Numerical Calculation of Vibrational Transition Probability for the Forced Morse Oscillator by Use of the Anharmonic Boson Operators

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The vibrational transition probability expressions for the forced Morse oscillator have been derived using the commutation relations of the anharmonic Boson operators. The formulation is based on the collinear collision model with the exponential repulsive potential in the framework of semiclassical collision dynamics. The sample calculation results for H_2 + He collision system, where the anharmonicity is large, are in excellent agreement with those from an exact, numerical quantum mechanical study by Clark and Dickinson, using the reactance matrix. Our results, however, are markedly different from those of Ree, Kim and Shin's in which they approximate the commutation operator I_0 as unity, the harmonic oscillator limit. We have concluded that the quantum number dependence in I_0 must be retained to get accurate vibrational transition probabilities for the Morse oscillator.

Keywords : Vibrational transition probability, Forced Morse oscillator, Anharmonic Boson operators.

Introduction

The Boson creation and annihilation operators for the harmonic oscillator are widely used in molecular vibrational energy transfer studies. This owes to their commutation relations, which make the interaction between the collision partners simpler and the Schrödinger equation easier to solve.[1-11] The angular momentum eigenvector problem encountered in the analysis of vibrational spectra is also one of the similar commutator algebras using the Boson creation and annihilation operators.[12,20-22]

Despite these apparent advantages, the use of Boson creation and annihilation operators requires that the vibrational motion of the colliding molecules be harmonic. Therefore, the Boson operator method can not be applied to molecules with large anharmonicity and/or with highly excited vibrational energy levels. Furthermore, this anharmonicity is known to have a significant effect, even on the lower vibrational energy levels of the polyatomic molecules and van der Waals molecules, which have shallow potential wells.

Recently Levine[23] derived the commutation relations for the anharmonic Morse oscillator from the Boson operators of the harmonic oscillator. The anharmonic Boson operators and their commutation relations derived by Levine have been used as the standard algebraic method in the collisional vibrational energy transfer for the forced Morse oscillator, and they also have proved very useful as the angular momentum generator in the coupled Morse oscillators.[13-22] Ballhausen[24] obtained the quantum mechanical solution of the forced Morse oscillator using the time-dependent step-up and step-down operators instead of the usual time-dependent perturbation theory. On the other hand, Ree *et al.*[25] developed an approximate method to obtain the perturbed vibrational states of the forced Morse oscillator, using Levine's anharmonic creation and annihilation operators and their commutation relations and derived expressions for vibrational excitation due to molecular collisions. In their study, however, to make it easier to obtain the time evolution operator for the wave function, they neglected the quantum number dependence of the anharmonicity parameter in describing the basic operators for Morse oscillator. That is, they approximated the commutator between the anharmonic creation and annihilation operators as the identity operator, which is true only in the harmonic oscillator limit. This approximation, however, can significantly affect the vibrational transition probabilities for molecules with large anharmonicity, especially when one deals with high vibrational levels.

In the present study, we incorporate the quantum number dependence of the anharmonicity parameter into the basic operators for the Morse oscillator. We have derived expressions for the final vibrational states and energy transfer probabilities of the Morse oscillator perturbed by molecular collisions. We have applied the expressions to a H_2 + He collision system, which has large anharmonicity and test the validity of the derived expressions by comparing the results with those of other exact calculation.[33] We have also shown the anharmonicity parameter dependence of the differential equations for the coefficients of the anharmonic Boson operators in the time evolution operator.

Algebraic Method

To handle the vibrational energy transfer problem for the forced Morse oscillator, it is essential to define the anharmonic Boson operators. In this section, we briefly summarize Levine's algebraic operator approach to the Morse oscillator.

