Exact Classical-Mechanical Calculation of the Translational-Vibrational Energy Transfer of Energized Anharmonic Diatomic Molecules

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(Received July 2, 1971)

The exact classical-mechanical calculation of the translational-vibrational energy transfer of diatomic molecules was extended to collisions between inert gas and anharmonic oscillator of varying initial vibrational energy. The systems investigated were H_2–He, N_2–Ar, and I_2–Ar. It was found that, at lower vibrational levels, the transitions in both upward and downward directions become more efficient with an increase in the initial vibrational energy of molecules. In a high vibrational energy region, however, vibrational deactivation reaches a maximum and then diminishes as the initial vibrational energy approaches the dissociation threshold. The results illuminate the essence of a "bottleneck" to vibrational energy flow involved in the activation process of bimolecular dissociation of diatomic molecules.

Several workers[1–9] have developed theories on the kinetics of diatomic molecules (and the three-body atomic recombination as the reverse reaction) coupled with molecular vibrational relaxation. Their theories all show that dissociation kinetics should receive a sizable draw-back effect from the limited rates of vibrational activation of molecules, the overall reaction being a process proceeding under vibrational non-equilibrium. Details of the non-equilibrium kinetics should essentially be subject to the vibrational transition probabilities of reacting molecules in their collisions with heat-bath molecules.

However, it is an extremely cumbersome problem to evaluate such probabilities for an anharmonic oscillator energized up to its dissociation threshold. In this high-energy region, the vibrational levels are in general not only densely spaced but also poorly definable because of the coupling between vibrational and rotational degrees of freedom. This constitutes an unsurmountable obstacle to an otherwise successful adaption of the concept of vibrational ladder climbing to the overall kinetics of bimolecular dissociations.

One way to overcome the difficulty is to consider the reaction in question as a process of energy flow, by assuming the vibrational energy to be indiscrete. In principle, the diffusion theory presented by Keck and Carrier[10] and the energy-band theory proposed by Rice[11] are both along this line. In this work we treat the average vibrational energy, $\Delta\varepsilon$, which could be gained or lost by Morse oscillators of arbitrary internal energy on their single collision with an inert gas molecule.

It should be noted that the vibrational energy increment, when calculated for an oscillator of relatively low internal energy, should be related, in its classical limit, to the quantum-mechanical vibrational transition probability, P_{ij}, through $P_{ij}=\Delta\varepsilon/(\varepsilon_i-\varepsilon_j)$, where ε_i and ε_j are the energies of the discrete vibrational levels i and j, respectively. Although a number of theoretical procedures (classical, semiclassical or quantum) have been given for such calculations in the literature,[12] any procedure assuming complete separability between the translational and vibrational motions is of little use for our purpose. Separability is justifiable only when the maximum displacement of an oscillating atom from its equilibrium position is considered to be sufficiently small compared with the range size of interaction between the atom and an incident sphere, which is certainly not the case for an energized anharmonic oscillator. Benson and Berend[13] were the first to calculate the 0→1 transition probabilities of diatoms under *mutual* interaction with the incident atom during a collision; exact collision trajectories were obtained by numerical integration of the classical equations of motion for the colinear system. An analogous "exact" classical-mechanical procedure has been used by Kelley and Wolfsberg[14] in order to calculate the energy transferred between harmonic oscillators and inert atoms. A quantum-mechanical version of these "exact" treatments was presented by Secrest and Johnson,[15] who calculated several lower-level transition probabilities of diatoms as a function of incident energy.

In the present paper, we have adopted the exact classical-mechanical procedure to calculate the energy transfer of Morse oscillators as a function of the initial vibrational energy of oscillators as well as the initial relative translational energy of the collision system. The main part of this paper will be bisected. The first half deals with the transition probabilities between lower vibrational levels. The exact quantum-mechanical results of Secrest and Johnson are used as a

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[1] E. W. Montroll and K. E. Shuler, *J. Chem. Phys.*, **26**, 454 (1957); *Advances Chem. Phys.*, **1**, 361 (1958).

