"In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institution shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.

[Signature]
STARK EFFECT AND NUCLEAR QUADRUPOLE SPLITTING
IN THE ROTATION SPECTRUM OF NITROSYL BROMIDE

A THESIS

Presented to
the Faculty of the Graduate Division
Georgia Institute of Technology

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in the School of Physics

By
Donald Frohlichstein Eagle

June 1956
STARK EFFECT AND NUCLEAR QUADRUPOLE SPLITTING
IN THE ROTATION SPECTRUM OF NITROSYL BROMIDE

Approved: 

[Signature]

Date Approved by Chairman: June 6, 1956
PREFACE

This work was sponsored by the Office of Ordnance Research, U. S. Army, under contracts No. DA-01-009-ORD-353 and No. DA-01-009-ORD-465. The author wishes to acknowledge Drs. T. L. Weatherly and J. Q. Williams both for suggesting the thesis topic and for supplying many hours of constructive consultation. The helpful advice of Dr. C. H. Braden is also gratefully acknowledged.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>PREFACE</td>
<td>ii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td><strong>CHAPTER</strong></td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. WEAK-FIELD THEORY</td>
<td>3</td>
</tr>
<tr>
<td>III. INTERMEDIATE FIELD THEORY</td>
<td>8</td>
</tr>
<tr>
<td>IV. EXPERIMENTAL RESULTS</td>
<td>18</td>
</tr>
<tr>
<td>APPENDIX</td>
<td>22</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>28</td>
</tr>
</tbody>
</table>
THESIS ABSTRACT

STARK EFFECT AND NUCLEAR QUADRUPOLE SPLITTING
IN THE ROTATION SPECTRUM OF NITROSYL BROMIDE

(29 pages)

by

Donald Frohlichstein Eagle

This thesis discusses the theory of the Stark effect of an asymmetric rotor with hyperfine structure resulting from nuclear quadrupole interaction. A calculation of the Stark effect and hyperfine splitting in the rotation spectrum of nitrosyl bromide is made according to the theory of Mizushima, and it is compared with the observed microwave spectrum of NOBr in order to determine the component of the electric dipole moment along the principal axis of least inertia.

When quadrupole interaction is present, it is convenient to discuss the Stark effect under three different conditions: weak field, strong field, and intermediate field. A brief qualitative discussion of each of these three cases is given. A partial, quantitative calculation of the weak field approximation is made and the explicit results quoted. Generalized perturbation theory is used to more fully develop the intermediate-field case, and the results of this computation are shown to agree with the theory of Mizushima.

Following a short general description of the microwave spectrometer, the spectrum of the $J = 2_o \rightarrow 3_1$ transition is used to calculate the value of the component of electric dipole moment along the axis of least inertia for nitrosyl bromide. The weak-field approximation is
initially used but it is found to be unsatisfactory. The more tedious intermediate field computation is then used to bring about good agreement between the calculated and the observed spectra. The value of \( \mu_a \) found by the latter computation is 1.76 Debye units. Since no transition sensitive to \( \mu_b \) could be found, it was not possible to calculate this component of the dipole moment. The third component, \( \mu_c \), which is perpendicular to the plane of the molecule is zero. The previously reported value for the total dipole moment of nitrosyl bromide in a solution of carbon tetrachloride is 1.87 Debye units.
CHAPTER I

INTRODUCTION

The theory of the interaction between nuclear electric quadrupole moments and molecular rotation in asymmetric top molecules has been worked out by Bragg (1), and the Stark effect for an asymmetric rotor was developed by Golden and Wilson (2). Mizushima (3) has considered the combined problem of the Stark effect of an asymmetric top with hyperfine structure resulting from nuclear quadrupole interaction. The present paper is based upon Mizushima's work; his theory will be used to interpret the observed spectrum of nitrosyl bromide and compute the electric dipole moment.

When hyperfine structure is present, it is convenient to discuss Stark effects under three different conditions: weak field, strong field, and intermediate field.

In the weak-field case, the electric field is so small that the Stark energy is considerably less than the quadrupole interaction energy. In this case the molecular wave functions and the hyperfine structure are only slightly perturbed by the electric field. This means that the precession of the molecule due to the applied field is slow enough that the interaction between the nucleus and the molecule is very little affected. The molecular state may be specified by the quantum numbers $J$, $I$, $F$, and $M$; where $J$ is the rotational angular momentum of the molecule, $I$ is the nuclear spin angular momentum, $F$ is the total angular momentum, and $M$ is the $z$-component of the total angular momentum. The Stark effect splits
each hyperfine line into a number of different components depending on
the value of \( N \); this splitting is small compared to the quadrupole
splitting.

In the strong-field case, the Stark energy is very much greater
than the quadrupole interaction energy. The molecule precesses so rapidly
that \( J \) and \( I \) are decoupled, and therefore \( F \) loses its significance as a
quantum number. In this case the molecular state may be specified by
the quantum numbers \( J, I, m_J \), and \( m_I \); where \( J \) and \( I \) are the same as defined
above, \( m_J \) is the component of \( J \) in the direction of the applied field,
and \( m_I \) is the component of \( I \) in the direction of the field. Under strong
field conditions the quadrupole interaction produces a splitting of each
Stark energy level which is considerably smaller than the separation be-
tween Stark levels.

