The polarization of molecular line radiation following electron impact.

Henricus William. Dassen

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LA THÈSE A ÊTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS REÇUE
THE POLARIZATION OF MOLECULAR LINE RADIATION

FOLLOWING ELECTRON IMPACT

by

Henricus William Dassen

A Thesis
submitted to the Faculty of Graduate Studies
through the Department of
Physics in Partial Fulfillment,
of the requirements for the Degree of
Master of Science at
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ABSTRACT
THE POLARIZATION OF MOLECULAR LINE RADIATION
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by

Henricus William Dassen

Considerable interest has developed recently in the polarization of radiation following electron impact excitation, particularly with the rapid advances made both theoretically and experimentally in the field of electron-photon coincidence measurements and their interpretation.

A full polarization analysis of the radiation, in which all the Stokes' parameters are measured, enables either the excitation process or the state of excitation of the target to be completely specified. These considerations had only been applied to atoms until recently when Malcolm and McConkey (1979) presented data on Werner band excitation of H₂.

A precursor to measurements of coincidence data is the more straightforward measurement of the linear polarization of the emitted light. This thesis presents the measurements of polarization for selected Lyman and Werner emissions in H₂. Both the integrated vibrational bands and resolved rotational structure have been studied. Also, the polarization of Lyman-α atomic fluorescence produced after dissociative excitation has been measured. In the cases of the Lyman and Werner transitions, relative excitation cross-sections have been deduced from the polarization data. The results have been com-
pared to the results of other workers whenever such data was available.

In addition to the polarization measurements, various theoretical predictions are examined. These theories use various assumptions about the conservation of angular momentum and dynamics of the collision. The predictions of each theory are compared with the experimental data, which was used to test the validity of these assumptions.
TO MY PARENTS
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'Trust in the LORD with all your heart, and do not lean on your own understanding; In all your ways acknowledge Him, and He will make your paths straight.' Proverbs 3:5,6 NIV
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CHAPTER 1

INTRODUCTION
This study of molecular line radiation polarization grew out of a similar study of atomic line radiation polarization in Ar (Dassen et al 1977). The polarization of atomic-line radiation excited by electron impact has been extensively studied, both experimentally and theoretically, but no such systematic investigation has been applied to molecules. The polarization of molecular line radiation is of considerable importance to excitation cross-section measurements. The radiation (particularly in the VUV) was always assumed to be unpolarized. This raises serious questions about the accuracy of these data since the optical dispersing elements used in such experiments are very often polarization sensitive. This was found to be the case in the present work.

In the literature considerable evidence exists to indicate that molecular line radiation may in fact be strongly polarized (Jette and Cahill 1968, Baltayan and Nedelec 1971). In addition, atomic line radiation produced following dissociative excitation of molecules may be polarized (Ott et al 1970, Karolis and Harting 1978). This was predicted by van Brunt and Zare in 1968 by considering the dynamics of the excitation process.

When electron-photon coincidence techniques were introduced, a renewed interest in polarization measurements occurred. With this method it is possible to study the orientation and alignment of atoms following electron impact (Eminyan et al
1974, Arriola et al. 1975, Tan et al. 1977). Also, the development of theoretical analyses along these lines has greatly increased the grasp of the dynamics involved, and the ability to extract useful information from such experiments (see Macek and Jaecks 1971, Wykes 1973, Pano and Macek 1973, and Blum and Kleinpoppen 1975). Recently Blum and Jakubowicz (1978) have extended the theory to cover electron-molecule scattering. As a special case of their theory, they have derived expressions for the threshold polarization of molecular radiation where Hund's case (b) applies.

This thesis presents the experimental results for the polarization of radiation following electron impact on H₂. Measurements were made on the Lyman (1^1Σ_u^+ - 1^1Σ_g^+) and Werner (1^1Π_u - 1^1Σ_g^+) transitions, as well as for Lyman-α atomic radiation produced by dissociative excitation. In the case of the Werner and Lyman bands, measurements of the entire vibrational band as well as resolved rotational structure were made. In addition to polarization measurements, the linearly polarized intensities were used to calculate relative excitation functions.

A theoretical discussion is presented in Chapter II, comparing the various theories of molecular radiation polarization, with calculated values of threshold polarization predicted by these theories. Not considered in some of these treatments are symmetry considerations, which were introduced by Malcolm et al. (1979) into the problem of predicting threshold polarization for molecular radiation. A rigorous treat-
ment is undertaken by Blum (1979).

Chapter III contains a description of the experimental arrangement. A discussion of each element of the apparatus is given, describing the method of operation and how the element was calibrated.

Chapter IV presents the experimental results obtained. The results of other workers are compared to the present results whenever such data was available. Also, a comparison with the theoretical values of the threshold polarization was made by extrapolating the experimental results back to the threshold.

Chapter V is a discussion of the results in the light of the theoretical predictions. Possible mechanisms are proposed to account for the differences in the predicted and extrapolated values.
CHAPTER II

THE THEORY
OF
THRESHOLD POLARIZATION
OF
MOLECULAR RADIATION
2.1 - AN INTRODUCTION TO MOLECULAR RADIATION POLARIZATION

As mentioned in the introduction, a knowledge of the polarization of molecular radiation following excitation by electron impact plays an important part in determining absolute excitation cross-sections. Measurements made with polarization sensitive optics (such as non-normal incidence grating spectrometers) without taking into account polarization effects can be in error. As will be shown in Chapter III, the correction for polarization can be significant.

In the theoretical discussions to follow, the polarization of the radiation is calculated at the excitation threshold of the upper state being considered. The reason for this is the availability of the approximation that the incident and scattered electron carries no orbital angular momentum, and this introduces many simplifying assumptions which makes the analysis possible. Such approximations are no longer valid at energies above threshold. It is also possible to calculate the polarization of the radiation at high incident electron energies where the Born approximation is valid. In between these extremes, however, there is a lack of any reasonable model with which to work.

Recently Chung and Lin (1978) have worked out excitation cross-sections for the $B_e^*\Sigma_u^+$ state of H$_2$ in a variety of theoretical approximations from 25 eV to 100 eV. They have used a close-coupling approximation with and without exchange, and Born and Born-Ochkur approximations. Their results for the close-coupling with exchange calculation are in fairly good
agreement with the experimental results presented in Chapter IV. However, as yet they have no polarizations calculated in this energy range.

Since the theory of molecular line radiation polarization is essentially an extension of the Percival and Seaton theory for atoms, a brief discussion of atomic radiation polarization follows.

* Chung and Lin have extended this energy range from 150 to 300 eV, where they use the Born-Ochkur approximation to calculate the cross-section.
2.2 - ATOMIC RADIATION POLARIZATION

For a full discussion of atomic radiation polarization the reader is referred to the work done by Percival and Seaton (1958). Jette and Cahill (1968) also give a brief discussion of the atomic case in their work.

The basic assumptions made by Percival and Seaton are:

(1) - Three atomic states are distinguished: the initial state 'a' (which is usually the ground state); an upper state 'b', populated only by collision with an incident electron; and a final state 'c', reached after photon emission from 'b'.

(2) - The distribution of spin directions of the electrons in the incident beam and of the initial states of the atom is isotropic.

(3) - The initial state of the atom is an S state, with L=0.

(4) - The interaction producing the collision is such that the total spin and the total angular momentum of the system are separately conserved.

Assumptions (3) and (4) lead to the conclusion that the angular momentum of the scattered electron, after exciting the upper state M_L, must be -M_L. At the excitation threshold the scattered electron has zero orbital angular momentum, and thus only states with M_L=0 can be excited.

The next step in determining the threshold polarization is to calculate the transition rates using radiative transition probabilities and excitation cross-sections. Both the total rate K and the rate K_z (for emission of photons whose electric vector is parallel to the incident electron beam) must
be calculated. The intensities of the emitted radiation are proportional to the emission rates, so that the polarization is given by:

$$J^P = \frac{3K_z - K}{K_z + K}$$  \hspace{1cm} (2.2.1)

In their calculation, Percival and Seaton consider the entire system of atom plus colliding electron. The expression obtained for the transition rate for the emission of an $x_i$-photon ($x_i$ represents $x$, $y$, or $z$ for $i = 1$, 2, or 3 respectively) of frequency $\nu_{bc}$ from state 'b' to state 'c' is given by:

$$K_{x_i} = \frac{64\pi \hbar^2 e^2 \nu_{bc} \nu_b}{3hc^3 \omega_a A} \sum_i \left| \sum_{\phi} \langle x_i | \phi \rangle G(\phi) f_{\phi}(x_{x_i} | \vec{k} | \vec{k}) \right|^2 \omega(\vec{k}) \hspace{1cm} (2.2.2)$$

where $v_b$ is the velocity of the scattered electron, $\omega_a$ is the statistical weight of level 'a', $\vec{k}$ is the wave vector of the incident electron, $\vec{k}$ is the wave vector of the scattered electron lying within the solid angle $d\omega(\vec{k})$, and $f_{\phi}(x_{x_i} | \vec{k} | \vec{k})$ is the scattering amplitude for excitation of level 'b' from level 'a'. The symbols $\alpha$, $\beta$, and $\gamma$ represent all the quantum numbers of levels 'a', 'b', and 'c' respectively. The total probability for photon emission from level 'b' is $A$, given by:

$$A = c(\nu_{bc}) \sum_{x_i} \left| \sum_{\phi} \langle x_i | \phi \rangle \right|^2 \hspace{1cm} (2.2.3)$$

where

$$c(\nu_{bc}) = \frac{64\pi \hbar^2 e^2 \nu_{bc}^3}{3hc^3}$$

The quantity $G(\phi)$ is a complex vector satisfying

$$G^*(\phi) \cdot G(\phi') = (1 + i\epsilon_{\phi\phi'})^{-1}$$  \hspace{1cm} (2.2.4)

where

$$\epsilon_{\phi\phi'} = 2\pi(\nu_\phi - \nu_{\phi'})/A$$  \hspace{1cm} (2.2.5)
This is a measure of the fine structure splitting in the levels of the atom compared to the natural linewidth of the transition. If $\xi_{ff} \ll 1$, the fine structure splitting can be ignored, and if $\xi_{ff} \gg 1$, a coupled representation which diagonalizes the interaction Hamiltonian must be used.

The transition rates $K_z$ and $K$ can be found from equation 2.2.2. The total rate $K$ is given by:

$$K = \sum x_i K_{\chi_i}$$  \hspace{1cm} (2.2.6)

Using these results Percival and Seaton calculated the threshold polarization for the 2p level of atomic hydrogen, taking into account both fine and hyperfine structure. They found that for the $2p_{1/2}$ level the polarization was always 0. For the calculation of the $2p_{3/2}$ level, they found that the polarization was given by:

$$P(2p_{3/2}) = 100(Q_0 - Q_1)/(1.694Q_0 + 2.388Q_1)$$

For the total radiation from the 2p level the polarization is:

$$P(2p) = 100(Q_0 - Q_1)/(2.375Q_0 + 3.749Q_1)$$

In these expressions $Q_0$ and $Q_1$ are the cross-sections for exciting the $M_L = 0$ and $M_L = \pm 1$ sublevels, respectively. If the threshold conditions are applied; i.e., only $M_L = 0$ is excited, then the threshold polarization values are given by:

$$P_{th}(2p_{3/2}) = 59.03\%$$
$$P_{th}(2p) = 42.11\%$$
2.3 - THE THEORY OF JETTE AND CAHILL

For a detailed discussion of Jette and Cahill's approach, the reader is referred to their work of 1968.

The treatment of molecular radiation polarization by Jette and Cahill is an extension of the work done by Percival and Seaton for atoms. Jette and Cahill applied the atomic results to homonuclear diatomic molecules.

In addition to the assumptions made in the atomic case, Jette and Cahill make some others:

(1) - Only a single vibrational-rotational state is populated by direct electron impact. They point out that in practice this is not the case because of the energy spread in the electron beam. However, even if the electron beam were totally monoenergetic this would not be the case because of the population distribution of rotational levels in the ground state. Thus, several ground state rotational levels could contribute to the excitation of the upper rotational level.

(2) - The radiation from a single vibrational-rotational excited electronic state to a lower electronic state in a single vibrational-rotational level is resolved, i.e., the rotational structure of the spectrum is resolved.

Jette and Cahill also point out that for homonuclear diatomic molecules there are no cascade effects from higher rotational levels within the same electronic state for dipole radiation. This is important since cascade effects would change the population distribution of the rotational sublevels in the excited state under consideration, and hence make the polari-
zation difficult, if not impossible, to calculate.

The procedure used to calculate the polarization of the radiation is as follows:

A molecule in an initial state \( \alpha \), with quantum numbers
\[
\alpha = n', \Lambda', N', S', M_N', M_S' \tag{2.3.1}
\]
is excited by electron impact to the state
\[
\beta = n, \Lambda, N, S, M_N, M_S \tag{2.3.2}
\]
which then decays by photon emission to the state
\[
\gamma = n'', \Lambda'', N'', S'', M_N'', M_S'' \tag{2.3.3}
\]
The \( n, n' \), and \( n'' \) denote all the non-angular momentum quantum numbers of the three states. \( \Lambda \) is the component of electronic angular momentum of the molecule along the internuclear axis, \( N \) is the rotational quantum number, with projection \( M_N \) on the \( \hat{z} \)-axis defined by the incident electron beam, and \( S \) and \( M_S \) are the spin quantum numbers of the molecule.

Now the total cross-section for exciting level \( \beta \) from level \( \alpha \) is given by:
\[
Q(\Lambda NM_{N}'M_{S}') = \frac{v_b}{v_a} \frac{1}{2(2S'+1)(2N'+1)} \sum_{M_N', M_S'} \left| \sum_{M_{N}'M_{S}'} \int \frac{\langle \Lambda N M_{N} M_{S} | k_a | k_b \rangle}{\omega(k_b)} \right|^2 \tag{2.3.4}
\]

Here \( v_a \) and \( v_b \) are the velocities of the incident and scattered electron, respectively; \( m_{S}' \) and \( m_{S} \) are the spin projections of the incident and scattered electrons on the \( \hat{z} \)-axis, and \( \vec{k}_a \) and \( \vec{k}_b \) are the incident and scattered electron wave vectors.

In equation 2.3.4, the spin polarizations of the incident electrons are averaged over, and the sum is over the spins of
the scattered electron. With the assumption of a spin-independent interaction and an initial electronic state of $\Lambda' = 0$ and the axial symmetry of the scattering plane, the expression for the total cross-section is:

$$ Q(\Lambda NS) = (2S+1)^{-1} Q |M_N| $$

and

$$ Q(\Lambda N) = \sum_{M_N} Q |M_N| $$

The spin independence of the interaction ensures that the orbital and spin angular momenta are separately conserved, and the axial symmetry of the scattering means that the cross-section is independent of the sign of $M_N$.

The conservation of orbital angular momentum is complicated due to the rotational states of the molecule. Jette and Cahill evaluate the expectation value of the angular momentum operator $L_\mu$ in the electron beam direction. $L_\mu$ is given by:

$$ L_\mu = \sum_1 (4\pi/3)^{1/2} L_1 \chi_1^\mu (\theta_1, \phi_1) $$

where the sum is over all the electrons of the molecule. They obtain:

$$ \langle NM_N \Lambda | L_\mu | NM_N \Lambda \rangle = \frac{M_N \chi^2}{N(N+1)} \delta_{\mu,0} $$

From this equation it can be seen that for other than $\Sigma$ states ($\Lambda = 0$), the components of the rotational state $N$ with $M_N \neq 0$ have a non-zero component of electronic angular momentum about the space-fixed z-axis.

Before excitation, a molecule in a $\Sigma$ state and the colliding electron at 'infinite' separation have a 0 component of electronic angular momentum about the $z$-axis. After scattering, the scattered electrons are isotropic near threshold.
since their velocities will be quite small (at threshold the scattered electron has almost zero energy and hence carries away no angular momentum). If the molecule is excited to a state with $\Delta \neq 0$ then only those states with $M_N = 0$ can be excited at threshold to conserve angular momentum. This follows from equation 2.3.8. According to Jette and Cahill, equation 2.3.8 allows the same symmetry arguments for molecules as for atoms: i.e., they assume that the interaction potential is spherically symmetric. As will be discussed later, the interaction potential is not spherically symmetric, and the asymmetry does indeed play a part in the determination of the polarization.

Jette and Cahill then go on to consider the effects of fine and hyperfine structure in the excited state.

(a) - Fine Structure Only

No fine or hyperfine structure is assumed in the initial state of the molecule. Because resolvable emission for rotational levels between two electronic states is expected for only the lightest molecules, the simplest possible coupling scheme, namely Hund's case (b) is assumed.

With fine structure in the excited state:

$$Q \equiv \Delta_{NS; JM_J}$$  (2.3.9)

The total cross-section then becomes:

$$Q(\Delta_{NS; JM_J}) = \sum_{NM_S} (2J+1) \left( \begin{array}{c} N \cdot S \cdot J \\ M_N M_S - M_J \end{array} \right)^2 Q(\Delta_{NS; M_{NS} M_{SJ}})$$  (2.3.10)

Summing equation 2.3.10 over $M_S$ and $M_J$, and using the orthogonality properties of the 3-j symbols, and using 2.3.5 and 2.3.6:
\[ Q(\text{ANS}; J) = \frac{(2J+1)}{(2N+1)(2S+1)} Q(\text{ANS}) \]  

(2.3.11)

By using a treatment similar to that of Percival and Seaton, Jette and Cahill arrive at an expression for the transition rate \( K_z \), given by:

\[ K_z = \frac{\nu_a (2N+1)}{(2S+1)} \sum_{J''} \sum_{M_J} (2J''+1) \left| \sum_J (2J+1) \begin{pmatrix} J'' & 1 & J \\ -M_J & 0 & M_J \end{pmatrix} \right|^2 \left| Q_{MN} \right| \]  

(2.3.12)

where \( G(J) \) is defined by 2.2.4. The total transition rate is:

\[ K = \nu_a \sum_{\text{MN}} Q_{\text{MN}} \]  

(2.3.13)

Since a detailed knowledge of the cross-sections \( Q_{\text{MN}} \) is not always available, the expression for the polarization obtained is:

\[ P = \frac{3K_z - K}{K_z + K} = \frac{\sum_{\text{MN}} A_{\text{MN}} Q_{\text{MN}}}{\sum_{\text{MN}} a_{\text{MN}} Q_{\text{MN}}} \]  

(2.3.14)

where \( A_{\text{MN}} \) is given by:

\[ A_{\text{MN}} = \frac{3(2N+1)}{(2S+1)} \sum_{M_J} (2J''+1) \left| \sum_J (2J+1) \begin{pmatrix} J'' & 1 & J \\ -M_J & 0 & M_J \end{pmatrix} \right|^2 \]  

(2.3.15a)

and \( a_{\text{MN}} \) is given by:

\[ a_{\text{MN}} = \frac{(2N+1)}{(2S+1)} \sum_{M_J} (2J''+1) \left| \sum_J (2J+1) \begin{pmatrix} J'' & 1 & J \\ -M_J & 0 & M_J \end{pmatrix} \right|^2 + 1 \]  

(2.3.15b)
In order to obtain the polarization, it is necessary to know the magnitude of $G(J)$. Jette and Cahill estimated $G(J)$ to be about 1.

(b) - Hyperfine Structure Included

In this case, the coupling is considered to be between the nuclear spin $\mathbf{I}$ and the electronic spin $\mathbf{S}$ to form a total spin $\mathbf{T} = \mathbf{I} + \mathbf{S}$. This couples with the rotation $\mathbf{N}$ of the molecule to form $\mathbf{F}$. Then the transition rate $K_z$ is given by:

$$K_z(J) = \frac{v_a(2N+1)}{(2S+1)(2I+1)} \sum_{T,M_N} (2J+1)^2(2T+1)(2J''+1)(2F''+1) \nu_{\mathbf{F},\mathbf{M}_F} \nu_{\mathbf{F''},\mathbf{M}_{F''}} \left[ \begin{array}{c} \text{N}, \text{J}, \text{S} \\ \text{J}, \text{N}, \text{1} \end{array} \right] \left[ \begin{array}{cc} \text{F}, \text{1}, \text{F''} \\ \text{M}_F, \text{0}, \text{M}_{F''} \end{array} \right] \left[ \begin{array}{ccc} \text{T} & \text{F} \\ \text{M}_N, \text{M}_F - \text{M}_N, -\text{M}_F \end{array} \right] \left[ \begin{array}{c} \text{1}, \text{S}, \text{T} \\ \text{N}, \text{F}, \text{J} \end{array} \right] G(F) \mid Q_{\mathbf{M}_N} \right|^2$$

(2.3.16)

The total transition rate is given by equation 2.3.13. The polarization is again given by:

$$P(J) = \frac{3K_z(J) - K}{K_z(J) + K} = \frac{\sum_{M_N} a_{M_N}(J)Q_{M_N}}{\sum_{M_N} a_{M_N}(J)Q_{M_N}}$$

(2.3.17)

The coefficients $A_{M_N}$ and $a_{M_N}$ are again given by equations of a form similar to equations 2.3.15a and 2.3.15b.

