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並進-振動에너지 變換에 있어서의 多量子 直接 振動 勵起

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Direct Non-stepwise Multiple Quantum Excitations in Translation-Vibration Energy Transfer

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要 約. 並進-振動에너지 變換에 있어서 中間에너지 準位를 거치지 않는 直接勵起가 多量子 振動 천이에 미치는 영향을 理論的으로 조사하였다. 衝突 모형은 直線 충돌이며, 分子間의 포텐셜은 指數函數型의 것을 振動좌표(q)로 전개하고 四次項 (q^4)까지 包含시켜 사용하였다. q^2, q^3, q^4를 포함시켰을 때의 천이 확율 ($p_{m\to n}$)에 對한 一般式을 各各 유도하고, 몇개의 충돌계에 대하여 그 값들을 計算하였다.

結果를 線型化시킨 포텐셜(q)을 사용한 경우의 結果와 比較하고 直接 多量子 振動遷移가 重要한 役割을 하게 되는 條件을 파라미터 α 및 m과 관련시켜 제시하였다.

ABSTRACT. Effects of *direct* multiple quantum excitations in vibrational energy transfer were investigated. Vibrational transition probabilities for 0→2, 0→3, and 0→4 excitations were explicitly formulated including both *direct* 0→*n* excitations and stepwise single quantum processes. For the formulation the perturbing force was derived from the exponential potential including terms up to fourth order in the vibrational amplitude. The head-on collinear collision model between a harmonic oscillator and an incident particle was employed, and the formulation was based on the semiclassical approximation.

Numerical results were obtained for five different collision systems (Ar···O—N, He···H—H, He···H—Cl, 5···1—2, 2···12—12). Comparison between the present results and those obtained using the linearized interaction potential showed that the overall effect of including the *direct* multiple quantum transition is to decrease the probabilities at low collision energies and to increase them at high energies. The present results were found to be significantly different from those obtained using the linearized potential for collision systems He···H—H, He···H—Cl, and 5···1—2. For systems Ar···O—N and 2···12—12 the differences were negligible.

1. INTRODUCTION

The vibrational transitions resulting from the collisional transfer of energy from the relative translational motion of the molecules as a whole to the vibrational degree of freedom of a diatomic molecule, or vice versa, is of particular importance to understand the molecular processes such as chemical activation, absorption and dispersion of ultrasonic waves, molecular beam, chemiluminescence, transport phenomena, and chemical lasers.[1]

Since the quantum mechanical study of a many particle system is extremely difficult, many simplifying assumptions are introduced. One of them is that the intermolecular potential can be expanded into a power series in terms of the vibrational amplitude, and then only the linear first order term is retained. All higher order terms are neglected. This is, so called, the linearized potential. For a collision model approximating a diatomic molecule as a harmonic oscillator, then, the selection rule permits only the single quantum transitions. Multiple quantum transitions such as (0→2), (0→3), etc. are achieved only by successive stepwise single quantum transitions, and nonstepwise direct multiple quantum transitions are forbidden.

At low collision energies, which are small compared with the vibrational quantum of the diatomic molecule, this has been the real case.[2~5] With the advent of the experimental techniques such as laser, however, very large collision energies in the range of 10~20 eV have been reported both in experimental[6] and in theoretical[7] studies. Since these energies are far greater than the vibrational quantum of usual diatomic molecules, the direct nonstepwise multiple quantum transitions are expected to play a significant role in inducing multiple quantum transitions.

In view of this, we wish to formulate explicitly the vibrational transition probabilities including the higher order terms in the potential as well as the linear term. By including the higher order terms we hope to establish the relative importance of the higher order terms in comparison with the linear term in inducing multiple quantum transitions. Also, by systematically varying the parameters which characterize the collision system, we hope to find the conditions under which the higher order terms become important in inducing the multiple quantum transitions.

2. COLLISION MODEL

Since we are interested only in the relative importance of the linear and higher order terms in the intermolecular potential, the simplest model, i.e., the collinear head-on collision model is employed. The diatomic molecule is approximated as a harmonic oscillator. The incoming atom or molecule is treated as a structureless mass point. The collision model and the coordinates used are illustrated in *Fig.* 1. The incident particle A collides with atom B of oscillator B–C with the initial relative velocity v_0.

The method of calculation is based upon the semiclassical approach developed by Rapp *et. al.*[8] using the linearized potential. In this method the oscillator is treated as a quantum mechanical system with discrete energy levels, while the relative translational motion of the incident

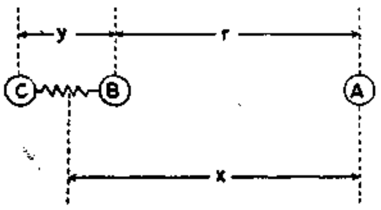

Fig. 1. Collision model.

particle is treated classically. This is permissible since the de Broglie wavelength associated with translational motion (in the order of $10^{-14}\sim10^{-15}$ cm for the collision energy of about 10 eV) is much smaller than the classical distance of closest approach[9] (in the order of 10^{-8} cm).

3. INTERMOLECULAR POTENTIAL

In the simple collinear collision model the most frequently used intermolecular potential is an exponential potential of the type

$$V'(r)=D\exp(-r/L) \tag{3-1}$$

where D and L are constants. We also use this potential.

The distance r between the atoms A and B is related to x and y by

$$r=x-\gamma y \tag{3-2}$$

where γ is the mass ratio defined as

$$\gamma=M_C/(M_B+M_C) \tag{3-3}$$

M_B and M_C denote the masses of B and C, respectively.

To obtain the time-dependent perturbing potential we want to convert the interatomic potential to one which is a function of time t and the vibrational amplitude q, which is equal to $y-y_e$, y_e being the equilibrium internuclear distance of the molecule B-C. In the semiclassical approach Rapp *et. al.*[8] have shown that the potential becomes

$$V'(t,q)=E_i'\operatorname{sech}^2\left[\left(\frac{E_i'}{2\mu'}\right)^{\frac{1}{2}}\frac{t}{L}\right]\exp\left(\frac{\gamma q}{L}\right) \tag{3-4}$$

where

$$E_i'=\frac{1}{2}\mu' v_0^2. \tag{3-5}$$

μ' is the reduced mass of A and B defined as

$$\mu'=M_A M_B/(M_A+M_B). \tag{3-6}$$

Expanding the potential into a power series in q, we obtain

$$V'(t,q)=E_i'\operatorname{sech}^2\left[\left(\frac{E_i'}{2\mu'}\right)^{\frac{1}{2}}\frac{t}{L}\right]\cdot\left[\sum_{j=0}^{\infty}\frac{1}{j!}\left(\frac{\gamma}{L}q\right)^j\right] \tag{3-7}$$

Since the harmonic oscillator approximation is valid only for the low lying energy levels, we take the terms up to the fourth power in q and neglect all higher order terms.