In the intermediate-field case, the Stark energy and the quadrupole
interaction energy are of the same order of magnitude. Their combined
effect is appreciably more difficult to treat than either of the previous
two cases. The parameters \( m_J \), \( m_I \), and \( F \) lose their significance as quantum
numbers, and the wave functions must be made up of linear combinations of
the weak- or strong-field case wave functions. Calculation of the
appropriate wave functions and of the energy levels is in general difficult.
Line splittings due to the two effects are comparable. A more quantitative
discussion of this case and of the weak field case is given below.
CHAPTER II

WEAK-FIELD THEORY

In connection with the weak-field case it is helpful to develop a few results from perturbation theory. Consider the Hamiltonian

$$H = H^0 + \epsilon H^1 + \epsilon^2 H^2 + \cdots,$$

the wave function $\Psi(n) = \psi^0(n) + \epsilon \psi^1(n) + \epsilon^2 \psi^2(n) + \cdots$, (1)

and the energy $E(n) = E^0(n) + \epsilon E^1(n) + \epsilon^2 E^2(n) + \cdots$.

where $n$ stands for all the quantum numbers that characterize the unperturbed wave function. Substituting the three above expressions into Schrödinger's equation,

$$H\Psi = E\Psi,$$

and equating coefficients of equal powers of $\epsilon$ gives the following:

0th order: $H^0 \psi^0(n) = E^0(n) \psi^0(n)$;

1st order: $H^1 \psi^0(n) + H^0 \psi^1(n) = E^0(n) \psi^1(n) + E^1(n) \psi^0(n)$; (2)

2nd order: $H^2 \psi^0(n) + H^1 \psi^1(n) + H^0 \psi^2(n)$

$$= E^0(n) \psi^2(n) + E^1(n) \psi^1(n) + E^2(n) \psi^0(n).$$
The first order wave function may be expressed as a combination of the zeroth order wave functions as follows:

$$\Psi_1(n) = \sum_n a_{nn} \Psi_0(n')$$

where

$$a_{nn'} = \frac{H_1}{E_0(n) - E_0(n')}$$

and

$$a_{nn} = 0$$

The results obtained for the energies are

$$E_0(n) = H_0^{nn},$$

$$E_1(n) = H_1^{nn},$$

$$E_2(n) = H_2^{nn} + \sum_{n'} \frac{H_1^{nn'} H_1^{n'n}}{E_0(n) - E_0(n')}.$$  

In the weak-field approximation, the Stark effect is considered as a perturbation on the rotational plus hyperfine energy and is calculated using zero-order wave functions specified by J, \( \tau \), I, F, and K. These wave functions diagonalize the rotational plus quadrupole Hamiltonian. The Hamiltonian to be considered is:

$$H = (H_r + H_Q) + H_E = H^0 + \epsilon H^1,$$

where \( H_r \) is the rotational energy Hamiltonian,

\( H_Q \) is the quadrupole interaction term,

and \( H_E \) is the Stark energy Hamiltonian.

Now

$$H_E = \sum_{g} \mu_g \mathcal{J} \cos \alpha_g.$$
where $\mu$ is the component of the dipole moment along the $g$th principal axis, $F$ is the external field, and $\alpha$ is the angle between the external field and the $g$th axis. From equation (4) above

$$ E_1(n) = H_{nn}^{1} = \langle J' | \mu_{g} \cos \alpha \mid J | J' \rangle $$

$$ = \langle J' | \mu_{g} \cos \alpha \mid J | J' \rangle $$

$$ = \sum_{g} \mu_{g} \langle J' | \cos \alpha \mid J | J' \rangle . $$

$$ E_2(n) = \sum_{n' \neq n} \frac{H_{n'n}^{1}}{E_0(n) - E_0(n')} $$

$$ = \sum_{J' \not'= J} \frac{\langle J' | \mu_{g} \cos \alpha \mid J | J' \rangle \langle J' | \cos \alpha \mid J | J' \rangle}{E_0(J | J') - E_0(J' \not'= J')} $$

Since the matrix is diagonal in $J$, the summation over $n'$ may be omitted in the above expression. The matrix elements of $\cos \alpha$ can be evaluated by using Racah's method. Kizushima (3) has solved the problem, and his result for the Stark energy due to the $g$th component of the dipole moment is quoted below:

$$ E_1(n) = \sum_{g} \mu_{g} \langle J | \mu_{g} \cos \alpha \mid J' \rangle = 0 , $$

$$ E_2(n) = W_{J' | J} = \sum_{g} W_{g} \langle J | J' \rangle $$

$$ (W_{g})_{J' | J} = \sum_{g} \mu_{g}^{2} \sum_{J' \not'= J} \chi_{g}(J', J+1 \not'= J) \frac{E_0(J' | J') - E_0(J | J')}{E_0(J' | J') - E_0(J+1 \not'= J')} \chi_{g}(J' | J') \chi_{g}(J' | J') $$
\[ \begin{align*}
\text{+} f_2(J_{\text{IFM}}) \sum_{t' \in \mathcal{T}} & \quad \frac{\lambda_g(J_t, J_{t'} \tau^t)}{E_o(J_{t'} F) - E_o(J_{t'} F + 1)} \\
\text{+} f_3(J_{\text{IFM}}) \sum_{t' \in \mathcal{T}} & \quad \frac{\lambda_g(J_t, J_{t'} \tau^t)}{E_o(J_{t'} F) - E_o(J_{t'} F - 1)} \\
\text{+} f_4(J_{\text{IFM}}) \sum_{t' \in \mathcal{T}} & \quad \frac{\lambda_g(J_t, J_{t'} \tau^t)}{E_o(J_{t'} F) - E_o(J_{t'} F + 1)} \\
\text{+} f_5(J_{\text{IFM}}) \sum_{t' \in \mathcal{T}} & \quad \frac{\lambda_g(J_t, J_{t'} \tau^t)}{E_o(J_{t'} F) - E_o(J_{t'} F)} \\
\text{+} f_6(J_{\text{IFM}-1}) \sum_{t' \in \mathcal{T}} & \quad \frac{\lambda_g(J_t, J_{t'} \tau^t)}{E_o(J_{t'} F) - E_o(J_{t'} F - 1)} \\
\text{+} f_7(J_{\text{IFM}-1}) \sum_{t' \in \mathcal{T}} & \quad \frac{\lambda_g(J_t, J_{t'} \tau^t)}{E_o(J_{t'} F) - E_o(J_{t'} F + 1)} \\
\text{+} f_8(J_{\text{IFM}-1}) \sum_{t' \in \mathcal{T}} & \quad \frac{\lambda_g(J_t, J_{t'} \tau^t)}{E_o(J_{t'} F) - E_o(J_{t'} F - 1)} \\
\text{+} f_9(J_{\text{IFM}-1}) \sum_{t' \in \mathcal{T}} & \quad \frac{\lambda_g(J_t, J_{t'} \tau^t)}{E_o(J_{t'} F) - E_o(J_{t'} F + 1)} \} \}
\end{align*} \]

