RAMAN EVIDENCE FOR THE
STRUCTURE OF THE
HYPONITRITE ION

by

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ACKNOWLEDGEMENT

I dedicate this thesis to my wife Mary for her numerous valuable suggestions and her patience and understanding during the preparation of this thesis.
TABLE OF CONTENTS

I  INTRODUCTION 1
II  DESIGN OF EQUIPMENT 3
III SAMPLE PREPARATION 16
IV OBSERVED SPECTRA 19
V  POLARIZATION OF RAMAN LINES 33
   A. THEORY OF THE POLARIZATION OF RAMAN LINES 33
   B. EXPERIMENTAL MEASUREMENT OF THE DEGREE OF DEPOLARIZATION OF THE 1383 cm⁻¹ LINE OF Na₂N₂O₂ 39
VI  THE GF MATRIX CALCULATION OF THE FORCE CONSTANTS OF THE HYPERNITRITE ION 55
VII A COMPARISON OF THE FORCE CONSTANTS CALCULATED FOR THE HYPERNITRITE ION WITH THE FORCE CONSTANTS OF SIMILAR SYSTEMS 83
VIII CONCLUSION 86
BIBLIOGRAPHY 87
LIST OF ILLUSTRATIONS

Stainless Steel Electrode for Lamp 8
Low Pressure Hg Lamp 9
Photographs of Lamp Assembly 10
Diagram of Optical System 11
Hilger E612 Spectrograph 12
Visible Absorption Curve for Sat. Aq. NaNO₂ 13
Visible Absorption Curve for Rhodamine Treated Cellophane 14
Sample Tube 15
Negative Logarithm of k Versus Temperature 21
β Versus Temperature 22
Log (Rate of N₂O Evolution) Versus pOH 23
Concentration of Sodium Carbonate Versus Equivalent Time 24
Internal Standardization for CO₃⁻ Impurity Determination 25
Raman Spectrum 30
Infrared Spectrum 31
Photographic Reproduction of the Plate Showing the Raman Spectrum of Aq. Na₂N₂O₂ 32
Visible Absorption Curve for HN₃ Linear Polaroid 42
The Observed Value of ρ Versus the Values of ρ Obtained by Crawford and Horwitz 46
Internal Calibration for CCl₄ Plate 48
Internal Calibration for C₆H₆ Plate 50
Internal Calibration for CHCl₃ Plate 52
Internal Calibration for Aq. Na₂N₂O₂ 54
<table>
<thead>
<tr>
<th>Illustration Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{r\alpha}$ Versus $F_{r}$</td>
<td>72</td>
</tr>
<tr>
<td>$F_{r\alpha}$ Versus $F_{\alpha}$ at Various Values of $r_2/r_1$</td>
<td>73</td>
</tr>
<tr>
<td>$F_{RR}$ Versus $r_2/r_1$ at 120° and $F_{r\alpha} = 0$</td>
<td>77</td>
</tr>
<tr>
<td>$\alpha$ Versus $F_{R\alpha}$ at $r_2/r_1 = 1.135$</td>
<td>78</td>
</tr>
<tr>
<td>$\alpha$ Versus $F_{R}$ at $r_2/r_1 = 1.135$</td>
<td>79</td>
</tr>
<tr>
<td>$\alpha$ Versus $F_{RR}$ at $r_2/r_1 = 1.135$</td>
<td>80</td>
</tr>
</tbody>
</table>
RAMAN EVIDENCE FOR THE STRUCTURE OF
THE HYponITRite ION

CHAPTER I
INTRODUCTION

The structure of the hyponitrite ion has been discussed in several papers, but a complete description of the ion has been lacking. This has resulted partly because in all the structures conceived for this ion, the number of observed Raman and infrared fundamental vibrational frequencies did not coincide with the number of predicted frequencies. Kuhn and Lippincott (9, p. 1820-1821) assigned to the ion $C_{2h}$ symmetry based on the number of observed frequencies and their mutual exclusion in the Raman and infrared spectra. Later, Millen et al. (12, p. 18) observed a slightly different set of values for the infrared and Raman frequencies but with essentially the same result. They (13, p. 687-691) also made some approximate force constant calculations to show that $C_{2h}$ symmetry was allowable from the observed spectra. In their discussion they predicted two new low frequencies, one in the Raman belonging to the $A_g$ species and one in the infrared belonging to the $B_u$ species, which would be consistent with $C_{2h}$ symmetry.

The work presented in this thesis was undertaken with the view that more Raman information was obtainable from
the hyponitrite ion. Since the two already observed Raman lines and the third, as yet unobserved, line necessarily belonged to the \( A_g \) species if the ion was to have \( C_{2h} \) symmetry, these lines should have depolarization ratios between 0 and 6/7. Thus, if the depolarization ratio could be measured as positively less than 6/7, then the lines must belong to the \( A_g \) species since the lines associated with all other species have depolarization ratios of 6/7. Also if there was a third Raman fundamental, it was thought that improved technique in preparing the sample and handling the sample during exposure could result in seeing this third line. Three Raman lines assignable to the hyponitrite ion were observed in this study. Two lines were identical with those observed by Millen \textit{et al.}. Thus, one will find in this paper a discussion of the force constants which would arise from these three Raman lines.
CHAPTER II
DESIGN OF EQUIPMENT

The equipment used to carry out this study was designed to use the Hg \( \lambda 4358 \) line to excite the molecule. Thus, methods were needed to excite the mercury spectrum, isolate the \( \lambda 4358 \) line, pass this near monochromatic light through the sample, and observe the resulting change in the exciting light.

Hg LAMP

The lamp was a modification of a low pressure Hg lamp described by Haunschild (7, p. 4-11) in which tap water was run through stainless steel electrodes (page 8) to cool the lamp. See page 9 for a drawing of the lamp.

This lamp was longer (the lamp in the illuminating region was of a smaller diameter) and four stainless steel fittings were employed instead of three in comparison to Haunschild's lamp. The lamp was usually operated at 10 amperes of current. At this current there was a voltage drop of 36 volts across the lamp. A ballast resistor of about 3.4 ohms was included in the circuit.

In starting the lamp a vacuum of about 4 microns of mercury pressure was first attained. Then the lamp would start with or without the tap water flowing through the electrodes and with or without the lamp connected to
the vacuum line (the lamp was usually continuously connected to the vacuum system during operation). The lamp was found to start readily if across the upper cold finger electrodes the voltage from a luminous gas tube transformer was impressed and simultaneously the mercury pool was activated through the glass wall at the surface of the mercury pool with a spark tester. The voltage across the mercury electrodes was kept at about 110 volts during this process. Upon starting the current would rise to about 28 amperes with this voltage across the system.

Actual photographs of the lamp may be seen on page 10. The upper picture shows the lamp in operation.

OPTICAL ARRANGEMENT

The optical arrangement which is diagramed on page 11 corresponds to the design suggested by Nielson (16, p. 494-499) for the efficient filling of a spectrograph with light from a Raman tube using a condensing lens. The focal length of the condensing lens was 65.6 mm. The effective diameter of the sample tube was 9.34 mm. (The actual diameter was 15.0 mm.) The prism height was 86 mm. The best slit height was 2.88 mm. The focal length of the collimating lens was 5.84 mm. The distance from the slit to the condensing lens, $z$, was 85.8 mm. The distance from the condensing lens to the front end of the Raman
tube, x, was 17 mm. The assumed index of refraction of the sample was 1.33 (water). The effective length of the Raman tube was 395 mm. For the data obtained in this thesis the slit width was 0.10 mm.

SPECTROGRAPH

The spectrograph used was the commercially available Hilger E612 Raman spectrograph with the F5.7 camera attachment (E614). For a diagram of the spectrograph see page 12.

FILTER SYSTEM

The filters used to isolate the $4358 \text{ Å} \ Hg$ line from the lamp were illustrated by Stamm (20, p. 318-331). A one centimeter path of saturated aqueous NaN02 was used to reduce the light of higher frequency than $4358 \text{ Å}$. See the diagram on page 13 for an absorption curve of this solution. This filter was circulated through the filter jacket which is shown in place in the lower left picture on page 10, and cooled by passing water through a coiled glass tube immersed in a reservoir of the filter solution. Instead of using the 0.5 cm. path of Rhodamine 5GDN Extra, 0.075 gram per liter (aq.), an equivalent filter was designed which had a similar absorption in the visible region with the advantage of
requiring less space. This was made by placing a sheet of uncoated cellophane, DuPont cellophane 600PD, in an aqueous solution of Rhodamine 5GDN Extra, 0.075 gram per liter, for about one hour. The absorption curve in the visible region for the filter used in this series of experiments prepared in the manner mentioned above is illustrated in the diagram on page 14. This filter was wrapped tightly around either the sample tube or a polaroid cylinder, which ever was appropriate to the experiment at hand.

SAMPLE TUBE AND SAMPLE TUBE HOLDER

The sample tube was essentially a Wood's type tube made of constant bore tubing of 15.0 mm. diameter. See diagram on page 15. The back portion of the tube was bent so that the opening could be kept upright when the tube was in place. The portion of the tube which was not illuminated and the cap were painted with a heavy coat of black enamel. The sample tube holder and its relation to the sample tube are illustrated by the photographs on page 10. The tube holder was supported on an extension of the spectrograph on a triangular mounting to insure proper alignment. The correct position of the tube was assured by a cone shaped rest for the front of the tube and a V shaped support for the rear of the tube.
Kodak 103a-0 spectroscopic plates were used throughout the experiment. These plates show good sensitivity in the 4358 Å Hg line region but become insensitive after about a 3000 cm⁻¹ shift on the red side of this line. The plates were developed for two minutes at about 25°C (room temperature) with D-8 diluted one part D-8 to two parts water (4, p. 268-274). After development they were placed in an acetic acid stop bath for about 30 seconds and then fixed for about 10 minutes in Kodafix diluted one part Kodafix to three parts water. After washing the plates were placed in Farmer's reducer solution A (3.75 g. K₃Fe(CN)₆ per liter) for two minutes and then in solution B for five minutes. After the hypo had been washed out the plate was placed in a Kodak Photo-Flo solution for about 30 seconds before drying.

