

# Molecular Structures of Gases by Electron-Diffraction:

## Improved Methods and Study of 1,1,3,3-tetramethylcyclobutane and spiropentane molecules

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### Background

The gas phase electron-diffraction (GED) technique has been the primary method used to expand our knowledge and understanding of gas-phase molecular structures. The technique yields interatomic distances and bond angles that are of use in both theoretical and experimental studies.

The GED structural parameters are thermal averages over all vibrational levels of a molecule that are occupied at the temperature of the experiment. Typical bond length accuracies are 0.01-0.004 Å and bond angles can be determined to a few tenths of a degree. In contrast, for small molecules, spectroscopic studies can give bond lengths of accuracy as good as 0.00001 Å for specific states, such as the vibrational ground state.

However spectroscopic measurements for a molecule can determine at most only three rotational constants, and hence only three structural parameters. Thus, for larger molecules, one would like to combine the results of both GED and spectroscopic experiments in determining the most accurate structures. To do this, one requires estimates of a number of small corrections which it is now possible to obtain from high-level quantum mechanical calculations. It is this approach that we have used in the work reported here.

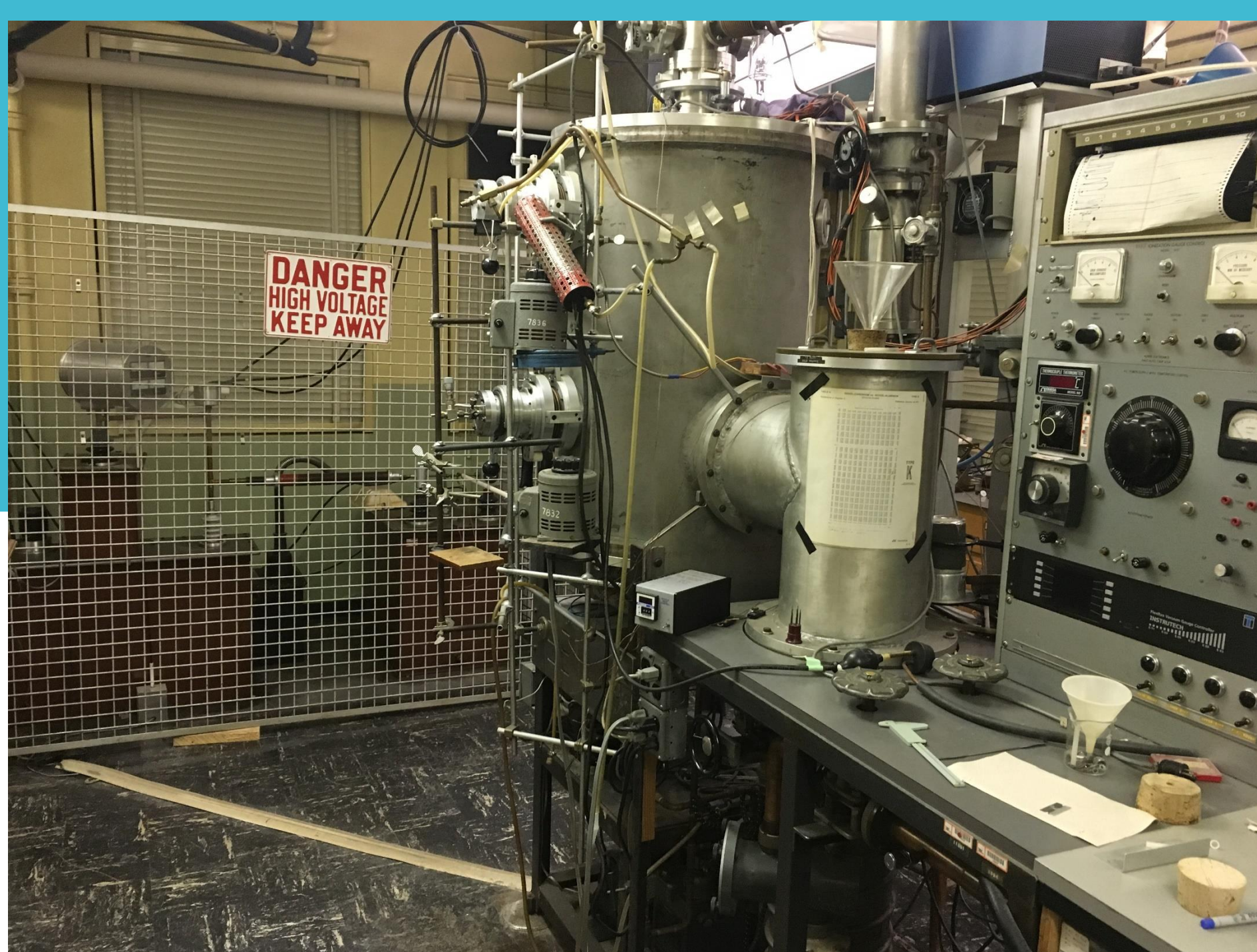
### GED Experimental Methods

Our GED experiments utilize a 60 kV beam of electrons of about 0.05 Å wavelength that intersects a jet of sample vapor emitted from a fine tip nozzle in a high-vacuum. The electrons interact with sample at this intersection and are scattered to a detector below the intersection. We use Kodak electron imaging films to collect an image of electron intensity versus distance. After development the scattered electron intensity appears as a set of diffuse rings symmetric about the center. Digitizing the intensity of the films is important to extract the pertinent molecular information from the experiment. As shown from equation 1, the  $r_{ij}$  separation between each pair of atoms  $i, j$  appears as a frequency term in the argument of the interference function that defines the scattered intensity:

$$s/m(s) \approx \sin[s(r_a + k s^2)]/sr_a \quad (1)$$

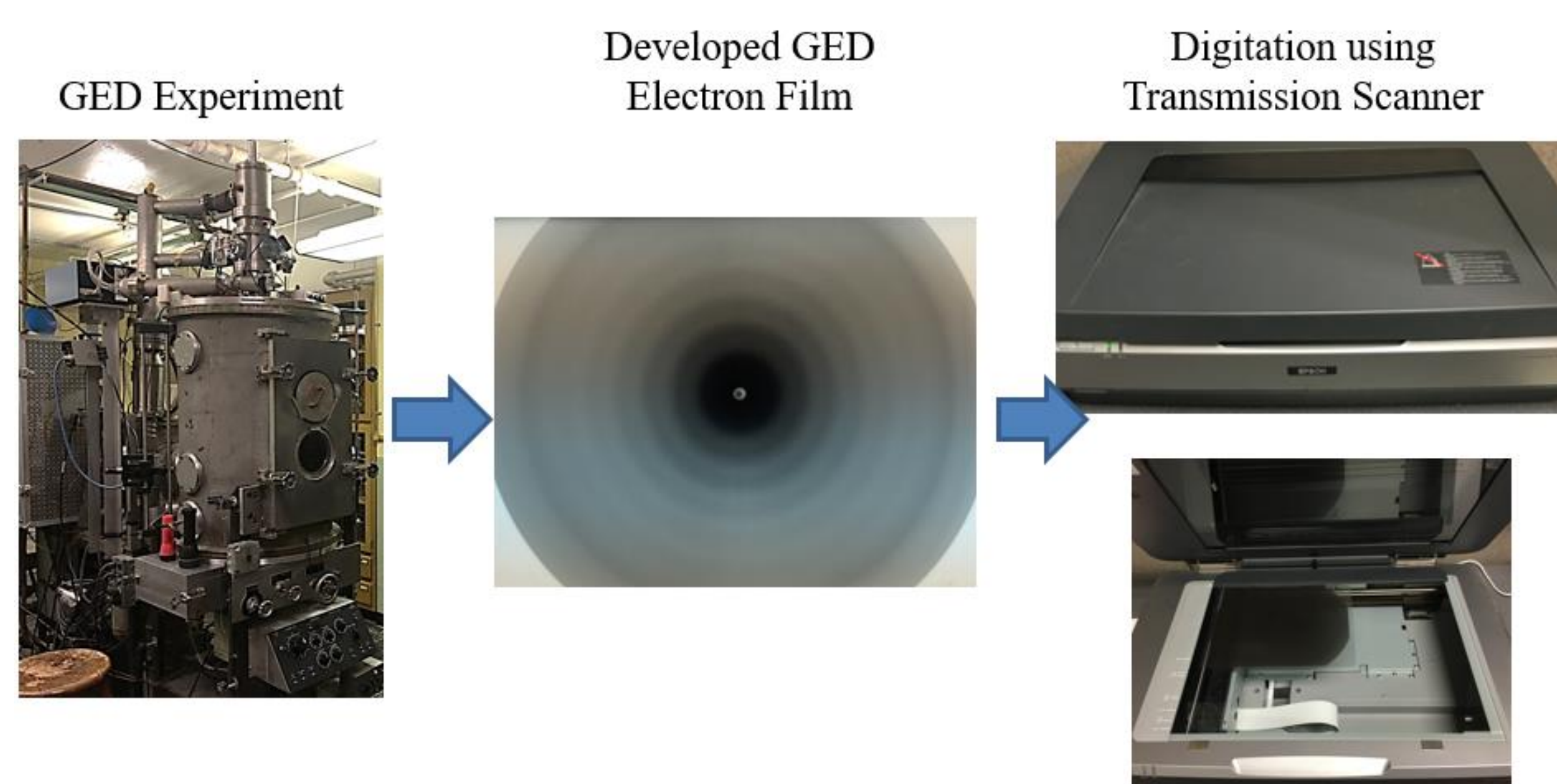
Here  $s$  is equal to  $4\pi\lambda^{-1} \sin(\theta/2)$  where  $\lambda$  and  $\theta$  denote the electron wavelength and scattering angle,  $k$  is a small higher-order phase correction and the total intensity is the sum of the contributions for all atom pairs.