The threshold polarizations obtained by Jette and Cahill were calculated by using the assumption that only states with $M_N = 0$ were excited. Thus the polarization expressions reduced to:

$$P_{th} = A_0/a_0 \text{ for fine structure only}$$

$$P_{th}(J) = A_0(J)/a_0(J) \text{ with hyperfine structure}$$
These results were used to calculate the threshold polarizations for rotational transitions in the Werner bands. The results of this calculation are shown in Table 2-2. Note that, because of their assumptions and equation 2.3.8, it is not possible to make any determination of which sublevels are excited preferentially for the Lyman transitions ($\Lambda_0 = \Lambda_1 = 0$).
2.4 - THE UNITED ATOM APPROXIMATION OF Baltayan AND NEDELEC

For a full treatment see Baltayan and Nedelec (1975). These authors use the united atom approximation to calculate molecular line radiation polarization. In doing so they make several assumptions. These assumptions, along with their validity, will be discussed.

(1) - The Born-Oppenheimer approximation describes the molecule; the electronic, vibrational, and rotational parts of the wavefunction are considered independent. This is not generally the case in \( \text{H}_2 \) because of the strong coupling between the rotation and vibration. However, Baltayan and Nedelec argue that the variation of the Franck-Condon factors with \( N \) is negligible when \( v=0 \) for one of the levels of the transition, or when the potential energy curves can be superposed by a translation in energy. If these conditions hold, then the relative transition probabilities between different rotational states can be expressed in terms of Wigner's 3-j and 6-j symbols. This condition is satisfied in the experimental case considered by Baltayan and Nedelec, where they studied the \( 3p^3 \Pi_u - 2s^3 \Sigma_g^+ \) Fulcher bands of \( \text{H}_2 \) with only the \( v=0 \) level populated in the ground state. This is also the case in the present work where the Werner (0,1) and (0,2) bands were studied.

(2) - The united atom approximation is valid, and the orbital angular momentum \( \ell \) is a good quantum number. This is valid for the highest excited states of \( \text{H}_2 \). For \( n=3 \), the internuclear distance is small (\( .1 \text{ nm} \)) compared to the diameter of the classical orbit (\( 1.3 \text{ nm} \)) (see Messiah Vol I). Thus \( \ell \).
is taken to be a good quantum number with the origin at the center of the molecule.

(3) - The scattering potential has spherical symmetry, so that the electron scattering is independent of the orientation of the internuclear axis. This follows from the united atom approximation. Baltayan and Nedelec refer to Herzberg, Vol I, page 352, where the probability distribution of the electrons in the $^1\Sigma$ ground state is shown. The distribution is almost spherically symmetric beyond 0.08 nm from the origin, and would tend to support the validity of this assumption. However, Dunn (1962) has shown that the orientation of the molecular axis is an important factor in determining the excitation probabilities. Other workers have used Dunn's 'symmetry rules' to calculate threshold polarizations, and this will be considered in the next section.

(4) - The molecule has $\mathbf{L}=0$ in the ground state, and the magnitude of $\mathbf{L}$ to be added to excite a given electronic state is uniquely defined.

(5) - The collision process is instantaneous. The nuclei of the molecule remain fixed (the Franck-Condon principle), and $\mathbf{L}$ in the excited state is that given by the incident electron. Baltayan and Nedelec estimate that the collision time is on the order of $10^{-16}$ sec. The period of the highest $v$ considered in their calculations ($v=3$) is $4 \times 10^{-15}$ sec (for $v=0$, 1, and 2 the period will be longer), and the rotational period for $N=4$ is $5 \times 10^{-14}$ sec. They deduce the period of precession of $\mathbf{L}$ from the energy separation between the $3p^3\Pi_u$ and the
$3p^3 \Sigma_u^+$ states to be about $10^{-14}$ sec.

It is evident that this approximation is not completely valid, especially near the excitation threshold where the scattered electron leaves with almost 0 velocity, thus greatly lengthening the collision time. Also, the presence of resonances near threshold can cause a strong depolarizing effect on the emitted radiation (see Dassen et al 1977). Recently, Heideman et al (1979) have proposed that a strong correlation effect can take place between the excited and scattered electron. This will have a depolarizing effect on the emitted radiation as well. Thus it is expected that this assumption will be valid only at energies well above the excitation threshold.

(6) - The addition of orbital and spin angular momentum may be considered independently, and the spins of the incident electrons are isotropic. Clearly this assumption is identical to the one made by Jette and Cahill about the interaction potential. Also, in practice, most electron guns produce unpolarized electron beams, so the spins are indeed isotropic.

(7) - Since Baltayan and Nedelec consider the polarization of resolved rotational lines, they assume that Hund's case (b) describes the coupling of angular momenta for the molecule.

The above assumptions enable the calculation of relative intensities and polarization of the emitted radiation to be done using simple vector addition, without having to resort to molecular wavefunctions.

A summary of Baltayan and Nedelec's calculation follows. They consider the density matrix of the excited state at thresh-
\[ N' \rho_{M'M'} = \sum_{M''} \left| \langle \psi_{N''}^{M''} | T_{M''}^{L} | \psi_{N'}^{M'} \rangle \right|^2 N'' \rho_{M''M''} \]  
(2.4.1)

where \( T_{M''}^{L} \) is an irreducible tensor operator, \( N' \) and \( N'' \) denote rotational levels in the excited and ground states, respectively.

Beyond threshold, the authors are not able to predict the probability \( |a_{LM_L}|^2 \) for adding an angular momentum \( |LM_L> \) to the molecule. The density matrix is expressed as a function of the \( a_{LM_L} \) given by:

\[ N' N'' \rho_{M'M''} = \sum_{M''M'''} \left| \langle \psi_{N''}^{M'''} | T_{M''}^{L} | \psi_{N'}^{M'} \rangle \right|^2 N'' N'''' \rho_{M''M'''} |a_{LM_L}|^2 \]  
(2.4.2)

with the condition

\[ \sum_{M''} |a_{LM_L}|^2 = 1 \]

Also, Baltayan and Nedelec assume that the ground state is isotropic, with the ground state density matrix given by:

\[ N'' \rho_{M''M''} = (2N'' + 1)^{-1} \]

The components of the density matrix in the basis of \( \sum_{T_Q} \) are given by:

\[ N' N'' K \rho_{Q=0}(N'') = (-1)^{N' + N''} (2N' + 1)(2K + 1)^{1/2} L K \rho_0 \]

\[ \times \left( \begin{array}{c} N' \\bar{L} \\bar{N} \\bar{N}' \bar{N}'' \end{array} \right)^2 L L K \]

\[ \times \left( \begin{array}{c} -\Lambda \Lambda' \\Lambda'' \\Lambda'' \end{array} \right) \left( \begin{array}{c} N' \\bar{N}' \\bar{N}'' \end{array} \right) \]

\[ \times \langle \psi_{v''} | \psi_{v'} \rangle^2 \left| \langle F_{\Lambda''} | (T_{\Lambda''}^{L} - \Lambda'' \Lambda'_{mol}) | F_{\Lambda'} \rangle \right|^2 \]  
(2.4.3)

where

\[ L K \rho_0 = \sum_{M_L} (-1)^{L+M_L} |a_{LM_L}|^2 \left( \begin{array}{c} L \\bar{L} \\bar{K} \end{array} \right) \left( \begin{array}{c} M_L \\bar{M}_L \bar{L}_0 \end{array} \right) \]

and \( \psi_{v} \) and \( F_{\Lambda} \) are the vibrational and electronic wavefunctions respectively. \( Q = 0 \) since the \( \bar{z} \) direction is defined by the
incident electron beam.

To describe the linearly polarized light emitted by the molecule, Baltayan and Nedelec consider the components of the density matrix with $K = 0$, which gives the relative populations, and $K = 2$, which gives the 'alignment'. It is not possible to calculate absolute values of the alignment for any electron energy, but the relative values can be found from equation 2.4.3. From this, they deduce that the relative values of the alignment in the rotational levels are independent of the incident electron energy.

The population of the rotational state $N'$ excited from $N''$ is given by:

$$P_{N',N''} = \frac{N'}{0} (2N'+1)^{1/2} P_{N''}$$

$$\approx (2N'+1) \begin{pmatrix} \Lambda' & \Lambda'' \\ \Lambda' & \Lambda'' \end{pmatrix} P_{N''}$$

(2.4.4)

where the $P_{N''}$ are the relative populations of the ground state rotational levels. The degree of alignment on a line $N' - N$ is defined as:

$$t_{N',N} = \frac{I_\parallel - I_\perp}{I_\parallel + 2I_\perp}$$

(2.4.5)

This can be written as:

$$t_{N',N} = \frac{\sum_{N''} t_{N',N''}(N'') P_{N',N''}}{\sum_{N''} P_{N',N''}}$$

(2.4.6)

where the $t_{N',N''}(N'')$ are given by:

$$t_{N',N''}(N'') = \frac{N'}{0} \begin{pmatrix} 1 & 1 & 2 \\ N' & N' & N'' \end{pmatrix}$$

$$- \frac{1}{\sqrt{2}} \frac{N'}{0} \begin{pmatrix} 1 & 1 & 0 \\ N' & N' & N'' \end{pmatrix}$$
The ratio of the matrix elements is given by:

\[
\frac{N' \rho_0^2}{N' \rho_0^2} = (5)^{1/2} (-1)^{k+N''+N'} [(2N'+1)(2k+1)]^{1/2} \begin{pmatrix} 2 & k & k \\ N'' & N' & N' \end{pmatrix} \\
\times (2k+1)^{1/2} \sum_{q} (-1)^{k-q} \begin{pmatrix} k & k & 2 \\ q & -q & 0 \end{pmatrix} |a_q|^2
\]

The quantities \( I_\parallel \) and \( I_\perp \) refer to the intensities of the emitted radiation with polarization vectors parallel and perpendicular to the electron beam, respectively.

Baltayn and Nedelec consider first the case where hyperfine structure is present and \( J \) and \( F \) are good quantum numbers. Here the natural line width is much less than the hyperfine structure splitting, which in turn is much less than the fine structure splitting. The alignment of a line originating from \( N' \) (an \( N' \to N \) transition) is then given by:

\[
\begin{pmatrix}
N' & N' & 2 \\
1 & 1 & N
\end{pmatrix}
\sum_{F', J'} (-1)^{2J'-F'} (2J'+1)(2F'+1)
\begin{pmatrix}
J' & J' & 2 \\
N' & N' & S
\end{pmatrix}
\times
\begin{pmatrix}
F' & F' & 2 \\
J' & J' & I
\end{pmatrix}
\rho_0
\]

\[
= (2)^{1/2} \begin{pmatrix}
N' & N' & 0 \\
1 & 1 & N
\end{pmatrix}
\sum_{F', J'} (-1)^{2J'-F'} (2J'+1)(2F'+1)
\begin{pmatrix}
J' & J' & 0 \\
N' & N' & S
\end{pmatrix}
\times
\begin{pmatrix}
F' & F' & 0 \\
J' & J' & I
\end{pmatrix}
\rho_0
\] (2.4.7)

For lines originating from levels \( N' \) which are excited from only one level \( N'' \) of the ground state, the alignment is:

\[
t = (-1)^{N+N''+L+1} \left( \frac{3 \sqrt{10}}{2} \right) \frac{(2N'+1)(2L+1)}{(2S+1)(2I+1)}^{1/2} \begin{pmatrix}
L & L & 2 \\
0 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
N' & N' & 2 \\
1 & 1 & N
\end{pmatrix}
\]
\[
x \sum_{j'} (2j'+1) \left\{ \frac{j' j' 2}{n' n' s} \right\}^2 \sum_{f'} (2f'+1) \left\{ \frac{f' f' 2}{j' j' i} \right\}^2 (2.4.8)
\]

The second case considered by Baltayan and Nedelec is the one where the hyperfine structure splitting is comparable to the fine structure splitting. Now \( J \) is no longer a good quantum number, and the transformation

\[
\left| (j') f'M_F' \right\rangle = \sum_{j'_1} C_{(j')j'_1}^{f'} \left| \gamma n'sj'_1 i; f'M_F' \right\rangle \quad (2.4.9)
\]

is made. The sum is over all \( j'_1 \) values for a single rotational level \( n' \). The wavefunction \( \left| (j') f'M_F' \right\rangle \) is an eigenfunction of the total Hamiltonian \( H = H_{\text{IS}} + H_{\text{HFS}} \). The quantity \( \gamma \) refers to the non-angular momentum quantum numbers of the old wavefunctions.

For the case when \( J \) is not a good quantum number, Baltayan and Nedelec found that the alignment is given by:

\[
x = \left( -1 \right)^{n+n''+l+1} \left( \frac{3\pi \alpha}{2} \right) \left( \frac{2n'+1}{2n'+1} \right)^{1/2} (L L 2) \left\{ \frac{n' n' 2}{1 1 n} \right\} \\
\times \left\{ \frac{n' n' 2}{L L n} \right\} \sum_{f', f''} (2f'+1) \left( \sum_{j'_1, j'_2} (-1)^{j'_1+j'_2} \left( \frac{2j'+1}{2j'+1} \right)^{1/2} \\
\times C_{(j')j'_1}^{f'} C_{(j')j'_2}^{f'} \left\{ \frac{j'_1 j'_2 2}{n' n' s} \right\} \left\{ \frac{j'_1 j'_2 2}{f' f' i} \right\} \right\}^2 \quad (2.4.10)
\]

Baltayan and Nedelec have calculated the alignment for various transitions and their results are shown in Table 2-2 along with the results of other workers for comparison.

Note that with the polarization defined to be:

\[
P = (I_{||} - I_{\perp})/(I_{||} + I_{\perp})
\]
the relationship of the polarization to Baltayan and Nedelec's alignment is given by:

\[ P = \frac{3t}{t+2} \]

These are the values tabulated in Table 2-2.
2.5 - THE APPROACH OF MALCOLM, DASSEN, AND McCONKEY

The symmetry considerations for excitation of molecules put forth by Gordon Dunn in 1962 were applied to the calculation of threshold polarizations by Malcolm et al (1979), Dassen and McConkey (1979), McConkey (1980), and Dassen and McConkey (1980).

Basically, Dunn's symmetry rules relate the orientation of the molecular axis with respect to the direction of the incident electron beam with the transition probability for excitation. By considering the symmetries involved in the collision, Dunn was able to show a correlation between the change in \( \Delta \) with the orientation of the molecular axis at the threshold for the process under consideration. For \( \Sigma^+ - \Sigma_u^+ \) excitation, the transition probability is zero when the molecular axis is perpendicular to the incident electron direction \( \hat{\mathbf{k}} \), and for \( \Sigma_g^+ - \Pi_u^+ \) excitation it is zero when the molecular axis is parallel to \( \hat{\mathbf{k}} \).

This has important consequences in the selection rules for the angular momentum of the initial and final states. For \( \Sigma^+_g - \Sigma_u^+ \) transitions, the state with \( M_{N_0} = 0 \) will be preferred since \( \hat{\mathbf{k}} \cdot \mathbf{N}_0 = 0 \). For \( \Sigma^+_g - \Pi_u^+ \) transitions, the states with \( M_{N_0} = \pm N_0 \) will be preferred since \( \hat{\mathbf{k}} \cdot \mathbf{N}_0 = \mp \hat{\mathbf{k}} \cdot \mathbf{N}_0 \). Applying conservation of angular momentum to the \( \hat{\mathbf{z}} \) component of the total orbital angular momentum at the excitation threshold:

\[
M_{N_0} + m_0 = M_{N_1} + m_1 \tag{2.5.1}
\]

where \( m_0 \) and \( m_1 \) are the initial and final \( z \) components of angular momentum of the electron, it is clear that \( m_0 = m_1 = 0 \) in
this case. Then equation 2.5.1 becomes:

\[ M_{N_0} = M_{N_1} \]

Thus, depending on the type of transition, only selected values of \( M_{N_1} \) will be populated.

Assuming that this selection rule can be strictly applied, it is possible to evaluate the relative intensities of the \( M_N = 0, +1, \) and \(-1\) components and obtain expressions for the threshold polarizations by evaluating the appropriate 3-\( j \) symbols. Table 2-1 (below) lists the polarization results for the \( P, Q, \) and \( R \) branches for different selection rules for \( M_{N_1} \).

<table>
<thead>
<tr>
<th>BRANCH</th>
<th>( N_1 )</th>
<th>( M_{N_1} )</th>
<th>0</th>
<th>[ M ]</th>
<th>0 = ( + (N_1 - 1) )</th>
<th>0 = ( + (N_1 - 1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R ) ( N_1 - 1 )</td>
<td>( N_1 + 1 )</td>
<td>( 3N_1 - 1 )</td>
<td>( \frac{N_1^2 + N_1 - 3M^2}{3N_1 - N_1 - M^2} )</td>
<td>( -2N_1^2 + 7N_1 - 3 )</td>
<td>( 2N_1^2 + N_1 - 1 )</td>
<td></td>
</tr>
<tr>
<td>( Q ) ( N_1 )</td>
<td>( -1 )</td>
<td>( M + N_1(N_1 + 1) )</td>
<td>( \frac{3M^2 - N_1(N_1 + 1)}{M^2 + N_1(N_1 + 1)} )</td>
<td>( 2N_1 - 1 )</td>
<td>( 2N_1 + 1 )</td>
<td></td>
</tr>
<tr>
<td>( P ) ( N_1 + 1 )</td>
<td>( 3N_1 + 4 )</td>
<td>( 3N_1 - 4M^2 )</td>
<td>( \frac{N_1^2 + N_1 - 3M^2}{3N_1 + 7N_1 - M^2 + 4} )</td>
<td>( -2N_1^2 + 7N_1 - 3 )</td>
<td>( 2N_1^2 + 9N_1 + 3 )</td>
<td></td>
</tr>
</tbody>
</table>

The first column in Table 2-1 shows the expression for the polarization when \( M_{N_1} = 0 \) only is selected; the second column shows the expression when \( M_{N_1} \) can take on any value; and the last column shows the expression when \( M_{N_1} \) takes its maximum value. The effects of fine and hyperfine structure do not appear in these calculations. The numerical results of this method are given in Table 2-2.

The results given here are only an upper limit to the po-
larization of the emitted radiation. In practice there will be a $\sin^2$ or $\cos^2$ distribution (relative to the $z$ direction) of the molecular axes, so this will relax the restrictions on $M_{N_1}$. This will have the effect of lowering the polarization values.

Blum has taken these qualitative symmetry arguments and developed them in a rigorous fashion. For complete details the reader is referred to Blum (1979).