The opacities of the lines of the plates were recorded with a Jarrell Ash #2105 Microphotometer. For the use of this instrument I am indebted to the Bureau of Mines in Albany, Oregon, and in particular Mr. George Kantas.
STAINLESS STEEL ELECTRODE
FOR LAMP
TO SCALE
PHOTOGRAPHS OF LAMP ASSEMBLY
Diagram of Optical System
HILGER E 612
SPECTROGRAPH
WITH E 614 CAMERA
APPROXIMATE DISPERSION
120 cm⁻¹/mm
VISIBLE ABSORPTION CURVE
FOR SAT. AQ. NaNO₂
VISIBLE ABSORPTION CURVE
FOR RHODAMINE TREATED
CELOPHANE
The sodium hyponitrite was prepared essentially by the method described by Partington and Shah (17, p. 2071-2080). In this method an aqueous solution of sodium nitrite is reduced to sodium hyponitrite with sodium amalgam.

\[ 2\text{NO}_2^- + 4\text{Na}(\text{Hg})_x + 2\text{H}_2\text{O} = \text{N}_2\text{O}_2^{2-} + 4\text{Na}^+ + 4\text{OH}^- + 4\text{xHg} \]

One hundred grams of Mallinckrodt U.S.P. sodium nitrite were dissolved in 200 cc. of distilled water. The sodium amalgam was prepared by slowly adding 100 grams of Baker reagent sodium to 555 cc. of mercury. After the aqueous solution was poured into a 2-liter round bottom flask and placed so that tap water could continuously cool the flask, the amalgam was slowly added. After the reaction had cooled and had been cool for at least one hour, the unreacted amalgam was separated from the reaction mixture. The reaction mixture was not shaken at this point (17, p. 2071-2080) since this tended to cause difficulties in the following filtration. The thick mixture was then filtered through Scientific Supplies filter paper number 28320 into a Büchner funnel. A stream of carbon dioxide free air or nitrogen should have been blown over the mixture at this point since the mixture was extremely basic and absorbed carbon dioxide from the air. The lack of this precaution probably
caused the carbonate contamination of the sodium hypno-
mitrite. The solid, impure sodium hyponitrite was re-
peatedly triturated with absolute ethanol until the
solid would fall freely. The mixture was then filtered
and washed with absolute ethanol.

At this point the collection of samples from two
or three runs was used. The impure sodium hyponitrite
was dissolved in the least amount of water. This solu-
tion was added to about 25 grams of activated charcoal
and mixed. After about five minutes the mixture was
filtered. The aqueous solution was concentrated by
placing the sample in a capped jar (the lid was screwed
on loosely) which held about twice the volume of liquid
present and then putting this jar in a vacuum desiccator
which had concentrated sulfuric acid as a desiccant.
The desiccator was evacuated with a fore-pump using a
dry ice-acetone cooled trap to prevent the water from
contaminating the fore-pump oil. Caution should be used
at this point not to dry the sample too fast or too much
since the octahydrate form probably has superior proper-
ties to the anhydrous form for purification.

After the sample had crystallized it was repeatedly
triturated with absolute ethanol, filtered, washed with
ethanol, and finally washed with absolute ether. Then
the sample was dried over concentrated sulfuric acid at
about 20 microns of mercury pressure.
An infrared spectrum of the sample at this stage showed the presence of carbonate and nitrite of which the nitrite could be almost entirely removed by repeating the process of dissolving the sample in water and allowing the octahydrate to precipitate. A medium intense band at 885 cm\(^{-1}\) appeared which could not be assigned to either carbonate or nitrite, but it tended to be removed upon trituration of the sample with absolute ethanol. Whether this band was due to NaH\(\text{N}_2\text{O}_2\) was not investigated further. This line was reported by Kuhn and Lippincott (9, p. 1820-1821) but they did not give it an assignment.

The yield was about 19 percent of the theoretical yield.
CHAPTER IV
OBSERVED SPECTRA

Just prior to making the Raman exposures of the aqueous Na$_2$N$_2$O$_2$, 50.0 grams of Na$_2$N$_2$O$_2$·xH$_2$O and 4.00 grams of reagent NaOH were dissolved in 140 cc. of solution. During the solution process the sample was cooled in an ice bath to avoid decomposition due to the heat generated upon solution. The solution was then filtered three times through a Corning fine sintered glass filter. During the filtering process the filter was capped with a tube containing ascarite so that the atmospheric air was required to pass through the ascarite tube.

NaOH was added to the solution to retard decomposition of the hyponitrite. If the rate determining step for the decomposition of the hyponitrite ion in water is (23, p. 55)

$$\text{H}_2\text{N}_2\text{O}_2 = \text{N}_2\text{O} + \text{H}_2\text{O}$$

the derived kinetic equation explains reasonably well the experimental findings on the rate of decomposition of hyponitrite. Thus one may write

$$\text{N}_2\text{O}_2^- + \text{H}_2\text{O} = \text{HN}_2\text{O}_2^- + \text{OH}^-$$

$$\text{HN}_2\text{O}_2^- + \text{H}_2\text{O} = \text{H}_2\text{N}_2\text{O}_2 + \text{OH}^-$$

$$K_1 = \frac{[\text{HN}_2\text{O}_2^-][\text{OH}^-]}{[\text{N}_2\text{O}_2^-]}$$
\[ K_2 = \frac{[\text{H}_2\text{N}_2\text{O}_2^-]}{\text{H}_2\text{N}_2\text{O}_2^-} \]

and

\[
\frac{d[N_2O]}{dt} = k'[\text{H}_2\text{N}_2\text{O}_2^-] 
\]

Then if one lets

\[
[N_2O_2^-]_s = [N_2O_2^-] + [\text{HN}_2\text{O}_2^-] ,
\]

the final result is

\[
\frac{d[N_2O]}{dt} = \frac{K_2k'[N_2O_2^-]_s}{[\text{OH}^-](1 + \frac{[\text{OH}^-]}{K_1})} 
\]

Let

\[ K_2k' = k \]

and

\[ \frac{1}{K_1} = \beta \]

A plot of \(-\log\)arithm \(k\) versus the temperature is shown on page 21. A plot of \(\beta\) versus the temperature is shown on page 22. On page 23 a plot of the logarithm of the rate of \(\text{N}_2\text{O}\) evolution versus the \([\text{OH}^-]\) is shown for 25°C and for 10°C. Thus, it is easily shown that several orders of magnitude reduction in the rate of the decomposition of the hyponitrite ion may be attained if the solution is made 1 M NaOH as compared to the addition of no NaOH. Also a reduction in the rate of decomposition is obtained in cooling the sample.

The sample was cooled to near the temperature of tap
NEGATIVE LOGARITHM OF $k$

VERSUS TEMPERATURE

NEGATIVE LOGARITHM OF $k$

TEMPERATURE DEGREES CENTIGRADE
LOG (RATE OF N₂O EVOLUTION)
VERSUS pOH

LOG (RATE OF N₂O EVOLUTION IN CC/MIN.)

25°C

10°C
CONCENTRATION OF SODIUM CARBONATE VERSUS EQUIVALENT TIME
INTERNAL STANDARDIZATION
FOR $\text{CO}_3^-$ IMPURITY
DETERMINATION

OPACITY

TIME IN SECONDS
water by circulating the NaNO\textsubscript{2} filter solution through the filter jacket. The filter solution was in turn cooled by passing tap water through a coiled glass tube immersed in the filter solution.

The exposure was made for one half hour with 15.0 amperes passing through the lamp. On the same plate samples of 1.00 M Na\textsubscript{2}CO\textsubscript{3} in 1.00 M NaOH, 0.50 M Na\textsubscript{2}CO\textsubscript{3} in 1.00 M NaOH, and 0.25 M Na\textsubscript{2}CO\textsubscript{3} in 1.00 M NaOH were exposed for the same time—one half hour. Along with these exposures an internal standard for the plate emulsion was made by exposing carbon tetrachloride for a range of times from two seconds to forty seconds with the lamp operating at 10.0 amperes. A more complete discussion of the use of an internal standard is given on page 141.

The Na\textsubscript{2}CO\textsubscript{3} exposures had two purposes. The first was to quantitatively estimate the concentration of Na\textsubscript{2}CO\textsubscript{3} in the hyponitrite sample (the carbonate 1065 cm\textsuperscript{-1} line was used for this purpose), and the second was to determine if the Na\textsubscript{2}CO\textsubscript{3} could introduce any other lines besides its 1065 cm\textsuperscript{-1} at the concentration present in the hyponitrite sample. Using the internal standard a plot, page 25, of the concentration of Na\textsubscript{2}CO\textsubscript{3} versus the equivalent time (see page 43 for an explanation of equivalent time) is shown on page 24. From this graph the estimated Na\textsubscript{2}CO\textsubscript{3} concentration turns out to be about
Even with 1.00 M Na$_2$CO$_3$ weak lines at 692 cm$^{-1}$ and 1115 cm$^{-1}$ were not observable in its spectrum. If either NaNO$_2$ or NaNO$_3$ appeared as contaminantes, lines should have appeared at 1331 cm$^{-1}$ for NaNO$_2$ and 1055 cm$^{-1}$ for NaNO$_3$. NaNO$_2$ has weaker lines at 720 cm$^{-1}$, 1381 cm$^{-1}$ and 1414 cm$^{-1}$. The absence of NaNO$_2$ and NaNO$_3$ was also confirmed by the infrared spectra.

<table>
<thead>
<tr>
<th>Material</th>
<th>Opacity</th>
<th>Eq. Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_3^-$ (N$_2$O$_2^-$)</td>
<td>2.00</td>
<td>14.0</td>
</tr>
<tr>
<td>0.5M CO$_3^-$</td>
<td>1.23</td>
<td>6.0</td>
</tr>
<tr>
<td>0.25M CO$_3^-$</td>
<td>1.545</td>
<td>10.03</td>
</tr>
<tr>
<td>1M CO$_3^-$</td>
<td>2.41</td>
<td>16.6</td>
</tr>
</tbody>
</table>

The graph on page 31 shows a diagram of the infrared spectrum in the rock salt region. The Na$_2$N$_2$O$_2$ absorptions were run as Nujol mulls while the strong Na$_2$CO$_3$ absorption at 1450 cm$^{-1}$ and the water absorptions around 3000-3600 cm$^{-1}$ were run as perfluorokerosene mulls. Due to the inherent Nujol absorptions perfluorokerosene was used as a complementary mulling agent. Thus, in a perfluorokerosene mull the sample was scanned from about 1200 cm$^{-1}$ to 1600 cm$^{-1}$ to bring out the 1450 cm$^{-1}$ carbonate band and from about 2800 cm$^{-1}$ to 3600 cm$^{-1}$ to give a clearer indication of the broad water absorption region. The diagram, of course, does not show the absorptions due to Nujol or perfluorokerosene. Thus, the absorption bands shown may be assigned as follows:
The graph on page 30 shows a drawing of the percent transmittance of the Raman plate spectrum illustrating the relative peak intensities. The scan was not carried further than about 1600 cm⁻¹ because no lines besides broad diffuse bands assignable to water or OH⁻ were observable. The line at 220 cm⁻¹ was caused by the 4358A₀ Hg line. This was apparent from observation of the plate itself. Thus, the lines seen may be assigned as follows:

