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COLLISION-INDUCED ABSORPTION IN DIATOMIC MOLECULE/RARE-GAS MIXTURES

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PREFACE

This analysis was conducted for the Advanced Research Projects Agency as part of RAND's continuing study of the propagation of laser beams through the atmosphere. It examines in detail the characteristics of the collision-induced absorption of infrared and far-infrared radiation by symmetrical diatomic molecules and rare-gas atoms in order to provide a broader basis for the theoretical understanding of collision-induced absorption, which is an important factor limiting transmission in some atmospheric spectral windows. It is believed that the results reported here represent substantial progress toward that end.
SUMMARY

A quantum mechanical calculation of collision-induced absorption in the infrared and far-infrared spectral regions for mixtures consisting of symmetrical diatomic molecules and rare-gas atoms is given. The induced moment consists of a short-range overlap term and a long-range quadrupole term. Near molecular transition lines the quadrupole term gives the main contribution to the absorption, while in the far wings the overlap term is dominant. The H$_2$-He, H$_2$-Ar and N$_2$-Ar systems are considered and an estimate for the absorption coefficient near 10$\mu$ for N$_2$-N$_2$ systems is given.
I would like to express my gratitude to H. A. Ory for suggesting the problem and Mrs. M. Lakatos for her endless patience in performing the numerical calculations.
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>PREFACE</td>
<td>iii</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>v</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>I.  INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. FORMAL EXPRESSION FOR THE INDUCED ABSORPTION COEFFICIENT</td>
<td>3</td>
</tr>
<tr>
<td>III. CALCULATION OF THE ABSORPTION SPECTRUM</td>
<td>10</td>
</tr>
<tr>
<td>Overlap-Induced Dipole Moment</td>
<td>10</td>
</tr>
<tr>
<td>Quadrupole-Induced Dipole Moment</td>
<td>13</td>
</tr>
<tr>
<td>Calculation of the Absorption Spectrum</td>
<td>16</td>
</tr>
<tr>
<td>IV. ABSORPTION SPECTRUM OF H₂-RARE ATOM AND N₂-Ar MIXTURES</td>
<td>23</td>
</tr>
<tr>
<td>Overlap Dipole Parameters for Diatomic Molecule/Rare-Gas Mixtures</td>
<td>23</td>
</tr>
<tr>
<td>Absorption Spectrum for H₂/Rare-Gas Atom</td>
<td>26</td>
</tr>
<tr>
<td>Absorption Spectrum for N₂-Ar</td>
<td>29</td>
</tr>
<tr>
<td>Estimates for N₂-N₂ Absorption in the Far Wings</td>
<td>33</td>
</tr>
<tr>
<td>V. CONCLUSIONS</td>
<td>40</td>
</tr>
<tr>
<td>Appendix</td>
<td></td>
</tr>
<tr>
<td>EVALUATION OF I(ω)</td>
<td>41</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>42</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

1. Absorption coefficient for H₂-He system at room temperature with contributions of Q and S branches indicated ............................................. 28

2. Absorption coefficient for H₂-Ar system at room temperature with contributions of Q and S branches indicated ............................................. 30

3. Absorption coefficient for N₂-Ar system at room temperature ......................................................... 32

4. Geometrical relationship for binary molecular collisions ......................................................... 35
I. INTRODUCTION

The purpose of this Memorandum is to calculate the binary absorption coefficient of infrared and far-infrared radiation in mixtures consisting of symmetrical diatomic molecules and rare-gas atoms. Atoms and molecules with no permanent dipole moment, and consequently no dipole absorption coefficient proportional to the density, are considered. The absorption mechanism considered here is that due to the dipole moment induced between a pair of colliding atoms or molecules. For small-impact parameters the induced moment arises as a consequence of the distortion of the electron cloud during the collision of two particles, atoms, or molecules, while for larger-impact parameters the induced moment arises from the polarization of one particle by the quadrupole field of the other. The induced dipole moment is expected to be nonzero when the colliding pair are within a few molecular radii of each other. Thus, absorption takes place within the duration of a collision and the probability of absorption is proportional to the product of the densities of the two species.

Collision-induced absorption in rare-gas mixtures was discovered experimentally by Kiss and Welsh \(^{(1)}\) and further studied by Bosomworth and Gush. \(^{(2)}\) Recently, Levine and Birnbaum \(^{(3,4)}\) have made a theoretical calculation of induced absorption in rare-gas mixtures using a simple model to describe the variation of the collision-induced dipole moment with internuclear separation. They obtain an analytic expression for the absorption spectrum which agrees well with the experiments. Previously, J. Van Kranendonk \(^{(5)}\) has presented a theory for the integrated absorption coefficient in diatomic molecules. Interest here is in
the absorption coefficient as a function of the frequency of the incident radiation field and not in this function integrated over all frequencies.

The energy absorbed during a collision between two dissimilar rare-gas atoms goes into increasing the translational kinetic energy only. The effects on the induced absorption due to the rotational transitions that occur in the diatomic molecule are investigated here. The frequency of the applied radiation field is taken to be less than the frequency of the first excited vibrational level of the diatomic molecule (4159.4 cm\(^{-1}\) for H\(_2\) and 2330.7 cm\(^{-1}\) for N\(_2\); see Ref. 6); consequently, vibrational effects on the absorption need not be considered. The absorbed energy in this case goes into both rotational and translational energy.

In Section II a formal expression for the absorption coefficient is written and the phenomenological induced dipole moment is introduced and discussed. In Section III an analytic expression for the absorption coefficient is derived, and in Section IV an estimate is made of the parameters for H\(_2\)-rare atom, N\(_2\)-rare atom, and N\(_2\)-N\(_2\) collisions, and numerical values of the absorption coefficient are given as calculated as a function of frequency for these cases.

These calculations are aimed at providing a broader basis for the theoretical understanding of collision-induced absorption, which is an important factor limiting transmission in some atmospheric spectral windows. For example, collision-induced absorption in O\(_2\) is dominant at the Nd laser wavelength of 1.06\,\mu m, and collision-induced absorption in the far wings of H\(_2\)O lines is important at the CO\(_2\) laser wavelength of 10.6\,\mu m. These absorptions involve more complicated mechanisms and require further development for their treatment.
II. FORMAL EXPRESSIONS FOR THE INDUCED ABSORPTION COEFFICIENT

Gaussian units are used with $h = c = 1$; then $e^2 = 1/137$. The absorption coefficient $\alpha = (2\pi/c)\Gamma$, where $\Gamma$ is the transition rate. That is,

$$\alpha(\omega) = \frac{(2\pi)^2}{V} \left\langle \sum_f \omega|\vec{\mu} \cdot \hat{e}\rangle_{1f} |^2(P_f - P_i) \delta(\omega_{fi} - \omega) \right\rangle_1 \quad (1)$$

In Eq. (1), $V$ is the volume of the sample, $\vec{\mu}$ is the induced dipole moment of the system of particles, $\hat{e}$ is the unit polarization vector of the incident radiation field of frequency $\omega$, $\omega_{fi} = E_f - E_i$ is the energy difference between a final state $f$ and an initial state $i$ of the molecular system respectively. $P_i$ and $P_f$ are the statistical weights of the initial and final particle states. Also, Eq. (1) indicates a sum over final states (denoted by $\Sigma$) and an average over initial states (denoted by $\langle \rangle_i$).

The appearance of the factor $(P_f - P_i)$ takes into account both absorption (the $P_i$ term) and the reverse process, spontaneous emission (the $P_f$ term). It is assumed throughout that the temperature $T$ of the system is so low that all of the particles may be taken to be in their electronic ground states.

Consider a system of rare-gas atoms (density $n_1$) and symmetrical diatomic molecules (density $n_2$). The dipole moment arises from binary collisions between atoms and molecules and between molecules. ** Consider first the term in $\alpha$ proportional to $n_1n_2$, that is, absorption

---

* Explicit expressions for $P_i$ and $P_f$ are given in Eq. (7) below.

** There can be no net induced dipole moment for two identical rare-gas atoms (in the same electronic state) since the system is completely symmetrical about the center of mass. However, this is not the case for two diatomic molecules.
by the induced moments arising from the collision of a rare-gas atom and a symmetrical diatomic molecule. Later on, the term proportional to $n_2^2$ (i.e., absorption arising from binary molecular collisions) is estimated. It is assumed that

$$\mu(R_1, \ldots, R_N) = \sum_{i=1}^{V_n_1} \sum_{j=2}^{V_n_2} \mu(R_{ij})$$

(2)

i.e., the dipole moment arises from binary collisions and is a function of the distance between the centers of mass ($R_{ij}$) of the two colliding particles. The wave functions describing the centers of mass motion of the particles can, in the first approximation, be taken as plane waves. Then by a straightforward procedure Eq. (1) may be reduced to a form expressing $\alpha$ in terms of two-particle matrix elements. Thus

$$\alpha = 4\pi^2 n_1 n_2 \omega \left\langle \sum_i \left| (\mu(R) \cdot e)_{i1} \right|^2 (P_{i1} - P_{i2}) \delta(\omega_{i1} - \omega) \right\rangle$$

(3)

where now the initial and final states refer to the two-particle system interacting with the radiation field,

$$|\mu(R) \cdot e|_{i1} = \int d^3R \varphi_i(R)^* (\mu(R) \cdot e) \varphi_i(R)$$

(4)

where

$$\varphi_i(R) = e^{i \mathbf{k} \cdot \mathbf{R}} u_k(R) \psi_i(\Omega) \approx e^{i \mathbf{k} \cdot \mathbf{R}} \psi_i(\Omega)$$

$$\varphi_f(n) = e^{i \mathbf{k}' \cdot \mathbf{R}} u_k'(R) \psi_f(\Omega) \approx e^{i \mathbf{k}' \cdot \mathbf{R}} \psi_f(\Omega)$$

(5) **

*Experimentally these two cases may be distinguished by, for example, arranging $n_1 >> n_2$ so that the absorption arises predominately from collisions between diatomic molecules and rare-gas atoms.