[2] E. V. Stupochenko and A. I. Osipov, *J. Fiz. Khim.*, **33**, 1526 (1959).

[3] H. O. Pritchard, *J. Phys. Chem.*, **65**, 504 (1961).

[4] O. K. Rice, *ibid.*, **65**, 1972 (1961); **67**, 1733 (1963).

[5] S. W. Benson and T. Fueno, *J. Chem. Phys.*, **36**, 1597 (1962).

[6] H. J. Kolker, *ibid.*, **44**, 582 (1966).

[7] H. J. Kolker, *Z. Naturforsch.*, **23a**, 1102 (1968).

[8] V. A. LoDato, D. L. S. McElwain, and H. O. Pritchard, *J. Amer. Chem. Soc.*, **91**, 7688 (1969).

[9] D. L. S. McElwain and H. O. Pritchard, *ibid.*, **91**, 7693 (1969).

[10] J. Keck and G. Carrier, *J. Chem. Phys.*, **43**, 2284 (1965).

[11] O. K. Rice, "Statistical Mechanics, Thermodynamics and Kinetics," Freeman and Co., San Francisco, Calif. (1967), Chapter 19.

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

[13] S. W. Benson and G. C. Berend, *J. Chem. Phys.*, **44**, 470 (1966).

[14] J. D. Kelley and M. Wolfsberg, *ibid.*, **44**, 324 (1966).

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

standard for comparison. The latter half deals with the energy transfer of energized anharmonic oscillators. Some important features of the mechanism of bimolecular dissociation of diatomic molecules are shown by comparison of the resulting energy transfer with that of harmonic oscillators.

Method of Calculation

The calculation is based on the classical colinear collision model. The coordinate system is as defined in Fig. 1; a Morse-type molecule BC is struck by an atom A.

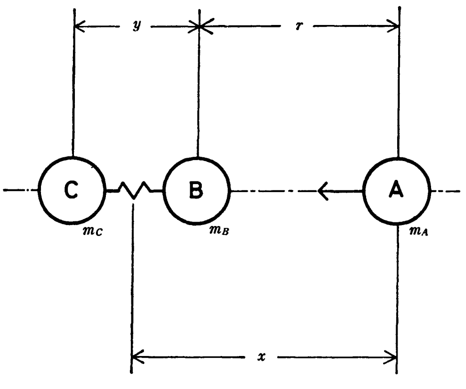


Fig. 1. The colinear collision model and its coordinate system.

The potential of the Morse oscillator is defined by

$$U(y) = D\{\exp[-a(y-y_e)]-1\}^2 \quad (1)$$

The potential acting between the colliding atoms A and B is assumed to be given by the Lennard-Jones 6—12 function:

$$V(r) = 4D_L[(r_L/r)^{12}-(r_L/r)^6] \quad (2)$$

where

$$r = x - ym_C/(m_B+m_C) \quad (3)$$

and m_B and m_C are the masses of atoms B and C respectively. In addition to the above potentials, the harmonic potentials and exponential repulsion potentials were also used for $U(y)$ and $V(r)$, whenever appropriate.

$$U(y) = \frac{1}{2}k(y-y_e)^2 \quad (4)$$

$$V(r) = A\exp(-r/L) \quad (5)$$

The total Hamiltonian of the collision system is expressed by

$$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2\mu} + U(y) + V(x,y) \quad (6)$$

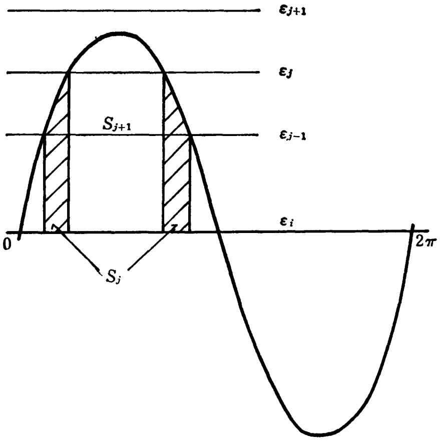
where p_x and p_y denote the momenta with respect to the ordinate variables x and y, respectively, and m and μ are the reduced masses of the collision system and the oscillator, respectively.

