AN ABSTRACT OF THE DISSERTATION OF

<u>Colin Harthcock</u> for the degree of <u>Doctor of Philosophy</u> in <u>Chemistry</u>, presented on <u>December 4, 2015</u> Title: <u>Zero Kinetic Energy Photoelectron Spectroscopy of Polycyclic Aromatic</u> Hydrocarbons.

Abstract approved:

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In this dissertation, I describe spectroscopic studies of jet-cooled polycyclic aromatic hydrocarbons (PAH) and one nitrogen substituted PAH (PANH) using pulsed field zero kinetic energy (ZEKE) photoelectron spectroscopy and resonantly enhanced multiphoton ionization (REMPI) spectroscopy. Recently, there has been a demand for far-infrared (FIR) spectral information of astrophysically relevant molecules by the National Aeronautics and Space Administration (NASA). Concurrent with the launching of the Herschel Space Observatory and the Stratospheric Observatory for Infrared Astronomy (SOFIA), NASA is on a mission to map out the chemical composition of the interstellar medium. In response to this call and in answering a broader interest in modeling the energy balance of the astrophysical environment, we have initiated a systematic study of polycyclic aromatic hydrocarbons, concentrating on the vibrational information in the FIR for the first electronically excited state and for the ground electronic state of the cation. From the REMPI experiment, we have learned that the vibronic structure of small stable PAHs generally follows the Franck-Condon principle, but vibronic coupling is prevalent for most larger sized PAHs. Nitrogen substitution can affect the nature of the electronic states and hence the vibronic distribution of the REMPI spectrum and ultimately the ZEKE spectra. Different from REMPI, ZEKE spectra typically follow the Franck-Condon principle, and spectral simulations using the Gaussian software package can typically reproduce the ZEKE spectrum obtained from the origin of the electronic transition qualitatively. Although ZEKE does not offer direction infrared transition intensities, our spectroscopic information in the FIR can benchmark theoretical values and offer guidance for NASA's astrophysical missions.

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by

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A DISSERTATION

submitted to

Oregon State University

in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Presented December 4, 2015 Commencement June 2016 Doctor of Philosophy dissertation of <u>Colin Harthcock</u> presented on <u>December 4, 2015</u> APPROVED:

Major Professor, representing Chemistry

Chair of the Department of Chemistry

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I understand that my dissertation will become part of the permanent collection of Oregon State University Libraries. My signature below authorizes release of me dissertation to any reader upon request.

Colin Harthcock, Author

ACKNOWLEDGEMENTS

After years of studious diligence; hours and hours spent in labs and tests, I am finally nearing my goal of earning a doctorate in chemistry. I know that my dream of a PhD in chemistry would not have been possible without the help of many people.

First, I would like to thank Dr. Chuck Williamson who first introduced me to the world of chemistry and laboratory research. Secondly, thank you Wei for the chance to be here at Oregon State University so that I can pursue my dream under her careful tutelage. Her availability and willingness to answer any question was and is extraordinary. I am forever in her debt. From the moment that I took my first step into the lab, Jie took me under her wing, going above and beyond to ensure that I knew everything when I took over her research.

I would also like to take a moment to acknowledge my lab mates, who have always been there to lend a helping hand when I needed it. Specifically I would like to thank Bill Freund who was always a fount of knowledge for all things electronic as well as Mark Warner, whose assistance proved invaluable. I would also like to thank the countless others at the university who helped me along the way.

My deepest appreciation goes out to my doctoral committee; Dr. Evans, Dr. Watson, Dr. Ostroverkhova, Dr. Strub, and Dr. McIntyre whose direction has been tremendously helpful.

Last but defiantly not least, I would like to express my most heartfelt thanks for my parents, whose unwavering support has helped me though the good and bad times.

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Chapter 1. Introduction

1.1 Background- Why PAH and PANH molecules?

Polycyclic aromatic hydrocarbons (PAHs) are a special group of hydrocarbons containing two or more fused aromatic rings without heteroatoms or substituents. The acronym PANH is used for PAHs which have undergone nitrogen substitution of a C-H moiety, and a PANH is isoelectronic to its PAH analog. The PAHs and PANHs included in this thesis are shown in Figure 1.1. Depending upon the bonding of the carbon atoms, PAHs and PANHs are classified into two subsets: cata-condensed and peri-condensed. The former contains no carbon atoms shared by more than two rings, while the latter contains at least one carbon atom shared by three aromatic rings. Peri-condensed PAHs can be quite large, owing to their increased conjugation as compared to the catacondensed type, while cata-condensed PAHs become unstable with more than six rings.

The importance of PAHs spans many different fields. For example, in atmospheric chemistry and biomedical researches, they are considered an important type of carcinogens.^{1,2} Atmospheric PAHs are typically formed during incomplete combustion of fossil fuels and are commonly found in smoke and tar. The carcinogenic effects of PAHs arise from their ability to bind or intercalate with DNA, causing transcription errors.^{1,2} In addition, PAHs are of interest in the field of astrobiology because they could be related to the origin of life through the formation of primitive organic molecules.³⁻⁹ The existence of PAHs in space has been confirmed in tails of comets using mass spectrometry.⁵ Without an ionosphere to block ionizing radiation, the

interstellar medium (ISM) is bathed in strong electromagnetic radiations. This environment can not only cause ionization, but can also trigger potentially biologically relevant chemistry on the surface of space ice. When PAHs were trapped in a matrix of ice and irradiated in conditions similar to the ISM, it was observed that ketones, alcohols, and ethers were produced.¹⁰ These chemicals could be important precursors to ribonucleic acids in a pre-DNA world. In particular, the quinolones found in this experiment closely resemble the molecules that facilitate light energy transfer from one part of a plant cell to another.^{3,10,11}



Figure 1.1. The PAH and PANH molecules included in this thesis.

In astrophysics, PAHs and PANHs are hypothesized to be constituents of the interstellar medium.^{5,7,8,12-14} From several space explorations, a set of emission bands at 3.3 μ m, 6.2 μ m, 7.7 μ m, 8.6 μ m and 11.3 μ m were observed from a wide variety of space

objects and regions. These bands are typically known as the unidentified infrared bands (UIBs).^{4,14,15} The frequencies of these bands correlate with a few of the signature vibrational transitions of PAHs: C-H in-plane stretching (3.3 μ m), C-C stretching (6.2, 7.7 μ m), C-H in-plane bending (8.6 μ m) and C-H out-of-plane bending (11.3 μ m).^{4,15} In addition, PANHs are also known to have strong vibrational modes in the spectral region of 5 - 10 μ m where PAHs do not have substantial oscillator strengths.^{7,8,16-18} Due to the low particle density in the ISM and the abundance of ionizing radiation in outer space, both cationic and anionic PAHs and PANHs may also contribute to the ISM and the UIBs.^{7,8,17-20}

The above situation has largely motivated the spectroscopic research of PAHs and PANHs, with the goal of identifying the chemical composition of the ISM.^{4,14,15,20-22} The history of PAH research goes back roughly four decades, starting with small molecules and working up to the larger, less volatile PAHs. As the research techniques matured over the years, the focus shifted from neutral molecules to both anions and cations. Some of the techniques employed include infrared absorption²³, single photon infrared emission²⁴, laser induced fluorescence²⁵, cavity ringdown²⁶ and photoionization spectroscopy.²⁷ The majority of these techniques are suited to the mid-infrared (MIR) spectral region between 3 and 25 µm, which is known to be representative of local vibrations and functional groups. As such, the MIR spectral region is ill suited to the identification of individual PAH or PANH molecules. Even with over four decades of work on a multitude of PAHs, not a single PAH has been positively identified in the ISM. On the other hand, the far-infrared (FIR) spectral region is indicative of skeletal vibrational modes, and is therefore useful for identification of specific PAHs or PANHs.^{20,28-31} However, there is very little

experimental information in this region owing to detector and light source issues associated with this low energy region.

The technique of zero kinetic energy photoelectron (ZEKE) spectroscopy offers a unique and powerful approach for tackling the usual issues of FIR spectroscopy of PAH and PANH cations.³²⁻³⁶ As will be shown in a later section, ZEKE relies heavily upon the lifetimes of high Rydberg states, which are much longer for low frequency modes; hence ZEKE is uniquely suited to probing FIR vibrational information of cations. By populating these long-lived high Rydberg states and then ionizing them with a pulsed electric field, ZEKE spectroscopy circumvents the ion density, light source, and detector issues associated with FIR cation spectroscopy.³⁷ The vibrational spectra from ZEKE obey the Franck-Condon principle, so primarily totally symmetric modes or even-number harmonics are observed. This means that for most species, the modes observed in the ZEKE experiment are IR inactive. Nevertheless, these modes help with scaling the frequency information from quantum mechanical calculation and they offer benchmark values whenever there is a vacuum of experimental data. Furthermore, all vibrational modes are needed to model the energy balance in the ISM and the universe. These IR forbidden bands are of direct value in astrophysical modeling.^{5,38}

1.2 The history and principle of ZEKE spectroscopy

Zero kinetic energy photoelectron spectroscopy was first implemented in 1984 by Mueller-Dethlefs and Schlag.³⁷ It is a specialized high resolution version of photoelectron spectroscopy (PES).³⁹ In typical PES experiments, a gas phase molecule is illuminated by a fixed wavelength light source, the energy of which surpasses the ionization threshold of the gas phase molecule. The resulting electrons have a wide range of kinetic energies, corresponding to the formation of different vibrational states of the cation. The resolution of PES is typically on the order of ± 10 meV, limited by the efficiency of the energy dispersion device.⁴⁰

Threshold photoelectron spectroscopy (TPES)⁴¹ is a higher resolution version of traditional PES. Instead of using a fixed wavelength light source and analyzing the kinetic energy of ejected photoelectrons, TPES collects threshold photoelectrons with a tunable light source. Because these electrons are near the ionization threshold, they have close to zero kinetic energy and can be collected with much higher efficiency than energetic electrons. Consequently, TPES can achieve a higher resolution by sheer steric discrimination of energetic electrons.⁴² Typical resolutions of TPES are on the order of 5 - 10 meV, while resolutions near 1 meV have been reported.⁴³

The initial idea of ZEKE was to detect only zero kinetic energy electrons, thereby maximizing spectral resolution.^{44,45} However, in practice, true zero kinetic energy electrons are impossible to capture because of the existence of stray fields in the ionization region. Instead, a tunable laser populates long lived high Rydberg states and after a delay, a pulsed electric field extracts the Rydberg electrons from the long lived Rydberg states.^{44,46} The delay allows the high energy prompt electrons to escape from the ionization region, leaving only neutral molecules in Rydberg states in the detection region.

A Rydberg state can be considered a hydrogen-like system with a cationic core. Differing from a proton, the cationic core has its own electronic, vibrational, and rotational quantum states. Each state of the cation has its own series of Rydberg states, and the limit of these states, corresponding to the principal quantum number *n* approaching infinity, is the actual cationic state. Due to the fact that Rydberg states exist close to an eigenstate of the cation, spectroscopy of the Rydberg states is considered the same as that of the cation. Hence ZEKE spectroscopy measures the vibrational states of the cation.

A unique and crucial property of Rydberg states is their exceedingly long lifetime, on the order of micro to milliseconds. Typical Rydberg states have lifetimes scaled by n^3 , but in ZEKE experiments, the observed lifetimes of Rydberg states are even longer than predicted. The origin of this increased lifetime is considered to be the spoiling and stray electric fields in the ionization region of a ZEKE experiment. These fields break the spherical symmetry of a hydrogen-like system, causing *l*-mixing. States with low orbital angular momentum l are close to the cationic core and are likely to autoionize, while states with high values of *l* have little interaction with the core. As such, *l*-mixing elongates the lifetime of Rydberg states by a factor of *n*. Moreover, the high density of charged particles in the ionization region further causes the magnetic quantum number mto be no longer conserved, mixing and elongating the lifetimes of Rydberg states. Because of these effects, the lifetime of experimental ZEKE Rydberg states follows n^{5} scaling. The lifetime of atomic hydrogen in the 2p electronic state is 1.600×10^{-9} seconds.^{44,46} If we know that the typical *n* values of ZEKE Rydberg states are greater than 100, the lifetime of these states is on the order of a few hundred milliseconds.^{44,46} Of course for a cationic core with internal electronic, vibrational, and rotational energies, mechanisms of autoionization can shorten the lifetime of these Rydberg states. In

particular, autoionization is the primary reason for the decreased lifetimes of ZEKE Rydberg states above a certain level of internal energy – the "cutoff energy" observed throughout our study.

The resolution of ZEKE is limited by the field strengths of the stray and extraction fields as well as the linewidth of the tunable light source. Typically resolutions are better than 5 cm⁻¹, while sub-wavenumber resolution has been reported.^{47,48} In addition to removing prompt electrons, the stray field also ionizes and therefore removes the top-most stack of Rydberg states with the highest principle quantum numbers. The size of the extraction field determines the range of Rydberg states that can be ionized by the field. The difference in the stray field and the pulsed extraction field determines the range of Rydberg states to be detected in a ZEKE experiment. This energy range is essentially the width of a ZEKE peak. The thus obtained ionization energy is close to the ionization threshold but lowered by the ionizing field. According to Schlag, the equation to correct the electric field is as follows⁴²:

$$\Delta \nu(cm^{-1}) = \alpha \sqrt{V_p\left(\frac{v}{cm}\right) + V_s\left(\frac{v}{cm}\right)}$$
(1.1)

where α is 5.1 V^{-1/2}cm^{-1/2}, V_s is the strength of the stray field (which was found experimentally to be -0.16 V/cm) and V_p is the strength of the pulsed field in V/cm.⁴⁹

In typical experiments performed in this thesis, two resonant lasers are used to reach the Rydberg states of a PAH or PANH molecule: one populating an intermediate vibrational state of the electronically excited molecule, while the other populates the Rydberg states which converge into a vibrational state of the cation. Through this scheme, the intermediate electronically excited state is also mapped out because only when the excitation laser is resonant with a vibronic level of the intermediate state can further excitation and ionization happen.

1.3 Summary

Zero kinetic energy photoelectron spectroscopy improves the spectral resolution over that of the traditional PES technique by approximately two orders of magnitude, and the application of ZEKE spectroscopy to the vibrational spectra of PAH and PANH cations is the central theme of this thesis. Not only is vibrational information collected from the cation, but also from the first electronically excited state. Information on the frequencies and charge distributions of the relevant electronic states help with the analysis of the structural stability of the cation. The insight from these studies and the actual values of vibrational frequencies are both necessary for modeling the energy balance of the universe and for deciphering the possible origin of the unidentified infrared bands.

In this thesis, the FIR modes of seven molecules are reported, the molecular structure of which can be found in Figure 1.1. About half of these publications were completed in collaboration with Dr. Jie Zhang, from whom I inherited the project. The presentation is arranged according to two subsets of PAHs: cata-condensed and peri-condensed. The cata-condensed group is first and includes triphenylene, chrysene, and benzo[h]quinoline. Among these, triphenylene relies entirely on vibronic coupling for excitation to vibrational levels of the first electronically excited S_I state, and it exhibits Jahn-Teller distortion in the cationic state. In contrast, chrysene does not exhibit

substantial vibronic coupling – an exception among all the PAHs in this thesis. The next

two cata-condensed molecules are PANHs and both exhibit interesting effects of nitrogen

substitution. The peri-condensed group starts out with benzo[a]pyrene and

benzo[*e*]pyrene which are structural isomers of each other, followed by

benzo[*g*,*h*,*i*]perylene, the largest PAH investigated in this thesis.

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Chapter 2. Experimental setup

2.1 General description

The experimental design consists of a laser system, a sample delivery system and a spectrometer. The sample is volatilized via heating then cooled with supersonic expansion through a pulse valve using an inert gas as a carrier, typically argon. The molecular beam passes through a skimmer, further selecting the coolest part of the pulsed sample at which point the sample reaches the inner (detection) chamber where the ZEKE spectrometer is housed. As the sample reaches the middle of the detection chamber, it is intersected by two counter-propagating laser beams (one of which is for excitation and the other is for ionization of the molecule) in between two electrodes. The resulting electrons or ions (depending on the experiment) are then detected by a time-of-flight spectrometer with a chevron-type multichannel plate (MCP) detector. Figure 2.1 includes details of the experimental setup.



Figure 2.1. Overall experimental setup and signal processing

The vacuum system consists of two chambers, the source chamber and the detection chamber, which are separated by a skimmer with an orifice of 2 mm in diameter. The source chamber is pumped with a diffusion pump (Varian, VHS 6) and is typically about 1×10^{-6} Torr, while the detection chamber is pumped via a turbo molecular pump (Varian, Turbo V-500) and is approximately 3×10^{-7} Torr with the pulse valve off and ~9 × 10⁻⁷ Torr with the pulse valve on. Details of the vacuum system are shown in Figure 2.2.



Figure 2.2. Details of the vacuum system

2.2 Laser systems

The ionization threshold of most polycyclic aromatic hydrocarbons is greater than $60,000 \text{ cm}^{-1}$ and is therefore in the vacuum ultraviolet. This energy is out of the range of

commercial lasers even with UV frequency doubling. To surmount this obstacle, we use a two photon process, the first of which is resonant with an intermediate vibronic state of the molecule, and the second is to ionize the sample. Both photons are typically in the ultraviolet range, which are generated through frequency doubling of visible dye lasers or optical parametric oscillators using either a KDP or a BBO crystal. The angle of the crystal is calibrated and tuned in synchronization with the scanning fundamental laser beam so that phase matching is maintained throughout the entirety of the scan. While two lasers are employed at any one time, some combination of two Nd:YAG pumped dye systems (Spectra Physics GCR 190, GCR 230 pumping Laser analytical systems; LDL 20505, LDL 2051) and an OPO system (Continuum, Precision I 8000 pumping Continuum, Panther OPO) is used.

At least one dye laser is employed in all of the experiments in this thesis. In most cases the dye is dissolved in pure methanol, however in some experiments a dioxane based dye is used. In most experiments, different dyes are mixed in order to maximize the intensity in a specific spectral region of interest. The dye laser is pumped at approximately 150 mJ/pulse and the dyes that we use regularly had an efficiency of 10 - 20%, thus resulting in ~15 mJ/pulse of fundamental tunable light. This light then passes through a doubling crystal which is also about 10% efficient, producing a final power of about 1.5 mJ/pulse of tunable UV light. The linewidth of the dye laser is 0.1 or 0.05 cm⁻¹ (depending on the dye laser).

Optical parametric oscillator (OPO) lasers are a convenient way of creating a tunable light source without the typical mess and trouble associated with liquid dyes. The process involves a 355 nm laser pumping a BBO crystal in an oscillator cavity, where the 2nd order nonlinear process generates two coexisting photons out of one photon at 355 nm -- signal and idler. The wavelength of the pair is dependent on the phase matching angle of the BBO. Either the signal or the idler can then be frequency doubled using another BBO crystal. While OPO laser systems are all solid state technology without the mess of dye systems, the trade-off of our current system is the limited linewidth of the output (3 cm^{-1}) , which is more than ten times of that of our dye lasers (0.1 cm^{-1}) .

2.3 Sample source

We use a pulse valve (General Valve, series 9) for supersonic cooling and entrainment of our non-volatile PAH and PANH samples. The samples are volatized by heating in a double walled cylinder directly attached to the valve's body and served also as a nozzle plate, as shown in Figure 2.3. A C-clamp type band heater with a 50 ohm coil is powered by a variac with a typical voltage range of 20 - 40 volts. The temperature of the nozzle is monitored via a thermistor with an Omega (CN370) controller. The highest temperature is 350 °C for the benzo[g,h,i]perylene experiment, but for most experiments the temperature does not exceed 200 °C. The heated volatized sample is seeded in a carrier gas, typically argon with a stagnation pressure of about 1 atm. The nozzle diameter of the pulse valve is 2 mm. The pulse valve is driven by a homemade driver circuit which allows for up to 10 A to be delivered to the pulse valve.¹ A few milligrams of sample are sufficient to supply the vapor pressure that is needed for the complete experiment. A general rule of thumb in forming supersonic molecular beams is that the ratio between the distance of the pulse valve and the skimmer to the nozzle diameter should be roughly $20:1^2$. Otherwise, shock waves from the gas plume might interfere

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with the supersonic expansion. Alignment of the skimmer and the pulse value is achieved with a HeNe laser directed opposite from the gas beam.



Figure 2.3. Details of the heatable pulse valve.

2.4 Spectrometer

The spectrometer contains two electrodes, a 2 inch long flight tube and a multichannel plate chevron detector for ion or electron detection. As shown in Figure 2.4, the two counter-propagating laser beams, the molecular beam, and the axis of the spectrometer are mutually perpendicular.



Figure 2.4. Details of the electrodes, TOF and sample source.

The spectrometer can be operated as a time-of-flight mass spectrometer (TOF-MS) for the detection of ions in the REMPI experiment and PFI-ZEKE spectrometer for the detection of field ionized electrons. The voltage settings of the different electrodes for the different experiments are listed in Table 2.1. Details of the MCP detection circuit are included in figure 2.5. A series of resistors form a voltage divider supplying equal voltage to the two multichannel plates, while the backside of the MCP is connected to capacitors to filter out ripples from the high voltage power supply. The resistor and capacitor connected to the back-plate form a high-pass RC filter, isolating the signal line from the high DC voltage. To detect ions, the front of the MCP is biased at a large negative voltage and the back is grounded, so ions can be accelerated to the detector. The opposite is true when detecting electrons.



Figure 2.5. The MCP detection circuit employed for the detection of cations and electrons.

Resonance enhanced multiphoton ionization spectra are obtained by scanning one laser (the excitation laser) which excites the molecule into an intermediate resonant state while fixing the wavelength of another laser for ionization. By scanning the excitation laser, the resonant vibrational levels of the intermediate electronic state can be mapped out. In the ZEKE experiment, the first laser is set to one of the vibrational intermediate states obtained in the REMPI experiment and the second laser is scanned through the ionization thresholds corresponding to different vibrationally excited cations.

In TOF-MS mode, the first electrode is grounded and the second electrode is negatively biased to help attract the cations to the TOF tube and ultimately to the MCP. Because of the diffusion pump, there are always oil molecules which get ionized along with the sample. This oil background signal is hard to remove from the ion signal and can cause serious problems in the detection of molecules that are of similar masses to the oil fragments.

Once the REMPI spectrum is collected, the first laser is set to the wavelength corresponding to one of the intermediate states so the ZEKE spectra can be collected. In order to do this, the MCP circuit is set to detect electrons and the electrodes are set to ZEKE mode (see Table 2.1). The second electrode provides a small positive DC spoiling field, on the order of 20 to 50 mV/cm, to accelerate prompt electrons out of the detection field thereby removing the spurious electrons, leaving only Rydberg state molecules within the spectrometer. After 300 - 600 ns, all prompt electrons have decayed away and the first electrode is pulsed to ionize, extract, and accelerate the Rydberg electrons to the detector. After the pulsed electric field, it takes approximately 30 ns for the electron to traverse the flight path to the MCP.

Table 2.1	. Electrode	voltages f	for the	REMPI	and PF	I-ZEKE	experiments

	REMPI (V)	PFI-ZEKE (V)			
First electrode	0	Pulsed*			
Second electrode	-80	~0.050			
TOF Tube	-255	+18			
MCP	-2100	+2100			
*Pulse amplitude -3 to -5 V, 0 V DC offset and width 0.1-0.5 μ s with a rise time of ~10					
ns					

The extraction pulse on the first electrode is supplied by a Systron Donner 114A pulse generator, allowing for timing control of the negative pulse. To minimize interference, the pulse is delivered to the electrode with a coaxial cable. Although the signal is terminated with a 50 ohm resistor, a ringing effect is observed and unavoidable.

2.5 Timing

The system operates in pulsed mode at a 10 Hz repetition rate, the master clock of which is supplied by a computer timing board (CIO-CTR 10). The rest of the timing control is achieved by delay generators (SRS DG535). A Q-switched laser requires at least 2 pulses, one to fire the lamps and the other to activate the Q-switch (on a 200 μ s delay). In a delay generator, channel A can be set for the delay of the flash lamp and channel B for the Q-switch of a laser. The pulse valve requires an up pulse and a down pulse, and the output channel C_T_D dictates the delay and duration for the pulse valve, typically 300 – 500 μ s. The pulse valve signal is significantly earlier than the two lasers

because of the relatively slow opening time of the solenoid and the fact that the molecular beam has to travel to the detection region. Figure 2.6 shows the relative timing profiles.



