

Vibrational energy transfer in a collinear HF-HF collision involving low-lying states in the presence of infrared laser beam

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MS received 9 March 1988, revised 9 January 1989

Abstract. An approximate method for the vibration-vibration (V-V) energy transfer process during collinear collisions of two HF molecules involving low-lying states in the presence of infrared laser beam using a quasi-energy approach (non-perturbative) is presented. The effect of radiation on V-V process is investigated by changing the laser field detuning and power for various values of collision velocities.

Keywords. Dressed states; quasi-energies; Rabi frequency

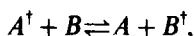
PACS Nos 34·40; 34·80

1. Introduction

The study of atomic and molecular collision process in the presence of radiation field is important due to their involvement in the field of laser-induced chemistry (DeVries *et al* 1980; George 1982; Mohan *et al* 1983), development of powerful laser etc. These processes have been investigated in detail both theoretically (Leasure and Wyatt 1979; DePristo *et al* 1980; Leasure *et al* 1981; Mohan *et al* 1983; Sharma and Mohan 1986a, b; Sharma *et al* 1988) and experimentally (Gudzenko and Yakovlenko 1972; Dingles *et al* 1980).

The advent of chemical and molecular lasers has made it important to understand energy transfer in molecular collisions in the presence of a radiation field. The exchange of quanta of vibrational energy from one molecule to another during a collision frequently plays a crucial role in the mechanism of lasers. This is true not only because lasers have proved to be an important tool in energy transfer research, but also because such processes are relevant to laser operation.

In V-V processes one is concerned with those collisions in which a vibrational quantum of one mode within a molecule may be transferred to another mode, either within the same molecule (intramolecular transfer) or into another molecule (intermolecular transfer). Collisions between two dissimilar diatomic species may produce transfer of the intermolecular energy transfer. For a mixture of two diatomic gases *A* and *B*, the V-V process is represented by



where the dagger denotes vibrational excitation. In many instances of V-V transfer, only one quantum of excitation is considered, although it may happen that higher

levels are important. In an intense laser beam the collision between atoms (molecules) can be modified in several ways. Kroll and Watson (1973) have used the quasi-molecular approach for studying the energy transfer process in a collision of two atoms (molecules) in the presence of a laser field. In their approach the adiabatic modified quasi-molecular states are assumed to be formed when two atoms (molecules) come closer in the presence of laser light. These quasi-molecular states are quite different from the quantum levels of individual atoms (molecules).

In this paper we treat the problem of vibrational energy transfer in collinear HF-HF collisions in the presence of laser beam using a quasi-energy (non-perturbative) approach (Shirley 1965; Zeldovich 1967; Ritus 1967; Ter-Mikaelyan 1979). Here during collisions the quantum levels of individual molecules are assumed to be modified due to laser light and the interaction potential between the molecules is assumed to cause a vibration energy exchange during impact with each other. The impacts between two molecules are assumed to be instantaneous, i.e., time τ_c between collision is shorter than the time of action of the laser τ_{pulse} .

2. Theory

Here we consider the collinear collision of two diatomic hetero molecules $A-B$ and $C-D$ in the presence of an infrared laser beam denoted by an electric field E_0 with frequency ω . Here the distance between the centres of mass of $A-B$ and $C-D$ is x , and the internuclear distances are taken to be y_1 and y_2 respectively.

The Schrödinger equation for the system can be written (in a.u.) as

$$\frac{i\partial\Psi}{\partial t} = (H_0^{AB}(y_1) + H_0^{CD}(y_2) + V(t; y_1, y_2) + V_M^L)\Psi, \quad (1)$$

where

$$H_0^{AB}(y_1) = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial y_1^2} + D_1[1 - \exp\{-\alpha_1(y_1 - y_{eq})\}]^2 \quad (2)$$

and

$$H_0^{CD}(y_2) = -\frac{1}{2\mu_2} \frac{\partial^2}{\partial y_2^2} + D_2[1 - \exp\{-\alpha_2(y_2 - y_{eq})\}]^2 \quad (3)$$

are the Morse oscillator Hamiltonians of the isolated $A-B$ and $C-D$ molecules satisfying the equation

$$H_0^{AB}(y_1)\psi_v(y_1) = E_v^{AB}\psi_v(y_1)$$

and

$$H_0^{CD}(y_2)\psi_v(y_2) = E_v^{CD}\psi_v(y_2),$$

where μ_1, D_1, α_1 and μ_2, D_2, α_2 are respectively the reduced mass, the dissociation energy and the Morse parameter for $A-B$ and $C-D$ molecules, E_v 's are the eigenvalues of the Morse oscillator wavefunctions ψ_v , defined by (in a.u.)

$$E_v = \omega_e[v + \frac{1}{2}] - \beta(v + \frac{1}{2})^2]$$

where $\omega_e\beta$ is an anharmonicity factor.