** The $\mu(R)$ term in the relative two-particle wave function, which is determined by solving the Schrödinger equation with the two-particle interaction, is taken to be unity in the first approximation. This corresponds to taking straight line collision paths in the classical approach. (3,4)
\( \psi \) are the rotational wave functions and \( k \) and \( k' \) are the relative momenta of the colliding particles before and after the collision, respectively.

For the atom-molecule system,

\[
\begin{align*}
E_i &= k^2/2m + E_{J_i} \\
E_f &= k'^2/2m + E_{J_f} \\
m &= \text{reduced mass} = m_1m_2/(m_1+m_2) \\
E_J &= \text{rotational energy} = B(J+1)
\end{align*}
\]

where \( J \) is the rotational quantum number and \( B \) is the rotational constant of the molecule. The statistical weights of the initial and final particle states are given by

\[
P_i = (2J_i+1)g_i \, e^{-E_i/kT} (1/2\pi m^*kT)^{3/2} \\
P_f = (2J_f+1)g_f \, e^{-E_f/kT} (1/2\pi m^*kT)^{3/2}
\]

where \( k \) is the Boltzmann constant, and \( g_i \) and \( g_f \) are the statistical weights for the nuclear spin states of the diatomic molecule. It is well known that the relative statistical weights for the symmetric and antisymmetric spin states are

\[
\frac{g(\text{sym})}{g(\text{antisym})} = \begin{cases} 
(I+1)/I \text{ for } I \text{ integral} \\
= 1/I + 1 \text{ for } I \text{ half-integral}
\end{cases}
\]

where \( I \) is the nuclear spin. Upon combining Eqs. (3)-(8),
\[ \sigma(\omega) = 4\pi^2 n_1 n_2 \omega (1/2\pi m \nu T)^{3/2} (2J_1 + 1)^{-1} \sum_{J_i, J_f, M_i, M_f} \int \frac{d^3 k}{(2\pi)^3} \int \frac{d^3 k'}{(2\pi)^3} \]

\[ \times |(\vec{u} \cdot \vec{e}_{k'}J_f, kJ_i)|^2 \frac{e^{-(k^2/2m \nu T)}}{\sum_i (2J_i + 1) g_i e^{\nu T} \frac{B}{\nu T} J_i (J_i + 1)} \{ (2J_f + 1) g_f e^{-\nu T} \frac{B}{\nu T} J_f (J_f + 1) \delta(\omega - \omega_{f_i}) \} \]

where

\[ \omega - \omega_{f_i} = \omega - \frac{1}{2m} (k^2 - k'^2) - E_{J_f} J_i \]

and

\[ E_{J_f} J_i = E_{J_f} - E_{J_i} \]

In Eq. (9) the summations over the initial and final continuum states \( k \) and \( k' \) have been replaced by integrations over \( d^3 k \) and \( d^3 k' \) respectively.

To proceed, an analytic form is specified for the induced dipole moment. The induced dipole moment of a pair of colliding particles may be resolved into two parts. One part is the overlap dipole moment which results from the distortion of the electron cloud during close collisions (\( r \lesssim \) collision diameter). The other part of the induced dipole moment arises from the polarization of one particle by the quadrupole field of the other and vice versa. The quadrupole-induced dipole moment arises from long-range collision (\( r \gtrsim \) collision diameter). These two parts of the moment are discussed separately.
In view of the close agreement of Levine and Birnbaum's\textsuperscript{(3,4)} theory with the experimental results, we use the same functional form for the overlap-induced dipole moment between the rare-gas atom and each nucleus of the diatomic molecule. The form they use is
\[ \mu(r) = \mu_c \gamma r \exp(-\gamma^2 r^2) , \]
where \( \gamma \) and \( \mu_c \) are the range and strength respectively of the dipole moment. In the cases considered here \( \gamma \sim (1-2) \text{Å}^{-1} \). That is, the important values of \( r \) are of the order of the internuclear separation of the molecule. For distance in this range the rare-gas atom "sees" each nucleus separately. This, however, would not be the case when \( \gamma^{-1} \) is much larger than the internuclear separation.

In the present calculation any interparticle potential is ignored, and hence straight line collision paths are assumed. Realistically, a potential exists between the particles which contains a repulsive part that prevents the two particles from approaching too close to one another, so there is actually a small moment for distances within the range of the repulsive part of the interparticle potential. The factor \( (\gamma r) \) in the moment cuts off the moment for \( r \lesssim \gamma^{-1} \). Similarly, for large interparticle separation, when the electron clouds do not overlap there is very little contribution to the overlap moment. The factor \( \exp(-\gamma^2 r^2) \) cuts off the moment for \( r \gtrsim \gamma^{-1} \). Strictly speaking, the repulsive and overlap ranges are not equal. In this calculation, as in Refs. 3 and 4, a single range is used to specify the induced moment.

By using the modified gaussian model for the induced overlap moment Levine and Birnbaum were able to obtain a simple analytic expression for the absorption spectrum. By matching the theoretical and experimental results (for Ne-Ne, He-Ar and Ne-Ar systems) at the
peak of the spectrum they obtained values of $\gamma$ and $\mu_0$. Using these values of $\gamma$ and $\mu_0$ they obtained good agreement over nearly the entire range of the spectrum (especially for He-Ar systems). For the cases considered here, $H_2$ and $N_2$/rare-gas atom absorption, no experimental results exist as yet. However, using the mathematical form for the moment that was used by Levine and Birnbaum leads to analytic expressions for the absorption spectrum in terms of $\mu_0$ and $\gamma$. Then physical arguments are used to estimate values for $\mu_0$ and $\gamma$ in terms of the values obtained by Levine and Birnbaum for the rare-gas cases. In view of their good agreement with the experimental results this procedure seems justifiable.

The main contribution to the induced dipole moment arises for values of $r$ where $r\gamma \sim 1$. In the cases considered here, $\gamma \sim (1-2)\text{Å}^{-1}$. That is, the important values of $r$ are of the order of the size of the atom or molecule (the electron clouds overlap and hence distort the charge distribution).

The quadrupole-induced dipole moment is equal to the quadrupole field of particle one at the position of particle two times the polarizability of particle two, and vice versa. In the case of a diatomic molecule/rare-gas atom collision there is only one term, since rare-gas atoms possess no quadrupole moment. Qualitatively the overlap-induced moment contributes to the high-frequency part of the absorption spectrum, since the overlap moment arises from close collision. On the other hand the quadrupole-induced moment contributes to low frequencies in the Q and O branches and frequencies near the rotational transitions in the S branches, since the quadrupole-induced
moment is due to distant collisions. (Near the rotational transition frequencies the momentum transfer is small.)
III. CALCULATION OF THE ABSORPTION SPECTRUM

OVERLAP-INDUCED DIPOLE MOMENT

The induced dipole moment between a colliding rare-gas atom and a symmetrical diatomic molecule is taken as a superposition of the atom interacting with each of the two atomic components of the molecule respectively. That is,

$$\vec{\mu}^{(o)}(r) = \vec{\mu}^{(o)}(r_1) + \vec{\mu}^{(o)}(r_2)$$  \hspace{1cm} (12)

where \(r_1\) and \(r_2\) are the separations of the atom from each of the two nuclei respectively. Choosing a coordinate system with the z-axis parallel to the polarization vector of the incident radiation field and calling the molecular internuclear separation vector \(2\vec{a}\) gives

$$\vec{u}(r) \cdot \vec{e} = u_o \sqrt{(r_1^z e^{-\gamma_1 r_1 z} + (r_2^z e^{-\gamma_2 r_2 z})}$$  \hspace{1cm} (13)

where

$$\vec{r}_1 = \vec{r} - \vec{a} \quad \text{and} \quad \vec{r}_2 = \vec{r} + \vec{a}$$