Since the excitation probability depends on the scattering amplitudes, Blum evaluates these and considers the final result for different types of excitation. From equation 13 of Blum (1978):

$$
I^{(2)}_{N_1 M_1 N_0 M_0} = \sum_{q,k} a_{kq} \langle \alpha_1 N_1 M_1 | T^k_q | \alpha_0 N_0 M_0 \rangle
$$

(2.5.2)

where $T^k_q$ represents an angular momentum change of $|kq\rangle$. The result is (upon evaluation of the matrix elements):

$$
I^{(2)}_{N_1 M_1 N_0 M_0} = \sum_{q,k} (-1)^{-M_0 - q} a_{kq} \langle \alpha_1 | T^k_q | \alpha_0 \rangle
$$

$$
x ((2N_1 + 1)(2N_0 + 1))^{1/2} \begin{pmatrix} N_0 & N_1 & k \\ -M_0 & M_1 & q \end{pmatrix}
$$

$$
x \begin{pmatrix} \alpha_0 & \alpha_1 & \alpha_1 \alpha_1 \end{pmatrix}
$$

(2.5.3)

Blum then transforms equation 2.5.2 to a frame attached to the molecule, to get:

$$
I^{(2)}_{N_1 M_1 N_0 M_0} = \sum_{q,k} a_{kq} \int D^{N_1}_{M_1 M_0} (\hat{n}) D^{k}_{q'q} (\hat{n}) D^{N_0}_{M_0 M_0} (\hat{n})
$$

$$
x \langle \alpha_1 N_1 M_1 | T^k_q | \alpha_0 N_0 M_0 \rangle \hat{n}
$$

(2.5.4)
For $\Sigma^+_{e} - \Sigma^+_{u}$ excitation, the scattering amplitude $f$ is non-zero only if the matrix elements of $T^k_{q}$ are:

$$\langle \chi_{1'N'1'N_1}^{N_1'N_1} | T^k_{q} | \chi_{0'N_0'N_0}^{N_0'N_0} \rangle = A \delta^3(\hat{n} - 0) \quad (2.5.5)$$

where $A$ is some constant. This means that the excitation cross-section will be non-zero only if the molecular axis $\hat{n}$ is parallel to the incident electron beam. Using this and the Born-Oppenheimer approximation ($|M_{N_1}' = \Lambda_1$ and $|M_{N_0}' = \Lambda_0$), and the properties of the rotation matrices, it follows that

$$M_{N_1}' = M_{N_1} = M_{N_0}' = \Lambda_0 = 0.$$  

This, then, confirms the qualitative arguments used by Malcolm et al.

Blum also considers $\Sigma^+_{e} - \Pi_{u}$ excitation. In this case, the matrix elements of $T^k_{q}$, are given by:

$$\langle \chi_{1'N'1'N_1}^{N_1'N_1} | T^k_{q} | \chi_{0'N_0'N_0}^{N_0'N_0} \rangle = A \delta^3(\hat{n} - \pi/2) \quad (2.5.6)$$

Then the scattering amplitude at threshold is given by:

$$f_{N_1'N_1 N_0'N_0} = \sum_{kq0} a_{k0} d_{M_{N_1}' N_1}^{N_1'} (\pi/2) d_{M_{N_0}' N_0}^{N_1} (\pi/2) d_{M_{N_0}' N_0}^{N_0'} (\pi/2) \delta_{N_1'} N_1 \delta_{N_0'} N_0 \quad (2.5.7)$$

This is non-zero if $M_{N_1} = \pm N_0$, but Blum points out that it is possible for states with $|M_{N_1}' \neq N_0$ to contribute also. However, states with $M_{N_1} = 0$ are not present in this case.

Finally, Blum accounts for all orientations of the molecule by assuming that

$$\langle \chi_{1'N'1'N_1}^{N_1'N_1} | T^k_{q} | \chi_{0'N_0'N_0}^{N_0'N_0} \rangle = A f(\Theta) \quad (2.5.8)$$
For \( \sum_{g}^{+} - \sum_{u}^{+} \) excitation \( f(\theta) = \delta \cos \theta = \mathcal{D}_{00}^{1}(\hat{n}) \), and from this:

\[
I_{N_{1}^{0}N_{1}^{0}N_{0}^{0}N_{0}^{0}} \begin{pmatrix} N_{1}^{0} & N_{0}^{0} & 0 & 0 \end{pmatrix} = \sum_{k,j}^{\infty} \delta_{q_{0}(2j+1)} a_{k_{0}0}^{j} \begin{pmatrix} N_{1}^{0} & N_{0}^{0} & 0 & 0 \end{pmatrix} (N_{1}^{0} & N_{0}^{0} & 0 & 0)
\begin{pmatrix} k & 1 & j & 0 \end{pmatrix}^{2} (-1)^{-M_{N_{1}^{0}}} \tag{2.5.9}
\]

For \( \sum_{u}^{+} \prod_{u}^{+} \) excitation \( f(\theta) = \sin \theta = (2)^{1/2} \mathcal{D}_{-10}^{1}(\hat{n}) \), and

\[
I_{N_{1}^{0}N_{1}^{0}N_{0}^{0}N_{0}^{0}} = (2)^{1/2} \sum_{k,j}^{\infty} \delta_{q_{0}a_{k_{0}0}^{j}} (-1)^{m_{1}^{0}+m_{-1}^{0} - M_{N_{1}^{0}}} (2j+1)
\begin{pmatrix} k & 1 & j & 0 \end{pmatrix} \begin{pmatrix} q & 1 & j & 0 \end{pmatrix} (N_{1}^{0} & N_{0}^{0} & 0 & 0)
\begin{pmatrix} N_{1}^{0} & N_{0}^{0} & 0 & 0 \end{pmatrix} \begin{pmatrix} N_{1}^{0} & N_{0}^{0} & 0 & 0 \end{pmatrix} \begin{pmatrix} N_{1}^{0} & N_{0}^{0} & 0 & 0 \end{pmatrix} \tag{2.5.10}
\]

The cross-section \( Q(N_{0}^{0}N_{1}^{0})_{M_{N_{1}^{0}}} \) for exciting a particular magnetic sub-level of the upper rotational state \( N_{1}^{0} \) from the ground state rotational level \( N_{0}^{0} \) is related to the \( f^{2} \) by:

\[
Q(N_{0}^{0}N_{1}^{0})_{M_{N_{1}^{0}}} = \frac{1}{2N_{0}^{0}+1} \sum_{M_{N_{1}^{0}}} \left| I_{N_{1}^{0}N_{1}^{0}N_{0}^{0}N_{0}^{0}} \right|^{2} d\Omega_{e} \tag{2.5.11}
\]

Thus a knowledge of the scattering amplitudes allows the threshold polarization to be calculated directly. However, unless the assumption is made that only one value of \( k \) (in \( T_{k_{0}0}^{0} \)) contributes in equations 2.5.9 and 2.5.10, the expansion coefficients \( a_{k_{0}0}^{j} \) must be calculated first. If only one value of \( k \) (e.g. only dipolar excitation takes place with \( k=1 \)) does contribute, then expressions for the threshold polarization depending on purely geometrical factors are obtained.

Equations 2.5.9, 2.5.10, and 2.5.11 were used in the ex-
pressions derived by Blum for the emitted intensities of the radiation (see section 2.6), and numerical values for the polarization were obtained. These results are shown in Table 2-2.

Recently Blum (in a private communication) has suggested an alternate approach showing that the preferential excitation of magnetic sublevels in the excited state follows directly from the selection rules involved in the calculation of the matrix elements of $T^k_q$.

The excitation amplitude can be written as:

$$\langle \alpha_1 \Lambda_1 N_1 M_1 | T | \alpha_0 \Lambda_0 N_0 M_0 \rangle$$

$$\sim \sum_{L_0} \begin{pmatrix} N_1 & N_0 & L_0 \\ -L_0 & -N_0 & -L_0 \end{pmatrix} \begin{pmatrix} N_1 & N_0 & L_0 \\ -M_0 & -M_0 & 0 \end{pmatrix} \langle \alpha_1 \Lambda_1 | T | \alpha_0 \Lambda_0, L_0 \rangle$$

For $\sum^+_g - \sum^+_u$ excitation $\Lambda_0 = \Lambda_1 = 0$, $L_0$ is odd, and $N_1 + N_0$ is odd. Then the factor

$$\begin{pmatrix} N_1 & N_0 & L_0 \\ 0 & 0 & 0 \end{pmatrix}$$

will be zero unless $N_1 + N_0 + L_0$ is even. It is this factor which contains the influence of the symmetry of the molecule on the excitation process. Only the 3-j symbols with $N_1 + N_0$ and $L_0$ odd will contribute to the excitation, and the 3-j symbols which are not maximal for $M_{N_0} = 0$ will vanish. Blum then points out that

$$\begin{pmatrix} N_1 & N_0 & 1 \\ -M_{N_0} & M_{N_0} & 0 \end{pmatrix} \sim \begin{cases} (N_0 + 1)^2 - M_{N_0}^2 & \text{for } N_1 = N_0 + 1 \\ M_{N_0} & \text{for } N_0 = N_1 \end{cases}$$

The previous selection rules forbid $N_0 = N_1$, so the selection rules enforce the preferential selection of $M_{N_0} = 0$. 
2.6 - THE DENSITY MATRIX FORMULATION OF BLUM AND JAKUBOWICZ

K. Blum and H. Jakubowicz (1978) have developed a density matrix formulation of the theory of electron-photon coincidence measurements in electron-molecule scattering, for molecules described by Hund's case (b). As a special case of their theory they derive expressions for the threshold polarization of the emitted radiation.

Basically, Blum and Jakubowicz construct a density matrix for the final state of the system, given by:

$$\langle \alpha_{1}^{N_{0}M_{0}} | \rho(\alpha_{1}^{N_{0}M_{0}}, \vec{P}_{1}) | \alpha_{1}^{N_{1}M_{1}} \rangle$$

$$= \frac{1}{2(2S_{0}+1)} \frac{W(N_{0})(2S+1)}{(2N_{0}+1)} \sum_{S_{1}} \sum_{M_{1}} \sum_{N_{1}} \sum_{M_{1}} f_{S_{1}M_{1}N_{1}N_{0}M_{0}} f_{S_{1}M_{1}N_{1}N_{0}M_{0}}$$

(2.6.1)

where $\alpha_{1} = n_{1}v_{1}\lambda_{1}$, $W(N_{0})$ is the probability of finding a molecule in the initial rotational level $N_{0}$, and the $f$'s are the scattering amplitudes to go from the initial state $N_{0}M_{0}$ to the excited state $N_{1}M_{1}$. The momentum of the scattered electrons is given by $\vec{P}_{1}$. For a discussion of the emitted radiation, the density matrix is decomposed into multipoles $T(N_{1}^{*}, N_{KQ})$ given by:

$$T(N_{1}^{*}, N_{KQ}) = \sum_{N_{1}M_{1}} (-1)^{N_{1}+M_{1}+K} (2K+1)^{1/2} \left( \begin{array}{ccc}
N_{1} & N_{1} & K \vspace{0.5em} \\
M_{1} & M_{1} & 0
\end{array} \right)$$

$$\times | \alpha_{1}^{N_{1}M_{1}} \rangle \langle \alpha_{1}^{N_{1}M_{1}} |$$

(2.6.2)

The density matrix is then expanded in terms of these multipoles, which yields:

$$\rho(\alpha_{1}, \vec{P}_{1}) = \sum_{KQ} \sum_{N_{1}} \left( \begin{array}{c}
T(N_{1}^{*}, N_{KQ})^{\dagger} \\
T(N_{1}^{*}, N_{KQ})
\end{array} \right)$$

(2.6.3)
The $\langle T(N'_1,N_1)^\dagger \rangle_{KQ}$ are the 'state multipoles' given by:

$$
\langle T(N'_1,N_1)^\dagger \rangle_{KQ} = \frac{1}{2(2S_0+1)} \sum_{M_{N_1}M'_{N_1}N_{N_0}N'_{N_0}} \frac{W(N_0)(2S+1)}{(2N_0+1)(2K+1)^{1/2}} \times N_{N_1}^{+K+Q-M_{N_1}} \times \left( \begin{array}{c} N_1' N_1' K \\ N_1 M_{N_1} Q \\ \end{array} \right) 
$$

$$
= \text{tr} \varrho(\alpha_1,\vec{F}_1) T(N'_1,N_1)^\dagger_{KQ}
$$

It can be seen that a knowledge of the state multipoles is equivalent to knowing the elements of the density matrix.

For photon emission the authors consider the time evolution of the state multipoles, using the evolution operator

$$
U(t) = e^{-iHt/\hbar} \Gamma t
$$

where $H$ is the Hamiltonian of the free molecule (including the fine structure interaction) and $\Gamma$ is the decay operator.

Then the density matrix, as a function of time, is given by:

$$
\varrho(t) = U(t) \varrho(\alpha_1,\vec{F}_1;0) U^\dagger(t)
$$

From this, the time evolution of the state multipoles is:

$$
\langle T(N'_1,N_1)^\dagger_{KQ} \rangle = \text{tr} \varrho(t) T(N'_1,N_1)^\dagger_{KQ}
$$

$$
= \sum_{K'Q} \langle T(N'_1,N_{10})^\dagger_{KQ} \rangle G(t)^{Q'Q}_{K'K}
$$

where

$$
G(t)^{Q'Q}_{K'K} = \text{tr} U(t) T(N'_1,N_1)_{K'Q} U^\dagger(t) T(N'_1,N_1)^\dagger_{KQ}
$$
are the perturbation coefficients in the expansion.

The density matrix for photon emission of frequency in the direction \( \hat{n} \) at time \( t \) is given by:

\[
\dot{\rho}(\hat{n},t)_{\lambda',\lambda} = \overline{\sigma(\omega)} \text{ tr } r_{-\lambda'} \rho(t) r_{-\lambda} \tag{2.6.9}
\]

where

\[
\overline{\sigma(\omega)} = \frac{e^2 \omega^4 d\Omega_{\nu}}{2 \pi c^3 h}
\]

and \( r_{-\lambda} \) is the component of the dipole transition operator in the helicity system, and \( d\Omega_{\nu} \) is the element of solid angle into which the photons are emitted. For a particular observation direction \( \hat{n} \), \( \dot{\rho} \) is a 2x2 matrix.

The molecular ensemble is characterized by the state multipoles at \( t=0 \) (eq 2.6.4) and at time \( t \) (eq 2.6.7). Using equation 2.6.6 in equation 2.6.9,

\[
\dot{\rho}(\hat{n},t)_{\lambda',\lambda} = \overline{\sigma(\omega)} \sum_{KQN'_{N'_{1}}N_{1}} [\text{ tr } r_{-\lambda'} T(N'_{1},N_{1})_{KQ} r_{-\lambda} ] \\
x \left< T(N'_{1},N_{1},t)_{KQ} \right> \tag{2.6.10}
\]

with \( \dot{\rho} \) normalized so that

\[
\text{ tr } \dot{\rho}(\hat{n},t) = I(\hat{n},t) \quad \phi
\]

where \( I(\hat{n},t) \) is the total intensity of photons emitted in the \( \hat{n} \) direction at time \( t \).

In the steady state case, the density matrix is integrated over all observation times since the time between excitation and emission is no longer uniquely defined. Also, since the scattered electrons are not observed, the results must be integrated over the scattered electron directions. Then the photon density matrix is:
\[
\rho \chi'\lambda = \frac{c(\omega)}{2} \left| \langle \chi_f | r_{\lambda_f} - \Lambda_{\lambda_f} | \chi_f \rangle \right|^2 \sum_{K N_1 N_1} (-1)^K W(N_f N_1)(2K+1) d_{\lambda_f}^K(\theta) \\
\times \left( \begin{array}{ccc} 1 & 1 & K \\ -\lambda & \lambda & Q \\ N_1 & N_1 & N_1 \end{array} \right) \frac{1}{(2S_1+1)} \sum_{J_1} \frac{1}{J_1} (2J_1+1)^2 \\
\times \left\{ \begin{array}{ccc} N_1 & J_1 & S_1 \\ J_1 & N_1 & K \end{array} \right\}^2 \sum_{N_0 N_1} W(N_0) (-1)^{N_1-M_1} \left( \begin{array}{ccc} N_1 & N_1 & K \\ -M_1 & M_1 & 0 \end{array} \right) \\
\times Q(N_0 N_1)_{M_1} \\
\]  

(2.6.11)

where \(Q(N_0 N_1)_{M_1}\) is the total cross-section for excitation of the state \(|\chi_{N_1 M_1}\rangle\) from the states \(\sum_{M_0} |\alpha_{N_0 M_0}\rangle\). It is given by:

\[
Q(N_0 N_1)_{M_1} = \frac{1}{2(2S_0+1)(2N_0+1)} \sum_{S_0, M_0} (2S+1) \left| \begin{array}{ccc} S_0 & N_0 & M_0 \\ N_1 & N_1 & N_1 \end{array} \right|^2 d_{\lambda_f}^2 \]

and \(\gamma_1\) is the lifetime of the excited state. The quantity \(W(N_f N_1)\) is:

\[
W(N_f N_1) = (-1)^{N_f - N_1 + f} (2N_1 + 1)(2N_f + 1) \left( \begin{array}{ccc} N_1 & N_f & 1 \\ -\Lambda_f & -\lambda_f & -\Lambda_f \end{array} \right) \\
\]

The polarization \(P\) is:

\[
P = (I_{||} - I_{\perp})/(I_{||} + I_{\perp}) = (3I_{||} - I_{\perp})/(I_{||} + I_{\perp})
\]

where \(I_{||} = I_I + 2I_\perp\). In terms of the elements of the density matrix,

\[
I_{||} = \frac{1}{2} \left[ \rho_{11} + \rho_{-1-1} - \rho_{1-1} - \rho_{-11} \right]
\]

Without taking into account hyperfine structure

\[
I_{||} = \frac{c(\omega)}{2} \left| \langle \chi_f | r_{\lambda_f} - \Lambda_{\lambda_f} | \chi_f \rangle \right|^2 \sum_{N_1 N_1 K} W(N_f N_1)(2K+1) \\
\times \sum_{J_1} (2J_1+1)^2 \left\{ \begin{array}{ccc} N_1 & J_1 & S_1 \\ J_1 & N_1 & K \end{array} \right\}^2 \left\{ \begin{array}{ccc} 1 & 1 & K \\ 1 & 1 & K \end{array} \right\} \left\{ \begin{array}{ccc} N_1 & N_1 & N_f \\ 0 & 0 & 0 \end{array} \right\}
\]
\[
\begin{align*}
x \sum_{N_0^M N_1^N} W(N_0)(-1)^{N_1-M_N_1} \begin{pmatrix} N_1 & N_1 & K \\ -M_N_1 & M_N_1 & 0 \end{pmatrix} Q(N_0N_1^M)_{N_1^N} \\
(2.6.12)
\end{align*}
\]

The total intensity \( \overline{I} \) is given by:
\[
\overline{I} = \overline{C(\omega)} \left| \langle \chi_f | r_{\lambda_1-\lambda_1'} | \chi_1 \rangle \right|^2 \sum_{N_1^N N_1^N} \frac{(-1)^{N_1+N_1'}W(N_1^N N_1')}{\gamma_1^N(2N_1+1)}
\]
\[
x \sum_{N_0^M N_1^N} W(N_0)Q(N_0N_1^M)_{N_1^N} \\
(2.6.13)
\]

When hyperfine structure is included in the calculation,
\[
\begin{align*}
I_{ij} &= \overline{C(\omega)} \left| \langle \chi_f | r_{\lambda_1-\lambda_1'} | \chi_1 \rangle \right|^2 \sum_{N_1^N K} W(N_1^N N_1') (2K+1) \\
&\times \sum_{J_1^F 1 I} \frac{(2J_1+1)^2(2F_1+1)}{\gamma_1^N(2S_1+1)(2I+1)} \begin{pmatrix} N_1 & J_1 & S_1 \\ J_1 & N_1 & K \end{pmatrix}^2 \begin{pmatrix} J_1 & F_1 & I \\ F_1 & J_1 & K \end{pmatrix} \\
&\times \begin{pmatrix} 1 & 1 & K \\ N_1 & N_1 & N_1' \end{pmatrix} \begin{pmatrix} 1 & 1 & K \\ 0 & 0 & 0 \end{pmatrix} \sum_{N_0^M N_1} W(N_0)(-1)^{N_1-M_N_1} \\
&\times \begin{pmatrix} N_1 & N_1 & K \\ -M_N_1 & M_N_1 & 0 \end{pmatrix} Q(N_0N_1^M)_{N_1^N} \\
(2.6.14)
\end{align*}
\]

The total intensity is again given by equation 2.6.13.

The above results depend on the following assumptions, as outlined by Blum (1979).

(a) - The excitation time is much shorter than the precession of the total angular momentum of the molecule, so that L-S coupling can be used to describe the molecule.

(b) - The fine-hyperfine structure separations are large compared to the level widths.