Levine introduced a pair of Boson creation (a_0^-, a_N^-) and annihilation (a_0^-, a_N^-) operators with the following commutation relations.[11]

$$[a_v^-, a_v^+] = [a_N^-, a_N^+] = 1 \tag{1a}$$

$$[a_v^-, a_N^+] = [a_v^-, a_N^-] = 0 \tag{1b}$$

Here, v is the vibrational quantum number and $N = x_0^{-1}$, where x_0 is the anharmonicity in the Morse oscillator energy expression

$$E_v = \hbar\omega_0\left(v + \frac{1}{2}\right) - \hbar\omega_0 x_0\left(v + \frac{1}{2}\right)^2 \tag{2}$$

Levine showed that the basic operators representing the Morse oscillator could be formed from the harmonic Boson operators as follows.

$$Q = (2N)^{-1/2}(a_v^- a_N^- + a_N^+ a_v^-) \tag{3a}$$

$$P = i(2N)^{-1/2}(a_v^- a_N^- - a_N^+ a_v^-) \tag{3b}$$

$$I_0 = N^{-1}(a_N^+ a_N^- - a_v^+ a_v^-) \tag{3c}$$

$$E_0 = N^{-1}(a_v^+ a_v^- + a_N^+ a_N^-) \tag{3d}$$

Here, P and Q are the basic operators for the Morse oscillator, derived from the harmonic creation and annihilation operators. The operator I_0 approaches the identity operator I only in the harmonic limit, where the anharmonicity becomes zero. From these basic operators one can write the Morse oscillator Hamiltonian as $H = \hbar\omega_0(P^2 + Q^2)/2$, where ω_0 is the vibrational frequency of the Morse oscillator. If we write the harmonic oscillator Hamiltonian as $H = (p^2 + M^2\omega_0^2 q^2)/2M$, then the position and momentum for the harmonic oscillator become $q = \hbar/(M\omega_0)^{1/2} Q$ and $p = (M\hbar\omega_0)^{1/2} P$, respectively. From Eqs. (3), one can obtain the commutation relation as follows.

$$[Q, P] = iI_0 \tag{4}$$

The anharmonic creation (A^+) and annihilation (A^-) operators for the Morse oscillator can be obtained by adding or subtracting Eqs. (3a) and (3b).

$$A^+ = 2^{-1/2}(Q - iP) = N^{-1/2} a_v^- a_N^- \tag{5a}$$

$$A^- = 2^{-1/2}(Q + iP) = N^{-1/2} a_N^+ a_v^- \tag{5b}$$

From these two operators one can obtain P and Q,

$$Q = 2^{-1/2}(A^- + A^-) \tag{6a}$$

$$P = 2^{-1/2} i(A^- - A^-) \tag{6b}$$

and the following commutation relations.

$$[I_0, P] = 2ix_0 Q \tag{7a}$$

$$[I_0, Q] = -2ix_0 P \tag{7b}$$

$$[A^-, A^+] = I_0 \tag{7c}$$

$$[I_0, A^-] = \mp 2x_0 A^- \tag{7d}$$

Also, in terms of anharmonic operators A^+ and A^-, the Morse oscillator Hamiltonian becomes

$$H = \hbar\omega_0\left(A^- A^- + \frac{1}{2} I_0\right). \tag{8}$$

Vibrational States for the Perturbed Morse Oscillator

We now write the Hamiltonian for the Morse oscillator perturbed by a time-dependent force $F(t)$ due to the interaction with an incident particle in the form

$$H(t) = \frac{1}{2}\hbar\omega_0(P^2 + Q^2) + (\hbar/M\omega_0)^{1/2} F(t)Q \tag{9}$$

or, in terms of the creation and annihilation operators,

$$H(t) = \hbar\omega_0\left(A^+ A^- + \frac{1}{2} I_0\right) + (\hbar/2M\omega_0)^{1/2}$$

$$\times F(t)(A^+ + A^-) \equiv H^0 + H'(t). \tag{10}$$

Long before $(t = -\infty)$ or long after $(t = +\infty)$ collision, where the perturbation term vanishes[23]

$$H|N, v\rangle = \hbar\omega_0(v - x_0 v^2)|N, v\rangle. \tag{11}$$

The Morse oscillator state $|N, v\rangle$ can be generated from the vacuum state $|0\rangle$ as follows.[12,23,27]

$$|N, v\rangle = [v!(N - v)!]^{-1/2}(a_v^+)^v (a_N^+)^{N-v}|0\rangle \tag{12}$$

From these normalized basis states $|N, v\rangle$, one can obtain the eigenvalue equations as follows.[23]