First the matrix element of \(\vec{u} \cdot \vec{e}\) between the initial and final continuum states is calculated. Suppressing the rotational quantum numbers for brevity, we have

$$\langle \vec{u}(o) \cdot \vec{e} \rangle_{k'}_{k} = \int d^3 r \ e^{-i\vec{k} \cdot \vec{r}} \ (\vec{u} \cdot \vec{e}) e^{i\vec{k} \cdot \vec{r}}$$  \hspace{1cm} (14)

\[
= \int d^3 r \ (\vec{u} \cdot \vec{e}) e^{-i\vec{Q} \cdot \vec{r}}
\]

where

$$\vec{Q} = \vec{k'} - \vec{k}$$
Substituting Eq. (13) into Eq. (14) gives

\[
(\mathbf{a} \cdot \mathbf{e})_k' = \left( \mu_z \right)_k' = \gamma \mu_0 \left\{ e^{iQ \cdot \mathbf{a}} \int d^3 \mathbf{r}_1 e^{-\mathbf{r}_1^2} \right. \\
+ e^{-iQ \cdot \mathbf{a}} \int d^3 \mathbf{r}_2 e^{-\mathbf{r}_2^2} \left\} \\
= \gamma \mu_0 e^{iQ \cdot \mathbf{a}} \int d^3 \mathbf{r} e^{i\mathbf{Q} \cdot \mathbf{r}} e^{-\mathbf{r}^2} + \text{terms } \mathbf{a} \rightarrow -\mathbf{a}
\]

The integral appearing in Eq. (15) is elementary and easily found to be:

\[
\int d^3 \mathbf{r} e^{i\mathbf{Q} \cdot \mathbf{r}} e^{-\mathbf{r}^2} = \frac{\pi^{3/2} \mathbf{Q}}{2l} e^{-(Q^2/4\gamma^2)}
\]

Substituting this value into Eq. (15) gives

\[
(\mathbf{a} \cdot \mathbf{e})_k' = \frac{\mu_0 \pi^{3/2} \mathbf{Q}^{-4} (\mathbf{Q} \cdot \mathbf{a})}{2l} e^{i\mathbf{Q} \cdot \mathbf{a}} e^{-(Q^2/4\gamma^2)} + \text{terms } \mathbf{a} \rightarrow -\mathbf{a}
\]

Next one must calculate the matrix element of Eq. (16) between initial and final rotational states of the molecule. Suppressing the subscripts '_1' and '_2',

\[
\langle J_{1M_1} | \mu_z | J_{2M_2} \rangle = \frac{\mu_0 \pi^{3/2} \mathbf{Q}^{-4} (\mathbf{Q} \cdot \mathbf{a})}{2l} e^{i\mathbf{Q} \cdot \mathbf{a}} e^{-(Q^2/4\gamma^2)} + \text{terms } \mathbf{a} \rightarrow -\mathbf{a}
\]

where the initial and final rotational states are referred to the z-axis. Suppressing, for brevity, terms that do not depend on angular coordinates,

*Due to the rapid convergence of the integrand for \( r > \gamma^{-1} \), negligible error is introduced upon extending the upper limit of the \( r \) integration to \( +\infty \).
we find

\[ \langle J_f M_f | u_z^G | J_i M_i \rangle = \langle J_f M_f | Q_z e^{i \mathbf{Q} \cdot \mathbf{a}} | J_i M_i \rangle + \text{terms } \mathbf{a} \to -\mathbf{a} \] (17)

For frequencies of the order of the peak in the absorption spectrum, \( |Q_a| \ll 1 \) and hence one may expand \( e^{i \mathbf{Q} \cdot \mathbf{a}} \) and retain the first nonvanishing term. In the case of diatomic molecule/rare-gas atom collisions the main contribution comes from setting \( e^{i \mathbf{Q} \cdot \mathbf{a}} \approx 1 \). That is, for diatomic molecule/rare-gas atom collisions the overlap-induced moment is independent of the orientation of the molecule. On the other hand, for molecular-molecular collisions involving identical molecules (in the ground electronic and vibrational states) the matrix elements of the angle-independent part of the overlap-induced moment are zero, since the colliding system possesses a center of symmetry. Hence, the lowest-order nonvanishing term for systems such as \( \text{N}_2-\text{N}_2 \), \( \text{H}_2-\text{H}_2 \) comes from the \( (Q\cdot a)^2 \) term in the expansion of \( e^{i \mathbf{Q} \cdot \mathbf{a}} \) (see Eq. (17)). The angle-dependent part of the overlap moment is small, and hence for frequencies of the order of the peak the overlap moment contributes to the Q branch only. For frequencies such that \( |Q_a| \ll 1 \) (tail of the spectrum), a power series expansion of \( e^{i \mathbf{Q} \cdot \mathbf{a}} \) is not valid and the overlap moment is strongly angle-dependent. For example, in \( \text{N}_2-\text{N}_2 \) absorption the peak in the spectrum is approximately 100 cm\(^{-1}\) and arises from quadrupole-induced dipole moments. Near 1000 cm\(^{-1}\) (\( \sim \text{CO}_2 \) laser wave number) where \( Q_a > 1 \), the main contribution to the absorption is expected to come from the angle-dependent terms in the overlap-induced moment. For the present, attention is focused on diatomic molecule/rare-gas atom collisions near the peak of the spectrum. Later on, the absorption in \( \text{N}_2-\text{N}_2 \) collisions near the \( \text{CO}_2 \) laser wavelength is estimated.
Setting \( e^{i \mathbf{\hat{n}} \cdot \mathbf{\hat{n}}} = 1 \) in Eq. (16), the overlap matrix element is given by

\[
(e \cdot e^0)_{k'k} = -i \mu_0 \gamma^{-4} (\mathbf{\hat{r}} \cdot \mathbf{n}) e^{-(q^2/4\gamma^2)} J_{J_k} J_{J_{k'}} M_{M_k} M_{M_{k'}}
\]

\[(18)\]

**QUADRUPOLE-INDUCED DIPOLE MOMENT**

For diatomic molecule/rare-gas atom systems the long range quadrupole-induced moment \( \mu(q) \), which can be inferred from Ref. 7, is given by

\[
\mu(q) = \frac{3 q_0 \alpha_o}{r^4} \left( \frac{4\pi}{5} \right) \sum_{m=-2}^{m=2} \mathbf{Y}_{2m}(\Omega_a) \mathbf{Y}_{2m}(\Omega_r) \mathbf{\hat{r}} \cdot \mathbf{\hat{r}} \quad \text{for } r \gg \sigma
\]

\[(19)\]

where the \( z \)-axis is taken parallel to \( \mathbf{\hat{r}} \), \( \mathbf{\hat{e}}_r \) is a unit vector in the \( r \)-direction, \( \Omega_a \) and \( \Omega_r \) are the angular coordinates of \( \mathbf{\hat{r}} \) and \( \mathbf{\hat{a}} \) respectively, \( \alpha_o \) is the polarizability of the rare-gas atom, and \( q_0 \) is the quadrupole moment of the diatomic molecule. The assumption is made that the quadrupole-induced moment has meaning only for values of \( r \gg \sigma \), which is the collision diameter of the colliding particles.

Upon taking matrix elements of Eq. (19) between initial and final continuum states,

\[
(e \cdot e^0(q))_{k'k} = \frac{12 \pi}{5} \alpha_o q_0 \mathbf{Y}_{20}(\Omega_a) \mathbf{\hat{e}}_r \mathbf{\hat{r}}
\]

\[(20)\]

where

\[
\mathbf{\hat{r}} = \int \mathbf{\hat{e}}_r \mathbf{Y}_{20}(\Omega) e^{i \mathbf{\hat{Q}} \cdot \mathbf{\hat{r}}} \frac{d^3 \mathbf{r}}{r^4}
\]

\[(21)\]

and \( \mathbf{\hat{Q}} = \mathbf{\hat{r}}' - \mathbf{\hat{r}} \). \( \mathbf{\hat{r}} \) is a vector and must be proportional to \( \mathbf{\hat{Q}} \). That is, \( \mathbf{\hat{r}} = I \mathbf{\hat{Q}} \) where \( I = (\mathbf{\hat{Q}} \cdot \mathbf{\hat{Q}})/q^2 \). Then

\[
\mathbf{\hat{Q}} \cdot \mathbf{\hat{r}} = \int \mathbf{\hat{Q}} \cdot \mathbf{\hat{e}}_r \mathbf{Y}_{20}(\Omega) e^{i \mathbf{\hat{Q}} \cdot \mathbf{\hat{r}}} \frac{d^3 \mathbf{r}}{r^4}
\]
Taking the z-axis of integration along $\mathbf{Q}$ and expanding $e^{-iQ \cdot r}$ in terms of spherical harmonics,

$$\mathbf{Q} \cdot \mathbf{r} = \mathbf{Q} \cdot \mathbf{r} \quad \text{(22)}$$

where $j_2\sigma$ is the spherical Bessel function of second order. The lower limit on the $r$ integration has been set equal to the collision diameter $\sigma$ appearing in the interparticle potential.