The first term in the perturbing potential does not contain q, so it has nothing to do with vibrational transitions. Therefore, it will also be dropped, and only the terms containing q will be retained. Then,

$$V'(t,q)=\sum_{j=1}^{4}\eta_j(t)q^j \tag{3-8}$$

with the time-dependent coefficients $\eta_j(t)$ defined as

$$\eta_j(t)=\frac{1}{j!}\left(\frac{\gamma}{L}\right)^j E_i'\operatorname{sech}^2\left[\left(\frac{E_i'}{2\mu'}\right)^{\frac{1}{2}}\frac{t}{L}\right] \tag{3-9}$$

4. FORMULATION of VIBRATIONAL TRANSITION PROBABILITIES

General Description. After taking out translational motion of the system as a whole, the Schrödinger equation for the molecular vibrational state becomes

$$i\hbar\frac{d\psi(t)}{dt}=H(t)\psi(t)=[H_0+H'(t)]\psi(t) \tag{4-1}$$

where H_0 is the Hamiltonian of the unperturbed diatomic molecule, and $H'(t)$ is the time-dependent perturbing Hamiltonian;

$$H_0=(p^2+\mu^2\omega^2q^2)/2\mu, \tag{4-2}$$

$$H'(t)=V'(t,q). \tag{4-3}$$

Here p is the momentum operator, μ the reduced mass, and ω the fundamental vibrational frequency of the oscillator B-C.

We now introduce a time development operator $U(t, t_0)$, which generates a vibrational wave function $\psi(t)$ at time t from the initial wave function $\psi(t_0)$ at time t_o,

$$\psi(t) = U(t, t_0)\psi(t_0). \qquad (4\text{-}4)$$

So $U(t, t_0)$ satisfies a differential equation

$$i\hbar\frac{dU(t, t_0)}{dt} = H(t)U(t, t_0) \qquad (5\text{-}5)$$

with the boundary condition $U(t_0, t_0) = 1$.
In the interaction representation,[10] the time dependence associated with H_0 is taken out by making a unitary transformation

$$\varphi(t) = \exp(iH_0t/\hbar)\psi(t). \qquad (4\text{-}6)$$

This gives

$$i\hbar\frac{dU(t, t_0)}{dt} = H_I'(t)U(t, t_0) \qquad (4\text{-}7)$$

with the interaction Hamiltonian $H_I'(t)$ defined by

$$H_I'(t) = \exp(iH_0t/\hbar)H'(t)\exp(-iH_0t/\hbar). \qquad (4\text{-}8)$$

In the limit of the sudden perturbation for which the vibrational energy levels are closely spaced compared to the translational energy, following approximate solution has been obtained for $U(t, t_0)$ and applied to various problems with good results[11~16].

$$U(t, t_0) = \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} H_I'(t')\,dt'\right]. \qquad (4\text{-}9)$$

Since we will deal with large collision energies in the electron volt range, this approximate solution is suitable for our calculation. In the present problem it is much more convenient to use, instead of q and p, a pair of operators $\boldsymbol{a}^+$ and $\boldsymbol{a}$[17] defined as

$$\boldsymbol{a}^+ = \left(\frac{\mu\omega}{2\hbar}\right)^{\frac{1}{2}}\left(q - i\frac{p}{\mu\omega}\right) \qquad (4\text{-}10)$$

and

$$\boldsymbol{a} = \left(\frac{\mu\omega}{2\hbar}\right)^{\frac{1}{2}}\left(q + i\frac{p}{\mu\omega}\right) \qquad (4\text{-}11)$$

with the commutation relation

$$[\boldsymbol{a}, \boldsymbol{a}^+] = \boldsymbol{a}\boldsymbol{a}^+ - \boldsymbol{a}^+\boldsymbol{a} = 1. \qquad (4\text{-}12)$$

These operators, when applied upon the harmonic oscillator wave function, have the following useful properties;

$$\boldsymbol{a}^+\psi_n = \sqrt{n+1}\ \psi_{n+1}, \qquad (4\text{-}13)$$
$$\boldsymbol{a}\Psi_n = \sqrt{n}\ \psi_{n-1}. \qquad (4\text{-}14)$$

Using these operators, one obtains for the perturbing Hamiltonian

$$\begin{aligned} H'(t) &= V'(t, q) \\ &= \sum_{j=1}^{4}\left(\frac{\hbar}{2\mu\omega}\right)^{\frac{j}{2}}\eta_j(t)\,(\boldsymbol{a}^+ + \boldsymbol{a})^j \qquad (4\text{-}15) \end{aligned}$$

Expanding the high order terms and using the cpmmutator, we obtain

$$(\boldsymbol{a}^+ + \boldsymbol{a})^2 = \boldsymbol{a}^{+2} + \boldsymbol{a}^+\boldsymbol{a} + \boldsymbol{a}\boldsymbol{a}^+ + \boldsymbol{a}^2, \qquad (4\text{-}16)$$
$$\begin{aligned} (\boldsymbol{a}^+ + \boldsymbol{a})^3 &= \boldsymbol{a}^{+3} + \boldsymbol{a}^3 + 3\boldsymbol{a}^2\boldsymbol{a}^+ + 3\boldsymbol{a}\boldsymbol{a}^{+2} \\ &\quad - 3\boldsymbol{a}^+ - 3\boldsymbol{a}, \qquad (4\text{-}17) \end{aligned}$$

and

$$\begin{aligned} (\boldsymbol{a}^+ + \boldsymbol{a})^4 &= \boldsymbol{a}^{+4} + \boldsymbol{a}^4 + 4\boldsymbol{a}^3\boldsymbol{a}^+ + 4\boldsymbol{a}\boldsymbol{a}^{+2} + 6\boldsymbol{a}^2\boldsymbol{a}^{+2} \\ &\quad - 12\boldsymbol{a}\boldsymbol{a}^+ - 6\boldsymbol{a}^{+2} - 6\boldsymbol{a}^2 + 3. \qquad (4\text{-}18) \end{aligned}$$

