

Collision Energy Dependence of Vibrational Transition in $I_2(v=5) + He$

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For many years the collision dynamics of the vibrational energy transfer of I_2 have been studied by various experimental techniques. Most of these studies have employed the vibrational and rotational states of the excited electronic state of I_2 because the experiments within the excited electronic state are relatively easier than those within the ground electronic state. Relatively a few workers have reported the vibrational energy transfer of the ground electronic state of $I_2(X^1\Sigma_g^-)$ which is of experimental¹⁻⁹ and theoretical¹⁰⁻¹³ interest for understanding of fundamental, microscopic kinetic processes.

In recent years Ma *et al.*⁴ have reported the vibrational excitation and deexcitation energy transfer cross sections from the $v=5$ excitation state of $I_2(X^1\Sigma_g^-)$ resulting from collision with He. They have measured the microscopic cross section as functions of kinetic energy using the crossed-beam technique. In their previous papers,^{2,3,6} they interpreted the gross features of their results for I_2+He , I_2+H_2 , and I_2+D_2 collision systems in terms of a simple dynamical mechanism in which most of the vibrational excitations come from nearly impulsive collisions along the steeply repulsive part of the interaction potential playing a dominant role. For $I_2(v=5)+He$ they also interpreted their experimental results using a simple theory.^{14,15} In this simple method calculating the vibrational energy transfer probability by perturbation theory a linear energy dependence is predicted. But the experimental observations for both $\sigma_{5\rightarrow4}$ and $\sigma_{5\rightarrow6}$ exhibit non-linear dependence on collision energy.

The purpose of this work is to study the kinetic energy dependence of the vibrational excitation and deexcitation energy transfer of $I_2(v=5)+He$ collision system using an operator solution of the time dependent Schrödinger equation with both the exact collision trajectory and rotation trajectory numerically from the equation of motion. Also, in order to compare with the cross sections, we have calculated the probability for $v=0 \rightarrow 1$.

Interaction Model and Transition Probability

The potential energy between I_2 and He is expressed as the sum of two I-He interactions:

$$V(R_1, R_2) = \frac{1}{2} D \sum \{ \exp[(R_e - R_i)/a] - 2 \exp[(R_e - R_i)/2a] \}; \quad i = 1, 2 \quad (1)$$

where $R_{1,2} = [R^2 \pm R(d+x)\cos\theta + \frac{1}{4}(d+x)^2]^{1/2}$, R_e is the equilibrium separation to be determined, and D and a are the inter-

action parameters. Here R is the distance between He and the center of mass of I_2 , θ is the angle between the molecular axis and the direction of approach of He, and x is the displacement of I_2 bond distance from its equilibrium value d . When these two atom-atom distances are introduced in Eq. (1), the potential becomes $V(R_1, R_2) = V(R, x, \theta)$. The straightforward expansion of $R_{1,2}$ in the exponent of $V(R, x, \theta)$ yields the interaction potential in the form

$$V(R, x, \theta) = V_0(R, \theta) + V_1(R, \theta)x + \dots \quad (2)$$

where

$$V_0(R, \theta) = \frac{1}{2} D \sum \{ \exp[(R_e - R_{i0})/a] - 2 \exp[(R_e - R_{i0})/2a] \}$$

$$V_1(R, \theta) = \frac{1}{2} D \sum \{ b_{i1} \exp[(R_e - R_{i0})/a] - c_{i1} \exp[(R_e - R_{i0})/2a] \}$$

$$R_{10} = (R^2 - Rd \cos\theta + \frac{1}{4}d^2)^{1/2}, \quad R_{20} = (R^2 - Rd \cos\theta + \frac{1}{4}d^2)^{1/2},$$

$$b_{11} = (R \cos\theta - \frac{1}{2}d) / \left[2a(R^2 - Rd \cos\theta + \frac{1}{4}d^2)^{3/2} \right],$$

$$c_{11} = (R \cos\theta + \frac{1}{2}d) / \left[2a(R^2 - Rd \cos\theta + \frac{1}{4}d^2)^{3/2} \right], \text{ etc.}$$

