Low energy vibrational relaxation of the diatomic molecule I₂ (B) by collision with He

P. Villarreal, G. Delgado-Barrio, and P. Mareca

Citation: [The Journal of Chemical Physics](#) **76**, 4445 (1982); doi: 10.1063/1.443560

View online: <https://doi.org/10.1063/1.443560>

View Table of Contents: <http://aip.scitation.org/toc/jcp/76/9>

Published by the [American Institute of Physics](#)

PHYSICS TODAY

WHITEPAPERS

ADVANCED LIGHT CURE ADHESIVES

Take a closer look at what these environmentally friendly adhesive systems can do

READ NOW

PRESENTED BY

Low energy vibrational relaxation of the diatomic molecule $I_2(B)$ by collision with He

P. Villarreal,^{a)} G. Delgado-Barrio, and P. Mareca

Instituto de Estructura de la Materia, C.S.I.C., Serrano 119, Madrid-6, Spain
(Received 18 February 1981; accepted 18 May 1981)

A quantum mechanical study of the collision $I_2(B \ ^3\Pi_{0g}, n=1, j=0) + He \rightarrow I_2(B \ ^3\Pi_{0g}, n=0, j') + He$ is reported here. The initial relative kinetic energies are lower than 0.7 cm^{-1} . The $I_2(B)$ diatom is approximated by a harmonic oscillator, while the atom-diatom interaction is described by two atom-atom Morse type potentials. The close-coupling equations for nuclear motion, within the body-fixed frame, have been solved numerically. The partial vibrational relaxation cross sections corresponding to the $J=0, 1, 2$ values of the total angular momentum, have been obtained as a function of energy. When several rotational channels in the $n=1$ vibrational level are introduced in the calculation, resonances do appear with lifetimes of the order of several ps. These resonances enhance the efficiency of the collision. Their positions, at very low energies, cause the dependence of the mean cross section with increasing temperature to be a fast decreasing function, in agreement with experimental results.

I. INTRODUCTION

The dynamics of Van der Waals molecules (VDWM's) has lately given rise to a considerable interest.¹ Several molecules of this type have been obtained following different methods² and some of their properties have been determined.³ In particular, the vibrational predissociation of VDWM's constitutes a clear and unique example of intramolecular vibrational redistribution on a single electronic potential energy surface.⁴⁻⁶ On the other hand, the quasibound states of VDWM's have been shown to be of high interest in the vibrational relaxation of gases at low temperatures⁷ as well as in supersonic beams and jets.⁸

Recently, the experimental vibrational predissociation of the $He \ I_2(B)$ molecule has been reported⁹ and several theoretical models have been used to study this process.¹⁰⁻¹²

The experimental vibrational relaxation of the $I_2(B)$ diatom by collision with He at low temperatures, starting from the excited levels in the range $n=14-25$, have also been studied.^{13,14} The efficiency of this collisional deexcitation must be taken into account when the vibrational distribution of the $I_2(B)$, product of the vibrational predissociation of the $He \ I_2(B)$ VDWM, is determined. The following experimental results have been reported:

(a) With respect to vibrational relaxation, low energy collisions are more effective than those occurring at high energy.^{13,14}

(b) The relaxation process is dominated by the formation of metastable complexes or "orbiting resonances".¹⁴

(c) In a similar way as in the vibrational predissociation of the $He \ I_2(B)$ molecule, the diatom shows a dominant vibrational variation of $\Delta n = -1$,^{13,14} although some transitions with $\Delta n = -2$ have also been reported.^{13b}

Given that all the variants of the forced oscillator

model of V-T transfer lead to a transition probability varying in the same direction with the energy,¹⁴ it seemed to us that the suitable approach to explain the experimental results should include the rotational degrees of freedom. The starting vibrational state for us is the first excited state of the diatom. The reason for this choice is twofold: (i) This level is accurately represented by a harmonic oscillator, and (ii) There is no possibility of transitions with $\Delta n = -2$. For reasons of computational economy, the diatomic initial rotational state considered here has been $j=0$.

The close-coupling equations for the atom-diatom relative motion, in a body-fixed frame of reference, are given in Sec. II. A linearized approximation for the atom-diatom interaction around the diatomic equilibrium distance is described in Sec. III. In the last section, we present the results obtained for the transition probabilities and the vibrational relaxation cross sections for the partial waves $J=0, 1, 2$. These results are given in form of functions of the initial relative kinetic energy and of the rotational channels considered. In this section we also report the mean values for the cross sections according to a Boltzmann distribution, together with the estimated lifetimes for the resonances.