where the \( \lambda_g \) are the line strengths defined by Golden and Wilson (2) and tabulated by Cross, Hainer, and King (5), and

\[
\begin{align*}
f_1(J_{\text{IFM}}) &= \frac{\mu^2(J+1+F+2)(J+1-F)(J+1+F+1)(J+1-I)}{4F^2(2F+1)^2(2J+3)(2J+1)(J+1)}, \\
f_2(J_{\text{IFM}}) &= \frac{(J+1+F+3)(J+1+F+2)(J-I+F+1)[(F+1)^2-J^2]}{4(F+1)^2(2F+1)(2F+2)(2J+3)(2J+1)(J+1)}, \\
f_3(J_{\text{IFM}}) &= \frac{(I+F-J)(I+F-J-1)(I+F-J+2)(I+F-J)[F^2-K^2]}{4F^2(2F-1)(2F+1)(2J+3)(2J+1)(J+1)}, \\
f_4(J_{\text{IFM}}) &= \frac{(I+F+2)(I+J+F)(I+J+F-1)(I+F-J+1)[(F+1)^2-J^2]}{4J(2J+1)(F+1)^2(2F-3)(2F+1)}.
\end{align*}
\]
The weak field approximation discussed here gives good qualitative results for the $2_0$ to $3_{-1}$ transition in nitrosyl bromide: it predicts the correct number of Stark components, the direction from the main line in which they are shifted, and the right order of magnitude for the shift. However, in order to obtain a more accurate prediction, it is necessary to consider the more difficult intermediate-field case.
For the development of the intermediate-field case, it is necessary to consider perturbation theory further. The previous results are still valid, and the discussion resumes from that point.

According to the matrix formulation of quantum mechanics, the perturbed energies of a system can be obtained by computing the Hamiltonian matrix $H$ in terms of the unperturbed wave functions $\Psi_0$ and diagonalizing this matrix. The allowed energies then appear as the diagonal elements. The elements of $H$ are of the form

$$\int \Psi_0(n) [H^0 + \epsilon H^1 + \ldots] \Psi_0(n') d\tau$$

$$= \int \Psi_0(n) H^0 \Psi_0(n') d\tau + \epsilon \int \Psi_0(n) H^1 \Psi_0(n') d\tau + \ldots$$

$$= E_0(n) \delta_{nn'} + \epsilon H_{nn'}^1 + \ldots.$$

The diagonal elements of this matrix are

$$H_{nn} = E_0(n) + \epsilon H_{nn}^1 + \ldots,$$

and the off-diagonal elements are

$$H_{nn'} = \epsilon H_{nn'}^1 + \ldots.$$
When the Hamiltonian matrix is diagonalized, it is found that the off-diagonal elements \( \epsilon H_{mn} \) contribute to the energy only in the next higher order—that is, in terms of order \( \epsilon^2 \). Thus, when the matrix elements of \( \mathcal{H} \) are computed using zero-order wave functions, one finds that the off-diagonal elements are zero to zero order in \( \epsilon \), and the diagonal elements are the perturbed energies correct to first order in \( \epsilon \).

This suggests that if wave functions correct to first order in \( \epsilon \) are used, the off-diagonal elements of \( \mathcal{H} \) would be zero to first order and the diagonal elements would be the perturbed energies correct to second order. To show that this is true define

\[
\Psi^I(n) = \psi^0(n) + \epsilon \psi^1(n) = \sum_{n'} b_{nn'} \psi^0(n')
\]

(7)

where \( b_{nn'} = \frac{\epsilon H_{nn'}}{E^0(n) - E^0(n')} \), \( n' \neq n \)

and

\[
|b_{nn}|^2 = 1 - \sum_{n' \neq n} |b_{nn'}|^2 = 1 - \epsilon^2 \sum_{n' \neq n} \left| \frac{\epsilon H_{nn'}}{E^0(n) - E^0(n')} \right|^2.
\]