Strictly speaking, setting the lower limit arbitrarily equal to $\sigma$ is incorrect. Upon introducing the two-particle distribution function into the integrand of Eq. (22), one can now integrate over all $r$. The two-particle distribution function, in the low density limit and at temperatures considered here, is proportional to $e^{-V(r)/kT}$ where $V(r)$ is the interparticle potential. Any realistic interparticle potential (for example the Lennard-Jones potential) becomes very large for small $r$ ($r \ll \text{size of molecule}$), and hence ($e^{-V(r)/kT} \ll 1$), a negligible contribution to the integral, comes from small $r$. For $r \gtrsim \text{size of the molecule}$, $V(r) \sim 0$ (i.e., the two-particle distribution function is constant). The main contribution to the integral comes from $r = \sigma$.

In view of other approximations involved in the calculation it is felt that unnecessary mathematical complexity is introduced by using the exact two-particle distribution function. Therefore we use, as an approximation, a distribution which is zero for $r < \sigma$ and is equal to unity for $r \geq \sigma$.

For frequencies $\omega \sim kT$ for the $Q$ branch, and frequencies near the rotational transition frequencies for the $S$ branch, $Q$, the momentum transfer, $\sim \sqrt{2m\omega}$. For $kT$ approximately equal to room temperature and
values of \( m \) and \( \sigma \) considered here, \( Q_\sigma \gg 1 \) and hence the asymptotic value of \( J_2 \) may be used. Setting \( x = Q_\sigma \), Eq. (22) becomes

\[
\tilde{q} \cdot \tilde{I} = \sqrt{20\pi} i Q^2 \int_{Q_\sigma}^\infty \frac{d[J_2(x)]}{x^2}
\]

\[
\approx \sqrt{20\pi} i Q^2 \frac{\sin Q_\sigma}{(Q_\sigma)^3} + 0(Q_\sigma)^{-4} + \ldots
\]

Therefore,

\[
\tilde{q} \cdot \tilde{e} = \frac{(\tilde{q} \cdot \tilde{e})(\tilde{q} \cdot \tilde{I})}{Q^2}
\]

Thus

\[
(\tilde{e} \cdot \mu'(q))_{k'k} = \sqrt{\frac{3}{5}} \sigma_0 q_0 (4\pi)^{3/2} (\tilde{q} \cdot \tilde{e}) \frac{\sin Q_\sigma}{(Q_\sigma)^3} Y_{20}(Q_\sigma)
\]

Taking matrix elements with respect to the rotational wave functions (suppressing factors that do not depend on rotational quantum numbers), it is found that

\[
\langle J_{1f} M_f | \tilde{e} \cdot \mu'(q) | J_{1i} M_i \rangle \sim \langle J_{1f} M_f | Y_{20} | J_{1i} M_i \rangle
\]

\[
= \left[ \frac{5(2J_1+1)}{4\pi(2J_f+1)} \right]^{1/2} C(J_{1f} 2J_f M_f 0) C(J_{1f} 2J_f 00)
\]

where the \( C's \) are the well-known Clebsch-Gordan coefficients.\(^{(3)}\) From Eq. (25) the selection rules for quadrupole absorption are easily obtained; they are \( \Delta J = \{J_{1f} - J_{1i} = 0, \pm 2 \) and \( \Delta M_i = 0 \). From Eqs. (24) and (25) it is found that
where $\bar{Q} = \bar{k}' - \bar{k}$.

CALCULATION OF THE ABSORPTION SPECTRUM

According to Eq. (5), it is necessary to square the matrix elements of $U\delta u_e (u = \delta u_o + \delta u(q))$ and then sum over final states (rotational and continuum) and average over initial states (rotational and continuum).

Consider the rotational part first: suppressing notation that does not depend on rotational quantum numbers, the average for a given initial rotational state takes the form

$$\bar{U}^2 = (2J_f + 1)^{-1} \sum_{M_i, M_f} |\langle J_f M_f | \bar{u} \cdot \bar{e} | J_i M_i \rangle|^2$$

where $\bar{u} \cdot \bar{e} = (\bar{u}(o) + \bar{u}(q)) \cdot \bar{e}$. From Eqs. (18) and (26) it is found that

$$\bar{U}^2 = (\bar{Q} \cdot \bar{e})^2 \left\{ A_o^2 e^{-(Q^2/2\gamma^2)} \delta_{J_f J_i} + A_q^2 (i, f) \frac{\sin \bar{Q} \cdot \bar{e}}{(Q \cdot \bar{e})^6} \right\}$$

$$= (\bar{Q} \cdot \bar{e})^2 (R_o + R_q)$$

(27)*

where

$$A_o = u_o \pi^{-3/2} \gamma^{-4}$$

and

$$A_q^2(i, f) = (12\pi \omega q)^2 \frac{1}{2J_f + 1} C^2(J_i 2J_f, 00)$$

*No cross term between overlap and quadrupole moment appears in Eq. (27). The cross term is proportional to

$$\sum_{M_i, M_f} C(J_i 2J_f, M_i 0) \delta_{J_i J_f} = \sum_{M_i} C(J_i 2J_f, M_i 0) = 0$$
The first term in Eq. (27) is the contribution from the overlap term, while the second is the contribution from the quadrupole term. The angle-independent overlap term contributes to the Q branches only, while the quadrupole term contributes to the S, Q and O branches.

To evaluate the integrals over $\bar{k}$ and $\bar{k}'$ indicated in Eq. (9), variables are changed from $\bar{k}$, $\bar{k}'$ to $k$, $Q$ respectively. Then (suppressing factors that do not depend on $k$ or $Q$),

$$\gamma(w) \sim \int \frac{d^3Q}{(2\pi)^3} \int \frac{d^3k}{(2\pi)^3} e^{-\frac{e k^2}{2}} \frac{-it}{\Delta^2} \delta \left[ (2m)^{-1} (Q^2 + 2Q \cdot \bar{r} - \Delta^2) \right]$$

where

$$\Delta^2 = 2m(w - E_{J=1})$$

and

$$\gamma = 1/2m_k T$$

Holding $\bar{Q}$ fixed for the $k$ integration,

$$\alpha(w) \sim (2\pi)^{-2}(m/Q) \int k \, dk \, (\cos \chi) e^{-\frac{e k^2}{2}} \delta (\cos \chi + \frac{Q^2 - \Delta^2}{2Qk})$$

where $\chi$ is the angle between $\bar{k}$ and $\bar{Q}$ and the $\bar{Q}$ integral is suppressed. Performing the integral over $\cos \chi$,

$$\alpha(w) \sim (2\pi)^{-2}(m/Q) \int k \, dk \, e^{-\frac{e k^2}{2}}$$

where

$$k_Q = \frac{\Delta^2 - Q^2}{2Q}$$

The limits on the $k$ integral are determined by requiring $|\cos \chi| \leq 1$ and $k \geq 0$. The integral appearing in Eq. (29) is elementary, and

$$\alpha(w) \sim (2\pi)^{-2}(m/2Q)e^{-\frac{e k^2}{2}}$$
Hence from Eq. (28),

\[ \alpha(\omega) \sim (2\pi)^{-4} (m/3\varepsilon) \int_0^\infty Q^2 dQ e^{-\varepsilon Q^2} (Q^2 + 1)^2 (R_0 + R_q) \]

\( R_0 \) and \( R_q \) are defined in Eq. (27). When the z-axis of integration is chosen to be parallel to \( \vec{e} \), the angular integration becomes elementary and gives

\[ \alpha(\omega) \sim (2\pi)^{-4} (m/3\varepsilon) \int_0^\infty Q^2 dQ e^{-\varepsilon Q^2} (R_0 + R_q) \]

\[ = (2\pi)^{-4} (m/3\varepsilon) e^{\Delta^2/2} \int_0^\infty Q^2 dQ \left\{ A_0^2 e^{-\varepsilon Q^2 \left( \frac{1}{2} \frac{Q^2}{\varepsilon} + \frac{1}{4} + \frac{\Delta^2}{4Q^2} \right)} + A_q^2 \sin^2 Q \right\} \]

\[ = (2\pi)^{-4} (m\Delta^2/3\varepsilon) e^{\Delta^2/2} \int_0^\infty x^3 dx \left\{ A_0^2 e^{-\varepsilon x^2 (a+b) + \frac{b}{x^2}} + A_q^2 \frac{\sin^2 Bx}{(\varepsilon x)^6} - b(x^2 + \frac{1}{x^2}) \right\} \]

where \( a = \frac{\Delta^2}{2\varepsilon} \), \( b = \varepsilon \Delta^2/4 \), and \( c = \Delta \sigma \). Two types of integrals appear in Eq. (30). The first is of the form

---

*Strictly speaking, the upper limit on the quadrupole term should be \( Q_{\text{max}} \sim 2\pi/\sigma \). However, due to the rapid convergence of the integrand for large \( Q \) the upper limit has been set to \( \infty \).
where $K_n$ is the modified Bessel function of the second kind of order $n$.

The second integral appearing in Eq. (30) cannot be expressed in closed form. However, the limiting cases of large and small C lead to closed form expressions.

