Semiclassical Calculation of the Vibrational Transition Probabilities of Diatomic Molecules in Collision. The Effect of Vibrational Anharmonicity

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The multi-state semiclassical method proposed by Sharp and Rapp for calculating the vibrational transition probabilities of harmonic oscillators in collision was extended to Morse oscillators. Model calculations have been carried out for the excitation of a vibrational ground-state hydrogen molecule colliding with a helium atom at varying relative velocity. It has been shown that the Morse oscillator model gives greater transition probabilities than the corresponding harmonic oscillator model.

The basic problem in quantitative investigations of molecular excitation processes involved in chemical reactions is to calculate the vibrational transition probabilities P_{ij} for a target molecule undergoing a transition from an initial state i to a final state j due to perturbation by incident particles. For the calculation of such probabilities, several theoretical treatments based on the classical, semiclassical, and quantum-mechanical approximations have been published.[1]

The purpose of the present work is to examine the effects of anharmonicity of molecular vibration on the transition probability. To this end, the multi-state semiclassical theory presented by Sharp and Rapp[2] has been extended to the treatment of Morse-type diatomic oscillators. A computer program was written out and applied to the vibrational excitation of a ground-state hydrogen molecule colliding with a helium atom at temperatures 1000—5000°K. It has been shown that even for lower level transitions a Morse oscillator model leads to transition probabilities several times greater than those obtained from the harmonic oscillator model.

Method of Calculation

We shall deal with a head-on collision between a mass point A and a diatomic molecule BC. The coordinate system is defined in Fig. 1. Two coordinates which characterize the collision are x, the distance between A and the center of mass of BC, and y, the internuclear separation of BC. The intramolecular potential $U(y)$ is approximated by the harmonic or Morse potential, both of which have well-known energy eigenvalues and eigenfunctions.

Let us denote the engenvalues and eigenfunctions of unperturbed oscillator hamiltonian H_0 by E_n and ϕ_n.

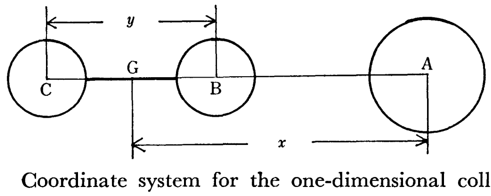

Fig. 1. Coordinate system for the one-dimensional collision between a BC molecule and an incident particle A.

When BC is a harmonic oscillator, we have

$$U_H(y) = \frac{1}{2}\mu\omega^2(y-y_e)^2 \tag{1}$$

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega \tag{2}$$

$$\phi_n(q) = M_n H_n(\sqrt{\alpha}\,q)\exp\left(-\frac{1}{2}\alpha q^2\right), \tag{3}$$

where ω is the angular frequency of the oscillator, y_e the equilibrium distance, H_n the Hermite polynomial, $q=y-y_e$ the instantaneous displacement of the oscillator, and μ, α, and M_n are quantities defined as follows:

$$\mu = m_B m_C/(m_B+m_C) \tag{4}$$

$$\alpha = \mu\omega/\hbar \tag{5}$$

$$M_n = (\alpha/\pi)^{1/4}/(2^n n!)^{1/2}. \tag{6}$$

When BC is a Morse oscillator, we can write[3]

$$U_M(y) = D_e[\exp\{-a(y-y_e)\}-1]^2 \tag{7}$$

$$E_n = \frac{4}{\beta}D_e\left\{\left(n+\frac{1}{2}\right)-\left(n+\frac{1}{2}\right)^2/\beta\right\} \tag{8}$$