Single quantum transitions are due to the operators $\boldsymbol{a}^+$, $\boldsymbol{a}$, $\boldsymbol{a}^2\boldsymbol{a}^+$ and $\boldsymbol{a}\boldsymbol{a}^{+2}$, the former two being much more important than the latter two. Single quantum transitions due to $\boldsymbol{a}^2\boldsymbol{a}^+$ and $\boldsymbol{a}\boldsymbol{a}^{+2}$ consist of two processes; one a direct double quantum transition, the other a single quantum transition. Hence, they are far less probable than those due to $\boldsymbol{a}^+$ and $\boldsymbol{a}$ by several orders of magnitude. The operators $\boldsymbol{a}^{+2}$, $\boldsymbol{a}^2$, $\boldsymbol{a}^3\boldsymbol{a}^+$ and $\boldsymbol{a}\boldsymbol{a}^{+3}$ cause double quantum transitions, with the first two playing a much greater role than the others.

The operators $\boldsymbol{a}^{+3}$ and $\boldsymbol{a}^3$ cause direct three quantum excitations and deexcitations, respectively. Direct four quantum transitions are due to $\boldsymbol{a}^{+4}$ and $\boldsymbol{a}^4$. The remaining operators $\boldsymbol{a}^+\boldsymbol{a}$, $\boldsymbol{a}\boldsymbol{a}^+$ and $\boldsymbol{a}^2\boldsymbol{a}^{+2}$, and the constant numerical term do not cause vibrational transitions. We simplify the Hamiltonian by taking only the more important excitation operators for the multiple quantum excitations. That is, we use $\boldsymbol{a}^+$ and $\boldsymbol{a}$ for single quantum transitions, and $\boldsymbol{a}^{+2}$, $\boldsymbol{a}^{+3}$ and $\boldsymbol{a}^{+4}$ for thedirect, non-stepwise double-, triple-, and quadruple-quantum excitations, respectively. Then the perturbing Hamiltonian reduces to

$$\begin{aligned} H'(t) &= \left[\left(\frac{\hbar}{2\mu\omega}\right)^{\frac{1}{2}}\eta_1(t) \right.\\ &\quad \left. -3\left(\frac{\hbar}{2\mu\omega}\right)^{\frac{3}{2}}\eta_3(t)\right](\boldsymbol{a}^+ + \boldsymbol{a}) \\ &\quad +\left[\left(\frac{\hbar}{2\mu\omega}\right)\eta_2(t) - 6\left(\frac{\hbar}{2\mu\omega}\right)^2\eta_4(t)\right]\boldsymbol{a}^{+2} \\ &\quad +\left(\frac{\hbar}{2\mu\omega}\right)^{\frac{3}{2}}\eta_3(t)\boldsymbol{a}^{+3} + \left(\frac{\hbar}{2\mu\omega}\right)^2\eta_4(t)\boldsymbol{a}^{+4} \\ &\equiv x(t)(\boldsymbol{a}^+ + \boldsymbol{a}) + y(t)\boldsymbol{a}^{+2} \\ &\quad + z(t)\boldsymbol{a}^{+3} + u(t)\boldsymbol{a}^{+4}. \end{aligned} \qquad (4\text{-}19)$$

Double-Quantum Transitions. To see the effect of the direct, as well as the stepwise, double-quantum transitions we include the terms containing $\boldsymbol{a}^{+2}$ as well as $\boldsymbol{a}^+$ and $\boldsymbol{a}$ in the perturbing Hamiltonian.

$$H'(t) = x(t)(\boldsymbol{a}^+ + \boldsymbol{a}) + y(t)\boldsymbol{a}^{+2}. \qquad (4\text{-}20)$$

After some elementary steps, one can obtain

$$\begin{aligned} H_I'(t) &= x(t)\exp(i\omega t)\boldsymbol{a}^+ + x(t)\exp(-iwt)\boldsymbol{a} \\ &\quad + y(t)\exp(2i\omega t)\boldsymbol{a}^{+2}. \end{aligned} \qquad (4\text{-}21)$$

From this, the time development operator becomes

$$U(+\infty, -\infty) = \exp[C_1(\boldsymbol{a}^+ + \boldsymbol{a}) + C_2\boldsymbol{a}^{+2}] \qquad (4\text{-}22)$$

where

$$\begin{aligned} C_1 &= -i\left(1-\frac{1}{4}\alpha^2\right) \\ &\quad \frac{\sqrt{2}\,\pi m}{\alpha(m+1)}\operatorname{csch}\left[\frac{\pi}{\alpha}\left(\frac{m}{2E_t}\right)^{\frac{1}{2}}\right], \end{aligned} \qquad (4\text{-}23)$$

and

$$\begin{aligned} C_2 &= -i\left(1-\frac{1}{4}\alpha^2\right) \\ &\quad \frac{\pi m}{m+1}\operatorname{csch}\left[\frac{2\pi}{\alpha}\left(\frac{m}{2E_0}\right)^{\frac{1}{2}}\right]. \end{aligned} \qquad (4\text{-}24)$$

The two dimensionless parameters, m and α, have been introduced to characterize the collision system, and they are defined as follows.

$$m = M_A M_C / M_B(M_A + M_B + M_C) \qquad (4\text{-}25)$$

$$\alpha = \frac{1}{L}\left[\frac{\hbar M_C}{\omega M_B(M_B + M_C)}\right]^{\frac{1}{2}} \qquad (4\text{-}26)$$

E_0 is the symmetrized energy defined as

$$E_0^{\frac{1}{2}} = \frac{1}{2}\left[\left(E_t - i - \frac{1}{2}\right)^{\frac{1}{2}} + \left(E_t - f - \frac{1}{2}\right)^{\frac{1}{2}}\right] \qquad (4\text{-}27)$$

where E_t is the total energy of the system. All energies are experssed in vibrational quantum unit($\hbar\omega$), and i and f denote the initial and final state of the oscillator, respectively.