$$E_0|N, v\rangle = |N, v\rangle \tag{13}$$

$$I_0|N, v\rangle = (1 - 2x_0 v)|N, v\rangle \tag{14}$$

The time-dependent Schrödinger equation for the forced Morse oscillator can be written as

$$i\hbar\frac{\partial|\Psi(t)\rangle}{\partial t} = [H^0 + H'(t)]|\Psi(t)\rangle. \tag{15}$$

where $|\Psi(t)\rangle$ is the vibrational state of the Morse oscillator induced by the perturbation term $H'(t)$, and can be expressed as a linear combination of the initial states $|N, v\rangle$. The solution to Eq. (15) can be written, in principle, in the form

$$|\Psi(t)\rangle = \left[\prod_{j=0}^{\infty} e^{G_j(t)\Omega_j}\right]|\Psi(t_0)\rangle \equiv U_0(t, t_0)|\Psi(t_0)\rangle, \tag{16}$$

where $U(t, t_0)$ is the time evolution operator, which converts the initial state $|\Psi(t_0)\rangle = |N, v\rangle$ into the perturbed states $|\Psi(t)\rangle$ in accordance with the perturbation $H'(t)$. Therefore, $G_j(t)$ terms in Eq. (16) are the time-dependent functions with complex values, and Ω_j's represent the anharmonic Boson operators $A^+, A^-, A^- A^-$ and I_0. Performing the time evolution operation on the initial state $|N, v\rangle$ one obtains

$$|\Psi(t)\rangle = \exp\{G_3(t)[1 - x_0(v - 1)]v\} \exp\{G_4(t)(1 - 2x_0 v)\}$$

$$\times \left\{ |N, v\rangle + \sum_{m=1}^{\infty} \frac{G_1^m(t)}{m!}\left(\prod_{k=v}^{v+m-1}(1 - kx_0)^{1/2}\right)\left[\frac{(v+m)!}{v!}\right]^{1/2} |N, v+m\rangle \right.$$

$$\left. + \sum_{n=1}^{\infty} \frac{G_2^n(t)}{n!}\left(\prod_{k=v-1}^{v-n}(1 - kx_0)^{1/2}\right)\left[\frac{v!}{(v-n)!}\right]^{1/2} |N, v-n\rangle \right.$$

$$+ \sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\frac{G_1^m(t)G_2^n(t)}{m!n!(v-n)!}[v!(v-n+m)!]^{1/2}$$

$$\times \left(\prod_{k=v-1}^{v-n}(1-kx_0)^{1/2}\right)\left(\prod_{k=v-n}^{v-n-m-1}(1-kx_0)^{1/2}\right)$$

$$\times |N, v-n+m\rangle\}. \tag{17}$$

which is a linear combination of all possible Morse oscillator states produced from the initial state $|N, v\rangle$. Here, the sum above m contains states that are higher than $|N, v\rangle$, whereas the sum over n contains the lower states. Thus, they represent the excited and de-excited vibrational states of the Morse oscillator due to the collision, respectively.

Formulation of Transition Probability

The probability of vibrational transition from the initial state $|N, v\rangle$ to the final state $|N, f\rangle$ can be written from Eq. (17) as

$$P_{v\to f} = \lim_{t\to\infty}\langle N, f|\Psi(t)\rangle|^2. \tag{18}$$

From Eqs. (17) and (18) one can obtain the excitation probability

$$P_{v\to f} = v!f!\,G_1^{2(f-v)}\exp\{2G_3[1-x_0(v-1)]v\}$$

$$\times \exp[2G_4(1-2x_0v)]\left|[v!(f-v)!]^{-1}\left[\prod_{k=v}^{f-1}(1-kx_0)^{1/2}\right]\right.$$

$$+ \sum_{n=1}^{v}\left[\prod_{k=v-1}^{v-n}(1-kx_0)^{1/2}\right]\left[\prod_{k=v-n}^{f-1}(1-kx_0)^{1/2}\right]$$