For the collinear arrangement $A-B+C-D$, atoms B and C are assumed to be

the innermost ones in the collision. The time-dependent interaction potential $V(t; y_1, y_2)$ between them is assumed to be of pure repulsive type (Rapp and Sharp 1963; Rapp and Englander-Golden 1964; Rapp and Kassal 1969) and is defined by

$$V(t; y_1, y_2) = E_T \operatorname{sech}^2(v_0 t/2L) \exp(\gamma_1 y_1/L) \exp(\gamma_2 y_2/L), \quad (4)$$

where

$$E_T = \frac{1}{2} \tilde{m} v_0^2$$

$\tilde{m} = (m_A + m_B)(m_C + m_D)/(m_A + m_B + m_C + m_D)$ is the reduced mass of the system, v_0 the collision velocity and L the potential parameter which determines the steepness of the potential. For the $A - B + C - D$ collinear collision, $\gamma_1 = m_A/(m_A + m_B)$ and $\gamma_2 = m_D/(m_C + m_D)$. Neglecting the polarizability of electron shells of molecules, we write the laser interaction with molecules in the electric-dipole approximation as

$$V_M^L(\mathbf{E}, y_1, y_2) = -\mathbf{d}_1 \cdot \mathbf{E}_0 \cos \omega t - \mathbf{d}_2 \cdot \mathbf{E}_0 \cos \omega t, \quad (5)$$

where \mathbf{d}_1 and \mathbf{d}_2 are dipole moments of molecules $A - B$ and $C - D$ respectively.

The total wavefunction $\psi(t, y_1, y_2)$ of the system is expanded in terms of the dressed states of the individual molecules. If $\Phi_J^{AB}(y_1)$ and $\Phi_n^{CD}(y_2)$ represent the dressed states of the molecules $A - B$ and $C - D$, we can write the total wavefunction of the system as

$$\psi(t, y_1, y_2) = \sum_J \sum_n C_{Jn}^{(0)} \Phi_J^{AB}(y_1) \Phi_n^{CD}(y_2), \quad (6)$$

where the dressed states $\Phi_J^{AB}(y_1)$ and $\Phi_n^{CD}(y_2)$ satisfy the following equations

$$(H_0^{AB}(y_1) + \mathbf{d}_1 \cdot \mathbf{E}_0 \cos \omega t) \Phi_J^{AB}(y_1, t) = i \frac{\partial \Phi_J^{AB}}{\partial t}(y_1, t) \quad (7)$$

and

$$(H_0^{CD}(y_2) + \mathbf{d}_2 \cdot \mathbf{E}_0 \cos \omega t) \Phi_n^{CD}(y_2, t) = i \frac{\partial \Phi_n^{CD}}{\partial t}(y_2, t). \quad (8)$$

Substituting (6) into (1) and using the orthogonality conditions for the dressed states of the molecules, we obtain the following set of coupled differential equations

$$i \frac{\partial C_{rs}}{\partial t} = \sum_J \sum_n C_{Jn}(t) B_{rs, Jn}(t) \quad (9)$$

where

$$B_{rs, Jn}(t) = \int_0^\infty \int_0^\infty dy_1 dy_2 \Phi_r^{AB}(y_1) \Phi_s^{CD}(y_2) V(t; y_1, y_2) \Phi_J^{AB}(y_1) \Phi_n^{CD}(y_2)$$

Using (4), we have

$$B_{rs, Jn}(t) = E_T \operatorname{sech}^2\left(\frac{v_0 t}{2L}\right) \left\langle \Phi_r^{AB}(y_1) \left| \exp\left(\frac{\gamma_1 y_1}{L}\right) \right| \Phi_J^{AB}(y_1) \right\rangle \\ \times \left\langle \Phi_s^{CD}(y_2) \left| \exp\left(\frac{\gamma_2 y_2}{2}\right) \right| \Phi_n^{CD}(y_2) \right\rangle \quad (10)$$

The solution of the above coupled equations gives the required probability for the V-V transfer process. In §3 we discuss the quasi-energy approach and describe the approximate solution of coupled equations (9).