II. CLOSE-COUPPLING EQUATIONS

Once the CM motion has been removed, the Schrödinger equation for a triatomic system $A+BC$, in a given electronic state, is of the form:

$$\left[\frac{-\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1^2}{2\mu R^2} + \frac{-\hbar^2}{2m r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{j^2}{2m r^2} + V_{BC}(r) + V_{A,BC}(R, r, \theta) \right] \psi^{JM} = E \psi^{JM}, \quad (1)$$

where R is the distance between the CM of BC and A ; r is the bond length of BC ; θ is the angle formed by the vectors R and r ; l is the angular momentum operator with respect to the $A-BC$ axis; j is the rotation angular momentum of the diatom BC ; $\mu = m_A(m_B + m_C)/(m_A + m_B + m_C)$ and $m = m_B m_C/(m_B + m_C)$ are the $A-BC$ and $B-C$ reduced masses respectively; and V_{BC} and $V_{A,BC}$ are

^{a)} Permanent address: Departamento de Química-Física y Química Cuántica, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, Madrid-34, Spain.

the interaction potentials between B and C and between A and BC respectively.

Due to the coupling between j and l , the only invariants are the total energy, the square of the total angular momentum J , and its z component in a space-fixed coordinate system. The eigenvalue of J_z is called M .

In the space-fixed frame (SF) of Arthurs and Dalgarno¹⁵ the total wave function, when J and M are fixed, is expanded in the basis Y_{ji}^{JM} of the eigenfunctions of J^2 , J_z , j^2 , and l^2

$$\psi^{JM} = \sum_{j,l} \phi_{jl}(R, r) Y_{ji}^{JM}(\hat{R}', \hat{r}'),$$

where

$$Y_{ji}^{JM}(\hat{R}', \hat{r}') = \sum_{m_j, m_l} C(jlJ; m_j m_l M) Y_{lm_l}(\hat{R}') Y_{jm_j}(\hat{r}')$$

and $\hat{R}' = (\phi_{R'}, \theta_{R'})$ and $\hat{r}' = (\phi_{r'}, \theta_{r'})$ are the angular components of R and r respectively in SF; the Y 's are the spherical harmonic functions; and the C 's are the Clebsch-Gordan coefficients in the Rose notation.¹⁶

When a rotation of the SF system through the Euler angles $w = (\phi_{R'}, \theta_{R'}, 0)$ is performed, keeping the Z axis pointing in the R direction, the body-fixed system (BF) of Curtiss¹⁷ is obtained. The result of this rotation on the Y_{ji}^{JM} functions is

$$Y_{ji}^{JM}(\hat{R}', \hat{r}') = \sum_{\Omega} C(jlJ; \Omega 0 \Omega) D_{\Omega M}^J(\omega) \times Y_{j\Omega}(\hat{r}) \left(\frac{2l+1}{4\pi} \right)^{1/2},$$

where $\hat{r} = (\phi_r, \theta_r)$ is the angular component of r in BF [in this system $\hat{R} = (0, 0)$]. The D 's are elements of the Wigner rotation matrix,¹⁸ and Ω is the component of the total angular momentum J (here it is equal to that of the diatomic rotational momentum j) in the R direction. Choosing the orthonormal set of functions of the type

$$X_{j\Omega}^{JM}(\hat{R}, \hat{r}) = \left(\frac{2J+1}{4\pi} \right)^{1/2} D_{\Omega M}^J(\omega) Y_{j\Omega}(\hat{r})$$

as a basis, the total wave function can be written as

$$\psi^{JM} = \frac{1}{Rr} \sum_{nj\Omega} \phi_{nj\Omega}^{JM}(R) \chi_{nj}(\mathbf{r}) X_{j\Omega}^{JM}(\hat{R}, \hat{r}), \quad (2)$$

where the χ 's are solutions of the equation for the isolated diatom

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 j(j+1)}{2mr^2} + V_{BC}(r) - \epsilon_{nj} \right] \chi_{nj}(r) = 0. \quad (3)$$

The l^2 operator, which is diagonal in j , is the only one coupling different Ω 's. The only nonzero elements

of the matrix representing this operator are¹⁸

$$\begin{aligned} [l^2]_{j\Omega; j\Omega}^{JM} &= \langle X_{j\Omega}^{JM} | l^2 | X_{j\Omega}^{JM} \rangle = \hbar^2 [J(J+1) + j(j+1) - 2\Omega^2], \\ [l^2]_{j\Omega; j\Omega \pm 1}^{JM} &= \langle X_{j\Omega}^{JM} | l^2 | X_{j\Omega \pm 1}^{JM} \rangle = -\hbar^2 [J(J+1) \\ &\quad - \Omega(\Omega \pm 1)]^{1/2} [j(j+1) - \Omega(\Omega \pm 1)]^{1/2}. \end{aligned} \quad (4)$$