The diagonal elements of \( \mathcal{H} \) are:

\[
\psi_2(n) = \int \overline{\Psi}_I^I(n) \mathcal{H} \Psi^I_I(n) d\tau
\]

\[
= \sum_{n'} \overline{b}_{nn'} \psi^0(n') \mathcal{H}^0 + \epsilon \mathcal{H}_{nn'}^1 \psi^0(n') d\tau
\]

\[
= \sum_{n'} \sum_{n''} \overline{b}_{nn'} \psi^0(n') \mathcal{H}^0 \psi^0(n'') d\tau
\]

\[
+ \epsilon \sum_{n'} \sum_{n''} \overline{b}_{nn'} \psi^0(n') \mathcal{H}^1 \psi^0(n'') d\tau.
\]
Denoting \( \int \Psi_n(n') H_{n' \sigma} \Psi_n(n'' \sigma) d\tau \) by \( H_{n' \sigma} \) and making use of the relation 
\( H_{n \sigma} \Psi_n = E_{n \sigma} \Psi_n \), the above expression reduces to

\[
\Psi_2(n) = \sum_{n'} \sum_{n''} b_{nn'} E_{n'}(n'' \sigma) \int \Psi_n(n') \Psi_n(n'') d\tau + \epsilon \sum_{n'} \sum_{n''} b_{nn'} H_{n' \sigma} \]

\[
= \sum_{n'} \sum_{n''} b_{nn'} E_{n'}(n'' \sigma) \delta_{n' n''} + \epsilon \sum_{n'} \sum_{n''} b_{nn'} H_{n' \sigma} \]

\[
= |b_{nn}|^2 E_{n}(n) + \sum_{n' \neq n} |b_{nn}||^2 E_{n'}(n') + \epsilon |b_{nn}|^2 H_{n n}^1 \]

\[
+ \epsilon \sum_{n' \neq n} \sum_{n'' \neq n} b_{nn'} E_{n''}(n') b_{nn''} H_{n n''}^1 \]

Substituting for \(|b_{nn}|^2\), and then for \(b_{nn}\),

\[
\Psi_2(n) = E_{n}(n) - \sum_{n' \neq n} |b_{nn}||^2 E_{n'}(n') + \epsilon H_{n n}^1 \]

\[
- \epsilon \sum_{n' \neq n} |b_{nn}||^2 H_{n n}^1 \]

\[
- \epsilon \sum_{n'' \neq n} \sum_{n'} b_{nn'} b_{nn''} H_{n n''}^1 \]

\[
= E_{n}(n) - \epsilon^2 \sum_{n' \neq n} (n') \]

\[
- \epsilon^3 \sum_{n' \neq n} \frac{|H_{n' \sigma}|^2}{E_{n}(n)} \cdot \left[ 1 - \frac{\epsilon^2 \sum_{n'' \neq n} \frac{|H_{n'' \sigma}|^2}{E_{n}(n)} \cdot \left[ E_{n}(n) - E_{n' \sigma} \right]^2 }{E_{n}(n)} \right]^{1/2} \]
Neglecting all terms of order higher than $\epsilon^2$, and noting that $\mathbf{H}_{nn'}^{-1} = \mathbf{H}_{nn'}^{-1}$,

$$\omega_2(n) = E_0(n) + \epsilon \mathbf{H}_{nn}^{-1} + \epsilon^2 \left\{ \sum_{n' \neq n} \frac{\mathbf{H}_{nn'}^{-1} \mathbf{H}_{n'n''}^{-1}}{E_0(n) - E_0(n')} \right\}$$

$$= E_0(n) + \epsilon \mathbf{H}_{nn}^{-1} + \epsilon^2 \sum_{n' \neq n} \left\{ \frac{2}{E_0(n) - E_0(n')} \frac{|\mathbf{H}_{n'n''}|^2}{E_0(n) - E_0(n')} \right\}$$

$$\omega_2(n) = E_0(n) + \epsilon \mathbf{H}_{nn}^{-1} + \epsilon^2 \sum_{n' \neq n} \frac{|\mathbf{H}_{n'n''}|^2}{E_0(n) - E_0(n')} \ . \quad (8)$$

These are the perturbed energies correct to second order in $\epsilon$ as given by non-degenerate perturbation theory.

The off-diagonal terms are of the form

$$\int \overline{\psi}_n \mathbf{H} \psi_m \, d\tau = \int \sum_{n'} \sum_{m'} \overline{\psi}_m(n') \mathbf{H}_n \psi_{n'}(n') \, d\tau + \epsilon \mathbf{H}_{nn'} \sum_{m'} \sum_{m''} \overline{\psi}_m(n') \mathbf{H}_{n'n''} \psi_{n''}(n'') \, d\tau$$

$$= \sum_{n'} \sum_{m'} \overline{\psi}_m(n') \mathbf{H}_{n'n''} \psi_{n''}(n') \, d\tau + \epsilon \mathbf{H}_{nn'} \sum_{m'} \sum_{m''} \overline{\psi}_m(n') \mathbf{H}_{n'n''} \psi_{n''}(n'') \, d\tau$$
Neglecting all terms of order higher than $\epsilon$, the above simplifies to

$$
\int \psi_i^* \psi_i \mathrm{d} \tau = \epsilon \frac{h_{mn}}{E_o(n) - E_o(m)} E_o(m) + \epsilon \frac{h_{nm}}{E_o(m) - E_o(n)} E_o(n) + \epsilon h_{nm} \quad n \neq m.
$$
Noting that $H_{nm}^1 = H_{nm}$ and collecting terms

$$
\int \psi_i^H \psi_i^H d\tau = \epsilon \frac{H_{nm}^1}{E_o(m) - E_o(n)} \left[ E_o(n) - E_o(m) \right] + \epsilon H_{nm}^1
$$

$$
= - \epsilon H_{nm}^1 + \epsilon H_{nm}^1
$$

$$
= 0 .
$$

Thus the perturbed wave functions diagonalize $H$ to first order in $\epsilon$, and the diagonal elements are the perturbed energies correct to second order.

The Hamiltonian for an asymmetric rotor containing a nucleus with an electric quadrupole moment and subjected to an electric field is

$$
H = H^0 + \epsilon_S \frac{Q}{H} + \epsilon Q
$$

where $H^0$ is the rotational energy Hamiltonian,

$\epsilon_S \frac{Q}{H}$ is the Stark energy term,

and $\epsilon Q$ is the quadrupole interaction term.