$$m = m_A(m_B+m_C)/(m_A+m_B+m_C) \quad (7)$$

$$\mu = m_Bm_C/(m_B+m_C) \quad (8)$$

Hamilton's equations of motion were solved numerically on a digital computer (NEAC 2200) with the aid of the Runge-Kutta-Gill procedure. The initial position of an incoming atom was so selected as to be large enough to render the initial interaction potential $V(x,y)$ negligibly small. The same criterion was applied for terminating the computations. The time step used for integration was 0.5×10^{-16} sec, which proved to be sufficiently small to warrant energy conservation.

For a given vibrational energy ε of the oscillator and a given translational energy E of the incident atom, the energy increment $\Delta\varepsilon$ of the oscillator was calculated as the function of the initial phase angle ϕ of the oscillator. Each initial phase was determined by dividing the period of oscillation into equal time increments. The corresponding initial bond length and momentum were calculated by use of the analytical solution of the internal motion of the Morse oscillator.[16] $\Delta\varepsilon$ was directly evaluated from the difference between the vibrational energies of the oscillator before and after the collision. The $\Delta\varepsilon$ values thus obtained were smooth functions of ϕ, as shown in Fig. 2.



$$P_{i\to j} = \frac{\Delta\varepsilon_{i\to j}}{\varepsilon_j-\varepsilon_i} \qquad \Delta\varepsilon_{i\to j} = S_j/2\pi$$

Fig. 2. Definitions of $\Delta\varepsilon_{i\to j}$ and the exact classical transition probability $P_{i\to j}$.

The average energy gain of the oscillator on a collision can be evaluated simply by integrating the $\Delta\varepsilon(E, \varepsilon, \phi)$ over the region where it is positive, and by dividing the results by 2π.

$$\Delta\varepsilon_{act}(E, \varepsilon) = \frac{1}{2\pi}\int_{\Delta\varepsilon>0}\Delta\varepsilon(E, \varepsilon, \phi)\mathrm{d}\phi \quad (9)$$

Likewise, the average energy loss, $\Delta\varepsilon_{deact}$, can be derived from $\Delta\varepsilon(E, \varepsilon, \phi)$ in the region where $\Delta\varepsilon<0$.

In cases where the initial vibrational energy is not very large, Eq. (9) should be related with the quantum-mechanical transition probability. Suppose the collision energy is relatively low, so that the maximum value of $\Delta\varepsilon(E, \varepsilon, \phi)$ for fixed E and ε is small compared with the energy difference between adjacent vibrational levels. The average energy gain of the oscillator which was initially at the i-th level, can then be expressed by

$$\Delta\varepsilon_{i\to i+1}(E) = \frac{1}{2\pi}\int_{\Delta\varepsilon>0}\Delta\varepsilon(E, \varepsilon_i, \phi)\mathrm{d}\phi \quad (10)$$

The transition probability $P_{i\to i+1}(E)$ can be defined as $\Delta\varepsilon_{i\to i+1}(E)$ divided by the energy difference be-

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[16] N. B. Slater, *Nature*, **180**, 1352 (1957).

tween the i-th and the $(i+1)$-th levels, *viz.*,

$$P_{i\to i+1}(E) = \Delta\varepsilon_{i\to i+1}(E)/(\varepsilon_{i+1}-\varepsilon_i) \tag{11}$$

$P_{i\to i-1}(E)$ can be obtained through an analogous procedure, except that $\Delta\varepsilon_{i\to i-1}(E)$ is calculated from $\Delta\varepsilon$ (E, ε, ϕ) in the region where $\Delta\varepsilon<0$.

On the high-energy collisions, however, the computed energy gain or loss exceeds the energy difference between adjacent levels (see Fig. 2), so that $\Delta\varepsilon_{i\to j}(E)$ should be properly defined so as to include the jumps over more than one quantum. The main problem is how $\Delta\varepsilon$ should be related with these various quantum jumps.