Figure 2.6. Relative timings for the PFI-ZEKE experiment

2.6 Typical experimental procedure

a. Choosing a viable sample

The first step of any experiment is to simulate the Herzberg-Teller spectrum for the first electronic transition $(S_1 \leftarrow S_0)$ and to simulate the Frank-Condon transition of the cation $(D_0 \leftarrow S_1)$ of the chosen sample, both of which predict the likelihood of success of the experiment. It is important to compare the absolute simulated intensity of a sample that ZEKE has been collected previously to that of a new system. If the simulated intensities are somewhat close, the ZEKE experiment is likely to be a success for the new system. It is also important to search the literature for the ionization threshold and the origin of the first electronic transition, as well as the symmetry of vibrations allowed for a specific transition.

Once a sample is considered viable according to the above simulation, the correct source conditions are determined to ensure sufficient vapor pressure, the best cooling condition, and the best signal-to-noise ratio. These are achieved by varying the carrier gas stagnation pressure, temperature of the sample holder, and the opening conditions of the pulse valve. Sometimes the lifetime of the excited state is so short that lifetime broadening washes out all observable vibronic transitions, and in this case, no REMPI or ZEKE experiments can be performed. If the energy of the intermediate state is less than half of the ionization threshold then two lasers are required (a two-color experiment) in REMPI: one for excitation and another for ionization. However, if the energy of the intermediate state is greater than half of the ionization threshold, the excitation laser can also act as the ionization laser, and only one laser is required (one-color).

b. Finding the ionization threshold and testing for ZEKE

Once the REMPI spectrum is completely mapped out, the ZEKE spectrum is ready to be obtained. The first step in the process is to set the first laser to the origin of the REMPI spectrum and then scan the energy of the second laser in the vicinity of the ionization threshold while monitoring the intensity of the ion signal (with the detector still in the TOF-MS mode). The thus obtained spectrum is called the photoionization efficiency (PIE) spectrum, and the sharpness of its onset is a general indication of the lifetimes of the corresponding Rydberg states.^{1,3} If the ion intensity shows a sharp change near the threshold, typically from maximum to near nothing within 2 nm of the scanning range, then it is very likely that there will be strong ZEKE signal. In our experience, if the intensity does not drop off within 5 nm by more than 50%, then signals from the ZEKE experiments are unlikely or very weak. This could be due to unfavorable Franck-Condon factors at the threshold.

c. Recording ZEKE spectra

If the ionization threshold scan is deemed sharp enough, ZEKE spectra can be collected. This is achieved by setting the MCP and electrodes to ZEKE mode, the first (excitation) laser to one of the intermediate states collected in the REMPI experiment, and scanning the second (ionization) laser. After the ZEKE spectrum is collected for a given intermediate, the excitation laser is moved to the next intermediate state and the process is repeated. Vibrational intermediates with energies above 1000 cm⁻¹ usually don't yield ZEKE spectra, perhaps due to reduced lifetime of Rydberg states with the opening of many more decay channels at higher energies.
2.7 Gaussian Calculations

The Gaussian suite⁴ is used to calculate frequencies of vibrational modes of the intermediate state as well as to simulate the spectra. Methods of Density Functional Theory (DFT) are used for all calculations of ground electronic states with the B3LYP functional, typically with the 6-31G basis set, and for excited states, time-dependent DFT is used. These calculations yield vibrational energies, symmetry properties, displacement vectors, and transition dipole moments, which are used in GaussView for animation. In addition, a checkpoint file could also be generated from the calculation and be used to simulate transitions using either Herzberg-Teller or Frank-Condon probabilities from which a complete REMPI or ZEKE spectrum can be generated.

2.8 References

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Chapter 3. Zero kinetic energy photoelectron spectroscopy of triphenylene

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Manuscript for submission to Journal of Chemical Physics, November 30, 2013

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Abstract

We report vibrational information of both the first electronically excited state and the ground cationic state of jet-cooled triphenylene via the techniques of resonantly enhanced multiphoton ionization (REMPI) and zero kinetic energy (ZEKE) photoelectron spectroscopy. The first excited electronic state S_I of the neutral molecule is of A_1 ' symmetry and is therefore electric dipole forbidden in the D_{3h} group. Consequently, there are no observable Franck-Condon allowed totally symmetric a_1 vibrational bands in the REMPI spectrum. All observed vibrational transitions are due to Herzberg-Teller vibronic coupling to the E' third electronically excited state S_3 . The assignment of all vibrational bands as e' symmetry is based on comparisons with calculations using the time dependent density functional theory and spectroscopic simulations. When an electron is eliminated, the molecular frame undergoes Jahn-Teller distortion, lowering the point group to C_{2v} and resulting in two nearly degenerate electronic states of A_2 and B_1 symmetry. Here we follow a crude treatment by assuming that all e' vibrational modes resolve into b_2 and a_1 modes in the C_{2v} molecular frame. Some observed ZEKE transitions are tentatively assigned, and the adiabatic ionization threshold is determined to be 63365 ± 7 cm⁻¹. The observed ZEKE spectra contain a consistent pattern, with a cluster of transitions centered near the same vibrational level of the cation as that of the intermediate state, roughly consistent with the propensity rule. However, complete assignment of the detailed vibrational structure due to Jahn-Teller coupling requires much more extensive calculations, which will be performed in the future.

3.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of molecules consisting of fused benzene rings. They are readily formed during incomplete combustion of fossil fuels and are considered potent pollutants due to their carcinogenic properties.¹⁻³ PAHs have also been observed in comet tails and are possibly a major component of the interstellar medium (ISM).^{4,5} They have been considered responsible for many of the spectroscopic features observed in the ISM and have substantial implications to the energy balance of the universe.⁶⁻¹³ In astrobiology, it has been hypothesized that PAHs could be related to the origin of life by forming the first primitive organic molecules including amino acids in the pre-DNA world.¹⁴⁻¹⁶

Many spectroscopic studies of neutral and cationic PAHs have been motivated by astrophysical modeling.¹⁷⁻²² Both the infrared and visible/ultraviolet regions have been extensively investigated using techniques of photoionization, cavity ring-down, photoabsorption, and photoemission spectroscopy.^{21,23-27} Unfortunately, the far-infrared (FIR) region has been largely untouched because of issues related to detector sensitivity and light source intensity. On the other hand, the FIR region is occupied by skeletal vibrations of the molecular frame, and it is considered the "finger-print region" for spectroscopic identification of astrophysical PAHs.^{28,29}

The technique of zero kinetic energy (ZEKE) photoelectron spectroscopy offers an indirect solution to the challenges in the FIR of cations for laboratory astrophysics.³⁰ In recent years, we have undertaken the mission of mapping out the low frequency vibrational modes of PAHs using ZEKE spectroscopy.³¹⁻³⁷ So far we have reported four peri-condensed species including pyrene, benzo[*a*]pyrene (B*a*P), benzo[*e*]pyrene (B*e*P), and benzo[g,h,i]perylene (BghiP) as well as three cata-condensed species including tetracene, pentacene, and chrysene.³¹⁻³⁷ Our results together with previous matrix isolation spectroscopy (MIS)³⁸⁻⁴¹ and other experimental efforts offer the possibility of a comprehensive analysis of the vibrational modes of a few selected cationic species, thereby benchmarking theoretical calculations and astrophysical modeling.

In this work, we report our new results on triphenylene, a highly symmetric neutral molecule with D_{3h} symmetry. The first electronically excited state S_I of triphenylene is electric dipole forbidden,^{38,39} hence all vibronic transitions originate from Herzberg-Teller (HT) vibronic coupling during resonantly enhanced multiphoton ionization (REMPI). The cationic state, on the other hand, is believed to be of C_{2v} symmetry, undergoing Jahn-Teller (JT) distortion when an electron is eliminated from the molecular frame.⁴²⁻⁴⁴ We offer vibrational analysis of both the REMPI and ZEKE spectra, and discuss the role of symmetry in affecting the vibronic activities of the system.

3.2 Experimental setup and calculation method

The experimental apparatus was a differentially pumped molecular beam machine, with the detection chamber enclosed inside the source chamber.³⁵ A time-of-flight mass spectrometer in the detection chamber also served as the pulsed field ionization zero kinetic energy photoelectron spectrometer. Triphenylene (Aldrich) was housed and heated to 260°C in the pulsed valve located in the source chamber. The vapor of the sample was seeded in 400 torr of argon and co-expanded into vacuum through a pulsed valve with a 1 mm orifice. After passing through a 2 mm skimmer, the cooled sample reached the detection chamber for laser excitation and ionization. The laser

systems for the REMPI experiment included two Nd:YAG (Spectra Physics, GCR 190 and GCR 230) pumped dye lasers (Laser Analytical System, LDL 20505 and LDL 2051), both equipped with frequency doublers. The excitation laser in the 304 - 340 nm range had a typical pulse energy of more than 1.0 mJ/pulse with a bandwidth of 0.5 cm⁻¹. The ionization laser in the 287 - 301 nm range had a pulse energy of ~1 mJ/pulse with a bandwidth of 0.3 cm⁻¹. The absolute wavelength of each laser was calibrated using an iron hollow-cathode lamp filled with neon. The pump laser and ionization laser were set to counter-propagate, and the light path, the flight tube, and the molecular beam were mutually perpendicular. Two delay generators (Stanford Research, DG 535) controlled the timing of the lasers and the pulsed valve, and the optimal signal was obtained under temporal overlap between the pump and ionization lasers. In the ZEKE experiment, molecules were excited to high Rydberg states for 400 ns in the presence of a small constant DC spoiling field, after which ionization and extraction were achieved by a pulsed electric field of ~2 V/cm.

The Gaussian 09 suite⁴⁵ was used to optimize the molecular structure, to obtain vibrational frequencies, and to simulate the observed vibrational structures from REMPI. For the ground state of the neutral and the cationic state, density functional theory (DFT) calculations using the B3LYP functional were performed with the 6-31+G basis set. The excited states S_1 and S_2 were calculated using both time dependent density functional theory (TDDFT) with the B3LYP functional and the 6-31+G basis set as well as configuration interaction singles (CIS) with the 6-31+G basis set. Details of the calculations will be provided in the following section.

3.3 Results

Two-color 1+1' REMPI spectroscopy

Figure 3.1 shows the two-color REMPI spectrum of triphenylene near the origin of the $S_1 \leftarrow S_0$ electronic transition. The ionization laser was set at 35090 cm⁻¹ and the excitation laser was scanned for resonant transitions. Table 3.1 includes the observed vibronic transitions, the corresponding calculated values from Gaussian 09 using TDDFT at the 6-31+G level, and the symmetry assignments in the D_{3h} point group. The labeling is by symmetry species and by numbering each species independently from low to high frequencies, a convention used by several groups since 2008.^{33,46} As will be discussed later, the electronic transition is dipole forbidden, resulting in no origin band, thus assignment of the origin is based on assignment of the vibronic bands. Our current value of 29618 cm⁻¹ for the origin of the electronic transition is in excellent agreement with the work of Kokkin *et. al.* in the gas phase,⁴⁷ but it is shifted by \sim 470 cm⁻¹ from the report of Merle, Campion and M. El-Sayed.³⁹ The blue shift of the latter work has been attributed to the effect of the *n*-heptane matrix. In Figure 3.1, the spectrum is shifted to the electronic origin to emphasize the vibronic structure. Typically, calculated vibrational frequencies for electronically excited states are over estimates, which can be corrected with a small scaling factor. In this case, a scaling factor of 0.964 has been used based on a least squares fit between the experimental and the putative theoretical values, and the resulting correlation of determination of the linear regression is 0.9999. The value of the scaling factor is within the typical range for calculations using the B3LYP functional.³¹⁻³⁷



Figure 3.1. REMPI spectrum of triphenylene shifted by 29618 cm⁻¹, the energy for the origin of the S_I state. The energy region below 180 cm⁻¹ was scanned with 180 laser shots for each data point in a failed attempt to observe the origin band, while the rest of the spectrum was the average of 100 laser shots. Modes in bold-faced italic fonts are the intermediate vibronic transitions which have yielded ZEKE spectra. The molecular structure with designations of axes is also included.

Experimental	Calculation [†]	Assignment	Matrix Isolation*	LIF**
249	252	<i>1e</i> '	249	247 (1e')
600	609	3e'	616	597 (3e')
748	748	4e'	769	745 (4e')
763	755	1e ^{,3}	789	
876	866	1e"4a ₁ "		
920	925	$1e'2a_1'$		
1026	1030	6e'	1036	
1163	1161	8e'	1172	
1269	1282	3e'2a ₁ '	1271	
1286	1306	1e'3a ₁ '		
1294	1307	10e'		
1335	1326	11e'	1336	1332 (11e')
1404	1405	4e'2a ₁ '	1410	1402 (4e'2a ₁ ')
1417	1424	12e'	1437	1414 (12e')
1478	1483	13e'	1480	
1576	1573	15e'	1576	
1624	1626	5e'2a ₁ '		
1976	1980	10e'2a ₁ '	1997	1973 (3e'7a ₁ ')
2124	2101	4e'6a ₁ '	2117	
2198	2197	4e'8a ₁ '	2184	
2709	2698	12e'5a ₁ '	2697	

Table 3.1. Observed vibrational bands for the S_I (A₁') state of triphenylene. Bands in bold-faced italic font are intermediate states which have yielded ZEKE spectra (units: cm⁻¹, uncertainty: ± 5 cm⁻¹).

2794	2790	14e'5a ₁ '	2777	2784 (12e'7a ₁ ')
3080	3085	16e'		

† Including a scaling factor of 0.964.

-

* Matrix isolation spectroscopy in *n*-heptane crystal with a scaling factor of 0.98.³⁹ ** Gas-phase laser induced fluorescence.⁴⁷

A feature of Gaussian 09 is inclusion of Herzberg-Teller coupling for simulations of vibronic transitions, often with very reasonable accuracy for intensity distributions.⁴⁵ The resulting spectrum can further assist with the assignment of the observed REMPI transitions. However, a problem with Gaussian 09, regardless of methods of calculation, is the uncertainty in the energy of closely spaced excited electronic states.³¹⁻³⁷ Consequently in Figure 3.2, we show the simulated spectra with Herzberg-Teller coupling for both the $S_1 \leftarrow S_0$ and the $S_2 \leftarrow S_0$ transitions of triphenylene. Although the lack of an origin band could potentially complicate the assignment of the spectrum, fortunately in this case, the agreement between simulation and experiment in Figure 3.2 is quite reasonable. The observed vibronic bands do indeed correspond to those from the $S_1 \leftarrow S_0$ transition.^{38-40,47}



Figure 3.2. Comparison between the experimental REMPI spectrum and the simulation using Gaussian 09 including Herzberg-Teller coupling.

The assignment in Table 3.1 is based on several considerations. First, even with HT coupling, selection rules for electric dipole transitions are still obeyed, hence only vibronic transitions with an overall symmetry species of e' are allowed. Second, given the symmetry constraint, the assignment of many low frequency bands is indisputable because of the discrete quantized fundamental frequencies. Third, the spectroscopic simulation presented in Figure 3.2 offers theoretical guidance for the observed transitions. Nevertheless, there are a few transitions that have unusually large deviations, but in general, the agreements between theory and experiment and between our assignment and two other previous works using different methods are quite satisfactory.^{39,47} The assignment for the transition at 1417 cm⁻¹ is based on a comparison with the calculated spectrum, hence it is different from that of a previous report.⁴⁷

ZEKE Spectroscopy

By setting the first laser at one of the intermediate states identified in the REMPI experiment and scanning the second laser, we have obtained the pulsed field ionization ZEKE spectra of triphenylene. Figures 3.3 and 3.4 show the ZEKE spectra via the first six vibronic transitions labeled in bold-faced font in Figure 3.1. Efforts of using intermediate states with vibrational energies higher than 900 cm⁻¹ have yielded no ZEKE signal. This kind of internal energy "cutoff" seems typical for the ZEKE experiments that we have performed.³¹⁻³⁷ The inconsistent signal-to-noise ratio (S/N) of Fig. 3.4c is due to the extra effort in the scan of the central region (marked by two arrows): while the rest of the region and the rest of all the ZEKE spectra have been results of averages over 100 laser shots, this central region has been the average of 170 laser shots per data point. The

data have also been recorded in different days, and slight variations in experimental parameters could also contribute to the difference in the S/N of the spectrum. The adiabatic origin of the cationic ground state is tentatively assigned to be $63365 \pm 7 \text{ cm}^{-1}$, corresponding to the observed lowest frequency band and taking into consideration the shift caused by the delayed electric pulse for ionization. This value is about 200 cm⁻¹ below that reported by Boschi, Clar and Schmidt via photoelectron spectroscopy.⁴⁸ The discrepancy is not surprising since the higher spectral resolution of ZEKE than that of typical photoelectron spectroscopy can effectively remove interferences from hot bands and from external electric and magnetic fields.



Figure 3.3. Experimental ZEKE spectra from intermediate vibronic states: (a) 1e', (b) 3e', and (c) 4e', shifted by 63365 cm⁻¹. Modes in bold-faced italic font are the correlated diagonal modes.



Figure 3.4. Experimental ZEKE spectra from intermediate vibronic states: (a) $1e^{3}$, (b) $1e^{4}a_{1}$, and (c) $1e^{2}a_{1}$, shifted by 63365 cm⁻¹. The top two panels are scaled up by a factor of 5. The inconsistent signal-to-noise ratio in panel (c) is due to the extra effort (170 laser shots vs. 100 laser shots per data point and perhaps better alignment on the day of the attempt) during the scan of the central region. Modes in bold-faced italic font are the correlated diagonal modes.

Compared with the ZEKE spectrum of benzene^{49,50} where coupling among different JT active modes is extensive, the ZEKE spectra of triphenylene are sparse and contain a recognizable pattern – a dominant single cluster of transitions. Jahn-Teller coupling results in splittings of vibrational levels, thus the individual transitions within each cluster could be related to the same doubly degenerate vibrational band of the intermediate state. This single cluster of transitions of each spectrum is thus an indicator of a propensity in preserving the vibrational excitation of the intermediate state.^{31-37,51,52}

Full assignment of the observed ZEKE transitions in the presence of Jahn-Teller distortion requires calculations similar to those of Applegate and Miller on the analysis of the ZEKE spectrum of benzene.⁵⁰ The inset of the bottom panel in Fig. 3.3 shows three transitions, two of which constitute a closely spaced doublet (7 cm⁻¹ apart), and the 3rd transition is nearly 50 cm⁻¹ above the doublet. This pattern is very similar to that of the ZEKE spectrum obtained via the 2¹18¹ vibrational level of the *S*₁ state of benzene.⁵⁰ A similar pattern is also observable in the inset of the middle panel of Fig. 3.3, although the doublet feature is now a triplet. However, the analysis of Applegate and Miller did not explicitly associate the observed vibrational transition with the unperturbed degenerate state.⁵⁰ In so doing, some physical insights related the ionization process could be missed.

In this work, we adopt the approach of Keszthelyi *et al.*^{43,53} by simply using the unperturbed vibrational frequencies from our DFT calculation for a preliminary analysis. The advantage of this treatment is the explicit symmetry information of the assigned vibrational transitions in the deformed molecular frame. Based on our calculations using unrestricted Hartree-Fock, Møller–Plesset second order perturbation theory, coupled cluster configuration interactions with single and double substitutions, and density

functional methods, the vibrational frequencies from the unperturbed electronic states in the C_{2v} symmetry that constitute the Jahn-Teller pair are almost identical (within 1 cm⁻¹). By using the frequencies of a single cationic state from our DFT calculation as a guide, we offer a tentative assignment as that listed in Table 3.II. As seen in the insets of Fig. 3.3, the current assignment leaves out many details revealed in the spectra. Nevertheless, the agreement in frequency between calculation and experiment in Table 3.2 is surprisingly good. A similar situation has also been reported by Keszthelyi *et al.*⁴³ on Raman spectroscopy of triphenylene cations. For bands with moderately high vibrational energies, we could attribute the agreement to the freedom in using combinations of low frequency modes just to match the transition wavenumbers, but this reason cannot be used to negate the agreement of the lower energy bands. One possibility of this surprisingly good agreement might be related to the strength of coupling specific to these vibrational modes. According to the report by Kato and Yamabe,⁴² only three e' modes are primarily responsible for JT coupling, and none of the three are accessed in the REMPI spectrum of Figure 3.1.

1e'	3e'	4e'	1e' ³	1e"4a ₁ "	1e'2a ₁ '	calc	Assignment
220						238	$1b_2^2$
267						265	$1a_1$
343						352	$2a_23b_1$
		423*				430	3a ₁

Table 3.2. Observed vibrational bands of the D_0 state of triphenylene from several intermediate vibronic transitions. The bands in bold-faced italic font are the correlated diagonal bands of the intermediate state (units: cm⁻¹, uncertainty: ± 7 cm⁻¹).

	586					584	4b ₂
	596*					594	1a ₂ 6a ₂
	610					623	5b ₂
	641					641	$4a_1$
685*						681	$1a_{1}2a_{1}$
		718				698	6b ₂
	730	732				735	$2b_22a_1$
		750				749	$2b_23a_1$
		785	785			778	3a ₂ 5a ₂
		806	795			801	6a ₁
			808			795	$1a_1^{3}$
			826			832	$2a_1^2$
				930		940	7b ₂
				950		963	$1b_111a_2$
					953	960	$2b_24a_1$
				974		975	$5a_11a_1$
	1004					1000	$4b_{2}2a_{1}$
	1015					1010	$1a_26a_22a_1$
	1028					1039	$5b_22a_1$
		1170				1165	$2b_23a_12a_1$
			1226			1211	$1a_1^{3}2a_1$
				1353		1356	$7b_22a_1$

*Modes that are observed in the matrix isolation resonant Raman experiment.⁴³

With this crude treatment, we can follow the transformation of vibrational modes from the S_1 to the D_0 states thereby peeking into the mechanism of ionization. We start by considering that when the electronic state exhibits JT distortion from D_{3h} to C_{2v} , the e' vibrational modes resolve into a_1 and b_2 modes. We can then construct a resolution map from the e' modes of the intermediate state to the a_1 and b_2 modes of the final ionic state. This correlation will in turn guide or confirm the vibrational assignment of both the REMPI and ZEKE spectra. Using GaussView⁴⁵ for visualization of the displacement vectors and using vibrational frequencies for guidance, we have concluded on a list of correlated vibrational modes as shown in Table 3.3. It is important to note that the a_1 modes of C_{2v} arise from both the a_1 ' as well as the e' modes of D_{3h} , and the b_2 modes of C_{2v} arise from both the a_2 ' modes of D_{3h} . This means that in the resolution table of the e' modes, the numbering of the modes in C_{2v} is not necessarily consecutive.

S_1 (D _{3h}) modes [†]	Correlated D_0 (C _{2v}) modes		
1-2 (252)	1b ₂ (119)		
1e (252)	1a ₁ (265)		
$2a^{2}(205)$	2b ₂ (319)		
2e (393)	2a ₁ (416)		
20' (600)	5b ₂ (623)		
3e (009)	4a ₁ (641)		
40' (748)	6b ₂ (698)		
46 (748)	6a ₁ (801)		

Table 3.3. The e' (D_{3h}) modes and the correlated a_1 and $b_2 (C_{2v})$ modes with the calculated frequencies in parenthesis (units: cm⁻¹).

5-2' (051)	7b ₂ (940)
56 (951)	7a ₁ (1012)
6°' (1020)	9b ₂ (1088)
0e (1050)	8a ₁ (1068)
7-2 (1021)	10b ₂ (1111)
/e (1081)	10a ₁ (1141)

[†]Including a scaling factor of 0.964.

Figure 3.5 shows the displacement vectors of the lowest frequency e' mode and the correlated a_1 and b_2 modes. This e' mode in D_{3h} can be regarded as two degenerate inplane vibrations, one of which is symmetric about the vertical plane σ_v (a_1) and the other is anti-symmetric (b_2). The b_2 mode in C_{2v} involves wagging of one terminal (top) ring relative to the somewhat rigid phenanthrene substructure, while the a_1 mode looks like scissoring of the two rings within the phenanthrene substructure while the top ring staying relatively still. In the ZEKE spectrum of Figure 3.3a, the strongest transition from the e' mode of the intermediate state is assigned as the a_1 mode of the cation. Although further calculations using the Applegate and Miller approach⁵⁰ will inevitably shift the theoretical transition frequency by introducing JT coupling terms, our current approach should capture the predominant feature of the observed transition.



Figure 3.5. The 1e' vibrational mode of S_1 (D_{3h}) and its resolution into the b₂ and a₁ modes of D_0 (C_{2v}). The displacement vectors (thinner arrows) are included as well as the vertical mirror plane σ_v (dashed line).

Many previous studies of ZEKE spectroscopy via resonantly excited states have reported a propensity rule, i.e. the strongest transition in the ZEKE spectrum can be assigned as the same vibrational mode as that of the intermediate state.^{31-37,51,52} If the propensity rule holds for triphenylene, we would expect many of the correlated a_1 and b_2 modes to be present in the ZEKE spectra. This is indeed the result from Figures 3.3 and 3.4, where the intense clusters of transitions contain one or both of the correlated modes of the intermediate state (labeled in bold). However, in Figures 3.3 and 3.4, weaker replicas of the strong cluster of transitions are also observable, and these replicas can be assigned as combinations of the original cluster of transitions with a $2a_1$ transition at 416 cm⁻¹. Clearly the Franck-Condon factor from the S_I intermediate state to the cationic state D_0 is not totally diagonal.