Substituting Eq. (2) into (1), and using Eqs. (3) and (4) after multiplication by $\chi_{n'j'} X_{j'\Omega'}^{JM}$, the Schrödinger equation leads to the following system of coupled equations once the integration over r and the angular variables is performed

$$\begin{aligned} \left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_{A,BC}^{nj\Omega}(R) - (E - \epsilon_{nj}) \right] \phi_{nj\Omega}^{JM}(R) \\ + \sum_{\delta=-1}^{+1} \frac{[l^2]_{j\Omega; j\Omega+\delta}^{JM}}{2\mu R^2} \phi_{nj\Omega+\delta}^{JM}(R) \\ = - \sum_{(n', j') \neq (n, j)} V_{A,BC}^{nj\Omega; n' j' \Omega'}(R) \phi_{n' j' \Omega'}^{JM}(R). \end{aligned} \quad (5)$$

In Eq. (5) the unknown ϕ 's describe the atom-diatom relative motion in BF. The potential matrix elements are

$$V_{A,BC}^{nj\Omega; n' j' \Omega'}(R) = \langle X_{j\Omega}^{JM} | \chi_{nj} | V_{A,BC}(R, r, \theta) | X_{j'\Omega'}^{JM} | \chi_{n'j'} \rangle. \quad (6)$$

Because the parity operator commutes with the Hamiltonian [Eq. (1)] it is useful to expand the total wave function by using a basis set of functions which are symmetrical (+) or antisymmetrical (−) under a change of sign in Ω such as:

$$F_{j\tilde{\Omega}}^{JM(+)} = \frac{1}{\sqrt{2}} (X_{j\tilde{\Omega}}^{JM} + X_{j-\tilde{\Omega}}^{JM}), \quad \text{note that } F_{j0}^{JM} = X_{j0}^{JM}, \quad (7a)$$

$$F_{j\tilde{\Omega}}^{JM(-)} = \frac{1}{\sqrt{2}} (X_{j\tilde{\Omega}}^{JM} - X_{j-\tilde{\Omega}}^{JM}), \quad (7b)$$

where $\tilde{\Omega} = |\Omega|$. Hence $\psi^{JM} = \psi^{JM(+)} + \psi^{JM(-)}$,

with

$$\psi^{JM(\pm)} = \frac{1}{Rr} \sum_{nj} \chi_{nj} \sum_{\tilde{\Omega}=0}^{\min(J, j)} \phi_{nj\tilde{\Omega}}^{JM} F_{j\tilde{\Omega}}^{JM(\pm)},$$

whose parity is $(-1)^J$ and $(-1)^{J+1}$ for the $\psi^{JM(+)}$ and the $\psi^{JM(-)}$ functions, respectively. The $F^{(+)}$ and $F^{(-)}$ functions defined in Eq. (7) are never coupled. Therefore substituting Eq. (7) into Eq. (1), two independent systems of equations are obtained. If the entrance channel is specified by means of the set of quantum numbers ($J, M, n=1, j=0, \tilde{\Omega}=0$), only the system of equations for the $\phi_{nj\tilde{\Omega}}^{JM(+)}$ functions must be considered. The solution of these C.C. equations with the boundary conditions

$$\phi_{n' j' \tilde{\Omega}'}^{JM(+)} \xrightarrow{R \rightarrow 0} 0,$$

$$\phi_{n' j' \tilde{\Omega}'}^{JM(+)} \xrightarrow{R \rightarrow \infty} \begin{cases} \frac{1}{\sqrt{K_{n' j'}}} \left(\delta_{nn'} \delta_{jj'} \delta_{\tilde{\Omega}\tilde{\Omega}'} \exp \left\{ -i \left[K_{n' j'} R - (J+j) \frac{\pi}{2} \right] \right\} - S_{n' j' \tilde{\Omega}'; nj\tilde{\Omega}} \exp \left\{ i \left[K_{n' j'} R - (J+j) \frac{\pi}{2} \right] \right\} \right) & \text{open channels} \\ 0 & \text{closed channels} \end{cases} \quad (8)$$

provides the following vibrational relaxation probabilities:

$$P_{n=0, j'; n=1, j=0}^J(E_R) = \sum_{\tilde{n}=0}^{\min(J, j)} |S_{0j', \tilde{n}', 100}^J(E_R)|^2. \quad (9)$$