3. Dressed states of a molecule using the quasi-energy approach and approximate solution of coupled equations

In the quasi-energy formalism (Shirley 1965; Ritus 1967; Zeldovich 1967; Ter-Mikaelyan and Melikyan 1970; Zeldovich 1973) dressed states of the molecule in the presence of a laser beam can be written as

$$\Phi_s = \exp[-i(E_1 + \lambda_s)t] \sum_{m=1}^k a_m^s \psi_m \exp[-i(m-1)\omega t], \quad (11)$$

where $\{\psi_m\}$ are the Morse oscillator wavefunctions (or bare states), $\{a_m^s\}$ are amplitudes corresponding to the bare states $\{\psi_m\}$ and $\{\lambda_s\}$ are defined as the quasi-energies. For the four-level system k is equal to 4 and the eigenvalues $\{\lambda_s\}$ and the corresponding eigenvectors $\{a_m^s\}$ are obtained from the secular equations

$$-\lambda_s a_1^s + E_{12} a_2^s + E_{13} a_3^s = 0, \quad (12)$$

$$E_{21} a_1^s + (\varepsilon_{21} - \lambda_s) a_2^s + E_{23} a_3^s = 0, \quad (13)$$

$$E_{32} a_1^s + (\varepsilon_{31} - \lambda_s) a_3^s + E_{34} a_4^s = 0, \quad (14)$$

$$E_{34} a_3^s + (\varepsilon_{41} - \lambda_s) a_4^s = 0, \quad (15)$$

where

$$E_{ij} = -(\mathbf{E}_0/2) \langle \psi_i | d | \psi_j \rangle$$

are the Rabi frequencies between adjacent molecular states, $|\mathbf{E}_0|$ is the amplitude of the laser field and $\varepsilon_{pq} = E_p - E_q - (p-1)\omega t$ is the field detuning term. Substituting these eigenvalues and eigenvectors in (11), we find the corresponding dressed states.

Considering V-V transfer between molecules $A-B$ and $C-D$ having two levels each, we have $J, n=0$ and 1. With these values for J and n , (9) reduces to 4×4 coupled equations, which in matrix notation can be written as

$$i\dot{\mathbf{C}}(t) = \mathbf{Q}(t)\mathbf{C}(t) \quad (16)$$

where $\mathbf{C}(t)$ is the column matrix given by $\{C_{00}(t), C_{01}(t), C_{10}(t), C_{11}(t)\}$ and

$$\mathbf{Q}(t) = \begin{pmatrix} B_{00,00} & B_{00,01} & B_{00,10} & B_{00,11} \\ B_{01,00} & B_{01,01} & B_{01,10} & B_{01,11} \\ B_{10,00} & B_{10,01} & B_{10,10} & B_{10,11} \\ B_{11,00} & B_{11,01} & B_{11,10} & B_{11,11} \end{pmatrix} \quad (17)$$

and the matrix elements $B_{rs,Jn}(t)$ are given by (10). Equation (9) represents a set of first-order differential equations in time t , therefore its approximate solution can be written as (Takayanagi 1952; Callaway and Bauer 1965; Sharma and Mohan 1986)

$$\mathbf{C}(t) = \exp\left[-i \int_{-\infty}^t \mathbf{Q}(t') dt'\right] \mathbf{C}(-\infty). \quad (18)$$

The above solution is exact if $\mathbf{Q}(t)$ and $\int_{-\infty}^t \mathbf{Q}(t') dt'$ commute (Callaway and Bauer 1965). We are interested in the transition probability at $t = +\infty$, therefore in this

limit (18) reduces to

$$C(+\infty) = \exp \left[-i \int_{-\infty}^{+\infty} Q(t') dt' \right] C(-\infty), \quad (19)$$

which we now solve using the diagonalization technique (Callaway and Bauer 1965; Sharma and Mohan 1986).

Let U be a unitary matrix which diagonalizes the matrix M given by

$$M = \int_{-\infty}^{+\infty} Q(t') dt' \quad (20)$$

i.e.

$$M_D = U^\dagger M U, \quad (21)$$

where M_D is a diagonalized matrix.