$$\phi_n(s) = N_n(-1)^n\Gamma(\beta-n)\exp(-s/2)s^{(\beta/2-n-1/2)} \tag{9}$$

$$\text{for } n = 0, 1, \cdots < (\beta-1)/2.$$

In Eq. (9), $\Gamma(x)$ is the gamma function and

$$\beta = (8\mu D_e)^{1/2}/\hbar a \tag{10}$$

$$s = \beta\exp(-aq) \tag{11}$$

$$N_n = \{(\beta-1-2n)a/n!\,\Gamma(\beta-n)\}^{1/2}. \tag{12}$$

The intermolecular potential $V(x, y)$ is assumed to be of the simple exponential repulsion type:

$$V(x,y) = C\exp\left\{-\left(X-\frac{m_C}{m_B+m_C}y\right)/R\right\} \tag{13}$$

with the collision length R. In the semiclassical method the effect of energy transfer upon the trajectory of A is usually ignored, so that $V(x,y)$ is reduced to the following form:

$$V(X, Y) = E\exp\left(-\frac{X(t)}{R}\right)\exp\left(\frac{m_C}{m_B+m_C}\cdot\frac{Y}{R}\right) \tag{14}$$

where

$$X = x - x_T \tag{15}$$

$$Y = y - y_T \tag{16}$$

$$E = \frac{1}{2}mv^2 \tag{17}$$

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[1] For review, see D. Rapp, and T. Kassel, *Chem. Revs.*, **69**, 61 (1969).

[2] T. E. Sharp and D. Rapp, *J. Chem. Phys.*, **43**, 1233 (1965).

[3] F. H. Mies, *ibid.*, **40**, 523 (1964).

$$m = m_A(m_B+m_C)/(m_A+m_B+m_C), \tag{18}$$

x_T and y_T being the values of x and y at the classical turning point in the relative motion of A to BC, and v the relative incident velocity. Reduction of Eq. (13) to Eq. (14) is justified when the total energy exchange ΔE is a small fraction of the relative translational energy E.

The classical trajectory $X(t)$ as a function of time t for the present collision model is obtained by neglecting the vibration of BC and solving the classical equation of motion

$$\frac{1}{2}m\left(\frac{\mathrm{d}X}{\mathrm{d}t}\right)^2 + E\exp(-X/R) = E. \tag{19}$$

The analytical solution of this equation is well-known, but we have made a computation program to solve it numerically, as we intend it to be useful for any assumed form of intermolecular potential between A and BC.

The behavior of the oscillator under the influence of intermolecular interaction can be traced by solving the time-dependent Schrödinger equation

$$\{H_0+V(t,Y)\}\Psi = i\hbar\frac{\partial\Psi}{\partial t}, \tag{20}$$

where $V(t, Y)$ involving t instead of X as a variable constitutes the time-dependent perturbation toward the oscillator.

The time-dependent wavefunction $\Psi(t)$ of the oscillator can be expanded with the complete set $[\phi_n(q)]$. Thus

$$\Psi(t) = \sum_n a_n(t)\phi_n(q)\exp(-iE_nt/\hbar). \tag{21}$$

Insertion of Eq. (21) into Eq. (20) gives

$$\frac{\mathrm{d}a_j}{\mathrm{d}t} = \frac{1}{i\hbar}\sum_n a_n(t)V_{nj}(t)\exp\{-i(E_n-E_j)t/\hbar\}, \tag{22}$$

where $V_{nj}(t)$ is defined by

$$V_{nj}(t) = \int\phi_n(q)V(t,Y)\phi_j(q)\mathrm{d}q. \tag{23}$$

In order to evaluate Eq. (23), Y must be related to the oscillator coordinate q for every collision of varying initial phase angle of the oscillator. To avoid this complexity in procedure, we have made use of an averaging convention by setting

$$Y = q - \langle q\rangle_n \tag{24}$$

for the initial nth vibrational state of the oscillator, where

$$\langle q\rangle_n = \int\phi_n(q)q\phi_n(q)\,\mathrm{d}q, \tag{25}$$

which represents the average displacement from the equilibrium nuclear separation of the oscillator in the nth level. Integration of Eq. (25) was carried out numerically for the Morse oscillator using Simpson's integration formula. Note that for a harmonic oscillator $\langle q\rangle_n=0$.