(c) - Hund's case (b) applies to the molecule.
There are certain restrictions at threshold discussed by Blum. The excitation is observed in L-S coupling, so this implies that the conservation of total angular momentum requires that total orbital angular momentum and total spin are separately conserved. This leads to the conclusion that $M_{N_1} = M_{N_0}$ at the threshold. This was also discussed in section 2.5.

It is clear from equations 2.6.12, 2.6.13, and 2.6.14 that the polarization will depend on the cross-sections for excitation of the different $M_{N_1}$, even at threshold. However, if only one sublevel is excited, the polarization will depend only on geometrical factors, as it does in the atomic case, where $M_L = 0$ only.

In his work, Blum also examines the assumptions of Jette and Cahill and those of Baltayan and Nedelec. Consider first Jette and Cahill.

For singlet excitation, Blum shows that the expression for the threshold polarization is given by:

$$P_{th} = \sum_{M_{N_0}} \left[ \sum_{M_{N_1}} \left[ \frac{3 \left( \frac{N_1}{M_{N_0}} 1 N_f \right)^2 - \frac{1}{(2N_1+1)}}{M_{N_0} 0 -M_{N_0}} \right] \frac{Q_{M_{N_0}}}{Q_{M_{N_0}}} \right]$$

(2.6.15)

If the selection rule of Jette and Cahill is used, then only the $M_{N_1} = M_{N_0} = 0$ term will contribute. Numerical evaluation of this expression shows that it does reproduce the results of Jette and Cahill. This is shown in Table 2-2. Furthermore, if the polarization is evaluated using equations 2.6.12 and
2.6.13, along with $S = 0$ and $M_{N_1} = 0$, exactly the same numerical values result. Thus the general expression derived by Blum reduces to the simple case above.

For the case of Baltayan and Nedelec's assumptions, Blum shows that the threshold polarization is given by:

$$P_{th} = \sum_{M_{N_0}} \left[ \left( \begin{array}{cc} N_1 & 1 \\ M_{N_0} & 0 \\ -N_{N_0} & M_{N_0} \end{array} \right) \right]^2 \left( 1 \over (2N_1 + 1) \right) \left( \begin{array}{ccc} N_1 & L_0 & N_0 \\ -M_{N_0} & 0 & M_{N_0} \end{array} \right)^2$$

(2.6.16)

The results of evaluating this expression are shown in Table 2-2. $L_0$ is the angular momentum that must be added to the molecule to define the upper state. $L_0 = 1$ was used.

Finally, if the case of $M_{N_1} = \pm N_0$ is considered, it can be seen that equation 2.6.15 reproduces the results of Table 2-1, when this form of selective excitation is used. However, if more than one ground state rotational level contributes to the upper rotational level, as is the case for P and R transitions, this no longer holds true.
2.7 - THE APPROACH OF FEOFILOV

(for a complete discussion the reader is referred to Feofilov (1959))

Feofilov developed a theory for the polarization of atomic fluorescence produced following excitation by linearly polarized light. The use of linearly polarized light automatically enforces the selection rule for the magnetic sublevels in the upper state:

\[ M_{L_1} = M_{L_0} \] \hspace{1cm} (2.7.1)

This follows directly from the dipole selection rules.

Based on dipole excitation and emission, Feofilov was able to evaluate the transition probabilities of the \( \Delta M_L = 0, \pm 1 \) components of the downward transitions, and hence determine the polarization of the emitted radiation. He then applied these results directly to diatomic molecules and obtained the following results:

\[ P(N_f - 2 \rightarrow N_f - 1 \rightarrow N_f) = \frac{1}{7} \] \hspace{1cm} (2.7.2)

\[ P(N_f \rightarrow N_f - 1 \rightarrow N_f) = \frac{[N_f - 1)(2N_f - 1)]}{14N_f^2 + 5N_f + 1} \] \hspace{1cm} (2.7.3)

for the P branch;

\[ P(N_f \rightarrow N_f \rightarrow N_f) = \frac{(2N_f + 3)(2N_f - 1)}{8N_f^2 + 8N_f - 1} \] \hspace{1cm} (2.7.4)

for the Q branch;

\[ P(N_f + 2 \rightarrow N_f + 1 \rightarrow N_f) = \frac{1}{7} \] \hspace{1cm} (2.7.5)

\[ P(N_f \rightarrow N_f + 1 \rightarrow N_f) = \frac{(N_f + 2)(2N_f + 5)}{14N_f^2 + 23N_f + 10} \] \hspace{1cm} (2.7.6)

for the R branch.

\( N_f \) is the rotational quantum number of the final state, and
$P(N_0 \rightarrow N_1 \rightarrow N_f)$ refers to the polariztion for the radiation emitted following excitation from $N_0$ to $N_1$ and decay to $N_f$. The numerical results of Feofilov are given in Table 2-2d. Also given are the net polarizations when the ground state rotational population distribution and the relative intensities of each transition are taken into account. Both $T=300^\circ K$ and $T=600^\circ K$ are used to calculate the relative intensities.

Although Feofilov's theory assumes excitation by linearly polarized light, it applies to threshold polarization of molecules excited by electron impact as well. Because the light is linearly polarized, the selection rule 2.7.1 for the molecular case becomes

$$M_{N_1} = M_{N_0} \quad (2.7.7)$$

This is precisely the selection rule obtained from equation 2.5.1 at the excitation threshold. Feofilov does not attempt to determine if there is preferential population of the magnetic sublevels of the upper state, but simply sums over all the possible sublevels of the initial, excited, and final states.
2.8 - NUMERICAL RESULTS OF THE VARIOUS THEORIES

The equations derived by the various authors were used to calculate numerical values for the threshold polarization of Lyman and Werner emissions, with the exception of Baltayan and Nedelec, who presented numerical results in their work of 1971 (Baltayan and Nedelec 1971). Table 2-2 presents these results.

Table 2-2a presents the calculated values of Jette and Cahill \((M_N=0)\), Baltayan and Nedelec, and Malcolm et al. The Lyman band results of Malcolm et al are given by \(M_N=0\).

Table 2-2b shows the calculated threshold polarizations when the expressions derived by Blum are used. For the preferential excitation, only one ground state rotational level was assumed to contribute to the excited state. For the united atom approximation, the contribution from both P and R channels to the excitation are given, as well as the resultant polarization. This was calculated by determining the relative intensities of the various transitions, obtained from the ground state rotational population distribution and the Hönle-London factors. A temperature of 600°K was assumed.

Table 2-2c shows the results for Lyman and Werner emissions calculated with Blum's expressions. Here the excitation cross-sections were given by equations 2.5.9, 2.5.10, and 2.5.11. Both \(k=0\) and \(k=1\) were used in the calculations.

Table 2-2d shows the numerical results of Feofilov. Again, the contributions from the P and R channels of the excitation are shown, and the resultant polarizations at \(T=300°K\) and 600°K
are given.

It is interesting to note that Feofilov's results are identical to the results of using equation 2.6.16. Upon consideration of the analysis used by Feofilov, it can be shown that his equations given in section 2.7 are identical with 2.6.16.

It is also interesting to note the disagreement between the various theories. Jette and Cahill's predictions are generally at odds with the predictions of the other workers. The predictions of Baltayan and Nedelec, Blum, Feofilov, and Malcolm et al are in fairly good agreement with each other, even though some of the assumptions made are quite different.
<table>
<thead>
<tr>
<th>ROTATIONAL LINE</th>
<th>$M_N^* = 0$</th>
<th>BALTAYAN &amp; NEDELEC (a)</th>
<th>MALCOLM et al. $M_N^* = \pm N$</th>
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</thead>
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<tr>
<td>$P(2)$</td>
<td>0.143</td>
<td>0.09</td>
<td>0.12</td>
</tr>
<tr>
<td>$P(3)$</td>
<td>0.200</td>
<td>0.12</td>
<td>0.13</td>
</tr>
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<td>$P(4)$</td>
<td>0.231</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>$P(5)$</td>
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<td>-</td>
</tr>
<tr>
<td>$P(6)$</td>
<td>0.263</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$P(7)$</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
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<td>$Q(6)$</td>
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<td>-</td>
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<tr>
<td>$R(5)$</td>
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</table>

(a) The authors assumed a target gas temperature of 600°K in their calculations.
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<th>P(3)</th>
<th>P(4)</th>
<th>P(5)</th>
<th>P(6)</th>
<th>P(7)</th>
<th>Q(1)</th>
<th>Q(2)</th>
<th>Q(3)</th>
<th>Q(4)</th>
<th>Q(5)</th>
<th>Q(6)</th>
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<th>R(1)</th>
<th>R(2)</th>
<th>R(3)</th>
<th>R(4)</th>
<th>R(5)</th>
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<tbody>
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<td>M_{N}^{1} = 0</td>
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<td>0.221</td>
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<td>0.253</td>
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<td>-1.000</td>
<td>-1.000</td>
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<td>-1.000</td>
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<td>-1.000</td>
<td>-1.000</td>
</tr>
</tbody>
</table>

**Table 2-2b:** Threshold Polarizations Calculated Using Blum's Theory

**With Different Assumptions**

- **UNITED ATOM APPROXIMATION**
  - N = N_{0}^{1/2} = 0.078

- **RESULTANT**
<table>
<thead>
<tr>
<th>Rotational Line</th>
<th>Lyman Bands K=0</th>
<th>Lyman Bands K=1</th>
<th>Werner Bands K=0</th>
<th>Werner Bands K=1</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(2)</td>
<td>0.135</td>
<td>-</td>
<td>0.141</td>
<td>-0.077</td>
</tr>
<tr>
<td>P(3)</td>
<td>0.080</td>
<td>-</td>
<td>0.082</td>
<td>0</td>
</tr>
<tr>
<td>P(4)</td>
<td>0.115</td>
<td>-</td>
<td>0.115</td>
<td>-0.021</td>
</tr>
<tr>
<td>P(5)</td>
<td>0.128</td>
<td>-</td>
<td>0.128</td>
<td>-0.027</td>
</tr>
<tr>
<td>P(6)</td>
<td>0.134</td>
<td>-</td>
<td>0.134</td>
<td>-0.032</td>
</tr>
<tr>
<td>P(7)</td>
<td>0.137</td>
<td>-</td>
<td>0.137</td>
<td>-0.037</td>
</tr>
<tr>
<td>Q(1)</td>
<td>-</td>
<td>-</td>
<td>0.333</td>
<td>0.333</td>
</tr>
<tr>
<td>Q(2)</td>
<td>-</td>
<td>-</td>
<td>0.500</td>
<td>-0.022</td>
</tr>
<tr>
<td>Q(3)</td>
<td>-</td>
<td>-</td>
<td>0.535</td>
<td>-0.292</td>
</tr>
<tr>
<td>Q(4)</td>
<td>-</td>
<td>-</td>
<td>0.538</td>
<td>-0.391</td>
</tr>
<tr>
<td>Q(5)</td>
<td>-</td>
<td>-</td>
<td>0.535</td>
<td>-0.430</td>
</tr>
<tr>
<td>Q(6)</td>
<td>-</td>
<td>-</td>
<td>0.530</td>
<td>-0.449</td>
</tr>
<tr>
<td>R(0)</td>
<td>0.960</td>
<td>-</td>
<td>0.990</td>
<td>-1.000</td>
</tr>
<tr>
<td>R(1)</td>
<td>0.264</td>
<td>-</td>
<td>0.269</td>
<td>0</td>
</tr>
<tr>
<td>R(2)</td>
<td>0.261</td>
<td>-</td>
<td>0.262</td>
<td>-0.051</td>
</tr>
<tr>
<td>R(3)</td>
<td>0.242</td>
<td>-</td>
<td>0.242</td>
<td>-0.053</td>
</tr>
<tr>
<td>R(4)</td>
<td>0.225</td>
<td>-</td>
<td>0.225</td>
<td>-0.056</td>
</tr>
<tr>
<td>R(5)</td>
<td>0.213</td>
<td>-</td>
<td>0.213</td>
<td>-0.060</td>
</tr>
</tbody>
</table>
### Table 2-2d: Calculation of Threshold Polarization Using the Results of Pefilov

<table>
<thead>
<tr>
<th>Rotational Line</th>
<th>Contribution from $N_0 = N_f$</th>
<th>Contribution from $N_0 = N_f^{1/2}$</th>
<th>Polarization $T=300^\circ K$</th>
<th>Polarization $T=600^\circ K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(2)</td>
<td>0.015</td>
<td>0.143</td>
<td>0.106</td>
<td>0.079</td>
</tr>
<tr>
<td>P(3)</td>
<td>0.042</td>
<td>0.143</td>
<td>0.135</td>
<td>0.117</td>
</tr>
<tr>
<td>P(4)</td>
<td>0.061</td>
<td>0.143</td>
<td>0.141</td>
<td>0.131</td>
</tr>
<tr>
<td>P(5)</td>
<td>0.074</td>
<td>0.143</td>
<td>0.143</td>
<td>0.137</td>
</tr>
<tr>
<td>P(6)</td>
<td>0.084</td>
<td>0.143</td>
<td>0.143</td>
<td>0.141</td>
</tr>
<tr>
<td>P(7)</td>
<td>0.091</td>
<td>0.143</td>
<td>0.143</td>
<td>0.143</td>
</tr>
<tr>
<td>Q(1)</td>
<td>0.333</td>
<td>-</td>
<td>0.333</td>
<td>0.333</td>
</tr>
<tr>
<td>Q(2)</td>
<td>0.447</td>
<td>-</td>
<td>0.447</td>
<td>0.447</td>
</tr>
<tr>
<td>Q(3)</td>
<td>0.474</td>
<td>-</td>
<td>0.474</td>
<td>0.474</td>
</tr>
<tr>
<td>Q(4)</td>
<td>0.484</td>
<td>-</td>
<td>0.484</td>
<td>0.484</td>
</tr>
<tr>
<td>Q(5)</td>
<td>0.490</td>
<td>-</td>
<td>0.490</td>
<td>0.490</td>
</tr>
<tr>
<td>Q(6)</td>
<td>0.493</td>
<td>-</td>
<td>0.493</td>
<td>0.493</td>
</tr>
<tr>
<td>R(0)</td>
<td>1.000</td>
<td>0.143</td>
<td>0.800</td>
<td>0.639</td>
</tr>
<tr>
<td>R(1)</td>
<td>0.447</td>
<td>0.143</td>
<td>0.426</td>
<td>0.373</td>
</tr>
<tr>
<td>R(2)</td>
<td>0.321</td>
<td>0.143</td>
<td>0.317</td>
<td>0.296</td>
</tr>
<tr>
<td>R(3)</td>
<td>0.268</td>
<td>0.143</td>
<td>0.267</td>
<td>0.258</td>
</tr>
<tr>
<td>R(4)</td>
<td>0.239</td>
<td>0.143</td>
<td>0.239</td>
<td>0.236</td>
</tr>
<tr>
<td>R(5)</td>
<td>0.221</td>
<td>0.143</td>
<td>0.221</td>
<td>0.221</td>
</tr>
</tbody>
</table>
2.9 - POLARIZATION OF ATOMIC LINE RADIATION FOLLOWING DISSOCIATIVE EXCITATION

The theory of polarization of atomic fluorescence produced after dissociative excitation of molecules was developed by van Brunt and Zare (1968). They show that two necessary conditions for the radiation to be polarized are:

(1) - There must be an anisotropic spatial distribution of the dissociation products; i.e., an anisotropic distribution of the orientation of the molecular axes just prior to dissociation.

(2) - There must also be a preferential population of the magnetic sublevels of the excited fragment.

Condition (1) has been demonstrated by Dunn (1962), and also by van Brunt in 1974, when he considered the breakdown of the dipole-Born approximation for predicting the angular distribution of the dissociation fragments.

Condition (2) provides an anisotropy in the relative intensities of the transitions from the magnetic sublevels, and condition (1) provides the spatial anisotropy. Together, these conditions ensure that the emitted radiation is polarized.

The authors argue that condition (2) will be satisfied in the following way: When the two atoms are brought close to each other, an inhomogeneous electric field is set up in the direction of the line joining the nuclei. This field produces space quantization of angular momentum. When the two atoms are brought together to form a molecule, each molecular state that could be formed is built up from atoms having well defined projections of angular momentum on the internuclear axis. Now,
when the atoms separate from a repulsive molecular state, they also have well defined \( M \) states with respect to the internuclear axis, and hence, a preferential population distribution.

A summary of their results is shown below in Table 2-3. The quantity \( \Theta \) is an asymmetry parameter, which comes from assuming an electric dipole transition in the dissociation of the molecule. For polarized light emission, \( \Theta \) can take on a range of values from 2 to -1.

**TABLE 2-3: POLARIZATION AS A FUNCTION OF THE ASYMMETRY PARAMETER FOR VARIOUS ATOMIC TRANSITIONS**

<table>
<thead>
<tr>
<th>M State Selected</th>
<th>( \frac{1S - 1P}{1S} )</th>
<th>( \frac{1P - 1S}{1P} )</th>
<th>( \frac{1P - 1D}{1D} )</th>
<th>( \frac{1D - 1P}{1D} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>( \frac{3\Theta}{10+\Theta} )</td>
<td>( \frac{3\Theta}{100+\Theta} )</td>
<td>( \frac{3\Theta}{40+\Theta} )</td>
</tr>
<tr>
<td>( \pm 1 )</td>
<td>-</td>
<td>( \frac{-3\Theta}{20-\Theta} )</td>
<td>( \frac{-3\Theta}{200-\Theta} )</td>
<td>( \frac{3\Theta}{40+\Theta} )</td>
</tr>
<tr>
<td>( \pm 2 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>( \frac{-3\Theta}{20-\Theta} )</td>
</tr>
</tbody>
</table>
CHAPTER III

THE EXPERIMENTAL DETAILS
3.1 - THE 3 MIRROR POLARIZER

At the wavelengths encountered in this experiment there are no transparent crystals available to analyze polarized radiation. Therefore the reflectance method was chosen to accomplish this. Such a polarization device is described in Sampson (1967), and is discussed briefly in Malcolm et al (1979).

The polarizer consists of 3 gold-coated, optically flat (Λ/4) mirrors oriented in such a way as to preserve the optical path of the incident beam. Fig 3-1 shows a diagram of the polarizer. Because of this arrangement the polarizer could be rotated about the optical axis of the system. In order to accomplish this, the three angles θ₁, θ₂, and θ₃ were chosen to satisfy the following two equations,

\[ \theta_3 = \theta_1 \]
\[ \theta_2 = 2\theta_1 - 90^\circ \]  \hspace{1cm} (3.1.1)

In addition to satisfying 3.1.1 the angles had to be chosen to obtain reasonable transmission and polarization over the wavelength range in which the polarizer would be used. This was done by calculating the transmission and polarization properties of the polarizer by using the generalized Fresnel equations (Sampson 1967):

\[ R_\perp = \frac{a^2 + b^2 - 2a\cos\theta + \cos^2\theta}{a^2 + b^2 + 2a\cos\theta + \cos^2\theta} \]  \hspace{1cm} (3.1.2)

\[ R_\parallel = R_\perp \frac{a^2 + b^2 - 2\sin\theta\tan\theta + \sin^2\theta\tan^2\theta}{a^2 + b^2 + 2\sin\theta\tan\theta + \sin^2\theta\tan^2\theta} \]  \hspace{1cm} (3.1.3)

where a and b are given by the following:
\[ 2a^2 = [(n^2-k^2-sin^2\theta)^2+4n^2k^2]^{1/2} + (n^2-k^2-sin^2\theta) \quad (3.1.4) \]
\[ 2b^2 = [(n^2-k^2-sin^2\theta)^2+4n^2k^2]^{1/2} - (n^2-k^2-sin^2\theta) \quad (3.1.5) \]

In these equations 'n' is the real part of the index of refraction and 'k' is the extinction coefficient. \( R_\perp \) is the reflectance of the mirror perpendicular to the plane of incidence and \( R_\parallel \) is the reflectance of the mirror parallel to the plane of incidence. Note that because of the complex index of refraction, only partially polarized light will be transmitted by the polarizer, and hence, its 'efficiency' is always less than 100%.