<table>
<thead>
<tr>
<th>Na₂N₂O₂</th>
<th>Na₂CO₃</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>692 cm⁻¹</td>
<td>1065 cm⁻¹</td>
<td>1690 cm⁻¹</td>
</tr>
<tr>
<td>1115 cm⁻¹</td>
<td>1383 cm⁻¹</td>
<td>3000-3600 cm⁻¹</td>
</tr>
</tbody>
</table>

One might also suspect that the decomposition products of the hyponitrite ion could yield a sufficient concentration to give a faint Raman line. N₂O has strong lines at 1286.5 and 2223.2 cm⁻¹ (8, p. 277). Thus, dissolved gaseous N₂O could not have accounted for either
the 1115 cm$^{-1}$ or the 692 cm$^{-1}$ lines. Also $\text{HN}_2\text{O}_2^-$ and $\text{H}_2\text{N}_2\text{O}_2$ could have possibly given new or shifted frequencies from those of $\text{N}_2\text{O}_2^2^-$. The addition of $\text{OH}^-$ to the hyponitrite solution reduced drastically the concentration of these species and decreased the probability that 1115 cm$^{-1}$ or 692 cm$^{-1}$ could have been assigned to them. Page 32 shows a photographic reproduction of part of the plate which shows the hyponitrite ion spectrum. Also shown is the spectrum of the 1.0 M sodium carbonate and xenon and krypton reference spectra. With the xenon and krypton spectra mercury and iron lines may also be seen.
RAMAN SPECTRUM

WAVE NUMBER SHIFT FROM Hg 4358 Å

% TRANSMITTANCE OF PLATE

1600 1200 800 400 0
INFRARED SPECTRUM

% TRANSMITTANCE

WAVE NUMBER

3800 3400 3000 2600 2200 1800 1400 1000 600
CHAPTER V
POLARIZATION OF RAMAN LINES

A. THEORY OF THE POLARIZATION OF RAMAN LINES

The classical rate of radiation from an induced dipole per unit solid angle in the X direction is given by

\[ I = \frac{16\pi^4 \nu^4}{c^2} (P_{oy}^2 + P_{oz}^2) \]

where \( \nu \) is the frequency of oscillation and of the emitted light and \( P_{oy} \) and \( P_{oz} \) are the amplitudes in the expressions

\[ P_y = P_{oy} \cos(2 \pi \nu t + \delta) \]
\[ P_z = P_{oz} \cos(2 \pi \nu t + \delta') \]

\( P_y \) and \( P_z \) are components of the induced dipole. Let us now consider the case of the intensity of scattered light. Assume that the "direction of propagation of the incident light coincides with the Y axis." (22, p. 45)

\[ I_T (OBS. I) \]
\[ I_N (OBS. II) \]
\( I_T(\text{obs.} \ 11) \) indicates the total intensity of scattered light if the incident light is polarized parallel to the X axis. \( I_T(\text{obs.} \ \perp) \) indicates the total intensity of scattered light if the incident light is polarized parallel to the Z axis. And \( I_{\|}(\text{obs.} \ \perp) \) indicates the intensity of the Z component of scattered light if the incident light is polarized parallel to the Z axis.

The depolarization ratio is "defined as the ratio of the scattered intensity which is polarized perpendicular to \( \overline{E} \), that is, in the direction of propagation of the incident light, to the intensity parallel to \( \overline{E} \)."

(22, p. 47) "If the incident light in natural (unpolarized), the depolarization ratio may be computed by considering the scattered light to represent the sum of the intensities of the observations made parallel and perpendicular to the incident electric vector of a polarized beam. That part of the light from the parallel observation, being unpolarized, contributes one-half its intensity to the scattered light polarized, respectively, parallel and perpendicular to \( \overline{E} \):

\[
\rho_n = \frac{I_T(\text{obs.} \ \perp) - I_{\|}(\text{obs.} \ \perp) + \frac{1}{2} I_T(\text{obs.} \ 11)}{I_{\|}(\text{obs.} \ \perp) + \frac{1}{2} I_T(\text{obs.} \ 11)}
\]

(22, p. 47)

In order to express \( \rho_n \) in terms of molecular parameters, let us consider a molecule acted upon by an
external light source. The induced dipole moment, $\vec{P}$, may be written in terms of the electric field, $\vec{E}$, acting on the molecule as

\begin{equation}
\vec{P} = \alpha \vec{E}
\end{equation}

where $\alpha$ is the polarizability tensor. It can be shown, however, that a set of axes in the molecule exists such that the relation between $\vec{P}$ and $\vec{E}$, when referred to these axes, assumes the simple form

\begin{equation}
\begin{align*}
P_1 &= \alpha_1 E_1 \\
P_2 &= \alpha_2 E_2 \\
P_3 &= \alpha_3 E_3
\end{align*}
\end{equation}

Thus, according to equations (1) and (4)

\begin{equation}
\begin{align*}
I_T(\text{OBS. } 11) &= \frac{2}{c^3} \frac{\nu^4}{\pi^3} (\alpha_{yx}^2 + \alpha_{zx}^2) E_0^2 \\
I_T(\text{OBS. } \perp) &= \frac{2}{c^3} \frac{\nu^4}{\pi^3} (\alpha_{yz}^2 + \alpha_{zz}^2) E_0^2 \\
I_\parallel(\text{OBS. } \perp) &= \frac{2}{c^3} \frac{\nu^4}{\pi^3} (\alpha_{zz}^2) E_0^2
\end{align*}
\end{equation}

Since the $\alpha_{FF'}$ refer to a laboratory fixed axis system the $\alpha_{FF'}$ should be averaged over all orientations of the molecular principal axes with respect to the fixed axes, $X, Y,$ and $Z$. Since the formulas of transformation for $\alpha_{FF'}$ are of the form

\begin{equation}
\alpha_{FF'} = \sum_{i=1}^{3} \alpha_i \Phi_{Fi} \Phi_{F'i}
\end{equation}

(22, p. 46)
where the i axes refer to the principal axes of the molecule and, therefore, the quantities $\alpha_i$ are constants under the averaging process, the averages required are expressible as

\[ \overline{\alpha_{PP}^2} = \sum_1 \alpha_i^2 \overline{\Phi_{F_1 F_1} \Phi_{F_1 F_1}^2} + 2 \sum_{1<j} \alpha_i \alpha_j \overline{\Phi_{F_1 F_1} \Phi_{F_1 F_1} \Phi_{F_1 F_1} \Phi_{F_1 F_1}} \]

The necessary averages of the direction cosines are

\[ \overline{\Phi_{F_1 F_1} \Phi_{F_1 F_1}^2} = \begin{cases} \frac{1}{15} & F = F' \\ \frac{1}{15} & F \neq F' \end{cases} \]

\[ \overline{\Phi_{F_1 F_1} \Phi_{F_1 F_1} \Phi_{F_1 F_1} \Phi_{F_1 F_1}} = \begin{cases} \frac{1}{15} & F = F' \\ \frac{1}{30} & F \neq F' \end{cases} \]

(22, p. 292)

Thus, for N molecules equations (6) become, using equations (8) and (9)

\[ I_T (OBS. I) = \frac{1}{15} \frac{2 \pi^3 \nu^4}{0^3} NE_o^2 \left( \sum_1 \alpha_i^2 - 2 \sum_{1<j} \alpha_i \alpha_j \right) \]

\[ I_T (OBS. \perp) = \frac{1}{15} \frac{2 \pi^3 \nu^4}{0^3} \left( 4 \sum_1 \alpha_i^2 + \sum_{1<j} \alpha_i \alpha_j \right) \]

\[ I_{11} (OBS. \perp) = \frac{1}{15} \frac{2 \pi^3 \nu^4}{0^3} \left( 3 \sum_1 \alpha_i^2 + 2 \sum_{1<j} \alpha_i \alpha_j \right) \]

Now if one makes the substitution of
\[ \alpha = \frac{1}{3} (\alpha_1 + \alpha_2 + \alpha_3) \]

\[ \beta^2 = \frac{1}{2} \left[ (\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2 \right] \]

where \( \alpha \) is the spherical part of the polarizability and \( \beta \) is the anisotropy, equations (10) become

\[ I_T(\text{OBS. } 11) = \frac{2\, \pi^3 \nu^4}{c^3} \frac{N}{E_0}^2 \left( \frac{2\, \beta^2}{15} \right) \]

\[ I_T(\text{OBS. } \perp) = \frac{2\, \pi^3 \nu^4}{c^3} \frac{N}{E_0}^2 \left( \frac{45\, \alpha^2 + 7\, \beta^2}{45} \right) \]

\[ I_\Pi(\text{OBS. } \perp) = \frac{2\, \pi^3 \nu^4}{c^3} \frac{N}{E_0}^2 \left( \frac{45\, \alpha^2 + 4\, \beta^2}{45} \right) \]

If now equations (12) are substituted into equation (3)

\[ \rho_n = \frac{6\, \beta^2}{45\, \alpha^2 + 7\, \beta^2} \]

These results are transformed into quantum mechanical expressions by considering that the intensities will be proportional to expressions of the form

\[ \frac{N_n}{g_n} \sum_{m, m'} \left| (\alpha_{pp})_{m m'} \right|^2 \]

(22, p. 50)

where \( N_n \) is the number of molecules initially in the energy level described by the quantum number \( n \), \( g_n \) is the number of degenerate initial states characterized
by the magnetic quantum number, \( m' \), and \( (\alpha_{m'm'})_{m''m'} \)
is given by

\[
(15) \quad (\alpha_{m'm'})_{m''m'} = \int \psi_{m''}^* \alpha_{m'm'} \psi_{m'} \, d\tau.
\]

Thus, equations (12) become

\[
(16) \quad I_T(\text{OBS. 11}) = \frac{8 \pi^3 \nu^4}{c^3} \frac{N_{m''}}{e_{m''}} E_o^2 \left( \frac{2}{15} \sum_{m''m'} \beta_{m''m'}^2 \right)
\]

\[
+ \frac{7}{45} \sum_{m''m'} (\beta_{m''m'})^2
\]

\[
I_{ll}(\text{OBS. 1}) = \frac{8 \pi^3 \nu^4}{c^3} \frac{N_{m''}}{e_{m''}} E_o^2 \left( \sum_{m''m'} (\alpha_{m''m'})^2 \right)
\]

\[
+ \frac{4}{45} \sum_{m''m'} (\beta_{m''m'})^2
\]

and equation (13) becomes

\[
(17) \quad \rho_n = \frac{\sum_{m''m'} (\beta_{m''m'})^2}{45 \sum_{m''m'} (\alpha_{m''m'})^2 + 7 \sum_{m''m'} (\beta_{m''m'})^2}.
\]