$$\left.\times \frac{G_1^n G_2^n}{n!(f-v+n)!(v-n)!}\right|^2 \tag{19}$$

and the de-excitation probability

$$P_{v\to f} = v!f!\,G_2^{2(v-f)}\exp\{2G_3[1-x_0(v-1)]v\}$$

$$\times \exp[2G_4(1-2x_0v)]\left|[f!(v-f)!]^{-1}\left[\prod_{k=v-1}^{f}(1-kx_0)^{1/2}\right]\right.$$

$$+ \sum_{m=1}^{f-m}\left[\prod_{k=v-1}^{f-m}(1-kx_0)^{1/2}\right]\left[\prod_{k=f-m}^{f-1}(1-kx_0)^{1/2}\right]$$

$$\left.\times \frac{G_1^m G_2^m}{m!(f-v+m)!(v-m)!}\right|^2 \tag{20}$$

Because of the presence of the k products containing the anharmonicity parameter, combining the two probabilities into one does not seem possible. However, in the harmonic oscillator limit, where x_0 becomes zero, the two expressions can be combined into the well-known probability expression for the harmonic oscillator.[7,28-30]

$$P_{v\to f} = v!f!\,G_{1,2}^{2|v-f|}\exp(2vG_3)\exp(2G_4)$$

$$\times \left|\sum_{j=0}^{l}\frac{G_1^j G_2^j}{j!(|v-f|+j)!(l-j)!}\right|^2 \tag{21}$$

Here, l is the smaller of v and f.

To calculate the probabilities, one must evaluate $G_j(t)$'s in Eqs. (19) and (20). To do this we express the Hamiltonian in Eq. (10) in the following form.

$$H(t) = \sum_{k=1}^{4}\lambda_k(t)\Omega_k. \tag{22}$$

where Ω_k's are the anharmonic operators A^-, A^+, A^-A^- and I_0, and λ_k's are their coefficients. To determine $G_j(t)$'s, we must therefore find the relationship between the functions $\lambda_k(t)$ and $G_j(t)$. For this purpose, we first differentiate $U(t, t_0)$ with respect to t.

$$\frac{dU(t, t_0)}{dt} = \sum_{i=1}^{4}\frac{dG_i(t)}{dt}$$

$$\times \left[\prod_{j=1}^{i-1}\exp[G_j(t)\Omega_j]\right]\Omega_i\left[\prod_{i=1}^{4}\exp[G_j(t)\Omega_j]\right]. \tag{23}$$

Multiplying U^{-1} and introducing the Baker-Hausdorff theorem,[31] we find

$$\left[\prod_{j=1}^{r}\exp[G_j(t)\Omega_j]\right]\Omega_i\left[\prod_{j=r}^{1}\exp[-G_j(t)\Omega_j]\right]$$

$$= \sum_{k=1}^{4}a_{ki}(t)\Omega_k. \tag{24}$$

From Eq. (22)-(24) we can thus obtain

$$\sum_{k=1}^{4}\lambda_k(t)\Omega_k = \sum_{i=1}^{4}\sum_{k=1}^{4}\frac{dG_i(t)}{dt}a_{ki}(t)\Omega_k. \tag{25}$$

This equation leads to the following four differential equations:

$$\frac{dG_1(t)}{dt} = x_0 G_1^2(t)\frac{dG_2(t)}{dt} + i\omega_0\frac{K_2}{K_1}$$
$$- 2x_0 G_1(t)\frac{dG_4(t)}{dt} - \frac{i}{\hbar}F(t) \tag{26a}$$

$$\frac{dG_2(t)}{dt} = i\omega_0\frac{K_3}{K_1} + 2x_0 G_2(t)\frac{dG_4(t)}{dt} - \frac{i}{\hbar}F(t) \tag{26b}$$

$$\frac{dG_3(t)}{dt} = -i\frac{\omega_0}{K_1} \tag{26c}$$

$$\frac{dG_4(t)}{dt} = i[1 + 2x_0 G_2(t) - 2x_0 G_1(t)G_2(t)]^{-1}$$
$$\times \left[\omega_0\frac{K_3 G_1(t)+K_4}{K_1} - \frac{1}{2}\omega_0 - \frac{i}{\hbar}F(t)\right] \tag{26d}$$