These equations were applied to each mirror in the polarizer, so that the net reflectance of the device was the product of the individual reflectances. Thus:

\[ R_\parallel = R_{\parallel}^{(1)}R_{\parallel}^{(2)}R_{\parallel}^{(3)} \quad (3.1.6) \]
\[ R_\perp = R_{\perp}^{(1)}R_{\perp}^{(2)}R_{\perp}^{(3)} \quad (3.1.7) \]

To obtain the expressions for the transmission and the polarization consider the following:

Light entering the polarizer has initial intensities \( I_\parallel \) and \( I_\perp \) with respect to a fixed direction in space (in the experiment this was defined by the electron beam, with the parallel component parallel to the electron beam, and the perpendicular component perpendicular to it). The polarizer is rotated so that \( I_\parallel \) lies in the plane of incidence of the mirrors. The measured intensity is then given by:

\[ I_{\parallel}^m = I_\parallel R_\parallel + I_\perp R_\perp \quad (3.1.8a) \]

Next the polarizer is rotated through \( 90^\circ \) bringing \( I_\perp \) into the plane of incidence. The measured intensity is now:
\[ I^m_\perp = I^m_\parallel + I^m_\perp \] (3.1.8b)

Now the polarization of the outgoing light is defined to be:
\[ P = \frac{I^m_\parallel - I^m_\perp}{I^m_\parallel + I^m_\perp} \] (3.1.9)

Using equations 3.1.8 in 3.1.9 it is found that
\[ P = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} \cdot \frac{R_\parallel - R_\perp}{R_\parallel + R_\perp} \] (3.1.10)

If the incoming light is completely polarized, with \( I_\perp = 0 \), then the polarization of the outgoing light is just
\[ \alpha = \frac{R_\parallel - R_\perp}{R_\parallel + R_\perp} \] (3.1.11)

The quantity \( \alpha \), given by equation 3.1.11 is defined to be the 'polarizer efficiency'.

To calculate the transmission properties of the polarizer consider the true and measured intensities of the light.

The true intensity is just
\[ I = I_\parallel + I_\perp \] (3.1.12a)

The measured intensity is
\[ I^m = I^m_\parallel + I^m_\perp \] (3.1.12b)

Again, using equations 3.1.8 in 3.1.12b,
\[ I^m = (I_\parallel + I_\perp)(R_\parallel + R_\perp) \]

Then the percentage transmission is
\[ T = 100\frac{I^m}{I} = 100(R_\parallel + R_\perp) \] (3.1.13)

The percent efficiency and transmission of the polarizer were calculated using incident angles \( \theta_\parallel \) from 46.0° to 89.5° over the wavelength range of 25.0 nm to 710.0 nm. The values of 'n' and 'k' were taken from Sampson, page 310. Gold was
chosen because of its uniform polarizing properties over the wavelength range used in the experiment. Table 3-1 shows the percentage transmission and efficiency as a function of wavelength for the angles $\Theta_1 = 70^\circ$ and $\Theta_2 = 50^\circ$. These angles were chosen to be used in construction of the polarizer, since they gave about the best combination of transmission and efficiency as well as being relatively easy to machine. Table 3-2 shows the transmission and efficiency of the polarizer at a wavelength of 120 nm as a function of the angles chosen.

The values of 'n' and 'k' for the gold coated mirrors actually depend a great deal on the surface conditions of the mirrors. Thus it was necessary to measure the efficiency experimentally. The method used is described in Sampson, on pp 312-317. Using the Ar resonance lines at 104.8 and 106.7 nm where the polarization is known to be 0 at 200 eV incident energy, the polarizer efficiency was found to be 0.85 \pm 0.12. The calculated value is 0.97. Using He 58.4 nm at 325 eV, where the polarization is about 0, the measured efficiency was about 0.99. The calculated value was again about 0.97. Having demonstrated the reliability of the calculated values it was decided that these would be used to make the corrections to the data for the polarizer efficiency.

When the measured signal is plotted against the angle of rotation of the polarizer it is found that there are 2 maxima and 2 minima. Fig 3-2 shows such a plot in polar coordinates. The maxima correspond to light whose electric vector is perpendicular to the electron beam and the minima corre-
spond to the electric vector parallel to the electron beam. The signal measured at these angles is called \( I_\perp \) and \( I_\parallel \), respectively. To measure polarization, the data collected at both maxima and both minima would be used. The parallel signal was taken to be the sum of the two minima, and the perpendicular signal was taken to be the sum of the two maxima. To do this the polarizer was rotated to each of the 4 angles in turn and the signal was measured. Using four angles instead of two has the advantage of averaging out any effects due to mechanical misalignment of the polarizer.

The polarizer itself was mounted on a rotary vacuum feed-through inside a stainless steel chamber, behind the exit slit of the spectrometer (see the following section for details). This chamber was maintained under high vacuum by an Edwards model E02 oil vapour diffusion pump and a Peltier thermoelectrically cooled baffle. In addition, when the experiment was not in progress, a butterfly valve was used to isolate the chamber from the pumping system. This was to minimize the migration of oil onto the mirrors of the polarizer and the channeltron detector. The pressure in the detector chamber was monitored with an ion gauge.

Initially the photon detector was mounted behind the polarizer and rotated with it. Rotation was accomplished manually, and a stop at 0° prevented more than one complete revolution in both directions. Since the detector rotated with the polarizer, care had to be taken so that the wiring was not put under any great strain or flexing. The manual system was
### TABLE 3-1: TRANSMISSION AND POLARIZATION PROPERTIES OF THE 3-MIRROR POLARIZER VS WAVELENGTH

\[ \theta_1 = 70^\circ, \quad \theta_2 = 50^\circ, \quad \theta_3 = 70^\circ \]

<table>
<thead>
<tr>
<th>WAVELENGTH (nm)</th>
<th>% TRANSMISSION</th>
<th>% POLARIZATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>3.07</td>
<td>93.37</td>
</tr>
<tr>
<td>30.0</td>
<td>3.01</td>
<td>94.14</td>
</tr>
<tr>
<td>40.0</td>
<td>5.52</td>
<td>93.24</td>
</tr>
<tr>
<td>50.0</td>
<td>8.13</td>
<td>90.64</td>
</tr>
<tr>
<td>60.0</td>
<td>8.34</td>
<td>96.15</td>
</tr>
<tr>
<td>70.0</td>
<td>5.68</td>
<td>96.51</td>
</tr>
<tr>
<td>80.0</td>
<td>7.84</td>
<td>95.33</td>
</tr>
<tr>
<td>90.0</td>
<td>8.45</td>
<td>95.99</td>
</tr>
<tr>
<td>100.0</td>
<td>8.12</td>
<td>97.23</td>
</tr>
<tr>
<td>105.0</td>
<td>8.62</td>
<td>97.28</td>
</tr>
<tr>
<td>110.0</td>
<td>9.49</td>
<td>97.08</td>
</tr>
<tr>
<td>115.0</td>
<td>9.94</td>
<td>97.23</td>
</tr>
<tr>
<td>120.0</td>
<td>10.03</td>
<td>97.36</td>
</tr>
<tr>
<td>125.0</td>
<td>11.00</td>
<td>97.30</td>
</tr>
<tr>
<td>130.0</td>
<td>11.71</td>
<td>97.36</td>
</tr>
</tbody>
</table>

### TABLE 3-2: TRANSMISSION AND POLARIZATION PROPERTIES OF THE 3-MIRROR POLARIZER VS ANGLE

\[ \lambda = 120.0 \text{ nm} \]

<table>
<thead>
<tr>
<th>ANGLE $\theta_1$ (DEG)</th>
<th>% TRANSMISSION</th>
<th>% POLARIZATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.0</td>
<td>1.80</td>
<td>91.04</td>
</tr>
<tr>
<td>55.0</td>
<td>2.49</td>
<td>94.80</td>
</tr>
<tr>
<td>60.0</td>
<td>3.74</td>
<td>96.63</td>
</tr>
<tr>
<td>65.0</td>
<td>5.97</td>
<td>97.34</td>
</tr>
<tr>
<td>70.0</td>
<td>10.03</td>
<td>97.36</td>
</tr>
<tr>
<td>75.0</td>
<td>17.54</td>
<td>96.11</td>
</tr>
<tr>
<td>80.0</td>
<td>32.34</td>
<td>89.22</td>
</tr>
<tr>
<td>85.0</td>
<td>67.97</td>
<td>62.25</td>
</tr>
</tbody>
</table>
replaced with an automatic system which allowed the experiment to be run continuously, even when unattended. With this system the detector was fixed, and a synchronous motor rotated the polarizer to each of the 4 angles in turn. The data at each angle was channelled into the appropriate counter. Section five of this chapter describes this in further detail.

Possible variations in the sensitivity of the detector as a function of the orientation of the electric vector of the incoming photons was minimized by arranging for the channeltron entrance axis to be coincident with the optical axis of the system. The $I(\theta)/I(\theta+180)$ and $I(\theta+90)/I(\theta+270)$ ratios were checked experimentally and found to be unity. This meant that the detector itself was not polarization sensitive in this arrangement.
FIG 3-2: INTERACTION REGION, SPECTROMETER, AND POLARIZER
3.2 - THE GRATING SPECTROMETER (see FIG 3-3)

The spectrometer used to select particular wavelengths for study was a McPherson model 235 half-meter vacuum-UV scanning spectrometer. The optical system employed by the instrument is the Seya-Namioka mounting of a concave grating. This has the entrance and exit slits and the grating mounted on the circumference of the Rowland circle, and scanning is accomplished by simply rotating the grating about the vertical axis through its center. A counter on the front of the instrument indicated the wavelength appearing at the exit slit when used with a 600 lines/mm grating. However, in the present work, a 1200 lines/mm platinized grating was used, making it necessary to calibrate the wavelength scale. This was done by locating first the central image and then Lyman-α from H₂(121.6 nm). From this it was found that the counter reading, n, for a particular wavelength was given by:

\[ n = 2\lambda + 401 \]

where the wavelength \( \lambda \) is given in Å.

The grating was blazed for 70.0 nm, which was not the ideal wavelength for the range over which the experiment was carried out. However, the reciprocal dispersion of the 1200 lines/mm grating was 1.7 nm/mm, twice as good as for the 600 lines/mm grating(3.4 nm/mm). Since resolving power was an essential factor in studying individual rotational lines, the 1200 lines/mm grating had to be used.

The entrance and exit slits were adjusted by means of micrometer screws on each. The width of each slit was contin-
nously adjustable from 0 to 2 mm. The slit widths used depended on the features to be studied. To resolve the rotational structure of the spectra narrow slits (0.05 mm) were used, and to examine an entire vibrational band much wider slits (0.175 mm) could be used. The entrance and exit slits were chosen to be the same width, and it was found that a resolution of 0.1 nm FWHM corresponded to a slit width of 0.05 mm.

The high vacuum needed in the spectrometer chamber was maintained by an Edwards model E04 oil vapour diffusion pump. To eliminate the possibility of oil vapour contaminating the surface of the grating and changing its reflective properties, both a Peltier baffle and a liquid nitrogen cold trap were included in the pumping system. In addition, a zeolite foreline trap was included to prevent backstreaming of oil from the rotary pump. A 4 inch butterfly valve was used to isolate the spectrometer from the pumping system when the experiment was not in progress. Butterfly flap valves at each slit assembly allowed isolation of the spectrometer from the detector chamber and the interaction region. Pressure in the spectrometer chamber was monitored by a Penning discharge gauge, and pressures on the order of $10^{-7}$ torr were obtained.

An essential property of the diffraction grating that was not known beforehand was its reflectivity to polarized light, and how it would affect the measured polarization of the radiation under study. Since there was no way available to calculate the 'instrumental polarization' this quantity had to be determined experimentally. This was done by using a
light source that was known to be unpolarized, such as the Ar resonance lines at 200.0 eV and He 58.4 nm at 325 eV. By simply measuring the signals \( I_\parallel \) and \( I_\perp \) for the unpolarized radiation, the effect of the grating could be calculated. Fig 3-2 shows a plot of \( I(\Theta) \) in polar coordinates using the Ar resonance lines at 200 eV. The data has been averaged for mechanical misalignments by adding \( I(\Theta) \) and \( I(\Theta + 180) \). Note that the angles of \( I_{\text{max}} \) and \( I_{\text{min}} \) correspond to the plane of incidence of the polarizer mirrors perpendicular and parallel to the rulings on the grating, respectively. Once the instrumental polarization was known for a particular wavelength, the polarization of molecular radiation at or near that wavelength could be measured. To measure the polarization of another transition at a different wavelength required that the instrumental effect be remeasured at the new wavelength. This was done by noting that the polarization was independent of the vibrational transition of the molecule. Thus the polarization behaviour of molecular radiation should be the same for different vibrational transitions, especially at high energy (see CHAPTER IV). Thus the true polarization of the incoming radiation for the same electronic transition was known for any vibrational transition. Hence the instrumental effect could be determined at the desired wavelength. Instrumental polarizations were measured that were in the range of about -0.4 to -0.5.
3.3 - THE INTERACTION REGION

The interaction region consists of the electron gun assembly, the gas beam assembly, and the Faraday Cup. FIG 3-4 shows the arrangement of each component.

THE ELECTRON GUN

The electron gun was based on the design of a commercially available gun, the Amperex DH3-91. This gun is also very similar to the one used by Donaldson (1972).

The cathodes used were oxide coated and indirectly heated. It was found that these cathodes had a very long useful lifetime when properly activated and maintained in a good vacuum. Activation was done by gradually increasing the filament current over a period of several hours until 0.4 amps was reached. The current was then brought up to 0.5 amps for 1 minute and returned to 0.4 amps thereafter. Electron beam currents as high as 2000 microamps were attained (at electron energies of 300 eV).

FIG 3-4 also shows the potentials applied to the lens elements of the gun. The surface of the cathode was driven to $-V_{CE}$ volts, and all the other lens elements were driven relative to the cathode. Voltages were monitored with a Dana model 5330 digital voltmeter, which had an accuracy of 0.05%. Stabilized power supplies were used to provide the required voltages to the gun, and energies up to 325 eV were attained.

The circuit diagram of the electron gun supply is shown in FIG 3-5.

The magnitude of the electron beam current was varied by adjusting the potential on L1. This also had the effect of al-
tering the focusing of the electron beam. Adjusting the potentials on L2 and L3 brought the beam back into focus, although L3 had a rather limited effect. The optimum focusing was judged to be when the current on the outer collector of the Faraday Cup was a minimum and the current on the inner collector was a maximum. Focusing was found to be much better at high energy than at low energy. FIG 3-6 shows a plot of the ratio $I_{\text{inner}}/I_{\text{outer}}$ as a function of electron energy. It can be seen that the focusing properties of the gun were essentially constant above 30 eV.

Because of surface and space-charge effects the cathode to interaction region potential did not represent the true energy of the electrons. An additional 'contact potential' was added to the desired energy to compensate for these effects. This contact potential was determined by locating the onset energy of Lyman-$\alpha$ radiation from the dissociative excitation of H$_2$. The difference between this value and the true energy gave the contact potential. FIG 3-7 shows a plot of signal vs $V_{CE}$ used to find the contact potential. It was found that the contact potential was usually on the order of several volts. Also, the contact potential tended to vary slightly over long periods of time due to changing surface conditions on the cathode, so it was monitored periodically during the course of the experiment to keep the energy calibration accurate. It was also found from measurements of the contact potential that the energy spread in the electron beam was on the order of 0.5 eV.

**THE GAS BEAM**

Initially the gas beam was produced by a rectangular slit
arrangement, 5.00 mm long by 1.00 mm wide. Because of the high throughput of gas, head pressures were limited to 1 torr or less. The pressure was monitored with an Edwards Pirani gauge. The limitation in pressure was due mainly to the pumping speed of the rotary pump of the system. At 1 torr head pressure the background gas pressure in the collision chamber was \(1 \times 10^{-4}\) torr.

This arrangement was used to carry out measurements of the integrated vibrational bands in hydrogen. To ensure that measurements were made at pressures where depolarization of the radiation did not occur, a check of signal vs head pressure was made. FIG 3-8 shows a plot of signal vs head pressure. Care was taken to operate only in the linear region on the graph.

When the rotational structure of the spectrum was to be resolved, the rectangular slit was replaced by a 21 gauge hypodermic needle, with the tip of the needle approximately 1 mm above the electron beam. This arrangement allowed head pressures in excess of 20 torr (measured with a Veeco model TG-27 thermocouple gauge), and background gas pressures of \(2 \times 10^{-4}\) torr. Again, a check of signal vs pressure was made. Also a check of polarization vs pressure was made to ensure that measurements were made in a region where the polarization was independent of pressure.

Because it was not possible to determine the head pressure above 20 torr with a TG-27 unit, all measurements were carried out at the same background gas pressure of \(2 \times 10^{-4}\) torr. Once the gas pressure was adjusted to the desired value it was found to remain stable for the entire duration of a mea-
SIGNAL vs HEAD PRESSURE
LYMAN - α

FIG 3-8

POLARIZATION vs PRESSURE
WERNER (2,5) BAND
THE FARADAY CUP

The Faraday Cup was used to monitor the electron beam current. It consisted of two collectors: an inner one which collected the majority of the electrons of the focussed beam, and an outer one which collected the rest of the electrons. FIG 3-4 shows this arrangement. The surface of the inner collector was coated with soot, and a small piece of steel wool was pushed into it to prevent electrons from bouncing around and perhaps finding their way back to the interaction region. The surface of the outer collector was similarly coated.

Currents reaching the inner and outer collectors were monitored by a Keithly model 414A picoammeter and a Keithly model 160B digital multimeter, respectively.
3.4 - THE COUNTING SYSTEM

FIG 3-9 shows a block diagram of the counting system. The detector used in this experiment was a Bendix Channeltron Electron Multiplier. A Tennelec model AEC-5000 HV supply was used to bias the channeltron. A 250 volt power supply was used to bias the front end of the channeltron to keep out any stray electrons.

Pulses from the channeltron were fed into a pre-amplifier and then into an Ortec model 454 Timing Filter Amplifier. The coarse and fine gains, and the integration and differentiation time constants of this unit were adjusted to obtain well defined, fast output pulses. It was found that both the coarse and fine gains had to be set to their maximum values, and the time constants used were: Integration - 20 nsec; Differentiation - 50 nsec.

An Ortec model 421 Integral Discriminator was used to cut out the noise pulses. Most of the noise pulses had amplitudes of 1 volt or less, while true data pulses had amplitudes of about 2 volts or more. To determine the optimum setting of the discriminator, a measurement of counts/minute vs the discriminator setting was made. FIG 3-10 shows this. The discriminator was set to a value on the 'plateau' of the curve.

The pulse inverter was used to convert the positive logic (0 to +5v) output of the discriminator to the negative logic (0 to -5v) required by the Ortec model 9315 Dual Photon Counter. This pulse inverter consisted simply of a pulse transformer with the output taken 180° out of phase with the input.
Thus a positive input pulse resulted in a negative output pulse. It was found that it was necessary to put 50 ohm terminations on the discriminator output, the inverter input, and the inverter output to keep ringing down to a minimum. Without such terminations spurious pulses arose that were counted as data.

The polarizer control unit determined the counter to send the data into, as well as controlling the rotation of the polarizer itself. A description of the working of the unit follows. FIG 3-11 shows the circuit diagram of the control unit. An Ortec model 719 timer was used to control the counting time at each position of the polarizer.

(a) - The 4 position sensors were placed at 90° intervals about the axis of rotation of the polarizer. These sensors consisted of an infrared emitting LED and a phototransistor in a single assembly, separated by a small gap. A slit in a cylinder which rotated with the polarizer allowed radiation from the LED to reach the phototransistor and turn it on. This signal was sent back to the control unit, which then turned the motor off, selected the counter gate appropriate to that position, and started the timer. The data was then counted by the counter. At the end of the timing interval the timer sent a stop pulse to the control unit. This caused the unit to turn off the counter and to start the motor. The polarizer rotated to the next position and the counting cycle began again.

(b) - To start the experiment with this unit the 'RESET' button was pressed to bring the polarizer to the 1st sensor position (marked 'A' in FIG 3-11). This set the unit up for
FIG 3-11
POLARIZER CONTROL CIRCUIT
FIG 3-11
INTERFACE CIRCUIT
counting. The 'STOP/RUN' switch was set to 'RUN'. To stop the experiment the switch was set to 'STOP'. After the completion of an entire cycle, the experiment would then stop. The number of cycles was counted by an Ortec model 775 counter. This was done by counting the number of start pulses issued by the control unit and dividing that by four.