### Oregon State University GED Apparatus



### Improved GED Calibration Methods

Modern developments in laser technology, Fourier-transform spectrometers, computers, and detectors have vastly improved the accuracy and precision of spectroscopic measurements. However experimental error for GED experiments has remained relatively constant over the past few decades. Part of this research was an effort to reduce experimental uncertainties in GED results by using a high precision transmission scanner to digitize the electron image films, and by developing a centering program with the use of a new software programs. In addition improved calibration of the GED apparatus was achieved by using nitrogen as a calibrant gas, as shown below. These modifications gave a 2- to 3-fold improvement in the GED accuracy and they have been used in our analysis of spiropentane and 1,1,3,3-tetramethylcyclobutane shown to the right.



### N<sub>2</sub> Calibration Results

Table 1: Summary of GED Calibration Experiments with N<sub>2</sub>

Expt.	V <sub>cal</sub> Volts	V <sub>M-V<sub>cal</sub></sub> Volts	Unc. Volts	Unc. in $r_a$ Å	Fit Quality
1	59836	-117	20	0.00037	0.100
2	59637	-336	14	0.00025	0.068
3a	59743	-183	20	0.00039	0.093
3b	59651	-280	20	0.00040	0.097
3c	59717	-214	18	0.00036	0.086
average		-226		0.00035	
st. dev.		85		0.00006	

Table 1 shows the voltage calibration of each of five nitrogen films. Experiments 1, 2 and 3 were run on different days, differences in other experimental conditions are taken into account through our refinement procedures and won't be discussed. Quality of fit values corresponds to the nonlinear least squares fit parameters between the experimental radial distribution curve and our fitted theoretical model. The measured voltage ( $V_m$ ) was measured from the high voltage multimeter and the calculated voltage ( $V_{cal}$ ) was calculated using an nitrogen bond length of 1.00087 Å.