In a similar way, we can define the probabilities for vibrational relaxation depending on the exit quantum number $\tilde{n}'$,

$$P_{n=0, \tilde{n}'; n=1, \tilde{n}=0}^J(E_R) = \sum_{j'} |S_{0j', \tilde{n}', 100}^J(E_R)|^2. \quad (10)$$

The K 's appearing in the previous relation (8) are the well known wavenumbers and E_R is the initial relative kinetic energy. Thus, the total cross section for vibrational relaxation can be written^{19(b)}

$$\sigma_{n=0 \rightarrow n=1}(E_R) = \frac{\pi \hbar^2}{2\mu E_R} \sum_J (2J+1) \sum_{j'} P_{0j', 10}^J(E_R). \quad (11)$$

III. POTENTIAL ENERGY SURFACE

We consider the motion of the triatomic He+I₂(B) on a single adiabatic potential energy surface which is approximated by the superposition of the intramolecular potential for the "free" diatomic molecule I₂ and the atom-diatom interaction

$$V = V_{I_2}(r) + V_{He-I_2}(R, r, \theta). \quad (12)$$

In this work, the diatomic potential is described as that of an harmonic oscillator

$$V_{I_2}(r) = \frac{1}{2} K_{I_2} (r - \bar{r})^2,$$

where $k_{I_2} = m\omega_{I_2}^2$ is the force constant and $\bar{r}$ is the bond equilibrium distance. The atom-diatom interaction has been specified in terms of two pairwise interactions between the He atom and each one of the I atoms, i.e.,

$$V_{He-I_2}(R, r, \theta) = V_{He-I}(R_1) + V_{He-I}(R_2). \quad (13)$$

The R_1 and R_2 in Eq. (13) are the two He-I distances which are related to the coordinates (R, r, θ) by the trigonometric relations

$$R_1 = \left[R^2 + \left(\frac{r}{2} \right)^2 - Rr \cos \theta \right]^{1/2},$$

$$R_2 = \left[R^2 + \left(\frac{r}{2} \right)^2 + Rr \cos \theta \right]^{1/2}.$$

These atom-atom interactions are described by means of the Morse potentials

$$V_{He-I}(R_i) = D \{ \exp[-2\alpha(R_i - \bar{R}_i)] - 2 \exp[-\alpha(R_i - \bar{R}_i)] \};$$

$$i = 1, 2,$$

where D is the bond dissociation energy, α is the characteristic inverse length, and $\bar{R}_i$ is the equilibrium distance. The following values

$$\omega_{I_2} = 128 \text{ cm}^{-1}; \quad \bar{r} = 3.016 \text{ \AA}; \quad D = 7 \text{ cm}^{-1};$$

$$\alpha = 1.24 \text{ \AA}^{-1}; \quad \text{and } \bar{R}_1 = \bar{R}_2 = 4 \text{ \AA}$$

have been chosen for the parameters. The oscillator parameters have been taken from the literature,²⁰ while the Morse potential parameters are those described in Eq. (36a) of Ref. 10(d).

Usually, the atom-diatom interaction is expanded in terms of the Legendre polynomials

$$V_{He-I_2}(R, r, \theta) = \sum_K v_K(R, r) P_K(\cos \theta), \quad (14)$$

where only the even terms appear due to the fact that the diatom is homonuclear. Once the variation range of θ ($0 - \pi/2$) is divided into a certain number of parts, the v_K coefficients in Eq. (14) were obtained by using the interpolation polynomials. We have only kept the terms in P_0 , P_2 , and P_4 in that expansion. Finally, these coefficients have been linearly approximated by keeping the first two terms in a Taylor expansion of them about the diatomic equilibrium distance $\bar{r}$:

$$v_K(R, r) \simeq v_K(R, \bar{r}) + (r - \bar{r}) \left. \frac{\partial v_K}{\partial r} \right|_{r=\bar{r}}. \quad (15)$$

Therefore, the potential matrix elements appearing in the close-coupling equations of Sec. II are of the type

$$V_{He-I_2}^{n_j \tilde{n}; n' j' \tilde{n}'}(R) = \sum_K \langle \chi_{n_j}(\mathbf{r}) | v_K | \chi_{n' j'}(\mathbf{r}) \rangle \times \langle F_{j\tilde{n}}^{JM(\cdot)} | P_K | F_{j' \tilde{n}'}^{JM(\cdot)} \rangle. \quad (16)$$