We here propose a working hypothesis that $\Delta\varepsilon$ can be partitioned into various $\Delta\varepsilon_{i\to j}$'s according to the relevant range of phase angles. That is, just as the activation and deactivation were discriminated according to the range of the phase angles which rendered the calculated $\Delta\varepsilon$ positive or negative, the various quantum jumps are considered to be properly characterized by the phase angle ranges which make such multi-step jumps possible on a single collision. Equation (10) can then be extended into a more general form

$$\Delta\varepsilon_{i\to j}(E) = \frac{1}{2\pi}\int_{\varepsilon_j-\varepsilon_i>\Delta\varepsilon>\varepsilon_{j-1}-\varepsilon_i} \Delta\varepsilon(E, \varepsilon_i, \phi)\mathrm{d}\phi \tag{12}$$

where $j=i+1,\ i+2,\cdots\cdots$. For deactivation, the corresponding expression will be as follows:

$$\Delta\varepsilon_{i\to j}(E) = \frac{1}{2\pi}\int_{\varepsilon_{j+1}-\varepsilon_i>\Delta\varepsilon>\varepsilon_j-\varepsilon_i} \Delta\varepsilon(E, \varepsilon_i, \phi)\mathrm{d}\phi \tag{13}$$

where $j=i-1,\ i-2,\cdots\cdots$. The transition probabilities are given by

$$P_{i\to j}(E) = \Delta\varepsilon_{i\to j}(E)/(\varepsilon_j-\varepsilon_i) \tag{14}$$

for either of the activation and deactivation processes. Plausibility of the above hypothesis can only be judged from its outcomings given in the following section.

Vibrational Transitions at Lower Levels

Before discussing the characteristic behavior of the energy transfer of energized molecules, we examine the reliability of the transition probabilities derived for lower levels. Let us compare the exact classical transition probabilities with those obtained by the approximate methods and by the exact quantum-mechanical calculations. In their exact quantum-mechanical theory, Secrest and Johnson[15] assumed a harmonic oscillator model struck by an atom through an exponential repulsion potential. In order to facilitate comparison, we have used the same collision model and potential parameters. Other approximate probabilities based on the classical,[17] semiclassical,[18] and quantum (distorted wave)[19] methods were also evaluated for the same model. The collision systems studied were H_2–He, N_2–Ar, and I_2–Ar. Both the intramolecular and intermolecular potential parameters used are listed in Table 1.

TABLE 1. PARAMETERS FOR THE HARMONIC-EXPONENTIAL-REPULSION POTENTIAL MODELS

System	Harmonic potential[a)]		Collision potential[b)]
	k, 10^4g/sec^2	y_e, Å	L, Å
H_2–He	57.494	0.7413	0.1576
N_2–Ar	229.43	1.0975	0.2041
I_2–Ar	17.202	2.667	0.2400

a) $U(y)=1/2\,k(y-y_e)^2$. k was evaluated from ω_e by use of the equation $k=(2\pi c\omega_e)^2\mu$, where c is the velocity of light and μ is the reduced mass of the oscillator. ω_e was taken from G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules," van Nostrand Reinhold Co., New York (1950).

b) $V(r)=A\exp(-r/L)$. A was taken to be equal to the initial translational energy E. L is evaluated from collision diameter σ by use of the equation $L=\sigma_{A-B}/17.5$ (K. F. Herzfeld and T. A. Litovitz, "Absorption and Dispersion of Ultrasonic Waves," Academic Press, New York (1959)). σ was taken from J. O. Hirschfelder *et al.*, "Molecular Theory of Gases and Liquids," Wiley, New York (1967).

H_2–He system. The values of $P_{0\to1}(E)$ calculated by the various methods as the functions of the initial translational energy of the incident atom are compared in Fig. 3. The approximate classical-, semicalssical-, and quantum-mechanical solutions all give $P_{0\to1}$ values exceeding unity at energetic collisions, whereas both the exact solutions give values which seem reasonable. The latter two solutions are in essential agreement with each other. In the lower collision energy region, however, the exact classical results are somewhat greater than those of the quantum-mechanical calculations.