On the above assumption, the factor $V_{nj}(t)$ can be written as

$$V_{nj}(t) = U_{nj}E\exp\{-X(t)/R\}\exp\left(-\frac{m_C}{m_B+m_C}\cdot\frac{\langle q\rangle_n}{R}\right), \tag{26}$$

where U_{nj} is a vibrational matrix element defined by

$$U_{nj} = \int\phi_n(q)\left\{\exp\left(\frac{m_C}{m_B+m_C}\cdot\frac{q}{R}\right)\right\}\phi_j(q)\mathrm{d}q. \tag{27}$$

When BC is a harmonic oscillator, Eq. (27) is reduced to[2)]

$$U_{ij} = \{\exp(\Delta^2)\}(2^{i-j}i!/j!)^{1/2}\Delta^{i-j}L_i^{(j-i)}(-2\Delta^2), \tag{28}$$

where $L_i^{(j-i)}$ is a generalized Laguerre polynomial and

$$\Delta = \{m_C\hbar/m_B(m_B+m_C)\omega\}^{1/2}/2R. \tag{29}$$

When BC is a Morse oscillator, Eq. (27) takes the form[3)]

$$U_{ij} = \{\beta^\eta N_iN_ji!\Gamma(\beta-i)/a\} \times\sum_{m=0}^{i}\frac{(-1)^{m+i-j}\Gamma(1+\eta+i-m)\Gamma(\beta-1-\eta-i-j+m)}{m!(i-m)!\Gamma(1+\eta+i-j-m)\Gamma(\beta-2i+m)}, \tag{30}$$

where

$$\eta = m_C/(m_B+m_C)Ra. \tag{31}$$

To obtain the transition probability P_{ij}, we must solve Eq. (22) for a_i.

For this purpose we used the Runge-Kutta-Gill method retaining lower N vibrational states of the oscillator. If before collision ($t=-\infty$) the molecule BC is in state i, the initial condition for Eq. (22) is $|a_j(-\infty)|^2=\delta_{ij}$. The probability of molecule undergoing the transition to the state j on collision is $P_{ij}=|a_j(+\infty)|^2$.

We have applied the above method of calculation to the excitation of a vibrational ground-state hydrogen molecule colliding with a helium atom at varying incident velocity. The appropriate molecular constants are $m_A=6.64\times10^{-24}$ g, $m_B=m_C=1.673\times10^{-24}$ g, $y_e=0.741$ Å, $\omega=9.378\times10^{14}$ sec^{-1}, $D_e=7.6\times10^{-12}$ erg, and $a=(\mu\omega^2/2D_e)^{1/2}=2.2$ Å^{-1}. R was assumed to be 0.2 Å.

All the numerical procedures were programmed in FORTRAN and calculations were carried out on the FACOM Computer at the Kyoto University Computation Center. Integration of Eq. (22) was started with a distance of 3 Å from the classical turning point and continued until the mass point A passed the 3 Å point on its departure. The integration step size was held below 1.0×10^{-16} sec, which required 1000 to 3000 steps to complete tracing one collision. The number of lower vibrational levels N included for solving Eq. (22) was 6. The incident velocity v was varied between 1.0×10^6 and 4.0×10^6 cm/sec.

Results and Discussion

For calculating the transition probability P_{ij}, it is necessary to evaluate the average displacements $\langle q\rangle_n$ and the vibration matrix elements U_{ij} of the oscillator.