The energy eigenvalues are obtained by computation of the Hamiltonian matrix in terms of a complete set of orthogonal functions, and diagonalization of that matrix. In this particular case it is desirable to use for the complete set wave functions of the type $\Psi^I$ which diagonalize $H^0 + \epsilon_S \frac{Q}{H}$ to first order in $\epsilon_S$. The only off-diagonal elements of $H$ will then be those of $\epsilon Q$. These wave functions will be designated $\Psi^S_n$ and are defined by
\psi^S_n = \psi^0_n + \epsilon_S^l \psi^1_n = \sum b_{nn'} \psi^0_{n'}

where \( b_{nn'} = \frac{\epsilon_S H^S n_1 n}{E_0(n) - E_0(n')} \), \( n' \neq n \).

\[ |b_{nn}|^2 = 1 - \sum_{n', \neq n} |b_{nn'}|^2 = 1 - \epsilon_S \frac{\sum_{n', \neq n} |n_1 n_{n'}|^2}{(E_0(n) - E_0(n'))^2}, \]

\[ \psi^0_n = \psi(J \tau \tilde{m}_j) = \psi(J \tau \tilde{m}_j) \tilde{\phi}(I m_1), \]

\( \psi(J \tau \tilde{m}_j) \) is an asymmetric rotor wave function,

and \( \tilde{\phi}(I m_1) \) is the nuclear spin wave function.

The matrix elements of \( H \) are

\[ \langle \psi^S_n | H | \psi^S_{n'} \rangle = \int \psi^S_n \overline{H} \psi^S_{n'} \, d\tau. \]

Diagonalization of \( H \) requires the solution of the following secular equation for the allowed energies:

\[ |(\psi^S_n | H | \psi^S_{n'}) - E \delta_{nn'}| = 0. \]

In this equation

\[ \langle \psi^S_n | H | \psi^S_{n'} \rangle = \langle \psi^S_n | H^0 + \epsilon_S H^S + \epsilon_S H^S | \psi^S_{n'} \rangle \]

\[ = \langle \psi^S_n | H^0 + \epsilon_S H^S | \psi^S_{n'} \rangle + \langle \psi^S_n | \epsilon_S H^S | \psi^S_{n'} \rangle. \]

The off-diagonal elements of the first term of (11) are zero to first order in \( \epsilon_S \), as shown above, and the diagonal elements are
where the matrix elements on the right, designated by subscripts, are evaluated using zero order wave functions. As stated previously (p. 5) the matrix elements of $\varepsilon_{S}^{H_{0}}_{nn} = 0$. Therefore

\[
(\psi_{n}^{S})_{H_{0}^{n}} + \varepsilon_{S}^{H_{0}}_{nn} = E_{n}^{0} + \sum_{n'n' \neq n} \frac{S_{nn'}^{2}}{E_{n'}^{0}(n') - E_{n}^{0}(n')}
\]

where $\eta_{n'}^{S}$, which has been substituted for the term involving the sum, is the Stark energy in the absence of quadrupole interaction. It is given by

\[
\eta_{n'}^{S} = \sum_{g=1}^{3} (w_{g}) Jn_{g} = \sum_{g=1}^{3} \mu_{g}^{2} J^{2} \left\{ \sum_{J=1}^{J} \frac{\lambda_{g}(J \tau, J \tau')}{E_{J \tau} - E_{J \tau'}} \right\}
\]

where as before $g$ denotes one of the principal axes, $\mu_{g}$ is the component of the electric dipole moment along the $g$th axis, $\mathbf{B}$ is the external field strength, and the $\lambda_{g}$ are the line strengths defined by Golden and Wilson (2) and tabulated by Cross, Haines, and King (5). The derivation of equation (13) is given in the Appendix.

Substituting equation (12) back into (11) and then putting this result into (10) gives
Now consider the matrix elements

\[ \left( \psi_n^S \left| \epsilon_Q^{H_Q} \psi_n^S \right. \right) = \left( \psi_n^O + \epsilon_S \psi_n^O \left| \epsilon_Q^{H_Q} \right| \psi_n^O \right) + \epsilon_S \psi_n^1 \]

\[ = \left( \psi_n^O \left| \epsilon_Q^{H_Q} \right| \psi_n^O \right) + \epsilon_S^2 \epsilon_Q \left( \psi_n^O \left| \epsilon_Q^{H_Q} \right| \psi_n^1 \right) \]

\[ + \epsilon_S \epsilon_Q \left( \psi_n^O \left| \epsilon_Q^{H_Q} \right| \psi_n^1 \right) + \epsilon_S \epsilon_Q \left( \psi_n^1 \left| \epsilon_Q^{H_Q} \right| \psi_n^0 \right). \]

The Stark splitting is a second order effect and the hyperfine splitting is a first order effect, but in the intermediate field case the magnitudes of the two splittings are comparable. Therefore \( \epsilon_Q \) is of order \( \epsilon_S^2 \).