Figure 1: Radial distribution and Scattering curve of N<sub>2</sub>

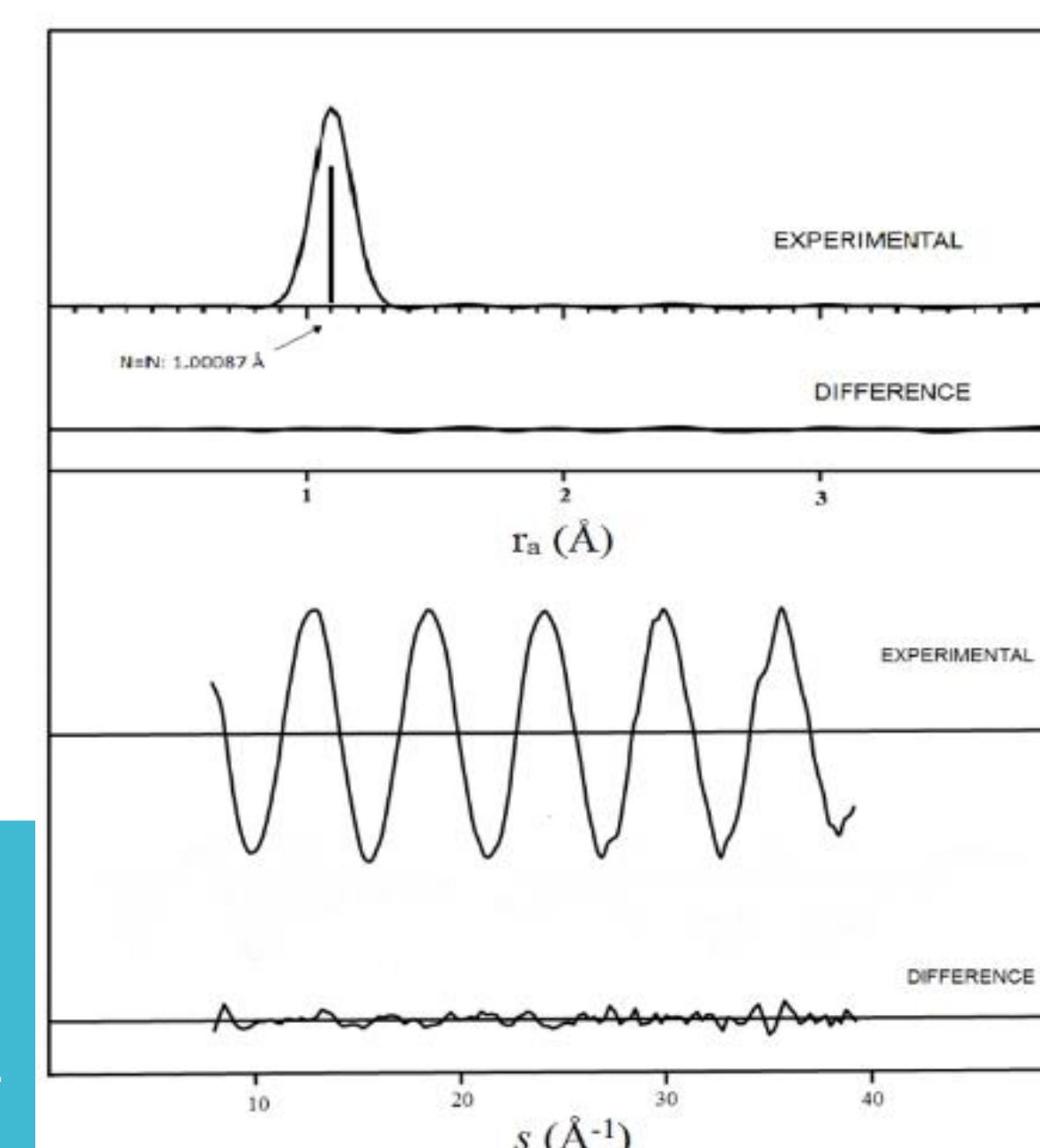


Figure 1: shows the average of the five experiments radial distribution curve and the scattering intensity curve. The difference is taken from the experimental curve minus the least squared fitted curve.