TABLE 1. THE ENERGY LEVELS, E_n, AND AVERAGE DISPLACEMENTS, $\langle q\rangle_n$, OF H_2

Vibrational state, n	E_n, 10^{-12} erg		$\langle q\rangle_n$, Å	
	Harmonic	Morse	Harmonic	Morse
0	0.4942	0.4862	0	0.0227
1	1.4827	1.4104	0	0.0707
2	2.4711	2.2702	0	0.1229
3	3.4595	3.0659	0	0.1800
4	4.4480	3.7972	0	0.2430
5	5.4364	4.4642	0	0.3130

TABLE 2. VIBRATION MATRIX ELEMENTS, U_{ij}, OF H_2

i	U_{ij}					
	j=0	1	2	3	4	5
			Harmonic			
0	1.0212					
1	2.0925×10^{-1}	1.0641				
2	3.0319×10^{-2}	3.0214×10^{-1}	1.1079			
3	3.5869×10^{-3}	5.3249×10^{-2}	3.7776×10^{-1}	1.1526		
4	3.6749×10^{-4}	7.2490×10^{-3}	7.6356×10^{-2}	4.4524×10^{-1}	1.1982	
5	3.3675×10^{-5}	8.2862×10^{-4}	1.1582×10^{-2}	9.9946×10^{-2}	5.0803×10^{-1}	1.2447
			Morse			
0	1.0823					
1	-2.3461×10^{-1}	1.2742				
2	4.3899×10^{-3}	-3.8356×10^{-1}	1.5176			
3	4.3230×10^{-4}	8.8579×10^{-3}	-5.4973×10^{-1}	1.8322		
4	8.0994×10^{-5}	1.0222×10^{-3}	1.4777×10^{-2}	-7.5354×10^{-1}	2.2478	
5	2.1238×10^{-5}	2.1801×10^{-4}	1.9362×10^{-3}	2.2837×10^{-2}	-1.0173	2.8110

Table 1 lists the values of $\langle q\rangle_n$ together with the energy E_n of the lowest six vibrational levels of a hydrogen molecule in its harmonic and Morse oscillator models. Table 2 gives U_{ij} pertinent to these levels in the harmonic and Morse oscillators.

The fractional populations $|a_j(t)|^2$ of various vibrational levels in a Morse oscillator H_2 molecule are shown in Fig. 2 as a function of time during its collision with an He atom incident with an initial velocity of 1.0×10^6 cm/sec. The H_2 molecule was assumed to be initially on the ground vibrational level. Thus the population of each given level at infinity of time should correspond to the transition probability from zero level to the level in question. It can be seen that P_{01} takes a value of approximately 0.01 on this collision, but the probabilities of transitions to higher levels are negligibly small. This is natural, since the initial velocity chosen in this specific example corresponds to $E_{tr}=1.112\times10^{-12}$ erg, which exceeds the vibrational quantum only slightly, so that none of the 0—2, 0—3, and 0—4 transitions is an energetically attainable transition in a classical-mechanical sense. Quantum-mechanically, however, the 2, 3, and 4 levels are all populated appreciably for some short period around $t=0$, which produces an important contribution to the final magnitude of P_{01}.

The transition probabilities P_{01} calculated for the harmonic model of H_2 are shown in Fig. 3 as the functions of collision velocity v. Figure 4 represents similar results obtained for the Morse model. All these probabilities initially increase with increasing v until they attain maximum values, and then decrease oscillatingly with v. Such a behavior is also observed in

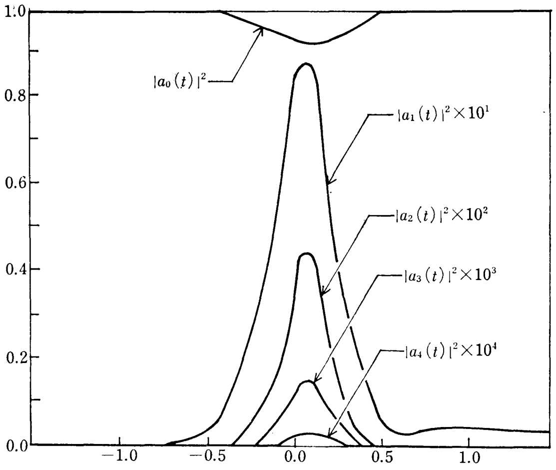

Fig. 2. Population of vibration levels, $|a_j(t)|^2$, as a function of time during a collision of a Morse oscillator H_2 molecule with an incident He.
$|a_j(-\infty)|=\delta_{0j}$; $v=1.0\times10^6$ cm/sec.