where

$$K_1 = 1 + 2x_0 G_1(t)G_2(t) + 2x_0 G_1^2(t)G_2^2(t) \tag{27a}$$

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$$K_2 = (2x_0 f - 1)G_1(t) - x_0(3 - 2x_0 - 6x_0 f)G_1^2(t)G_2(t)$$
$$- 2x_0^2(1 - x_0 - 2x_0 f)G_1^3(t)G_2^2(t) \tag{27b}$$

$$K_3 = (1 + 2x_0 - 2x_0 f)G_2(t) + 2x_0(1 + x_0 - 2x_0 f)$$
$$\times G_1(t)G_2^2(t) \tag{27c}$$

$$K_4 = (2x_0 f - 1)G_1(t)G_2(t) - x_0(1 - x_0 - 2x_0 f)$$
$$\times G_1^2(t)G_2^2(t) \tag{27d}$$

Here f is the vibrational quantum number of the final state $|N, f\rangle$ resulting from the initial state $|N, v\rangle$ due to collisional interaction. Thus, $G_j's$ can be determined by solving four differential equations subject to the initial conditions, $G_j(t_0)=0$. These simultaneous differential equations will be solved numerically. We note that in the limit $x_0 \to 0$ these differential equations reduce to the following well-known equations for the harmonic oscillator, as they must.[32]

$$\frac{dG_1(t)}{dt} = -i\omega_0 G_1(t) - i\hbar^{-1}F(t) \tag{28a}$$

$$\frac{dG_2(t)}{dt} = i\omega_0 G_2(t) - i\hbar^{-1}F(t) \tag{28b}$$

$$\frac{dG_3(t)}{dt} = -i\omega_0 \tag{28c}$$

$$\frac{dG_4(t)}{dt} = -\frac{1}{2}i\omega_0 - i\hbar^{-1}F(t) \tag{28d}$$

One can calculate the transition probabilities for the harmonic oscillator from Eqs. (21) and (28). In the next section, we will use these equations to calculate the vibrational transition probabilities for the harmonic oscillator and compare them with those for the Morse oscillator.

Results and Discussion

To test the probability expressions for the Morse oscillator derived from the commutation relations of the anharmonic Boson operators, we have chosen the collinear $H_2 +$ He collision as our model system. The reason we have chosen this particular system is two-fold. The first is that the H_2 molecule has large anharmonicity, and the second is that the exact quantum mechanical (Clark and Dickinson; Ref. 33) and approximate semiclassical (Ree, Kim and Shin; Ref. 25) calculations are already available with which we can compare the results.

The interaction potential between the collision partners is also the simplest one, *i.e.*, the exponential repulsive potential, which is the most often used potential for this kind of model calculations.

$$V(z) = D \exp(-z/a). \tag{29}$$

Here z is the distance between He and the nearer H, and D and a are the steepness and the range parameter, respectively. Since $z = R - \gamma (d + q)$, where R is the distance between the He atom and the center of mass of the H_2 molecule, γ the mass ratio $\gamma = m_H/(m_H + m_H) = 1/2$. d the equilibrium bond length

of H_2, and q the vibrational amplitude of H_2, respectively, the potential can be represented as

$$V(z) = V(R, q) = D \exp(\gamma d/a)\exp(-R/a) \exp(\gamma q/a) \tag{30}$$

Expanding the $\exp(\gamma q/a)$ term into a power series in the vibrational amplitude coordinate q, gives

$$V(R, q) = D'\exp(-R/a) + (D'\gamma/a)\exp(-R/a)q + ..., \tag{31}$$

where $D' = D\exp(\gamma d/a)$. Therefore, the perturbing force $F(t)$ in Eq. (9) becomes $(D'\gamma/a)\exp(-R/a)$ and $q = (\hbar/M\omega_0)^{1/2} Q$.

