EFFECT OF MOLECULAR ROTATION ON VIBRATIONAL RELAXATION

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EFFECT OF MOLECULAR ROTATION ON VIBRATIONAL RELAXATION

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Molecular rotation
Vibrational relaxation

This final report for Contract F29601-74-A-0023-0061 studies the effect of molecular rotation on vibrational relaxation. A model for complicated vibrational collisions is developed. Changes in the molecular rotation are of significant importance in vibration collision processes and dominate deactivation processes at thermal velocities.
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DISTRIBUTION OF DOCUMENT CONTROLLED BY KIRTLAND AFB, NM 87117. THIS DOCUMENT INFORMATION SUPPLIED BY AIR FORCE WEAPONS CENTER. THIS FINAL REPORT STUDIES THE EFFECT OF A MODEL FOR COMPLICATED VIBRATIONAL COUPLING OF MOLECULAR ROTATION AND MOLECULAR COLLISIONS DOMINATE DEACTIVATION PROCESSES AT THE
PORT STUDIES THE EFFECT OF MOLECULAR ROTATION ON VIBRATIONAL RELAXATION.

OXYGEN VIBRATIONAL COLLISIONS IS DEVELOPED. CHANGES IN THE RELAXATION ARE OF SIGNIFICANT IMPORTANCE IN VIBRATION COLLISION PROCESSES AND TIVATION PROCESSES AT THERMAL VELOCITIES.
SECTION I

INTRODUCTION

The purpose of this contract is to develop a theory that describes the vibrational-vibrational collision processes within the bending mode of CO₂ and the cross collisions between the bending mode and the symmetric stretch mode. These processes play a vital role in the deactivation of the lower state of the CO₂ laser transition. The technical problems associated with the problem are simply stated. First, CO₂ is a linear triatomic molecule, and it is unclear whether existent theories, which are restricted to diatomic systems, will work. Second, since CO₂ is linear, the bending mode is degenerate, which leads to an ambiguity between vibrational and rotational motion (called "vibrational angular momentum"), which gives rise to a doubling of the bending mode. Because of the uncertainty with how to proceed, a Born theory is used, which is relatively simple conceptually and which can, in principle, lead to the information needed to rationally attack the problem.
SECTION II

TECHNIQUE

In this section, a simple technique is presented for calculating the matrix elements of the intermolecular potential between colliding molecules undergoing vibrational energy transfer or conversion processes. The theory of vibrational relaxation processes in diatomic or polyatomic molecular gases (Refs. 1 and 2) depends critically on these matrix elements. To date, most calculations of (molecular) inelastic collision cross sections have employed a set of questionable approximations in computing the relevant matrix elements (Refs. 3 through 5). While these approximations greatly simplify the calculations, they lack sound justification and in some cases are not valid. For collisions between two molecular systems, most calculations consider only (1) collinear collisions and (2) interactions between nearest neighbors. In addition, the colliding potential is approximated by a simple repulsive exponential.

The first two approximations are kinematic, and their effect is to eliminate all of the angular factors that would otherwise arise in the collision process. To simulate the full set of possible initial collision orientations, a steric factor $P_0 = 1/3$ for each molecule is introduced into the transition amplitude. The second approximation is justified on the grounds that it is the short-range portion of the collision potential that dominates the dynamics of vibrational transfer
and conversion processes. Unfortunately, the steric factor tends to vary with the colliding molecular species, and there does not exist a reliable quantitative theory for calculating this factor for collisions involving nonlinear polyatomic molecules (Ref. 6). The second approximation is clearly invalid for initial collision orientations in which one atom of one molecule is very close to a number of atoms in the second molecule. Furthermore, one cannot investigate the possibility of rotational transfer or conversion occurring simultaneously with vibrational processes. Finally, with regard to these kinematic approximations, it should be noted that Mies (Ref. 7) has carried out a first-principle's calculation using the full-angle-dependent potential for the excitation of hydrogen molecules by helium atoms. His results have raised grave doubts about the validity of items (1) and (2) above.