3.4 Discussions

--The S_1 electronic state and vibrational assignment

The symmetry of several low lying electronic states and the corresponding electronic orbitals are informative in understanding the origin of the vibronic coupling in triphenylene. Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are e" in symmetry, and every e" orbital consists of a symmetric and anti-symmetric molecular orbital with respect to the vertical mirror plane σ_v (symmetry plane shown in Figure 3.5). Excitation from the doubly degenerate HOMO to the doubly degenerate LUMO can result in four possible transitions, corresponding to three possible electronic states with symmetry terms of A₁', A₂' and E'. Based on the output from TDDFT calculations, the transition to the *S*₁ state contains equal contributions from transitions between orbitals of the same symmetry, hence the *S*₁ state can be assigned as A₁'. The situation for the transition to the *S*₂ state is the opposite, consisting of equal contributions between molecular orbitals of different symmetry,

hence the S_2 state can be assigned as A_2 '. The transitions to the S_3 state consist of a degenerate pair, which confirms the E' assignment for S_3 .³⁸ The transition dipole for the D_{3h} group is either e' or a_2 ", hence both S_1 and S_2 are electric dipole forbidden. Any observed vibronic transitions to S_1 are therefore due to vibronic coupling with the dipole allowed S_3 state.

It might seem surprising that all observed vibronic bands from REMPI are results of coupling to the third electronically excited state S_3 . The energy difference between S_3 and S_1 is ~7000 cm⁻¹ by our calculation, which agrees with that of Chojnacki *et al.*³⁸ This energy gap is the largest although not totally out of reason when compared with those in other PAHs that we have studied. For example, the energy gap is 1200 cm⁻¹ for B*a*P,³⁴ 3000 cm⁻¹ for pyrene,³⁵ and 5000 cm⁻¹ for B*e*P.³¹ However, all of these PAHs couple to the S_2 electronic state. We have previously concluded and once again confirm in this study that the degree of Herzberg-Teller coupling does not necessarily correlate with the energy gap.^{31-37,51,52} A somewhat surprising realization is that despite the large energy difference and the complete electric dipole forbidden nature of the S_1 state, the vibronic transitions are strong and the corresponding Rydberg states are stable enough for further ZEKE spectroscopy.

With the exception of a missing origin band, the REMPI spectrum of triphenylene is similar to those of other PAHs that our group has studied.^{31-37,51,52,54,55} The observed vibrational modes are in-plane, and the simulated spectrum captures the essence of the experimental data, despite the dominance of vibronic coupling. Based on our calculation, the molecular frame hardly changes upon excitation, expanding only by about half a

percent in all directions because of the increased nodal character in the excited electronic state.³¹⁻³⁷

The first electronically excited state of triphenylene has been studied by several groups using a variety of techniques including gas phase laser induced fluorescence $(LIF)^{47}$ and matrix isolation spectroscopy.³⁸⁻⁴¹ The LIF study by Kokkin *et al.* is in close agreement with our work in terms of frequency, intensity, and assignment, as shown in Table 3.1.⁴⁷ The frequencies from matrix isolation spectroscopy at 1.6 K³⁹ are also included in Table 3.1 for comparison. In general, frequencies from MIS experiments either at 77 K^{38,41} or at 1.6 K³⁹ require a scaling factor of 0.98 to agree with the corresponding values from gas phase studies. The scaling factor is indicative of deformation of the molecular frame relative to that of free space gas phase molecules.^{39,40} This effect is not too surprising given the seemingly floppy shape of the molecular frame. Furthermore, all MIS studies have shown a small but observable origin band, implying that the symmetry of the electronic state has perhaps been distorted.³⁸⁻⁴⁰ Based on polarization analysis, Lamotte *et al.* have indeed confirmed the symmetry of the *S*₁ state to be C_{2y} in their matrix.⁴⁰

--Geometry and vibrational assignment of the D_0 state

After photoionization, the resulting electron configuration for triphenylene is $(e'')^3$, a prime candidate for Jahn-Teller distortion. There have been several studies, both theoretical and experimental, indicating that both the cation and anion are of C_{2v} symmetry.^{42-44,56,57} In particular, Keszthelyi *et al.*⁴³ have reported the resonant Raman spectroscopy of triphenylene cation along with Hartree-Fock and density functional

calculations, and the authors have simulated the experimental spectrum based on parameters from the C_{2v} molecular frame.⁴³

Jahn-Teller distortion results in two electronic states A_2 and B_1 for triphenylene. Based on calculations of our own and those of Keszthelyi *et al.*⁴³ using a range of methods, the two states are nearly degenerate. In the A_2 state, one of the arms is compressed, while in the B_1 state, the arm is elongated. We have then calculated the energy of the D_{3h} conical intersection by averaging the geometric parameters of the Jahn-Teller pair, and the resulting barrier is ~1000 cm⁻¹. This value is on par with that from Keszthelyi *et al.*⁴³ Given the scope of the current work and our emphasis for the correlation between the vibrational levels of the intermediate state and those of the final state, we will leave the full Jahn-Teller analysis for the future.

Interestingly, the change in symmetry only exerts minor effect on the actual dimension of the molecular frame, resulting in observable propensity in preserving the vibrational excitation of the intermediate state. This result is not too surprising given the relatively large number of rings of triphenylene thereby its capacity to accommodate the positive charge of the cation.

There are some similarities between our data and those from the resonant Raman experiment of Keszthelyi *et al.*⁴³ While the intensities should be different between these two experiments because of different selection rules, some common vibrational modes particularly the a_1 modes should be observable in both experiments. In Table 3.2, three reported a_1 modes from Keszthelyi *et al.*⁴³ are marked with asterisks. However in our case, the two higher frequency bands are better assigned as combination bands based on correlations with the intermediate vibrational level. It is possible that the bands observed

in the matrix are different from ours since no matrix effect has been considered in the original report.

--Comparisons with other PAHs

With the exception of JT distortion, triphenylene is in many ways similar to the other PAHs that we have studied.³¹⁻³⁷ The observable modes from both the S_I and D_0 electronic states are restricted to in-plane vibrations, and the scaling factor for the vibrational frequency of the S_I state is also within the range of expected values.³¹⁻³⁷ In pyrene and a few cata-condensed PAHs,^{32,35,36} we have observed out-of-plane vibrations due to vibronic coupling, and in all cases, the out-of-plane modes have been electric dipole allowed because of the symmetry of the coupled higher electronic state. Although the degree of vibronic coupling is extraordinary in triphenylene, no out-of-plane modes are allowed because of the symmetry of the S_3 (E') electronic state. Hence the existence and intensity of out-of-plane modes are not indicative of molecular rigidity.

Coronene and benzene are both similar to triphenylene in that they are highly symmetric PAHs and they exhibit JT distortion upon ionization. In terms of structural distortion, based on our calculation, the $D_0 \leftarrow S_0$ transition in triphenylene shrinks the overall dimension along one of the principal axes by less than 0.25% and expands the dimension in the perpendicular direction by a little less than 0.5%. The structural change in coronene is similar, consistent with the trend that larger molecules tolerate more disturbances in the electronic structure. In contrast, the JT distortion of benzene cation is much more pronounced, with the dimension along the elongated axis increasing by 4%. Consequently, the ZEKE spectrum of benzene contains an extensive progression of vibrational bands, including several out-of-plane modes,^{49,50} while the ZEKE spectra of triphenylene mostly contain diagonal vibrational bands.

3.5 Conclusions

The vibrational information of triphenylene for both the first electronically excited state and the cationic ground state is reported based on REMPI and ZEKE spectroscopy. The $S_1 \leftarrow S_0$ electronic transition is electric dipole forbidden and all vibrational bands are results of vibronic coupling with a high lying S_3 (E') electronic state. Using Gaussian 09, we are able to simulate the vibronic spectrum of the S_1 state, from which we have determined the origin of the S_1 state to be 29618 ± 5 cm⁻¹. Removal of an electron results in a symmetry change from D_{3h} to $C_{2\nu}$, but the actual changes in structural parameters are still small. Based on a resolution of the intermediate e' modes from D_{3h} to the a_1 and b_2 modes of C_{2v} , some transitions in the ZEKE spectra can be tentatively assigned, and the propensity of preserving the vibrational excitation of the intermediate state can be observed. No ZEKE signal has been observed from intermediate states with vibrational energy excesses higher than 900 cm⁻¹, similar to many of the PAHs we have investigated. Given the complexity of the ZEKE spectra, however, a complete understanding and assignment will require a detailed calculation of vibronic wavefunctions of the Jahn-Teller pair, a task that awaits future effort.

Acknowledgments

This work is supported by the National Aeronautics and Space Administration under award No. NNX09AC03G.

3.6 References

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Chapter 4. Resonantly enhanced multiphoton ionization and zero kinetic energy photoelectron spectroscopy of chrysene: A comparison with tetracene

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Manuscript for submission to J. Phys. Chem. A, April 6, 2012

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Abstract

We report electronic and vibrational spectroscopy of chrysene using resonantly enhanced multiphoton ionization (REMPI) and zero kinetic energy (ZEKE) photoelectron spectroscopy. As an isomer of tetracene, chrysene contains a kink in the middle of the four fused hexagonal rings, which complicates not just the symmetry, but more importantly, the molecular orbitals and hence vibronic transitions. Incidentally, the two nearby electronically excited states of chrysene have the same symmetry, and vibronic coupling introduces no out-of-plane vibrational modes. As a result, the REMPI spectrum of chrysene contains essentially only in-plane ring deformation modes, similar to that of However, density functional calculations using Gaussian even after the tetracene. inclusion of vibronic coupling can only duplicate the observed REMPI spectrum in a qualitative sense, and the agreement is considerably worse than our recent work on a few pericondensed polycyclic aromatic hydrocarbons and on tetracene. The ZEKE spectrum of chrysene via the origin band of the intermediate electronic state S_{l} , however, can be qualitatively reproduced by a straight-forward Franck-Condon calculation. The ZEKE spectra from vibrationally excited states of the S_1 , on the other hand, demonstrate some degree of mode selectivity: the overall intensity of the ZEKE spectrum can vary by an order of magnitude depending on the vibrational mode of the intermediate state. A scaling factor in the theoretical vibrational frequency for the cation is also needed to compare with the experimental result, unlike tetracene and pentacene.

4.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds consisting of more than two fused aromatic rings without any heteroatoms or substituents. Depending on the number of shared carbon atoms between adjacent hexagonal rings, PAHs can be further separated into two categories: cata-condensed species with no carbon atoms shared by more than two rings, and otherwise, peri-condensed species. Although conceptually simple in atomic structure, PAHs have a range of properties in electronic structures.¹⁻³ As a few groups including our own have discovered, many PAHs exhibit strong configuration interactions, and great care has to be exerted in calculating properties of excited electronic states.⁴⁻¹⁰ Closely spaced electronic states complicate the assignment of vibronic transitions, and vibronic coupling in PAHs is prevalent.¹¹ The chemical stability and structural rigidity of these species are tied to the detailed connectivity of each carbon atom and the symmetry of the overall molecular structure.

Aside from their fundamental interests in physical chemistry, PAHs are also studied in environmental sciences because of incomplete combustion of carbonaceous fuels,^{12,13} in biology because of their carcinogenicity,¹⁴⁻¹⁷ in molecular electronics because of their readily available mobile π electrons,¹⁸⁻²⁰ and in astrophysics as a candidate species in the interstellar medium.²¹⁻²⁹ The possibility of neutral and charged PAHs as carriers of the unidentified infrared bands and/or diffuse interstellar bands has been investigated for over four decades. Apart from identification of functional groups in the mid-infrared (MIR) spectral region, however, confirmation of specific PAHs in the interstellar medium is still yet to be achieved.^{25,30-32} Establishment of a database in the fingerprint far infrared (FIR) region of PAHs and their cationic and anionic species is therefore instrumental for the next phase of space exploration.

Our research group has been engaged in a series of investigations of PAH cations in the far-infrared using resonantly enhanced multiphoton ionization (REMPI) and zero kinetic energy (ZEKE) photoelectron spectroscopy.^{8-10,33,34} We have reported spectroscopic analysis of cata-condensed species including tetracene and pentacene, and peri-condensed species including pyrene, benzo[a]pyrene, and benzo[g,h,i]perylene. In this work, we report another cata-condensed species chrysene, an isomer of tetracene but with a kink in the chain of the fused hexagonal rings. We analyze the observed vibronic transitions of the excited electronic state based on density functional theory (DFT) calculations using the Gaussian 09 suites,³⁵ but with a cautious interpretation of the theoretical result. We notice that the kink in the chain structure has a profound effect on the molecular orbitals of chrysene. Furthermore, the stability of ZEKE Rydberg states demonstrates mode dependence, implying a mode-specific decay mechanism of the relevant states. This situation is drastically different from the other two cata-condensed species tetracene and pentacene.^{33,34} Rather, the complication of the molecular orbitals is similar to that of a peri-condensed species pyrene.⁸ Our results on chrysene will be compared with previous reports using several different experimental techniques.^{3,36-39} In addition, we offer the first experimental result on several ag modes of this C2h molecular cation in the FIR. Assignment of these bands further provides a scaling factor of 0.9766, which is smaller than those from our previous studies of PAHs, and quite different from tetracene and pentacene. Our results, in combination with those from matrix isolation studies, offer the possibility of fitting both IR active and forbidden modes of chrysene cation from FIR to MIR.^{40,41}

4.2 Experimental

The experimental apparatus and procedure have been published earlier.^{8,33} The title compound chrysene (Aldrich) was heated to 200°C for sufficient vapor pressure, and a small time-of-flight mass spectrometer confirmed the intact molecular structure of the sample. In the REMPI experiment, the ionization laser was set at 300 nm while the resonant laser scanned across the vibronic structures of the first excited electronic state of chrysene. In the ZEKE experiment, the resonant laser was set at the chosen vibronic structure from the REMPI experiment while the ionization laser scanned across the ionization laser was set at the chosen vibronic structure from the REMPI experiment while the ionization laser scanned across the was 1 - 2 μ s in a DC spoiling field of ~ 1 V/cm, and the amplitude of the electric pulse was ~ 5 V/cm.

4.3 Results

Two-color 1+1' *REMPI spectroscopy*

The two-color 1+1' REMPI spectrum of chrysene near the origin of the $S_1 \leftarrow S_0$ electronic transition is displayed in Figure 4.1. The observed lowest energy transition is also the most intense in the spectrum, and it is assigned as the origin band. To emphasize the frequencies of the observed vibronic bands, the spectrum in Fig. 4.1 is shifted by 28195 cm⁻¹, i. e. the transition energy of the electronic origin. The wavelengths of the lasers have been calibrated using neon transitions from an opto-galvanic lamp, and the


uncertainty in wavelength is about 1 cm⁻¹. The observed linewidth, on the other hand, is 3 - 4 cm⁻¹.

Figure 4.1. (1+1') REMPI spectrum of jet-cooled chrysene. The spectrum is shifted by 28195 cm⁻¹ (the origin of the electronic transition) to highlight the frequencies of the different vibronic transitions. The molecular structure is also included in the inset. The top panel (a) is the experimental spectrum, and the calculation using the Franck-Condon principle in the bottom panel (b) is inverted for comparison. The inset in panel (b) shows the overall intensity distribution without scaling of the origin band. Only the bold-phased transitions have yielded observable ZEKE spectra as shown in Fig. 4.2.

We have performed calculations of both the ground and excited electronic states of chrysene using the Gaussian 09 suite³⁵ to assist with the spectroscopic assignment. The ground electronic state was obtained from the density functional theory method and the B3LYP functional with the 6-311G (d,p) basis set. For the excited electronic state, time dependent density functional theory (TDDFT) with the 6-31G (d,p) basis set was used. The REMPI spectrum was calculated with the Herzberg-Teller (HT) vibronic coupling option. The resulting spectrum is also plotted in Fig. 4.1 for comparison.

The calculation is only in qualitative agreement with the experimental results, and the agreement is substantially inferior to our previous work on BaP and BghiP.^{9,10} Other than the overly strong origin band, the cluster of modes 23 - 26 misses two major peaks, and modes 13 and 14 are also mismatched in intensity. Nevertheless, this degree of agreement offers some guidance to the assignment of the observed vibronic bands. Table 4.1 lists the observed vibronic transitions, all of which are of a_g symmetry. Based on the spectroscopic convention, these modes are numbered 1 - 29 in the order of decreasing frequencies. The resulting scaling factor based on a least squares fitting is 0.964, with a coefficient of determination (R^2) of 0.9998.

Experiment	Calculation*	Assignment
278	281	55 ¹ 54 ¹
290	283	29^{1}
543	532	<i>26¹</i>

666

 25^{1}

655

Table 4.1 Observed and calculated vibrational frequencies for the excited electronic state of chrysene[&]

752	755	24^{1}
842	835	$28^{1}27^{1}$
851	851	23^{1}
1237	1245	16 ¹
1343	1346	14^{1}
1369	1369	13 ¹
1442	1441	10 ¹

 $^{\&}$ All observed modes are of a_g symmetry, and only the bold-phased transitions have yielded observable ZEKE spectra.

* A scaling factor of 0.964 is included in the calculation result.

Previous spectroscopic reports on the vibronic structures of chrysene are limited.³⁷ The work by Borisevich et al using laser induced fluorescence and dispersed fluorescence techniques has identified the majority of the a_g modes of the S_I state.³⁷ Our assignments of the band origin and most of the features below 1250 cm⁻¹ are the same as those of Borisevich et al, but higher vibrational bands differ both in experimental values and in assignment.

ZEKE spectroscopy

By setting the resonant laser at each vibronic transitions observed in the REMPI experiment and scanning the ionization laser, we attempted to obtain ZEKE spectroscopy of the cation. However, this effort was only successful for the origin band and modes 23, 25 and 26. The intensity of mode 13 is comparable to those of the lower frequency modes in Fig. 4.1, but repetitive efforts resulted in no ZEKE signal. In addition, the ZEKE spectra obtained via the origin and via mode 25 were about an order of magnitude

stronger than those from modes 26 and 23. Figure 4.2 shows the resulting spectra, with qualitative indications of the signal intensity. The identity of the vibrational level of the intermediate state for each ZEKE spectrum is labeled in the corresponding panel by a black dot. The experimental and theoretical values are shown in Table 4.2, and the assignment of the cation is noted by a superscript "+". Limited by the linewidth of the resonant transitions and the pulsed electric field, the uncertainty of the experimental values of the ZEKE spectra is 7 cm⁻¹.



Figure 4.2. Two-color ZEKE spectra of chrysene recorded via different vibrational levels of the intermediate electronic state: (a) 0^0 , (b) 26^1 , (c) 25^1 , and (d) 23^1 . The energy in the *x*-axis is relative to the ionization threshold at 61219 cm⁻¹. The assignment in the figure refers to the vibrational levels of the cation, and the corresponding vibrational level of the intermediate state is labeled by a black dot in each panel.

Intermediate vibronic level			Cation		
origin	26 ¹	25 ¹	23 ¹	Calculation*	Assignment ^{&}
0				0	origin
280				280	29^{+}
369				368	28^+
471				466	27^{+}
535	534			545	26^{+}
671		670		671	25^{+}
	833			826	$26^{+}29^{+}$
			866	864	23^{+}
			883	890	$39^{2+}(b_g)$
	912			913	$26^{+}28^{+}$
		1040		1040	$25^{+}28^{+}$
	1077			1090	26^{2+}
		1202		1216	25 ⁺ 26 ⁺

Table 4.2 Observed and calculated vibrational frequencies of chrysene cation

*A scaling factor of 0.9766 is included in the calculation result. [&]All modes are of a_g symmetry except for mode 39^+ (b_g) as noted.

The spectrum from the origin band in the bottom panel is by far the most intense, resulting in the appearance of several low frequency ag modes of the cation that were unobservable in the REMPI spectrum. From the energy of the origin band, taking into consideration of the shifts due to the pulsed ionization field in the ZEKE experiment, the ionization threshold is determined to be 61219 cm⁻¹. This value is 163 cm⁻¹ above that reported by Schmidt from photoelectron spectroscopy.²

Vibrational assignment of the observed bands was mostly based on our calculation of the cationic state using the density functional theory method, the B3LYP functional, and the 6-311G (d,p) basis set. The FC calculation of the ZEKE spectrum from the origin of the S_1 state is shown in Figure 4.3. Given the limited qualitative agreement in the REMPI spectrum of Fig. 4.1, the agreement in Fig. 4.3 is quite Although the origin band is still too strong for the calculation, the remarkable. distribution of vibrational modes is every similar between the two spectra. Based on the spectral assignment, a least squares fitting of the observed fundamental frequencies of modes 23 - 29 resulted in a scaling factor was 0.9766 with a R² value of 0.9994. The reduction in theoretical vibrational frequencies reduces the deviation from experimental values to within 6 cm⁻¹, except for mode 26, in which case, the theoretical value is 9 cm⁻¹ above that of the experiment. This scaling factor is within the range of those of Langhoff,⁴¹ but smaller than our previous values from other PAHs.^{8,33,34} In particular, our earlier studies of tetracene and pentacene have both concluded on the high accuracy in frequency calculations from DFT for the cation,^{33,34} and no scaling was needed to fit the experimental values.



Figure 4.3. Comparison between experimental (top) and simulated (bottom) ZEKE spectra from the origin of the S_1 state.

Regardless of the overall strength of the ZEKE signal, interestingly, all spectra are dominated by the same vibrational mode of the intermediate state, and all the combination bands of each individual spectrum contain the same vibrational mode as that of the intermediate state, except for trace (d). This observation is in line with the propensity rule observed from our previous studies of PAHs^{8,33,34} and a series of substituted benzene derivatives.⁴²⁻⁴⁴

The weaker ZEKE spectra from modes 26 and 23 both demonstrate a doublet feature for the strongest band, and assignment of these bands has proven challenging. In the top panel (d), the separation of the doublet is nearly 20 cm⁻¹, but no other fundamental modes of a_g symmetry from calculation are close to the value of 883 cm⁻¹ after scaling. However, the fundamental frequency of a b_g mode and a second harmonic of yet another b_g mode are both close in energy to the observed band. Taking the symmetry selection rule into consideration, we therefore tentatively assign the higher energy component $39b_g^{2+}$. The doublet feature in panel (b) from mode 26 has a splitting of 7 cm⁻¹, and in Table 4.2, mode 26 demonstrates the largest deviation between calculation and experiment. At ~540 cm⁻¹, this band is unlikely to be the 2nd harmonic of lower frequency Franck-Condon forbidden modes with non- a_g symmetry, since our calculation only shows 6 modes that are below the fundamental frequency within 100 cm⁻¹. Currently we do not have an explanation for this doublet splitting.

Our ZEKE result complements previous work on infrared spectroscopy of PAH cations using matrix isolation spectroscopy.⁴⁰ In the work of Hudgins and Allamandola,⁴⁰ IR active modes from 676 cm⁻¹ to 1593 cm⁻¹ were reported. Even within

the overlapping spectral region, none of our modes are IR active, hence our results offer more data points for the vibrational spectroscopy of the cation. Combination of the two different types of measurements offers the possibility of global fitting for the best scaling factor, which could assist with astrophysical modeling and chemical identification of PAH compounds.

4.4 Discussion

Electronic state

The calculation for the vibrational frequencies of the electronically excited neutral state was obtained by setting the keyword in Gaussian 09 root = 2, i. e., we believe that the TDDFT calculation reversed the order of the S_1 and S_2 states.⁸ This belief is based on our analysis of the molecular orbitals and previous theoretical and experimental reports.^{2,3,36,38} Figure 4.4 shows the highest occupied molecular orbital (HOMO), the next lower energy orbital HOMO-1, the lowest unoccupied molecular orbitals (LUMO), and the next higher energy orbital LUMO+1 with the corresponding nodal planes. The HOMO and HOMO-1 orbitals both have 4 nodal planes each, and the LUMO and LUMO+1 orbitals both have 5 nodal planes each. This qualitative result implies that the energies of the HOMO and HOMO-1 orbitals are probably similar, while those of the LUMO and LUMO+1 orbitals are similar. A potential complication is thus configuration interaction, which could result in a wrong order from the straightforward calculation. Our previous experience with peri-condensed PAHs has confirmed this situation,⁸⁻¹⁰ and to obtain a reasonable vibrational assignment, the keyword has to be set with root = 2 for pyrene, BaP, and BghiP.