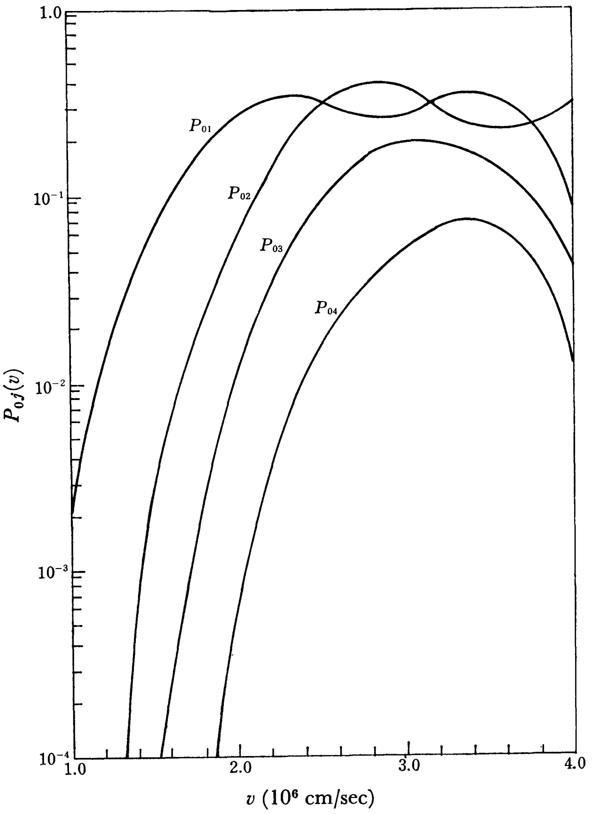

Fig. 3. Vibrational transition probabilities, $P_{ij}(v)$, of a ground-state H_2 (harmonic) molecule on collision with an He atom as the functions of velocity.

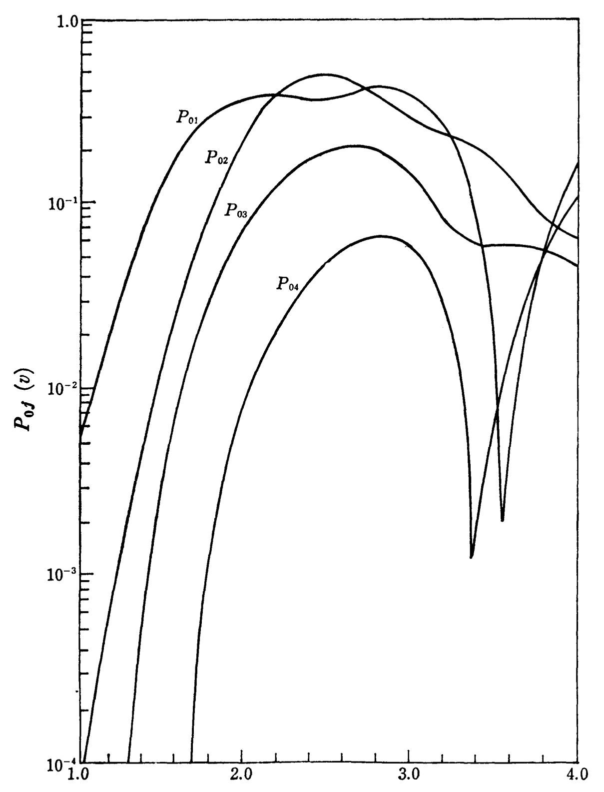

Fig. 4. Vibrational transition probabilities, $P_{ij}(v)$, of a ground-state H_2 (Morse) molecule on a collision with an He atom as the functions of velocity.

both the "exact" classical[4] and quantum-mechanical[5] transition probabilities.