Invoking the well-established semiclassical procedure in which the translational motion is treated classically, the collision trajectory is found to be[34]

$$\exp[-R(t)/a] = \text{sech}^2[(E/2 \mu)^{1/2} (t/a)], \tag{32}$$

where E is the collision energy and μ is the reduced mass of the collision system. The collision energy is symmetrized before and after the collision and is related to the total energy E_T as $E^{1/2} = 1/2[(E_T - E_{v,i})^{1/2} + (E_T - E_{v,f})^{1/2}]$, where $E_{u,i}$ and $E_{u,f}$ are the initial and final vibrational energies. The molecular spectroscopic constants are taken from the standard table[26] and the range parameter a is set at 0.02 nm, which is the most frequently used value in this type of model calculations.[25,33,34]

Our results are in excellent agreement with those from the exact quantum mechanical numerical calculation of Clark and Dickinson, using the reactance matrix method.[33] To show this we have grouped together in Table 1 the transition probabilities for Morse (P_{MO}) and the harmonic oscillator (P_{HO}), their ratios (P_{MO}/P_{HO}) and harmonic scaling law ($P_{v \to v-1}/(v + 1)P_{0 \to 1}$) for the Morse oscillator at the collision energy $\varepsilon = 1$. For example, for the $v \to v + 1$ transitions $P_{MO}'s$ by Clark and Dickinson are 2.46×10^{-4}, 1.25×10^{-3}, 5.29×10^{-3}, 1.92×10^{-2} and 5.97×10^{-2} for $v = 0, 1, 2, 3, 4$, respectively, whereas those in the present study are 2.41×10^{-4}, 1.31×10^{-3}, 5.09×10^{-3}, 1.59×10^{-2} and 4.58×10^{-2}, respectively. The small differences can be attributed to the difference in calculation methods (exact quantum mechanical *vs.* semiclassical) and/or difference in the interaction potential (full exponential repulsive potential in Clark and Dickinson *vs.* expanded first order term in q in this work). Note that the differences between the two calculations are larger at high v than at low v. This is because the effect of the potential difference is expected to be more pronounced at higher vibrational levels. The possibility of multiple quantum transitions is omitted in our calculation and this omission leads to larger errors at larger v. Our results for other quantities P_{HO}, P_{MO}/P_{HO} and $P_{v \to v+1}/(v + 1)P_{0 \to 1}$ are in excellent agreement with those of Clark and Dickinson.

Figure 1 shows the transition probability ratios P_{MO}/P_{HO} for various one quantum vibrational transitions against the reduced collision energy $\varepsilon = E/\hbar\omega_0$. P_{MO} is the vibrational transition probability for the Morse oscillator calculated using

Eq. (19) and P_{HO} is the vibrational transition probability for the harmonic oscillator calculated using Eq. (21). As can be seen from Figure 1, the ratio P_{MO}/P_{HO} for the lower vibrational levels v = 0-2 when the anharmonicity effect is small increases slowly as ε increases. For the higher vibrational levels v = 3-5, however, the ratio increases rapidly with ε at low collision energies, reaches maximum, and then decreases at high collision energies.

This clearly shows that the vibrational transition for the Morse oscillator is quite different from that for the harmonic oscillator at higher vibrational levels where the anharmonicity effect becomes increasingly important. For example, the ratios P_{MO}/P_{HO} for v = 0 → 1 transition at ε = 0.5, 1.0, 1.5, 2.0 and 3.0 are 0.01, 0.48, 0.85, 1.22 and 1.31, respectively, whereas those for v = 5 → 6 transitions are 14.2, 15.8, 12.3, 9.65 and 4.75, respectively, at the same ε values. The effect of anharmonicity on the transition probability becomes much more pronounced as v increases.

For the harmonic oscillator, the so-called harmonic scaling law should hold. $P_{v \to v-1}/(v+1)P_{0 \to 1} = 1$. As can be seen from Table 1, this law holds well for the harmonic oscillator by both exact quantum mechanical numerical calculation of Clark and Dickinson and semiclassical operator algebra calculation in the present study. As v increases from 1 to 5 the ratios from the Clark and Dickinson's results vary from 0.986 to 0.944, whereas those from our results vary from 0.997 to 0.999.

For the Morse oscillator, however, the law does not hold at all due to the anharmonicity effect. See the last column of Table 1 and Figure 2(a). The ratio $P_{v \to v-1}/(v+1)P_{0 \to 1}$ increases rapidly with v rather than staying close to unity in both calculations. This fact is in complete disagreement with the results of Ree *et al.*'s approximate operator algebraic calculation.[25] Their results at ε = 1.0 are shown in Figure 2(b) and the ratio decreases linearly with v and is less than unity at all v.