Using the Baker-Hausdorff theorem[18,19] we put the time development operator just derived into a more convenient form to use,

$$\begin{aligned} U(+\infty, -\infty) &= \exp\left(\frac{1}{2}C_1^2 + \frac{1}{3}C_1^2 C_2\right)\cdot \\ &\quad \exp[C_1(1+C_2)\boldsymbol{a}^+]\cdot \\ &\quad \exp(C_2\boldsymbol{a}^{+2})\cdot\exp(C_1\boldsymbol{a}). \end{aligned} \qquad (4\text{-}28)$$

When the oscillator is originally in its m-th state,

$$\begin{aligned} \psi &= U(+\infty, -\infty)\psi_m \\ &= \exp\left(\frac{1}{2}C_1^2 + \frac{1}{3}C_1^2 C_2\right) \\ &\quad \cdot\left[\sum_{i=0}^{m}\frac{C_1^i}{i!}\sqrt{\frac{i!}{(m-i)!}}\right. \\ &\quad \sum_{j=0}^{\infty}\frac{C_2^j}{j!}\sqrt{\frac{(m-i+2j)!}{(m-i)!}} \end{aligned}$$

$$\sum_{k=0}^{\infty} \frac{[C_1(1+C_2)]^k}{k!} \sqrt{\frac{(m-i+2j+k)!}{(m-i+2j)!}}\Bigg]\psi_{m-i+2j+k} \qquad (4\text{-}29)$$

from which we get the transition probability from the m-th to the n-th level as

$$\begin{aligned} P_{m\to n} &= |\langle\psi_n|U(+\infty,-\infty)|\psi\rangle|^2 \\ &= \Bigg[\exp\left(\frac{1}{2}C_1^2+\frac{1}{3}C_1^2C_2\right) \\ &\cdot\left(\sum_{i=0}^{m} \frac{C_1^i}{i!}\sqrt{\frac{m!}{(m-i)!}} \sum_{j=0}^{(n-m-i)/2} \frac{C_2^j}{j!}\right. \\ &\sqrt{\frac{(m-i+2j)!}{(m-i)!}}\, \frac{[C_1(1+C_2)]^{n-m+i+2j}}{(n-m+i-2j)!} \\ &\left.\sqrt{\frac{n!}{(m-i+2j)!}}\right)\Bigg]^2 \end{aligned} \qquad (4\text{-}30)$$

Specifically for $P_{0\to 2}$, this general expression reduces to

$$\begin{aligned} P_{0\to 2} &= \exp(-|C_1|^2)\Big[\frac{1}{2}|C_1^4|(1-|C_2|^2)^2 \\ &+2|C_2|^2(|C_1|^2-1)^2\Big]. \end{aligned} \qquad (4\text{-}31)$$

Three-Quantum Transitions. Direct three-quantum excitations are due to the operator $\boldsymbol{a}^{+3}$. To study the effect of this non-stepwise transition we include $\boldsymbol{a}^{+3}$ term as well as $\boldsymbol{a}^{+}$ and $\boldsymbol{a}$ in the perturbing Hamiltonian,

$$H'(t)=x(t)(\boldsymbol{a}^{+}+\boldsymbol{a})+z(t)\boldsymbol{a}^{+3}. \qquad (4\text{-}32)$$

Following the same procedure outlined for double-quantum transition case, we obtain

$$\begin{aligned} H_I'(t) &= x(t)\exp(i\omega t)\boldsymbol{a}^{+}+x(t)\exp(-i\omega t)\boldsymbol{a} \\ &+z(t)\exp(3i\omega t)\boldsymbol{a}^{+3}, \end{aligned} \qquad (4\text{-}33)$$

and

$$U(+\infty,-\infty)=\exp[C_1(\boldsymbol{a}^{+}+\boldsymbol{a}]+C_3\boldsymbol{a}^{+3}] \qquad (4\text{-}34)$$

with

$$C_3=-i\frac{\pi\alpha m}{2\sqrt{2}\,(m+1)}\operatorname{csch}\left[\frac{3\pi}{\alpha}\left(\frac{m}{2E_0}\right)^{\frac{1}{2}}\right] \qquad (4\text{—}35)$$

Again using the Paker-Hausdorff theorem, one finds

$$\begin{aligned} U(+\infty,-\infty) &= \exp[C_1(\boldsymbol{a}^{+}+\boldsymbol{a})+C_3\boldsymbol{a}^{+3}] \\ &= \exp\left(\frac{1}{2}C_1^2+\frac{1}{4}C_1^3C_3\right) \\ &\cdot\exp[C_1(1+C_1C_3)\boldsymbol{a}^{+}] \\ &\cdot\exp\left(\frac{3}{2}C_1C_3\,\boldsymbol{a}^{+2}\right) \\ &\cdot\exp[C_3\boldsymbol{a}^{+3})\cdot\exp(C_1\boldsymbol{a}). \end{aligned} \qquad (4\text{-}36)$$

From this

$$\begin{aligned} P_{m\to n} &= \Bigg|\exp\left(\frac{1}{2}C_1^2+\frac{1}{4}C_1^3C_3\right) \\ &\Bigg\{\sum_{i=0}^{m}\frac{C_1^i}{i^i}\sqrt{\frac{m!}{(m-i)!}} \\ &\sum_{j=0}^{(n-m+i)/3}\frac{C_3^j}{j!}\sqrt{\frac{(m-i+3j)!}{(m-i)!}} \\ &\sum_{k=0}^{(n-m+i-3j)/2}\frac{\left(\frac{3}{2}C_1C_3\right)^k}{k!}\sqrt{\frac{(m-i+3j+2k)!}{(m-i+3j)!}} \\ &\frac{[C_1(1+C_1C_3)]^{n-m+i-3j-2k}}{(n-m+i-3j-2k)!} \\ &\sqrt{\frac{n!}{(m-i+3j+2k)!}}\Bigg\}\Bigg|^2, \end{aligned} \qquad (4\text{-}37)$$

and

$$\begin{aligned} P_{0\to 3} &= 6\exp\left(-|C_1|^2+\frac{1}{2}|C_1^3C_3|\right)\cdot \\ &\Big\{\frac{1}{6}|C_1|^3(1-|C_1C_3|)^3+\frac{3}{2}|C_1^2C_3| \\ &(1-|C_1C_3|)-|C_3|\Big\}^2 \end{aligned} \qquad (4\text{—}38)$$

Four-Quantum Transitions. For the perturbing Hamiltonian we take

$$H'(t)=x(t)(\boldsymbol{a}^{+}+\boldsymbol{a})+u(t)\boldsymbol{a}^{+4}. \qquad (4\text{—}39)$$