Assume that the potential can be approximated by

\[ U = \sum_{i,j} U_{i,j} |\vec{r} - \vec{R}_i(a) + \vec{R}_j(b)| \]  

Here, \( U_{i,j} \) is the interaction between atom \( i \) in polyatomic molecule \( A \) and atom \( j \) in polyatomic molecule \( B \), \( \vec{r} \) is the vector between the molecular center of masses, and \( \vec{R}_i(a) \), \( \vec{R}_j(b) \) is the position vector of atom \( i(j) \) from the center of mass of molecule \( A(B) \). Equation (1) assumes that the electronic degrees of freedom are not excited by the collision and in addition, that \( \vec{s} = \vec{r} - \vec{R}_i(a) + \vec{R}_j(b) \) is the only vector direction that is significant. Thus, one neglects (orientational) dipole-dipole forces, etc., which are believed to dominate only the long-range portion of the intermolecular potential (Ref. 8). This part of the intermolecular
force gives rise only to rotational processes and plays no role in vibrational relaxation.

For situations in which the Born approximation applies, the matrix elements of equation (2) are required between the states \(|\vec{k}; \alpha, \beta>\) and \(|\vec{k}'; \alpha', \beta'>\). Here \(\vec{k}(\vec{k}')\) is the relative center-of-mass wave vector before (after) the collision, \(\alpha(\alpha')\) is the initial (final) rotation-vibration state of molecule \(A\), and \(\beta(\beta')\) is the same, but for molecule \(B\). The relevant matrix element is then

\[
<\vec{k}'; \alpha', \beta' | U | \vec{k}; \alpha, \beta> = \sum_{\ell, j} U_{\ell, j}(\vec{q}) \hat{F}_{\ell}^{\alpha} (-\vec{q}) \hat{F}_{\ell}^{\alpha'} (\vec{q})
\]

where \(\vec{q}\) is the momentum transfer vector and \(\hat{F}_{\ell}^{\alpha} (-\vec{q}) = \langle \alpha' | \exp(-i\vec{q} \cdot \vec{R}_{\ell}(\alpha)) | \alpha \rangle\) is the form factor of atom \(i\) between molecular states \(|\alpha>\) and \(|\alpha'>\) at wave vector \(\vec{q}\). These quantities, which also appear in neutron scattering, depend only on the molecular structure, the initial and final rotation-vibration states, and the wave vector \(\vec{q}\). They are independent of the colliding potential and for some transitions may be obtainable from neutron scattering experiments (Ref. 9). The factors \(U_{\ell, j}(\vec{q})\) are the Fourier transform of the atom-atom interaction. This approach separates the internal dynamics of the molecule (i.e., the form factors \(\hat{F}_{\ell}^{\alpha} (-\vec{q})\)) from the center-of-mass motion (i.e., the \(U_{\ell, j}(\vec{q})\)) and is formally similar to the approach taken for inelastic collisions between fast electrons and atoms (Ref. 10). Finally, it should be noted that all of the approximations mentioned above have been avoided.

For most molecular systems one cannot use the Born approximation for collisions occurring at thermal velocities and one must resort to
other techniques. One approach is the Born approximation to the reactance matrix. This technique was used by Burke and Seaton (Ref. 11) to study e-H collision cross sections. Their efforts were successful and can be adapted readily to our problem.

In general, one expects that many partial waves will be required to adequately describe the cross section for inelastic processes. Consequently, one should avoid a partial wave analysis and use the expression

\[
<\vec{k}',\alpha',\beta'|\vec{k},\alpha,\beta> = \frac{-2\varepsilon(2\hbar k/k^2)<\vec{k}',\alpha',\beta'|U|\vec{k},\alpha,\beta>}{1 - i(2\hbar k/k^2)<\vec{k}',\alpha',\beta'|U|\vec{k},\alpha,\beta>}
\]  

(3)

for the transmission matrix.
SECTION III

DISCUSSION

As discussed in Section II, the collision matrix elements decompose into individual atom-atom contributions times a term describing the center-of-mass motion. This leads to a model of collisions that is called the "form factors" model following the usage of this model in nuclear theory. The basic idea is to regard each pair of components (e.g., O and C) to be the same independent of the molecule in which it is situated. In practice, the atmosphere has only four interesting atoms (H, O, C, and N) and the CO$_2$ laser only one more (He); thus, one can describe all collisions of interest with a relatively limited number of parameters. In the case of the collision of CO$_2$ molecules, there are only three collision potentials (O-O, O-C, C-C) that can be determined by comparison with the collisions of CO with itself—a problem that is fairly well developed both theoretically and experimentally.