Thus

\[ \left( \psi_n^S \left| \epsilon_Q^{H_Q} \psi_n^S \right. \right) \approx \left( \psi_n^O \left| \epsilon_Q^{H_Q} \right| \psi_n^O \right) + \epsilon_S \left( \psi_n^O \left| \epsilon_Q^{H_Q} \right| \psi_n^1 \right) \]

\[ + \epsilon_S^3 \left( \psi_n^O \left| \epsilon_Q^{H_Q} \right| \psi_n^1 \right) + \epsilon_S \left( \psi_n^1 \left| \epsilon_Q^{H_Q} \right| \psi_n^0 \right). \]

Neglecting terms of order higher than \( \epsilon_S^2 \), there remains

\[ \left( \psi_n^S \left| \epsilon_Q^{H_Q} \psi_n^S \right. \right) \approx \left( \psi_n^O \left| \epsilon_Q^{H_Q} \right| \psi_n^O \right) = \epsilon_Q^{H_Q} \psi_n^O. \]

Therefore to the degree of approximation desired here (namely, energy correct to second order), the secular equation may be written

\[ \left| \epsilon_Q^{H_Q} \psi_n^O + (S_n^S + E_n^O - E_n^O) \sigma_{nn'} \right| = 0. \]

(15)

where the matrix elements \( \epsilon_Q^{H_Q} \psi_n^O \) are calculated using zero-order wave functions. In (15) \( n \) stands for all the quantum numbers \( J, I, m_j, m_\perp \).
The explicit form of the quadrupole interaction Hamiltonian is (6)

\[ \xi Q H^Q = eQ \left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{AV} \left\{ 3(I^*J)^2 + \frac{3}{2} (I^*J) - I^2 J^2 \right\} \left[ 2I(2I-1)J(2J-1) \right]^{-1} \]

(16)

where \( Q \) is the nuclear quadrupole moment,

\( V \) is the potential caused by all charges within the molecule except that of the nucleus under consideration,

\( Z \) is the direction of the external field, and

\[ \left\langle \right\rangle_{AV} \] means a quantum mechanical average over the different spatial orientations for a given rotational state. The matrix elements of \( \xi Q H^Q \) are diagonal in \( J, I, \) and \( M = m_J + m_I \). This means that the secular determinant can be separated into blocks for each particular value of \( J \) and \( M \). Within each block \( E^0_n \) will be constant and we may set \( E_n - E^0_n = E^1_n \), the perturbation energy. Thus equation (15) can be rewritten in the form

\[ eQ \left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{AV} \left( J \left| \frac{3}{2} \left( I^*J \right) - \frac{I^2 J^2}{2} \right| \right)^{-1} \left[ 2I(2I-1)J(2J-1) \right]^{-1} \]

\[ + \left( \frac{\delta^S}{J \tau m_J} - \frac{1}{2} \right) \delta m_J m_I, \delta m_I m_I \]

\[ = 0 \]  

(17)

This is the secular equation that was used to compute the energy splitting when both the Stark effect and hyperfine structure were present and were of the same order of magnitude. The explicit expression for \( \left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{AV} \) in the case of the asymmetric rotor is given by Bragg (1); the matrix elements of \( 3(I^*J)^2 + \frac{3}{2} (I^*J) - I^2 J^2 \) are given by Kellogg et.al. (7); and \( \delta^S_{J \tau m_J} \) is obtained from equation (13) above. Equation (16) is the same result that Kizushima reports for the intermediate field case.
CHAPTER IV

EXPERIMENTAL RESULTS

The experimental data was obtained from a Stark modulated microwave spectrograph of the type first described by Hughes and Wilson (8). A reflex klystron oscillator supplied microwave energy through a mica window to the absorption cell, which consisted of a nineteen foot section of X-band waveguide with a horizontal brass Stark electrode supported on teflon strips running down the center. At the far end of the absorption cell was a crystal detector whose output was fed into a phase sensitive detector and then into an Enterline-Augus recorder for display of the results. Stark modulation was provided by an eighty-five kilocycle square wave generator whose output could be varied from approximately twenty volts up to seven hundred volts. The bottom side of the applied square wave was held at zero potential.

The frequency of the klystron was varied slowly by a mechanical drive. A cavity wavemeter attached to the waveguide near the klystron served to give a rough determination of the absorption frequencies. Precise frequency measurement was accomplished with the aid of a crystal controlled frequency standard that was calibrated against WWV.

In the attempt to determine the dipole moment of nitrosyl bromide from its microwave spectrum, all the lines of the $J = 2$ to $J = 3$ transition were examined in order to find one whose Stark components could be clearly resolved. The best possibility seemed to be the $J = 2^o \rightarrow 3^{-1}$ lines.
FIGURE 1 - J_γ = 2 \rightarrow 3_1 \text{ TRANSITION OF NITROSYL BROMIDE}
Two of these, the $F = \frac{7}{2} \rightarrow \frac{9}{2}$ and $F = \frac{1}{2} \rightarrow \frac{3}{2}$ lines, lie very close together and split into five Stark components which can be identified. The selection rule on $M$ is $\Delta M = 0$. Strictly speaking, this is true only where the Stark field is uniform, that is, near the center of the waveguide. However, the rf field out near the edges is sufficiently weak and the number of transitions sufficiently few that it is a good approximation to assume the $\Delta M = 0$ selection rule holds everywhere. Then the $F = \frac{7}{2} \rightarrow \frac{9}{2}$ line has four Stark components corresponding to $M = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$, and the $F = \frac{1}{2} \rightarrow \frac{3}{2}$ line has one Stark component corresponding to $M = \frac{1}{2}$. Recordings were made of these lines at Stark field intensities of 255, 281, 295, 343, and 367 volts per centimeter. Figure 1 shows one of the recorder traces for a Stark field of 367 volts per centimeter.

The $J_c = 2 \rightarrow 3$ transition considered in this work allows one to compute $\mu_a$, the component of the electric dipole moment along the principal axis of least inertia. The contribution of $\mu_o$ is negligible for this transition (as the weak field calculations showed) and $\mu_c$ is zero for nitrosyl bromide. No transition could be found which was similarly sensitive to $\mu_b$. A diagram showing the location of the principal axes of NOBr is given below in Figure 2.