For $C \ll 1$ the $\sin^2$ term varies slowly over the region where the exponential term is nonzero. Applying the method of steepest descent to $I_2$ it is found that

$$I_2 = \frac{(a/\beta)^{1/2}}{(2c^2)} \sin^2[C(B/\alpha)^{1/2}] K_0(2 \sqrt{\alpha \beta}), \ C \ll 1$$

For $C \gg 1$ the $\sin^2$ term oscillates rapidly over the region where the exponential term is nonzero, and hence its average value, $\frac{1}{2}$, may be substituted, yielding

*See Ref. 9.*
The integrals appearing in Eq. (30) may be obtained by substituting
$\alpha = a+b$, $\beta = b$ in $I_1$ and $\alpha = \beta = b$ in $I_2$. The result is

$$\sigma(\omega) \sim (2\pi)^{-4}(m \hbar/3 \epsilon) \cdot e^{\Delta^2/2} \left\{ \frac{A_0^2}{1+\delta} K_2(2b \sqrt{1+\delta}) + \frac{A_0^2}{C^6} I_q \right\}$$

(31)

where

$$\delta = a/b = 4\pi \hbar /\gamma^2$$

and

$$I_q = \int_0^\infty \frac{dx}{x^3} e^{-x^2/2} \sin^2 Cx$$

$$- C^2 K_0(2b) \text{ for } C \ll 1$$

$$- \frac{1}{2} K_1(2b) \text{ for } C \gg 1$$

Replacing all of the factors previously withheld, it is found that

$$\sigma(\omega) = \frac{n_i n_e m \epsilon}{3n^3(2\pi \hbar \gamma)^{3/2}} \sum_{J_i, J_f} \left\{ (\omega-E_{J_f J_i})^2 e^{\frac{\omega-E_{J_f J_i}}{2\hbar \gamma}} \frac{g_i}{2} \right\}$$

$$- (2J_f + 1) e^{-\omega/\gamma T} \left[ \frac{B}{J_i} J_i (J_i + 1) \right]$$

$$\left\{ \frac{A_0}{1+\delta} K_2(2b \sqrt{1+\delta}) \frac{\epsilon}{J_f} + \frac{A_q^2(i, \ell)}{C^6} I_q \right\}$$

(32)
where

\[ b = \frac{(\omega - E_{J_i} J_i)}{4\kappa T} \]

\[ \delta = 4m\kappa T/\gamma^2 \]

\[ C = \Delta \sigma \]

\[ Z = \sum_{J_i} (2J_i + 1) g_i e^{-\frac{B_i}{\kappa T} J_i (J_i + 1)} \]

\( A_0 \), \( A_q \), and \( I_q \) are given in Eqs. (27) and (31) respectively. In obtaining Eq. (32) \( g_f \) has been set equal to \( g_4 \), since the interaction does not change the nuclear spin.

Examining the overlap term in Eq. (32) it is found that it is identical to the results given by Levine.\(^{(4)}\) This is expected, since in the present approximation the molecular overlap term is independent of molecular orientations and hence is formally the same as the rare-gas case. Examining this term further it is found that the peak \( \omega_0 \) in spectrum is given by \( \omega_0 = 6\kappa T[(1+6)^{1/2}-1]^{-1} \) where \( \delta = 4m\kappa T/\gamma^2 \). For low temperatures \( (\kappa T \ll \kappa T_0 = \frac{\gamma^2}{4m}) \alpha \) is independent of temperature, while for high temperatures \( (\kappa T \gg \kappa T_0 = \frac{\gamma^2}{4m}) \alpha \sim (\kappa T)^k \exp \left[-(\omega\kappa T^k/\gamma(\kappa T)^3)\right] \).

The values of \( \kappa T_0 \) for the systems considered here are 100 cm\(^{-1}\), 40 cm\(^{-1}\), and \( \sim 6 \) cm\(^{-1}\) for \( \text{H}_2-\text{He}, \text{H}_2-\text{Ar}, \) and \( \text{N}_2-\text{Ar} \) respectively. Room temperature \( (\kappa T \sim 200 \text{ cm}^{-1}) \) lies in the high temperature region for the cases considered here. Also, the temperature dependence of the location of the peak in the absorption spectrum is given by

\( (\kappa T \ll \kappa T_0) \omega_0 \sim \text{constant independent of temperature for low temperatures, and (} \kappa T \gg \kappa T_0) \omega_0 \sim (\kappa T)^k \) for high temperatures. That is, for low temperatures the peak in the spectrum remains fixed as the
temperature is varied, while for high temperature the peak moves toward higher wave numbers as the temperature is increased (and vice versa).

The width of the absorption spectrum $\Delta \omega$ is approximately $6\kappa T[(1 + T/T_0)^{\frac{3}{2}} - 1]^{-1}$. For low temperatures ($T \ll T_0$), $\Delta \omega \sim 12\kappa T_0$ (i.e., independent of temperature), while for high temperatures ($T \gg T_0$), $\Delta \omega \sim 6(\kappa T_0)^{\frac{3}{2}} (\kappa T)^{\frac{1}{2}}$ (i.e., proportional to the square root of the temperature). These two limiting cases may also be obtained directly from physical arguments. The low temperature case, $T \ll T_0$, implies $P \ll \gamma$ where $P$ is the relative momentum of the colliding particles. The induced moment gives rise to an attractive force which increases the relative kinetic energy from a very small value $(P^2/2m)$ at large distances to a value $\Delta E \sim \gamma^2/2m$ at distances of the order $\gamma^{-1}$. From the uncertainty principle ($\Delta E \Delta t \sim 1$), the transition rate ($\sim \Delta t^{-1}$) and hence the width of the spectrum $\Delta \omega = 2\pi \Delta E = \Delta t^{-1} \sim \pi \gamma^2/m = 4\pi \kappa T_0$ (i.e., independent of temperature). For the high temperature case, $T \gg T_0$, we have $\Delta \omega \sim 2\pi \Delta t^{-1}$. In this case the rate is approximately $(\kappa T/m)^{\frac{3}{2}}$ and the distance approximately $\gamma^{-1}$ (as can be inferred from the uncertainty principle). Therefore, $\Delta \omega \sim 4\pi (\kappa T)^{\frac{3}{2}} (\kappa T_0)^{\frac{1}{2}}$

Numerical estimates of the overlap-induced dipole parameters in $H_2$, $N_2$/rare-gas atom systems and quantitative results for the absorption coefficients for these cases are given in the next section.
IV. ABSORPTION SPECTRUM OF H₂-RARE ATOM AND N₂-Ar MIXTURES

OVERLAP DIPOLE PARAMETERS FOR DIATOMIC MOLECULE/RARE-GAS MIXTURES

In order to obtain numerical results, estimates of the phenomenological parameters $\mu_0$ and $\gamma$ are required. Levine and Birnbaum have determined these parameters for three cases of rare-gas atoms; values are given in the following table.

DIPOLe PARAMETERS FOR RARE-GAS MIXTURES

<table>
<thead>
<tr>
<th>Parameter</th>
<th>System</th>
<th>He-Ne</th>
<th>He-Ar</th>
<th>Ne-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ (Å$^{-1}$)</td>
<td>1.920</td>
<td>1.357</td>
<td>1.446</td>
<td></td>
</tr>
<tr>
<td>$\mu_0$ (debyes)</td>
<td>0.121</td>
<td>0.166</td>
<td>0.223</td>
<td></td>
</tr>
</tbody>
</table>

In order to estimate $\mu_0$ and $\gamma$ for systems considered here it is assumed that $\gamma^{-1}$ is proportional to the collision diameter $\sigma$ occurring in the interparticle potential and that $\mu_0$ is proportional to both the collision diameter and the number of electrons in the outer shells of the component particles. The first assumption seems reasonable, since the range of the induced moment is proportional to the separation of the particles when their electron clouds are overlapping and hence to the collision diameter characteristic of the interparticle potential. The second assumption also seems reasonable since the magnitude of the dipole moment is proportional to the mean separation of charges (which is taken to be $\gamma^{-1}$) and the mean number of electrons involved in the
collision (taken as the electrons in the outer shells of the colliding particles). The inner electrons are too closely bound to be of much consequence to the induced moment.