(c) - A continuous rotary mode was also available. This mode allowed a continuous scan of signal vs polarizer angle to be made. The sensors and the timer were inoperative in this mode, and the polarizer simply rotated continuously until it was stopped. A potentiometer on the shaft of the polarizer provided a voltage linearly proportional to the polarizer angle. Signal pulses from the discriminator were multiplied by this voltage in an analog multiplier. The output of the multiplier went into a Pulse Height Analyzer. Since the height of the pulses was proportional to the angle of the polarizer, a PHA spectrum of signal vs polarizer angle was obtained. Once the horizontal axis of the spectrum was calibrated, determination of the maximum and minimum transmission angles of the polarizer was done. Position sensor 'A' was then set to the angle corresponding to a minimum in the transmission ($I_\parallel$).
3.5 - DETERMINATION OF THE TRUE POLARIZATION AND INTENSITY

In order to obtain the true polarization of the radiation, as well as the true emitted intensities, the polarizing effects of the spectrometer and the polarizer had to be corrected for. This was done in the following way:

Consider the simplified diagram of the experimental arrangement shown in FIG 3-12. The radiation produced in the interaction region has true signal intensities $I_{\|}$ and $I_{\perp}$ with respect to the electron beam direction. After being wavelength selected by the spectrometer the signal intensities are $I'_{\|}$ and $I'_{\perp}$. This radiation then passes through the polarizer where it is polarization analyzed. The measured signal is then $I^m_{\|}$ and $I^m_{\perp}$.

The spectrometer grating has reflectances $R_{\|}$ and $R_{\perp}$. The polarizer has transmittances $T_{\|}$ and $T_{\perp}$. The following quantities are defined:

$$\alpha = \left| \frac{T_{\|} - T_{\perp}}{T_{\|} + T_{\perp}} \right|$$  \hspace{1cm} 'Polarizer Efficiency' \hspace{1cm} (3.5.1)

$$P_I = \frac{R_{\|} - R_{\perp}}{R_{\|} + R_{\perp}}$$  \hspace{1cm} 'Instrumental Polarization' \hspace{1cm} (3.5.2)

$$P_m = \frac{I^m_{\|} - I^m_{\perp}}{I^m_{\|} + I^m_{\perp}}$$  \hspace{1cm} 'Measured Polarization' \hspace{1cm} (3.5.3)

$$P = \frac{I_{\|} - I_{\perp}}{I_{\|} + I_{\perp}}$$  \hspace{1cm} 'True Polarization' \hspace{1cm} (3.5.4)
CALCULATION OF THE TRUE POLARIZATION

Consider what happens to the light after being reflected by the grating. The resultant intensities are:

\[ I'_{||} = I_{||} R_{||} \] \hspace{1cm} (3.5.5a)
\[ I'_{\perp} = I_{\perp} R_{\perp} \] \hspace{1cm} (3.5.5b)

Now consider the case when the polarizer is oriented in such a way that the plane of incidence of the mirrors is parallel to the electron beam direction. The measured signal is then:

\[ I_{||}^m = I_{||}^t T_{||} + I_{\perp}^t T_{\perp} \] \hspace{1cm} (3.5.6a)

When the polarizer is rotated by 90°, the measured signal is:

\[ I_{\perp}^m = I_{||}^t T_{\perp} + I_{\perp}^t T_{||} \] \hspace{1cm} (3.5.6b)

Using equations 3.5.5 in 3.5.6 results in:

\[ I_{||}^m = I_{||} R_{||} T_{||} + I_{\perp} R_{\perp} T_{\perp} \] \hspace{1cm} (3.5.7a)
\[ I_{\perp}^m = I_{||} R_{\perp} T_{\perp} + I_{\perp} R_{||} T_{||} \] \hspace{1cm} (3.5.7b)

Thus equations 3.5.7a and 3.5.7b are two equations in two unknowns, \( I_{||} \) and \( I_{\perp} \). Solving for these using Cramer's rule:

\[ I_{||} = \frac{I_{||}^m - I_{\perp}^m}{R_{||} (T_{||}^2 - T_{\perp}^2)} \] \hspace{1cm} (3.5.8a)
\[ I_{\perp} = \frac{I_{\perp}^m - I_{||}^m}{R_{\perp} (T_{\perp}^2 - T_{||}^2)} \] \hspace{1cm} (3.5.8b)

Now the individual components of the grating reflectance and the polarizer transmittance are not known, but the ratios \( R_{||}/R_{\perp} \) and \( T_{||}/T_{\perp} \) can be determined from equations 3.5.1 and 3.5.2. Using equations 3.5.8, the ratios \( R_{||}/R_{\perp} \), \( T_{||}/T_{\perp} \), and \( I_{||}^m/I_{\perp}^m \) (from eq 3.5.3) in equation 3.5.4, the true polarization
\[ P = \frac{P_m - \alpha P_I}{\alpha - P_m P_I}. \]  

(3.5.9)

When calculating the measured polarization \( P_m \), the contribution due to background noise was first subtracted from \( I_{\parallel}^m \) and \( I_{\perp}^m \). Background noise was measured by allowing the experiment to collect data with the electron beam turned off. Thus the measured intensities due to purely radiation from the interaction region are given by:

\[ I_{\parallel}^m = I_{\parallel}^{m'} - I^b \]

where \( I_{\parallel}^{m'} \) is the total signal plus background and \( I^b \) is the background contribution.

To calculate the error in the measured polarization, consider the following:

\[ \sigma^2(P_m) = \left( \frac{\partial P_m}{\partial I_{\parallel}^m} \right)^2 \sigma^2(I_{\parallel}^m) + \left( \frac{\partial P_m}{\partial I_{\perp}^m} \right)^2 \sigma^2(I_{\perp}^m) \]

Now \( \sigma^2(I^m) = I_{\parallel}^{m'} + I^b \). Using these equations in equation 3.5.3 it is found that the error in the measured polarization is:

\[ \sigma^2(P_m) = \frac{4[I_{\parallel}^m(I_{\parallel}^{m'}+2I^b) + I_{\perp}^m(I_{\perp}^{m'}+2I^b)]}{(I_{\parallel}^m + I_{\perp}^m)^4} \]  

(3.5.10)

A similar consideration of the error in the corrected polarization gives the result:

\[ \sigma(P) = \frac{\alpha(1-P_m^2)}{(\alpha - P_m P_I)^2} \sigma(P_m) \]  

(3.5.11)

Note that this error depends only on the error in \( P_m \). The errors in \( \alpha \) and \( P_I \) were treated as systematic errors, and thus were not included in the final calculation. Variations in these quantities only shifted the entire curve up or down slightly.
CALCULATION OF APPARENT EXCITATION FUNCTIONS

The apparent excitation cross-section $Q$, is proportional to the quantity $I_{\parallel} + 2I_{\perp}$. This corresponds to three dipoles oscillating along mutually perpendicular axes, 2 perpendicular to the electron beam direction and 1 parallel to it.

The apparent excitation cross-sections were obtained in two ways. In the case of the integrated vibrational bands, $I_{\parallel}$ and $I_{\perp}$ were obtained directly from the polarization measurements, and an expression relating $Q$ to the measured intensities was derived. When the rotational structure was resolved, however, the polarizer was removed from the detector chamber. This was done to obtain greater intensity. Since $I_{\parallel}^m$ and $I_{\perp}^m$ were no longer separately available, it was the sum of these intensities that was measured. In this case a different expression was derived relating $Q$ to the total intensity and the polarization of the radiation.

(a) - Integrated Band Calculation

The cross-section $Q$ is given by:

$$Q \sim I_{\parallel} + 2I_{\perp} \quad (3.5.12)$$

Using equations 3.5.8a and 3.5.8b in the above expression, it is found that:

$$Q \sim \frac{(T_{\parallel}R_{\perp} - 2T_{\perp}R_{\parallel})I_{\parallel}^m - (T_{\parallel}R_{\perp} - 2T_{\perp}R_{\parallel})I_{\perp}^m}{R_{\parallel}R_{\perp}(T_{\parallel}^2 - T_{\perp}^2)} \quad (3.5.13)$$

Since $Q$ is proportional to this, equation 3.5.13 can be rewritten as:

- 83 -
\[ Q \sim I_{\|}^m + \left( \frac{2T_{\|} \left[ R_{\|} / R_{\perp} \right] - T_{\perp}}{T_{\|} - 2T_{\perp} \left[ R_{\|} / R_{\perp} \right]} \right) I_{\perp}^m \]  

(3.5.14)

Multiplying the numerator and denominator of the coefficient of \( I_{\perp}^m \) by \( 1/T_{\perp} \) and after some algebra, it is found that:

\[ Q \sim I_{\|}^m + \left[ \left( \frac{1-P_{\perp}}{1+P_{\perp}} \right) - 2 \left( \frac{1-\alpha}{1+\alpha} \right) \right]^{-1} + \left[ \left( \frac{1+P_{\perp}}{1-P_{\perp}} \right) - 2 \left( \frac{1+\alpha}{1-\alpha} \right) \right]^{-1} I_{\perp}^m \]  

(3.5.15)

Since

\[ \sigma^2(Q) \sim \left( \frac{\partial Q}{\partial I_{\|}^m} \right)^2 \sigma^2(I_{\|}^m) + \left( \frac{\partial Q}{\partial I_{\perp}^m} \right)^2 \sigma^2(I_{\perp}^m) \]

the error in the cross-section is:

\[ \sigma^2(Q) \sim (I_{\|}^m + I_{\perp}^b) + C^2(I_{\perp}^m + I_{\perp}^b) \]  

(3.5.16)

where \( C \) is the coefficient of \( I_{\perp}^m \) given in equation 3.5.15.

The cross-sections were calculated for different electron energies. The values were normalized to the total electron beam current, total counting time, and gas pressure. Current and gas pressure were assumed to remain constant over the duration of a run. The fact that small variations in these parameters sometimes occurred meant that additional systematic errors had to be included.

(b) - Resolved Rotational Structure Calculation

With the polarizer no longer in place the measured signal was given by:

\[ S = I_{\|} R_{\|} + I_{\perp} R_{\perp} \]  

(3.5.17)

Since the instrumental polarization and the true polarization of the radiation were known from previous measurements, it was possible to obtain the values of the true signal intensities. Using equations 3.5.2, 3.5.4, and 3.5.8 along with
3.5.17 it was found that the true intensities were:

\[ I_{II} = \frac{(1 + P)(1 - P_I)}{(1 + PP_I)} S \]

\[ I_I = \frac{(1 - P)(1 - P_I)}{(1 + PP_I)} S \]

From these equations the cross-section is:

\[ Q \sim \left( \frac{2 - P}{1 + PP_I} \right) S \quad -(3.5.18) \]

The error in \( Q \) is given by:

\[ \sigma(Q) \sim \frac{1}{1 + PP_I} \left( \left( \frac{3P_I + 1}{1 + PP_I} S \right)^2 \sigma^2(P) + (3 - P)^2 S \right)^{1/2} \quad -(3.5.19) \]

Again, the value of \( Q \) was normalized to the total counting time, the total electron beam current, and the gas pressure. Also, systematic errors due to variations in current and pressure were not included.
CHAPTER IV

EXPERIMENTAL RESULTS
4.1 - INTRODUCTION AND IDENTIFICATION OF SPECTRA

The data presented in this chapter shows the polarization and relative excitation cross-sections as a function of incident electron energy for selected transitions in H₂. Measurements have been carried out for the integrated vibrational bands (no resolved rotational structure) and for resolved rotational structure in both Lyman and Werner band transitions. Polarization measurements carried out near the excitation threshold have been compared to the various theoretical predictions considered in Chapter II. Excitation cross-sections have been compared to the results of other workers whenever such data was available.

FIG 4-1 shows the energy level diagrams and the observed vibrational transitions \( B^1 \Sigma_u^+(v'=6) - X^1 \Sigma_g^+(v''=1) \) (Lyman band) and \( C^1 \Pi_u(v'=0) - X^1 \Sigma_g^+(v''=1) \) and \( C^1 \Pi_u(v'=0) - X^1 \Sigma_g^+(v''=2) \) (Werner bands). FIG 4-2 shows the energy level diagrams and the rotational structure observed for the transitions \( B^1 \Sigma_u^+(v'=6) - X^1 \Sigma_g^+(v''=1) \) R(0)+R(1) branches, and the \( C^1 \Pi_u(v''=2) - X^1 \Sigma_g^+(v''=5) \) Q(1)+Q(2), P(3), and R(0)+R(1)+R(2) branches. The energy levels were determined from the equation:

\[
\nu = \nu_e' + \left[ \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 + \omega_e y_e (v + 1/2)^3 \right] \\
+ \left[ (B_e - \alpha_e (v + 1/2))N(N + 1) - D_e N^2(N + 1)^2 \right] \text{ cm}^{-1}
\]

(Hezberg (1950) p 149). \( N \) is the rotational quantum number and \( v \) is the vibrational quantum number. The constants for the three states of H₂ studied are given below.
<table>
<thead>
<tr>
<th>CONSTANT</th>
<th>$x^1\Sigma_g^+$</th>
<th>$b^1\Sigma_u^+$</th>
<th>$c^1\Pi_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_e$</td>
<td>0</td>
<td>91689.9</td>
<td>100043.0</td>
</tr>
<tr>
<td>$\omega_e$</td>
<td>4395.2</td>
<td>1356.90</td>
<td>2442.72</td>
</tr>
<tr>
<td>$\omega_e x_e$</td>
<td>117.90</td>
<td>19.932</td>
<td>67.03</td>
</tr>
<tr>
<td>$\omega_e y_e$</td>
<td>0.29</td>
<td>0.4029</td>
<td>1</td>
</tr>
<tr>
<td>$B_e$</td>
<td>69.80</td>
<td>20.0159</td>
<td>31.340</td>
</tr>
<tr>
<td>$\alpha_e$</td>
<td>2.993</td>
<td>1.1933</td>
<td>1.626</td>
</tr>
<tr>
<td>$D_e$</td>
<td>$4.65 \times 10^{-2}$</td>
<td>$1.74 \times 10^{-2}$</td>
<td>$2.06 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

All the above constants are in units of cm$^{-1}$.

FIG's 4-3 through 4-6 show the observed spectra of the above transitions. FIG's 4-3 and 4-4 refer to the (0,2) and (0,1) integrated Werner bands, respectively. The identification of the features was done using the work of Jeppessen (1933). FIG 4-5 shows the rotational structure of the Werner (2,5) band. The features were identified using the work of Stone and Zipf (1972). FIG 4-6 shows the rotational structure of the Lyman (6,1) band. The initial identification was done with Jeppessen, and was later refined using the above equation and the given constants. The vertical lines in the figures indicate the calculated positions of the transitions.

Note that in the cases of the Werner (2,5) band and the Lyman (6,1) band it was not always possible to completely resolve the rotational structure. Thus, measurements were made on several $P$, $Q$, or $R$ lines.
FIG 4-1
ENERGY LEVEL DIAGRAM
FOR THE INTEGRATED BANDS
FIG 4-2
ROTATIONAL ENERGY LEVELS

Lyman
(6,1) R(0) + R(1)

Werner
(2,5) P(3), Q(1)+Q(2), R(0)+R(1)
(6,0) Lyman P(7)?

(0,1) Werner Q(1) + R(3)

(0,1) Werner Q(3)
(0,1) Werner P(3)

Instrumental Resolution = 0.1 nm FWHM

FIG 4-4
4.2 - WERNER BAND EXCITATION

(a) - INTEGRATED BANDS

Polarization measurements were carried out on the Werner (0,1) and (0,2) vibrational bands at 105.4 nm and 110.0 nm, respectively. Because of intensity limitations no rotational structure was resolved. The instrumental resolution used was 0.35 nm for the (0,2) band and 1.0 nm for the (0,1) band. It was estimated that the Q(1), Q(3), R(3), and P(3) lines contributed to the observed signal for the (0,1) band, and only the Q(1), Q(2), R(0), and R(3) lines contributed to the (0,2) band.

Table 4-1 presents the polarization data for the (0,1) and (0,2) bands, and these are plotted in FIG's 4-7 and 4-8, respectively. As can be seen, the basic shape of the polarization curve is the same in both cases, with only small differences in magnitude. The (0,1) band shows a pronounced maximum of about 0.23 at 20 eV, while the maximum is not so well defined in the (0,2) band, with a value of 0.24 at about 22.5 eV. At 50 eV, both polarizations have fallen off to about 0.15, and by 300 eV, the polarization is small and positive in both cases.

The threshold polarization values suggested by the data is about 0.15 or less. However, the rapid decrease in the polarization near threshold may be due to resonance effects or a correlation between the excited and scattered electrons (see Chapter V for a full discussion of this). Based on the dominance of the Q(1), Q(2), and R(3) lines in the (0,1) band, the
<table>
<thead>
<tr>
<th>ENERGY (eV)</th>
<th>(0,2) BAND</th>
<th>% POLARIZATION</th>
<th>(0,1) BAND</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.0</td>
<td>-</td>
<td>17.0 ± 5.0</td>
<td></td>
</tr>
<tr>
<td>15.0</td>
<td>-</td>
<td>14.9 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>17.5</td>
<td>-</td>
<td>19.5 ± 1.0</td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>23.5 ± 1.0</td>
<td>23.0 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>22.5</td>
<td>24.1 ± 1.0</td>
<td>22.0 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>24.1 ± 0.7</td>
<td>18.9 ± 0.7</td>
<td>17.7 ± 0.8</td>
</tr>
<tr>
<td>30.0</td>
<td>20.9 ± 0.6</td>
<td>14.7 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>19.8 ± 0.6</td>
<td>14.0 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>50.0</td>
<td>14.2 ± 0.8</td>
<td>11.1 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>75.0</td>
<td>11.4 ± 1.0</td>
<td>9.7 ± 0.7</td>
<td></td>
</tr>
<tr>
<td>100.0</td>
<td>10.8 ± 1.0</td>
<td>6.8 ± 1.0</td>
<td></td>
</tr>
<tr>
<td>125.0</td>
<td>10.2 ± 1.1</td>
<td>6.7 ± 1.0</td>
<td></td>
</tr>
<tr>
<td>130.0</td>
<td>6.8 ± 1.0</td>
<td>5.9 ± 1.4</td>
<td></td>
</tr>
<tr>
<td>145.0</td>
<td>6.7 ± 1.0</td>
<td>7.7 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>147.5</td>
<td>5.9 ± 1.4</td>
<td>5.3 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>150.0</td>
<td>7.7 ± 1.1</td>
<td>6.2 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>175.0</td>
<td>5.3 ± 1.1</td>
<td>4.6 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>200.0</td>
<td>6.2 ± 1.1</td>
<td>2.8 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>225.0</td>
<td>4.6 ± 1.1</td>
<td>3.6 ± 1.0</td>
<td></td>
</tr>
<tr>
<td>250.0</td>
<td>2.8 ± 1.1</td>
<td>2.1 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>275.0</td>
<td>3.6 ± 1.0</td>
<td>4.0 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>300.0</td>
<td>2.1 ± 1.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIG 4-7
WERNER (0,1) INTEGRATED BAND POLARIZATION

% POLARIZATION

INCIDENT ELECTRON ENERGY (eV)
FIG 4-8
WERNER (0,2) INTEGRATED BAND POLARIZATION

% POLARIZATION

INCIDENT ELECTRON ENERGY (eV)
simplified theory of Malcolm et al gives a threshold polarization value of 0.3. The theory of Jette and Cahill gives -0.82; that of Baltayan and Nedelec, 0.34; that of Blum, 0.24; and the theory of Feofilov, 0.355.

Table 4-2 gives the relative excitation cross-section for the Werner (0,2) band, and this is plotted as a function of incident electron energy in FIG 4-9. The present results are compared with the work of Gerhart(1975), who used the work of de Heer and Carrère(1971), and Stone and Zipf(1972). Gerhart combined the data of these workers and arrived at a 'best estimate' of the excitation cross-section of the C1\textsuperscript{1}\Pi_u state. The data of the present work has been normalized to the data of Gerhart at 50 eV. Note the good agreement in shape between the two curves, particularly above 50 eV.