In the present semiclassical procedure, we consider the translation to be classical and determine the collision trajectory from $V_0(R, \theta)$ given in Eq. (2); *i.e.*, $R \equiv R(t)$ and $\theta \equiv \theta(t)$. Since the x dependent terms in Eq. (2) are responsible for one-quantum vibrational transition, we can express the Hamiltonian in terms of ladder operators (a^+ , a) in the form

$$H(t) = \hbar\omega(a^+ a + \frac{1}{2}) + (\hbar/2m\omega)^{1/2} V_1(t)(a^+ + a), \quad (3)$$

where m and ω are the reduced mass and the angular frequency of I_2 , respectively. Then the time dependent Schrödinger equation can be written as

$$i\hbar \frac{\partial}{\partial t} | \Psi(t) \rangle = H(t) | \Psi(t) \rangle \quad (4)$$

Since the operators a^+ , a , a^+a , and \mathbf{I} form a close family with respect to commutation, we look for the solution of this equation in the form^{16,17}

$$| \Psi(t) \rangle = e^{g_-(t)a^+} e^{g_+(t)a} e^{g_-(t)a^+ a} e^{g_+(t)\mathbf{I}} | i \rangle \quad (5)$$

where \mathbf{I} is the identity operator and $|i\rangle$ represents the initial state $|\Psi(t_0)\rangle$. Here $g(t)$'s are complex-valued functions of time to be determined for the Hamiltonian given by Eq. (4). In Eq. (5), the product of exponential operators plays the role of a time development operators transforming the initial state into various states at time t . After the initial state has evolved into the asymptotic region, the transition probability can be obtained by projecting onto the known asymptotic state $|f\rangle$:

$$P_{i \rightarrow f} = \lim_{t \rightarrow \infty} |\langle f | \Psi(t) \rangle|^2 = \lim_{t \rightarrow \infty} |\langle f | e^{g_3(t)a^\dagger} e^{g_2(t)a} e^{g_1(t)a^\dagger} e^{g_4(t)t} |i\rangle|^2 \quad (6)$$

For $0 \rightarrow 1$, $5 \rightarrow 4$, and $5 \rightarrow 6$, the exponential operation gives the transition probabilities

$$P_{0 \rightarrow 1} = \lim_{t \rightarrow \infty} |g_1(t) e^{g_4(t)^2}|^2 \quad (7a)$$

$$P_{5 \rightarrow 4} = \lim_{t \rightarrow \infty} 5 \left[|1 + 2g_1(t)g_2 + g_1^2(t)g_2^2(t) + \frac{1}{6}g_1^3(t)g_2^3(t) + \frac{1}{120}g_1^4(t)g_2^4(t)| e^{15g_3(t)+g_4(t)} \right]^2 \quad (7b)$$

$$P_{5 \rightarrow 6} = \lim_{t \rightarrow \infty} 6 \left[|1 + \frac{5}{2}g_1(t)g_2(t) + \frac{5}{3}g_1^2(t)g_2^2(t) - \frac{5}{12}g_1^3(t)g_2^3(t) - \frac{1}{24}g_1^4(t)g_2^4(t) + \frac{1}{720}g_1^5(t)g_2^5(t)| g_1(t) e^{15g_3(t)+g_4(t)} \right]^2 \quad (7c)$$

To determine $g(t)$'s, we derive a linear relation between the coefficients of a^\dagger , a , $a^\dagger a$, and \mathbf{I} in the Hamiltonian and those in $\partial|\Psi(t)\rangle/\partial t$ by substituting Eqs. (3) and (5) in Eq. (4):

$$\frac{dg_1}{dt} = -i\omega g_1(t) - i(2\hbar m\omega)^{-\frac{1}{2}} V_1(t) \quad (8a)$$

$$\frac{dg_2}{dt} = -i\omega g_2(t) - i(2\hbar m\omega)^{-\frac{1}{2}} V_1(t) \quad (8b)$$

$$\frac{dg_3}{dt} = -i\omega \quad (8c)$$

$$\frac{dg_4}{dt} = -\frac{i}{2}\omega - i(2\hbar m\omega)^{-\frac{1}{2}} V_1(t) g_1(t) \quad (8d)$$

Thus, g_i 's can be determined by solving four first-order differential equations subject to the initial conditions $g_i(t_0) = 0$. These equations will be solved for $V_1(t)$ numerically using the fourth-order Runge-Kutta method.