After the approximation (15) is used

$$\langle \chi_{n_j} | v_K | \chi_{n' j'} \rangle = v_K(R, \bar{r}) \delta_{nn'} \delta_{jj'} + \left. \frac{\partial v_K}{\partial r} \right|_{r=\bar{r}} \times \langle \chi_{n_j} | (r - \bar{r}) | \chi_{n' j'} \rangle. \quad (17)$$

If the interdiatomic potential V_{I_2} is approximated by a harmonic oscillator, and the rotational dependence is not considered, the following result is obtained^{10(a)}

$$\langle \chi_{n_j} | (r - \bar{r}) | \chi_{n' j'} \rangle = \left(\frac{\hbar}{m\omega_{I_2}} \right)^{1/2} \left[\left(\frac{n}{2} \right)^{1/2} \delta_{n, n'+1} + \left(\frac{n+1}{2} \right)^{1/2} \delta_{n, n'-1} \right]. \quad (18)$$

Now, from Eq. (7) and considering the matrix elements of the Legendre polynomials between $X_{j\tilde{n}}^{JM}$ functions given by Pack,¹⁸ we obtain

$$\langle F_{j\tilde{n}}^{JM(\cdot)} | P_K(\cos \theta) | F_{j' \tilde{n}'}^{JM(\cdot)} \rangle = \delta_{\tilde{n}\tilde{n}'} \left[\frac{1 + (-1)^{j+k-j'}}{2} \right] \left(\frac{2j+1}{2j'+1} \right)^{1/2} \times C(jk j'; 000) C(jk j'; \tilde{n} 0 \tilde{n}). \quad (19)$$

If the collisional energies are lower than the vibrational excitation threshold, the relations (17) and (18) explain the tendency of the diatom I₂ to lose one vibrational quantum after the collision. On the other hand, the relation (19) imposes the following selection rules (a) $\Delta j = 2n - k$, $n = 0, 1, 2, \dots$, (b) $|j - k| \leq j' \leq j + k$.

IV. RESULTS

The close-coupling equations described in Sec. II have been numerically solved according to the standard methods of the reactance matrix propagation.²¹ Once the total angular momentum J is fixed, the elements of the scattering matrix S^J are calculated for each initial

FIG. 1. Transition probabilities $(n=1, j=0) \rightarrow (n=0, j')$ vs the initial relative kinetic energy E_R , for the values 0, 1, and 2 of the total angular momentum J , obtained from the 4×1 calculation.

relative kinetic energy E_R . This magnitude has been divided into 30 steps of $2.19502 \times 10^{-2} \text{ cm}^{-1}$ each, starting at $2.19502 \times 10^{-2} \text{ cm}^{-1}$. (These "unround" values come from the fact that atomic units were used in the calculation.) Because the energies are not high, we have considered for J the values 0, 1, and 2; the diatomic vibrational levels taken into account here have been the ground and the first excited ones. As for the diatomic rotational levels, only the even ones have to be considered.

The number of the rotational levels taken into account defines each calculation. In the following we shall call " $p \times q$ " the calculation with " p " levels corresponding to the ground vibrational state and " q " levels in the excited vibrational state of the diatom.

The quantum number $\tilde{\Omega}$ belongs to the interval $[0, \min(j, J)]$, where $\min(j, J)$ represents the lowest of the j and J values.

For the different partial waves the transition probabilities $(n=1, j=0) \rightarrow (n=0, j')$ are plotted versus E_R in Fig. 1 for the 4×1 calculation. As it was previously mentioned, the diatomic vibro-rotational levels $(n=0, j=0)$, $(0, 4)$, $(0, 6)$, and $(1, 0)$ are the levels included in this calculation. For each partial wave and each E_R value, the higher probabilities correspond to the transition to the $(n=0, j=2)$ level. This fact reflects the dominance of the first anisotropic term $v_2(R, r) P_2(\cos \theta)$ in the expansion of the atom-diatom interaction.

The cross sections for the diatomic vibrational de-excitation $(n=1) \rightarrow (n=0)$, obtained from the 1×1 , 2×1 , 3×1 , and 4×1 calculations, are plotted versus E_R in Fig. 2. These cross sections have been calculated by using the expansion (11) up to the $J=2$ value. The 4×1 calculation does not enhance significantly the cross-section obtained with the 3×1 one. Indeed convergence

is practically achieved by including three rotational levels in the $n=0$ vibrational ground state. Because the transition probabilities increase more slowly than the energy E_R , the cross sections for the vibrational relaxation are decreasing functions. This result is qualita-

FIG. 2. Cross sections for the vibrational de-excitation $n=1 \rightarrow n=0$ vs E_R , obtained from the 1×1 , 2×1 , 3×1 , and 4×1 calculations by using a partial waves expansion up to the $J=2$ value.