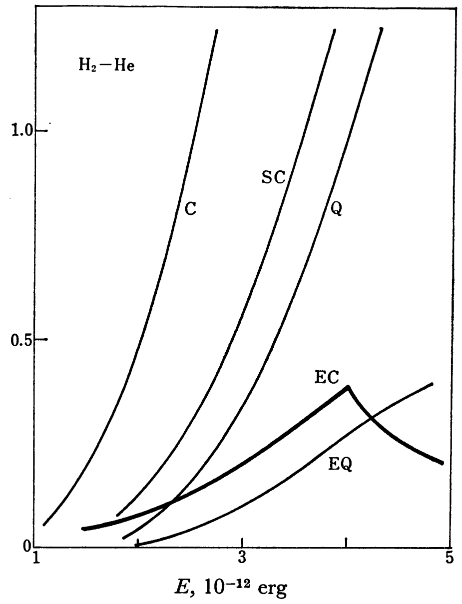

Fig. 3. The 0→1 transition probability of a harmonic H_2 molecule on its collision with an He atom as a function of incident energy.
C, classical[17]; SC, semiclassical[18]; Q, quantum(DW)[19]; EC, exact classical; EQ, exact quantum[15]

The exact classical probabilities calculated for several upward transitions are shown in Fig. 4, and the exact quantum-mechanical results obtained for the same transitions in Fig. 5. A comparison of Figs. 4 and 5

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[17] D. Rapp, *J. Chem. Phys.*, **32**, 735 (1960).

[18] D. Rapp and T. E. Sharp, *ibid.*, **38**, 2641 (1963); **43**, 1233 (1965).

[19] J. D. Jackson and N. F. Mott, *Proc. Roy. Soc.* (London), **A137**, 703 (1932).

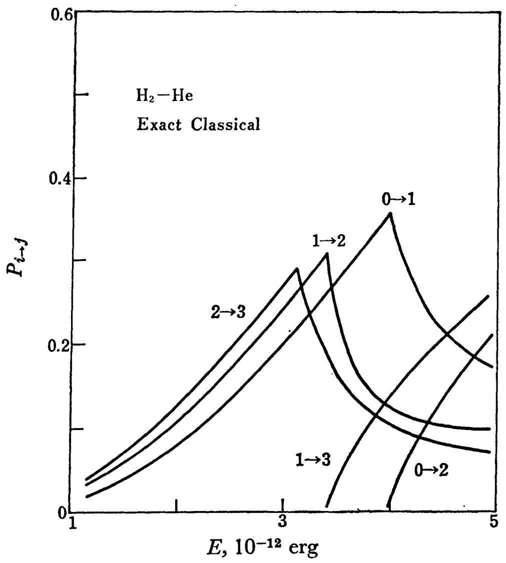

Fig. 4. Exact classical transition probabilities of a harmonic H_2 molecule colliding with a He atom as functions of incident energy.

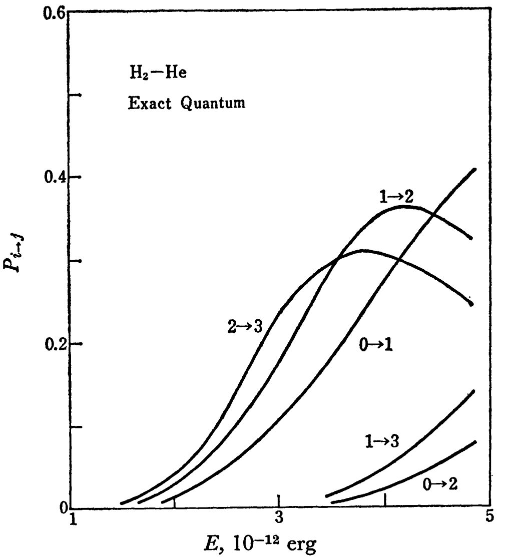

Fig. 5. Exact quantum transition probabilities of a harmonic H_2 molecule colliding with an He atom as functions of incident energy.