HOMO-1



HOMO



LUMO



Figure 4.4. Calculated molecular orbitals of chrysene with nodal planes. The broad arrow in the top panel for the HOMO represents the general direction of the long axis in the discussion.

The distribution of the nodal planes is also indicative of the nature of the electronic transitions and the direction of the transition dipole. Due to the low symmetry of the molecular structure, the nodal planes do not have a consistent direction, and for the

ease of discussion, we designate the long axis to be along the general direction shown by the arrow in the inset of the HOMO. We notice that both near degenerate transitions of HOMO-1 to LUMO and HOMO to LUMO+1 involve the addition of a nodal plane along the long axis of the molecular frame, and the transition dipoles should therefore be along the long axis. The HOMO-LUMO transition, on the other hand, involves multiple rearrangements of nodal planes: those along the long axis are increased from 2 to 5, and those along the short axis disappear. The direction of the transition dipole, however, should still be along the long axis. We therefore expect two electronic transitions that are of similar energies and of the same symmetry, one from the HOMO-LUMO transition, and the other from the nearly degenerate pair of HOMO-1 to LUMO or HOMO to LUMO+1. This situation of chrysene is drastically different from that of tetracene, where the nodal planes of HOMO-1, HOMO, LUMO, and LUMO+1 increase consecutively from 3 to 6. In this clear-cut case of tetracene, the Gaussian program, regardless of calculation method, has no problem in calculating the order and symmetry of related electronic states.

Our belief that the S_2 state from TDDFT is actually the observed electronic state agrees with previous experimental and theoretical reports.^{2,3,36,38} According to Schmidt,² the electronic transitions in PAHs could be categorized into two cases, and chrysene belonged to case B with the lowest transition α (${}^{1}L_{b}$) type and a transition dipole moment along the long axis. In contrast, tetracene belonged to type A with the lowest transition p (${}^{1}L_{a}$) and a transition dipole along the short axis. Schmidt also suggested that this inversion in transition order of case B molecules was due to the strong configuration interactions of the nearly degenerate transitions of HOMO-1 to LUMO and HOMO to LUMO+1. This inversion would happen if the difference in orbital energies between HOMO and HOMO-1 was less than 0.5 eV. From polarization dependence of two photon excitation spectroscopy, Liem *et al* confirmed the symmetry of the first electronically excited state at ~27730 cm⁻¹ to be ${}^{1}B_{u}$ (${}^{1}L_{b}$).³⁶ From single photon excitation at 257 nm, Langelaar et al observed dual fluorescence from chrysene corresponding to two electronically excited states separated by ~4000 cm⁻¹,³⁸ and the lower component was considered ${}^{1}L_{b}$ of chrysene. The fluorescence lifetime was also observed to decrease with increasing internal energy. Nijegorodov and Winkoun established a correlation diagram for the electronic energy levels of a few cata-condensed PAHs,³ and their analysis agrees with our results on both chrysene and tetracene. The linear and magnetic circular dichroism measurements by Spanget-Larsen, Waluk, and Thulstrup³⁹ reported two closely spaced electronic states of chrysene, and the *S_I* state at 27600 cm⁻¹ was assigned the ${}^{1}L_{b}$ state. However, the authors concluded on a transition dipole direction along the short axis, opposite to the general belief for a ${}^{1}L_{b}$ transition.

In our previous work on pyrene where similar confusion of S_1 and S_2 states was reported,⁸ some evidence for the inversion in state order was obtained from assignment of the vibrational spectroscopy. For chrysene, this effort was futile partially because of the small number of observed modes. Furthermore, the two electronically excited states have the same symmetry, and vibronic coupling does not activate any new types of modes. The corresponding vibrational frequencies of both electronic states are also similar, and we only need to adjust the scaling factor slightly to obtain the same assignment in terms of mode number and fitting quality for both states. In this sense, the experimental vibrational frequencies cannot offer any definitive clue as to the nature of the observed electronic state.

The unusual discrepancy between calculation and experiment for the REMPI spectrum in Fig. 4.1 is puzzling considering the fact that even when there was an ordering problem with the excited electronic states of BghiP and BaP,^{9,10} we were able to duplicate the REMPI spectra by setting "root = 2" in our CIS calculations and by taking HT coupling into consideration. For chrysene, neither CIS nor TDDFT could improve the agreement to any observable degree, with or without HT coupling. Perhaps more extensive configuration calculations, such as complete active space self-consistent field or perturbation theory methods, are required for this system.

Transition from S_1 *to* D_0

The overall intensity of a ZEKE spectrum from different intermediate vibronic levels of S_I demonstrates mode dependence: the fundamental frequency of mode 25 is in between those of modes 23 and 26, but the intensity of its ZEKE spectrum is about one order of magnitude stronger. In addition, the intensity of mode 13 in Fig. 4.1 is similar to those of modes 23 – 26, but there was no ZEKE signal to be observed in our experiment. Although we do expect that the stabilities of ZEKE Rydberg states decrease with increasing internal energy of the ionic state, the strong ZEKE signal for mode 25 is inconsistent with this trend. The calculation in Fig. 4.3 shows regular Franck-Condon behavior for mode 25 when ionized from the origin band of the S_I state. However, opposite from all previous studies of ZEKE spectroscopy of PAHs,^{8-10,33,34} the origin band from calculation is actually a few folds weaker than that from the experiment. In Fig. 4.1, the calculation of the REMPI spectrum considerably underestimates the intensities of modes 25 and 23. These discrepancies are all manifestations of complicated vibronic dynamics in the seemingly simple molecule chrysene. To our knowledge, there has been just one similar report in the literature on vibrational mode dependence of ZEKE states.⁴⁵ In the work from Grant's group on three photon ionization of NO₂,⁴⁵ the ZEKE intensity was observed to be weaker for the symmetric stretching mode than for other modes of the cation, and vibrational autoionization of ZEKE Rydberg states was proposed for this intensity abnormally. In diatomic molecules such as CO,⁴⁶ some degree of relaxation between two nearly degenerate series of Rydberg states was proposed, but by and large, the ionic core was proven to exert minimal effect on the Rydberg electron, even when the core goes through radiative decay or dissociation.^{47,48}

Nevertheless, each ZEKE spectrum in Fig. 4.2 is dominated by one single transition, showing clear preference for preserving the vibrational excitation of the intermediate state. This propensity is considered a sign of molecular rigidity during ionization.^{8,33,34,42-44} In this aspect, chrysene seems to have even more capacity to accommodate the additional charge than tetracene.³⁴ Similar to tetracene, Mulliken population analysis also reveals that the central rings have more positive charges than the side rings: 0.30 vs 0.20 electrons, in agreement with the reactivity of different carbon atoms from organic chemistry.

Comparisons with tetracene and other PAHs

In our previous work on tetracene and pentacene prior to the availability of Gaussian 09,^{33,34} we have reported excellent agreement between the experimental and

DFT calculations for the frequency of the cation. However, the intensity distributions were way off. The availability of TDDFT and Herzberg-Teller coupling and our success with a few peri-condensed PAHs⁸⁻¹⁰ prompted us to revisit the calculation of the two cata-condensed PAHs. Unlike the cases of peri-condensed PAHs and chrysene, neither tetracene nor pentacene is plagued by two nearby electronic states, hence there is no confusion as to the molecular orbitals of the excited state, and vibronic coupling should be minimal. Figure 4.5 shows the REMPI and ZEKE spectra of tetracene overlapped with our new calculation using the Gaussian 09 suite. Both the neutral and ionic ground state were calculated using DFT with the B3LYP functional and the 6-31G basis set, and the electronic excited state was obtained using TDDFT with the 6-31G basis set. The calculated REMPI spectrum in Fig. 4.5 was obtained with the HT option, but the results remain the same even without vibronic coupling. For pentacene, however, the situation is

still hopeless for any qualitative agreement in the intensity distribution, with or without the HT option.





Figure 4.5. REMPI (a) and ZEKE (b) spectra of tetracene from the origin band of the REMPI spectrum. The grey lines are calculations using DFT (a) and TDDFT (b) from Gaussian 09, and the dotted lines are experimental results from reference ³⁴. The frequency scaling factor for the REMPI spectrum is 0.9862, but no scaling is necessary for the ZEKE spectrum from the origin band of S_1 .

The additional kink in the molecular structure of chrysene seems to have an effect not only on the molecular orbitals and the relaxation dynamics of vibronic states, but also on the rigidity of the molecular frame of the cation. In the case of tetracene, one out-ofplane mode was observed in both the REMPI and the ZEKE spectra, while in chrysene, only in the ZEKE spectrum is one out-of-plane mode observable. The lower symmetry of chrysene seems to have enhanced the rigidity of the cation, in agreement with our previous conclusions on a few peri-condensed species.⁸⁻¹⁰ For pentacene, in contrast, only out-of-plane rippling modes of the ribbon were observed, and no FC allowed transitions were detected. Pentacene is perhaps an extreme case that cannot be resolved with our limited computational resources.

Among the sampled PAHs that demonstrate reasonable agreements between calculations and experiments, tetracene³⁴ is an isomer of chrysene, and the pericondensed systems⁸⁻¹⁰ span a range of sizes, with some smaller while others bigger than chrysene. The success of these samples makes it difficult to understand the discrepancy in the REMPI spectrum of chrysene in Fig. 4.1. In addition, the frequency calculations for cata-condensed PAHs tetracene and pentacene require no scaling,^{33,34} but the situation is different for chrysene.

4.5 Conclusion

Compared with tetracene, chrysene is only different by a kink in the fused hexagonal chain. Yet this kink seems to wrack havoc, both in terms of molecular orbitals and vibrational frequencies. Configuration interaction dominates the first electronic transition, and careful tweaking of the calculation keywords is needed to obtain the correct nature of the relevant electronic state. The stability of the ZEKE Rydberg states, on the other hand, demonstrates dependence on the vibrational mode of the ionic core. Although for the straight cata-condensed polyacenes such as tetracene and pentacene, DFT calculations have proven reliable in predicting the vibrational frequencies of the cations, a kink in the linear structure calls for a scaling factor of 0.9766 from the calculation. Our conclusion demonstrates the complexity of this seemingly simple group

of PAH compounds.

Acknowledgement

This work is supported by the National Aeronautics and Space Administration under

award No. NNX09AC03G.

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Chapter 5. Zero Kinetic Energy Photoelectron Spectroscopy of Benzo[*h*]quinoline

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Manuscript for submission to the Journal of Physical Chemistry A, Special Issue entitled: Dynamics of Molecular Collisions XXV: Fifty Years of Chemical Reaction Dynamics, June 19, 2015

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Abstract

We report zero kinetic energy (ZEKE) photoelectron spectroscopy of benzo[h]quinoline (BhQ) via resonantly enhanced multiphoton ionization (REMPI) through the first electronically excited state S_I . From the simulated REMPI spectra with and without Herzberg-Teller coupling, we conclude that vibronic coupling plays a minor but observable role in the electronic excitation to the S_1 state. We further compare the S_1 state of BhQ with the first two electronically excited states of phenanthrene, noticing a similarity of the S_1 state of BhQ with the second electronically excited state S_2 of phenanthrene. In the ZEKE spectra of BhQ, the vibrational frequencies of the cationic state D_0 are consistently higher than those of the intermediate neutral state, indicating enhanced bonding upon ionization. The sparse ZEKE spectra, compared with the spectrum of phenanthrene containing rich vibronic activities, further imply that the nitrogen atom has attenuated the structural change between S_1 and D_0 states. We speculate that the nitrogen atom can withdraw an electron in the S_1 state and donate an electron in the D_0 state, thereby minimizing the structural change during ionization. The origin of the first electronically excited state is determined to be 29410 ± 5 cm⁻¹ and the adiabatic ionization potential is determined to be 65064 ± 7 cm⁻¹.

Key words: zero kinetic energy photoelectron spectroscopy, resonantly enhanced multiphoton ionization, benzo[*h*]quinoline, polycyclic aromatic hydrocarbons, far infrared spectroscopy

5.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) consist of fused benzene rings without any heteroatoms and with characteristic delocalized π electrons. When one or more nitrogen atoms are included in the molecular frame, the resulting molecule is denoted as PANH. Spectroscopy of PAHs and PANHs is not only interesting from a fundamental point of view, but also of practical value in the fields of astrophysics and astrobiology.¹⁻⁴ Infrared (IR) and far-infrared (FIR) bands have been observed to emanate from deep space since the 1970s and more recently by the Herschel Space Telescope and the Stratospheric Observatory for Infrared Astronomy.^{2,5-11} These ubiquitous unidentified infrared bands (UIB) are thought to contain spectroscopic signatures of molecules that constitute the interstellar medium (ISM), hence identification of these suspected molecules through spectroscopic assignments could help to determine the chemical composition of the ISM.^{12,13} The close match between the UIB spectra and transitions of several functional groups of aromatic molecules alludes to the possibility of PAHs in the ISM.^{2,5,7,14,15} The existence of PANHs has been postulated because of their relatively strong bands between 1000 - 1750 cm⁻¹; a region associated with the C-N-C in-plane vibrations.¹⁶⁻¹⁸ The presence of stray interstellar ionizing radiations further suggests the possibility of ionized PAHs and PANHs.^{7,15,19} From the perspective of astrobiology, PAHs and PANHs are of particular interest because of their potential relation to the origin of life through the formation of primitive organic molecules, including ribonucleic acids in a pre-DNA environment.^{3,20} Fundamentally, comparative studies of PAHs and PANHs are also of interest in physical chemistry; nitrogen substitution into the molecular frame of a polycyclic aromatic hydrocarbon lowers the molecular symmetry and interrupts the aromaticity of the molecule.^{1,19,21}

Far-infrared spectra are considered to be fingerprints for PAH species because of their sensitivity to molecular skeletal modes,²²⁻²⁴ and zero kinetic energy (ZEKE) photoelectron spectroscopy offers a unique and powerful approach for obtaining frequency information of FIR bands.²⁵ The mid and near infrared spectral regions contain localized vibrational modes which are characteristic of specific functional groups, and experimental studies in these regions have been prolific: examples include single-photon infrared emission spectroscopy, matrix isolation spectroscopy (MIS), and cavity ringdown spectroscopy.^{7,26-30} The far-infrared spectral region, on the other hand, suffers from low oscillator strength as well as other experimental difficulties, including inadequate light sources and insensitive detectors. Zero kinetic energy photoelectron spectroscopy, governed by a completely different set of selection rules from infrared spectroscopy, however, is ideal for detecting low energy vibrational modes of cations using commercially available light sources and efficient microchannel plate detectors.³¹ Using ZEKE, we have studied four peri-condensed species including pyrene, benzo[a]pyrene, benzo[e]pyrene and benzo[ghi]perylene as well as four cata-condensed species including triphenylene, tetracene, pentacene and chrysene.³²⁻³⁹ Our ZEKE data, supplemented by matrix isolation spectroscopy and other excitation and fluorescence spectroscopy,^{7,26-30} allow for a comprehensive analysis of the vibrational states of cationic PAHs. These experimental results can further benchmark theoretical calculations and astrophysical modeling.40,41

In this work, we report resonantly enhanced multi-photon ionization (REMPI) spectroscopy of the first electronically excited state S_I as well as ZEKE spectroscopy of the cationic state D_0 of benzo[h]quinoline (BhQ). We compare the spectroscopic features of BhQ with those of two isoelectronic systems phenanthrene and anthracene, and comment on the unique contribution of the nitrogen atom.^{16,18,42-46} We observe that in terms of molecular orbitals, the first two electronic states of BhQ are in reverse order relative to those of phenanthrene, a not-so-subtle effect of the heteroatom in the molecular frame.⁴⁴⁻⁴⁷ The low molecular symmetry has relaxed the selection rule in vibronic transitions, allowing all in-plane modes to be observable. Nevertheless, the ZEKE spectra are sparse, implying structural similarities between the cation and the first excited electronic state. We also notice a consistent increase in the vibrational frequencies of several observed modes in the D_0 state compared with those from the S_I state, an indication of increased aromaticity upon ionization.

5.2 Experimental Setup and Calculation Method

The experimental apparatus consisted of a differentially pumped molecular beam apparatus with the detection chamber enclosed inside the source chamber, as detailed in several of our previous publications.³²⁻³⁹ A time-of-flight mass spectrometer in the detection chamber also served as the pulsed field ionization zero kinetic energy spectrometer. Benzo[*h*]quinoline (Aldrich) was housed and heated to 84°C in a pulsed valve (Parker Finnegan, Series 9) with a 1 mm orifice located in the source chamber. The sample vapor was seeded in 1700 Torr of argon and co-expanded into vacuum through

the pulsed valve. The sample beam was further collimated by passing through a 2 mm skimmer before reaching the detection chamber for laser excitation and ionization. The laser system for the REMPI experiment included a Nd:YAG (Spectra Physics, GCR 190) pumped dye laser (Laser Analytical System, LDL 20505) equipped with a frequency doubler for excitation and an optical parametric oscillator (Continuum, Panther, pumped by Precision I 8000) for ionization. The excitation laser in the 322.5 - 342.6 nm range had a typical pulse energy of ~ 1 mJ/pulse with a bandwidth of 0.5 cm⁻¹. The ionization laser in the 273 - 281 nm range had a pulse energy of ~ 0.5 mJ/pulse with a bandwidth of 0.3 cm⁻¹. The absolute wavelengths of both lasers were calibrated using an iron hollowcathode lamp filled with neon based on values from the National Institute of Standards and Technology. The excitation and ionization lasers were set to counter-propagate, and the light path, the flight tube, and the molecular beam were mutually perpendicular. Two delay generators (Stanford Research, DG 535) controlled the timing of the lasers, and the optimal signal was obtained via temporal and spatial overlap of the two lasers. In the ZEKE experiment, molecules were excited to high Rydberg states for 400 ns in the presence of a constant DC spoiling field (below 50 mV/cm), after which ionization and extraction were achieved by a pulsed electric field of 2 V/cm.

The Gaussian 09 suite⁴⁸ was used to optimize the molecular structure, to obtain frequencies from the optimized molecular frame and to simulate the observed vibrational structures from the REMPI and ZEKE experiments. For the ground state of the neutral and cationic state, density functional theory (DFT) calculations using the B3LYP functional were performed with the 6-31G basis set. The S_1 and S_2 electronically excited states were calculated using time dependent density functional theory (TD-DFT) with the B3LYP functional and the 6-31G basis set. Further details of the calculation will be provided in the following section.

5.3 Results

Two-color 1+1' REMPI spectroscopy

The two-color 1+1' REMPI spectroscopy of benzo[h]quinoline near the origin of the $S_1 \leftarrow S_0$ electronic transition is displayed in Figure 5.1. The ionization laser was set at 280 nm and was temporally and spatially overlapped with the scanning resonant laser. After each laser shot, a complete time-of-flight mass spectrum could be observed, and clear presence of intact molecular ions of BhQ could be identified as the excitation laser was scanned through the recorded spectral region. Other than the appearing and disappearing parent ion with wavelength, the mass spectrum contained no sign of molecular clusters or other impurities. We briefly varied the stagnation pressure and the heating temperature of the sample, with no effect on the resulting mass spectrum, further eliminating the possible contribution of molecular clusters. Each data point was an average of over 100 laser shots, and the spectrum was repeated over a period of three months. The band second to the lowest energy transition at 29410 ± 5 cm⁻¹ was assigned as the origin and was the second most intense in the spectrum. The assignment for the lowest energy transition as a hot band of $(1a'')^2$ was based on two considerations. First, by improving the cooling condition of the supersonic molecular beam, we were able to lower the intensity of the putative hot band, and second, the simulated REMPI spectrum agreed with the current assignment (see Fig. 5.2).



Figure 5.1. REMPI spectrum of benzo[h]quinoline shifted by 29410 cm⁻¹. The peak observed at -183 cm⁻¹ is assigned as a hot band based on simulations and experimental observations. The molecular structure with designations of axes is also included.



Figure 5.2. Comparison between the experimental REMPI spectrum from Fig. 5.1 and simulation using DFT at the B3LYP/6-31G level, with and without Herzberg-Teller coupling.

Table 5.1 lists the frequencies of the observed vibrational bands, frequencies from the calculation, and spectroscopic assignments. The vibrational frequencies were calculated using TDDFT at the B3LYP/6-31G level. Based on our current assignment and using the least-squares fitting procedure, we obtained a scaling factor of 0.963 for the calculated frequency with a coefficient of determination of 0.9998. The experimental data were limited by the linewidth of each band, which resulted in an uncertainty of 5 cm⁻¹.

Experimental	Calculation [†]	Assignment
-185	-204*	1a" ²
230	223	1a'
307	308	1a"4a"
<u>395</u>	<u>394</u>	<u>2a'</u>
399	400	3a'' ²
<u>409</u>	<u>416</u>	<u>3a"4a"</u>
446	435	3a'
492	488	4a'
521	521	5a'
<u>584</u>	<u>586</u>	<u>6a'</u>
<u>669</u>	<u>674</u>	<u>7a'</u>
<u>705</u>	<u>700</u>	<u>8a'</u>
709	711	1a'4a'
720	719	5a" ²
733	737	5a"6a"
797	788	2a ^{,2}
834	835	9a'
841	849	10a'

Table 5.1. Observed vibrational bands for the S_1 (A') state of benzo[*h*]quinoline. Bands in bold-faced italic font are intermediate states which have yielded ZEKE spectra (units: cm⁻¹, uncertainty: \pm 5 cm⁻¹).

846	843	5a"8a"
872	870	3a ^{,2}
937	936	2a"15a"
973	980	2a'6a'
1011	1010	12a'
1021	1021	3a'6a'
1028	1010	4a'5a'
1034	1037	13a'
1061	1068	2a'7a'
1075	1089	15a'
1115	1110	3a'7a'
1208	1193	19a'
1322	1327	23a'
1335	1338	7a' ²
1365	1363	24a'
1375	1376	7a'8a'
1390	1378	25a'
1392	1392	3a ^{,2} 5a [,]
1395	1396	26a'
1407	1416	27a'
1416	1415	1a'19a'
1438	1441	29a'
1459	1452	30a'
1493	1498	32a'
1507	1506	33a'
1510	1509	7a'9a'
1515	1502	2a'16a'
1518	1512	13a" ²
1525	1527	34a'

[†] Including a scaling factor of 0.963.

* Including the scaling factor of 0.961 obtained for the cationic ground state D_0 .

The first two electronically excited states of BhQ are closely spaced in energy, and the proximity can be a source of confusion for the DFT calculation.^{32-38,48} We simulated the excitation spectra to both the putative S_1 and S_2 electronic states, and to further illustrate the effect of Herzberg-Teller (HT) vibronic coupling, we also calculated a spectrum containing only the Franck-Condon factor for the vibronic bands to the S_1 state. The calculation results are shown in Fig. 5.2 for comparison with the experimental data. The similarity between panels (c) and (d) confirms the assignment of the $S_1 \leftarrow S_0$ transition. Moreover, HT coupling introduces few new vibrational modes; rather the intensities of some vibronic bands, in particular, the 7a' band, are visibly enhanced.

The agreement between simulation and experiment can further assist with spectral assignment. For example, the band at 446 cm⁻¹ has a deviation of 11 cm⁻¹ from the calculation, but because of its presence in the simulated spectrum, we are comfortable in its identity as the 3a' band. A similar situation exists for the band at 1208 cm⁻¹ (19a'). The experimental spectrum contains several clusters of congested transitions above 700 cm⁻¹. Although the calculation has reproduced some of the clusters of transitions, the density of transitions from the calculation is still below that of the experiment. Consequently, assignment within each cluster is difficult and tentative, and some unusually large deviations are noticeable. Moreover, the transition at 409 cm⁻¹ is clearly missing in the calculation. Our tentative assignment of a combination band 3a"4a" is based on possible combinations of low frequency bands and the selection rule for vibronic transitions. The assignment of this band will be discussed again in the ZEKE

experiment. Overall mostly in-plane vibrational modes can be observed, for example, the 2a' mode involving elongation along the long axis and the 7a' mode corresponding to breathing of the molecular frame.

The observed vibronic distribution of Fig. 5.1 is largely similar to the fluorescence excitation spectrum reported by Prochorow, Deperasińska and Stepanenko (PDS).⁴⁹ However, the spectrum of the PDS report contains two bands below the strongest band at 29409 cm⁻¹, and the lowest energy band at 29226 cm⁻¹ is considered the origin band. If we revise the PDS assignment by shifting all vibronic bands by 184 cm⁻¹, the reported vibrational frequencies agree with our result within our uncertainty. Unfortunately, there is no symmetry assignment associated with the PDS report and hence no direct comparisons can be made.