We use the following property of the diagonalized matrix during exponentiation, i.e.

$$[\exp[-iM_D]]_{ij} = \delta_{ij} \exp[-iM_D]_{ii}. \quad (22)$$

Using (21) and (22) in (20) we obtain the $\exp[-iM]$ as

$$\exp[-iM] = U \exp[-iM_D] U^\dagger. \quad (23)$$

Substitution of (23) in (19) and matrix multiplication yield the required value of the transition amplitude and transition probabilities.

4. Results and discussion

Here we take an example of V-V energy transfer between HF molecules. The dressed states of HF molecule with only two low-lying vibrational states ($J=0$ and 1) are calculated using the quasi-energy approach as described in §3. The dipole matrix element between adjacent levels was calculated using Morse oscillator wavefunctions (Mies 1964; Clark and Dickinson 1973). The parameters for HF molecule are given in table 1 (Huber and Herzberg 1979) in which d_0 is the dipole moment of the HF molecule when the displacement of the bond length of the HF molecule is zero and d_1 is the first derivative of the dipole moment with respect to displacement of the bond length.

Table 1. Molecular parameters for HF-molecule in $1\Sigma^+$ state.

$\omega_e(\text{cm}^{-1})$	4138.52
$\omega_e x_e(\text{cm}^{-1})$	90.069
$\beta_e(\text{cm}^{-1})$	20.4
$\alpha_e(\text{cm}^{-1})$	0.789
$D_e(\text{cm}^{-1})$	2.2×10^{-3}
$\gamma_e(\text{\AA})$	1.7320
$d_0(D)$	1.82
$d_1(D/\text{\AA})$	0.7876

The quasi-energies, i.e. the $\{\lambda_s\}$ and the corresponding eigenfunctions $\{a_m^s\}$ were calculated by diagonalizing the characteristic equation of the quasi-energy matrix, i.e. equations (12)–(15), using a standard routine. These $\{\lambda_s\}$ and $\{a_m^s\}$ are then substituted into (11) to obtain the dressed states of the system. The dressed states thus obtained are substituted into (10) to obtain the coupling matrix elements $B_{rs,jn}(t)$. The vibrational-matrix elements of the type $V_{sn} = \langle \psi_s | \exp(\gamma y/L) | \psi_n \rangle$ involved in the coupling matrix $B_{rs,jn}$ are known in a closed form (Mies 1964; Clark and Dickinson 1973).

In order to solve the coupled equations (9) by the procedure described in §3, we have to determine the value of \mathbb{M} governed by (20). The integration over time in \mathbb{M}_{ij} was done analytically and one such element i.e. \mathbb{M}_{11} is obtained in the following form

$$\begin{aligned} \mathbb{M}_{11} &= \int_{-\infty}^{+\infty} B_{00,00}(t') dt' \\ &= E_T \left[\{ (a_1^0)^4 V_{11}^{AB} V_{11}^{CD} + (a_1^0)^2 (a_2^0)^2 (V_{11}^{AB} V_{11}^{CD} + V_{12}^{AB} V_{21}^{CD} \right. \\ &\quad + V_{21}^{AB} V_{12}^{CD} + V_{22}^{AB} V_{11}^{CD}) + (a_2^0)^4 V_{22}^{AB} V_{22}^{CD} \} \times \frac{4\pi L^2}{v_0^2} \\ &\quad + \{ (a_1^0)^3 a_2^0 V_{11}^{AB} V_{12}^{CD} + (a_1^0)^3 a_2^0 V_{12}^{AB} V_{11}^{CD} + a_1^0 (a_2^0)^3 V_{12}^{AB} V_{22}^{CD} \\ &\quad + (a_1^0) (a_2^0)^3 V_{22}^{AB} V_{12}^{CD} \} \frac{4\pi L^2}{v_0^2} \operatorname{csch} \left(\frac{\pi \omega L}{v_0} \right) + \{ (a_1^0)^3 a_2^0 V_{11}^{AB} V_{21}^{CD} \\ &\quad + (a_1^0)^3 a_2^0 V_{12}^{AB} V_{11}^{CD} + (a_2^0)^3 a_1^0 V_{22}^{AB} V_{21}^{CD} \} \frac{4\pi L^2}{v_0^2} \operatorname{csch} \left(\frac{2\pi \omega L}{v_0} \right) \\ &\quad + \{ (a_1^0) (a_2^0)^3 V_{12}^{AB} V_{22}^{CD} \} \frac{8\pi L^2}{v_0^2} \operatorname{csch} \left(\frac{4\pi \omega L}{v_0} \right) \\ &\quad \left. + \{ (a_1^0)^2 (a_2^0)^2 V_{21}^{AB} V_{12}^{CD} \} \frac{8\pi L^2}{v_0^2} \operatorname{csch} \left(\frac{8\pi \omega L}{v_0} \right) \right], \end{aligned}$$

where

$$V_{ij}^{AB} = \left\langle \psi_i \left| \exp \left(\frac{\gamma_1 y_1}{L} \right) \right| \psi_j \right\rangle$$

$$V_{ij}^{CD} = \left\langle \psi_i \left| \exp \left(\frac{\gamma_2 y_2}{L} \right) \right| \psi_j \right\rangle$$