TABLE 2. DETAILED BALANCINGS OF THE $P_{i\to j}$ VALUES CALCULATED FOR THE H_2–He SYSTEM

Method	Transition probability	
	$P_{0\to1}$ (E=3.0×10⁻¹² erg)	$P_{1\to0}$ (E=2.17×10⁻¹² erg)
Semiclassical	0.60	0.19
Quantum(DW)	0.35	0.35
Exact Quantum	0.11	0.11
Exact Classical	0.20	0.20
	$P_{1\to2}$ (E=3.0×10⁻¹² erg)	$P_{2\to1}$ (E=2.22×10⁻¹² erg)
Semiclassical	1.21	0.41
Quantum(DW)	0.70	0.70
Exact Quantum	0.18	0.18
Exact Classical	0.29	0.30

a) $\varepsilon_1-\varepsilon_0=0.83\times10^{-12}$erg
b) $\varepsilon_2-\varepsilon_1=0.78\times10^{-12}$erg

shows that the general features of the numerical results reached from the two methods agree fairly well.

One criterion for testing the soundness of the theoretical procedure can be brought about from the microscopic reversibility relationship, which demands that $P_{1\to0}$ at an incident energy E be equal to $P_{0\to1}$ at the energy $E+(\varepsilon_1-\varepsilon_0)$. Table 2 presents a part of such tests. The exact classical method is seen to be at least as good as the quantum-mechanical methods.

N_2–Ar system. The $P_{0\to1}(E)$ values calculated by the various methods are shown in Fig. 6. Here also, the results of the exact quantum-mechanical calculations and those of exact classical calculations closely resemble each other. Although the approximate theories again give too high values of $P_{0\to1}(E)$ for energetic collisions, the differences between the approximate and exact calculations are not as great as those in the case of the H_2–He system, provided the probabilities are compared in the range of ε between 2×10^{-12} and 4×10^{-12}erg.

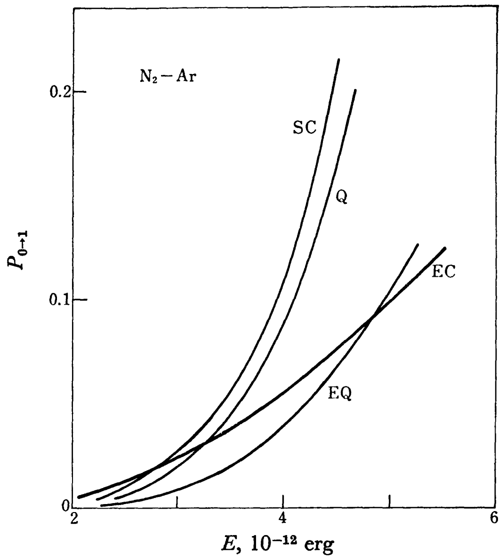

Fig. 6. The 0→1 transition probability of a harmonic N_2 molecule on its collision with an Ar atom as a function of incident energy.
SC, semiclassical[18]; Q, quantum(DW)[19]; EC, exact classical; EQ, exact quantum[15]

The calculations showed that the 1→2 and 2→3 transition probabilities are nearly two- and threefold the 0→1 probability, respectively. This is to be expected, since nitrogen is recognized as the least anharmonic oscillator, to which the well-known Landau-Teller formula,[20] $P_{i\to i+1}=(i+1)P_{0\to1}$, could be applied at lower levels.

I_2–Ar system. Iodine molecules have a very shallow potential and a small vibrational quantum, and the transition probabilities are relatively great even at lower vibrational levels. The first excited vibrational level of iodine molecule lies only 0.035×10^{-12}erg above the ground state. Comparing this value with 0.04×10^{-12}erg, the ***RT*** value at 300°K, one may expect that the 0→1 transition probability will be large

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[20] L. Landau and E. Teller, *Physik. Z. Sowjet Union*, **11**, 18 (1937).

even at room temperature. This in turn implies that at higher temperatures the multi-quantum transition might be more efficient than the 0→1 transition. As an example, the average energy transferred at the collision of $E=0.87\times10^{-12}$erg (the corresponding temperature being as high as 5000°K) is about 0.2×10^{-12}erg, which corresponds to the 0→6 transition.