FIG. 3. Vibrational de-excitation probabilities $n=1 \rightarrow n=0$ vs E_R , obtained from the 1×2 , 2×2 , and 3×2 calculations, for the values 0, 1, and 2 of the total angular momentum J .

tively correct. However, the decrease with the energy is not steep enough, and the values obtained for the cross sections are too low when compared with the experimental ones.

For the 1×2 , 2×2 , and 3×2 calculations, and for the different partial waves, the probabilities for the transition $(n=1) \rightarrow (n=0)$ are plotted versus E_R in Fig. 3. In these calculations, two rotational levels (i.e., $j=0, 2$) corresponding to the $n=1$ vibrational level have been considered. Again, the transition probabilities increase as we add more rotational levels in the vibrational ground state. For the partial wave corresponding to $J=2$, a resonance in the neighbourhood of $E_R \approx 0.40$ cm⁻¹ appears in all these calculations. By fitting a Lorentzian function to the resonance by means of a least-squares method, we have estimated its lifetime to be about 50 psec. Therefore, the inclusion of the $j=2$ rotational level in the excited $n=1$ vibrational one allows us to observe the formation of a collisional complex with a long lifetime. To explain the existence of this resonance in the $(n=1, j=2)$ vibro-rotational state for $J=2$, we have fitted, by the least-squares method, a Morse function to the diagonal portion of the atom-diatom interaction. This potential has been approximated in the form

$$V_{\tilde{Q}}(R) \approx \sum_{k=0}^4 v_k(R, \tilde{r}) \langle P_k(\cos \theta) \rangle + \frac{\langle I^2 \rangle}{2\mu R_{\min}^2},$$

where $R_{\min}$ is R corresponding to the minimum of the series. So, by using a well known formula which gives the energy levels of a Morse potential,^{10(a)} a bound level for $\tilde{Q}=0$ is found with an initial relative kinetic energy of about 0.43 cm⁻¹. Because the dissociation energy of the $(n=1, j=2)$ vibro-rotational state is about 0.18 cm⁻¹ higher than that corresponding to the $(n=1, j=0)$ one, it is clear that this level should be a triatomic metastable level.

In Fig. 4 we present the cross-sections for the vibrational relaxation $(n=1) \rightarrow (n=0)$ versus E_R obtained from the 3×2 and 3×3 calculations. In the first case, a maximum appears at the energy corresponding to the greatest probability for $J=2$ in Fig. 3. However, in the

FIG. 4. Cross sections for the vibrational de-excitation $n=1 \rightarrow n=0$ vs E_R , obtained from the 3×2 and 3×3 calculations by using a partial waves expansion up to the $J=2$ value.

TABLE I. Vibrational de-excitation probabilities depending on the initial relative kinetic energy and the exit quantum number $\tilde{\Omega}$ for $J=2$ in the 3×3 calculation. (The initial relative kinetic energy E_R ranges in the neighborhood of the resonance obtained in this calculation.)

Energy (cm^{-1})	$P_{\tilde{\Omega}=0}$	$P_{\tilde{\Omega}=1}$	$P_{\tilde{\Omega}=2}$
0.022	0.50×10^{-4}	0.17×10^{-4}	0.47×10^{-5}
0.044	0.70×10^{-3}	0.24×10^{-3}	0.67×10^{-4}
0.066	0.13×10^{-1}	0.41×10^{-2}	0.12×10^{-2}
0.088	0.46×10^{-1}	0.15×10^{-1}	0.46×10^{-2}
0.110	0.73×10^{-2}	0.23×10^{-2}	0.11×10^{-2}
0.132	0.38×10^{-2}	0.11×10^{-2}	0.37×10^{-3}
0.154	0.26×10^{-2}	0.78×10^{-3}	0.27×10^{-3}

3×3 calculation, this maximum is shifted to about 0.08 cm^{-1} . By fitting a Lorentzian function to this new resonance, we have estimated about 350 psec for its lifetime. This high value is of the order of those reported in theoretical calculations^{10c,d} for the $\text{He} \dots I_2(B)$ VDWm at higher excited diatomic vibrational levels.