In the specific approach, a relatively simple problem was chosen, the collision of He with N$_2$, because of its significance to the CO$_2$ laser problem and because it involves one of the simplest of the homonuclear diatomics. Furthermore, it is somewhat analogous to collisions involving hydrogen, which is a system about which a great deal is known. This work was initially developed into a short paper whose material is included in this report. Several purposes were served in the study. It showed that the results of the calculation were
sensible and that calculations were possible. More subtly it demonstrated that quantum mechanical effects were important.

The investigation given in the paper involved relative cross sections, which are used to determine the range but not the magnitude of the potential. For that, one must be able to calculate the absolute cross sections. To do this, it is necessary to unitarize the calculation, i.e., to correct for the fact that probability conservation is violated in the Born approximation. Many unitarization schemes exist and are tested for collisions with hydrogen. The scheme outlined in Section II was tried and proved to be successful for e\textsuperscript{−} and He collisions. However, an unresolved difficulty was encountered. The unitarization procedure involves the computation of all nonunitarized cross sections before the unitarized values can be found. As is seen in Section IV, there are significant contributions from large values of angular momentum transfer (\( \Delta J = 12 \)) and therefore intricate dependences on the \( m \) values (i.e., angular dependences). These numerical problems become worse as \( J \) increases, and there are enormous problems in finding an appropriate cutoff point. At the end of the contract year, this problem had not been solved. However, unitarization may not be as important as first believed, and the difficulties may not be fatal to the scheme.
SECTION IV  

CALCULATIONS

In this section, the method described above is applied to calculate the scattering cross sections for vibrational, rotational, translational collision rates between He and N$_2$. In particular, excitation from the vibrational ground state ($v = 0$) to the $v = 1$ state is considered and the following three features are examined: (1) The effect of the initial rotational state, (2) the importance of angular momentum transfer during a vibrational encounter, and (3) the effects of molecular orientation (i.e., the $M_j$ quantum number) in these collisions.

For the purposes of illustration, the inelastic scattering of He with N$_2$ is treated within the first Born approximation. As inelastic vibrational processes generally involve the short-range portion of the collision potential, which is quite large, the first Born approximation will not yield collision cross sections whose absolute magnitudes are reliable. However, it does yield accurate results for the relative sizes of such cross sections for different inelastic processes. For example, in charge transfer collisions between alpha particles and hydrogen, the ratios of the inelastic cross sections to different final states remain unchanged in going from the Born approximation to much more sophisticated approaches although the magnitude of the various cross sections varies by several factors of 10 (Refs. 12 and 13). Furthermore, experimental results for these ratios are within 10%.
agreement with those predicted by the Born approximation.* For our present purposes, these ratios are sufficient, and our results are qualitatively reliable.

Using the techniques described in Section II, it can be assumed for the purposes of vibrational collisions that the short-range piece of the He-N$_2$ interaction can be written as

\[ U(\vec{r}; \vec{R}_1, \vec{R}_2) = U_1(\vec{r} - \vec{R}_1) + U_2(\vec{r} - \vec{R}_2) \]  

(4)

where $\vec{r}$ is the vector distance between the He atom and the center of mass of the N$_2$ molecule. The vectors $\vec{R}_1$ and $\vec{R}_2$ locate the position of the nitrogen atom in question relative to the molecular center of mass. The quantity $U_1(\vec{r} - \vec{R}_1)[U_2(\vec{r} - \vec{R}_2)]$ is the interaction potential between atom 1[2] and the He atom. For homonuclear diatomic molecules $U_1 = U_2$, and for simplicity a Yukawa type interaction with a range of 0.1 nm has been assumed.

Within the first Born approximation, the inelastic scattering cross section between the (initial) molecular state $|\nu M_j>$ and the (final) molecular state $|\nu' J'M'_j>$ is (the He atom is assumed to remain in its ground state)

\[ \sigma_{\nu M_j \rightarrow \nu' J'M'_j}(k_f) = \left( \frac{\mu}{2\pi\hbar^2k_f} \right)^2 \int \frac{d^2q}{4\pi^2} U_1^2(\vec{q}) \left| \mathcal{F}_{\nu M_j \rightarrow \nu' J'M'_j}(\vec{q}) \right|^2 \]  