Several transition probabilities calculated for the I_2–Ar system by the exact classical method are shown in Fig. 7. It may be seen that the 0→1 transition probability reaches its maximum at a collision energy of 0.3×10^{-12}erg and then gradually decreases. The 0→2 transition becomes significant around this energy, attains its maximum at 0.4×10^{-12}erg, and then is replaced by the 0→3 transition.

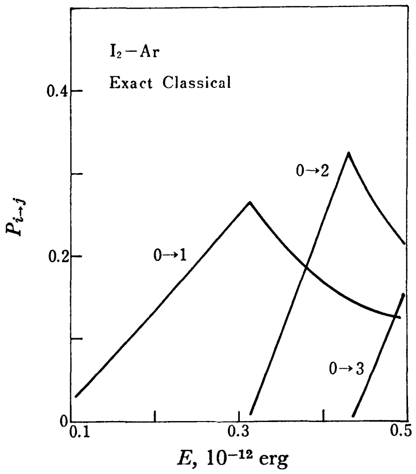

Fig. 7. Exact classical transition probabilities of a harmonic I_2 molecule colliding with an Ar atom as functions of incident energy.

In the case of iodine molecule, one significant transition from a given level is liable to be replaced quickly by another as the incident energy increases. Moreover, the level spacings are so dense that the transition probabilities of each level lose their meaning. Therefore, $\Delta\varepsilon$ will be a more convenient measure of the energy transfer even in the room temperature region.

Energy Transfer in the Higher Vibrational Energy Region

We have extended the exact classical-mechanical calculations to the energy transfer of vibrationally activated diatomic molecules. The collision system consists of a Morse oscillator and an atom interacting with it through the Lennard-Jones potential, a collision model which is more realistic for energized molecules. The systems investigated are H_2–He and I_2–Ar. Various potential parameters used are summarized in Table 3. A harmonic oscillator model was also used for the sake of comparison. Both oscillator models lead to the same results only at lower vibrational levels.

H_2–He system. As an illustrative example, typical trajectories of an atom and a Morse oscillator are shown in Fig. 8. The solid lines represent the motions of an oscillator initially at the 12-th vibrational level and of an atom colliding with the incident energy of 0.5×10^{-12}erg (the corresponding temperature being *ca.* 3620°K). The trajectories of an atom and an oscillator initially at the ground vibrational level are given by broken lines. The amplitude of the energized oscillator is so large, about 1.5 Å at the 12-th level, which is 8 times greater than that of the ground state oscillator, that the assumption $|\Delta y|\ll L$ used in the approximation does not hold. The time duration for the maximum extension is much more prolonged in the energized H_2, thus facilitating its excitation on collision. These facts clearly indicate the necessity of adopting exact treatments, if reliable results are to be obtained for energized diatomic molecules.

Table 3. Parameters for the Morse–Lennard-Jones potential models

System	Morse Potential[a)]			Collision Potential[b)]	
	D, 10^{-12} erg	a, Å^{-1}	y_e, Å	D_L, 10^{-12} erg	r_L, Å
H_2–He	7.602	2.284	0.7413	0.002633	2.759
N_2-Ar	15.88	2.452	1.0975	0.01357	3.576
I_2–Ar	2.495	1.546	2.667	0.0465	4.20

a) $U(y)=D\{\exp[-a(y-y_e)]-1\}^2$. Parameters were taken from G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules," van Nostrand Reinhold Co., New York (1950).

b) $V(r)=4D_L[(r_L/r)^{12}-(r_L/r^6)]$. Parameters were taken from J. O. Hirschfelder *et al.*, "Molecular Theory of Gases and Liquids," Wiley, New York (1967).