The trajectory needed to parameterize V_1 will be obtained from the solutions of the equations of motion $\mu d^2R/dt^2 = -\partial V/\partial R$, $m d^2x/dt^2 = -\partial V/\partial x$, and $I d^2\theta/dt^2 = -\partial V/\partial\theta$ for the initial conditions (at $t=t_0$).¹⁸

$$R(t_0) = 2a \ln \left\{ \cosh(T_0/\sqrt{2}) - \sqrt{(D/E+D)} \sqrt{\sqrt{(D/E)} + (D/E)^2} \right\} \quad (9a)$$

$$x(t_0) = (2E_v/m\omega^2)^{1/2} \sin(\omega t + \delta_0) \quad (9b)$$

$$\theta(t_0) = \Omega t_0 + \theta_0 \quad (9c)$$

where $T_0 = (E/\mu)^{1/2}(t_0/a)$, E is the initial collision energy, E_v is the initial vibrational energy, Ω is the angular velocity (rad/s), and δ_0 and θ_0 are the initial vibrational and rotational phases, respectively. Since the classical expression for the rotational energy of I_2 is $E_R = \frac{1}{2}I\Omega^2$, we express $\Omega = (2E_R/I)^{1/2}$. At a given collision energy E , we take the most probable rotation energy for the present calculation. For example, at $E=0.02$ eV, $E_R=6.51 \times 10^{-3}$ eV.

Results and Discussion

The potential parameters employed in the calculations^{19,20} are $D=52.1$ cm⁻¹, $a=0.278$ Å, and $d=2.6635$ Å. Using the spectroscopic constants given in Ref. 20, we find the vibrational energy spacings ΔE_{10} , ΔE_{54} , and ΔE_{56} to be 213.30, 208.34, and 207.08 cm⁻¹, respectively. We sample 1000 trajectories for various set of δ_0 and θ_0 , and integrate the differential equations for a time step of 0.5 fs or approximately 1/20th the period of I_2 vibration. Trajectories are initiated at a distance of 15 Å, and the equations are integrated until trajectories reach at least the same distance after the collision.

In addition to the collision energy E , the transition probabilities obtained above are dependent on the impact parameter b and the initial phase δ_0 and θ_0 . To calculate transition probabilities, it is necessary to make some modifications to the expressions given above. First, the energy E will have to be symmetrized because it does not represent the collision energy after energy transfer. We take the symmetrized energy²¹ to be $E_s = \frac{1}{4}[(E \pm \Delta E_{if})^{1/2} + E^{1/2}]^2$ for $i \rightarrow f$, where ΔE_{if} is the VT energy transfer for $i \rightarrow f$ and the upper and lower signs are for exothermic and endothermic directions, respectively. Second, we consider the colliding partners approaching each other from noncollinear direction by introducing the impacter parameter. For this consideration, we modify the collision energy as $E(1-b^2/R^{*2})$ in the range $0 \leq b \leq R^*$. Thus, the initial collision energy can be replaced by $E_s(E, b) = \frac{1}{4} \{ [E(1-b^2/R^{*2}) \pm \Delta E_{if}]^{1/2} + [E(1-b^2/R^{*2})]^{1/2} \}^2$, i.e., $P_{i \rightarrow f}(E) \equiv P_{i \rightarrow f}(E, b, \delta_0, \theta_0)$. With these modifications, we average the probability over impact parameters from 0 to R^* and over the initial phases as

$$P_{if}(E) = (2\pi)^{-2} (\pi R^{*2})^{-1} \int_0^{2\pi} d\delta_0 \int_0^{2\pi} d\theta_0 \int_0^{R^*} 2\pi b db P_{if}(E, b, \delta_0, \theta_0) \quad (10)$$

The calculated values of the transition probabilities for $v = 0 \rightarrow 1$, $5 \rightarrow 4$, and $5 \rightarrow 6$ are plotted in Figure 1, where the experimental data are reproduced from Ref. 4. In order to compare with normalized cross sections, we have reduced the calculated probabilities by a factor of 0.08. As shown in Figure 1, the slopes of calculated results are in reasonable agreement with the experimental data. The magnitudes, however, are little different. This discrepancy is understandable from the fact that the calculated results take into account one-dimensional collision trajectory. The actual dynamics even for this collision system is much more com-