(5)

where $\mu$ is the reduced mass of the He-N$_2$ system, and $U_1(\vec{q})$ is the Fourier transform of the Yukawa potential. For a homonuclear diatomic molecule such as N$_2$, the form factor $\mathcal{F}_{\nu M_j \rightarrow \nu' J'M'_j}(\vec{q})$ is given by

---

*Yale data, unpublished.
\[ \mathcal{F}_{\omega M_j \to \omega' M_j'}(\mathbf{g}) = 2\langle \omega' M_j' | \cos(\frac{i}{\hbar} \mathbf{g} \cdot \mathbf{R}) | \omega M_j \rangle \]  

where \( \mathbf{R} \) is the instantaneous vector distance between the two nitrogen atoms (in the \( \text{N}_2 \) molecule). If the axis of quantization is taken parallel to the momentum transfer vector (\( \mathbf{g} \)), then the selection rule \( M_j = M_j' \) follows. A similar situation arises in neutron scattering (Ref. 9). Finally, note that symmetry demands that both \( J \) and \( J' \) be even.
SECTION V

RESULTS

For convenience, this discussion is confined to vibrational excitation (de-excitation) from the ground (first-excited) to the first-excited (ground) vibrational state. In problems involving atmospheric propagation or in typical laser systems one generally finds that a large number of different rotational states are occupied. This is especially true for molecules such as CO₂ or N₂. Consequently, one must investigate the effect of the initial angular momentum state on the collision process. One can readily convince oneself that the best measure of this feature is to examine V-T collision process, i.e., inelastic events in which ΔJ = 0 (but with Δν = 1, of course). In Figure 1 the collision cross section for J = 0 to J = 10 is plotted in arbitrary units for an incoming velocity of ν = 1.14 νₜ, where νₜ is the threshold velocity for such inelastic processes. For J ≥ 4, the total inelastic cross sections scale with the multiplicity of the state, which implies that the probability for inelastic scattering (with ΔJ = 0) is independent of J for the higher rotational states. This feature is unaffected by increasing the initial velocity. In addition, by ν = 1.8 νₜ, the J = 2 state grows until it scales with its multiplicity, and for very high velocities (ν = 4νₜ) the ground rotational states also do the same. In addition, this feature is further reinforced by the fact that, at a distance from threshold,
Figure 1. Plot of normalized calculated cross sections (in arbitrary units) as a function of $J$.

$$\sigma_{J'\rightarrow J}/\sigma_{J'\rightarrow J} = 1 \pm 0.05$$  \hspace{1cm} (7)

for all states through $J = 12$. In equation (7), $\sigma_{J'\rightarrow J}/(\sigma_{J'\rightarrow J})$ is the total inelastic scattering cross section for processes in which $\Delta v = 1$ and the rotational quantum number changes by means of $J \rightarrow J' (J' \rightarrow J')$. (The small deviation from unity is due to small changes in the available phase space for collision.)

Next, the importance of angular momentum in a vibrational-roational-translational (V+R+T) collision is examined. Processes in which $\Delta \omega \neq 0$ represent additional channels through which the vibrational mode can be excited or de-excited and as a result may play an important role in gas kinetics. This will occur if the cross sections for $\Delta \omega \neq 0$ processes are of the same order of magnitude as the $\Delta \omega = 0$ channel. In Figure 2 the quantities

$$R_{1,2-0,\omega}^{(v)} \equiv \frac{\sigma_{1,2-0,\omega}^{(v)}}{18} \sum_{J'=0}^{J} \sigma_{1,2-0,\omega}^{(v)}$$  \hspace{1cm} (8)
Figure 2. Plot of normalized calculated cross sections (in arbitrary units) for de-excitation of \( \text{N}_2 \) by He as a function of velocity.

are plotted for de-excitation of \( \text{N}_2 \) by He as a function of \( v \), the incident velocity. Note that large quantities of angular momentum are readily transferred. In particular, \( \Delta J = 0 \) processes amount to less than 10% of the possible processes for thermal velocities of 1200°K or greater. In addition, for thermal velocities of 300°K, processes with \( \Delta J = 12 \) are of greater importance than those in which \( \Delta J = 0 \). Furthermore, for a cold gas (105°K), processes with \( \Delta J = 14 \) are as significant as those with \( \Delta J = 0 \). Thus, angular momentum transfer plays an extremely important role in vibrational excitation. Note that, except for the \( \mathcal{J} = 2 + \mathcal{J} = 0 \) processes, these effects are not due to multiplicity of the final state but arise from the selection rule.
$\Delta M_J = 0$ state. Therefore only one $M_J$ (i.e., $M_J = 0$) state can participate, which gives rise to an anomalously small cross section. In Figure 3 a similar plot has been made for vibrational excitation including states through $J = 12$. For convenience, the relative cross sections have been plotted as a function of $\nu/\nu_t$, where $\nu_t$ is the threshold velocity for excitation of $N_2$ by He to the first excited vibrational state. The situation is essentially identical, although a much greater range of impact velocities is displayed.