![Figure 2](image_url)
Initially the weak field approximation discussed in Chapter II was used to compute $\mathcal{M}_a$ from the observed spectrum for three different values of Stark field strength. The value obtained was $\mathcal{M}_a = 1.69$ Debye units. However, results were not as good as had been hoped for, so the calculation was performed under the intermediate field assumptions. Using the value previously obtained, namely, $\mathcal{M}_a = 1.69$ Debye units, the microwave spectrum for the $J = 2 \rightarrow 3$ transition was computed for Stark field intensities of 255 volts per centimeter, 281 volts per centimeter, and 294 volts per centimeter, and then compared with the observed spectrum. In all cases, the calculated line shifts were found to be too small. Since the Stark energy for this transition is proportional to $(\mathcal{M}_a^2)^2$, a parabolic correction was applied to $\mathcal{M}_a$ in order to force agreement between the computed and observed spectra. The value of $\mathcal{M}_a$ that gave the best overall fit was $\mathcal{M}_a = 1.76$ Debye units. This value was then substituted back into the secular determinant (16) and the spectrum recomputed. This time it was found that the differences between the calculated and the observed spectra approached the reliability of the experimental values. Table 1 reproduces these results in concise form. The third column listing the weak field theory predictions is included to show how the accuracy of this approximation compares with that of the more rigorous intermediate field development. The numbers in the table represent the separations in megacycles of the Stark components from the main line. The negative sign means they are shifted toward lower frequencies.
TABLE 1

Stark splitting in the $J = 2 \rightarrow 3 \rightarrow 1$ transition of NOBr.

Stark field = 367 volts/cm; $\mu_a = 1.76$ Debye units.

<table>
<thead>
<tr>
<th>Calculated Splitting</th>
<th>Observed Splitting</th>
<th>Calculated Splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermediate Field Case</td>
<td>Weak Field Case</td>
<td></td>
</tr>
<tr>
<td>$F = \frac{7}{2} \rightarrow \frac{7}{2}; M = \frac{7}{2}$</td>
<td>$-20.27 mc$</td>
<td>$-20.0 mc$</td>
</tr>
<tr>
<td>$\frac{5}{2}$</td>
<td>$-10.35$</td>
<td>$-10.7$</td>
</tr>
<tr>
<td>$\frac{3}{2}$</td>
<td>$-4.97$</td>
<td>$-5.0$</td>
</tr>
<tr>
<td>$\frac{1}{2}$</td>
<td>$-2.42$</td>
<td>$-2.7$</td>
</tr>
<tr>
<td>$F = \frac{1}{2} \rightarrow \frac{3}{2}; M = \frac{1}{2}$</td>
<td>$-9.61$</td>
<td>$-10.2$</td>
</tr>
</tbody>
</table>

The value of $\mu_a$ reported here -- 1.76 Debye units--compares favorably with the value of 1.87 Debye units for the total dipole moment previously reported for a solution of nitrosyl bromide in carbon tetrachloride (10). It is also interesting to compare this value with the value of 1.70 Debye units for $\mu_a$ reported by Magnuson (11) from a microwave study of nitrosyl fluoride. He also found a value of 0.62 Debye units for $\mu_b$. These together give a total dipole moment of 1.81 Debye units for nitrosyl fluoride.
APPENDIX

The expression for the Stark energy of an asymmetric rotor may be obtained from 1st order non-degenerate perturbation theory. The Hamiltonian involved is

\[ \hat{H} = \hat{H}^0 + \hat{H}^S = \hat{H}^0 + \sum_{g} \mu_g \hat{J} \cos \alpha_g, \]

where \( \hat{H}^0 \) is the rotational energy Hamiltonian for an asymmetric top, \( \hat{H}^S = \sum_{g} \mu_g \hat{J} \cos \alpha_g \) is the Stark energy Hamiltonian, \( \mu_g \) is the component of the electric dipole moment along the \( g \)th principal axis, and \( \alpha_g \) is the angle between the \( g \)th axis and the applied external field \( \mathbf{\hat{J}} \). In terms of asymmetric top wave functions, the rotational energy is given by

\[ \hat{W}^0 = (J^m_j | \hat{H}^0 | J^m_j) . \]

The first order Stark correction is

\[ \hat{W}^1 = (J^m_j | \hat{H}^S | J^m_j) = 0 . \]

The second order term is

\[ \hat{W}^{(2)} = \sum_{j' m' j} \frac{(J^m_j | \hat{H}^S | J^{m'}_{j'}) (J^{m'}_{j'} | \hat{H}^S | J^m_j)}{\hat{W}(J^m_j) - \hat{W}(J^{m'}_{j'})} . \]

For a particular dipole moment component \( \mu_n \), the contribution to the energy is
\[ w(2) = \sum_{J'} \sum_{m_J' \neq m_J} \mu_g^2 \left( \frac{|(Jm_J| \cos \alpha | J' \tau_m J') (J' \tau_m' m_J') \cos \alpha | Jm_J |^2}{w^0(Jm_J) - w^0(J' \tau_m J')} \right). \]

The symbol \( \sum' \) means the sum is taken over all elements for which the denominator is not zero. The matrix elements of \( \cos \alpha \) vanish except for

\[ \Delta J = 0, \pm 1 \text{ and } \Delta m_J = 0. \]

Thus

\[
\begin{align*}
\frac{w(2)}{\mu_g^2} = & \sum_{J'} \left( \frac{\sum_{m_J'} \frac{|(Jm_J| \cos \alpha | J' \tau_m J') (J' \tau_m' m_J') \cos \alpha | Jm_J |^2}{w^0(J \tau') - w^0(J - 1, \tau')} \right) \\
+ & \sum_{\tau' \neq \tau} \frac{|(Jm_J| \cos \alpha | J' \tau_m J') (J' \tau_m' m_J') \cos \alpha | Jm_J |^2}{w^0(J \tau') - w^0(J - 1, \tau')} \\
+ & \sum_{\tau'} \left( \frac{|(Jm_J| \cos \alpha | J' \tau_m J') (J' \tau_m' m_J') \cos \alpha | Jm_J |^2}{w^0(J \tau') - w^0(J + 1, \tau')} \right). 
\end{align*}
\]