It is well to note at this point that "any vibration that is antisymmetric or degenerate with respect to any other symmetry element will give a Raman line with the maximum degree of depolarization if it occurs at all"
and "therefore, only Raman lines corresponding to
totally symmetric vibrations can have a degree of de-
polarization smaller than the maximum value 6/7."
(8, p. 249) In the "cubic point groups, the totally
symmetric Raman lines are completely polarized (\(\rho_n = 0\))."
(8, p. 271) "For all other molecules, that is, for all
non-cubic point groups, the degree of depolarization of
the totally symmetric Raman lines is intermediate between
0 and 6/7." (8, p. 271) Also one might note that the
observation of the width of the Raman lines sometimes
supplements the observation of their state of depolariza-
tion "When a degree of depolarization of 6/7 is observed,
for a Raman line it is probable, but not certain, that
it corresponds to a non-totally symmetric vibration.
Observation of a great width of the Raman line would make
this certain. On the other hand, if a Raman line is
quite sharp (even under fairly high dispersion) it is not
certain, although probable, that the line corresponds to
a totally symmetric vibration." (8, p. 491)

B. EXPERIMENTAL MEASUREMENT OF THE DEGREE OF DEPOLARIZA-
TION OF THE 1383 cm\(^{-1}\) LINE OF Na\(_2\)N\(_2\)O\(_2\)

The depolarization ratio was measured, taking cer-
tain precautions, by using two polaroid cylinders, one
with its polarizing axis parallel to the sample tube and
the other with its axis perpendicular to the sample tube.
(5, p. 124-127) The lamp, sample tube, filters, and
polaroid were placed in a cylindrical reflector coated with magnesium oxide according to the following diagram.

R is the cylindrical reflector.
L is the low pressure Hg lamp.
F is a one centimeter path of saturated aq. NaNO₂.
F' is a cylindrical cellophane treated rhodamine GDN extra.
P is the polaroid cylinder.
S is the sample tube.

A separate discussion of the design of the apparatus concerning the low pressure Hg lamp, the light filters, and the sample tube was made in Chapter II. The polaroid used was Polaroid HN 32 plastic linear polarizer 0.010 inch in thickness of cellulose acetate butyrate purchased from the Polaroid Corporation, Cambridge 39, Mass. Its absorption curve in the visible region is shown on page 42.

The polaroid cylinder was made by wrapping the polaroid about the sample tube and uniting the two sides of the polaroid with cellophane tape. A sheet of rhodamine GDN extra treated cellophane was then wrapped about the
outside of the polaroid cylinder and again fastened with cellophane tape. The rhodamine GDN extra filter was attached permanently to the polaroid cylinder. The filter-polaroid cylinder thus made could be slid easily on or off a given sample tube.

Rank and Kagarise (19, p. 89-92) described a method in which the convergence error of such a system as this one may be corrected. However, they used a photoelectric means of detecting the spectra and did not encounter the problem of interpreting relative intensities from photographic plates. In order to attempt an interpretation from the photographic plates $\rho_o$, the observed depolarization ratio, was plotted as a function of $\rho_t$, the true or accepted value of the depolarization ratio using the following scheme for chloroform (262, 0.86; 366, 0.18; 668, 0.08), carbon tetrachloride (218, 0.83; 314, 0.82; 459, 0.044), and benzene (606, 0.8; 992, 0.04; 1177, 0.8). (4, p. 272) The first number in the series behind the given molecule represents the wave number shift of the line, and the second number gives $\rho_t$ for that line.

An internal standard was produced by exposing $\text{CCl}_4$ from two seconds to 40 seconds. Eight different exposures of this type were made such that the logarithm of the time of exposure changed by about 0.15 units. On the same plate the required exposure was made. The zero density was taken as the region of maximum light
VISIBLE ABSORPTION CURVE FOR
HN32 LINEAR POLAROID

% TRANSMITTANCE

WAVE LENGTH IN MILLIMICRONS
transmittance on the side of the Raman line nearer the exciting line. (4, p. 273) Thus, two exposures of the sample were taken of the same duration and identical conditions except that the polaroid cylinders were interchanged. In order to compare the intensities of a given band in the two exposures, a plot of the logarithm of the peak opacity, peak density, versus the logarithm of the time of the exposure was first plotted for the internal standard at 459 cm\(^{-1}\) (see the respective graphs for each plate). Next the logarithm of the peak opacity for the line in question in the two cases was measured. Using the calibration curve for the emulsion, these densities corresponded to two times (the equivalent times). The ratio of the time calculated for the perpendicular case to the time calculated for the parallel case was taken as the observed depolarization ratio, \(\rho_0\).

In order to make the results have more meaning and as an attempt to correct for experimental fluctuations, such as the variable light intensity output of the H\(_g\) lamp, the calibration curve of \(\rho_0\) versus \(\rho_t\) was made from the average of six observations of each case. See the charts on pages 47, 49, and 51. Even with this method the curve came out so that one could only estimate the value of \(\rho_t\) within \(\pm .08\) units. See the graph on page 46.

Three lines were observed for sodium hyponitrite: 1383 (s), 1115 (w), and 682 (vw). Although the lines at
1115 cm$^{-1}$ and 692 cm$^{-1}$ were visually apparent on the plate they were too weak to measure the depolarization ratio by the method employed. Besides general fogging which occurs because of light scattering from the gas bubbles upon decomposition of the hyponitrite, the line at 1115 cm$^{-1}$ is very close to the carbonate impurity line at 1065 cm$^{-1}$. Because of this, only the measurement of the depolarization ratio of the line at 1383 cm$^{-1}$ was attempted. Three exposures of about 2.5 M Na$_2$N$_2$O$_2$ with 1 M NaOH were made for each of the polaroid cylinders. Each exposure was for one hour with the lamp operating at 10.0 amperes. The average values for the opacity of the 1383 cm$^{-1}$ line for each polaroid was calculated. The value was related to an equivalent time from the internal calibration spectra of carbon tetrachloride (page 54). The appropriate ratio of these values was taken as $\rho_o$ (page 53). Then from the calibration chart of $\rho_o$ versus $\rho_t$ the value of $\rho_t$ was estimated for the 1383 cm$^{-1}$ line. $\rho_o$ turned out to be 0.85. Thus, $\rho_t$ is 0.82 ± 0.08 (page 53). It is apparent that one cannot tell conclusively that $\rho_t$ is not 6/7. The lines at 692 cm$^{-1}$ and 1383 cm$^{-1}$ appeared sharp. The line at 1115 cm$^{-1}$ appeared slightly diffuse but this was not certain because the 1065 cm$^{-1}$ line of the carbonate impurity tended to complicate this region of the spectrum.
Thus, only inconclusive information was obtainable from this approach. But it appeared probable that the lines belonged to totally symmetric modes from the apparent sharpness of the lines.
THE OBSERVED VALUE OF $\rho$
VERSUS THE VALUES OF
$\rho$ OBTAINED BY
CRAWFORD AND HORWITZ
(4, p. 268-274)
CARBON TETRACHLORIDE

<table>
<thead>
<tr>
<th>Line (cm⁻¹)</th>
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<th>314</th>
<th>459</th>
<th>218</th>
<th>314</th>
<th>459</th>
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<td></td>
<td></td>
<td>Opacity</td>
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<td>2.29</td>
<td>2.29</td>
<td>2.30</td>
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<td>218</td>
<td>2.63</td>
<td>2.68</td>
<td>2.53</td>
<td>2.61</td>
<td>2.57</td>
<td>2.60</td>
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<tr>
<td>314</td>
<td>1.24</td>
<td>1.26</td>
<td>1.26</td>
<td>1.21</td>
<td>1.22</td>
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<td>459</td>
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<table>
<thead>
<tr>
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<th>218</th>
<th>314</th>
<th>459</th>
<th>218</th>
<th>314</th>
<th>459</th>
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</thead>
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<tr>
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<td>3.16</td>
<td>2.94</td>
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<td>3.02</td>
<td>2.89</td>
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<td>3.20</td>
<td>3.11</td>
<td>3.08</td>
<td>3.09</td>
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<tr>
<td>314</td>
<td>7.48</td>
<td>7.64</td>
<td>6.97</td>
<td>6.82</td>
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<td>6.42</td>
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<table>
<thead>
<tr>
<th>Line (cm⁻¹)</th>
<th>Equivalent Time</th>
<th>P₀</th>
<th>Pₜ</th>
<th>*</th>
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<tbody>
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<td>.83</td>
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</tr>
<tr>
<td>↓</td>
<td>12.0</td>
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<td></td>
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</tr>
<tr>
<td>314 II</td>
<td>10.5</td>
<td>.840</td>
<td>.82</td>
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</tr>
<tr>
<td>↓</td>
<td>12.5</td>
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<td>459 II</td>
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<td>.163</td>
<td>.044</td>
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<tr>
<td>↓</td>
<td>23.0</td>
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</table>

* (I, p. 268-274)
INTERNAL CALIBRATION FOR
CCl₄ PLATE

OPACITY

TIME IN SECONDS

15
10
5
0
**BENZENE**

<table>
<thead>
<tr>
<th>Line (cm(^{-1}))</th>
<th>(\parallel) Opacity</th>
<th>(\perp) Opacity</th>
<th>Average</th>
<th>(P_0)</th>
<th>(P_t)</th>
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<td>1.31 1.34 1.28 1.26 1.29 1.25</td>
<td>1.33 1.33 1.34 1.34 1.38 1.34</td>
<td>1.29</td>
<td>.883</td>
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<td>992</td>
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<td>21.1 21.1 19.4 19.1 21.1 18.3</td>
<td>2.99</td>
<td>.246</td>
<td>0.04</td>
</tr>
<tr>
<td>1177</td>
<td>1.42 1.46 1.42 1.38 1.35 1.36</td>
<td>1.50 1.50 1.52 1.50 1.45 1.44</td>
<td>1.40</td>
<td>.910</td>
<td>0.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Line (cm(^{-1}))</th>
<th>Equivalent Time</th>
<th>(P_0)</th>
<th>(P_t)</th>
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</thead>
<tbody>
<tr>
<td>606 (\parallel)</td>
<td>5.00</td>
<td>.883</td>
<td>0.8</td>
</tr>
<tr>
<td>(\perp)</td>
<td>5.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>992 (\parallel)</td>
<td>14.3</td>
<td>.246</td>
<td>0.04</td>
</tr>
<tr>
<td>(\perp)</td>
<td>58.2</td>
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<td></td>
</tr>
<tr>
<td>1177 (\parallel)</td>
<td>6.20</td>
<td>.910</td>
<td>0.8</td>
</tr>
<tr>
<td>(\perp)</td>
<td>6.80</td>
<td></td>
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</tbody>
</table>