![Figure 3](image)

Figure 3. Plot of normalized calculated cross sections (in arbitrary units) for excitation of $N_2$ by He as a function of velocity.

An examination of Figure 3 reveals that as the incident velocity increases, the $\Delta J = 0$ channel tends to dominate and the probability of creating large quantities of angular momentum tends to decrease. However, even at an incident velocity of $4\nu_t$, the $\Delta J = 0$ channel accounts for only half the possible processes, so $V\!\rightarrow\!R\!\rightarrow\!T$ processes are always of importance. These features, i.e., large $\Delta J$, are quantum mechanical effects, which
would not appear in semiclassical theories. This can be seen from the following semiclassical argument. The torque \( \mathbf{\tau} \) exerted on the \( \text{N}_2 \) molecule is

\[
\mathbf{\tau} = \frac{d\mathbf{J}}{dt} = \mathbf{r} \times \mathbf{F}
\]  

(9)

where \( \mathbf{r} \) is the impact parameter and must lie within the range \( a \) of the force. The change in the rotational motion is approximately \( \frac{\mathbf{a}}{r} \) torque, i.e.,

\[
\delta J = Fa^2/r
\]  

(10)

In equation (7), \( \bar{v} \) is the average of the initial and final velocities. Thus, on the basis of semiclassical considerations one expects that \( \Delta J \) should be small and that the cross sections \( \sigma_{J \rightarrow J'} \), with \( J \neq J' \) should fall off rapidly with increasing velocity. These features tend to appear only at high incident velocities (\( v \sim 4v_t \)), but note that even at \( v = 5.5 v_t \) quantum effects still remain.

Finally, the effect of molecular orientation on \( V-T \) processes is examined. For large values of \( J \), the angular momentum behaves like a classical variable (with regard to the orientation of the molecule) and one can make a correspondence between the \( M_J \) state and a classical angle \( \theta \equiv \cos^{-1}(M_J/J) \), which specifies the orientation of the molecule. Now, for situations in which the incident velocity is slightly greater than the threshold velocity, the momentum transfer vector is nearly parallel to the initial wave vector, i.e., the incident velocity. Since the momentum transfer vector defines the axis of quantization,
it follows that states with $M_J = 0$ correspond to head-on or collinear collisions (see inset in Fig. 4), whereas states in which $M_J = \pm J$ correspond to the case in which the $N_2$ molecule is normal to the incident velocity. In Figure 4, the inelastic collision cross section is plotted in arbitrary units for the $V \rightarrow T$ process with $J = 12$ and $\Delta v = 1$, as a function of $M_J$ (or $\theta$). The large central peak corresponds to the fact that head-on collisions tend to dominate $V \rightarrow T$ rates. Furthermore, the configuration in which the molecule is normal to the incident velocity (i.e., $M_J = \pm J$) does not participate in the collision. These features are expected within a classical model. However, the cross section does not fall off smoothly as $|M_J|$ varies from zero to $J$, but instead displays considerable structure with intermediate peaks. Again, these features arise from quantum effects.

Figure 4. Plot of normalized calculated cross sections (in arbitrary units) as a function of the $M$ quantum number.
In conclusion, changes in the molecular rotation are of significant importance in vibration collision processes and dominate deactivation processes at thermal velocities.
SECTION VI
FIFTH WINTER COLLOQUIUM

As required by the Statement of Work, the Fifth Winter Conference on Quantum Electronics was held from February 1-6, 1975, at Snowmass, Colorado. The emphasis was on electronic transitions, chemical and collisional pumping of electron transitions, and short wavelength optics. Particular emphasis was paid to molecular physics, E-collision pumping, excitation mechanics, short wavelength lasers, and short wavelength resonators.
REFERENCES