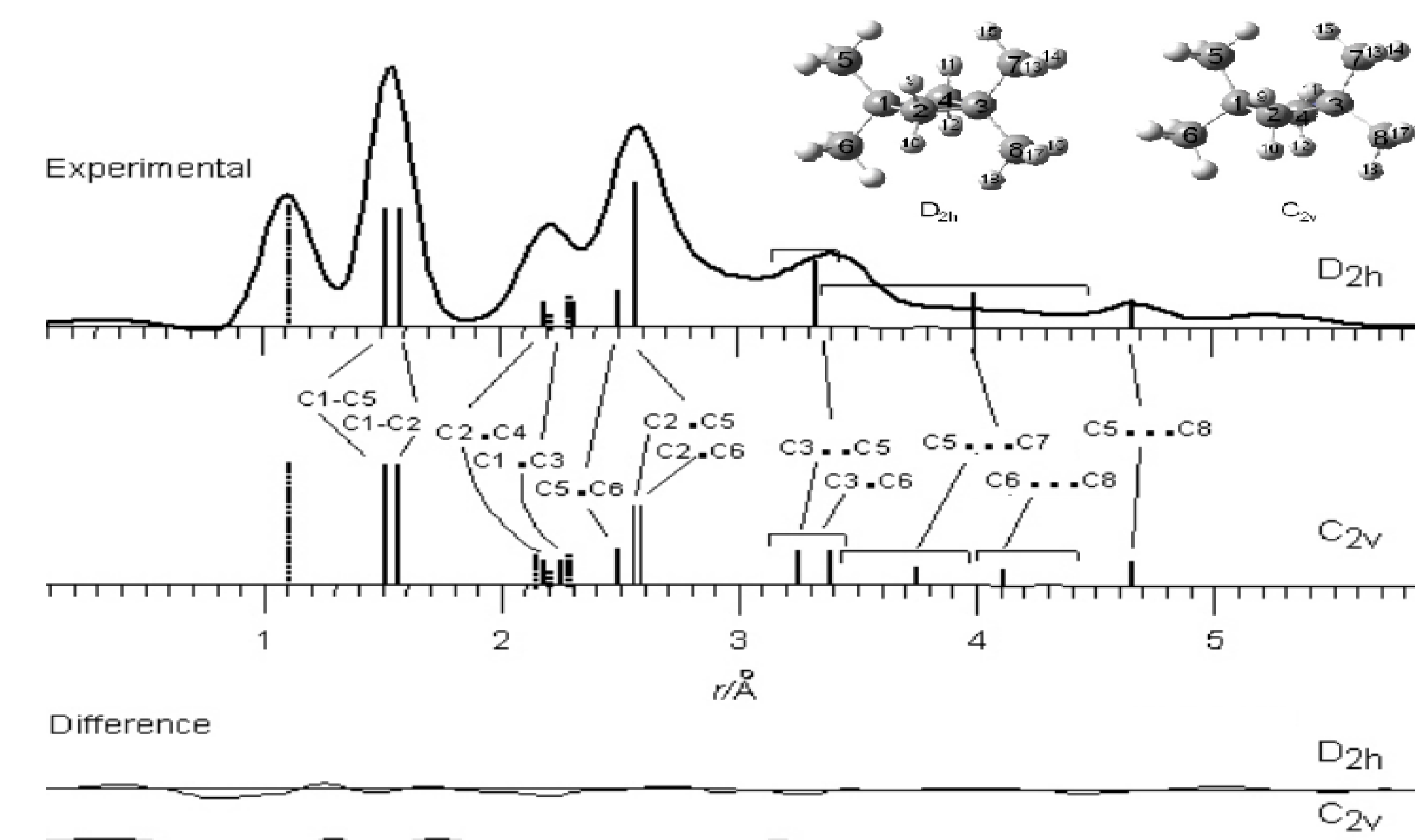
### Acknowledgments

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### 1,1,3,3-tetramethylcyclobutane

A GED experiment was conducted on 1,1,3,3-tetramethylcyclobutane (TMCB). The investigation sought to determine if TMCB would have the same thermal equilibrium structure as all previously studied cyclobutane (CB) compounds, i. e. a configuration of C<sub>2v</sub> symmetry with the ring bent due to ring strain. Our GED results below suggest that, due to increased repulsions of the methyl groups, TMCB actually has a thermal equilibrium structure with a planar ring and a molecular symmetry that is D<sub>2h</sub>. However since the ring bending motion has a very low frequency, <100 cm<sup>-1</sup> as predicted by density functional theory, a precise equilibrium structure at zero K could not be determined.

Figure 2: Radial distribution curve comparing the C<sub>2v</sub> and D<sub>2h</sub> theoretical model to experimental



### Spiropentane

A high resolution infrared spectroscopy study of spiropentane was recently carried out at OSU, yielding a very accurate value of the B<sub>0</sub> rotational constant for this molecule, 0.1394741(1) cm<sup>-1</sup>. The result was within 0.6% of a value obtained from density functional theory (DFT) but was in poor agreement with a value calculated from an earlier GED determination of the structure. The HCH bond angle obtained in this GED study was also much larger, 118.4(9)°, than the DFT value of 114.4° and a value of 115.0(7)° from an NMR study. Using the improved scanning and calibration methods developed in this work, we obtained a more accurate structure from a combined GED-spectroscopy analysis that gave a more reasonable HCH angle of 113.7(13)° and also resolved the B<sub>0</sub> inconsistency.