* (4, p. 268-274)
INTERNAL CALIBRATION FOR

$C_6H_6$ PLATE

OPACITY

TIME IN SECONDS
### CHLOROFORM

| Line (cm⁻¹) |   || Opacity  | Average |
|-------------|----------------|---------|
|             |   | 2.60 | 2.58 | 2.65 | 2.41 | 2.41 | 2.53 |
| 262         |   | 1.35 | 1.34 | 1.35 | 1.34 | 1.36 | 1.35 |
| 366         |   | 1.18 | 1.17 | 1.22 | 1.21 | 1.18 | 1.19 |

<table>
<thead>
<tr>
<th>Line (cm⁻¹)</th>
<th>( \perp ) Opacity</th>
<th>Average</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>3.05</td>
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<tr>
<td>262</td>
<td></td>
<td>3.64</td>
</tr>
<tr>
<td>366</td>
<td></td>
<td>3.80</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Line (cm⁻¹)</th>
<th>Equivalent Time</th>
<th>( \rho_0 )</th>
<th>( \rho_t ) *</th>
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<tbody>
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<td>( \perp )</td>
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<td>366 ( \parallel )</td>
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<td>.18</td>
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<td>668 ( \parallel )</td>
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<td>.08</td>
</tr>
<tr>
<td>( \perp )</td>
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* (4, p. 268-274)
INTERNAL CALIBRATION FOR
CHCl₃ PLATE

OPACITY

TIME IN SECONDS

2

3

4

6

8

10

15

20

30

40

2

3

4

5
AQUEOUS SODIUM HYPOXONITRITE
(2-3 M)
1383 cm\(^{-1}\)

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<tr>
<td>(\perp)</td>
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<td>4.28</td>
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<table>
<thead>
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<th>Polaroid</th>
<th>Equivalent Time</th>
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<th>(\rho_t)</th>
</tr>
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<tbody>
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<td>(\parallel)</td>
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<td>.848</td>
<td>.82±.08</td>
</tr>
<tr>
<td>(\perp)</td>
<td>15.3</td>
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</table>
INTERNAL CALIBRATION FOR

AQ. $Na_2N_2O_2$ PLATE

OPACITY

TIME IN SECONDS
Let

\[ G_{tt'} = \sum_{\alpha=1}^{N} \mu_{\alpha} \overline{s}_{t\alpha} \cdot \overline{s}_{t'\alpha} \]  

(22, p. 61)

where \( \overline{s}_{t\alpha} \) is defined as follows: "The direction of \( \overline{s}_{t\alpha} \) is the direction in which a given displacement of atom \( \alpha \) will produce the greatest increase of \( S_t \). The magnitude of \( \overline{s}_{t\alpha} \) is equal to the increase of \( S_t \) produced by a unit displacement of the atom \( \alpha \) in this most effective direction." (22, p. 55) The quantity \( \mu_{\alpha} \) is the reciprocal mass of atom \( \alpha \). Then it can be shown "that the kinetic energy of vibration can be written in terms of internal coordinates in the form

\[ 2T = \sum_{tt'} (G^{-1})_{tt'} \hat{S}_t \hat{S}_{t'} \]  

(22, p. 63)

where the matrix \( G^{-1} \) is the inverse of \( G \). "If the potential energy is expressed in the same internal coordinates so that

\[ 2V = \sum_{tt'} F_{tt'} \hat{S}_t \hat{S}_{t'} \]  

(19)

\( F_{tt'} \) being the force constants, the vibrational problem leads to a secular equation" (22, p. 64)
where \( \lambda = 4 \pi^2 \nu^2 \) and the determinant has \( n \) rows and \( n \) columns. \( n \) is the number of internal coordinates. Thus, if equation (20) is multiplied by the determinant of the matrix \( G \) the final result is

\[
|G_{ij} - \nu \lambda| = 0
\]

or

\[
|F_{ij} - \nu \lambda| = 0
\]

since \( F \) and \( G \) are both symmetrical matrices.

Now, consider the hyponitrite ion for which the structure has been proposed to be \( G_{2h} \) (9, p. 1820-1821) (For a discussion which discounts some other possible structures see Millen, et al.'s paper (12, p. 687-691).)

\[ \begin{align*}
N & = \frac{\sqrt{\alpha_2^2 + \alpha_3^2}}{N} \\
O & = \frac{1}{\sqrt{\alpha_1^2}} \end{align*} \]

Let the internal coordinates be defined in terms of the above diagram by

\[
\begin{align*}
S_1 &= r_{23} = r_1 \\
S_2 &= r_{12} = r_2 \\
S_3 &= r_{34} = r_3
\end{align*}
\]
(23 continued)

\[ s_4 = \sqrt{r_{12}^{-1}r_{23}} \alpha_1 \]
\[ s_5 = \sqrt{r_{34}^{-1}r_{23}} \alpha_2 \]

Then the \( \vec{s}_{\text{tt'}} \) vectors may be written as follows: (\( \vec{e}_{\alpha \alpha'} \) is a unit vector from atom \( \alpha \) to atom \( \alpha' \).)

\[
\begin{align*}
\vec{s}_{11} &= 0 & \vec{s}_{21} &= \vec{e}_{21} & \vec{s}_{31} &= 0 \\
\vec{s}_{12} &= \vec{e}_{32} & \vec{s}_{22} &= -\vec{e}_{21} & \vec{s}_{32} &= 0 \\
\vec{s}_{13} &= -\vec{e}_{32} & \vec{s}_{23} &= 0 & \vec{s}_{33} &= -\vec{e}_{34} \\
\vec{s}_{14} &= 0 & \vec{s}_{24} &= 0 & \vec{s}_{34} &= \vec{e}_{34} \\
\vec{s}_{41} &= \sqrt{r_{23}^{-1} \left( \frac{\vec{e}_{21} \cos \alpha_1 + \vec{e}_{32}}{\sin \alpha_1} \right)} \\
\vec{s}_{42} &= -\sqrt{r_{23}^{-1} \left( \frac{\vec{e}_{21} \cos \alpha_1 + \vec{e}_{32}}{\sin \alpha_1} \right)} \sqrt{r_{12}^{-1} \left( \frac{-\vec{e}_{32} \cos \alpha_1 - \vec{e}_{21}}{\sin \alpha_1} \right)} \\
\vec{s}_{43} &= \sqrt{r_{12}^{-1} \left( -\vec{e}_{32} \cos \alpha_1 - \vec{e}_{21} \right)} \\
\vec{s}_{44} &= 0 \\
\vec{s}_{51} &= 0 \\
\vec{s}_{52} &= -\sqrt{r_{34}^{-1} \left( \frac{\vec{e}_{32} \cos \alpha_2 - \vec{e}_{34}}{\sin \alpha_2} \right)}
\end{align*}
\]
Thus, the $G$ matrix for the hyponitrite ion may be constructed from equation (17) and equations (24)

\[
G_{11} = \frac{1}{m_2} + \frac{1}{m_3}
\]

\[
G_{12} = \frac{\cos \alpha_1}{m_2}
\]

\[
G_{13} = \frac{\cos \alpha_2}{m_3}
\]

\[
G_{14} = -\sqrt{\frac{r_{12}}{r_{23}}} \frac{\sin \alpha_1}{m_2}
\]

\[
G_{15} = -\sqrt{\frac{r_{12}}{r_{34}}} \frac{\sin \alpha_2}{m_3}
\]

\[
g_{22} = \frac{1}{m_1} + \frac{1}{m_2}
\]

\[
g_{23} = 0
\]
(25 continued)

\[ G_{24} = -\sqrt{\frac{r_{12}}{r_{23}}} \sin \alpha_1 \]

\[ G_{25} = -\sqrt{\frac{r_{34}}{r_{23}}} \sin \alpha_2 \]

\[ G_{33} = \frac{1}{m_3} + \frac{1}{m_4} \]

\[ G_{34} = -\sqrt{\frac{r_{12}}{r_{23}}} \sin \alpha_1 \]

\[ G_{35} = -\sqrt{\frac{r_{34}}{r_{23}}} \sin \alpha_2 \]

\[ G_{44} = \frac{r_{23}}{r_{12}} \left( \frac{1}{m_1} + \frac{1}{m_2} \right) + \frac{r_{12}}{r_{23}} \left( \frac{1}{m_3} + \frac{1}{m_2} \right) - \frac{2\cos \alpha}{m_2} \]

\[ G_{45} = \frac{r_{12}}{r_{23}} \left( \frac{1}{m_2} + \frac{1}{m_3} \right) - \cos \alpha \left( \frac{1}{m_2} + \frac{1}{m_3} \right) \]

\[ G_{55} = \frac{r_{34}}{r_{23}} \left( \frac{1}{m_2} + \frac{1}{m_3} \right) + \frac{r_{23}}{r_{34}} \left( \frac{1}{m_4} + \frac{1}{m_3} \right) - \frac{2\cos \alpha}{m_3} \]

\[ r_{12} = r_{34} \quad \alpha_1 = \alpha_2 \]

\[ m_1 = m_4 \quad m_2 = m_3 \]
Now in terms of these internal coordinates the potential energy may be written as

\[
2V = F_R S_1^2 + F_r (S_2^2 + S_3^2) + F_\alpha (S_4^2 + S_5^2) \\
+ 2F_{R\alpha} (S_1 S_4 + S_1 S_5) + 2F_{r\alpha} (S_2 S_4 + S_3 S_5) \\
+ 2F_{r'\alpha} (S_2 S_5 + S_3 S_4) + 2F_{rr} (S_1 S_2 + S_1 S_3) \\
+ 2F_{rr'} (S_2 S_3) + 2F_{\alpha'\alpha} (S_4 S_5)
\]

or

\[
2V = \begin{pmatrix}
F_R & F_{Rr} & F_{Rr} & F_{R\alpha} & F_{R\alpha'} \\
F_{Rr} & F_{rr} & F_{r\alpha} & F_{r'\alpha} \\
F_{r\alpha} & F_{r'\alpha} & F_{\alpha} & F_{\alpha'\alpha} \\
F_{\alpha'\alpha} & F_{\alpha} & F_{\alpha} & F_{\alpha} \\
F_{\alpha} & F_{\alpha} & F_{\alpha} & F_{\alpha}
\end{pmatrix}
\]

In order to simplify the form of the GF matrix the F and G matrices which have been found will be transformed to correspond with a set of internal symmetry coordinates. (22, p. 117) Hence, let

\[
S^{(r)} = N \sum_R \chi^{(r)}_R R_S
\]

where \( S^{(r)} \) is a symmetry coordinate, \( N \) is a normalizing
factor, $\chi_R^{(\nu)}$ is the character for a given species and symmetry operation, and $RS_1$ "stands for the coordinate to which the displacement of $S_1$ is transferred by the operation $R$." (22, p. 119) Using this procedure the symmetry coordinates for this ion are

\begin{align*}
S_R^{(Ag)} &= R \\
S_r^{(Ag)} &= \frac{1}{\sqrt{2}} (r_1 + r_2) \\
S_\alpha^{(Ag)} &= \frac{1}{\sqrt{2}} (\alpha'_1 + \alpha'_2) \\
S_r^{(Bu)} &= \frac{1}{\sqrt{2}} (r_1 - r_2) \\
S_\alpha^{(Bu)} &= \frac{1}{\sqrt{2}} (\alpha'_1 - \alpha'_2)
\end{align*}

Next the $G$ and $F$ matrices will be transformed to correspond to these symmetry coordinates.