This apparently opposite trend can be attributed to the difference in operator I_0, one of the basic operators for the Morse oscillator. This operator reduces to the identity operator only in the harmonic limit. That is, $\lim_{x_0 \to 0} I_0|N,f\rangle = \lim_{x_0 \to 0} (1 - 2x_0 f)|N,f\rangle \approx |N,f\rangle$. We have already defined this operator in Eqs. (3c) and (14). When I_0 is inserted in Eq. (25). $2x_0 f$ terms appear in the differential equations (26). These terms are responsible for the rapid increase in probabilities with increasing v.

In carrying out the time-evolution operation Ree *et al..* however. approximated G as $G_{1,2}(t) = (2M\hbar\omega_0)^{-1/2} \int_{-\infty}^{t} F(t)\exp[\pm i\omega_0(I_0 \pm x_0)t]dt$. In addition to this approximation, they then took the harmonic oscillator limit for I_0, *i.e.*, they approximated I_0 as unity. $I_0|N,f\rangle = |N,f\rangle$ for ease of calculation. which is correct only when x_0 approaches zero. Therefore, $G_{1,2}(t)$ was approximated as $G_{1,2}(t) \approx (2M\hbar\omega_0)^{-1/2} \int_{-\infty}^{t} \exp[\pm i\omega_0(1 + x_0)t]dt$. And also, the term in the exponent $(I_0 \pm x_0)$ was replaced by $(1 \pm x_0)$, which has no quantum number (f) dependence. These approximations cause the ratio $P_{v \to v+1}/(v+1)P_{0 \to 1}$ to decrease with increasing v.

Of course, when we replace the operator I_0 with identity operator I in our formulation. our results also reduce to the results by Ree *et al..* as they must. Specifically, when we replace I_0 with I in carrying out $\Omega_k(A^-, A^-, A^-A^-, I_0)$ operations in Eq. (25). the following K_i's are obtained

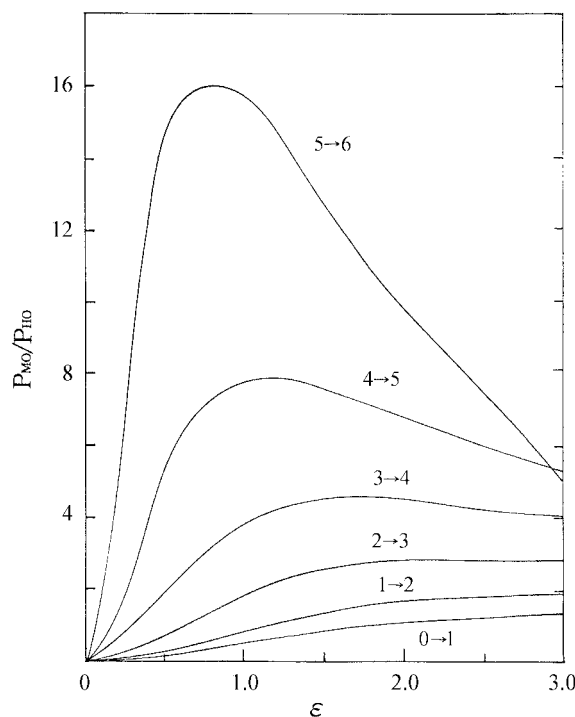$$K_1 = 1 + 2x_0 G_1(t)G_2(t) + 2x_0 G_1^2(t)G_2^2(t) \tag{33a}$$

Figure 1. The ratios P_{MO}/P_{HO} for one quantum vibrational transitions as a function of the reduced collision energy $\varepsilon = E/\hbar\omega_0$.