Hence,

\[ \frac{\mu_o}{N^2} = \text{constant} \]  \hspace{1cm} (33a)

and

\[ \gamma = \text{constant} \]  \hspace{1cm} (33b)

where \( \sigma \) is the collision diameter and \( N \) is the number of electrons in the outer shells of the colliding particles. From the values given in the Table, for example, Eq. (33a) is fairly well satisfied. From Eqs. (33a) and (33b)

\[ \frac{\mu_o_A}{\mu_o_B} = \frac{(N_\sigma)_A}{(N_\sigma)_B} = \frac{(N\gamma^{-1})_A}{(N\gamma^{-1})_B} \]  \hspace{1cm} (34)

where the subscripts refer to two different mixtures. For the three cases given in the Table:

*Since the induced dipole moment is taken as a superposition of two terms (the rare-gas atom interacting with each of the two atomic components of the molecule respectively) the molecular electron contribution to \( N \) is taken as one half of the number of outer shell molecular electrons while all of the outer shell electrons in the rare-gas atom are counted.
1) \[ A = \text{He-Ne} \quad B = \text{He-Ar} \]

\[
\frac{\mu_A}{\mu_B} = 0.73 \\
\frac{(NY^{-1})_A}{(NY^{-1})_B} = 0.71
\]

2) \[ A = \text{He-Ne} \quad B = \text{Ne-Ar} \]

\[
\frac{\mu_A}{\mu_B} = 0.54 \\
\frac{(NY^{-1})_A}{(NY^{-1})_B} = 0.47
\]

3) \[ A = \text{He-Ar} \quad B = \text{Ne-Ar} \]

\[
\frac{\mu_A}{\mu_B} = 0.74 \\
\frac{(NY^{-1})_A}{(NY^{-1})_B} = 0.68
\]

The ratios agree fairly well for these cases.

Values of \( \gamma \) and \( \mu_0 \) for \( H_2\)-He, \( H_2\)-Ar and \( N_2\)-Ar systems are now estimated. Equation (33b) implies \( \gamma_A/\gamma_B = \sigma_B/\sigma_A \). Then

\[
\gamma_{H_2\text{-He}} = (\gamma_{\text{He-Ar}}) \frac{\sigma_{\text{He-Ar}}}{\sigma_{H_2\text{-He}}} = 1.6 \text{ Å}^{-1} \quad (35a)
\]

\[
\gamma_{H_2\text{-Ar}} = (\gamma_{\text{He-Ar}}) \frac{\sigma_{\text{He-Ar}}}{\sigma_{H_2\text{-Ar}}} = 1.2 \text{ Å}^{-1} \quad (35b)
\]

and

\[
\gamma_{N_2\text{-Ar}} = (\gamma_{\text{He-Ar}}) \frac{\sigma_{\text{He-Ar}}}{\sigma_{N_2\text{-Ar}}} = 1.1 \text{ Å}^{-1} \quad (35c)
\]
to two significant figures. In arriving at these results the value of the collision diameter \( \sigma \) was obtained in the usual way as the arithmetic mean of the values for the component gases. \(^{(10)}\) \( \sigma_{\text{H}_2-\text{He}} = 2.46 \text{Å}, \sigma_{\text{H}_2-\text{Ar}} = 3.19 \text{Å}, \sigma_{\text{N}_2-\text{Ar}} = 3.7 \text{Å}, \text{and } \sigma_{\text{He}-\text{Ar}} = 2.91 \text{Å}. \) From Eq. (34),

\[
\left(\mu_o\right)_{\text{H}_2-\text{He}} = \frac{(N\gamma^{-1})_{\text{H}_2-\text{He}}}{(N\gamma^{-1})_{\text{He}-\text{Ar}}} \left(\mu_o\right)_{\text{He}-\text{Ar}} = 0.044 \text{ debyes} \tag{36a}
\]

\[
\left(\mu_o\right)_{\text{H}_2-\text{Ar}} = \frac{(N\gamma^{-1})_{\text{H}_2-\text{Ar}}}{(N\gamma^{-1})_{\text{He}-\text{Ar}}} \left(\mu_o\right)_{\text{He}-\text{Ar}} = 0.16 \text{ debyes} \tag{36b}
\]

and

\[
\left(\mu_o\right)_{\text{N}_2-\text{Ar}} = \frac{(N\gamma^{-1})_{\text{N}_2-\text{Ar}}}{(N\gamma^{-1})_{\text{He}-\text{Ar}}} \left(\mu_o\right)_{\text{He}-\text{Ar}} = 0.27 \text{ debyes} \tag{36c}
\]

The quantitative results for the absorption spectrum follow.

**ABSORPTION SPECTRUM FOR H\(_2\)/RARE-GAS ATOM**

First consider the H\(_2\)-He system. The reduced mass \( \mu \) for H\(_2\)-He is approximately \( 4/3 \text{ amu (atomic mass unit)} \) and the rotational constant \( B \) for H\(_2\) is \( 59.3 \text{ cm}^{-1}. \) \(^{(6)}\) In this example and the following the temperature \( T \) is taken to be of the order of room temperature (i.e., \( kT \approx 200 \text{ cm}^{-1} \)). Using these values for \( B \) and \( kT \) it is easy to see that only the ground and first few (about three) excited rotational states of H\(_2\) are appreciably excited under equilibrium conditions. The nuclear spin of H\(_2\) is \( \frac{1}{2} \), hence the total wave function must be antisymmetric. This implies
that the relative nuclear statistical weights are 1 and 3 for even and odd rotational states respectively. The polarizability of He is $\mu = 0.21 \times 10^{-24}$ cm$^3$ (Ref. 11) and the quadrupole moment of $H_2$ is $Q = 0.49 e^2/\alpha_0^2$ (Ref. 7) where $e$ is the electron charge and $\alpha_0$ is the Bohr radius. Substituting numerical values in Eq. (32) gives (at $\mu T = 200$ cm$^{-1}$)

$$\alpha_{H_2-He}(k) = 1.53 \times 10^{-46} \left[ Q + \sum_{J=0}^{3} S(J) \right] n_1 n_2 (\text{cm}^{-1})$$

(37) where $Q$ is the sum given in Eq. (32) with $J_L = J_F$, $J_L = 0, 1, 2, 3$, $S(J)$ is given by the summand in Eq. (32) with $J = J_L$, $J_F = J_L - 2$, and the wave number is $k$ cm$^{-1}$. In Fig. 1 the contributions of the various branches and the sum of these branches are plotted as a function of the wave number $k$ (i.e., $k = \omega/2\pi$). The Q branch contains contribution from both the overlap and quadrupole-induced dipole moments (the overlap term being $\sim 90$ percent of the Q branch contribution), while only the quadrupole-induced moment contributes to S branches.

As another example the $H_2$-Ar system is considered. The reduced mass $H_2$-Ar is approximately 1.91 amu, and the polarizability of Ar is $\mu = 1.63 \times 10^{-24}$ cm$^3$ (Ref. 12). Substituting numerical values into Eq. (32) gives (at $\mu T = 200$ cm$^{-1}$)

**In all cases discussed here the contribution to $\alpha$ from the O branches was found to be negligible compared to the contributions from the Q and S branches.

** At $\omega = E_{J_L}^{-J_F}$ (resonance) Eq. (32) indicates that the quadrupole contribution becomes very large. $I_\alpha \sim \log (\omega - E_{J_L}^{-J_F})$. Strictly speaking, the rotational transition lines are not infinitely short but have very narrow pressure broadened lines ($\ll 1$ cm$^{-1}$) at room temperature and atmospheric pressure. The absorption at resonance is finite; $I_\alpha \sim \log \left[ (\omega - E_{J_L}^{-J_F})^2 + \gamma^2/4 \right]$ where $\gamma$ is the half width of the line. Due to the lack of knowledge of these line widths, the increase in the absorption spectrum very near a resonance is indicated schematically.
\[ \alpha_{\text{H}_2-\text{Ar}}(k) \approx 3.75 \times 10^{-46} \left[ Q + \sum_{J=0}^{3} S(J) \right] n_1 n_2 (\text{cm}^{-1}) \]  

(38)

In Fig. 2 the contribution of the various branches and the sum of these branches are plotted as a function of wave number. In this case the absorption coefficient is roughly an order of magnitude larger than the H$_2$-He case. This is due mainly to the larger reduced mass of the H$_2$-Ar system and the larger polarizability and induced moment of Ar and H$_2$-Ar system as compared with H$_2$-He.

**ABSORPTION SPECTRUM FOR N$_2$-Ar**

Due to the relatively large rotational constant of H$_2$ (\( B_0 = 59.3 \text{ cm}^{-1} \)), the absorption spectrum, at room temperature, can be resolved into two parts; a pure translational component (Q branch), and a rotation-translation component (S branch). On the other hand, in the case of N$_2$ the rotational constant is much smaller than for H$_2$ (\( B_{N_2} \approx 2 \text{ cm}^{-1} \)), with the result that at room temperature the Q and S branches completely overlap. That is, a resolution of the absorption spectrum of N$_2$/rare-gas atom systems into a translational component and a rotation-translation component is not possible. The N$_2$-Ar system is considered. The reduced mass of N$_2$-Ar is approximately 10.4 amu, the quadrupole moment of N$_2$ is \( \approx 1.1 \text{ ea}^2 \) (Ref. 13). The nuclear spin of N$_2$ is 1, which implies that the relative nuclear statistical weights are 2 and 1 for even and odd rotational states respectively. At room temperature it is necessary to include the ground and about the first twenty excited rotational states in the statistical average. Substituting numerical values into Eq. (32) gives (\( \hbar T \approx 30 \text{ cm}^{-1} \))
Fig. 2—Absorption coefficient for H₂-Ar system at room temperature with contributions of Q and S branches indicated
\[ \alpha_{N_2-Ar}(k) = 2.6 \times 10^{-27} R(k) = n_1 n_2 (\text{cm}^{-1}) \]  

where \( R(k) = Q + \sum_{j=0}^{20} S(j) \). The absorption coefficient for \( N_2-Ar \) is plotted in Fig. 3 (the S branch contributes about 90 percent of the total to \( R(k) \)). Very close (\(< < 1 \text{ cm}^{-1}\)) to a transition line the absorption becomes large, but this occurs in a very narrow region about each line (compared to the spacing between them). Due to lack of knowledge of the relevant line widths, the curve shown in Fig. 3 is the envelope of points away from rotational transition lines. Very close to the resonances the absorption spectrum has a series of very narrow spikes. The contribution of these resonance lines to the integrated absorption coefficient is negligible, since these lines are so narrow; therefore they are not indicated in Fig. 3.