ZEKE Spectroscopy

By scanning the ionization laser while setting the resonant laser at one of the intermediate states identified in the REMPI experiment, we obtained pulsed field ionization ZEKE spectra as shown in Figure 5.3. Similar to the REMPI spectrum, the ZEKE spectra were obtained with about 100 laser pulses per data point over a three month period. The ZEKE experiment was only successful with a few intermediate vibronic states that had relatively strong intensities in the REMPI spectrum and had internal vibrational energies below 710 cm⁻¹. The vibrational identity of the intermediate state for each ZEKE spectrum is labeled in Figure 5.3 with a black dot. The theoretical vibrational frequencies were calculated using DFT at the B3LYP/6-31G level, and a least-squares fitting procedure, similar to that used in the REMPI experiment, was used to
obtain a scaling factor of 0.961 with a coefficient of determination of 0.9983. Table 5.2 lists the observed transitions, the corresponding theoretical values, and the assignment. The experimental uncertainty of 7 cm⁻¹ is restricted by the uncertainty of the intermediate state, the linewidth of the lasers, and the pulsed electric field for ionization.



Figure 5.3. Experimental ZEKE spectra from a few selected intermediate vibronic states: (a) origin, (b) 2a', (c) 3a"4a", (d) 6a', (e) 7a' and (f) 8a'. All spectra are shifted by the adiabatic ionization threshold of 65064 cm⁻¹. Modes marked with a black dot are the correlated modes of the intermediate state.

Origin	2a'	3a"4a"	6a'	7a'	8a'	Calc [†]	Assignment
	<u>395</u>					395	2a'
		<u>477</u>				447	3a"4a"
			<u>600</u>			604	ба'
688				<u>700</u>		692	7a'
					<u>719</u>	712	8a'
					807	787	5a"6a"
	1075					1087	2a'7a'
			1281			1296	6a'7a'
				1383		1384	7a ^{,2}

Table 5.2. Observed vibrational transitions of the D_0 state of benzo[*h*]quinoline from several intermediate vibronic transitions. The bands in bold-faced italic font are the correlated diagonal bands of the intermediate state (units: cm⁻¹, uncertainty: ± 7 cm⁻¹).

† Including a scaling factor of 0.961

Panel a in Figure 5.3 contains the ZEKE spectrum recorded from the origin of the first electronically excited state, and the calculated spectrum is overlaid with the experimental data in grey based on the Franck-Condon factors of the electronic transition $D_0 \leftarrow S_1$. Once again the calculation has captured the essence of the experimental spectrum, with a predominant origin and a few much weaker vibrational bands, particularly the 7a' band corresponding to the breathing mode of the whole molecular frame. The adiabatic ionization threshold of BhQ is thus determined to be 65064 ± 7 cm⁻¹ (8.067 ± 0.001 eV) after taking into consideration the effect of the ionization field. This value is approximately 200 cm⁻¹ higher than that from the photoelectron spectroscopy study conducted by Hush, Cheung and Hilton (8.04 ± 0.02 eV), and our value represents more than an order of magnitude increase in precision.⁵⁰

All panels in Fig. 5.3 are characteristically sparse, containing primarily the band corresponding to the same vibrational excitation of the intermediate state. The 7a' breathing mode is present in four out of the six spectra as a combination with the predominant vibrational band. Panel c was obtained via the 3a"4a" intermediate level and the observed ZEKE transition was assigned as 3a"4a" in keeping with the propensity rule,³²⁻³⁹ although just from vibrational frequency and selection rule points of view, the observed strongest transition could be assigned as (4a")² at 470 cm⁻¹. The weaker transition in panel f was also assigned as a combination band of two out-of-plane modes because the next nearest in-plane vibration was at 837 cm⁻¹, 30 cm⁻¹ above the observed transition.

5.4 Discussion

*Nature of the S*₁ *State*

Aromaticity leads to degenerate or near degenerate molecular orbitals, which can produce closely spaced excited electronic states. With the introduction of a nitrogen atom in BhQ, reorganization of the nearly degenerate electronic states can be expected. Based on our calculation, the majority of the oscillator strength (60%) of the $S_1 \leftarrow S_0$ transition is derived from the transition between the highest occupied molecular orbital to the lowest unoccupied molecular orbital (the LUMO \leftarrow HOMO transition), and it is $\pi\pi^*$ in character. The resulting change in the molecular frame is elongation along the long axis by 0.04 Å (0.5%) and contraction along the short axis by 0.02 Å (0.5%). In contrast, for phenanthrene, an isoelectronic and structural analogue of BhQ, the first electronic transition is a mixture of transitions involving LUMO \leftarrow HOMO - 1 and LUMO + 1 \leftarrow HOMO, while the second electronic transition is LUMO \leftarrow HOMO.⁴⁶ Based on our calculation, the molecular frame of the S_I state of phenanthrene exhibits elongation along the long axis by 0.6% and minimal change along the short axis (0.05%), while that of the S_2 state has an elongated molecular frame by 0.06 Å (0.8%) along the long axis and a contracted frame by 0.03 Å (0.7%) along the short axis. The similarity in the structural change and in the nature of electronic transitions both testify to the correlation between the two electronic states of the two molecular systems, i. e., the S_1 state of BhQ corresponds to the S_2 state of phenanthrene.

The elongation along the long axis and the contraction along the short axis of the frame dimension account for the activities of the stretching mode 2a' and the breathing mode 7a' in the REMPI spectrum of BhQ. Comparable modes and frequencies have also been observed in the study of phenanthrene,⁴⁴ although for phenanthrene, the vibrational frequencies for both the S_1 and the S_2 states are similar. It appears that while the introduction of a nitrogen atom into the molecular frame affects the nature of electronic states, it has little effect on the bond strength and thereby the vibrational frequencies of the molecule.

This effect of the nitrogen atom on the nature of the electronic state has also been reported previously.⁴⁷ Yi, Alvarez-Valierra and Pratt have studied the electronic transitions of fluorene and its nitrogen and oxygen substituted analogues carbazole and dibenzofuran.⁴⁷ The authors have concluded that the introduction of a heteroatom causes the transition moment of the first electronic excitation to rotate by 90° relative to that of fluorene. This rotation is a direct result of reordering of the closely spaced molecular

orbitals and related transitions, similar to the case of BhQ. The authors have further observed, as we do here, that the overall geometry of the molecular system is minimally affected by the introduction of a heteroatom in the ground state.

Nature and vibrational spectroscopy of the D_0 *state*

Based on our calculation, the optimized structure of the cationic state of BhQ shows further contraction along the short axis compared with the first electronically excited state, by about 0.5%, while the dimension along the long axis remains unchanged. This progressive shortening of the short axis from S_0 to S_1 to D_0 is unique to BhQ since for all the PAHs we have observed previously, the structures of S_0 and D_0 are similar while that of S_1 is distorted.³²⁻³⁹ Nevertheless, the degree of change upon ionization is still low enough that a propensity of preserving the vibrational excitation of the intermediate state is still observable in Fig. 5.3 for all ZEKE spectra.

While the states D_0 and S_1 may be structurally similar, there is a notable difference in the vibrational frequencies, possibly denoting a difference in the bond strength or rigidity of the two states. Almost all observed vibrational frequencies for the D_0 state, with the exception of the 2a' mode, are blue shifted from those of the S_1 state, as shown in Table 5.3. An increase in out-of-plane vibrational frequencies implies an increase in planar rigidity, a trait that is directly correlated to aromaticity.

Mode	S_{I}	D_0	$D_0 - S_1$
2a'	395	395	0
3a"4a"	409	477	68
6a'	584	600	16
7a'	669	700	31
8a'	705	719	14
5a"6a"	733	807	74

Table 5.3. Frequencies of several observed vibrational modes in the cationic state D_0 and the first electronically excited state S_I of benzo[h]quinoline (units: cm⁻¹, uncertainty: \pm 7 cm⁻¹)

Compared with the mass analyzed threshold ionization (MATI) spectroscopy of phenanthrene reported by Piest *et al*, the ZEKE spectra of BhQ are much sparser.⁴³ Although the MATI spectrum from the origin of the S_I state of phenanthrene also contains a predominant origin band, many more low frequency bands have been reported, with three particularly strong features centering at 240, 550, and 700 cm⁻¹, and some out-of-plane modes.⁴³ Using DFT at the B3LYP/6-31G level and based on the Franck-Condon factor from S_I to D_0 , we have qualitatively reproduced the vibronic activities in the MATI/ZEKE spectrum of phenanthrene from the origin of the S_I state. For comparison, we have also calculated the MATI/ZEKE spectrum of phenanthrene from the origin of the S_2 state. Different vibronic bands in the resulting spectra are observed from the two different electronic states, but both spectra show similar levels of vibronic activities. In contrast, the ZEKE spectrum of BhQ contains essentially only one in-plane vibrational band of 7a'.

The difference in vibronic structures of the ZEKE/MATI spectra between BhQand phenanthrene is intriguing. Our group has investigated the ZEKE spectroscopy of a series of benzene derivatives via resonantly enhanced multiphoton ionization.⁵¹⁻⁵⁴ In all cases, we have discovered that the electron rich substituent attenuates the geometric change from S_1 to D_0 , resulting in a vibronically active REMPI spectrum but sparse ZEKE spectra. In the MATI experiment of pyridine through REMPI,⁵⁵ with the exception of one spectrum obtained through an out-of-plane mode, all other spectra follow the propensity rule. These results are in direct contrast to the ZEKE spectrum of benzene where extensive vibrational progressions have been reported.⁵⁶ It seems that the nitrogen atom in BhQ has a similar effect as the substituent in the benzene derivatives and pyridine, maintaining the molecular frame during ionization from S_1 to D_0 .

Our assessment of the effect of the nitrogen atom in the S_1 and D_0 states of BhQ has been implied in the literature.^{16-18,21} Several groups have investigated the cationic ground state of BhQ using matrix isolation spectroscopy and infrared multiphoton dissociation (IRMPD).^{16,18} The work of Mattioda *et al.* using MIS has revealed that PANHs does not present new signature vibrational bands, but rather, some transitions in the region of 1100 - 1600 cm⁻¹ and 500 - 600 cm⁻¹ are enhanced, corresponding to the C-C and C-N stretching, C-N-C in-plane bending, and C-N-C out-of-plane vibrational modes.¹⁷ Using a free electron laser for multiphoton dissociation, Galue *et al.* have discovered enhanced vibrational activities in the same region of cationic PANHs, although many bands from their IRMPD experiment are red-shifted due to vibrational anharmonicity.¹⁸ Based on these enhancement effects, Mattioda *et al.* have made an interesting observation that "the nitrogen atom in the aromatic network of the PANHs

produces a pseudo-ionization effect.¹⁷ Incidentally, the ZEKE spectra of anthracene, an isomer of phenanthrene without the kink in the structure, defy the propensity rule and contain a vibrational progression.²⁷

A plausible interpretation of the effect of the nitrogen atom can be glimpsed from the charge distribution among the relevant electronic states. Based on the Mulliken population analysis from our calculation, the $S_1 \leftarrow S_0$ transition increases the negative charge on the nitrogen atom from -0.41 to -0.46 electron, and shifts ~ 0.1 electron from the farthest ring to the nitrogen containing ring. Upon ionization, on the other hand, the nitrogen containing ring loses 0.44 electron, while the farthest ring loses 0.35 electron. We therefore speculate that the stabilizing effect of the nitrogen atom comes from its electron withdrawing effect in the S_1 state and its electron donating ability in the D_0 state. Thus electron rich and electronegative substituents can buffer the geometric change from S_1 and D_0 by modifying the S_1 state to be more like the ionic state, and by modifying the D_0 state to be more like the S_1 state.

5.5 Conclusion

The vibrational characteristics of the first electronically excited state and the ground cationic state were studied using 1+1' two-color REMPI and two-color ZEKE spectroscopic techniques. The closely spaced excited electronic states of aromatic systems could easily be switched in order by the addition of a heteroatom, which was the case when we compare BhQ and its isoelectronic system phenanthrene. Using DFT at the B3LYP/6-31G level, we were able to qualitatively reproduce the observed REMPI

spectrum and assign the vibrational bands. The ZEKE spectra obtained from a few intermediate vibronic states were sparse, following the propensity of preserving the vibrational excitation of the intermediate state. However, the vibrational frequencies of the cation were all higher than those of the S_I state, implying stronger bonding in the cationic state. From comparisons between the MATI spectrum of phenanthrene and the ZEKE spectra of BhQ, we believe that similar to the case of electron rich substituents of benzene,⁵¹⁻⁵⁴ the nitrogen atom has played an important role in the bonding of both S_I and D_0 states, resulting in the extra geometrical stability upon ionization. This is in contrast to the ZEKE or MATI spectra of phenanthrene and anthracene, where neither show strong propensity in vibrational distribution.

Acknowledgments

This work is supported by the National Aeronautics and Space Administration under award No. NNX09AC03G.

5.6 References

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Chapter 6. Resonantly enhanced multiphoton ionization and zero kinetic energy

photoelectron spectroscopy of Benzo[e]pyrene

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Manuscript for submission to the journal of Chemical Physics Letters, September 13, 2012

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Abstract:

We report zero kinetic energy (ZEKE) photoelectron spectroscopy via resonantly enhanced multiphoton ionization (REMPI) for benzo[e]pyrene. Extensive vibronic coupling between the first electronically excited state and a nearby state allows b₂ symmetric modes to be observed which would normally be Franck-Condon (FC) disallowed. These vibronic modes are comparable in intensity to the FC allowed a₁ modes. Gaussian 09 is able to qualitatively simulate the vibronic spectra of the REMPI and the ZEKE experiment using density functional methods. The ZEKE spectra demonstrate propensity in preserving the vibrational excitation of the intermediate electronic state. These results suggest a remarkable structural stability of BeP in accommodating the additional charge.

Key words:

photoionization spectroscopy, polycyclic aromatic hydrocarbons, zero kinetic energy photoelectron spectroscopy, far infrared vibrational spectroscopy, vibronic coupling.

6.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of molecules that are observed in pollution, in comet tails, and possibly in the interstellar medium. In biology, PAHs are lipophilic and many are known carcinogens.¹⁻³ In astrobiology, it has been hypothesized that PAHs could be related to the origin of life by forming the first primitive organic molecules including amino acids in the pre-DNA world.⁴⁻⁶ In astrophysics, PAHs have been observed in a wide range of galactic and extragalactic environments.^{7,8} They are considered responsible for a range of spectroscopic absorption and emission features, and hence their rovibronic quantum states have substantial implications to the energy balance in the universe.⁹⁻¹⁶

Many spectroscopic studies of neutral and cationic PAHs have been motivated by astrophysical modeling.¹⁷⁻²⁴ Both the infrared and visible/ultraviolet regions have been extensively investigated using photoionization spectroscopy, cavity ringdown, as well as infrared absorption and emission spectroscopy techniques.^{18,25-29} The far-infrared (FIR) region has been largely untouched because of issues related to the detector sensitivity and light source intensity. On the other hand, the FIR region is occupied by skeletal vibrations of the molecular frame, and it is considered the "finger-print region" for spectroscopic identification of astrophysical PAHs.

The technique of zero kinetic energy (ZEKE) photoelectron spectroscopy offers an indirect solution to the challenges in the FIR for laboratory astrophysics.³⁰ In recent years, we have undertaken the mission of mapping out the low frequency vibrational modes of PAHs using ZEKE spectroscopy.³¹⁻³⁶ So far we have reported 3 peri-condensed species including pyrene, benzo[*a*]pyrene (B*a*P), benzo[*g*,*h*,*i*]perylene (B*ghi*P), and 3 cata-condensed species including tetracene, pentacene, and chrysene.³¹⁻³⁶ In this report, we investigate the vibronic spectra of benzo[*e*]pyrene, an isomer of B*a*P as shown in the inset of Figure 6.1. While the highly carcinogenic isomer B*a*P has been extensively investigated previously,³⁶⁻⁴¹ B*e*P has only been

reported in a few studies.^{21,42,43} We use resonantly enhanced multiphoton ionization (REMPI) to probe the vibronic structure of the first excited electronic state S_I , and the ZEKE technique to probe the skeletal modes of the cationic state D_0 . Additional insights can be obtained from comparisons with other PAHs and theoretical calculations.

6.2 Experimental setup

The experimental apparatus is a differentially pumped molecular beam machine, with the detection chamber enclosed inside the source chamber.^{32,44} A time-of-flight mass spectrometer in the detection chamber also serves as the pulsed field ionization zero kinetic energy photoelectron spectrometer. The sample benzo[e]perylene (Aldrich) was housed and heated to 260 °C in the pulsed valve located in the source chamber to achieve sufficient vapor pressure. The vapor was seeded in 400 torr of argon and co-expanded into vacuum through a pulsed valve with a 1 mm orifice. After passing through a 2 mm skimmer, the cooled sample reached the detection chamber for laser excitation and ionization. The laser systems for the REMPI experiment included two Nd:YAG (Spectra Physics, GCR 190 and GCR 230) pumped dye lasers (Laser Analytical System, LDL 20505 and LDL 2051), both equipped with frequency doublers. The excitation laser in the 370 - 350 nm range had a typical pulse energy of > 1.0 mJ/pulse with a bandwidth of 0.5 cm^{-1} . The ionization laser in the 300 - 309 nm range had a pulse energy of ~1 mJ/pulse with a bandwidth of 0.3 cm⁻¹. The absolute wavelength of each laser was calibrated using an iron hollow-cathode lamp filled with neon. The pump laser and ionization laser were set to counterpropagate, and the light path, the flight tube, and the molecular beam were mutually perpendicular. Two delay generators (Stanford Research, DG 535) controlled the timing of the lasers, and the optimal signal was obtained under temporal overlap between the pump and ionization lasers. In the ZEKE experiment, molecules were excited to high Rydberg states for 600 ns in the presence of a small constant DC spoiling field, after which ionization and extraction were achieved by a pulsed electric field of ~ 2 V/cm.

The Gaussian 09 suite ⁴⁵was used to optimize the molecular structure, to obtain vibrational frequencies, and to simulate the observed vibronic structures from REMPI and ZEKE.⁴⁵ For the ground state of the neutral and the cationic state, density functional theory (DFT) calculations using the B3LYP functional were performed with the 6-311G basis set. The excited state S_I was calculated using both time dependent density functional theory (TD-DFT) with the B3LYP functional and the 6-311G basis set and the configuration interaction singles (CIS) with the 6-31G basis set. Details of the calculations will be provided in the following.

6.3 Results

Two-color 1+1' REMPI spectroscopy

The 1+1' REMPI spectrum was collected near the origin of the $S_1 \leftarrow S_0$ electronic transition of BeP and is displayed in Figure 6.1. The ionization laser was set at 33,000 cm⁻¹ and was temporally and spatially overlapped with the scanning resonant laser. The origin was observed to be 26,983 ± 5 cm⁻¹, which is 9 cm⁻¹ higher than the origin reported by Misawa *et. al.* (no uncertainty was reported in this reference).⁴³ The other observed vibronic transitions are listed in Table 6.1, with the labeling scheme following the Herzberg convention. For clarity, the molecular axes have been included in an inset of the figure.



Figure 6.1. REMPI spectrum of benzo[*e*]pyrene. The spectrum is shifted by 26,983 cm⁻¹ -- the origin of the $S_1 \leftarrow S_0$ transition -- to emphasize the frequencies of the different vibrational modes of the S_1 state. The molecular structure and the definition of molecular axes are also shown in the inset.

Experimental	Calculation*	Assignment	Symmetry
251	245	90 ¹	1b ₂
374	377	30^{1}	$2a_1$
401	402	89 ¹	$2b_2$
537	533	28^1	$4a_1$
746	748	84^{1}	7b ₂
753	753	26^{1}	6a ₁
755	754	30^{2}	$2a_1^2$
917	929	83 ¹	8b ₂
1200	1199	78^{1}	13b ₂
1282	1266	76 ¹	15b ₂
1312	1305	16 ¹	16a ₁
1321	1317	15 ¹	17a ₁
1378	1386	73 ¹	18b ₂
1415	1397	13 ¹	19a ₁
1478	1480	70^1	21b ₂
1571	1586	7^1	25a ₁

Table 6.1 Observed and calculated vibrational frequencies of the S_1 state of benzo[e]pyrene.

*The calculation result includes a scaling factor of 0.973.

Based on our previous experience, PAHs are prone to vibronic coupling.^{32-36,44} Fortunately, Gaussian 09 incorporates a new feature of Herzberg-Teller (HT) coupling, which in general, yields outstanding accuracy in transition frequencies and vibrational intensity distribution. Figure 6.2 shows the comparison of calculation results with the experimental spectrum. Given the possibility of order switching in the calculated electronic states,^{33-36,46-48} we performed two calculations, one to the putative $S_1(A_1)$ state with the keyword root = 1 and the other to the putative $S_2(B_2)$ state with root = 2. Both were at the B3LYP/6-311G level for the excited electronic state. In Fig. 6.2, the transition to the $S_1(A_1)$ state is clearly a better match to the experimental spectrum, with a diminished origin band and an intense cluster of bands at ~ 750 cm⁻¹. The calculation for the $S_1(A_1) \leftarrow S_0(A_1)$ transition also states that the oscillator strength derives from the near degenerate pairs of LUMO \leftarrow HOMO-1 and LUMO+1 \leftarrow HOMO, where HOMO and LUMO represent the highest occupied molecular orbital and the lowest unoccupied molecular orbital respectively. The transition to the S_2 state, on the other hand, is of LUMO \leftarrow HOMO in nature.



Figure 6.2. Comparison between different calculations of the vibronic spectra using Gaussian 09 for both the $S_1 \leftarrow S_0$ (b & c) and the $S_2 \leftarrow S_0$ transitions (a) with the experiment (d). The calculation without Herzberg-Teller coupling for the $S_1 \leftarrow S_0$ transition (b) is also shown for comparison. An inset is included in the calculation with HT coupling (c) to show the detail in the 730-765 cm⁻¹ region.

While the agreement between calculation and experiment is not quantitative, it is good enough for a general guidance regarding vibrational assignment. In Table 6.1 and Fig. 6.1, most bands are assigned as a_1 or b_2 modes of the C_{2V} point group, and the presence of the latter modes is a pure result of vibronic coupling with the nearby $S_2(B_2)$ state. The current assignment further results in a scaling factor of 0.973 for the theoretical frequencies. Overall the spectrum has a weak origin band, and the relative intensities of the Franck-Condon (FC) allowed a_1 bands and the FC forbidden but vibronic allowed HT bands are similar.

Assignment of the vibronic structure is straightforward for the first few low frequency modes, but high energy bands are problematic. The cluster of peaks at 750 cm⁻¹ is challenging to assign for several reasons. The theoretical calculation could only reproduce the first two peaks of the triplet feature (inset of Fig. 6.2c), which can be assigned as mode 84 (7b₂) and 26 (6a₁). In Table 6.1, the second harmonic of mode 2a₁ and the fundamental frequency of 6a₁ are essentially degenerate, and both are higher than the 7b₂ band by ~5 cm⁻¹. We believe that the high intensity of the 2a₁² band is related to the complication of this Fermi resonance among all three bands. The band at 917 cm⁻¹ could be assigned as a combination of 2a₁ and 4a₁, but based on the calculation, it probably belongs to a 8b₂ band, which has a larger deviation (12 cm⁻¹) than the combination band (7 cm⁻¹). A few other bands, such as those at 1282, 1378, and 1571 cm⁻¹, can also be assigned as combination bands or fundamental bands of higher frequency modes. Unlike the 8b₂ bands, however, these bands are not reproduced from the simulation spectrum and hence the only criterion for their assignment comes from the theoretical frequencies. The listed assignment in Table 6.1 is therefore tentative for these bands.