From this, we obtain

$$\begin{aligned} H_I'(t) &= x(t)\exp(i\omega t)\boldsymbol{a}^{+}+x(t)\exp(-i\omega t)\boldsymbol{a} \\ &+u(t)\exp(4i\omega t)\boldsymbol{a}^{+4}, \end{aligned} \qquad (4\text{—}40)$$

and

$$
\begin{aligned}
U(+\infty, -\infty) &= \exp[C_1(a^+ + a) + C_4 a^{+4}] \\
&= \exp\left(\frac{1}{2}C_1^2 + \frac{1}{5}C_1^4 C_4\right) \\
&\quad \cdot \exp[C_1(1 + C_1^2 C_4)a^+] \cdot \\
&\quad \cdot \exp(2C_1^2 C_4 a^{+2}) \\
&\quad \exp(2C_1 C_4 a^{+3}) \\
&\quad \exp(C_4 a^{+4}) \cdot \exp(C_1 a)
\end{aligned}
\tag{4-41}
$$

where

$$C_4 = -i\frac{\pi\alpha^2 m}{12(m+1)} \operatorname{csch}\left[\frac{4\pi}{\alpha}\left(\frac{m}{2E_0}\right)^{\frac{1}{2}}\right], \tag{4-42}$$

$$
\begin{aligned}
P_{m-n} = \Bigg| &\exp\left(\frac{1}{2}C_1^2 + \frac{1}{5}C_1^4 C_4\right) \\
&\Bigg\{\sum_{i=0}^{m} \frac{C_1^i}{i!}\sqrt{\frac{m!}{(m-i)!}} \\
&\sum_{j=0}^{(n-m+i)/4} \sqrt{\frac{(m-i+4j)!}{(m-i)!}} \\
&\sum_{k=0}^{(n-m+i-4j)/3} \frac{(2C_1C_4)^k}{k!}\sqrt{\frac{(m-i+4j+3k)!}{(m-i+4j)!}} \\
&\sum_{l=0}^{(n-m+i-4j-3k)/2} \sqrt{\frac{(m-i+4j+3k+2l)!}{(m-i+4j+3k)!}} \\
&\frac{[C_1(1+C_1^2C_4)]^{n-m+i-4j-3k-2l}}{(n-m+i-4j-3k-2l)!} \\
&\sqrt{\frac{n!}{(m-i+4j+3k+2l)!}}\Bigg\}\Bigg|^2,
\end{aligned}
\tag{4—42}
$$

and

$$
\begin{aligned}
P_{0-4} = 24\exp(-|C_1|^2) \times \\
\Bigg[\Bigg\{&\frac{|C_1|^4}{24}(1 - 6|C_1^4C_4^2| + |C_1^8C_4^4|) \\
&+ 2|C_1^4C_4^2|(|C_1|^2 - 2)\Bigg\}^2 \\
&+ \Bigg\{|C_1^4C_4|(1 - |C_1^4C_4^2|)\left(\frac{1}{6}|C_1|^2 - 1\right) \\
&+ |C_4|(2|C_1^2| - 1)\Bigg\}^2\Bigg]
\end{aligned}
\tag{4-43}
$$

Our derived transition probabilities, however formidable they may look, should reduce to the simple form derived by Rapp *et. al.*[8] in the limit of stepwise transitions. This can be easily shown by letting C_2, C_3, and C_4 equal to zero for double-, three-, and four-quantum excitations, respectively. Then our experessions reduce to

$$P_{0-n} = \exp(-|C_1|^2)\frac{|C_1|^{2n}}{n!} \tag{4-44}$$

which is just what Rapp *et al.*[8] obtained for multiple quantum transitions permitting only the successive, stepwise single quantum transitions.

5. CALCULATION AND RESULTS

To study the effect of nonstepwise direct multiple quantum excitations, we have carried out numerical calculations for five collision systems details of which are shown in *Table* 1. To make

Table 1. Collision parameters.

System	1	2	3	4	5
Description	Ar···O—N	2···12-12	He···H—H	5···1—2	He···HCl
m	0. 500	0. 0769	0. 667	1. 25	3. 50
L(Å)	0. 2	0. 2214	0. 2	0. 2214	0. 2
$\omega(10^{+14}\ \mathrm{sec}^{-1})$	3. 587	3. 257	8. 279	9. 772	5. 632
α	0. 114	0. 1287	0. 31	0. 2973	0. 52

a. Systems 2 and 4 are imaginary systems first used by Kelley and Wolfsberg[20], and later used by other workers.[8,21] The symbol 5···1—2, for example, denotes a collision between an incident particle of mass 5 a. m. u. and a diatomic molecule B-C with $M_B = 1$ a. m. u. and $M_C = 2$ a. m. u.

b. The fundamental vibrational frequencies are calculated based on the following spectroscopic constants.[21]

$NO(^2\Pi_{\frac{1}{2}})$: $\omega_e = 1904.03\ \mathrm{cm}^{-1}$, $H_2(X^1\Sigma_g^+)$: $\omega_e = 4395.24\ \mathrm{cm}^{-1}$, $HCl(X^1\Sigma^+)$: $\omega_e = 2989.74\ \mathrm{cm}^{-1}$

For Systems 2 and 4, the force constant $k = 10.57$ mdyne/Å given by Kelley and Wolfsberg[20] is used.

Table 2. 0→2 Transition probabilities.