Figure 3: Comparison of experimental and calculated radial distribution function for spiropentane.

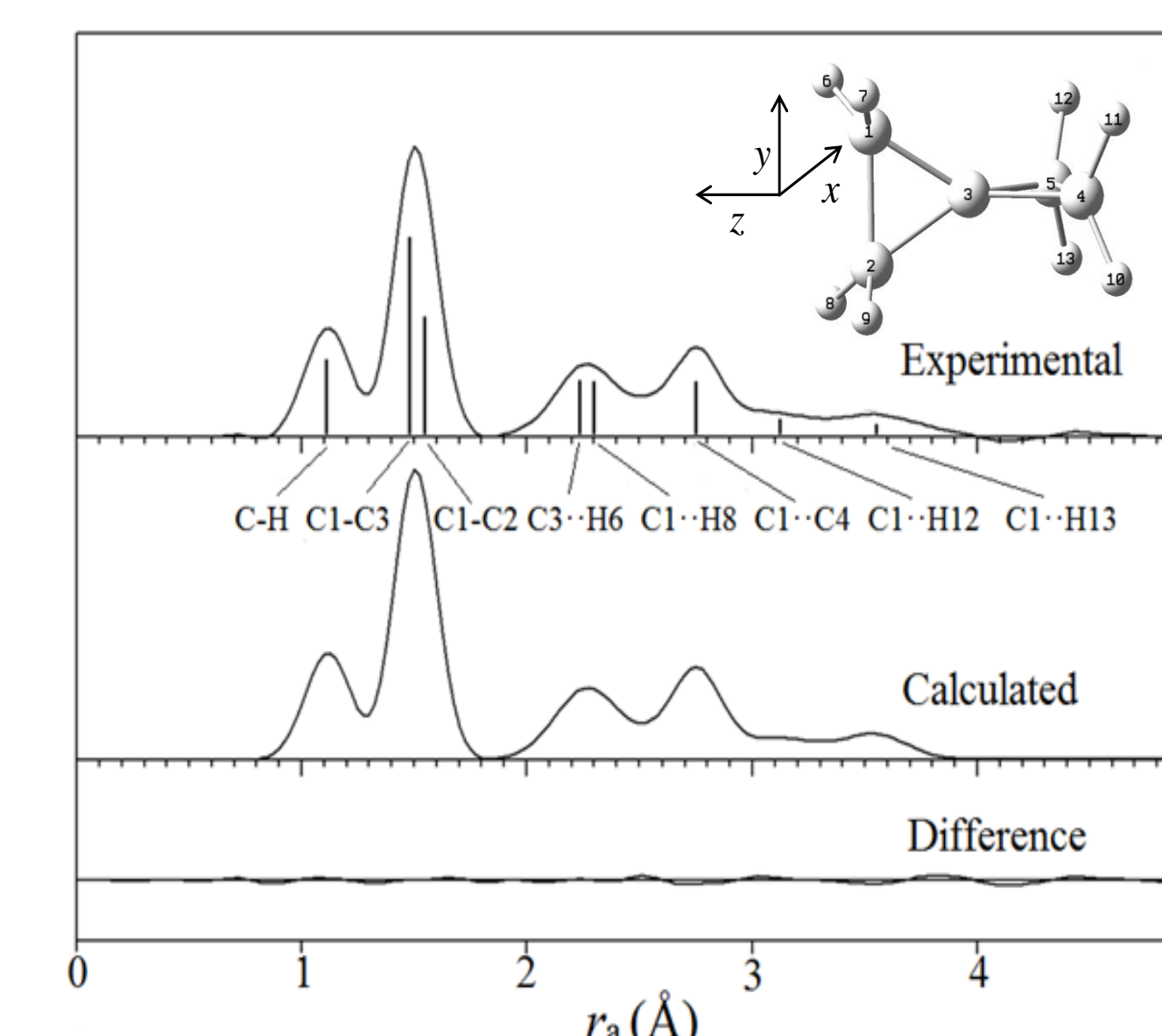


Figure 4: Comparison of experimental and calculated scattering intensities  $s/m$  for spiropentane. The dotted trace shows results from a scan of a similar curve reported from a prior ED experiment