Comparison of Fig. 4 with Fig. 3 shows that the Morse oscillator model leads to greater P_{0j} values than the harmonic model, until the P_{0j}'s calculated from the former model reach maximal values. The results are apparently contradictory to the theoretical demonstration of Mies,[3] who claims that the anharmonicity of diatomic molecules generally reduces the "usually" calculated P_{01} values by a factor of 10^{-1} to 10^{-2}. In order to avoid confusion between these two results, some comments are desirable.

The "anharmonicity factor" proposed by Mies is essentially a correction factor for the conventional adiabaticity assumption $U_{ii}=U_{jj}$, which was invoked in the original two-state distorted-wave approximation (DWA) of Jackson and Mott.[6] In the harmonic oscillator model the assumption is tolerably satisfied. However, if a Morse model is adopted, the assumption becomes no longer justifiable as can be seen in Table 2. Calculations show that use of precisely evaluated U_{ii}'s generally tends to reduce the P_{ij} values. Even in the case of harmonic oscillators, the Jackson-Mott transition probabilities need to be corrected by a factor of 10^0 to 10^{-1}.[7] Thus, in this sense the "anharmonicity factor" might better be termed the "nonadiabaticity correction factor."

In the case of the two-state approximation, the effects of nonadiabaticity are certainly more conspicuous in Morse oscillators than in harmonic oscillators, as Mies emphasizes. Such nonadiabaticity corrections have authomatically been embodied in our multi-state semiclassical treatments. Auxiliary calculations made by forcing all the U_{ii} elements to be 1 have led to the P_{0j} values which are 10^0 to 10^1 times greater than those of more precise calculations. The P_{01} values for the Morse model relative to the harmonic were not altered materially from those given in Figs. 3 and 4. That the Morse model gives greater P_{0j} values than the harmonic model is due primarily to the narrower spacings of the vibrational levels in the former.

The effects of narrow energy level spacings may become clearer in the energy exchange of a highly excited oscillator. We calculated P_{ij} of excited Morse oscillator ($i=10$) at the initial velocity of 1.0×10^{-6}cm/sec. The multi-state semiclassical method gave $P_{10-11}=0.820$, $P_{10-12}=0.158$, $P_{10-13}=0.281$ and $P_{10-14}=0.102$. The two-state approximation (Jackson-Mott-Mies), on the other hand, resulted in $P_{10-11}=4.79\times10^{-3}$, $P_{10-12}=6.22\times10^{-6}$, $P_{10-13}=9.21\times10^{-4}$, and $P_{10-14}=1.47\times10^{-4}$. It seems that these values are unreasonably small.

The effects of anharmonicity are thus reflected in both the vibrational matrices U_{ij} and the level heights E_i. Whether the anharmonicity enhances or diminishes the calculated transition probabilitics depends on the approximation used as well as the collision ve-

Table 3. Average transition probabilities, $\langle P_{ij}\rangle$

Transition $i\to j$	$\langle P_{ij}\rangle$				
	$T=1000$	2000	3000	4000	5000°K
			Harmonic		
0→1	1.544×10^{-6}	1.520×10^{-4}	1.043×10^{-3}	3.210×10^{-3}	6.820×10^{-3}
0→2	7.261×10^{-10}	1.728×10^{-6}	3.505×10^{-5}	2.030×10^{-4}	6.657×10^{-4}
0→3	1.682×10^{-12}	4.254×10^{-8}	1.992×10^{-6}	1.810×10^{-5}	7.872×10^{-5}
0→4	2.852×10^{-15}	9.871×10^{-10}	1.009×10^{-7}	1.303×10^{-6}	6.905×10^{-6}
			Morse		
0→1	3.787×10^{-6}	3.486×10^{-4}	2.256×10^{-3}	6.572×10^{-3}	1.326×10^{-2}
0→2	3.075×10^{-8}	1.405×10^{-5}	1.848×10^{-4}	8.612×10^{-4}	2.447×10^{-3}
0→3	1.505×10^{-11}	3.218×10^{-7}	1.321×10^{-5}	1.090×10^{-4}	4.301×10^{-4}
0→4	1.457×10^{-14}	8.569×10^{-9}	1.090×10^{-6}	1.367×10^{-5}	6.555×10^{-5}