$E_t(\hbar\omega)$	$\|C_1\|$	$\|C_2\|$	$P_{0\to2}$	$P_{0\to2}^{HWR}$	$P_{0\to2}/P_{0\to2}^{HWR}$
System 1 (Ar···O—N)					
3	1.524(−4)	7.232(−11)	2.699(−16)	2.734(−16)	0.9870
8	1.146(−1)	4.079(−5)	8.612(−5)	8.612(−5)	0.9872
12	3.669(−1)	4.188(−4)	7.916(−3)	8.013(−3)	0.9879
16	6.900(−1)	1.480(−3)	7.040(−2)	7.110(−2)	0.9901
20	1.048	3.404(−3)	2.009(−1)	2.021(−1)	0.9942
24	1.415	6.198(−3)	2.707(−1)	2.707(−1)	1.000
28	1.782	9.794(−3)	2.106(−1)	2.089(−1)	1.008
System 2 (2···12—12)					
3	7.486(−2)	1.038(−4)	1.564(−5)	1.585(−5)	0.9850
8	7.646(−1)	1.035(−2)	9.524(−2)	9.637(−2)	0.9883
12	1.180	2.327(−2)	2.407(−1)	2.421(−1)	0.9942
16	1.519	3.636(−2)	2.647(−1)	2.643(−1)	1.002
20	1.808	4.879(−2)	2.033(−1)	2.011(−1)	1.011
24	2.064	6.042(−2)	1.284(−1)	1.259(−1)	1.020
28	2.295	7.129(−2)	7.189(−2)	6.975(−2)	1.031
System 3 (He···H—H)					
3	5.865(−2)	6.299(−5)	5.905(−6)	6.459(−6)	0.9144
8	1.082	2.109(−2)	2.125(−1)	2.206(−1)	0.9634
12	1.832	5.859(−2)	1.964(−1)	1.840(−1)	1.067
16	2.467	1.026(−1)	4.243(−2)	3.471(−2)	1.223
20	3.019	1.480(−1)	4.683(−3)	3.269(−3)	1.432
24	3.510	1.929(−1)	3.564(−4)	2.089(−4)	1.706
28	3.955	2.365(−1)	2.146(−5)	1.044(−5)	2.056
System 4 (5···1—2)					
3	1.095(−2)	1.552(−6)	7.189(−9)	7.858(−9)	0.9149
8	6.079(−1)	4.771(−3)	4.719(−2)	5.073(−2)	0.9303
12	1.236	1.956(−2)	2.532(−1)	2.583(−1)	0.9801
16	1.831	4.232(−2)	1.968(−1)	1.846(−1)	1.066
20	2.375	7.010(−2)	5.667(−2)	4.771(−2)	1.188
24	2.874	1.008(−1)	8.923(−3)	6.617(−3)	1.349
28	3.333	1.331(−1)	9.450(−4)	6.076(−4)	1.555
System 5 (He···H—Cl)					
3	1.147(−2)	3.900(−6)	8.668(−9)	1.143(−8)	0.7586
8	5.351(−1)	8.465(−3)	3.084(−2)	3.903(−2)	0.7903
12	1.057	3.266(−2)	2.036(−1)	2.283(−1)	0.8920
16	1.541	6.833(−2)	2.616(−2)	2.431(−2)	1.076
20	1.980	1.108(−1)	1.330(−1)	1.120(−1)	1.366
24	2.379	1.568(−1)	5.677(−2)	3.152(−2)	1.801
28	2.746	2.045(−1)	1.557(−2)	6.437(−3)	2.450

a. The numbers in parentheses denote the power of 10, so, for example, 1.524(−4) = 1.524×10^{-4}.

b. P_{0-2}'s are calculated using the Eq. (4—31).

c. P_{0-2}^{HWR}'s are calculated using the results given in reference 8, and checked with those listed therein.

a systematic variation of α we have included two imaginary systems, systems 2 and 4. These two systems have also been used by other workers.[8,20,21]

Our results are compared with those obtained by Heidrich, Wilson, and Rapp (HWR) who employed the same method with the same collision model but using the linearzed potential.

The effect of the inclusion of direct double-quantum excitations can be investigated by calculating $P_{0\to2}$. The results are tabulated in *Table* 2. In *Fig.* 2 the transition probabilities $P_{0\to2}$ are plotted for system 5. All other systems show similar behavior. The effect of three-quantum excitations are fully realized in the transitions from the ground to the third excited energy level, so $P_{0\to3}$ is chosen for the comparison purpose. The results are shown in *Table* 3 and in *Fig.* 3. In *Table* 4 and *Fig.* 4, the effect of the direct four-quantum excitations are shown. The transition (0→4) is chosen for numerical comparison.

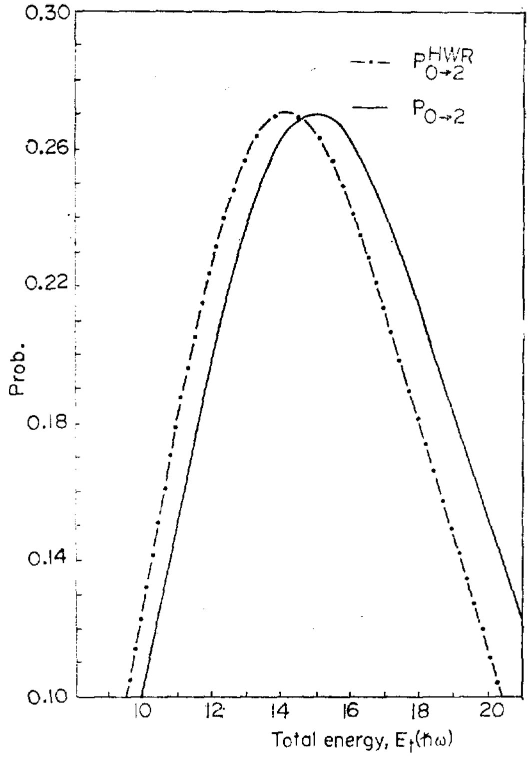

Fig. 2. $P_{0\to2}$ for He···HCl.

6. DISCUSSION

General Trend. From *Tables* 2 through 4 and *Figs.* 2, 3, and 4 we can see that the main effect of the inclusion of direct, non-stepwise multiple quantum excitation operators is to shift the probability *vs.* energy curves to the higher energy side. When direct multiple quantum excitations are included the maximum probability occurs at a slightly higher energy than when only single quantum transitions are considered. The modification to the probability *vs.* energy curve consists of a depression before the maximum and an elevation after it. These general features are in agreement with the conclusions drawn by Robinson[23] in his treatments of the coulomb excitation including two-phonon processes as well as one-phonon processes.

Effect of α. The coefficients C_1, C_2, C_3,

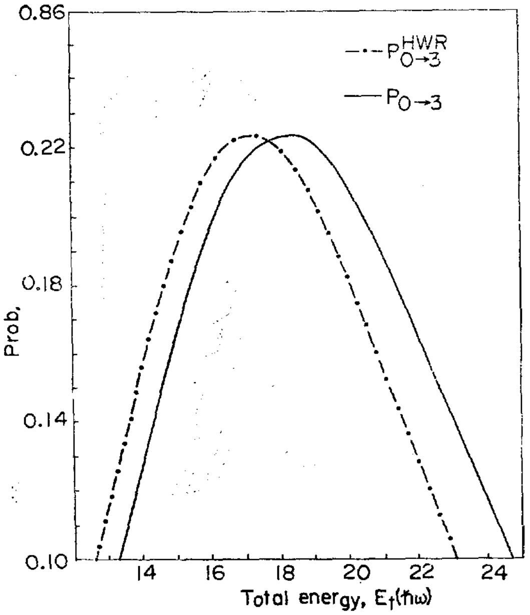

Fig. 3. $P_{0\to3}$ for He···HCl.