Next we diagonalized \mathbb{M} to obtain \mathbb{M}_D and \mathbb{U} , where \mathbb{M}_D is the diagonalized matrix and \mathbb{U} is the unitary matrix which diagonalizes \mathbb{M} . Substitution of \mathbb{M}_D , \mathbb{U} , \mathbb{U}^\dagger and $\mathbb{C}(-\infty)$ into (19) gives in the required $\mathbb{C}(+\infty)$ i.e. final transition amplitude matrix.

We assume that initially both the molecules are in the ground state i.e. $C_{00}(-\infty) = 1$, $C_{01}(-\infty) = C_{10}(-\infty) = C_{11}(-\infty) = 0$, therefore $P_{00 \rightarrow n_1 n_2} = |C_{n_1 n_2}(+\infty)|^2$ represents the collision-aided vibration-vibration energy transfer process for the transition $0 \rightarrow n_1$ in $A - B$ and $0 \rightarrow n_2$ in $C - D$.

In tables 2 and 3 we have shown the variation of transition probabilities $P_{00 \rightarrow n_1 n_2}$ with frequency of the laser beam for laser intensities $I = 10^7$ and 10^8 W/cm² and collision velocity $v_0 = 0.01$ a.u. It is clear from table 2 that as the frequency of the

Table 2. Frequency variation of transition probability $P_{00 \rightarrow n_1 n_2}$ for collision velocity $v_0 = 0.01$ a.u. and intensity $I = 10^7$ W/cm².

Frequency ω (cm ⁻¹)	Transition probability			
	$P_{00 \rightarrow 00}$	$P_{00 \rightarrow 01} \times 10^{-6}$	$P_{00 \rightarrow 10} \times 10^{-6}$	$P_{00 \rightarrow 11}$
3952	0.9824	0.4338	0.4338	0.01309
3953	0.9822	0.4630	0.4651	0.0142
3954	0.9821	0.5073	0.5071	0.0151
3955	0.9811	0.5829	0.5821	0.01625
3956	0.9810	0.7386	0.7214	0.01639
3957	0.9815	1.214	1.254	0.01694
3958	0.1387×10^{-3}	7.973	7.921	0.9923
3958.25	0.2742×10^{-3}	901.12	901.15	0.9924
3959	0.9072	1.384	1.321	0.08698
3960	0.9582	0.0152	0.0148	0.0390
3961	0.9605	0.0378	0.0372	0.02796

Table 3. Frequency variation of transition probability $P_{00 \rightarrow n_1 n_2}$ for collision velocity $v_0 = 0.01$ a.u. and intensity $I = 10^8$ W/cm².

Frequency ω (cm ⁻¹)	Transition probability			
	$P_{00 \rightarrow 00}$	$P_{00 \rightarrow 01} \times 10^{-6}$	$P_{00 \rightarrow 10} \times 10^{-6}$	$P_{00 \rightarrow 11} \times 10^{-1}$
3952	0.9839	0.4981	0.4981	0.1609
3953	0.9818	0.9828	0.9827	0.1616
3954	0.9818	1.209	1.219	0.1619
3955	0.9817	1.627	1.614	0.17495
3956	0.9795	2.557	2.557	0.18953
3957	0.1154×10^{-6}	6.216	6.227	9.925
3958	0.1191×10^{-6}	852.7	852.5	9.927
3958.25	0.1192×10^{-6}	163.96	162.91	9.973
3959	0.2154×10^{-3}	31.18	31.17	9.910
3960	0.9675	2.465	2.214	0.1068
3961	0.9720	0.5199	0.5187	0.06469

laser beam is increased from $\omega = 3952$ cm⁻¹, the transition probability $P_{00 \rightarrow 11}$ increases upto $\omega = 3958.25$ cm⁻¹. This happens because near $\omega = 3958.2$ cm⁻¹, the laser detuning ϵ_{21} ($= E_2 - E_1 - \omega$) is at a minimum with respect to the ground and first excited energy level spacing of the HF molecule. However, with further increase in the frequency, the probability $P_{00 \rightarrow 11}$ decreases upto $\omega = 3961$ cm⁻¹. Similar behaviour near the resonant frequency is also shown in table 3 at laser intensity $I = 10^8$ W/cm².