In an energy range near to that of the resonance obtained from the 3×3 calculation, the dependence of the vibrational de-excitation probabilities on the exit quantum number $\tilde{\Omega}$ is reported in Table I. It is clear that the most probable value after the collision, in the neighbourhood of the resonance, is $\tilde{\Omega}=0$. Therefore, it seems that this resonance corresponds to a bending level^{10d} of the $\text{He} \dots I_2$ complex which is oscillating around the T -shaped equilibrium configuration,^{10c} i.e., $\tilde{\Omega}=0$. In Table II, the probabilities depending on the exit rotational diatomic momentum j are reported. The dominance of the $j=2$ and $j=4$ values can be observed, and their probabilities are very close.

On the other hand, in order to explain the observed shift of the resonance when comparing the 3×2 calculation to the 3×3 one, we have extended this last calculation to higher energies than 0.70 cm^{-1} . In this way, with $J=2$ fixed, we get a second resonance at 0.86 cm^{-1} . In order to analyse the contribution of the ($n=1, j=4$) vibro-rotational state, a model 3×2 calculation with $j=0$ and $j=4$ rotational levels in the $n=1$ vibrational level was performed. This calculation gives the first resonance at 0.66 cm^{-1} for $J=2$. Thus, the resonance shifting seems to be mainly due to an effect of interaction of configurations among two meta-

TABLE II. Vibrational de-excitation probabilities depending on the initial relative kinetic energy and the exit diatomic rotation j for $J=2$ in the 3×3 calculation. (E_R ranges in the neighborhood of the resonance.)

Energy (cm^{-1})	$P_{j=0}$	$P_{j=2}$	$P_{j=4}$
0.022	0.10×10^{-4}	0.31×10^{-4}	0.30×10^{-4}
0.044	0.12×10^{-3}	0.45×10^{-3}	0.44×10^{-3}
0.066	0.18×10^{-2}	0.81×10^{-2}	0.80×10^{-2}
0.088	0.55×10^{-2}	0.30×10^{-1}	0.31×10^{-1}
0.110	0.68×10^{-3}	0.47×10^{-2}	0.49×10^{-2}
0.132	0.27×10^{-3}	0.24×10^{-2}	0.26×10^{-2}
0.154	0.14×10^{-3}	0.17×10^{-2}	0.18×10^{-2}

TABLE III. Mean cross sections for the vibrational de-excitation as functions of the temperature. (I) 3×2 calculation. (II) 3×3 calculation. (III) From Table I of Ref. 9d.

T (K)	I. $\langle \sigma_{1-0} \rangle$ ($\text{\AA}^2$)	II. $\langle \sigma_{1-0} \rangle$ ($\text{\AA}^2$)	III. $\sigma_{v \rightarrow v-1}$ ($\text{\AA}^2$)
0.02	1.07	4.97	
0.04		17.76	
0.05	1.90	21.45	
0.06		23.40	
0.07	2.41	24.18	24.8
0.08		24.21	
0.09	3.19	23.79	
0.10		23.12	
0.11	4.19	22.31	15.5
0.13	6.35	18.79	
0.18	7.74	16.44	8.9
0.20	8.50	15.08	
0.25	9.75	12.32	
0.30	10.32	10.28	
0.40	10.28	7.54	
0.50	9.58	5.82	
0.75	7.56	3.53	
1.00	5.83	2.43	

stable levels and the several continua involved in the collision. This effect causes an asymmetrical separation of those metastable levels which, in the 3×3 calculation, appear about 0.08 cm^{-1} and 0.86 cm^{-1} of E_R , respectively.

In order to calculate mean cross sections for the vibrational relaxation, we have assumed a Boltzmann distribution for the E_R in the temperature range of 0–1 K. The results corresponding to the 3×2 and 3×3 calculations are reported in Table III. In the 3×2 calculation, the maximum of the mean cross section is placed at about 0.35 K with a value of the order of $10 \text{ \AA}^2$. The result for the 3×3 calculation is better, as it shows its maximum at 0.07 K, with a value of about $24 \text{ \AA}^2$. Our results are close to the experimental data reported by Levy *et al.*^{9d} corresponding to higher initial vibrational diatomic states. A late estimation of cross sections for the vibrational relaxation by Levy *et al.*¹³ is of the order of several hundreds of $\text{\AA}^2$. Nevertheless, a fast decreasing behaviour of the mean cross section when the temperature increases from 0.07 K is described by our 3×3 calculation.

We are aware that in order to achieve convergency, it should be necessary to take into account a great number of diatomic rotational channels. Also higher values of the total angular momentum should in principle be considered. However, the increase on the number of rotational channels would render the calculation very expensive without providing any new significant information. In this paper, our most complete calculation has been of the 3×3 type, up to the $J=2$ value. We found a high efficiency of the collisional process due to the existence of resonances as well as the behaviour of the vibrational de-excitation cross section with the temperature.