Table 3. 0→3 Transition probabilities.

$E_t(\hbar\omega)$	$\lvert C_1\rvert$	$\lvert C_3\rvert$	P_{0-3}	P_{0-3}^{HWR}	P_{0-3}/P_{0-3}^{HWR}
		System 1 (Ar⋯O—N)			
4	5.898(−4)	9.971(−16)	6.979(−21)	7.153(−21)	0.9758
8	8.926(−2)	3.456(−9)	8.360(−8)	8.524(−8)	0.9807
12	3.278(−2)	1.711(−7)	1.857(−4)	1.892(−4)	0.9813
16	6.485(−1)	1.323(−6)	8.140(−3)	8.278(−3)	0.9833
20	1.005	4.913(−6)	6.257(−2)	6.339(−2)	0.9871
24	1.374	1.250(−5)	1.697(−1)	1.709(−1)	0.9928
28	1.742	2.536(−5)	2.240(−1)	2.239(−1)	1.000
		System 2 (2⋯12—12)			
4	1.198(−1)	2.963(−7)	4.856(−7)	4.988(−7)	0.9736
8	6.984(−1)	5.540(−5)	1.187(−2)	1.213(−2)	0.9787
12	1.130	2.149(−4)	9.691(−2)	9.827(−2)	0.9862
16	1.478	4.376(−4)	1.955(−1)	1.968(−1)	0.9939
20	1.773	6.907(−4)	2.233(−1)	2.230(−1)	1.001
24	2.032	9.562(−4)	1.997(−1)	1.870(−1)	1.009
28	2.266	1.225(−3)	1.327(−1)	1.305(−1)	1.017
		System 3 (He⋯H—H)			
4	1.062(−1)	2.057(−7)	2.366(−7)	2.716(−7)	0.8711
8	9.684(−1)	1.526(−4)	5.381(−2)	5.905(−2)	0.9113
12	1.740	8.458(−4)	2.241(−1)	2.230(−1)	1.005
16	2.390	2.076(−3)	1.026(−1)	9.029(−2)	1.136
20	2.952	3.692(−3)	1.818(−2)	1.385(−2)	1.313
24	3.450	5.563(−3)	1.954(−3)	1.254(−3)	1.559
28	3.900	7.593(−3)	1.575(−5)	8.206(−5)	1.920
		System 4 (5⋯1—2)			
4	2.488(−2)	1.319(−9)	3.944(−11)	4.514(−11)	0.8736
8	5.223(−1)	1.217(−5)	2.574(−3)	2.908(−3)	0.8849
12	1.154	1.297(−4)	1.039(−1)	1.118(−1)	0.9296
16	1.756	4.481(−4)	2.238(−1)	2.223(−1)	1.007
20	2.308	9.923(−4)	1.224(−1)	1.099(−1)	1.115
24	2.812	1.749(−3)	3.032(−2)	2.415(−2)	1.256
28	3.276	2.686(−3)	4.528(−3)	3.144(−3)	1.440
		System 5 (He⋯H—Cl)			
4	2.514(−2)	7.500(−9)	4.179(−11)	6.396(−11)	0.6534
8	4.628(−1)	4.659(−5)	1.316(−3)	1.947(−3)	0.6759
12	9.889(−1)	4.480(−4)	5.863(−2)	7.703(−2)	0.7612
16	1.480	1.467(−3)	1.969(−1)	2.146(−1)	0.9175
20	1.925	3.141(−3)	2.083(−1)	1.818(−1)	1.146
24	2.330	5.397(−3)	1.165(−1)	7.883(−1)	1.478
28	2.701	8.138(−3)	4.388(−2)	2.238(−2)	1.961

a. P_{0-3}'s are calculated by use of Eq. (4-38).

b. P_{0-3}^{HWR}'s are calculated using the results given in reference 8.

Table 4. 0→4 Transition probabilities.

$E_t(\hbar\omega)$	$\lvert C_1\rvert$	$\lvert C_4\rvert$	P_{0-4}	P_{0-4}^{HWR}	$P_{0-4}/P_{0-4}^{\mathrm{HWR}}$
		System 1 (Ar…O—N)			
5	1.520(−3)	2.692(−20)	1.187(−24)	1.219(−24)	0.9743
10	1.615(−1)	3.430(−12)	1.877(−8)	1.927(−8)	0.9745
16	6.030(−1)	6.652(−1)	5.063(−4)	5.184(−4)	0.9766
20	9.572(−1)	4.211(−9)	1.175(−2)	1.199(−2)	0.9800
24	1.326	1.541(−8)	6.855(−2)	6.955(−2)	0.9855
30	1.878	6.140(−8)	1.895(−1)	1.901(−1)	0.9970
34	2.237	1.227(−7)	1.753(−1)	1.741(−1)	1.007
		System 2 (2…12—12)			
5	1.666(−1)	8.171(−10)	2.404(−8)	2.485(−8)	0.9676
8	6.252(−1)	1.528(−7)	6.576(−4)	6.776(−4)	0.9705
12	1.077	1.199(−6)	2.369(−2)	2.426(−2)	0.9761
16	1.435	3.331(−6)	9.553(−2)	9.708(−2)	0.9841
20	1.736	6.324(−6)	1.688(−1)	1.702(−1)	0.9920
24	2.000	9.927(−6)	1.954(−1)	1.953(−1)	1.000
28	2.237	1.394(−5)	1.753(−1)	1.738(−1)	1.009
		System 3 (He…H—H)			
5	1.610(−1)	7.028(−10)	1.838(−8)	2.196(−8)	0.8346
8	8.445(−1)	5.214(−7)	5.283(−3)	6.130(−3)	0.8617
12	1.642	7.042(−6)	1.486(−1)	1.572(−1)	0.9451
16	2.309	2.560(−5)	1.629(−1)	1.524(−1)	1.068
20	2.882	5.754(−5)	4.899(−2)	3.992(−2)	1.227
24	3.388	1.017(−4)	7.480(−3)	5.258(−3)	1.423
28	3.844	1.561(−4)	7.592(−4)	4.577(−4)	1.659
		System 4 (5…1—2)			
5	4.416(−2)	1.407(−12)	6.019(−13)	7.196(−13)	0.8364
8	4.331(−1)	1.298(−8)	4.279(−5)	5.073(−5)	0.8435
12	1.068	4.732(−7)	2.256(−2)	2.560(−2)	0.8754
16	1.678	2.815(−6)	1.569(−1)	1.649(−1)	0.9512
20	2.238	8.616(−6)	1.752(−1)	1.666(−1)	1.051
24	2.749	1.892(−5)	7.101(−2)	6.012(−2)	1.181
28	3.218	3.420(−5)	1.522(−2)	1.134(−2)	1.343
		System 5 (He…HCl)			
5	4.353(−2)	1.677(−11)	5.363(−13)	9.386(−13)	0.5714
8	3.869(−1)	1.042(−7)	1.800(−5)	3.081(−5)	0.5842
12	9.184(−1)	3.250(−6)	9.072(−3)	1.399(−2)	0.6484
16	1.417	1.789(−5)	9.098(−2)	1.178(−1)	0.7725
20	1.869	5.219(−5)	1.886(−1)	1.954(−1)	0.9656
24	2.279	1.108(−4)	1.683(−1)	1.350(−1)	1.247
28	2.654	1.951(−4)	8.947(−2)	5.434(−2)	1.646