This is accomplished by the rule for diagonal constants: "Multiply the force constant in the first row and in the column labeled by a given internal coordinate by the coefficient with which that internal coordinate appears in the symmetry coordinate. Then divide by the coefficient of the first internal coordinate (row label). Do this for each column and add the results." (22, p. 130) And for off diagonal constants: "Multiply the force constants in the first row and in the column labeled by a given internal coordinate by the coefficient with which
that internal coordinate appears in the symmetry coordinate. Then divide by the coefficient of the first internal coordinate of the other set (row label). Do this for each column and add." (22, p. 131) Using these rules the G and F matrices become

\[ G^{(Ag)} = \begin{pmatrix}
G_{11} & \frac{1}{\sqrt{2}}(G_{12} + G_{13}) & \frac{1}{\sqrt{2}}(G_{14} + G_{15}) \\
\frac{1}{\sqrt{2}}(G_{12} + G_{13}) & G_{22} + G_{23} & G_{24} + G_{25} \\
\frac{1}{\sqrt{2}}(G_{14} + G_{15}) & G_{24} + G_{25} & G_{44} + G_{45}
\end{pmatrix} \]

\[ F^{(Ag)} = \begin{pmatrix}
F_R & \sqrt{2}F_{RR} & \sqrt{2}F_R \\
\sqrt{2}F_{RR} & F_R + F_{RR} & F_R + F_{RR} \\
\sqrt{2}F_{R} & F_R + F_{RR} & F_R + F_{RR}
\end{pmatrix} \]

\[ G^{(Bu)} = \begin{pmatrix}
G_{22} - G_{23} & G_{24} - G_{25} \\
G_{24} - G_{25} & G_{44} - G_{45}
\end{pmatrix} \]

\[ F^{(Bu)} = \begin{pmatrix}
F_R - F_{RR} & F_R - F_{RR} \\
F_R - F_{RR} & F_R - F_{RR}
\end{pmatrix} \]

However, it was shown in equations (25) that \( G_{12} = G_{13}, \) \( G_{14} = G_{15}, \) \( G_{23} = 0, \) and \( G_{24} = G_{25}. \) Thus,
Next let us tabulate the components of the GF matrix.

\[
\begin{pmatrix}
G_{11} & \sqrt{2} G_{12} & \sqrt{2} G_{14} \\
G_{22} & 2G_{24} & \\
G_{44} & G_{45} & 0
\end{pmatrix}
\]

\[
\text{and}
\begin{pmatrix}
G_{22} & 0 \\
G_{44} & G_{45}
\end{pmatrix}
\]

\[
(GF)_{11} = G_{11} F_R + 2G_{12} F_{Rr} + 2G_{14} F_{R\alpha}
\]

\[
(GF)_{12} = \sqrt{2} G_{11} F_{Rr} + \sqrt{2} G_{12} (F_R + F_{rr}) + \sqrt{2} G_{14} (F_\alpha + F_{r\alpha})
\]

\[
(GF)_{13} = \sqrt{2} G_{11} F_{R\alpha} + \sqrt{2} G_{12} (F_{R\alpha} + F_{r\alpha}) + \sqrt{2} G_{14} (F_\alpha + F_{r\alpha})
\]

\[
(GF)_{22} = 2G_{12} F_{Rr} + G_{22} (F_R + F_{rr}) + 2G_{24} (F_\alpha + F_{r\alpha})
\]

\[
(GF)_{23} = 2G_{12} F_{R\alpha} + G_{22} (F_{R\alpha} + F_{r\alpha}) + 2G_{24} (F_\alpha + F_{r\alpha})
\]

\[
(GF)_{33} = 2G_{14} F_{R\alpha} + 2G_{24} (F_{R\alpha} + F_{r\alpha}) + (G_{44} + G_{45})(F_\alpha + F_{r\alpha})
\]

\[
(GF)_{44} = G_{22}(F_R - F_{rr})
\]

\[
(GF)_{45} = G_{22}(F_{R\alpha} - F_{r\alpha})
\]

\[
(GF)_{55} = (G_{44} - G_{45})(F_\alpha - F_{r\alpha})
\]
If $F_{R\alpha}$, $F_{RR}$, and $F_{\alpha\alpha}$ are neglected, being considered insignificant, there are two bond distances ($r_1$ and $r_2$), one angle ($\alpha$), one angle force constant ($F_{\alpha}$), two major bond force constants ($F_R$ and $F_r$), one bond-bond interaction force constant ($F_{RR}$), and two bond-angle interaction force constants ($F_{R\alpha}$ and $F_{r\alpha}$) to determine from the known data neglecting the out of plane distortion force constant. Thus, if two infrared $\nu$ vibrational frequencies are known the problem is underdetermined, since for the five vibrational frequencies there are nine parameters to determine. Hence, it is easy to see that exact values or even correct values for the force constants will be difficult to calculate. However, intuition may be used to obtain a reasonable estimate of the free constants. First, the bond angle, $\alpha$, may be guessed to be near $120^\circ$ if the hyponitrite ion has $C_{2h}$ symmetry. Second, the unknown parameters may be reduced to eight, since only the ratio of the bond distances ($r_2/r_1$) occurs in the FG matrix. Third, a value of $r_2/r_1$ may be estimated from the observed values of the N-O and N-N distances in other molecules. In light of these remarks the calculation will be continued in such a manner as to assign reasonable values to $\alpha$ and $r_2/r_1$, and then determine $F_R$, $F_{\alpha}$, $F_{RR}$, $F_r$, and $F_{R\alpha}$ as a function of $F_{r\alpha}$. 
The following table lists the values of several bonds which have similarities to the bonds of the hyponitrite ion.

Table of Bond Lengths

<table>
<thead>
<tr>
<th>Bond</th>
<th>Molecule</th>
<th>Distance (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-O</td>
<td>NH₂OH</td>
<td>1.46</td>
<td>6, p. 147</td>
</tr>
<tr>
<td>N≡O</td>
<td>NNO</td>
<td>1.191</td>
<td>3, p. 178</td>
</tr>
<tr>
<td>N≡O</td>
<td>NO₂</td>
<td>1.19</td>
<td>20, p. 1248-1251</td>
</tr>
<tr>
<td>N=O</td>
<td>ONF</td>
<td>1.13</td>
<td>10, p. 1071</td>
</tr>
<tr>
<td>N=O</td>
<td>NO₂⁻</td>
<td>1.13</td>
<td>13, p. 444-446</td>
</tr>
<tr>
<td>N≡N</td>
<td>N₂H₄</td>
<td>1.47±.02</td>
<td>17, p. 228</td>
</tr>
<tr>
<td>N≡N</td>
<td>HN'N''N''</td>
<td>1.240±.003</td>
<td>1, p. 1422</td>
</tr>
<tr>
<td>N≡N</td>
<td>HN'N''N''</td>
<td>1.134±.003</td>
<td>1, p. 1422</td>
</tr>
<tr>
<td>N≡N</td>
<td>NNO</td>
<td>1.126</td>
<td>2, p. 72; 3, p. 178</td>
</tr>
</tbody>
</table>

In order to compare the bonds in the preceding table with those of the hyponitrite ion, something must be said on the type of bonds expected in the hyponitrite ion. The structure which is considered dominant by considerations of the C₂h symmetry is

But, structures such as

\[
\text{N} = \text{N}^\text{-} \quad \text{O}^- \\
\text{O}^- \quad \text{N} \quad \text{N}^\text{-} \quad \text{O}^- \\
\text{N} - \text{N} \quad \text{O}^- \\
\text{O}^- \quad \text{N} \quad \text{N}^\text{-} \quad \text{O}^- 
\]
and

\[ \text{O} \quad \text{N} - \text{N}'' \quad \text{O} \]

may also play a significant role in the ion's structure. One may make an estimate of the ratio of the bond distances, \( r_2/r_1 \) by assigning to \( r_2 \) the N-O bond distance of \( \text{NH}_2\text{OH} \) and to \( r_1 \) the \( \text{N}''\text{N}'' \) bond distance of \( \text{HN}'\text{N}''\text{N}'' \). Thus, \( r_2/r_1 \) becomes 1.176. The value of the ratio is only an estimate and it cannot be considered as the correct value to use. However, this does give a starting point for the calculations, and on page 81 reasoning is given for the selection of 1.135 as the value for the ratio of the bond distances.

Next, in order to assess a logical assignment of the fundamental vibrational frequencies, the assignment of the vibrational frequencies previously published and those which I have reported in the previous sections will be compared. Kuhn and Lippincott (9, p. 1820-1821) have reported the following values for the infrared and Raman spectra of the hyponitrite ion.
<table>
<thead>
<tr>
<th>IR ($\omega$ cm$^{-1}$)</th>
<th>RAMAN ($\Delta \omega$ cm$^{-1}$)</th>
<th>ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1392</td>
<td>N=N stretch</td>
</tr>
<tr>
<td>1090</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1035 mw</td>
<td></td>
<td>antisym. N-O stretch</td>
</tr>
<tr>
<td></td>
<td>958</td>
<td>sym. N-O stretch</td>
</tr>
<tr>
<td>885 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>629 m</td>
<td></td>
<td>NNO bend</td>
</tr>
<tr>
<td>492 w</td>
<td></td>
<td>ONNO distortion</td>
</tr>
</tbody>
</table>

Millen, Polydoropoulos, and Watson (13, p. 687-691) have also reported values for the Raman and infrared spectra of the hyponitrite ion.