All observed modes are in-plane deformation modes. Similar to our previous observation on BaP,³⁶ the modes of BeP can be categorized into three groups, including two groups localized in the pyrene (modes 30, 89, and 28) and the benzene (modes 90) moieties, and the overall skeletal deformation of the molecular frame (modes 84, and 26).^{31,36} The lowest frequency mode 90 is essentially wagging of the benzene ring around the short axis of the pyrene backbone. The next three low frequency modes are in-plane deformations or wagging of the pyrene moiety, with the additional benzene ring tagging along and making no observable internal structural changes. It is interesting to note that while B*a*P and B*e*P belong to very different point groups, they both seem to surrender to the extreme stability of the pyrene moiety in exhibiting localized vibrational modes on pyrene or the additional benzene ring.^{36,44}

6.4 ZEKE Spectroscopy

By setting the first laser at one of the intermediate states identified in the above experiment and scanning the second laser, we were able to observe the vibrational bands of the D_0 electronic state using pulsed field ionization ZEKE. Figures 6.3 and 6.4 show the ZEKE spectra collected from the eight intermediate states labeled in Fig. 6.1 in bold-phased fonts. Unfortunately, efforts of recording more ZEKE spectra for intermediate levels with more than 800 cm⁻¹ vibrational energies were unsuccessful, particularly for the 16a₁ band at 1312 cm⁻¹, which is the strongest band in the REMPI spectrum. The spectral assignment, together with the calculation results scaled by 0.9697, is listed in Table 6.2. The spectrum from the origin band of Fig. 6.1a corresponds to the origin of the cation, which results in an adiabatic ionization threshold of $59,766 \pm 7$ cm⁻¹, including corrections due to the pulsed electric field. This value is about 100 cm⁻¹ below what reported by Clar and Schmidt based on photoelectron spectroscopy (7.41 eV).⁴⁹

0	90 ¹	30 ¹	89 ¹	28^{1}	84 ¹	26 ¹	30^{2}	Calc*	Assignment
0								0	0
	248							247	$90^{1} (1b_{2})$
		379						379	$30^{1}(2a_{1})$
			394					394	89 ¹ (2b ₂)
				542				544	$28^{1} (4a_{1})$
				555				558	87 ¹ (4b ₂)
					753			753	84 ¹ (7b ₂)
							759	753	$30^2 (2a_1^2)$
					766			768	$89^{1}30^{1}(2b_{2}+2a_{1})$
					775	777		771	$26^{1}(6a_{1})$
					801	801	796	801	$90^{1}87^{1}$ (1b ₂ +4b ₂)
				1084				1083	$28^2 (4a_1^2)$
				1094				1098	$87^{1}28^{1} (4b_{2}+4a_{1})$
					1295			1297	$84^{1}28^{1}$ (7b ₂ +4a ₁)
					1306			1307	89 ¹ 30 ¹ 28 ¹

 Table 6.2 Observed and calculated vibrational frequencies of BeP cation.

*The calculation result includes a scaling factor of 0.9697.

The most striking feature of Figure 6.3 is the lack of any vibrational structure beyond the single transition corresponding to the same vibrational mode (termed diagonal bands in the following) of the intermediate state. This simplicity in the ZEKE spectra is an exemplary case of propensity reported in our studies of substituted aromatic compounds and a few PAHs.^{32-36,44,50,51} The dominance of the diagonal band manifests the diagonal Franck-Condon factor between the intermediate state and the cationic state. This means that the geometry and normal modes of B*e*P do not change upon ionization. Based on this belief, assignment of the ZEKE spectra in Figure 6.4 relies on the correlation with the mode of the resonant state. For example, similar to the REMPI spectrum, the cluster of vibrational bands near 750 cm⁻¹ is again congested with many closely spaced transitions. In Table 6.2, although the 7b₂ and $2a_1^2$ because of the identity of the intermediate vibronic state.



Figure 6.3. Two-color ZEKE spectra of B*e*P recorded via the following vibrational levels of the S_I state as intermediate states: (a) 0^0 , (b) 90^1 , (c) 30^1 , and (d) 89^1 . The energy in the figure is relative to the ionization threshold at 59,766 cm⁻¹. The assignment in the figure refers to the vibrational levels of the cation, and the corresponding vibrational level of the intermediate state is labeled by a black dot in each panel. An inset is included in (a) to show the Franck-Condon result from the origin band of S_I .



Figure 6.4. Two-color ZEKE spectra of B*e*P recorded via the following vibrational levels of the S_1 state as intermediate states: (a) 28^1 , (b) 84^1 , (c) 26^1 , and (d) 30^2 . The energy in the figure is relative to the ionization threshold at 59,766 cm⁻¹. The assignment in the figure refers to the vibrational levels of the cation, and the corresponding vibrational level of the intermediate state is labeled by a black dot in each panel.

Simulation of the ZEKE transition from the origin of the intermediate state is shown in the inset of Fig. 6.3a. The simulated ZEKE spectrum has an intense origin, with essentially no other observed transitions on the scale of the inset. Although vibronic coupling plays an important role in the REMPI process, the next step of ionization strictly follows the Franck-Condon principle. Moreover, there is minimal structural change upon elimination of the excited electron from S_1 .

6.5 Discussions

Vibrational band distributions and implications in geometry variation

The REMPI spectrum contains both Franck-Condon allowed a_1 bands and vibronic allowed b_2 bands, and overall the two types of bands are of comparable intensity. In addition, the origin band is considerably weaker than a few of the vibronic bands. While the former observation implies extensive vibronic coupling, the latter seems to imply large geometry changes upon electronic excitation. Upon ionization, the ZEKE spectra contain almost exclusively diagonal bands, alluding to an invariant molecular frame with the removal of the electron from the intermediate state. In addition, the vibrational frequencies of the corresponding modes of the S_1 and D_0 states are similar. Although one electron is missing between the two states, the bond strengths, at least for those related to the skeletal motions below 1500 cm⁻¹, remain largely unchanged.

Our calculated molecular structures, on the other hand, paint a picture of stability of B*e*P for all three related electronic states. The overall length and width of the molecular structure vary less than 1% in all cases, similar to the degree of variation for tetracene and pentacene, and

slightly larger than the other peri-condensed systems we have reported ($\sim 0.5\%$).^{32-34,36,44} The weak origin band thus seems to be not related to large geometry changes.

The extensive vibronic coupling in the REMPI spectrum of BeP is confirmed from the Franck-Condon calculation without the HT option in Fig. 6.2b. The resulting origin band becomes so strong that it dominates the REMPI spectrum. Among all the peri-condensed PAHs we have investigated,^{34,36,44} the degree of vibronic coupling in BeP is by far the most extensive. For cata-condensed species, an even more extreme case was observed in pentacene.^{32,33,35} While our Gaussian calculation with and without HT both predicted overwhelmingly strong totally symmetric a₁ modes for the REMPI spectrum of pentacene, the experimental spectrum contained only FC forbidden out-of-plane waving modes. On the other hand, the electronic transition in pentacene was fully symmetry allowed, and the S_2 state was over 5000 cm⁻¹ higher in energy than the S_1 state. The energy gaps between the two lowest excited electronic states vary from 2000 cm⁻¹ to over 5000 cm⁻¹ among Bep, B*a*p, B*ghi*p, pyrene, tetracene, chrysene, and pyrene, and these values do not seem to have a direct correlation with the degree of HT coupling.^{32-36,44} Currently, we do not have an explanation for the seemingly extraordinary degree of vibronic coupling in BeP and in pentacene.

All observed modes are in plane deformation modes, and all are IR active for this C_{2v} system. The vibrational levels of the neutral ground state S_0 and the cationic state D_0 of BeP have been probed by gas chromatography/Fourier transform infrared spectroscopy (GC/FT-IR) and matrix isolation spectroscopy (MIS) in the region above 600 cm⁻¹.^{17,21} Neither groups performed high level *ab initio* or density functional calculations, hence the vibrational assignment was based on comparisons with other PAHs. For the S_0 state, several bands between 700 and 900 cm⁻¹ were considered out-of-plane C-H bending modes, and one band at ~700 cm⁻¹ was assigned as C-C inplane bending. The corresponding modes of the D_0 state were compared with those of the S_0 states, and the result was regarded as unusual by the authors.¹⁷ While the C-C in-plane mode was

red shifted by 62 cm⁻¹, the C-H out-of-plane modes were *blue* shifted by nearly ~80 cm⁻¹. Furthermore, the intensities of these bands were also an order of magnitude too low compared with those of their neutral counterparts. Within the region of spectral overlap, unfortunately, we did not observe any common modes with the previous studies, hence no direct frequency comparisons are possible. We do notice interestingly that the general spectral intensity distribution of the GC/FT-IR spectrum is somewhat similar to our REMPI spectrum of Fig. 6.1, with intense activities between 700 and 900 cm⁻¹. Since the two techniques probe two different electronic states and follow completely different selection rules, this similarity should be a mere coincidence. Nevertheless, bands in this region seem to be particularly sensitive to any changes in the internal energy of the molecular system, as observed in our other studies of PAHs.^{32-36,44} As to the unusual vibrational frequency shifts in the D_0 state,¹⁷ the similarity in frequency between the neutral and the cationic state of our gas phase experiment implies nothing extraordinary in the force field and molecular structure of B*e*P. Most likely, these shifts were due to the influence of the argon matrix in the MIS experiment.

The geometry, Mulliken charge distribution and IR spectroscopy have all been calculated in a separate work by Pathak and Rastogi for both the neutral and cation using B3LYP/4-31G.⁵² The reported geometries and charge distributions can be related to our results by a scaling factor, arising from the difference in the two basis sets.

Comparisons with other PAHs

Most of the peri-condensed PAHs that we have investigated so far, including B*a*P, B*e*P, and B*ghi*P, have been reasonably successful for vibrational assignment and spectral simulation, particularly with the vibronic coupling feature of Gaussian 09.^{34,36,45} All peri-condensed PAHs and chrysene have at least two closely spaced excited electronic states. In many cases, CIS

calculations from Gaussian suffer from the confusion of the closely spaced states, and a keyword has to be set artificially to avoid the problem.^{44,46-48} Even with this confusion, on the other hand, HT calculations based on the displacement vectors and frequencies are still satisfactory in reproducing the observed REMPI spectrum, and with the use of scaling factors, the observed vibrational bands for both S_I and D_0 can be assigned.

This situation is somewhat different for the cata-condensed species including tetracene, pentacene, and chrysene.^{32,33,35} While tetracene is an example of mostly Franck-Condon behavior for REMPI, chrysene, an isomer with just a kink in the ribbon structure, could not be reproduced satisfactorily in vibronic transition intensities.^{32,35} With an additional ring than tetracene, pentacene is an extreme with no Franck-Condon allowed vibrational bands observable in the REMPI spectrum and no calculation methods were able to even qualitatively reproduce the vibronic features.^{32,33} However, the vibrational frequencies for cationic tetracene and pentacene obtained from DFT calculations are so close to the experimental values that no scaling factors are necessary. Moreover, neither molecule has closely spaced excited electronic states for vibronic coupling.

Although seemingly simple, the above comparison alludes to the fact that each PAH has its unique situation, and a generalization of properties is questionable at this stage. Overall, the HT feature in Gaussian 09 has dramatically improved our abilities in modeling the REMPI and ZEKE spectroscopy of peri-condensed species. However, human interference is still necessary for the choice of the correct electronic state and for vibrational scaling. The cata-condensed systems are still difficult to model for *ab initio* or DFT calculations.

An interesting observation in the ZEKE experiment of the PAHs is the existence of a cutoff energy of the intermediate state: when the excess vibrational energy of the intermediate state is above a certain value, for example, 800 cm^{-1} for BeP, no more ZEKE signal can be

observed from the intermediate state. In chrysene, we also observed mode selectivity in the overall ZEKE signal.³⁵ The cutoff energy does not seem to have a direct correlation with the size of the molecular system; for the largest molecule BghiP among our studies, we were able to record ZEKE spectrum from bands with nearly 1100 cm⁻¹ vibrational energy.³⁴

6.6 Conclusion

The vibrational spectra of benzo[*e*]pyrene were recorded for both the first electronically excited state and the ground state of the cation. Vibronic coupling was observed to play a major role in the REMPI spectrum, and the intensities of FC forbidden but vibronic allowed bands are similar to those of FC allowed bands. Using the relatively new feature of Gaussian 09, we were able to include Herzberg-Teller coupling for the simulation of the REMPI spectrum with satisfactory results. The ZEKE spectra demonstrate a propensity for preserving the vibrational excitation of the intermediate state, but as the energy excess from the origin of the *S*₁ state increases to ~800 cm⁻¹, no more ZEKE signal was observable, similar to our previous report on B*ghi*P and chrysene. All observed modes are IR active, but a direct comparison with results from matrix isolation spectroscopy is impossible due to lack of common vibrational modes. Nevertheless, the small variation of vibrational frequency from *S*₁ to *D*₀ of our experiment does reveal some unsettling effect of the argon matrix in shifting the frequency and changing the transition intensity.

Acknowledgement

This work is supported by the National Aeronautics and Space Administration under award No. NNX09AC03G.

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Chapter 7. Zero Kinetic Energy Photoelectron spectroscopy of jet cooled benzo[*a*]pyrene from resonantly enhanced multiphoton ionization

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Manuscript for submission to J. Chem. Phys., September 12, 2011

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Running title: ZEKE and REMPI spectroscopy of benzo[a]pyrene

Key words: photoionization spectroscopy, vibrational spectroscopy, polycyclic aromatic hydrocarbons, ZEKE spectroscopy

Significance: This work maps out many of the low frequency vibrational modes of cationic benzo[a]pyrene, and clarifies the electronic configuration of the 1st electronically excited state. The former type of information is difficult if possible to obtain using other experimental techniques, and the experimental data not only help with calibration of theoretical calculations but also shed light on the fundamental effect of electronic excitation and ionization.

Abstract

We report zero kinetic energy (ZEKE) photoelectron spectroscopy of benzo[a]pyrene (BaP) via resonantly enhanced multiphoton ionization (REMPI). Our analysis concentrates on the vibrational modes of the first excited state (S_1) and those of the ground cationic state (D_0) . Similar to pyrene, another peri-condensed PAH we have investigated, the first two electronically excited states of BaP exhibit extensive configuration interactions. However, the two electronic states are of the same symmetry, hence vibronic coupling does not introduce any out-of-plane modes in the REMPI spectrum, and Franck-Condon analysis is qualitatively satisfactory. The ZEKE spectra from the in-plane modes observed in the REMPI spectrum demonstrate strong propensity in preserving the vibrational excitation of the intermediate state. Although several additional bands in combination with the vibrational mode of the intermediate state are identifiable, they are much lower in intensity. This observation implies that the molecular structure of BaP has a tremendous capability to accommodate changes in charge density. All observed bands of the cation are IR active, establishing the role of ZEKE spectroscopy in mapping out far infrared bands for astrophysical applications.

7.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrocarbon molecules with fused six member aromatic ring frames terminated with peripheral hydrogen atoms. They are an important group of molecules for laboratory astrophysical studies because of their possible role in infrared emission in the interstellar medium (ISM) and their potential as an energy and carbon storage reservoir.¹⁻⁷ In the mid 1970s, a series of unidentified infrared (UIR) bands, including features at 3.3, 6.2, 7.7, 8.6, and 12.7 μ m, have been discovered in a spectroscopic study of planetary nebulae.¹ Later on, these UIR bands have been shown to be ubiquitous for a variety of astronomical sources. It is well accepted now that these 3.3 – 17.4 μ m features can be characterized as C-H, C-C or C-C-C stretching modes.²⁻⁷ Polycyclic aromatic hydrocarbons have since been considered an important subject of astrophysical investigations. Given the abundant radiation sources in the ISM, ionic PAHs have also been considered promising carriers of the UIR bands.⁸

For comparisons with astrophysical observations, efforts have been made on the study of laboratory infrared spectroscopy of PAHs and their cations, including matrix isolation spectroscopy,^{11,12} infrared emission,¹³ laser induced fluorescence, photoionization spectroscopy,¹⁴ and carvity ringdown spectroscopy.¹⁵ Unfortunately, identification of specific PAHs has been unsuccessful so far, largely due to the fact that mid-IR bands only represent local motions or functional groups of a molecule. In contrast, far-infrared (FIR) bands are sensitive to the molecular size and structure, hence FIR spectroscopy is considered "fingerprint" of individual molecule or ion. The *Herschel Space Observatory* launched in May, 2009 is aimed for the FIR and submillimeter

(submm) wavelength region of the ISM. One of the goals of Herschel is to map out the chemical composition of the ISM and the atmospheres and surfaces of comets, planets, and satellites.

Laboratory FIR spectroscopy has always been challenging due to the lack of light sources and detectors. Moreover, spectroscopy of ions is further hindered by the low achievable particle density. The technique of zero kinetic energy photoelectron (ZEKE) spectroscopy serves as an ideal tool, albeit indirect, for the study of low frequency vibrational modes of cations,¹⁶⁻¹⁸ ZEKE is known for its high resolution of cation rovibrational spectroscopy. The high Rydberg states in ZEKE are longer lived when they are associated with lower vibronic states of the cation, and this feature makes ZEKE particularly suitable for studies of lower frequency vibrational modes. Thus by detecting electrons from pulsed field ionization in ZEKE spectroscopy via resonantly enhanced multiphoton ionization (REMPI), we can avoid both the light source and the detector problems in typical FIR and sub-millimeter wave experiments. The vibrational information from ZEKE is largely governed by the Franck-Condon (FC) principle, hence the information from ZEKE might not be directly applicable for line identification in astronomy, but the information of IR inactive modes can be used for frequency calibrations of FIR spectroscopy from theoretical calculations and for modeling of the energy and chemical balance in the ISM.^{19,20}

Benzo[*a*]pyrene (B*a*P) is a five ring PAH as shown in Figure 7.1. It is the most abundant PAH in the earth's atmosphere and it is highly carcinogenic.²¹⁻²³ Although it has been more than seventy years since the first study of B*a*P,²⁴ spectroscopic information is still limited. Imasaka *et al* performed the first fluorescence excitation

spectrum in a supersonic jet and identified the origin of the first electronically excited state S_1 around 393 nm.²⁵ Greenblatt *et al* later determined the origin of the $S_1 \leftarrow S_0$ transition at 25265±20 cm⁻¹ and measured the lifetime of the first excited state to be 270 ns.²⁶ The authors further discussed the second excited state S_2 which was considered to be 1500 cm⁻¹ higher than S_1 , and attributed the long lifetime of the S_2 state to strong vibronic coupling with the S_1 state. In the work of Gittins *et al*, the first excited state was studied in a supersonic jet using fluorescence excitation and two color REMPI, and 32 modes were assigned based on their configuration interaction singles (CIS) calculation.²⁷ However, as will be discussed later, the authors did not distinguish the two closely coupled electronic states explicitly, and there might be some complications with the calculation procedure. Additional infrared spectroscopy of B*a*P and its radical ion was reported from doped wax films and argon matrices²⁸ between 400 and 2000 cm⁻¹.



Figure 7.1. Structure of benzo[a]pyrene and definition of the molecular coordinate system.

7.2 Experimental setup

The experimental apparatus is a differentially pumped high vacuum molecular beam machine, with the detection chamber enclosed inside the source chamber.¹⁶⁻¹⁸ The sample benzo[a]pyrene (Aldrich) was housed and heated to 170 °C in the pulsed valve located in the source chamber to achieve sufficient vapor pressure. The vapor was seeded in 1600 torr of argon and co-expanded into vacuum through a pulsed valve with a 1 mm orifice. After passing through a 2 mm skimmer, the cooled sample reached the detection chamber for laser excitation and ionization. The laser systems included two Nd:YAG (Spectra Physics, GCR 190 and GCR 230) pumped dye lasers (Laser Analytical System, LDL 20505 and LDL 2051). The excitation laser in the 398 - 382 nm range (Exalite 389) had a pulsed energy of 1.5 mJ/pulse with a bandwidth of 0.5 cm⁻¹. The ionization laser in the 312.3 - 304.6 nm range from the frequency-doubled dye laser (Rhodamine 610 and sulforhodamine 640) had a pulse energy of 1 mJ/pulse with a band width of 0.3 cm⁻¹. The absolute wavelength of each laser was calibrated using an iron hollow-cathode lamp filled with neon. The relative timing between the two laser pulses was controlled by two delay generators (Stanford Research, DG 535), and the optimal signal was obtained under temporal overlap between the pump and ionization lasers. In the ZEKE experiment, molecules excited to high Rydberg states were allowed to stay for 1 - 2 µs in the presence of a constant DC spoiling field of ~ 0.5 V/cm, after which ionization and extraction were achieved by a pulsed electric field of ~5 V/cm.

Gaussian 09 suite was used to optimize the molecular structure and to obtain vibrational frequencies for assignment of the observed vibronic structures from REMPI and ZEKE. For the ground state of the neutral and the cationic state, density functional theory (DFT) calculations using the B3LYP functional were performed with the 6-31+G (d,p) basis set. The excited state S_1 was calculated using the time-dependent density functional theory (TDDFT) with the 6-31G basis set.

7.3 Results

Two-color 1+1' *REMPI spectroscopy*

The two-color 1+1' REMPI spectrum of BaP near the origin of the $S_1 \leftarrow S_0$ electronic transition is displayed in Figure 7.2. The ionization laser was set at 290 nm and was temporally overlapped with the scanning resonant laser. The most intense peak at $25,205\pm3$ cm⁻¹ is assigned as the origin band, which is 28 cm⁻¹ to the red compared with the report by Gittins et al.²⁷ and 60 cm⁻¹ to the red of Greenblatt et al.²⁶ The experimental uncertainty of 3 cm⁻¹ is mostly due to the linewidth of the vibronic bands, since the linewidth of the excitation laser beam is only 0.3 cm⁻¹. Other observed vibronic transitions are listed in Table 7.1. The labeling of each vibrational mode is based on spectroscopic conventions, i. e. by using consecutive numbers in reference to the symmetry species and the frequency in decreasing order. The listed theoretical values were obtained from our TDDFT calculations by setting the keyword "root = 2" in the input file, i. e. the nominally 2nd excited electronic state, and this choice will be discussed in the latter part of this section. The values include a scaling factor of 0.9633, which was derived from a least-squares linear regression method with a coefficient of determination (R^2) of 0.9983.



Figure 7.2. REMPI spectrum of benzo[*a*]pyrene. The spectrum is shifted by 25205 cm⁻¹ - the origin of the $S_1 \leftarrow S_0$ transition -- to emphasize the frequencies of the different vibrational modes of the S_1 state.

Table 7.1. Observed and calculated vibrational frequencies of the S_1 state of benzo[*a*]pyrene

Experimental	Calculation (TDDFT) ^{&}	Assignment	Description of modes
373	369	59 ¹	Phenyl swing
451	451	58 ¹	Pyrene modes
515	505	56 ¹	Pyrene modes
523	515	55 ¹	Skeletal, longitudinal stretch

551	557	54 ¹	Pyrene modes			
593	597	53 ¹	Skeletal, transverse stretch			
626	629	52 ¹	Phenyl stretch			
688	683	51 ¹	Skeletal			
749	748	50 ¹	Pyrene modes			
793	791	49 ¹	Pyrene modes			
829	837	48 ¹	Skeletal			

[&] Scaled by 0.9633.

BaP is a planar molecule with C_s symmetry. There are altogether 90 vibrational normal modes, with 61 a' modes that are numbered 1 - 61, and 29 a" modes numbered 62 – 90. Within the range of our REMPI spectrum, 13 of the a' modes should be observable, from mode 61 to mode 48, and these modes constitute the central cluster of vibronic transitions in the spectrum. The intensities of the two lowest a' modes 60 and 61 are much weaker than those of other a' modes, and they are buried in the low frequency region leading to the major vibronic bands. Mode 57 at 473 cm⁻¹ seems to be completely missing. With the exception of mode 56, the agreement between theory and experiment is within 8 cm⁻¹, somewhat larger than the experimental uncertainty of 3 cm⁻¹. The theoretical frequency for mode 56 is significantly lower than the experimental value. As will be observed in the ZEKE experiment, the same trend of disagreement persists for the same mode in the cation. Below 350 cm⁻¹, there are several weak bands that could be tentatively assigned as overtones or combination bands of out-of-plane a" modes. These bands are barely above the noise level in the spectrum, hence their assignment is not listed in Table 7.1.

The observed Franck-Condon allowed totally symmetric a' modes can be grouped into three categories. The first type are modes located mainly on the pyrene ring structure,¹⁶ including modes 58, 56, 54, 50 and 49. In particular modes 58 and 50 have very similar displacement vectors as two of the b_{3g} modes of pyrene. Due to the additional ring (I, Fig. 7.1) attached to the pyrene moiety in BaP, both modes shift to lower frequencies by about 10% from those of pyrene. The second type of observed modes including modes 59 and 52 are related to the motion of the extra phenyl ring (I). Mode 59 involves swinging and mode 52 involves stretching of the extra phenyl ring. The third type of modes are skeletal modes of the whole molecular frame, including modes 55, 53, 51, and 48. Mode 55 is the longitudinal stretching mode, and mode 53 is the transverse stretching mode. Mode 55 and 53 are widely reported among PAHs, and the frequencies of which are observed to be inversely proportional to the dimension of the molecule.¹⁷ Consistent with this trend, the frequencies of both stretching modes in BaP are lower than those in pyrene. The rest of the skeletal modes involve mixed motions of stretching and ring deformation.

A typical complication in vibronic assignment of PAHs is caused by two closely spaced electronically excited states S_1 and S_2 .³⁰ Several work including our own have discovered that CIS and TDDFT calculations can sometimes predict the wrong order of states.^{17,31-33} For this reason, we calculated the vibrationally resolved spectra for both transitions of $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ based on the Franck-Condon principle,³⁴ and the results are shown in Figure 7.3. The displacement vectors and vibrational frequencies were taken from the output files of Gaussian 09: root = 2 for S_1 and root = 1 for S_2 . It is evident from Fig. 7.3 that the simulation of $S_1 \leftarrow S_0$ agrees with the experimental result in both line positions and intensity distribution.³² As for the simulation of the $S_2 \leftarrow S_0$ transition, the disagreement further confirms our assignment of the S_1 electronic state and the observed vibrational bands. It is worth noting that among the three PAHs that we have investigated,¹⁶⁻¹⁸ B*a*P is the first case when we used the newly available vibronic coupling feature of Gaussian 09 to calculate the REMPI spectrum. The remarkable agreement in this case and the disagreements of our previous work on tetracene, pentacene, or pyrene testify to the importance of vibronic coupling in PAHs.