a. P_{0-4}'s are obtained using the Eq. (44-3).

b. P_{0-4}^{HWR}'s are calculated with the results given in the reference 8.

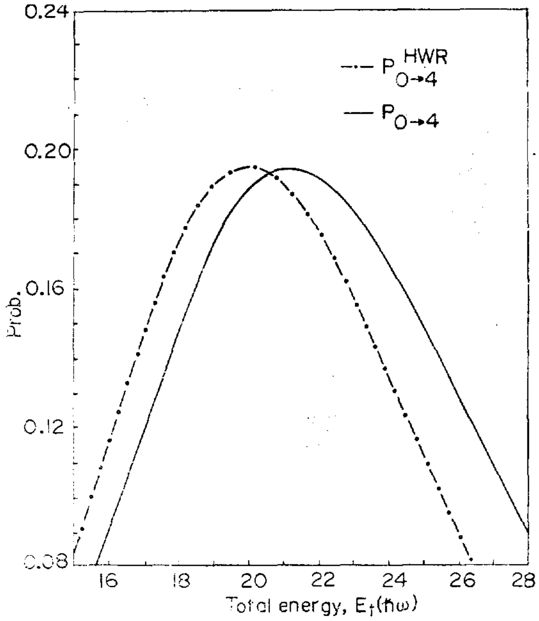

Fig. 4. $P_{0\to4}$ for He···HCl.

Table 5. Calculated values of α.

Molecule	α
H_2	0.315
N_2	0.112
O_2	0.129
S_2	0.135
F_2	0.158
Cl_2	0.143
Br_2	0.127
I_2	0.124
CO	0.102(0.135)
NO	0.114(0.128)
HF	0.023(0.43)
HCl	0.015(0.52)
HBr	0.071(0.56)
HI	0.0048(0.60)

a. $L=0.2$ Å has been used for all cases.[24]
b. For all molecules calculations have been based on the ground electronic state.
c. The number in parenthesis is for the light atom of the molecule being in the center.

and C_4 for the operators a^+, a^{+2}, a^{+3}, and a^{+4} are a measure of the relative importance of the single-, double-, three-, and four-quantum excitations, respectively. The functional dependence of the coeffients on α is, approximately,

$$C_n \simeq \alpha^{n-2}\operatorname{csch}\left(\frac{n}{\alpha}\right) \qquad (5\text{-}1)$$

Therefore, when α is small, C_2, C_3, and C_4 become negligible when compared to C_1, and the effects of direct multiple-quantum transitions also become very small. On the other hand, when α is large, the magnitudes of C_2, C_3, and C_4 become quite appreciable, and the corresponding effects of the double- triple-, and quadruple-quantum transitions become large too. This situation is clearly exhibited in *Tables* 2 through 4. For systems 1 and 2, α's are about 0.1, and the ratio $P_{0\to n}/P_{0\to n}^{HWR}$ are very close to unity. So the higher order terms in the interaction potential which cause direct multiple quantum transitions are not imprtant for these two systems. For systems 3, 4, and 5 with $\alpha=0.3$, 0.2973, and 0.5, respectively, the ratios are significantly different from unity. For these collision systems one must consider the higher order terms in the interaction potential when one calculates the multiple quantum transition probabilities.

The calculated values of α for some typical diatomic molecules are listed in *Table* 5. From this table, one can see α for usual diatomic molecules is about 0.1. For these molecules direct multiple quantum transitions are not important. For hydrogen containing molecules, however, α can be quite large especially when the light atom is hit by the incident particle. For these molecules direct multiple quantum transitions should be included as well as the stepwise single quantum transitions.

Effect of *m*. The functional dependence of the coefficients C_1, C_2, C_3, and C_4 on m is the same for all cases. The coefficients may be represented as

$$|C_n| = (\text{constant})\,(1+m^{-1})^{-1} \times \operatorname{csch}\,[n\pi\alpha^{-1}(m/2E_0)^{\frac{1}{2}}]. \qquad (5\text{-}2)$$

The preexponential factor is same for all coefficients, but the exponents are different because of the factor n. If m is large, the exponents of C_1, C_2, C_3, and C_4 are becoming progressively larger, thus making C_1, C_2, and C_4 very small compared to C_1. If m is small, the preexponential factor becomes very small. Even though the preexponential factor is same for all C_n's, small m still makes the absolute values of C_n's small. To see the effect of m more clearly we fixed the value of α at 0.5 and varied m systematically from 0.1 to 0.7. The effect of the inclusion of the multiple-quantum transitions is most marked at about $m=0.5$, and tapers off when m is too small or too large. This fact is also evident from the data for systems 3 and 4. For these two systems, α's are almost the same ($\alpha=0.3$ for system 3, and 0.2973 for system 4). However, m for system 3 is 0.667, while that for system 4 is 1.25, and the ratios $P_{0\to n}/P_{0\to n}{}^{\mathrm{HWR}}$ differ more from unity for system 3 than for system 4.

Generally m is large when the incoming particle A is heavy. For homonuclear diatomic molecules the optimum value of m (about 0.5) is realized when the incoming particle has the same mass as the diatomic molecule.

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