<table>
<thead>
<tr>
<th>IR ($\omega$ cm$^{-1}$)</th>
<th>RAMAN ($\Delta \omega$ cm$^{-1}$)</th>
<th>ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>2207</td>
<td>$\nu_{2} + \nu_{5}$ Bu</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1383</td>
<td>$\nu_{1}$ Ag</td>
</tr>
<tr>
<td>1129</td>
<td>$2\nu_{4} + \nu_{6}$ Au</td>
<td></td>
</tr>
<tr>
<td>1020</td>
<td>$\nu_{5}$ Bu</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1115</td>
<td>$\nu_{2}$ Ag</td>
</tr>
<tr>
<td>863</td>
<td>$\nu_{3} + \nu_{4}$ Bu</td>
<td></td>
</tr>
<tr>
<td>504</td>
<td>$\nu_{6}$ Au</td>
<td></td>
</tr>
<tr>
<td>(485)</td>
<td></td>
<td>$\nu_{3}$ Ag</td>
</tr>
<tr>
<td>(370)</td>
<td></td>
<td>$\nu_{4}$ Bu</td>
</tr>
</tbody>
</table>

In comparison with these two papers I have found the following spectra to be consistent with my observations.
<table>
<thead>
<tr>
<th>IR (ω cm⁻¹)</th>
<th>RAMAN (Δω cm⁻¹)</th>
<th>ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1383 s</td>
<td>N=N stretch</td>
<td>( \nu_1 )</td>
</tr>
<tr>
<td>1115 w</td>
<td>sym. N-O stretch</td>
<td>( \nu_2 )</td>
</tr>
<tr>
<td>1020 s</td>
<td>antisym. N-O stretch</td>
<td>( \nu_4 )</td>
</tr>
<tr>
<td>895 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>692 w</td>
<td>sym. NNO bend</td>
<td>( \nu_3 )</td>
</tr>
<tr>
<td>629 m</td>
<td>CNNO distortion</td>
<td>( \nu_6 )</td>
</tr>
<tr>
<td>492 w</td>
<td>NNO bend</td>
<td>( \nu_5 )</td>
</tr>
</tbody>
</table>

The 492 cm⁻¹ band was observed in connection with another study being carried on at Oregon State University. This band was observed as a broad band somewhere in the vicinity of 480-495 cm⁻¹.

Now, from \( \nu_1, \nu_2, \nu_3, \nu_4, \) and \( \nu_5 \) the required \( \lambda_1, \lambda_2, \lambda_3, \lambda_4, \) and \( \lambda_5 \) may be evaluated from the expression given on page. Hence,

\[
\lambda = 4 \pi^2 \nu^2 = 4 \pi^2 c^2 \omega^2 = \left( \frac{\omega}{1303.1} \right)^2
\]

where the last form is consistent with the following system of units: masses in atomic weight units, lengths in angstroms, and the force constants in \( 10^5 \) dynes cm⁻¹.
The results may be summarized in the following table:

<table>
<thead>
<tr>
<th>( \nu )</th>
<th>( \omega_{(cm^{-1})} )</th>
<th>( \lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 )</td>
<td>1383</td>
<td>1.125</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>1115</td>
<td>.726</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>692</td>
<td>.285</td>
</tr>
<tr>
<td>( \nu_4 )</td>
<td>1020</td>
<td>.6126</td>
</tr>
<tr>
<td>( \nu_5 )</td>
<td>492</td>
<td>.1426</td>
</tr>
</tbody>
</table>

In a consideration of the \( B_u \) species part of the FG matrix it was found that only \( r_2/r_1 \), \( F_\alpha \), \( F_r \), and \( F_{r\alpha} \) need be considered. From this viewpoint then \( F_\alpha \) and \( F_r \) may be expressed as a function of \( F_{r\alpha} \) for a given value of \( r_2/r_1 \). From equations (31) the \( B_u \) part of the secular determinant becomes

\[
\begin{vmatrix}
G_{22}F_r - \lambda & G_{22}F_{r\alpha} \\
G_{22}F_{r\alpha} & (G_{44} - G_{45})F_\alpha - \lambda
\end{vmatrix} = 0
\]

Hence, for \( \nu_4 \) and \( \nu_5 \)

\[
(34) \quad F_\alpha = \frac{\lambda_4 + \lambda_5 + \sqrt{(\lambda_4 + \lambda_5)^2 - 4(\lambda_4\lambda_5 + G_{22}^2F_{r\alpha}^2)}}{2(G_{44} - G_{45})}
\]

and

\[
(35) \quad F_r = \frac{\lambda_4 + \lambda_5 + \sqrt{(\lambda_4 + \lambda_5)^2 - 4(\lambda_4\lambda_5 + G_{22}^2F_{r\alpha}^2)}}{2G_{22}}
\]
Since $G_{22}$ is only a function of the masses of the nitrogen and oxygen atoms, $F_r$ is also independent of $r_2/r_1$. Since equations (34) and (36) would give two sets of solutions for each value of $F_{r\alpha}$, a selection must be made as to which is the most appropriate solution. For comparison let us select $F_{r\alpha} = 0$ and $r_2/r_1 = 1.135$. First, select the negative sign before the square root symbol in equation (34). This means that the corresponding solution in equation (35) is given by using the positive sign before the square root symbol in this equation. Hence, $F_r = 4.57$ and $F_{\alpha} = 1.205$. The other set of solutions is obtained by reversing the signs before the square root symbols in the two equations. Hence, $F_r$ now becomes 1.06 and $F_{\alpha}$ equals 5.18. One can conclude from this that the negative sign must be used in equation (34) and the positive sign in equation (35) because 5.18 is extremely large for a bending force constant such as $F_{\alpha}$ and 1.06 is extremely small for a bond force constant such as $F_r$. The results for a set of selected values of $r_2/r_1$ are given next and graphed on pages 72 and 73. The force constants are in $10^5$ dynes/cm.
<table>
<thead>
<tr>
<th>$r_2/r_1$</th>
<th>$F_{\alpha}$</th>
<th>$F_r$</th>
<th>$F_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.107</td>
<td>0</td>
<td>4.57</td>
<td>1.177</td>
</tr>
<tr>
<td></td>
<td>.25</td>
<td>4.55</td>
<td>1.198</td>
</tr>
<tr>
<td></td>
<td>.50</td>
<td>4.50</td>
<td>1.258</td>
</tr>
<tr>
<td></td>
<td>.75</td>
<td>4.40</td>
<td>1.365</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>4.26</td>
<td>1.522</td>
</tr>
<tr>
<td>1.124</td>
<td>0</td>
<td>1.177</td>
<td>1.196</td>
</tr>
<tr>
<td></td>
<td>.25</td>
<td>1.218</td>
<td>1.218</td>
</tr>
<tr>
<td></td>
<td>.50</td>
<td>1.280</td>
<td>1.280</td>
</tr>
<tr>
<td></td>
<td>.75</td>
<td>1.388</td>
<td>1.388</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.548</td>
<td>1.548</td>
</tr>
<tr>
<td>1.135</td>
<td>0</td>
<td>1.177</td>
<td>1.205</td>
</tr>
<tr>
<td></td>
<td>.25</td>
<td>1.228</td>
<td>1.228</td>
</tr>
<tr>
<td></td>
<td>.50</td>
<td>1.291</td>
<td>1.291</td>
</tr>
<tr>
<td></td>
<td>.75</td>
<td>1.400</td>
<td>1.400</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.561</td>
<td>1.561</td>
</tr>
<tr>
<td>1.150</td>
<td>0</td>
<td>1.177</td>
<td>1.221</td>
</tr>
<tr>
<td></td>
<td>.25</td>
<td>1.245</td>
<td>1.245</td>
</tr>
<tr>
<td></td>
<td>.50</td>
<td>1.307</td>
<td>1.307</td>
</tr>
<tr>
<td></td>
<td>.75</td>
<td>1.418</td>
<td>1.418</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.580</td>
<td>1.580</td>
</tr>
</tbody>
</table>
$F_{\alpha}$ VERSUS $F_r$
A: \( \frac{r_2}{r_1} = 1.107 \)
B: \( \frac{r_2}{r_1} = 1.121 \)
C: \( \frac{r_2}{r_1} = 1.135 \)
D: \( \frac{r_2}{r_1} = 1.150 \)

F\text{r, vs. F}_4 \) at various values of \( \frac{r_2}{r_1} \).
In using the Ag species part of the secular determinant simple expressions giving $F_R\alpha$, $F_{RR}$, and $F_R$ in terms of $F_\alpha$, $F_R$, and $F_{R\alpha}$ are not easily found. Because of this difficulty a different procedure will be outlined whereby the values of $F_R\alpha$, $F_{RR}$, and $F_R$ may be evaluated.

The expressions for the components of the GF matrix are

\[
(GF)_{11} = G_{11}F_R + 2G_{12}F_{RR} + 2G_{14}F_{R\alpha}
\]

\[
(GF)_{12} = \sqrt{2} G_{11}F_{RR} + \sqrt{2} G_{12}F_R + \sqrt{2} G_{14}F_\alpha
\]

\[
(GF)_{13} = \sqrt{2} G_{11}F_{R\alpha} + \sqrt{2} G_{12}F_{R\alpha} + 2G_{14}F_\alpha
\]

\[
(GF)_{22} = 2G_{12}F_{RR} + G_{22}F_R + 2G_{24}F_{R\alpha}
\]

\[
(GF)_{23} = 2G_{12}F_{R\alpha} + G_{22}F_{R\alpha} + 2G_{24}F_\alpha
\]

\[
(GF)_{33} = 2G_{14}F_{R\alpha} + 2G_{24}F_{R\alpha} + (G_{44} + G_{45})F_\alpha
\]

Next the expressions for the GF matrix will be written in a way to show only their dependence upon $F_R$, $F_{RR}$, and $F_{R\alpha}$.

\[
(GF)_{11} = G_{11}F_R + 2G_{12}F_{RR} + 2G_{14}F_{R\alpha}
\]

\[
(GF)_{12} = \sqrt{2} G_{11}F_{RR} + a
\]

\[
(GF)_{13} = \sqrt{2} G_{11}F_R + b
\]

\[
(GF)_{22} = 2G_{12}F_{RR} + c
\]
A comparison of equations (36) and (37) defines a, b, c, d, and e which are functions of $F_{r\alpha}$ at a given bond angle, $\alpha$, and $r_2/r_1$. Now, equation (21) may be applied and the secular determinant evaluated.