(b) RESOLVED ROTATIONAL STRUCTURE

To study the polarization of individual rotational lines, the Werner (2,5) band at 117.6 nm was used. An instrumental resolution of 0.1 nm was used in this work. At this resolution it was possible to resolve the P(3), Q(1)+Q(2), and R(0)+R(1)+R(2) rotational transitions.

Table 4-3 shows the polarization data for the Q(1)+Q(2), P(3), and R(0)+R(1)+R(2) lines, and FIG's 4-10, 4-11, and 4-12 plot these data as a function of incident electron energy, respectively. Again, the basic shape of the polarization curve is the same as in the integrated case, but with differences in magnitude. Notice that the P(3) curve is smaller than both the Q and the R curves. The appearance of structure in these
<table>
<thead>
<tr>
<th>ENERGY (eV)</th>
<th>CROSS-SECTION (ARB. UNITS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5</td>
<td>0</td>
</tr>
<tr>
<td>15.0</td>
<td>0.34 ± 0.08</td>
</tr>
<tr>
<td>17.5</td>
<td>0.64 ± 0.07</td>
</tr>
<tr>
<td>22.5</td>
<td>0.99 ± 0.01</td>
</tr>
<tr>
<td>25.0</td>
<td>1.62 ± 0.01</td>
</tr>
<tr>
<td>30.0</td>
<td>3.10 ± 0.02</td>
</tr>
<tr>
<td>40.0</td>
<td>3.18 ± 0.02</td>
</tr>
<tr>
<td>50.0</td>
<td>3.18 ± 0.07</td>
</tr>
<tr>
<td>75.0</td>
<td>2.95 ± 0.03</td>
</tr>
<tr>
<td>100.0</td>
<td>2.67 ± 0.03</td>
</tr>
<tr>
<td>125.0</td>
<td>2.46 ± 0.02</td>
</tr>
<tr>
<td>145.0</td>
<td>2.34 ± 0.02</td>
</tr>
<tr>
<td>147.5</td>
<td>2.26 ± 0.03</td>
</tr>
<tr>
<td>150.0</td>
<td>2.24 ± 0.02</td>
</tr>
<tr>
<td>175.0</td>
<td>2.13 ± 0.02</td>
</tr>
<tr>
<td>200.0</td>
<td>2.04 ± 0.02</td>
</tr>
<tr>
<td>225.0</td>
<td>1.87 ± 0.02</td>
</tr>
<tr>
<td>250.0</td>
<td>1.90 ± 0.02</td>
</tr>
<tr>
<td>300.0</td>
<td>1.66 ± 0.02</td>
</tr>
</tbody>
</table>
**TABLE 4-3: POLARIZATION vs INCIDENT ELECTRON ENERGY for the WERNER (2, 5) P, Q, R BRANCHES**

<table>
<thead>
<tr>
<th>ENERGY (eV)</th>
<th>P(3)</th>
<th>q(1)+q(2)</th>
<th>R(0)+R(1)+R(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>12.9 ± 2.4</td>
<td>23.4 ± 3.5</td>
<td>25.9 ± 3.0</td>
</tr>
<tr>
<td>22.5</td>
<td>-</td>
<td>25.0 ± 3.1</td>
<td>27.0 ± 2.8</td>
</tr>
<tr>
<td>25.0</td>
<td>11.1 ± 2.4</td>
<td>25.9 ± 1.9</td>
<td>27.1 ± 1.8</td>
</tr>
<tr>
<td>30.0</td>
<td>11.7 ± 1.3</td>
<td>21.8 ± 1.5</td>
<td>26.1 ± 1.2</td>
</tr>
<tr>
<td>35.0</td>
<td>-</td>
<td>-</td>
<td>23.6 ± 1.1</td>
</tr>
<tr>
<td>40.0</td>
<td>11.5 ± 1.2</td>
<td>17.6 ± 1.3</td>
<td>23.4 ± 1.2</td>
</tr>
<tr>
<td>50.0</td>
<td>9.9 ± 1.6</td>
<td>16.4 ± 1.5</td>
<td>21.7 ± 1.7</td>
</tr>
<tr>
<td>60.0</td>
<td>-</td>
<td>14.6 ± 1.4</td>
<td>-</td>
</tr>
<tr>
<td>75.0</td>
<td>7.1 ± 1.4</td>
<td>-</td>
<td>15.0 ± 1.8</td>
</tr>
<tr>
<td>100.0</td>
<td>7.0 ± 1.4</td>
<td>10.4 ± 1.3</td>
<td>11.4 ± 1.4</td>
</tr>
<tr>
<td>150.0</td>
<td>3.8 ± 1.4</td>
<td>8.6 ± 1.7</td>
<td>4.2 ± 1.4</td>
</tr>
<tr>
<td>200.0</td>
<td>1.3 ± 1.1</td>
<td>4.5 ± 1.6</td>
<td>5.5 ± 1.3</td>
</tr>
<tr>
<td>250.0</td>
<td>1.3 ± 1.5</td>
<td>6.0 ± 1.6</td>
<td>7.2 ± 1.8</td>
</tr>
<tr>
<td>300.0</td>
<td>3.1 ± 2.0</td>
<td>2.0 ± 1.4</td>
<td>-0.6 ± 1.0</td>
</tr>
</tbody>
</table>
FIG 4-10
WERNER (2,5) Q(1)+Q(2)
Polarization

% POLARIZATION

INCIDENT ELECTRON ENERGY (eV)
FIG 4-11
WERNER (2,5) P(3)
POLARIZATION

% POLARIZATION

INCIDENT ELECTRON ENERGY (eV)
FIG 4-12
WERNER (2,5) R(0)+R(1)+R(2)
POLARIZATION

% POLARIZATION

INCIDENT ELECTRON ENERGY (eV)
data at energies above 200 eV may be due to the presence and effects of low energy secondary electrons in the electron gun, although the design of the gun was such that secondary electron effects were minimized.

By extrapolating the curves back to the excitation threshold (indicated by the vertical lines on the graphs), and assuming that the decrease in polarization is actually due to other depolarizing effects, it was possible to obtain estimates of the threshold polarization. These values, along with the predictions of the various theories, are shown below.

<table>
<thead>
<tr>
<th>ROTATIONAL LINE</th>
<th>ESTIMATE FROM DATA</th>
<th>JETTE AND CAHILL</th>
<th>BALTAYAN &amp; NEDRELEC (k=1)</th>
<th>BLUM ET AL</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(3)</td>
<td>0.13</td>
<td>0.20</td>
<td>0.13</td>
<td>0.0</td>
</tr>
<tr>
<td>Q(1)+Q(2)</td>
<td>0.35</td>
<td>-1.00</td>
<td>0.37</td>
<td>0.26</td>
</tr>
<tr>
<td>R(0)+R(1)+R(2)</td>
<td>0.35</td>
<td>0.65</td>
<td>0.45</td>
<td>-0.12</td>
</tr>
</tbody>
</table>

The results of Feofilov's theory for these rotational lines are: P(3) 0.14; Q(1)+Q(2) 0.36; and R(0)+R(1)+R(2) 0.47. From this comparison, it can be seen that the predictions of Jette and Cahill are much farther out than any of the other theoretical predictions. More will be said about this in Chapter V.

Table 4-4 presents the relative excitation cross-sections for the P, Q, and R branches. FIG 4-13 plots these cross-sections as a function of incident electron energy. These results were normalized with respect to total counting time, total electron beam current, and gas pressure. Also, since the polarizer was removed when these measurements were performed, the time taken to acquire all the data was only a few days. Thus
<table>
<thead>
<tr>
<th>ENERGY (eV)</th>
<th>P(3)</th>
<th>Q(1)+Q(2)</th>
<th>R(0)+R(1)+R(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>18.1 ± 0.6</td>
<td>36.3 ± 0.8</td>
<td>14.7 ± 0.3</td>
</tr>
<tr>
<td>22.5</td>
<td>-</td>
<td>-</td>
<td>18.0 ± 0.4</td>
</tr>
<tr>
<td>25.0</td>
<td>28.0 ± 0.9</td>
<td>39.1 ± 0.5</td>
<td>21.6 ± 0.3</td>
</tr>
<tr>
<td>30.0</td>
<td>35.2 ± 0.7</td>
<td>47.3 ± 0.5</td>
<td>24.8 ± 0.2</td>
</tr>
<tr>
<td>35.0</td>
<td>-</td>
<td>-</td>
<td>28.5 ± 0.4</td>
</tr>
<tr>
<td>40.0</td>
<td>36.3 ± 0.6</td>
<td>54.1 ± 0.6</td>
<td>31.0 ± 0.3</td>
</tr>
<tr>
<td>50.0</td>
<td>39.0 ± 0.8</td>
<td>58.0 ± 0.7</td>
<td>31.3 ± 0.4</td>
</tr>
<tr>
<td>60.0</td>
<td>-</td>
<td>58.5 ± 0.7</td>
<td>-</td>
</tr>
<tr>
<td>75.0</td>
<td>32.4 ± 0.7</td>
<td>-</td>
<td>28.6 ± 0.4</td>
</tr>
<tr>
<td>100.0</td>
<td>32.8 ± 0.6</td>
<td>53.8 ± 0.6</td>
<td>24.7 ± 0.3</td>
</tr>
<tr>
<td>150.0</td>
<td>27.6 ± 0.6</td>
<td>48.4 ± 0.7</td>
<td>19.5 ± 0.2</td>
</tr>
<tr>
<td>200.0</td>
<td>25.4 ± 0.5</td>
<td>42.3 ± 0.6</td>
<td>17.6 ± 0.2</td>
</tr>
<tr>
<td>250.0</td>
<td>20.5 ± 0.5</td>
<td>38.1 ± 0.5</td>
<td>16.2 ± 0.2</td>
</tr>
<tr>
<td>300.0</td>
<td>17.8 ± 0.5</td>
<td>34.5 ± 0.4</td>
<td>14.0 ± 0.1</td>
</tr>
</tbody>
</table>
FIG 4-13
APPARENT EXCITATION CROSS-SECTION
FOR THE WERNER (2,5) P, Q, & R BRANCHES

○ - Q(1)+Q(2)
● - P(3)
▲ - R(0)+R(1)+R(2)

EXCITATION CROSS-SECTION (ARB. UNITS)

INCIDENT ELECTRON ENERGY (eV)
it is expected that the efficiency of the channeltron remained constant during this time, and it is possible to compare the relative cross-sections of the P, Q, and R branches with each other. Note that the Q branches are the strongest, then the P branch, and finally the R branches. This is to be expected from the Hönl-London formulae (Herzberg 1950, p 208).

The maximum values of the three branches appear to be at 50 eV, although there also seems to be a shift in the position of the maximum going from the R branch to the Q branch. Also, at first glance, the shape of the curve appears to be the same in each case, but upon closer inspection this is not so. The peak-to-high energy ratio is about the same for the P and R branches, but different for the Q. It is possible that this is related to the change in rotational quantum number, which is 0 for the Q branch, +1 for the P branch, and −1 for the R branch.
4.3 - LYMAN BAND EXCITATION

(a) - INTEGRATED BANDS

The only Lyman band of sufficient intensity which could be isolated from the dominant Werner emission in the wavelength range available was the Lyman (6,1) band at 107.0 nm. There is the presence of the Lyman (3,0) R(4) branch at 107.1 nm, but it is unlikely that it made any significant contribution to the observed intensity. This is based on the known ground state rotational population distribution, the dipole selection rule $\Delta N = \pm 1$ for the upward transition, and on the known oscillator strengths (Allison and Dalgarno 1970).

Table 4-5 presents the polarization of the (6,1) band, and FIG 4-14 plots this data as a function of incident electron energy. The instrumental resolution used was 0.35 nm. From this it is expected that the R(0), R(1), R(2) and P(1) lines all contributed to the measured intensity.

It can be seen from FIG 4-14 that the data suggests a threshold value of about 0.2. The simplified theory of Malcolm et al predicts a threshold value of 0.5; Baltayan and Nedelec predict 0.42; Blum predicts 0.4. The rather low threshold polarization indicated by the data is not at all unreasonable when compared with the theoretical predictions in the light of the depolarizing effects that can occur.

One other feature that is evident from FIG 4-14 is the apparent secondary structure near 175 eV. This could be due to the effects of low energy secondary electrons, as mentioned in the discussion of the Werner transitions.
<table>
<thead>
<tr>
<th>ENERGY (eV)</th>
<th>% POLARIZATION</th>
<th>CROSS-SECTION (x10^{-21} m^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5</td>
<td>-</td>
<td>0.35 ± 0.17</td>
</tr>
<tr>
<td>15.0</td>
<td>-</td>
<td>0.83 ± 0.48</td>
</tr>
<tr>
<td>20.0</td>
<td>17.4 ± 2.0</td>
<td>1.88 ± 0.04</td>
</tr>
<tr>
<td>25.0</td>
<td>17.0 ± 1.1</td>
<td>-</td>
</tr>
<tr>
<td>50.0</td>
<td>13.7 ± 1.5</td>
<td>4.50 ± 0.04</td>
</tr>
<tr>
<td>75.0</td>
<td>9.4 ± 2.0</td>
<td>4.50 ± 0.04</td>
</tr>
<tr>
<td>100.0</td>
<td>8.5 ± 2.0</td>
<td>-</td>
</tr>
<tr>
<td>150.0</td>
<td>7.1 ± 1.2</td>
<td>3.62 ± 0.04</td>
</tr>
<tr>
<td>200.0</td>
<td>7.0 ± 2.0</td>
<td>-</td>
</tr>
<tr>
<td>250.0</td>
<td>3.3 ± 1.3</td>
<td>2.62 ± 0.04</td>
</tr>
</tbody>
</table>

**NOTE** - The cross-section data has been normalized to that of Gerhart (1975).
FIG 4.15
LYMAN (6,1) INTEGRATED BAND
EXCITATION CROSS-SECTION

- Present Work
- Chung & Lin (1978)
- Gerhart (1975)
- Srivastava & Jensen (1977)

EXCITATION CROSS-SECTION (10^-21 m^2)

INCIDENT ELECTRON ENERGY (eV)
Table 4-5 also presents the relative excitation cross-section for the \((6,1)\) band. This data is plotted in FIG 4-15, along with the work of Gerhart(1975), the calculations of Chung and Lin(1978), and the measurements of Srivastava and Jensen (1977). The data of the present work has been normalized to that of Gerhart at 250 eV. The only previous measurements of the cross-section were made by Srivastava and Jensen in 1977. They measured the differential inelastic scattering, cross-sections, and deduced the integral cross-sections from this. Their data lies about a factor of two lower than our data, although a direct comparison between our data and the electron scattering work at low energy is not strictly justified, since no allowance for cascade has been made in the present work.

The calculations of Chung and Lin(1978) are in good agreement with our data. However, if the data is normalized to the calculations at high energy rather than to Gerhart's, significantly poorer agreement with Chung and Lin's data occurs in the region near the maximum of the curve.

(b) **RESOLVED ROTATIONAL STRUCTURE**

The only rotational lines of significant intensity that could be resolved were the \(R(0)+R(1)\) branches of the Lyman \((6,1)\) band. An instrumental resolution of 0.1 nm was used. Table 4-6 presents the polarization vs incident electron energy for these transitions, and FIG 4-16 plots this data. The shape of the curve is the same as in the integrated case. It can be seen from FIG 4-16 that the threshold polarization is about 0.2, as it was in the integrated case. The prediction of Mal-
colm et al is 0.71; Baltayan and Nedelec predict 0.47; Blum predicts a value of 0.48; and Feofilov predicts 0.5. Again, the rather low value suggested by the data may be due to the depolarizing effects mentioned earlier.
<table>
<thead>
<tr>
<th>ENERGY (eV)</th>
<th>% POLARIZATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.5</td>
<td>17.5 ± 1.0</td>
</tr>
<tr>
<td>25.0</td>
<td>15.3 ± 0.9</td>
</tr>
<tr>
<td>30.0</td>
<td>15.1 ± 0.9</td>
</tr>
<tr>
<td>40.0</td>
<td>13.0 ± 0.9</td>
</tr>
<tr>
<td>50.0</td>
<td>11.8 ± 0.9</td>
</tr>
<tr>
<td>75.0</td>
<td>8.1 ± 0.6</td>
</tr>
<tr>
<td>100.0</td>
<td>6.2 ± 0.9</td>
</tr>
<tr>
<td>150.0</td>
<td>5.6 ± 1.1</td>
</tr>
<tr>
<td>200.0</td>
<td>4.6 ± 0.9</td>
</tr>
<tr>
<td>250.0</td>
<td>1.9 ± 0.9</td>
</tr>
<tr>
<td>300.0</td>
<td>2.5 ± 1.1</td>
</tr>
</tbody>
</table>
FIG 4-16
LYMAN (6,1) R(0)+R(1)
POLARIZATION

% POLARIZATION

100  200  300
INCIDENT ELECTRON ENERGY (eV)
4.4 - LYMAN-\( \alpha \) ATOMIC FLUORESCENCE

Table 4-7 presents the polarization vs incident electron energy for Lyman-\( \alpha \) radiation at 121.6 nm. The instrumental resolution was 0.35 nm. FIG 4-17 displays this data, along with the results of Ott et al (1970), who used an O\(_2\) filter and a LiF polarization analyzer to measure the polarization of Lyman-\( \alpha \). Also shown are the results of Karolis and Harting (1978) for the polarization of Balmer-\( \alpha \) radiation from H\(_2\) dissociation.

It can be seen that there is good agreement between our results and those of Ott et al. Both sets of results show the same features: a dip near 17 eV rising to a higher value at lower energies; a gradual rise above threshold to a maximum of 0.08 near 30 eV; and a gradual fall-off towards high energy. The signal obtained below threshold in the present work is attributed to Werner emissions. It is in this region that our data seriously departs from that of Ott et al. Their data indicates a peak of 0.12 at 1 eV below the threshold energy, whereas our data indicates 0.24. This difference is to be expected since the resulting polarization is sensitive to the rotational lines contributing to the signal. The choice of an O\(_2\) filter or a monochromator for wavelength selection will result in large differences in the relative contributions of different rotational lines.

It is possible to use the results of van Brunt and Zare discussed in Chapter II to get an approximate value for the threshold polarization for Lyman-\( \alpha \). Consideration of the the
<table>
<thead>
<tr>
<th>ENERGY (eV)</th>
<th>% POLARIZATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5</td>
<td>24.7 ± 2.5</td>
</tr>
<tr>
<td>15.0</td>
<td>8.9 ± 1.9</td>
</tr>
<tr>
<td>16.0</td>
<td>4.6 ± 0.7</td>
</tr>
<tr>
<td>20.0</td>
<td>7.1 ± 0.6</td>
</tr>
<tr>
<td>22.5</td>
<td>7.6 ± 0.8</td>
</tr>
<tr>
<td>37.5</td>
<td>6.7 ± 0.8</td>
</tr>
<tr>
<td>47.5</td>
<td>7.6 ± 0.8</td>
</tr>
<tr>
<td>57.5</td>
<td>7.1 ± 0.8</td>
</tr>
<tr>
<td>80.0</td>
<td>5.9 ± 0.6</td>
</tr>
<tr>
<td>100.0</td>
<td>5.4 ± 0.6</td>
</tr>
<tr>
<td>110.0</td>
<td>5.8 ± 0.5</td>
</tr>
<tr>
<td>120.0</td>
<td>5.8 ± 0.5</td>
</tr>
<tr>
<td>130.0</td>
<td>4.8 ± 0.7</td>
</tr>
<tr>
<td>150.0</td>
<td>3.1 ± 0.4</td>
</tr>
<tr>
<td>175.0</td>
<td>4.5 ± 0.7</td>
</tr>
<tr>
<td>200.0</td>
<td>4.2 ± 0.6</td>
</tr>
<tr>
<td>250.0</td>
<td>1.8 ± 0.4</td>
</tr>
<tr>
<td>260.0</td>
<td>1.3 ± 0.7</td>
</tr>
<tr>
<td>297.5</td>
<td>-1.2 ± 0.9</td>
</tr>
</tbody>
</table>
FIG 4-17
LYMAN-α POLARIZATION
• - Present Work
○ - Ott et al (1970)
- - Karolis and Harting (1978)
    Balmer-α

% POLARIZATION

INCIDENT ELECTRON ENERGY (eV)
position of the Franck-Condon region and use of the correlation diagram given by Sharp (1971) shows that of the states giving rise to a separated atom in the 2p state, only the \( \Sigma^+_g \), \( \Pi^+_u \), \( \Sigma^+_g \), and \( \Pi^+_u \) states are excited near threshold. It is also possible that predissociation processes may contribute, and in the case of photodissociation this occurs via the \( \Pi^+_u \) state (Mentall and Guyan 1977). Other predissociation modes may be present in the case of electron impact excitation but it is probable that this optically-allowed process is dominant.