The effect of intensity on the transition probabilities $P_{00 \rightarrow n_1 n_2}$ at $\omega = 3952$ cm⁻¹ is shown in table 4. It is seen that as the intensity increases from $I = 10^7$ to $I = 10^{10}$ W/cm², the transition probability $P_{00 \rightarrow 11}$ increases from 0.01309 to 0.9929. This is due to the fact that the full width at half maximum (FWHM) increases as laser intensity is increased as this is directly related to the Rabi frequency.

Table 5 shows the variation of various inelastic transition probabilities, e.g., (0, 0) to (0, 1), (1, 0) and (1, 1) with collision velocity v_0 for $\omega = 3952$ cm⁻¹ and laser intensity

Table 4. Intensity variation of transition probability $P_{00 \rightarrow n_1 n_2}$ for velocity $v_0 = 0.01$ a.u. at $\omega = 3952 \text{ cm}^{-1}$

Intensity I (W/cm^2)	Transition probability			
	$P_{00 \rightarrow 00}$	$P_{00 \rightarrow 01} \times 10^{-6}$	$P_{00 \rightarrow 10} \times 10^{-6}$	$P_{00 \rightarrow 11}$
10^7	0.9824	0.4338	0.4338	0.01309
10^8	0.9879	0.4981	0.4981	0.01609
10^9	0.6071	3.3228	3.1248	0.3872
10^{10}	0.004978	1058.0	1092.1	0.9929

Table 5. Variation of transition probabilities $P_{00 \rightarrow n_1 n_2}$ with collision velocity v_0 (in a.u.) For $\omega = 3952 \text{ cm}^{-1}$ and $I = 10^8 \text{ W}/\text{cm}^2$.

Velocity v_0	Transition probability			
	$P_{00 \rightarrow 00}$	$P_{00 \rightarrow 01}$	$P_{00 \rightarrow 10}$	$P_{00 \rightarrow 11}$
0.001	0.9988	0.4685×10^{-10}	0.4685×10^{-10}	0.1650×10^{-2}
0.01	0.9839	0.4981×10^{-6}	0.4981×10^{-6}	0.1609×10^{-1}
0.1	0.9984	0.1035×10^{-3}	0.1099×10^{-3}	0.3699×10^{-2}
1.0	0.5567	0.6683×10^{-1}	0.6583×10^{-1}	0.3095

$I = 10^8 \text{ W}/\text{cm}^2$. It is found that the probability flows back and forth between (0, 0) to (1, 1) transition as the collision velocity is varied from $v_0 = 0.001$ to 1.0 a.u. For (0, 0) to (0, 1) or (1, 0), however, the transition probability increases as the collision velocity v_0 is increased. This is an interesting result and is expected because for identical molecules the detuning ϵ_{21} at $\omega = 3952 \text{ cm}^{-1}$ is least for the (0, 0) to (1, 1) transition as compared to (0, 0) to (1, 0) or (0, 1) transitions. Furthermore, it may be shown that at resonance, the transition probability $P_{01 \rightarrow 10}$ achieves a peak at a low velocity v_0 because at low v_0 , the probability for resonant exchange increases at v_0^2 . However, when the velocity is increased further the symmetrical nature of the interaction between the identical molecules causes the probability to flow back and forth between (0, 0) and (1, 1) transitions. This type of oscillatory behaviour of probability for high velocity has also been observed by others (Rapp and Sharp 1963; Rapp and Kassal 1969).

5. Conclusion

We have presented a simple approximate method for the transfer process between identical molecules in the presence of a laser beam. Further, we have clearly shown the influence of various radiation field parameters on the V-V transfer process. Finally this theory can be easily extended to V-V transfer processes for any two heteronuclear molecules.

Acknowledgements

We are thankful to Prof S N Biswas for constant encouragement during this work. Two of us (BS) and (VP) are grateful to CSIR, New Delhi for financial assistance in the form of fellowships. One of the authors (MM) is thankful to the Department of Science and Technology, New Delhi for financial support.

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