From the \( N_2-Ar \) spectrum an estimate of the absorption in \( N_2-N_2 \) that involves single rotational transitions may be easily obtained. Single (as opposed to double) rotational transitions are those which involve a rotational transition in one of the colliding molecules but not in both. To obtain this, one substitutes the polarizability, reduced mass, the collision diameter for the \( N_2-N_2 \) system, and an overall factor of two for that of the \( N_2-Ar \) system. This method treats one of the \( N_2 \) modules essentially as a rare-gas atom—that is, as having no internal energy levels to excite it. It is found that at the peak of the spectrum (\(~ 100 \text{ cm}^{-1}\), room temperature and atmospheric pressure) the absorption coefficient is of the order of \( 0.8 \times 10^{-6} \text{ cm}^{-1} \). Bosomworth and Gush (2) report an experimental absorption coefficient of \(~ 4 \times 10^{-6} \text{ cm}^{-1} \) at \(~ 100 \text{ cm}^{-1} \). Presumably the reason for this discrepancy of values lies,
Fig. 3—Absorption coefficient for N – Ar system at room temperature
in part, in the failure of our analysis to include the contribution of double rotational transitions.

**ESTIMATES FOR N₂-N₂ ABSORPTION IN THE FAR WINGS**

For frequencies \( \omega \gg \kappa T \) and \( E_j J_i \) the momentum transfer \( Q \) becomes large (\( Q a \gg 1 \) where \( a \) is one-half the internuclear spacing \( \approx 0.5 \) Å for \( N_2 \)). This can be seen as follows: \( Q = |\vec{k}' - \vec{k}| \) and \( k'^2/2m = k^2/2m + \omega - E_j J_i; \) \( k'^2/2m \sim \kappa T \), hence for \( \omega \gg \kappa T \), \( E_j J_i \) implies \( Q \sim (2\mu \omega)^{1/2} \).

Thus for large \( \omega \), \( Q \sim \omega^{1/2} \). At the CO₂ laser wavelength (\( k \approx 10^3 \) cm⁻¹) we find \( Q a \approx 1 \), and hence the overlap moment is angle-dependent (i.e., \( e^{iQ \cdot \vec{a}} \neq 1 \)). Large \( Q \) implies close collisions and hence the quadrupole-induced moments do not contribute. Also, since the overlap moment is angle-dependent the \( N_2-N_2 \) system no longer possesses a center of symmetry and can have a nonzero overlap-induced dipole moment. By a process similar to that which led to Eqs. (35) and (36), it is found that \( (\sigma_{N_2-N_2} = 3.75 \) Å)

\[
\gamma_{N_2-N_2} = (\gamma_{He-Ar}) \sigma_{He-Ar}/\sigma_{N_2-N_2} = 1.05 \text{ Å}^{-1}
\]

and

\[
(\mu_0)_{N_2-N_2} = \frac{(N\gamma^{-1})_{N_2-N_2}}{(N\gamma^{-1})_{He-Ar}} (\mu_0)_{He-Ar} = 0.11 \text{ debyes}
\]

Instead of using Eq. (12), we take the overlap-induced dipole moment of the two molecule system to be

\[
\mathbf{\mu}(r) = \mathbf{\mu}(r_1) + \mathbf{\mu}(r_1') + \mathbf{\mu}(r_2) + \mathbf{\mu}(r_2')
\]
The vectors $\vec{r}_1$, $\vec{r}_1'$, $\vec{r}_2$, and $\vec{r}_2'$ are defined in Fig. 4. Letting $\vec{r}$ be the vector between the centers of mass of the two molecules, and calling the molecular internuclear separation vector $2\vec{a}_1$ and $2\vec{a}_2$, where the subscripts 1 and 2 refer to the two molecules respectively, it is seen that

$$
\begin{align*}
\vec{r} - \vec{a}_2 - \vec{r}_2 - \vec{a}_1 &= 0 \\
\vec{r} + \vec{a}_2 - \vec{r}_1 - \vec{a}_1 &= 0 \\
\vec{r} - \vec{a}_2 - \vec{r}_2' + \vec{a}_1 &= 0 \\
\vec{r} + \vec{a}_2 - \vec{r}_1' + \vec{a}_1 &= 0
\end{align*}
$$

(43)

The integral over the relative coordinate ($\vec{r}$) is the same as before, that is, in place of Eq. (17), it can be shown that

$$
H = \left\langle (JM)^{(1)}_f (JM)^{(2)}_f | \mu_z | (JM)^{(1)}_1 (JM)^{(2)}_1 \right\rangle = A_o Q_z \left[ \int \left| f e^{iQ\cdot\vec{a}_1} \right|_1 \right]^{(1)}
$$

$$
\times \left[ \int \left| f e^{iQ\cdot\vec{a}_2} \right|_2 \right]^{(2)} + \left[ \int \left| f e^{iQ\cdot\vec{a}_1} \right|_1 \right]^{(1)} \left[ \int \left| f e^{-iQ\cdot\vec{a}_2} \right|_2 \right]^{(2)}
$$

+ terms $a_1 \rightarrow -a_1$, $a_2 \rightarrow -a_2$

(44)

where the sub- and superscripts 1 and 2 refer to each of the two molecules respectively and

$$
A_o = \frac{\mu_o^{3/2}}{2} \gamma^4 e^{-Q^2/4\gamma^2}
$$

(45)
Fig. 4—Geometrical relationship for binary molecular collisions
Taking the $z$-axis parallel to the polarization vector of the photon, we expand $e^{i\mathbf{Q} \cdot \mathbf{a}}$ in terms of spherical harmonics; that is,

$$e^{i\mathbf{Q} \cdot \mathbf{a}} = 4\pi \sum_{J=0}^{\infty} i^J j_j(Qa) \sum_{M=-J}^{+J} Y_{J}^{M}(\Omega_a) Y^{*}_{J}(\Omega_Q)$$

(46)

where $Y_{JM}$ are spherical harmonics, and $\Omega_a$ and $\Omega_Q$ are the angular coordinates of the vectors $\mathbf{a}$ and $\mathbf{Q}$ respectively. Because of the symmetry of the $N_2$ molecule about its center of mass, only even $J$'s will contribute (as can be deduced from Eq. (44)). Also, since $Qa \gtrsim 1$ the asymptotic form of the spherical Bessel function is used:

$$j_J(Qa) \sim \sin(Qa - \frac{Jm}{2})/Qa = (-1)^J/2 \sin Qa/Qa \text{ for even } J.$$

The average over the azimithal quantum numbers takes the form

$$\overline{H^2} = (2J+1)^{-1} \left( \begin{array}{c} (2J+1)^{-1} \ 1 \ 1 \\ M_1 \ M_2 \ end{array} \right) \ H^* H$$

(47)

Substituting Eq. (46) into Eq. (44) and obtaining the indicated rotational matrix elements (which can be expressed in terms of Clebsch-Gordan coefficients), the operations indicated in Eq. (47) are then performed. The sums over the $M$ values can be obtained by using the orthogonality conditions on the Clebsch-Gordan coefficients, and it is found that

$$\overline{H^2} = 16Qa^2 \left[ \frac{\sin Qa_1}{Qa_1} \right]^2 \left[ \frac{\sin Qa_2}{Qa_2} \right]^2 (1)^{(1)} (2)^{(2)} F(i,f) F(i,f)$$

(48)

*Since $J$ is even, it can be deduced that $J_1 + J_f$ must be even.*
where

\[ F(i,f) = \left( \frac{2J_i+1}{2J_f+1} \right) \sum_{J(\text{even})} (2J+1)^2 c^2(J_i,J,J_f,00) \]  

(49)

In the following, \( a_1 = a_2 = a \). Replacing Eq. (30), it is found that

\[ \alpha(\omega) \sim (2\pi)^{-4} (4m/3\epsilon a^4) \int_0^\infty \frac{d\Omega}{\Omega} \sin^4 \Omega a \frac{e^{k_2^2}}{e^{-Q^2/2\gamma^2}} \]

\[ = (2\pi)^{-4} (4m/6\epsilon a^4) e^{\Delta^2/2} \int_0^\infty \frac{dQ}{Q^2} \sin^4 \Omega a \]

\[ \times \exp \left[ -Q^2 \left( \frac{1}{2\gamma^2} + \frac{\Delta^2}{4} - \frac{\epsilon a^4}{4Q^2} \right) \right] \]

\[ = (2\pi)^{-4} (4m/6\epsilon a^4) e^{\Delta^2/2} I_1(\omega) \]

where

\[ I_1(\omega) = \int_0^\infty \frac{dx}{x} e^{-[x(A+B) + \frac{B}{x}] \sin^4 \Omega x^{1/2}} \]  