Figure 7.3. Calculations of the vibronic spectra using Gaussian 09 for both the $S_1 \leftarrow S_0$ and the $S_2 \leftarrow S_0$ transitions.

By scanning the ionization laser while setting the resonant laser at one of the intermediate vibronic states identified in the above REMPI experiment, we obtained pulsed field ionization ZEKE spectra as shown in Figures 7.4 and 7.5. The assignment of the vibrational levels of the cation is noted by a superscript "+". The identity of the vibrational level of the intermediate state for each ZEKE spectrum is labeled in the corresponding panel by a black dot. The experimental and theoretical values are shown in Table 7.2. Limited by the linewidth of the resonant transitions and the pulsed electric field, the uncertainty of the experimental values from ZEKE is 5 cm⁻¹. The calculation was performed at the B3LYP/6-31+G (d,p) level, and a scaling factor of 0.9803 was obtained from a least-squares fitting procedure with a coefficient of determination of 0.9991. The agreement between theory and experiment is within a few wavenumbers for most transitions below 1000 cm⁻¹, with the exception of a few transitions involving modes 55^+ and 56^+ . Higher frequency transitions are combination bands and overtones, which have larger deviations, particularly for bands with modes 55^+ and 56^+ . If we reset the frequencies of both modes 55^+ and 56^+ to be 10 cm⁻¹ higher, the agreement between calculation and experiment in Table 7.2 would be within 10 cm⁻¹. In addition, because of the large number of possible combinations at high internal energies, some of these assignments are tentative. In several cases, the choice was made to preserve the vibrational mode of the intermediate state, and the rationale for this choice is the propensity rule, which will be discussed in the following. Nevertheless, the resulting assignment has yielded a consistent presence of combination bands with modes 55⁺ and 52^+ regardless of the initial vibrational excitation.

	Intermediate level in the S_1 state						Cal	Assignm					
0^0	59 1	58 ¹	56 ¹	55 ¹	54 ¹	53 ¹	52 ¹	51 ¹	50 ¹	49 ¹	48 ¹	&	ent
0												0	0^{0+}
20 4												209	61+
32 6												327	60^{+}
	36 9											372	59 ⁺
		451										449	58 ⁺
		472										476	57 ⁺
			522	523		524						508	56+
53 2			532	535								523	55 ⁺
				561	554							557	54+
	57 5											581	61 ⁺ 59 ⁺
						607						608	53 ⁺
62 7						628	633					632	52 ⁺
65 0												654	60^{2+}
								699				695	5 1 ⁺
72 2			729					724				717	61 ⁺ 56 ⁺
				741				737				732	61 ⁺ 55 ⁺
	74 3							745				744	59 ²⁺
								755	755			752	50^{+}
				803						803		808	49 ⁺
						816						817	61 ⁺ 53 ⁺

Table 7.2. Observed and calculated vibrational frequencies of BaP cation

						8	346	852	48^{+}
852								837	60 ⁺ 56 ⁺
	867							852	60 ⁺ 55 ⁺
						8	366	863	61 ⁺ 60 ²⁺
89 7								895	59 ⁺ 55 ⁺
		937						937	60 ⁺ 53 ⁺
984								972	58 ⁺ 55 ⁺
99 6								100 4	59 ⁺ 52 ⁺
101 7								100 6	58 ⁺ 54 ⁺
104 5								105 3	58 ⁺ 53 ⁺
105 8								103 1	56 ⁺ 55 ⁺
	107 0							104 6	55 ²⁺
107 7								108 1	58 ⁺ 52 ⁺
		114 6						113 1	55 ⁺ 53 ⁺
115 1								114 0	56 ⁺ 52 ⁺
	116 6		116 9					115 5	55 ⁺ 52 ⁺
	118 1							118 9	54 ⁺ 52 ⁺
		123 9						124 0	53 ⁺ 52 ⁺
			126 0					126 4	52 ²⁺
				129 0				130 3	53 ⁺ 51 ⁺
				132 9				132 7	52 ⁺ 51 ⁺
						133 5		133 1	55 ⁺ 49 ⁺
				137 0				139 0	51 ²⁺
				-	138 3			138 6	52 ⁺ 50 ⁺

	138 7	137 5	55 ⁺ 48 ⁺
143 0		144 0	52 ⁺ 49 ⁺
	148 4	148 4	52 ⁺ 48 ⁺

[&] Scaled by 0.9803.

The most striking feature of all the ZEKE spectra is the dominance of one vibrational band corresponding to the same vibrational excitation of the intermediate state. Unlike all the other PAH molecules we have studied,¹⁶⁻¹⁸ a clear propensity of preserving the vibrational excitation of the intermediate state can be identified in the ZEKE spectra of B*a*P, with negligible vibrational relaxation or mode mixing.³⁵⁻³⁹ When ambiguities arise in the assignment of combination bands, we therefore believe that the combination containing the original vibrational excitation is the most probable.

Figure 7.4a was recorded via the origin of the S_I state, and the most intense peak corresponds to the origin of the cation. The adiabatic ionization potential is thus determined to be 57271 ± 5 cm⁻¹ (7.1006 ± 0.0006 eV), taking into account the shift caused by the pulsed electric field. This value is 20 cm⁻¹ lower than the ionization threshold extrapolated from the two color REMPI experiment by Gittins *et al.*²⁷ The discrepancy is mostly related to the red shift of the origin of the S_I state. In addition, a major vibrational band in Figure 7.4a is mode 52⁺, which is about 1/6 of the intensity of the origin band (the unattenuated intensity distribution is shown Fig. 7.6a). All vibrational transitions with observable intensities in the ZEKE spectrum of Figure 7.4a correspond to excitations of a' modes. Both REMPI and ZEKE are governed by the Franck-Condon overlap, so if there are no major changes in the molecular frame upon electronic excitation and further ionization, the spectra of Fig. 7.2 and Fig. 7.4a should both have limited vibronic activities. Although not quantitative, the overall intensity distributions of the two spectra do look similar, with the exception of the overwhelming origin band and the mode 52^+ band of Fig 7.4a.



Figure 7.4. Two-color ZEKE spectra of B*a*P recorded via the following vibrational levels of the S_1 state as intermediate states: (a) 0^0 , (b) 59^1 , (c) 58^1 , (d) 56^1 , (e) 55^1 , (f) 54^1 . The energy in the figure is relative to the ionization threshold at 57271 cm⁻¹. The assignment in the figure refers to the vibrational levels of the cation, and the corresponding vibrational level of the intermediate state is labeled by a black dot in each panel.



Figure 7.5. Two-color ZEKE spectra of B*a*P recorded via the following vibrational levels of the S_I state as intermediate states: (a) 53^1 , (b) 52^1 , (c) 51^1 , (d) 50^1 , (e) 49^1 , (f) 48^1 . The energy in the figure is relative to the ionization threshold at 57271 cm⁻¹. The assignment in the figure refers to the vibrational levels of the cation, and the corresponding vibrational level of the intermediate state is labeled by a black dot in each panel.

All ZEKE spectra were obtained from in-plane stretching modes, since the out-ofplane bending modes in the REMPI spectrum were too weak for further ZEKE experiments. None of the in-plane vibrational excitations of S_1 has activated any observable out-of-plane bending modes in ZEKE. Instead, a few limited stretching modes seem to have universal presence in the form of combination bands, such as modes 55^+ and 52^+ , thus the resulting ZEKE spectra have a similar intensity distribution, with a cluster of transitions between 500 and 700 cm^{-1} above the most intense transition. It is also interesting to notice that modes 60^+ and 61^+ are barely observable in the REMPI spectrum, but they can be clearly identified in the ZEKE spectra of Figure 7.4a, 7.4d and 7.5a as isolated bands and as combination bands. In addition, the missing mode 57^+ in the REMPI spectrum is now observed in the ZEKE spectrum through the excitation of mode 58 of the S_1 state in Figure 7.4c. Altogether from modes 61^+ to 48^+ , the frequencies of the in-plane stretching modes of the cation are spaced by 30 - 70 cm⁻¹, a situation prone to mode coupling and to complications in frequency assignment. The displacement vectors of the observed modes of the cationic state correlate with those from the S_1 state on a one-to-one basis, including the localized pyrene modes, the localized phenyl modes (ring I, Fig. 7.1), and the overall skeletal modes.

7.4 Discussion

Similar to pyrene, another peri-condensed PAH we have studied,¹⁷ B*a*P exhibits extensive configuration interactions, and in this situation, ab initio and DFT calculations typically fail to predict the correct order of the two nearby electronically excited

states.^{32,33} The gap between the two lowest excited states of BaP is less than 2000 cm⁻¹ and both states have the same symmetry. The first excited electronic state S_1 with a relatively small oscillator strength is a mixed transition of LUMO+1← HOMO and LUMO \leftarrow HOMO-1, and the second excited state S_2 with a larger oscillator strength is a LUMO + HOMO transition.⁴⁰ This type of energy level inversion has also been observed in pyrene.^{17,31,41-44} Consequently, to obtain the correct geometry and vibrational frequencies from either CIS or TDDFT calculations, we need to set the keyword "root = 2" in the input file. However, in comparing our results with those of Gittins *et al*, 2^{27} we discovered that there were substantial differences between the two calculations in both geometry and frequency. We then calculated the S_2 state by setting root = 1 using the same method, and reproduced the calculation result of Gittins et al (all bond lengths in our results were shorter by about 0.003Å-0.004Å due to the higher basis set used in our calculation). Gittins et al. also pointed out that the Franck-Condon calculation based on their geometry file was in poor agreement with the experiment, opposite from our observation in Fig. 7.3. We therefore suspect that the assignment of Gittins et al for the vibronic transitions in the REMPI spectrum was affected by the wrong keyword in the input file.

Although B*a*P has one additional ring compared with pyrene, and the two systems belong to different symmetry groups, it is still insightful to compare the vibrational modes of the two molecules. The extra ring (I) degrades the D_{2h} symmetry of pyrene to C_s for B*a*P. One would expect that B*a*P should have more flexibility and less rigidity than pyrene, and hence it should have more vibrational activities involving out-of-plane modes. In the REMPI spectrum of B*a*P (Fig 7.2), however, the out-of-plane butterfly waving motions are overshadowed by the a' modes by orders of magnitude. This result is surprising since the corresponding out-of-plane modes in pyrene are on par with the Franck-Condon allowed bands. In addition, only even quanta levels of the out-of-plane a" modes are observable in B*a*P, strictly obeying the FC principle, while for pyrene, the FC principle is essentially obliterated. In fact, a similar FC calculation for pyrene is qualitatively different from the experimental spectrum, with deviations of orders of magnitude for the FC allowed and forbidden bands.

The weak out-of-plane modes in B*a*P might be related to the symmetry of the nearby S_2 state. Vibronic coupling with the S_2 (A') state in B*a*P does not expand the selection rule to out-of-plane modes. Similar Franck-Condon distributions might be possible for both S_1 and S_2 states in this case, and vibronic interaction might not change the spectral distribution to a noticeable degree. In contrast, the S_2 state of pyrene is ${}^{1}B_{1u}$, and vibronic coupling expands the selection rule to the out-of-plane b_{3g} modes. Thus the intensity of out-of-plane modes or the degree of violation of the Franck-Condon principle might be more reflective of the molecular symmetry than of the molecular rigidity.

The strong propensity for preserving the vibrational excitation of the intermediate level in ZEKE is an indicator of similarity in geometry between the intermediate state and the cation ground state. This point is further confirmed from the calculated geometries of the neutral ground state S_0 , the first excited state S_1 and the cationic ground state D_0 . The overall change in size is within 0.5% of the linear dimensions of the molecular frame upon excitation or ionization. In contrast, for tetracene and pentacene, the width of the molecular frame increases by 1~2% upon electronic excitation and shrinks back to nearly the same size as that of the original neutral ground state upon ionization.^{16,18} Although we have only a small set of samples, our studies of PAHs¹⁶⁻¹⁸ seem to suggest that highly symmetric species are easily deformed upon excitation or ionization, while low symmetry species have more ability to absorb the positive charge upon ionization.

We performed a Franck-Condon calculation³⁴ using the Gaussian suite to simulate the $D_0 \leftarrow S_I$ transition from the origin of the S_I state, and the results are shown in Figure 7.6. Similar to the experimental result, the origin band overwhelms the whole spectrum, in qualitative agreement with the experimental observation, and mode 52⁺ is the most intense vibrational band in the ZEKE spectrum. However, the agreement is not quite quantitative, and the intensities of modes 61⁺ and 55⁺ are overestimated in the calculation. We have also used a program from Dr. Dongsheng Yang for the same calculation^{34,45} and obtained the same qualitative agreement, although some details in the weak vibronic structures differ.



Figure 7.6. Comparison between the experimental ZEKE spectrum for the origin of S_1 (Fig 7.4a) (a) and Franck-Condon simulation (b).

An interesting question for the cationic state is the location of the positive charge. We have calculated the Mulliken charge distribution and performed the natural population analysis for the S_0 and D_0 states, by including the charges on the peripheral hydrogen atoms in the adjacent rings and dividing the charges on the shared carbon atoms among conjoint rings. The results from the two types of charge analysis differ, but the change upon ionization is consistent: the positive charge of the cation is by no means localized in the phenyl group ring I or the pyrene group, and all rings share about the same amount of charge loss. Although we can categorize the observed vibrational modes into phenyl modes, pyrene modes, and skeletal modes, the fact that all three categories are observed with similar intensities supports the calculation result of a delocalized charge. Based on our calculation, C8 is the most positively charged among all the carbon atoms connected with a hydrogen atom, and interestingly C8 is the most favorable for nucleophilic substitutions in organic chemistry.

All a' modes are IR active, hence our results of BaP can directly assist with line identification in astrophysical surveys. Khan and Dwayyan studied the infrared spectrum of BaP cation doped in a wax film as well as in an argon matrix from 400 cm⁻¹ to 2000 cm⁻¹.²⁸ Four a' modes 59⁺, 55⁺, 54⁺ and mode 50⁺ from the Khan and Dwayyan report are within our scanning range. The frequencies in wax films are 5 cm⁻¹ higher than our values, but are still within our experimental uncertainty. Our work has further extended the experimental observation to below 400 cm⁻¹, including more than ten IR allowed modes of the cation and some of their overtones. In addition, some of the observed modes are discovered to deviate from DFT calculations by over 10 cm⁻¹, and the need of a scaling factor is also troublesome. This situation calls for precautions in relying exclusively on theoretical predictions for astrophysical fingerprints of PAHs.

7.5 Conclusion

Spectroscopic properties of electronically excited and ionic states of BaP have been studied using 1+1' two-color REMPI and two-color ZEKE. The observed vibronic transitions in the REMP spectrum qualitatively agree with the Franck-Condon principle, dominated by in-plane stretching and bending modes. This result is different from that of pyrene, a PAH with one fewer ring but a much higher symmetry point group. The lack of or weak out-of-plane waving modes in BaP is a result of the same symmetry of the interfering S_2 state as that of the S_1 state. Consequently, the vibrational selection rule does not relax or expand to other types of modes even when vibronic coupling is present. The intensity of the out-of-plane modes is therefore reflective of the molecular symmetry, not indicative of the rigidity of the molecular frame. In addition, our TDDFT calculation using the Gaussian 09 suite²⁹ with the 6-31G basis set is incapable of predicting the energy order of the two interfering electronic states, and the need to artificially "tweak" the calculation is also exemplified. For the cationic state, all observed vibrational modes are IR active, and with the exception of two modes, the DFT calculation, after scaling by a factor of 0.9803, are in agreement with the experimental data. However, the necessity of the scaling factor and the inability to predict all modes with the same accuracy raise the issue of reliability of DFT calculations. The limit of our calculation methods further calls for laboratory experimental efforts, particularly in the context of astrophysical studies. In this favorable case of BaP, ZEKE offers direct information for astrophysical line identifications.

Acknowledgement

This work is supported by the National Aeronautics and Space Administration under

award No. NNX09AC03G.

7.6 References

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Chapter 8. Resonantly enhanced multiphoton ionization and zero kinetic energy photoelectron spectroscopy of Benzo[*g*,*h*,*i*]perylene

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Manuscript for submission to J. Phys. Chem. A, November 14, 2011

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Abstract

We kinetic (ZEKE) photoelectron of report energy spectroscopy zero benzo[g,h,i] perylene (BghiP) via resonantly enhanced multiphoton ionization (REMPI). Our analysis concentrates on the vibrational modes of both the first electronically excited state and the ground cationic state. Extensive vibronic coupling due to a nearby electronically excited state manifests through strong Franck-Condon (FC) forbidden bands, which are stronger than even the FC allowed bands in the REMPI spectrum. Theoretical calculations using Gaussian are problematic in identifying the electronic configurations of the excited electronic states and predicting the transition energies. However, by setting the keyword for the second excited electronic state, both density functional theory and configuration interaction methods can reproduce the observed spectrum qualitatively. The general agreement significantly helps with the vibrational assignment. The ZEKE spectra demonstrate propensity in preserving the vibrational excitation of the intermediate electronic state. In addition, almost all ZEKE spectra exhibit a similar vibrational distribution, and the distribution can be reproduced by a Franck-Condon calculation from the vibronic origin of the first excited electronic state to the cationic state using Gaussian 09. These results suggest a remarkable structural stability of BghiP in accommodating the additional charge. All observed vibrational bands of the cation are IR active, establishing the role of ZEKE spectroscopy in mapping out far infrared bands for astrophysical applications.

8.1 Introduction

Polycyclic aromatic hydrocarbons (PAH) are a group of compounds distributed in the environment, in comet tails, and perhaps in the outerspace.¹ Environmental PAHs are formed during incomplete combustion of organic substances and are related to environmental toxicity and carcinogenicity.^{2,3} In astrophysics, PAHs have been observed in a wide range of galactic and extragalactic regions, and they have been further suggested to be related to the origin of life via the formation of primitive organic molecules including amino acids in the pre-DNA world.⁴⁻⁷

Both neutral and ionic PAHs are considered promising candidates for the interstellar absorption and emission bands,⁸⁻¹⁵ hence spectroscopic investigations of PAHs and their cations in both infrared and ultraviolet/visible regions have been explored using photoionization spectroscopy¹⁶, cavity ringdown¹⁷, and infrared absorption and emission spectroscopy.¹⁸ The far-infrared (FIR) region is occupied by skeletal modes of the molecular frame, and it is considered the "finger-print region" for spectroscopic identification of astrophysical PAHs.^{12,19,20} However, the FIR region has been once considered "no man's land" because of the low sensitivity of available detectors and the low intensity of available light sources. Moreover, laboratory experiments of ions are further challenged by the achievable low ion densities.

The technique of zero kinetic energy (ZEKE) photoelectron spectroscopy offers an indirect solution to these challenges in laboratory astrophysics in the FIR.²¹⁻²³ ZEKE is known for its high resolution (on the order of ~100 kHz) of cation rovibrational spectroscopy.²⁴ The high Rydberg states in ZEKE are longer lived when they are associated with lower vibronic states of the cation, which makes it particularly suitable for studies of low frequency vibrational modes. By detecting electrons from pulsed field ionization in ZEKE spectroscopy via multiphoton excitation, both the light source and the detector problems in typical FIR and sub-millimeter wave experiments can be avoided. Controlled by the Franck-Condon (FC) principle, the vibrational modes from ZEKE are different from those governed by single photon vibrational transitions. However, the IR forbidden modes from ZEKE are useful for frequency calibration and for determination of scaling factors from theoretical calculations. Moreover, to model the energy balance in the interstellar medium,^{8,25-27} both IR allowed and forbidden modes are necessary.

In this report, we investigate the electronic and vibrational spectroscopy of benzo[g,h,i]perylene, also known as 1,12-benzoperylene, as shown in the inset of Figure 8.1. The first two excited electronic states of this peri-condensed PAH have been widely studied both experimentally and theoretically in the gas phase and in the solution phase.²⁸⁻³³ Helium droplet studies have explored the vibrational spectroscopy of the S_1 state up to 3530 cm⁻¹ above the electronic origin, well into the S_2 electronically excited state.²⁸ Matrix isolation spectroscopy of the cation in argon matrix³⁴ and in solid H₂O³⁵ has been reported in the mid-IR and near-IR region from 600 to 1600 cm⁻¹In this paper, we use resonantly enhanced multiphoton ionization (REMPI) to probe the vibronic structure of the first excited electronic state S_1 , and the ZEKE technique to probe the skeletal modes of the cationic state D_0 . Additional insights can be obtained from the results of *ab initio* and density functional calculations.

8.2 Experimental setup

The experimental apparatus is a differentially pumped molecular beam machine, with the detection chamber enclosed inside the source chamber.^{21,23} A time-of-flight mass spectrometer in the detection chamber also serves as the pulsed field ionization zero kinetic energy photoelectron spectrometer. The sample benzo[g,h,i] perylene (Aldrich) had a specified purity of 98%, and altogether less than 100 mg was used throughout the whole experiment. It was housed and heated to 260°C in a modified pulsed valve (General Valve, series 9) located in the source chamber to achieve sufficient vapor pressure. The vapor was seeded in 470 torr of argon and co-expanded into vacuum through a pulsed valve with a 1 mm orifice. After passing through a 2 mm skimmer, the cooled sample reached the detection chamber for laser excitation and ionization. The laser systems for the REMPI experiment included two Nd:YAG (Spectra Physics, GCR 190 and GCR 230) pumped dye lasers (Laser Analytical System, LDL 20505 and LDL 2051). The pump laser in the 397-372 nm range, obtained from the dye laser system (exalite 389, 384 and 376), had a pulsed energy of >1.0 mJ/pulse with a bandwidth of 0.5 cm⁻¹. The ionization laser in the 300-309 nm range from the frequency-doubled output of the other dye laser (rhodamine 610 and sulforhodamine 640 mix) had a pulse energy of ~1 mJ/pulse with a bandwidth of 0.3 cm⁻¹. The absolute wavelength of each laser was calibrated using an iron hollow-cathode lamp filled with neon. The pump laser and ionization laser were set to counter-propagate, and the light path, the flight tube, and the molecular beam were mutually perpendicular. The relative timing between the two laser pulses was controlled by two delay generators (Stanford Research, DG 535), and the optimal signal was obtained under temporal overlap between the pump and ionization

lasers. In the ZEKE experiment, molecules excited to high Rydberg states were allowed to stay for 600 ns in the presence of a constant DC spoiling field of ~160 mV/cm, after which ionization and extraction were achieved by a pulsed electric field of ~2 V/cm.

Gaussian 09W suite³⁶ was used to optimize the molecular structure, to obtain vibrational frequencies, and to simulate the observed vibronic structures from REMPI and ZEKE. For the ground state of the neutral and the cationic state, density functional theory (DFT) calculations using the B3LYP functional were performed with the 6-31G (d,p) basis set. The excited state S_1 was calculated using both time dependent density functional theory (TDDFT) with the B3LYP functional and the 6-31G basis set and the configuration interaction singles (CIS) with the 6-31IG basis set. Details of the calculations will be provided in the following.

8.3 Results

Two-color 1+1' REMPI spectroscopy

The two-color 1+1' REMPI spectrum of BghiP near the origin of the $S_1 \leftarrow S_0$ electronic transition is displayed in Figure 8.1. The ionization laser was set at 33,280 cm⁻¹ and was temporally and spatially overlapped with the scanning resonant laser. Each data point was an average of 100 laser shots, and the spectrum was repeatable over a twoyear period. The peak at 25,027 ± 3 cm⁻¹ is assigned as the origin band, which agrees with the absorption study of 25,027.1 ± 0.2 cm⁻¹ by Rouillé *et al.*²⁹ Other observed vibronic transitions are listed in Table 8.1. Two labeling schemes are used in the Table for comparison: one is to follow previous reports by numbering each symmetry species independently from low to high frequencies,^{28,29} and the other is to follow the order of the symmetry species in the Character Table, and for a given species, in descending order of the frequency. Different definitions of the molecular axes result in different symmetry species for both the electronic state and the vibrational modes, and for clarity, the molecular axes of this work is also shown in the inset of Figure 8.1.