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[4] J. D. Kelley and M. Wolfsberg, *J. Chem. Phys.*, **44**, 324 (1966).

[5] D. Secrest and B. R. Johnson, *ibid.*, **45**, 4556 (1966).

[6] J. M. Jackson and N. F. Mott, *Proc. Roy. Soc.*, **A137**, 703 (1932).

[7] R. E. Roberts, *J. Chem. Phys.*, **49**, 2880 (1968).

locity chosen.

The 0—j vibrational transition probability averaged over thermal velocity distributions for collisions at a temperature T may be written as

$$\langle P_{0j}\rangle = \int_{v_c}^{\infty} P_{0j}(v)\,\mathrm{d}n(v), \tag{32}$$

where

$$\mathrm{d}n(v) = (m/\boldsymbol{k}T)v\exp(-mv^2/2\boldsymbol{k}T)\mathrm{d}v \tag{33}$$

and

$$v_c = \{2(E_j-E_0)/m\}^{1/2}. \tag{34}$$

We calculated the $\langle P_{0j}\rangle$ at temperatures 1000—5000°K for every 1000°. The results are given in Table 3, where it may be seen that the $\langle P_{0j}\rangle$ values calculated for the Morse oscillator are always larger than the corresponding values obtained from the harmonic oscillator model.

Our value of $\langle P_{01}\rangle$, 3.486×10^{-4}, calculated for the Morse model at 2000°K agrees well with the value 3.7×10^{-4} which McElwain and Pritchard[8] assumed (based on DWA method) for an anharmonic H_2 molecule at the same temperature. Although the agreement may be fortuitous, the $\langle P_{01}\rangle$ value of *ca.* 10^{-4} will probably be in a correct order of mganitude for the H_2—He system at 2000°K. The $\langle P_{0j}\rangle$ values decrease with the increasing quantum number j of the final state. The decrease is, however, much more moderate than that derived from the usual two-state approximations. The conclusion stresses the need of care in the choice of the $\langle P_{ij}\rangle$ values to be used for high-energy collision processes.

It should be noted that we have used the classical trajectories for the present inelastic collision processes. In the "exact" semiclassical method proposed by Locker and Wilson,[9] the effect of energy exchange on the $X(t)$ and hence on the P_{ij} is evaluated properly. However, the method gives different transition probabilities for different initial phase angles, so that an appropriate averaging procedure is required, if the method is to be really useful for obtaining the average probability on a collision. In our method, on the other hand, such an averaging process is included automatically, though in a crude manner. Thus, our method may be less rigorous but is certainly more tractable than the method of Locker and Wilson.

Conclusion

The multi-state semiclassical method coupled with a proper procedure of averaging the initial vibration phase angles provides a tractable means of evaluating the vibrational transition probabilities of diatomic molecules. When the H_2 molecule is assumed to be a Morse oscillator the probabilties calculated for the H_2 ($i=0$)—He system at 1000—5000°K are greater than when it is assumed to be harmonic. This seems to have an important bearing with the kinetics of the bimolecular dissociation process of diatomic molecules.

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[8] D. L. S. McElwain and H. O. Pritchard, *J. Amer. Chem. Soc.*, **91**, 7693 (1969).

[9] D. J. Locker and D. J. Wilson, *J. Chem. Phys.*, **52**, 271 (1970).