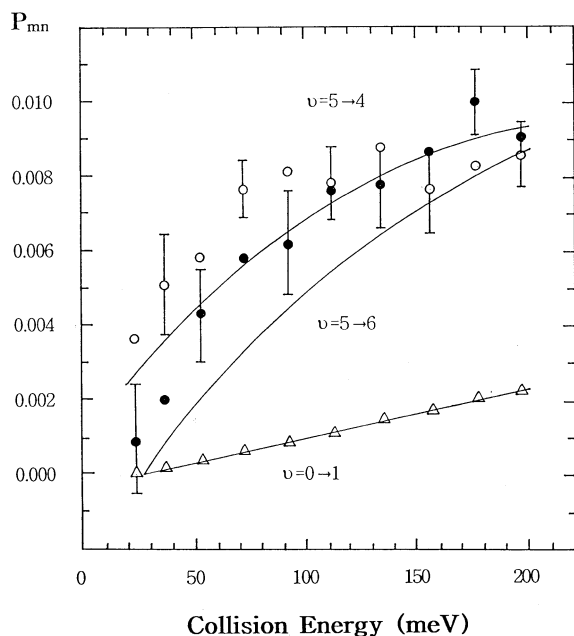


Figure 1. Collision energy dependence of the vibrational transition probabilities. The solid curves are the present calculations. All experimental data are reproduced from Ref. 4. Experimental data: for $\nu = 5 \rightarrow 4$; \bullet for $\nu = 5 \rightarrow 6$; \triangle for $\nu = 0 \rightarrow 1$.

plicated, but the present calculation gives the transition probabilities which agree with experimental data, in despite of one-dimensional collision trajectory and the simple collision model. The other point worth noting is that although there is a large experimental scatter, the experimental result for $\sigma_{5 \rightarrow 4}$ tends to exceed that for $\sigma_{5 \rightarrow 6}$ at the higher end of the collision energies. However, the calculation does not show such a reversal. This result can be explained in terms of the sign of ΔE and the impact parameter b in the symmetrized energy E_s . In this calculation the collision energy is replaced by $E_s - \frac{1}{4} \{ [E(1-y^2) - \Delta E]^{1/2} + [E(1-y^2)]^{1/2} \}^2$, where $y = b/R^*$. In the case of $\nu = 5 \rightarrow 6$ transition, y have to be smaller than $1 - \Delta E/E$ because in the endothermic process the sign of ΔE is negative. As this result also brings about the reduction to the upper integral limit for b in Eq. (10), the calculated probability $P_{5 \rightarrow 6}$ becomes less efficient than $P_{5 \rightarrow 4}$ at the collision energy range of 20-200 meV.

Table 1. Comparison of $P_{5 \rightarrow 6}/P_{5 \rightarrow 4}$ for the collinear collision and the result of Eq. (10)

| E (meV) | $P_{5 \rightarrow 4} / P_{5 \rightarrow 6}$ | |
|---------|---|---------|
| | Eq. (10) | $b = 0$ |
| 40 | 4.19 | 1.63 |
| 60 | 2.11 | 1.24 |
| 80 | 1.62 | 1.11 |
| 100 | 1.41 | 1.05 |
| 120 | 1.29 | 1.02 |
| 140 | 1.21 | 1.00 |
| 160 | 1.17 | 0.99 |
| 180 | 1.14 | 0.99 |
| 200 | 1.11 | 0.99 |

On the other hand, when only collinear collisions are considered, we can set $b = 0$ and define the calculated probability simply as $P(E) = (2\pi)^{-2} \int_0^{2\pi} d\delta_0 \int_0^{2\pi} d\theta_0 P_{ij}(E, \delta_0, \theta_0)$, with $E_s = \frac{1}{4} \{ [E(1-y^2) - \Delta E]^{1/2} + [E(1-y^2)]^{1/2} \}^2$. This expression leads to the reversal between $P_{5 \rightarrow 4}$ and $P_{5 \rightarrow 6}$. The values of $P_{5 \rightarrow 4}/P_{5 \rightarrow 6}$ from Eq. (10) and the collinear ($b = 0$) collision are listed in Table 1. At higher collision energies, $P_{5 \rightarrow 4}/P_{5 \rightarrow 6}$ for the collinear collision is about 0.99, indicating that the collinear treatment is a valid approach. But at all collision energy range the collinear collision probability is nearly two times that obtained from Eq. (10) including $b \neq 0$ collisions. Therefore, it may be too early to conclude the validity of the collinear treatment.

In summary, a semiclassical calculation using an operator solution of the time-dependent Schrödinger equation has been performed for the $I_2(\nu = 5) + \text{He}$ collision system. Even though the collision model and potential used in this study is very simple, it can explain essential features of the vibrational excitation and deexcitation energy transfer of $I_2(\nu = 5) + \text{He}$.

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