Figure 8.1. The (1+1') REMPI spectrum of jet-cooled benzo[g,h,i]perylene in the S_I electronic state. The spectrum is shifted by 25,027 cm⁻¹ (the origin of the $S_I \leftarrow S_0$ transition) to emphasize the frequencies of the different vibrational levels of the S_I state. The assignments to these transitions are listed in Table 8.1. Both the vibrational energies in cm⁻¹ and symmetry assignments are labeled in the figure. Bold and italicized labels represent intermediate states from which ZEKE spectra were collected. The inset shows the molecular structure and the orientation of molecular axes.
REMP I	Calc.	Assi	ign.	Droplet	Calc.	Assign.	Abs.	Calc.	Assign.
449	443	3a ₁	31 ¹	450.3					
472	471	$4a_1$	30^{1}	471.4	461.8	$4a_1$			
518	521	3b ₁	79 ¹	517.3	504.9	3b ₁	517.5	509.1	3b ₁
553	559	4 b ₁	78^1	552.6	533.7	$4b_1$	552.7	533.2	$4b_1$
				611.2	603.4	$5b_1$			
675	670	6b ₁	76 ¹	676.1	664.7	6b ₁			
748	749	7a ₁	27^{1}						
750	769	7b ₁	75 ¹	752.5	759.5	7b ₁	749.7	749.9	7b ₁
757	773	$8b_1$	74^{1}	760.1			757.1	789.3	8b ₁
				779.8	777.2	$1a_13b_1$			
				903.6	905.1	9b ₁			
<i>938</i>	935	9b 1	73 ¹	936.6	950.1	$3a_13b_1$	937.1	908.2	9b ₁
979	966	9a ₁	25^{1}	978.4	978.9	$3a_14b_1$			
1002	1002	$3a_14b_1$	$31^{1}_{1}78$	1001. 1	995.5	$4a_{1}4b_{1}$			
1014	1012	10b1	72 ¹	1013. 1	1025. 2	$10b_1$	1012. 8	1010. 6	10b ₁
1074	1072	11b ₁	71 ¹	1073. 1	1077. 6	11b ₁	1072	1067	11b ₁
1080	1081	$5a_14b_1$	$29^{1}_{1}78$	1075					
1132	1131	12b ₁	70^{1}	1132		$1a_13b_1$	1131. 7	1117	13b ₁
1193	1193	14b ₁	68^{1}	1194		$3a_17b_1$			
1196				1196. 3					
1206				5 1207. 5			1205. 1	1204	16b ₁

Table 8.1. Assignment of vibrational transitions (cm⁻¹) of the S_I state of benzo[g,h,i] perylene.* The bands that have yielded ZEKE spectra are in bold and italicized typeset.

* Results from helium droplet are based on reference²⁸, and results from absorption (Abs.) are from reference.²⁹ & The calculation was performed using TDDFT (root = 2) with a 6-31G basis set. The

listed values include a scaling factor of 0.9549.

The two closely spaced electronically excited states of BghiP imply potential confusions from TDDFT and CIS calculations. We calculated both electronic states using both methods. To our satisfaction, the results from both TDDFT and CIS are similar in terms of electronic configurations of the excited states and in vibrational The putative S_1 state from the Gaussian program corresponds to an frequencies. electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) with a transition dipole perpendicular to the $C_2(z)$ symmetry axis and an oscillator strength of ~0.3. The putative S_2 state corresponds to electronic excitations of LUMO \leftarrow HOMO-1 and LUMO+1 \leftarrow HOMO, with ${}^{1}A_{1}$ symmetry and an oscillator strength of 0.002. We then further calculated the REMPI excitation spectra using the new vibronic coupling feature of Gaussian 09, and the resulting spectra from TDDFT calculations are shown in Figure 8.2. The transition to the ${}^{1}B_{1}$ state has a strong origin band and relatively weak vibronic activities, while the transition to the ${}^{1}A_{1}$ state qualitatively agrees with the experimental observation. We therefore believe that the observed transition correspond to the ${}^{1}B_{1}$ state, i. e. the putative S_2 state. On the other hand, no experimental evidence of lower lying electronic states was observed either in the solution or in the vapor phase from UV/VIS spectrometers. Since the S_1 state has a much higher oscillator strength and is within 2000 cm⁻¹ of the origin of the S_2 state, we then concluded that the order of states from Gaussian is switched, and hence we labeled the ${}^{1}A_{1}$ state to be S_{1} , in agreement with previous literature reports.^{28,29,37}



Figure 8.2. Excitation spectra calculated from Gaussian 09 for the two different electronic states. The experimental spectrum from Fig. 8.1 is reproduced for comparison.

The agreement in Figure 8.2 greatly simplifies the vibrational assignment of the REMPI spectrum. All the observed vibrational modes can be assigned as either a_1 or b_1 symmetry species. B*ghi*P has 33 a_1 modes allowed by the Franck-Condon principle in

the ${}^{1}A_{1} \leftarrow {}^{1}A_{1}$ transition, and among the 11 a_{1} modes in the current spectral region, only 5 can be identified either as independent vibrational bands or in combination bands. Herzberg-Teller vibronic coupling with the ${}^{1}B_{1}$ state activates the Franck-Condon forbidden but vibronically allowed b_{1} modes. Interestingly for B*ghi*P, the frequency distributions of a_{1} and b_{1} modes are similar, and within the current spectral range, a few more b_{1} modes than a_{1} modes can be identified. In addition, the intensities of the b_{1} modes seem to be higher than those of the a_{1} modes in Figure 8.1. The a_{2} and b_{2} modes are mostly out-of-plane bending motions that are only allowed for transitions to even quantum states, and they are not observable in the current spectrum.

Our assignment is in general agreement with previous literature reports.^{28,29} The scaling factors, however, seem to vary substantially depending on the calculation method. The two different calculation methods from our own Gaussian 09 also resulted in very different scaling factors: 0.9549 for TDDFT 6-31G and 0.9049 for CIS 6-311G. Nevertheless, the qualities of both linear regressions are similarly high, with only the 7a₁ and 10b₁ modes that have discrepancies larger than 6 cm⁻¹ for CIS (not listed in Table 8.1), and 7b₁, 8b₁ and 9a₁ modes for TDDFT (Table 8.1).

8.4 ZEKE spectroscopy

By scanning the ionization laser while setting the resonant laser at one of the intermediate states identified in the above REMPI experiment, we obtained pulsed field ionization ZEKE spectra as shown in Figures 8.3 and 8.4. The reproducibility of the spectra was tested over a two year period. The spectra in Fig. 8.3 were obtained with about 100 laser shots per data point, but the spectra in Fig. 8.4 were recorded with more

than 200 laser shots per data point due to the low signal intensity. The two figures are plotted on different horizontal scales for clarity and compactness. The identity of the vibrational level of the intermediate state for each ZEKE spectrum is labeled in the corresponding panel by a black dot. The experimental and theoretical values are shown in Table 8.2. The calculation for the cation vibrational frequencies was performed at the B3LYP/6-31G (d,p) level. Using a least-squares fitting procedure similar to that for the S_1 state, we obtained a scaling factor of 0.9983 with a coefficient of determination 0.9995. Limited by the linewidth of the resonant transitions and the pulsed electric field, the uncertainty of the experimental values of the ZEKE spectra is ± 7 cm⁻¹.

0^0	3b ₁	4b ₁	7b ₁	9b ₁	$4a_13b_1$	10b ₁	11b ₁	$5a_14b_1$	Calc*	Ass	ignment
410									390	2a ₁	32+
	531								531	3b ₁	79^{+}
		574							567	$4b_1$	78^+
	673								686	6b ₁	76^{+}
			781						783	$7b_1$	75 ⁺
	919					920			921	$2a_13b_1$	32 ⁺ 79 ⁺
				960				962	949	9b ₁	73 ⁺
		961							957	$2a_14b_1$	32 ⁺ 78 ⁺
	980			980		980			988	$3a_13b_1$	31+79+
					1014			1019	1024	$4a_13b_1$	30 ⁺ 79 ⁺
						1051			1054	$10b_1$	72^{+}
						1063			1062	$3b_1^2$	79^{2+}
						1075			1073	$5a_13b_1$	29 ⁺ 79 ⁺
						1084			1082	$6a_11b_1$	$28^{+}81^{+}$

Table 8.2. Vibrational assignment of benzo[g,h,i] perylene cation relative to the 57623 cm⁻¹ ionization threshold. Transitions in bold typeface are of the same symmetry as that of the intermediate state.

		1107		1115	11b ₁	71 ⁺
1108			1106	1109	$5a_14b_1$	$29^{+}78^{+}$
			1138	1134	$4b_1^2$	78^{2+}
1165				1173	$2a_17b_1$	32 ⁺ 75 ⁺
1365				1348	$2a_19b_1$	32 ⁺ 73 ⁺
	1397			1415	$2a_14a_13b_1$	32 ⁺ 30 ⁺ 79 ⁺
		1495		1505	$2a_111b_1$	32 ⁺ 71 ⁺

*The calculation result includes a scaling factor of 0.9983.

Trace 8.3a was recorded via the origin of the S_I state, and the most intense peak corresponds to the origin of the cation. The adiabatic ionization potential is thus determined to be 57,623 ± 7 cm⁻¹ (7.1443 ± 0.0006 eV). This value is about 300 cm⁻¹ lower than that of 7.19 ± 0.01 eV from photoelectron spectroscopy by Boschi, Murrell and Schmidt in 1972³⁸ and close to the result of 7.15 eV from gas phase ion equilibrium measurements by Meot-Ner in 1980³⁹. Our new value represents an improvement of one order of magnitude in precision for the ionization threshold.

In addition to the origin band, trace 8.3a also contains a $2a_1$ band of the cation, in agreement with the symmetry selection rule dictated by the Franck-Condon factor. Using Gaussian 09 and based on the geometry and vibrational information of the intermediate (TDDFT 6-31G) and the cationic state (DFT B3LYP/6-31G (d,p)), we were able to calculate the ionization spectrum from the origin band and the comparison is shown in Figure 8.5. The excellent agreement between calculation and experiment further confirms the assignment of the $2a_1$ mode for the cation, although the frequency difference between experiment and calculation, even after a scaling factor of 0.9983, is still on the order of 20 cm^{-1} .

Except for Trace 8.3a, the rest of the ZEKE spectra were obtained from b_1 intermediate vibronic states and almost all observed vibrational bands in the ZEKE spectra are of b_1 symmetry. Most vibronic transitions in the REMPI spectrum of Fig. 8.1 that are of b_1 symmetry with a signal-to-noise ratio above 5 were successful candidates as intermediate states for ZEKE experiments. The only exception is the 8b₁ band, which is in close proximity to the 7b₁ band and is of similar intensity, but no ZEKE signal was observable from this band.

The ZEKE spectra in Figures 8.3 and 8.4 are sparse, and the most salient feature is the dominance of the same vibrational level as that of the S_I intermediate state, with the exception of trace 8.4d. This propensity in preserving the vibrational excitation of the intermediate state can also offer further guidance in assignment of both the REMPI and ZEKE spectra, particularly for high energy bands where more than one potential candidate of combination bands might exist. For example, the peak at 961 cm⁻¹ in trace 8.3c and the peak at 960 cm⁻¹ in trace 8.3e are assigned as two different transitions, despite of the fact that our experimental uncertainty is 7 cm⁻¹. Trace 8.3c was recorded from the 4b₁ intermediate state, hence it would be more reasonable to assign the transition at 961 cm⁻¹ a combination band with mode 4b₁ than to assign it as a completely different vibrational mode. On the other hand, trace 8.3e was recorded via the 9b₁ level of the *S_I* state, and its dominant transition should correspond to the same vibrational mode of the cation. Given the fact that the calculated frequencies for both vibrational levels of the cation are virtually degenerate, we thus believe that the two peaks from the two different spectra should have two different identities. A similar argument holds for the transitions between 1106 and 1108 cm^{-1} in trace 8.3c, 8.4c and 8.4d.

Another noticeable feature of the ZEKE spectra is the repetition of the vibrational pattern of trace 8.3a: most ZEKE traces contain a dominant band and a combination band with mode $2a_1$, similar to the ZEKE spectrum from the electronic origin of the S_1 state. This consistency further offers confirmation of the vibrational assignment. More importantly, the qualitative agreement between the Franck-Condon calculation in Figure 8.5 and trace 8.3a implies that although vibronic coupling is extensive for the intermediate state, the ionization process is largely unperturbed, and the Franck-Condon principle is more or less preserved.

The two ZEKE spectra that do not exhibit the same pattern as trace 8.3a are traces 8.4b and 8.4d. The overall intensities of these two spectra are also substantially lower than those from Fig. 8.3. The quartet feature of trace 8.4b poses a challenge for a definitive assignment. Based on the frequent appearance of mode $3b_1$ at 920 and 980 cm⁻¹, two of the four peaks can be assigned as combination bands with mode $3b_1$. The triplet feature at 980 cm⁻¹ is also present in traces 8.3b and 3e, although because of the compact horizontal scale, the splitting is not discernable in Figure 8.3. We could only attribute the lowest energy component to a combination band of mode $3b_1$.



Figure 8.3. Two-color ZEKE spectra of B*ghi*P recorded via five of the vibrational levels of the S_1 state as intermediate states. The energy in the *x*-axis is relative to the ionization threshold at 57,623 cm⁻¹. The labels in the figure refer to the vibrational energies in cm⁻¹ and symmetry assignments of the cation, and the corresponding vibrational assignment of the intermediate state is labeled by a black dot in each panel. The assignment can be found in Table 8.2.



Figure 8.4. The two-color ZEKE spectra of B*ghi*P recorded via four of the vibrational levels of the S_1 state as intermediate states. The energy in the *x*-axis is relative to the ionization threshold at 57,623 cm⁻¹. The labels in the figure refer to the vibrational energies in cm⁻¹ and symmetry assignments of the cation, and the corresponding vibrational assignment of the intermediate state is labeled by a black dot in each panel. The assignment can be found in Table 8.2.



Figure 8.5. Franck-Condon calculation using Gaussian 09 from the origin of the S_1 state to the D_0 state. The experimental spectrum from trace 8.3a is reproduced for comparison.

8.5 Discussion

S_1 state

The new capability of Gaussian 09 to include vibronic coupling for calculations of excitation spectroscopy is truly remarkable. The agreement between simulation and experiment for both the REMPI and ZEKE spectra helps greatly with the vibrational assignment and determination of symmetry and electronic orbitals of the related states. Discussions on the symmetry and nature of the first two electronically excited states of B*ghi*P have had a long history. Based on experiments both in the gas phase and in the solution phase and on advanced theoretical calculations, the S_1 state is generally considered ${}^{I}A_{I}$ and the S_2 state ${}^{I}B_{I}$.^{29,31,33,40-42} Our work confirms the previous conclusion

based on simulations of the excitation spectra. However, even with Gaussian 09, the order of the electronic excitation is still switched. To obtain the current calculation result, the keyword for the Gaussian input has to be set to root = 2.

The vibrational distribution of BghiP should be compared with those of pyrene²¹ and benzo[a]pyrene $(BaP)^{43}$, two other peri-condensed PAH that have been investigated in our group, and those of a few cata-condensed PAHs^{22,23,44,45}. In the REMPI spectrum of pyrene,²¹ two types of vibrational bands were observed, and the FC allowed in-plane stretching modes were relatively stronger than the out-of-plane vibronic modes. The addition of another ring off the symmetry axis of pyrene in BaP lowered the symmetry point group to C_s ⁴³ Although configuration interaction remained, the two interacting electronic states in BaP were of the same symmetry and the resulting FC profiles were similar. Consequently, a FC calculation from our TDDFT results had qualitatively reproduced the observed spectrum. As the molecular frame expanded symmetrically from pyrene to BghiP, the symmetry point group lowered to C_{2v} , and vibronic modes overtook the FC modes, dominating the REMPI spectrum. In contrast, cata-condensed PAHs including tetracene and pentacene were not affected by configuration interactions.^{22,23} The REMPI spectrum of tetracene was dominated by FC bands,²³ although FC simulations without vibronic coupling resulted in an overly strong origin band. Pentacene was sufficiently flexible in the molecular frame,²² and out of plane waving modes of the ribbon dominated the REMPI spectrum. Within this selected group of PAHs, we therefore conclude that both symmetry and size affect the vibrational distribution upon electronic excitation. Lower symmetry systems exhibit more FranckCondon behavior, and expansion of the molecular frame exacerbates non-Franck-Condon behaviors.

D_{θ} state

In contrast to the strong vibronic activities of the REMPI spectrum, the ZEKE spectra of B*ghi*P exhibit strong Franck-Condon behavior. The pattern for the vibrational distribution of the origin band is repeated in most of the observed ZEKE spectra originating from different intermediate vibrational states. This situation is also an indicator of the capacity of the molecular frame for accommodating the additional charge upon ionization. Among the PAHs that we have investigated,^{21-23,43} only B*a*P has demonstrated a propensity of preserving the vibrational excitation of the intermediate state,⁴³ which agrees with the high structural stability of the low symmetry PAHs. No obvious propensity has been observed in pyrene, tetracene, and pentacene.²¹⁻²³

Based on our previous studies of cata-condensed PAHs and a series of small benzene derivatives,^{21-23,46-50} DFT calculations typically yield reliable vibrational frequency information for the cation. In the case of B*ghi*P, a scaling factor of 0.9983 is needed to fit the experimental frequencies, and mode $2a_1$ is proven an outlier with a deviation much larger than the experimental uncertainty. This agreement is on par with the case of B*a*P⁴³ but worse than the cases of pyrene, tetracene, and pentacene where no scaling factor was needed.²¹⁻²³ This variation of scaling factors is unsettling, particularly for predictions of vibrational bands from unknown substances.

All observed modes including b_1 and a_1 modes in ZEKE are IR active, however, a direct frequency comparison with results from literature reports is still impossible.

Hudgins and Allamandola reported the cation IR spectroscopy of B*ghi*P in argon matrices from 600 cm⁻¹ to 1600 cm⁻¹.⁵¹ Bernstein et al studied the cation IR spectroscopy in solid water from 1120 cm⁻¹ to 1600 cm⁻¹.³⁵ Within the range of frequency overlap with our current work, unfortunately, these two studies failed to observe any b₁ or a₁ modes, perhaps due to the low transition intensities of these modes. This situation alludes to the value of ZEKE spectroscopy for astrophysical studies: although the vibrational intensities from ZEKE are not representative of single photon absorption or emission, the frequency information is still valuable for calibration and for optimization of scaling factors from calculation. Furthermore, for non-central symmetric PAHs such as B*ghi*P, vibrational frequencies from ZEKE can be used for direct line identification.

8.6 Conclusion

Vibrational properties of the electronically excited and ionic states of benzo[g,h,i]perylene have been studied using REMPI and ZEKE. Due to strong Herzberg-Teller coupling, vibronic allowed bands of the first excited state dominate the REMPI spectrum, much stronger in intensity than those of Franck-Condon allowed a_1 modes. With the vibronic coupling feature of Gaussian 09, on the other hand, the REMPI spectrum can be simulated with remarkable success. The ZEKE spectra demonstrate a propensity for preserving the vibrational excitation of the intermediate state. The vibrational pattern of the ZEKE spectrum from the origin of the S_1 state can be reproduced by a direct Franck-Condon calculation, and the vibrational pattern is more or less repeated for most ZEKE spectra originating from intermediate vibronic b_1 states.

observed modes in ZEKE are IR active, but none of the observed modes have ever been

reported from previous IR experiments. This result establishes the role of ZEKE in

mapping out the vibrational mode distribution of PAHs for astrophysical studies.

Acknowledgements

This work is supported by the National Aeronautics and Space Administration

under award No. NNX09AC03G.

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Chapter 9. Concluding Remarks

9.1 General Implications

This thesis presents our investigation on excited and cationic state vibrational spectroscopy of select PAH and PANH species using the REMPI and PFI-ZEKE techniques.¹⁻⁵ The work was motivated by the desire to obtain the "finger-print" of the relevant species for astrophysical applications.⁶⁻¹⁰ This spectral region has always been plagued with issues related to the light source, detector and particle density. Zero kinetic energy photoelectron spectroscopy, as evidenced in this thesis, is a way around many of the issues, and it allows for the collection of vibrational information of cationic species following the Franck-Condon overlap integral between the two related electronic states.^{1-5,11-13} Unfortunately for centrally symmetric molecules, this selection rule dictates that only infrared inactive modes are observed in ZEKE spectroscopy.^{12,13} Nevertheless, the intensity and frequency information of even the IR forbidden modes is still invaluable to benchmark modern calculation methods and for astrophysical modeling in general.^{14,15}

The vast majority of the systems investigated in this thesis exhibit vibronic coupling in the electronically excited state used as an intermediate state in ZEKE spectroscopy.¹⁻⁵ This is because of the close proximity of electronically excited states in aromatic systems.¹⁻⁵ This situation can also cause Gaussian calculations to switch the orders of electronic states, which means that it is important to simulate all low-lying electronic states and compare the results with the experimental spectrum.^{1-5,16-18} Vibronically coupled intermediate states can expand the detectable vibrational modes in

the final ZEKE spectrum, allowing for measurements of more vibrational frequencies and intensities for astrophysical modeling.^{1-5,14,15}

The strong aromaticity of PAHs and PANHs determines their structural stability, upon electronic excitation and ionization.¹⁻⁵ In most of the systems studied in this thesis, the ZEKE spectra are sparse, exhibiting only the vibrational excitation of the intermediate state used to collect the ZEKE spectrum.¹⁻⁵ This propensity implies diagonal Franck-Condon factors due to similar vibrational mode distributions between the intermediate electronic state and the ionic state, a signature of strong structural similarity between the two electronic states.^{12,13} Nitrogen substitution is particularly favorable for accommodating the extra charge in the ionic state, since the lone pair on the nitrogen atom can adapt to the charge condition of the whole molecular system.

This work offers experimental vibrational frequencies for benchmarking far infrared modes for astrophysical modeling.^{1-5,14,15} Comparisons between our experimental frequency values with calculations using DFT or other methods indicate that even with modern software packages and supercomputers, there is still a distance between reliable theoretical values for astrophysical observations.^{1-5,14,15} Table 9.1 includes the scaling factors for both the intermediate electronic state and the cationic state: they range from 0.96 to 1, depending on the system. Typically cationic states require less scaling than the S_1 state. The notable cases are triphenylene which requires no scaling for the cation, and B*h*Q which requires the largest scaling, possibly due to the effect of the nitrogen atom. This situation precipitated an immense desire for improved range and resolution of modern day laboratory observations. For example, the HI-FI detector from Herschel is limited to 16 - 42 cm⁻¹ and 47 - 64 cm⁻¹ in frequency ranges

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(480 - 1250 and 1410 - 1910 GHz) with a resolution of \pm 5 x 10⁻⁶ cm⁻¹ (\pm 0.14 MHz). An uncertainty of several wavenumbers could mean a "YES" or "NO" answer for the identification of some species. More experimental efforts and theoretical improvements in calculation methods are clearly needed from this perspective.

Species	S ₁ Scaling	D_0 Scaling		
triphenylene	0.964	1		
chrysene	0.964	0.977		
benzo[h]quinoline	0.963	0.961		
benzo[<i>e</i>]pyrene	0.973	0.97		
benzo[a]pyrene	0.963	0.98		
benzo[g,h,i]perylene	0.955	0.998		

 Table 9.1 Scaling factors for the calculated vibrational frequencies obtained using the B3LYP functional

9.2 Extreme vibronic coupling in triphenylene

For the majority of the systems in this thesis, vibronic coupling plays a key role in the S_I state.¹⁻⁵ In fact, with the exception of chrysene, every molecule in this thesis exhibits vibronic coupling to a nearby electronic state. In the unique case of triphenylene, due to the high symmetry of the molecular frame, the HOMO and LUMO are of the doubly degenerate e" symmetry species, and the first two electronic states are transition dipole forbidden. Transitions to the S_I state therefore arise solely from Herzberg-Teller coupling to the S_3 electronic state, and only vibrational transitions with e' in total symmetry are observable.

The nature of the cationic state of triphenylene is an interesting and unique case. When an electron is removed from the e'' HOMO, the system undergoes Jahn-Teller distortion, lowering the overall point group from D_{3h} to C_{2v} . The doubly degenerate e' vibrational modes in the S_1 state thus resolve into a_1 and b_2 modes in the cation, the latter of which is IR active. Consequently, the propensity rule is no longer prominent, and clusters of transitions due to the Jahn-Teller distortion are observed.

9.3 Effect of nitrogen substitution in PANHs

Aromatic systems are known for having closely spaced, nearly degenerate molecular orbitals, hence the introduction of a perturbation can shift the relative energies of the related orbitals. A kink in the molecular frame in anthracene and a heteroatom in BhQ (compared with phenanthrene) are proven to be sufficient to switch the nearby energy levels. In the S_I state, a nitrogen atom can absorb a significant amount of the electron density, making the charge distribution resemble that of the cationic state. While in the cationic state, the nitrogen back-donates to the molecular frame, making it resemble the neutral state. The resulting spectroscopic manifestation is the strong propensity in the ZEKE spectra through the REMPI process.

9.4 References

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