Table 1. Vibrational transition probabilities of H_2 + He for the harmonic oscillator (H.O.) and Morse oscillator (M.O.) and the harmonic scaling relation $P_{v \to v+1}/(v+1)P_{0 \to 1}$ for Morse oscillator at collision energy $\varepsilon = 1$

Vibrational Transition	H.O.		M.O.		P_{MO}/P_{HO}		$P_{v \to v-1}/(v+1)P_{0 \to 1}$	
	P_{CD}[a]	P_T[b]	P_{CD}	P_T	P_{CD}	P_T	P_{CD}	P_T
0 → 1	7.20(-4)[c]	7.07(-4)	2.46(-4)	2.41(-4)	0.34	0.34	1.0	1.0
1 → 2	1.42(-3)	1.41(-3)	1.25(-3)	1.31(-3)	0.88	0.93	2.5	2.7
2 → 3	2.10(-3)	2.12(-3)	5.29(-3)	5.09(-3)	2.52	2.40	7.2	7.0
3 → 4	2.76(-3)	2.82(-3)	1.92(-2)	1.59(-2)	6.96	5.64	19.5	16.5
4 → 5	3.40(-3)	3.53(-3)	5.97(-2)	4.58(-2)	17.6	12.8	48.5	38.0
5 → 6	–	4.23(-3)	–	1.15(-1)	–	27.2	–	79.5

[a]Exact numerical calculation results by Clark and Dickinson (Ref. 33). [b]This work. [c]Parentheses include power of ten.

$$K_2 = -G_1(t) - x_0(3 - 2x_0)G_1^2(t)G_2(t)$$
$$+ 2x_0^2(1 - x_0)G_1^3G_2^2(t) \tag{33b}$$

$$K_3 = (1 + 2x_0)G_2(t) + 2x_0(1 + x_0)G_1(t)G_2^2(t) \tag{33c}$$

$$K_4 = -G_1(t)G_2(t) - x_0(1 - x_0)G_1^2(t)G_2^2(t) \tag{33d}$$

in which all the $2x_0 f$ terms in Eq. (27) have vanished. The $P_{v \to v+1}/(v + 1)P_{0 \to 1}$ ratios calculated with these new K_i's are shown in Fig. (2c), and we can see that the results reproduce exactly those of Ree *et al.* in Fig. (2b).

Conclusion

We have derived vibrational transition probability expressions for the Morse oscillator, using anharmonic creation and annihilation operator algebra. The collinear collision model and the exponential repulsive potential were employed in the formulation.

Our model can be extended to other types of interaction potentials, even to the *ab initio* numerical potentials. However. they must first be converted into a form that has functional dependency on the vibrational displacement coordinate.

Sample calculation results for H_2 + He collision system in which the anharmonicity effect is large are in excellent agreement with those obtained from exact numerical quantum mechanical calculations by Clark and Dickinson.[33] Our results. however, are markedly different from those of Ree *et al.*,[25] who performed essentially the same calculation but replaced the quantum number dependent commutation operator I_0 with the unit operator I. Our results show that the integrity of the I_0 operator must be kept and its operation is essential in the anharmonic vibrational transitions. especially for high
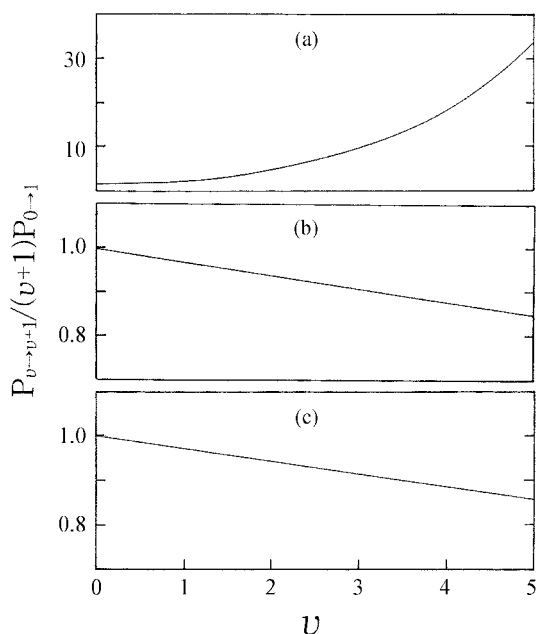

Figure 2. Dependence of $P_{v \to v-1}/(v+1)P_{0 \to 1}$ on vibrational quantum number v. (a) This work (b) The result from Eq. (33) (c) The result by Ree *et al.*[25]

energy levels.

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