In terms of the $\lambda$'s

(38) \[ \lambda^3 - A \lambda^2 + B \lambda - C = 0 \]

where

(39) \[ A = \lambda_1 + \lambda_2 + \lambda_3 \]

(40) \[ B = \lambda_1 \lambda_2 + \lambda_1 \lambda_3 + \lambda_2 \lambda_3 \]

(41) \[ C = \lambda_1 \lambda_2 \lambda_3 \]

The next step is to express the values of A, B, and C in terms of $F_{R}$, $F_{Rr}$, $F_{Rd}$, $a$, $b$, $c$, $d$, and $e$. Thus,

(42) \[ A = G_{11}^2 F_{R} + 4G_{12}^2 F_{Rr} + 4G_{14}^2 F_{Rd} + e \]

(43) \[ B = 2G_{11} G_{14} F_{R} F_{Rd} + 12G_{12} G_{14}^2 F_{Rr} + (a+c) G_{11}^2 F_{R} \]

\[ + (4G_{14}^2 - 2G_{11}^2 - 4G_{12}^2) F_{Rd}^2 + (2a+4c) G_{11} F_{R} \]

\[ + [(2e+2c) G_{12} - 2\sqrt{2}a G_{11}] F_{Rr}^2 + [(2e+4c) G_{14} \]

\[ - 2\sqrt{2}b G_{11} - 4G_{12}] F_{Rd} + [4G_{12}^2 - 2G_{11}^2] F_{Rr}^2 \]

\[ + 2G_{11} G_{12} F_{R} F_{Rr} + ec-a^2-b^2-d^2 \]
It is quite apparent at this point that complications would arise if one were to try to solve for $F_R$, $F_{RR}$, and $F_{R\alpha}$ analytically from equations (42), (43), and (44). But the complexity may be reduced to that of only solving quadratic equations. The procedure undertaken may be described as follows: $F_R$ and $F_{RR}$ were determined from (42) and (43) at several values of $F_{R\alpha}$ (set I) and also from (42) and (44) at several values of $F_{R\alpha}$ (set II). Hence, if the values of $F_{RR}$ versus $F_{R\alpha}$ from set I are plotted on the same graph paper as those from set II,
$F_{Rr}$ VERSUS $r_2/r_1$ AT 120° AND $F_{ra} = 0$
$\alpha$ VERSUS $F_{R\alpha}$

AT $r_2/r_1 = 1.135$
$\alpha$ VERSUS $F_R$

AT $r_2/r_1 = 1.135$

$F_{r\alpha} = 0$

$F_{r\alpha} = \frac{1}{2}$
$\alpha$ VERSUS $F_{Rr}$
AT $r_2/r_1 = 1.135$

$F_{r\alpha} = \frac{1}{2}$

$F_{r\alpha} = 0$
the intersection of these two curves gives a set of force 
constants consistent with the observed fundamental 
vibrational frequencies and the assumed values of $\alpha$, 
$r_2/r_1$, and $F_{R\alpha}$.

First, consider $\alpha = 120^\circ$ and $F_{R\alpha} = 0$ and then vary 
$r_2/r_1$. The results are summarized in the graph on page 77. 
$F_{Rr}$ appears quite high in comparison with other similar 
interaction constants. Because of this, the remaining 
calculations were carried out at $r_2/r_1 = 1.135$ where $F_{Rr}$ 
appears to experience a minimum.

Thus, with $r_2/r_1$ fixed only $\alpha$ and $F_{R\alpha}$ remain as 
variable parameters. The next task is to determine $F_{Rg}$, 
$F_R$ and $F_{Rr}$ at various values of $\alpha$ and $F_{R\alpha}$. These 
results are shown in the graphs on pages 78, 79, and 80. 
Negative values of $F_{R\alpha}$ were not included in the graphs.
The values of $F_R$ and $F_{\alpha}$ depend only upon the magnitude 
of $F_{R\alpha}$, hence it may seem logical in this treatment to 
consider negative values of $F_{R\alpha}$. However, as hinted by 
the graph of $\alpha$ versus $F_{Rr}$, $F_{Rr}$ becomes larger as $F_{R\alpha}$ 
decreases. For $\alpha = 120^\circ$, $r_2/r_1 = 1.135$, and $F_{R\alpha} = -0.50$, 
$F_{Rr}$ becomes 2.93. Because of this only positive values 
of $F_{R\alpha}$ were considered. Several interesting facts may 
be extracted from the curves shown.

First, $F_{R\alpha}$ decreases as $\alpha$ increases, whereas, both 
$F_R$ and $F_{Rr}$ increase as $\alpha$ increases. Still retaining the 
theme that $F_{Rr}$ should be as small as possible this would
indicate that the angle should be less than 120°. But $F_{R\alpha}$ must also be kept small. With this reasoning, $\alpha$ probably should not be too much less than 120°. Second, $F_{R\alpha}$ and $F_R$ increase as $F_{R\alpha}$ increases, whereas $F_{RR}$ decreases as $F_{R\alpha}$ increases. Since at the angles involved $F_{R\alpha}$ remains less than $F_{R\alpha}$ at $F_{R\alpha} = .50$, the increase in $F_{R\alpha}$ with $F_{R\alpha}$ will not be considered significant. But since $F_R$ for a pure double N-N bond is around $13 \times 10^5$ dynes/cm, it is desirable to keep $F_R$ relatively large. This indicates the larger values of $\alpha$ and $F_{R\alpha}$. The smaller values of $F_{R\alpha}$ indicate the smaller values of and larger values of $F_{R\alpha}$. Thus, for the sake of comparison of the values of force constants obtained here with those of other molecules and ions, $F_{R\alpha}$ will be assumed to be .50 and $\alpha$ will be assumed to be 115°. Thus,

\[
\begin{align*}
\alpha & = 115^\circ & F_R & = 9.00 \\
r_2/r_1 & = 1.135 & F_{RR} & = 2.14 \\
F_{R\alpha} & = .50 & F_r & = 4.50 \\
F_{R\alpha} & = .325 & F_\alpha & = 1.29
\end{align*}
\]
At first glance the values of $F_x$ and $F_{rr}$ seem rather large. However, both NO$_2^-$ (14, p. 444-446) and NO$_2$ (21, p. 1248-1251) have large bending force constants and large interaction constants. In the following table N$_2$O (18, p. 174) has been added for comparison.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$F_R$</th>
<th>$F_P$</th>
<th>$F_x$</th>
<th>$F_{rr}$</th>
<th>$F_{pp}$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2^-$</td>
<td>7.5</td>
<td>1.8</td>
<td></td>
<td>1.5</td>
<td></td>
<td>132</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>10.4</td>
<td>1.10</td>
<td></td>
<td>2.0</td>
<td></td>
<td>134</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>14.6</td>
<td>13.7</td>
<td>0.49</td>
<td></td>
<td></td>
<td>180</td>
</tr>
<tr>
<td>N$_2$O$_2$</td>
<td>9.00</td>
<td>4.50</td>
<td>1.29</td>
<td>2.14</td>
<td></td>
<td>115</td>
</tr>
</tbody>
</table>

These values appear to be of similar magnitude. But we still have not discussed the similarity in the bonds involved. Let the structures be represented as follows:

\[
\begin{align*}
\text{NO}_2^- & : \quad \alpha = 132^\circ \\
\text{NO}_2 & : \quad r_{NO} = 1.15 \text{ Å}^\circ \\
\text{N}_2\text{O} & : \quad \alpha = 134^\circ \\
\text{N}_2\text{O}_2 & : \quad r_{NO} = 1.19 \text{ Å}^\circ 
\end{align*}
\]
Resonance may be suggested to be present in the hypochlorite ion by writing the structures

$$\begin{align*}
\alpha &= 115^\circ \\
R_{NO} &\approx 1.36 \text{ Å} \\
R_{NN} &\approx 1.20 \text{ Å}
\end{align*}$$

Thus, in each case the bending motion is in connection with bonds involved in resonance of what may be written as a double and a single bond about a central nitrogen atom. Millen et al. (13, p. 687-689) have treated the case of the hypochlorite ion in terms of normal coordinate theory for the $C_{2v}$ symmetry. They also give reasons why such structures as

$$\begin{align*}
&D_{\alpha h} \\
&G_{2v}
\end{align*}$$

should not account for the observed spectra of the hypochlorite ion. In their treatment, however, they neglected the interaction constants $F_{R\alpha}$, $F_{R\alpha}$, and $F_{R\alpha}$. In this
way they obtained the following force constants:

\[
\begin{array}{ccc}
F_r & F_\alpha & F_R \\
4.6 & 0.6 & 6.9
\end{array}
\]

\(F_\alpha\), of course, was small in their calculation because they used \(\nu_5\) as about 370 cm\(^{-1}\), an unobserved frequency. They used a value of 504 cm\(^{-1}\) for \(\nu_6\), the out-of-plane distortion. This value corresponds to the value of 492 cm\(^{-1}\) used in my calculations for \(\nu_5\), the antisymmetric in plane bending frequency. It was shown here, however, that a high bending force constant is reasonable for the assumed structure and that \(\nu_5 = 492\) cm\(^{-1}\) is a very likely assignment. The assignment of \(\nu_6\) as 630 cm\(^{-1}\) does not involve the Raman frequencies and hence will not be discussed in detail. This assignment leads to a force constant of 1.7 md/Å\(^0\). This value being rather high tends to make one feel that perhaps a fundamental lower than 400 cm\(^{-1}\) does indeed exist. If 630 cm\(^{-1}\) is not a fundamental then it should be accountable as a combination of two fundamental frequencies. Since this frequency is infrared active, it should be the sum of a g and a u species. If 492 cm\(^{-1}\) represents the u species, then this would require that a Raman active line lies at about 138 cm\(^{-1}\). This last statement is in contradiction to the proposed hyponitrite ion structure and the observed Raman frequencies.
CHAPTER VIII
CONCLUSION

The new frequency for the hyponitrite ion at 692 cm$^{-1}$, although weak in the Raman effect, appears to be quite consistent with the other observed frequencies in relation to the calculated force constants. More accurate values for the force constants, bond distances, and the bond angle may be obtained if more information, such as the isotopically substituted hyponitrite spectra, were available. But the data available does point to the fact that the symmetry of the ion belongs to the $C_{2h}$ point group. At least no contradictions are present to discredit this theory.
BIBLIOGRAPHY