Using the change of notation \( (Jm_J| \cos \alpha | J' \tau_m J') = (\Phi_{Fg})_{Jm_J; J' \tau_m J'} \),

where \( F \) denotes one of the space fixed axes \( X, Y, Z \), equation (17) becomes

\[
\begin{align*}
\frac{w(2)}{\mu_g^2} = & \sum_{J'} \left( \frac{\sum_{m_J'} \frac{|(\Phi_{Fg})_{Jm_J; J' \tau_m J'}|^2}{w^0(J \tau') - w^0(J - 1, \tau')} \right) \\
+ & \sum_{\tau' \neq \tau} \frac{|(\Phi_{Fg})_{Jm_J; J' \tau_m J'}|^2}{w^0(J \tau') - w^0(J - 1, \tau')} \\
+ & \sum_{\tau'} \left( \frac{|(\Phi_{Fg})_{Jm_J; J' \tau_m J'}|^2}{w^0(J \tau') - w^0(J + 1, \tau')} \right). 
\end{align*}
\]

Now, from Cross, Hainer, and King (5) II,
\[
\sum_{F_{m_j, m_j'}} \left| \Phi_{F_{m_j}} \right|^2 J_{m_j, m_j'} \right| \Phi_{Z_g} \right|^2 J_{J, J'} \sum_{J_{m_j, m_j'}} \left| \Phi_{Z_g} \right|^2 J_{m_j, m_j'}
\]

or when \( m_j' = m_j \),

\[
\sum_{F_{m_j}} \left| \Phi_{F_{m_j}} \right|^2 J_{m_j, m_j'} = 3 \left| \Phi_{Z_g} \right|^2 J_{J, J'} \sum_{J_{m_j}} \left| \Phi_{Z_g} \right|^2 J_{m_j, m_j'}
\]

and for Z axis and a particular \( m_j \)

\[
\left| \Phi_{Z_g} \right|^2 J_{m_j, J_{m_j}} \right| \Phi_{Z_g} \right|^2 J_{J, J'} \right| \Phi_{Z_g} \right|^2 J_{m_j, m_j'}
\]

From table I of Cross, Hainer, and King (9)

\[
\left| \Phi_{Z_g} \right|^2 J_{m_j, J-1 \tau' m_j} = [16J^2(J^2 - 1)]^{-1} \left| \Phi_{Z_g} \right|^2 J_{J, J-1 \tau'} \frac{\hbar(J^2 - m_j^2)}{m_j^2}
\]

\[
= \frac{J^2 - m_j^2}{4J^2(J^2 - 1)} \left| \Phi_{Z_g} \right|^2 J_{J, J-1 \tau'}
\]

\[
\left| \Phi_{Z_g} \right|^2 J_{m_j, J \tau' m_j} = [16J^2(J+1)^2]^{-1} \left| \Phi_{Z_g} \right|^2 J_{J, J+1 \tau'} \frac{\hbar m_j^2}{m_j^2}
\]

\[
= \frac{m_j^2}{4J^2(J+1)^2} \left| \Phi_{Z_g} \right|^2 J_{J, J+1 \tau'}
\]

\[
\left| \Phi_{Z_g} \right|^2 J_{m_j, J+1 \tau' m_j} = [16(J+1)^2(2J+1)(2J+3)]^{-1} \left| \Phi_{Z_g} \right|^2 J_{J, J+1 \tau'} \frac{\hbar(J^2 - m_j^2)(J+1)(J-1 \tau)}{4(J+1)^2(2J+1)(2J+3)}
\]

\[
= \frac{(J+1)^2 - m_j^2}{4(J+1)^2(2J+1)(2J+3)} \left| \Phi_{Z_g} \right|^2 J_{J, J+1 \tau'}
\]

Substituting equations (19) into equation (18) gives
\[ w_2^{(2)} = \mathcal{L}_E^2 \frac{m_j^2}{j(J+1)^2} \sum_{\tau} \left( \frac{\lambda_{\tau}(J \tau, J-l \tau')}{w^0(J \tau') - w^0(J-l \tau')} \right) \]

From the definition of the line strength \( \lambda \) and Table I of Cross, Hainer and King II (5), one can obtain the results, as quoted in Golden and Wilson (2):

\[ \left| \Phi_{Zg} \right|^2 \]

Substituting these into equation (20) gives

\[ w_2^{(2)} = \mathcal{L}_E^2 \frac{m_j^2}{j(J+1)^2} \sum_{\tau} \left( \frac{\lambda_{\tau}(J \tau, J-l \tau')}{w^0(J \tau') - w^0(J-l \tau')} \right) \]

\[ + \frac{m_j^2}{j(J+1)(2J+1)} \sum_{\tau \neq \tau'} \left( \frac{\lambda_{\tau}(J \tau, J-l \tau')}{w^0(J \tau') - w^0(J-l \tau')} \right) \]

\[ + \frac{(J+1)^2 - m_j^2}{j(J+1)(2J+1)(2J+3)} \sum_{\tau} \left( \frac{\lambda_{\tau}(J \tau, J+1 \tau')}{w^0(J \tau') - w^0(J+1 \tau')} \right) \]
This is just equation (13) above—the one used to calculate the Stark energy in the present work.
BIBLIOGRAPHY  
LITERATURE CITED


OTHER REFERENCES