(50)

and

\[ A = \Delta^2/2\gamma^2 = m\omega/\gamma^2 \]

\[ B = \epsilon a^2/4 = \omega/4K_T \]

\[ C = \Delta a = (2m\omega)^{1/2}a \]

For \( \omega \approx C_0^2 \) laser frequency, \( C > 1 \) and hence the \( \sin^4 \) term in the integrand of \( I_1 \) oscillates rapidly over the region where the exponential is nonzero. Hence, \( \alpha(\omega) \) may be used, yielding
\[
I_1 = \frac{3}{8} \int_0^\infty \frac{dx}{x} e^{-[(A+B)x + \frac{B}{x}]} \\
= \frac{3}{4} \left( \frac{1}{1+5} \right) K_0(2B \sqrt{1+5})
\]

where

\[5 = \frac{B}{A} = 4mKT/\gamma^2\]  

Hence it is found for \(\omega \gg \kappa T\), \(E_{J_f J_1}\) that

\[
\alpha_{N_2-N_2}(\omega) \equiv \frac{(n^2/2) \text{ max } \omega_o^2 e^{\omega/2\kappa T} K_0(\omega \sqrt{1 + 4mKT/\gamma^2})}{8(2\pi mKT)^3/8 a^4 (1 + 4mKT/\gamma^2)} \\
\times \left\{ \begin{array}{c}
20 \\
\sum_{J_1=0}^{J_f=J_1+1+\Delta J} e^{-\frac{B}{\kappa T} J_1(J_1+1)} F(1,f) g_1(2J_1+1) \\
\end{array} \right\}^2
\]  

(52)

where

\[
Z = \sum_{J_1=0}^{20} e^{-\frac{B}{\kappa T} J_1(J_1+1)} g_1(2J_1+1)
\]

\(F(1,f)\) is given by Eq. (49), and the molecular density is \(n \text{ cm}^{-3}\). In obtaining Eq. (52) the term \((2J_1+1)e^{-\omega/\kappa T}\) has been dropped since \(\omega \gg \kappa T\). For \(N_2-N_2\) systems the reduced mass is 7 amu and \(a = .505 \text{ A}^{-1}\). Hence from Eqs. (40), (41) and (52) it is found that at room temperature

\*The factor \(n^2/2\) appears in Eq. (52) (instead of \(n^2\)) in order to count each collision once.
\[ \alpha_{N_2-N_2}(k) \approx 4.5 \times 10^{-42} n^2 \left\{ k K_0(3.17k) e^{-k/4} \right\} \text{ (cm}^{-1}) \]  \hspace{1cm} (53)

\[ \approx 3.2 \times 10^{-42} n^2 \left\{ \frac{1}{k} e^{-2.92k} \right\}, \text{ for } k \gg 1/3.17 \]

where \( k = 10^{-2} k \). In obtaining these results only those final states corresponding to \( \Delta J = 0, \pm 2 \) have been included. Since the overlap-induced moment falls off very rapidly with increasing interparticle separation (the moment having a maximum for \( r = \gamma^{-1} < \text{molecular separation} \)), angular momentum considerations imply that \( \Delta J = |J_f - J_i| < 2 \) for \( N_2 \). This can be seen by estimating the order of magnitude of the relative angular momentum of the colliding particles, \( mvr \), with

\[ \gamma \approx (kT/m)^{1/2} r \approx \gamma^{-1} \text{ and noting that the photon contributes one unit of angular momentum. At the CO}_2 \text{ laser wave number } k = 9.44 \text{ it is found that} \]

\[ \alpha(k_{CO}_2) \approx 3.3 \times 10^{-54} n^2 \text{ (cm}^{-1}) \]  \hspace{1cm} (54)

\[ = 2.5 \times 10^{-15} \text{ cm}^{-1} \]

at atmospheric pressure \( (n \approx 2.7 \times 10^{19}) \), which is very small. Even at high pressures the absorption coefficient remains small. For example, at 100 atmospheres the absorption coefficient at 10.6\( \mu \) is \( 2 \times 10^{-11} \text{ cm}^{-1} \).

Finally it is noted that the absorption coefficient is relatively insensitive to temperature; therefore no large change in \( \alpha \) is obtained by varying the temperature.
V. CONCLUSIONS

The results obtained for $N_2$/rare-gas atom and $N_2-N_2$ absorption in the far wing were deduced from a model which assumes a specific functional form for the overlap-induced dipole moment. The dependence on interparticle separation is of the form used by Levine,\(^{(4)}\) while the angular dependence is introduced by assuming that the total overlap moment is a superposition of one particle interacting with each of the atomic components of the molecule respectively, the latter assumption having important effects for close collision, when details of the intermolecular potential become important. For close collisions the assumption of plane waves to describe the relative translational motion of the two particles is offset by assuming that the dipole moment goes to zero for small $r$, i.e., $\mu = \mu_0 \gamma r - \frac{2}{2}$. The factor $\gamma r$ is used to simulate the effect of the scattering wave functions. Levine\(^{(4)}\) has shown that this model is relatively insensitive to the effects of the interparticle potential for wave numbers near the peaks in the rare-gas spectrum (100-400 cm\(^{-1}\)). No experimental results as yet exist for the far wings, and hence the accuracy of an extrapolation of the overlap model into the far wings cannot be ascertained. The results obtained here for $N_2-N_2$ absorption at $k \approx 1000$ cm\(^{-1}\) have been based on an extrapolation of this model. The absorption coefficient obtained is very small and it is not felt that any refinement of the model will produce orders of magnitude changes in $\alpha$. Therefore it is concluded that this mechanism does not play an important role in the atmosphere for the absorption of 10.6$\mu$ radiation by nitrogen.
Consider the integral $I(\omega)$ defined in Eq. (28):

$$I(\omega) = \int_0^\infty dx \ e^{-Ax - \frac{B}{x}} \sin^2 \left( \frac{C}{x} \right)$$

(55)

$A$, $B$ and $C$ are given in Eq. (28). At $x \to 0$ and $x \to \infty$ the integrand approaches zero exponentially and has a maximum for $x = (B/A)^{\frac{1}{2}}$. Upon examining the numerical values of parameters for the cases discussed in the text it can be seen that the $\sin^2 \left( \frac{C}{x} \right)$ term is a slowly varying function of $x$ in the region where the exponential term is nonzero. Hence, upon substituting those values of $x$ in which the exponential term is maximum into the $\sin^2 \left( \frac{C}{x} \right)$ term,

$$I(\omega) = \sin^2 \left[ \frac{C}{(B/A)^{\frac{1}{2}}} \right] \int_0^\infty dx \ e^{-Ax - \frac{B}{x}}$$

$$= - \sin^2 \left[ \frac{C}{(B/A)^{\frac{1}{2}}} \right] \frac{\partial}{\partial A} \left\{ \int_0^\infty dx \ e^{-Ax - \frac{B}{x}} \right\}$$

(56)

$$= -2 \sin^2 \left[ \frac{C}{(B/A)^{\frac{1}{2}}} \right] \frac{\partial}{\partial A} \left\{ K_0 \left[ 2(BA)^{\frac{1}{2}} \right] \right\}$$

The formula

$$\int_0^\infty \frac{dx}{x} \ e^{-Ax - \frac{B}{x}} = 2K_0 \left[ 2(BA)^{\frac{1}{2}} \right]$$

has been used. (9) It can be shown that

$$\frac{\partial K_0 \left[ 2(BA)^{\frac{1}{2}} \right]}{\partial A} = - \left( B/A \right)^{\frac{1}{2}} K_1 \left[ 2(BA)^{\frac{1}{2}} \right]$$

(57)

Hence, from Eqs. (56) and (57),

$$I(\omega) = 2 \sin^2 \left[ \frac{C}{(B/A)^{\frac{1}{2}}} \right] \left( B/A \right)^{\frac{1}{2}} K_1 \left[ 2(BA)^{\frac{1}{2}} \right]$$

(58)
REFERENCES


A quantum mechanical calculation is given for collision-induced absorption in the infrared and far-infrared spectral regions for mixtures consisting of symmetrical diatomic molecules and rare-gas atoms. The induced moment consists of a short-range overlap term and a long-range quadrupole term. Near molecular transition lines, the quadrupole term gives the main contribution to the absorption, while in the far wings, the overlap term is dominant. The Hydrogen(sub 2)-Lelium, Hydrogen(sub 2)-Argon, and Nitrogen(sub 2)-Argon systems are considered, and an estimate is given of the absorption coefficient near 10 millimicrons for Nitrogen(sub 2)-Nitrogen(sub 2) systems.