Using the symmetry rules of Dunn (1962), electron impact excitation of a \( \Sigma^+_g \) state from a \( \Sigma^+_g \) state occurs with a non-zero probability for both parallel and perpendicular alignment of the internuclear axis with respect to the momentum transfer vector (which is parallel to the incident electron direction \( \hat{z} \) at threshold). Thus, for excitation of the \( \Sigma^+_g \) states, an isotropic distribution of internuclear axes (\( \varphi = 0 \)) is assumed. For the \( \Pi^+_u \) states, Dunn's symmetry rules give a non-zero transition probability for the internuclear axis perpendicular to the \( \hat{z} \) direction. In this case a \( \sin^2 (\varphi = 1) \) distribution of internuclear axes is assumed.

The possible values of \( M_L \) selected by the excitation can be determined by assuming Hund's case (a) coupling for which the sum of the \( M_L \) for the separated atoms is a good quantum number and is equal to \( \Lambda \). At the threshold for Lyman-\( \alpha \) one of the separated atoms is always in the ground state, and \( M_L = 0 \) for this atom. Thus \( M_L = \Lambda \) for the excited atom. The contributions to the threshold polarization are given below.
<table>
<thead>
<tr>
<th>STATE</th>
<th>$Q$</th>
<th>$M_L$</th>
<th>THRESHOLD POLARIZATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^1\Sigma_g^+$</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>$h^3\Sigma_g^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D^1\Pi_u$, $C^1\Pi_u$</td>
<td>-1</td>
<td>$^1$</td>
<td>0.143</td>
</tr>
<tr>
<td>$c^3\Pi_u$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is expected that the threshold polarization should lie between 0 and 0.143, the exact value depending on the relative cross-sections of the $\Sigma_g^+$ and the $\Pi_u$ states. The $\Sigma_g^+$ states lie closer to the center of the Franck-Condon region, and so it is expected that excitation of these will dominate, and the threshold polarization should be close to zero. This is in fact what is observed both in the present results and those of Ott et al, where the data indicates a threshold polarization of 0.05 or less.

At higher energies $Q$ changes in value as the momentum transfer direction rotates with respect to the $\Sigma$ direction, and additional states of different symmetries begin to contribute to $H(2p)$ production.
CHAPTER V

DISCUSSIONS AND CONCLUSIONS
5.1 - EXPERIMENTAL RESULTS

The polarization curves for the Werner (0,1) and (0,2) vibrational bands, and the (2,5) P(3), Q(1)+Q(2), and R(0)+R(1)+R(2) rotational transitions, as well as the Lyman (6,1) vibrational band and the R(0)+R(1) rotational transitions have been measured. As seen from the results for the Werner bands, the polarization appears to be essentially independent of the vibrational transitions involved, and, from the measurements of the (2,5) rotational structure, depends only on the rotational states involved. This is expected because the vibrational motion does not contribute to the angular momentum of the system.

A comparison of the Lyman (6,1) R(0)+R(1) polarization curve with the Werner (2,5) R(0)+R(1)+R(2) polarization curve shows the difference between these transition types (Σ-Σ and Σ-Π, respectively), especially near the excitation threshold. The extrapolated threshold value for the Lyman transition is 0.2, whereas for the Werner transition, it is 0.35, a significant difference. This would support the theoretical considerations of the excitation process where the orientation of the molecular axis is different for Σ-Σ excitation than it is for Σ-Π excitation; i.e., that Dunn's symmetry rules as developed rigorously by Blum (see section 2.5) must be applied.

It is instructive to consider the extrapolation of the experimental results to the excitation threshold. When this was done, any depolarizing effects that could occur were not
properly taken into account. There are several possible sources of depolarization of the radiation:

(a) - Negative ion resonances, when the scattered electron and the molecule form an ion for a short time.

(b) - Recently, Heideman et al (1979) have shown that there is a possibility of correlation between the motion of the excited and the scattered electron in electron-atom scattering. This results in a 'dip' in the polarization curve near the ionization threshold. Such dips have been observed in several spectral lines of He (Heddle et al 1977) and in the Ar resonance lines (Dassen et al 1977). They point out that this could be due to negative ion resonances, cascade from higher levels, or collisional energy transfers. However, none of these effects totally account for the decrease in polarization near threshold. Fano (1974) has emphasized that the incident and atomic electron may become closely correlated in collisions near the ionization threshold. Ionization near threshold can only occur if the distances and velocities of the two escaping electrons with respect to the nucleus remain nearly equal up to large distances. If this radial correlation is disturbed within a critical radius, an exchange of energy occurs, and the slower electron is recaptured by the residual ion, and excitation has taken place instead of ionization. If the collision energy is slightly below the ionization threshold, the excitation of states with energies near the available energy is possible only if the electrons remain correlated in the same way as in near threshold ionization. Fano argued that the Coulomb repulsion
between the two electrons causes a stable angular correlation, and as a result, the two electrons may acquire significant orbital angular momenta (with opposite signs) even if their velocities are small. Thus excitation of states with $M_L \geq 1$ is possible, resulting in a decrease in the observed polarization.

The same effect occurs in molecular excitation near threshold as seen from a combination of FIG's 4-17 and 4-10, 4-11, and 4-12. The latter shows the fall-off from about 30 eV to lower energies while the former illustrates the very sharp rise again very close to threshold. Clearly there is a need for further polarization measurements very close to the threshold with a better energy resolution than was possible in this experiment.

(c) - Another effect which will reduce the polarization of the emitted radiation is the distribution of the orientation of the molecular axes with respect to the incident electron beam. In the interaction region all orientations of the molecules are equally likely. This introduces a $\sin^2 \theta$ or a $\cos^2 \theta$ factor into the transition probability for exciting the rotational sublevels which must be integrated over all possible angles. In the theoretical discussions this fact has not been taken into account, except by Blum, who considered the case where the transition probability was some function of $\theta$, in conjunction with Dunn's symmetry arguments. This must be kept in mind when comparing the theoretical predictions with the data.

One final point about using the data of Chapter IV to ex-
trapolate threshold polarization. Because of the very low signal intensities at or near the excitation threshold, measurements were extremely difficult to make. The statistics are very poor in all the data near the threshold, so the extrapolated values cannot be determined with any real certainty. It has been suggested by King et al (1972) that "pseudo-threshold" excitation could be used to examine the dynamics of 'real' threshold' excitation. With this method, the decay photons are observed in coincidence with the forward scattered electrons, which carry away no orbital angular momentum (with respect to the scattering center). This then satisfies equation 2.5.1, with $m_1=m_0=0$. This approach was used by Malcolm and McConkey (1979) to measure the 'threshold' polarization of the Werner system. Forward scattered electrons which had excited the $^1\Sigma^+$ ($v'=0$) state at an incident energy of 50 eV were detected in coincidence with the decay photons. The polarization state of the photons was selected by a 2-mirror reflectance polarizer (Tan et al 1977). No wavelength selection was made other than that which occurred because of the rapid fall-off in the detector sensitivity towards the longer wavelengths. For this reason a number of vibrational bands contribute to the observed signal, but this is not a major problem since no dependence of polarization on vibrational transition is expected. The pseudo-threshold polarization value obtained with this technique was $0.17 \pm 0.03$, close to the extrapolated values of the Werner (0,1) and (0,2) transitions. More experimental work with the pseudo-threshold excitation technique is needed, and under
stringent wavelength selection, if intensity limitations are not too severe. In practice this is not always the case, where trade-offs between intensity and resolution are always made.

It is also interesting to examine the high energy behavior of the polarization. At high incident electron energies the Born approximation may be used. This predicts that the excitation probability depends on $|\vec{\mu} \cdot \vec{k}|^2$, where $\vec{\mu}$ is the electric dipole moment and $\vec{k}$ is the momentum transfer vector. At high energies $\vec{k}$ is predominantly directed perpendicular to the incident ($\hat{z}$) direction, and preferential excitation will occur for molecules and transitions where $\vec{\mu}$ is also in this direction. In the case of $\chi^1\Sigma_g^+ - B^1\Sigma_u^+$ excitation $\vec{\mu}$ is aligned along the internuclear axis, whereas for $\chi^1\Sigma_g^+ - C^1\Pi_u$ excitation it is perpendicular to the internuclear axis. This means that for B(C) state excitation at high energy, molecules oriented perpendicular (parallel) to the $\hat{z}$ direction will be preferred, and it is expected that preferential population of $M_{N_1} = \pm N_0 (0)$ will occur. The results in Table 2-1 can then be used to obtain the expected polarizations for the different rotational lines involved.

However, this simplified discussion must be modified for the reasons outlined by Zare (1967). He points out that when the integration over all scattered electron directions is carried out for the initial excitation process a strong weighting occurs for the electrons whose momentum transfer vectors lie at significantly smaller angles than $\phi_0$ to the incident $\hat{z}$ direction. This, along with the effects of fine and hyperfine
structure, will produce a significant reduction in the anisotropies and resultant polarizations obtained. When a number of rotational lines are included in the measured intensity, the polarization will be reduced even more. It is expected that at high energies (a few hundred eV) the polarization will be small. Looking at the polarization data in Chapter IV confirms this.

It is clear from the data that the polarization of the molecular radiation will not go negative until energies in excess of 300 eV are reached. It was recently shown by Heddle (1979) that, for optically allowed transitions, where the Bethe approximation could be applied, the polarization should go through zero at an energy \( E \) given by:

\[
\ln(CE/R) = 3
\]

where \( C \) is a constant and \( R \) is the Rydberg energy. This constant has been shown by de Heer and Carriere (1971) to be 1.29 for the Werner system. Thus the polarization of the Werner lines should be zero at 212 eV. The failure of the data to do so may be due to cascade effects or the presence of low energy secondary electrons in the electron beam. The lower energy electrons will cause radiation with large polarization to contribute to the total intensity, and thus bring the polarization up to a value higher than it normally would have been.

McConkey and Donaldson (1972) determined \( C \) for Lyman-\( \alpha \) to be 1.44. Thus the polarization should go through zero at an energy of about 190 eV. The data of FIG 4-17 indicates that the polarization is zero at about 280 eV.
The apparent optical excitation functions for the Lyman and Werner transitions have been derived from the polarization measurements. It is interesting to note the level of agreement between these results and the results of other workers. The Lyman results have been compared with the semi-empirical work of Gerhart (1975), the integral cross-section measurements of Srivastava and Jensen (1977), and the calculations of Chung and Lin (1978). Our results are in good agreement with Gerhart's work and the calculations of Chung and Lin. The Werner results were compared with the work of Gerhart, which was based on the data of Stone and Zipf (1972) in our energy range. Again, there is good agreement between the two sets of data.

The relative cross-sections for the Werner (2,5) P(3), Q(1)+Q(2), and R(0)+R(1)+R(2) branches have also been determined. It is interesting to note the difference in the shape of the curve between the Q branch and the P and R branches. As was mentioned earlier, this might be due to the difference in ΔN for these transitions.

The polarization of Lyman-α was also measured, and the results obtained confirm and extend those of Ott et al. (1970). These results were also compared with the measurements of Karolis and Harting (1978) of the polarization of Balmer-α radiation following electron impact dissociation of H₂. The close agreement between these and our results reflects the similarity in the dissociation modes of H₂ leading to the emissions of Lyman-α and Balmer-α.
5.2 - THEORETICAL RESULTS

First, a comparison of the theoretical predictions among themselves shows a variety of results depending on the initial assumptions employed. Jette and Cahill assumed that conservation of the z-component of the total electronic angular momentum could be applied. They also assumed that the molecule was spherically symmetric. These assumptions led to the conclusion that, for excitation from a state with \( \Lambda = 0 \) to a state with \( \Lambda \neq 0 \), only \( M_N = 0 \) was excited at threshold. However, they were not able to use equation 2.3.8 to predict the selection of magnetic sublevels for excitation to a state with \( \Lambda = 0 \). Blum (1978) has pointed out that the conservation of the z-component of electronic orbital angular momentum is not in agreement with the threshold selection rule \( M_{N_0} = M_{N_1} \). Blum argues that, in the molecular frame, the incident and outgoing electron does not generally have \( m_1 = 0 \) and so, the expectation value of \( L_z \) must be evaluated in the molecular frame, and not in the laboratory frame.

The approach of Baltayan and Nedelec, who assumed that total electronic orbital angular momentum is conserved, yields a set of results different from those of Jette and Cahill. In their work (Baltayan and Nedelec 1975), they performed measurements on the Fulcher Bands \( 3p^3 \Pi_u^0 - 2s^3 \Sigma_g^+ \) of \( H_2 \) and obtained good agreement between theory and experiment. This suggests that conservation of total electronic orbital angular momentum is a good starting point for evaluating threshold polarizations.
The predictions of Feofilov are based on the use of linearly polarized light to excite the upper state. He derives the polarization for the atomic case, and then applies it to molecules. The reason for the good agreement between his results and the molecular case is that the use of \( \pi \)-polarized light forces \( M_{L_1} = M_{L_0} \) in the atomic case, which carries over to \( M_{N_1} = M_{N_0} \) in the molecular. This is just the selection rule applied at threshold for electron scattering.

It can be seen from the results in Table 2-2 that the predictions of Feofilov are the same as those of Blum's equation 2.6.16. Blum assumed that only one partial wave would contribute to the excitation at threshold, namely the \( l=1 \) partial wave for Werner excitation. The dipole excitation used by Feofilov corresponds to this exactly.

Malcolm, Dassen, and McConkey, using the assumption of conservation of total orbital angular momentum and the symmetry rules of Dunn (1962), obtained expressions for the threshold polarization. In this case they predicted that the polarization should depend not only on the rotational levels involved, but also on the change in \( \Lambda \). As was discussed in Chapter II, Blum developed these symmetry rules in a rigorous fashion. He showed that for Lyman excitation \( M_{N_1} = 0 \) was indeed preferentially populated, and that for Werner excitation \( M_{N_1} \neq \pm N_0 \) was populated, but other sublevels with \( M_{N_1} \neq \pm N_0 \) could also be populated. Unlike the theories of Jette and Cahill and Baltayan and Nedelec, which use a simple, spherically symmetric excitation, the theory of Malcolm et al predicts that the dynamics of the
excitation process is not that simple.

The density matrix formulation of Blum and Jakubowicz (1978) gives the most general expression for the threshold polarization. By using the appropriate assumptions in this expression, the results of Jette and Cahill and Malcolm et al can be reproduced. The results of Baltayan and Nedelec and Feofilov are approximated by this expression. Blum has also derived expressions for the excitation cross-sections that have the asymmetry of the excitation process built into them. The relevance of the values of $k$ that can contribute to the excitation process (in equations 2.5.9 and 2.5.10) is discussed in Dassen and McConkey (1980).

None of the above theories take into account the possible effects of resonances or the electron correlation described by Heideman et al. Blum does take into account all orientations of the molecule, which reduces the predicted polarization at the excitation threshold. Baltayan and Nedelec consider the effects of cascade contributions from higher levels on the polarization, although this was not discussed in Chapter 2.

Secondly, there is the comparison of the theoretical predictions with the experimental values obtained. One of the first points to take note of is the significant difference between the polarization of Lyman transitions and Werner transitions. This tends to give support to the idea that the interaction potential is not spherically symmetric, as assumed by Jette and Cahill, and Baltayan and Nedelec. Baltayan and Nedelec predict that the polarization of the Lyman transitions
is not very different from the polarization of the Werner transitions (see Table 2-2a). Clearly the data indicates that this is not the case. Also, the comparison of Jette and Cahill's predictions with the experimental results clearly indicate the incorrectness of their assumptions; i.e., that conservation of the z component of electronic orbital angular momentum and a spherically symmetric interaction cannot be applied to the evaluation of threshold polarizations. Rather, the experimental data supports the assumptions of conservation of total angular momentum and the asymmetries involved in the excitation process. The level of agreement (in the light of possible depolarizing effects) between the simplified theory of Malcolm et al, Blum's theory, Baltayan and Nedelec's theory, and the approach of Feofilov and the experimental data is rather good. It must be emphasized, however, that the agreement of our theory with that of Baltayan and Nedelec, even though the symmetry of the interaction potential assumed is different, might indicate that the dependence on the orientation of the molecule is not that stringent.
5.3 - CONCLUSIONS AND SUGGESTIONS

From the previous discussions concerning the theoretical and experimental results, it can be concluded that:

(1) - The conservation of total orbital angular momentum and its z-component is more applicable to the excitation process than the conservation of electronic orbital angular momentum only. As could be seen from the theoretical predictions, the assumptions made about the conservation of angular momentum had a great effect on the threshold polarization.

(2) The orientation of the molecular axes with respect to the incident electron beam is important in determining the threshold polarization, since the population distribution of the magnetic sublevels in the excited state will be different for different orientations of the molecule during the collision. One aspect of this that was not taken into account is the rotation of the molecule during the collision. All of the theories discussed assumed that the molecule remained stationary during the collision. At the excitation threshold, the fact that the scattered electron has practically zero energy means that the interaction time will be greatly lengthened. For this reason, measuring the polarization at threshold is not really a good test of this aspect of the theory. Using the 'pseudo-threshold' technique would be a far better test, since the scattered electron will still have significant energy. Thus the interaction time will be much shorter than at threshold, and the rotation of the molecule will not be important.

In addition to providing some insight into the dynamics
of the excitation of molecules, this study has also raised
some new questions. Blum's approach to the evaluation of the
excitation cross-sections appears to suggest that there is a
difference in the type of scattering involved in Lyman excita-
tion and in Werner excitation. The only measurements of the
electron scattering at low energy for H₂ are the results of
Srivastava and Jensen(1977), and they did not approach the
excitation threshold. Near threshold measurements of the scattered electron angular distribution for Lyman and Werner excita-
tion would provide information on the scattering processes
involved.

The behavior of the polarization at energies close to the
excitation threshold is also well worth investigating. This
study would have to be done with a higher energy resolution
than was used in the present work. Such data is available for
atoms, but there have been no results for molecules published
at this time.

On the theoretical side it can be seen that much more work
is needed to account for the complexity of the molecular case.
There are approximations that can be used at the threshold re-
gion and ones that are used at the high energy region of the
excitation which enable the calculation of polarizations, but
there is a lack of suitable approaches for the intermediate
energies. Also, the presence of resonances has not been taken
into account in the various theoretical approaches. Heideman
et al(1979) have developed a model which they use to calculate
the effect of the electron correlation in atoms on the resul-
tant polarization, but no such treatment is available for molecules.

Clearly, then, there is a need for further investigation, both experimentally and theoretically, into the nature and dynamics of the polarization of molecular line radiation.
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A list of publications that deal with the polarization of radiation is given below.

Dassen, H. W., Malcolm, I. C., and McConkey, J. W.
Polarization of the Ar 106.7 and 104.8 nm Resonance Lines

Dassen, H. W., and McConkey, J. W. Abstracts XI ICPEAC, Kyoto 1979
Electron Impact Excitation of \( H_2 \) -- Individual Line Polarizations

Malcolm, I. C., Dassen, H. W., and McConkey, J. W.
Polarization of Radiation from \( H \) Excited by Electron Impact: Lyman and Werner Emissions and Lyman-

McConkey, J. W., Dassen, H. W., and Malcolm, I. C.
Optical Polarization Studies in \( H_2 \) Following Electron Impact

Other publications not related to polarization studies are:

Dassen, H. W., Huschilt, J. C., King, G. C. M., and McConkey, J. W.
Structure in Cross-sections for Ar Metastable Production in the 25 - 35 eV Region