ACKNOWLEDGMENTS

The original idea of this work came from a series of interesting discussions with Dr. A. Beswick, whom we

also wish to thank for the set of programs that he kindly made available to us. We also acknowledge the helpful comments of Dr. O. Atabeck and Dr. C. Valdemoro on the manuscript.

- ¹(a) G. E. Ewing, *Angew. Chem. Int. Ed., Engl.* **11**, 486 (1972); (b) W. Klemperer, *Ber. Bunsenges. Phys. Chem.* **78**, 129 (1974); (c) G. E. Ewing, *Acc. Chem. Res.* **8**, 185 (1975).
- ²(a) K. C. Janda, J. M. Steed, S. E. Novick, and W. Klemperer, *J. Chem. Phys.* **67**, 5162 (1977); (b) L. Wharton, D. Auerbach, D. H. Levy, and R. Smalley, *Advances in Laser Chemistry*, edited by A. H. Zewail (Springer, New York, 1978), Sec. V.
- ³S. J. Harris, K. C. Janda, S. E. Novick, and W. Klemperer, *J. Chem. Phys.* **63**, 881 (1975).
- ⁴B. L. Blaney and G. E. Ewing, *Annu. Rev. Phys. Chem.* **27**, 553 (1976).
- ⁵R. E. Smalley, L. Wharton, and D. H. Levy, *Acc. Chem. Res.* **10**, 139 (1977).
- ⁶J. A. Beswick and J. Jortner, *Adv. Chem. Phys.* (to be published).
- ⁷G. E. Ewing, *Chem. Phys.* **29**, 253 (1978).
- ⁸G. M. McClelland, K. L. Saenger, J. J. Valentine, and D. R. Herschbach, *J. Phys. Chem.* **83**, 974 (1979).
- ⁹(a) R. E. Smalley, D. H. Levy, and L. Wharton, *J. Chem. Phys.* **64**, 3266 (1976); (b) M. S. Kim, R. E. Smalley, L. Wharton, and D. H. Levy, *J. Chem. Phys.* **65**, 1216 (1976); (c) K. E. Johnson, L. Wharton, and D. H. Levy, *J. Chem. Phys.* **69**, 2719 (1978); (d) W. Sharfin, K. E. Johnson, L. Wharton, and D. H. Levy, *J. Chem. Phys.* **71**, 1292 (1979).
- ¹⁰(a) J. A. Beswick and J. Jortner, *J. Chem. Phys.* **68**, 2277, 2525 (1978); (b) **69**, 512 (1978); (c) J. A. Beswick, G. Delgado-Barrio, and J. Jortner, *J. Chem. Phys.* **70**, 3895 (1979); (d) J. A. Beswick and G. Delgado-Barrio, *J. Chem. Phys.* **73**, 3653 (1980).
- ¹¹S. B. Woodruff and D. L. Thompson, *J. Chem. Phys.* **71**, 376 (1979).
- ¹²R. Ramaswamy and A. E. DePristo, *J. Chem. Phys.* **72**, 770 (1980).
- ¹³Reference 9(d); T. D. Russell, B. M. DeKoven, J. A. Blazy, and D. H. Levy, *J. Chem. Phys.* (to be published).
- ¹⁴(a) J. Tusa, M. Sulkes, and S. A. Rice, *J. Chem. Phys.* **70**, 3136 (1979); (b) M. Sulkes, J. Tusa, and S. A. Rice (preprint).
- ¹⁵A. M. Arthurs and A. Dalgarno, *Proc. R. Soc. London Ser. A* **256**, 540 (1960).
- ¹⁶M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).
- ¹⁷C. F. Curtiss and F. T. Adler, *J. Chem. Phys.* **20**, 249 (1952).
- ¹⁸R. T. Pack, *J. Chem. Phys.* **60**, 633 (1974).
- ¹⁹(a) G. C. Schatz and A. Kuppermann, *J. Chem. Phys.* **65**, 4642 (1976); (b) **65**, 4668 (1976).
- ²⁰G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1966).
- ²¹For a description of the method see, for example, F. A. Gianturco, "Lecture Notes in Chemistry," *The Transfer of Molecular Energies by Collision: Recent Quantum Treatments*, edited by G. Berthier, M. J. S. Dewar, H. Fischer, K. Fukui, H. Hartmann, H. H. Jaffé, J. Jortner, W. Kutznigg, K. Ruedenberg, E. Scrocco, and W. Zeil (Springer, Berlin, 1979), Vol. 11.