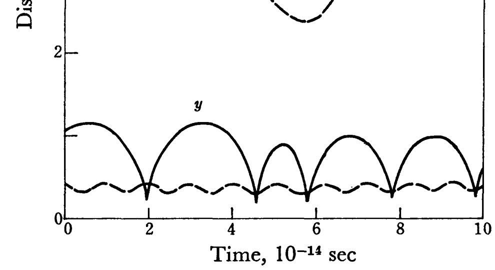

Fig. 8. Trajectories for collisions between a Morse H_2 molecule and an He atom with the incident energy fixed at 0.5×10^{-12} erg.
The initial vibrational levels of H_2 are the 0th (------) and the 12th (——).

The phase-averaged $\Delta\varepsilon$ is calculated for each level for various collision energies ranging from 0.51×10^{-12} to 5.62×10^{-12}erg. Figure 9 shows the results obtained for $E=2.02\times10^{-12}$erg. For the E value chosen, the energy transferred in either of the upward and downward directions increases at first with the level height, and the downward transitions tend to dominate over the upward transitions, except for the 0-th level. Above the 9-th level, however, the energy transferred downward gradually decreases with the level height, until it becomes overshadowed by that for the upward transition, which is capable of leading to dissociation. The higher levels must then be kept depopulated below their thermal-equilibrium populations during the course of overall dissociation reaction.

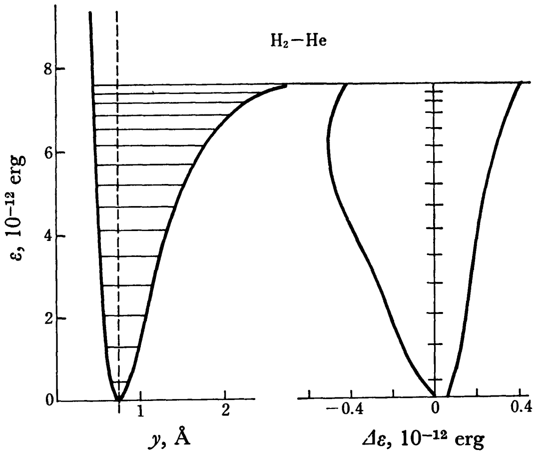

Fig. 9. The average energy change of a Morse H_2 molecule in collision with an He atom as a function of initial vibrational energy. The incident energy is fixed at 2.02×10^{-12} erg.

I_2–Ar system. Dependence of the vibrational energy increment $\Delta\varepsilon$ on the initial vibrational energy of the oscillator is shown in Fig. 10. The features of energy transfer are similar to those noted for the H_2–He system. Occurrence of the maximal deactivation in the vicinity of the threshold region is even more marked than in the H_2–He system.

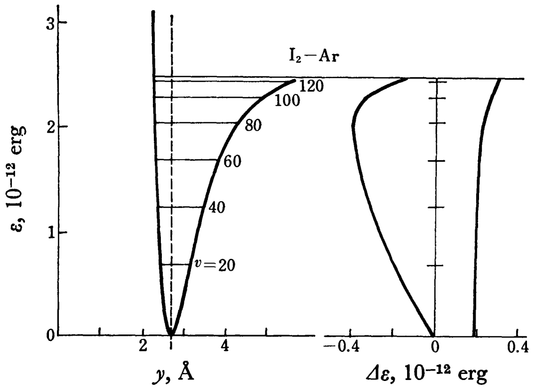

Fig. 10. The average energy change of a Morse I_2 molecule in collision with an Ar atom as a function of initial vibrational energy. The incident energy is fixed at 0.87×10^{-12} erg.

For the sake of comparison, calculations were also carried out for the hypothetical harmonic iodine molecule colliding with an argon atom of $E=0.87\times10^{-12}$erg. The results are shown in Fig. 11, where it is apparent that no such maximal efficiency for deactivation shows up; the deactivation becomes more efficient monotonously with an increase in the initial vibrational energy, and always exceeds the efficiency of activation except in the very low vibrational energy region.

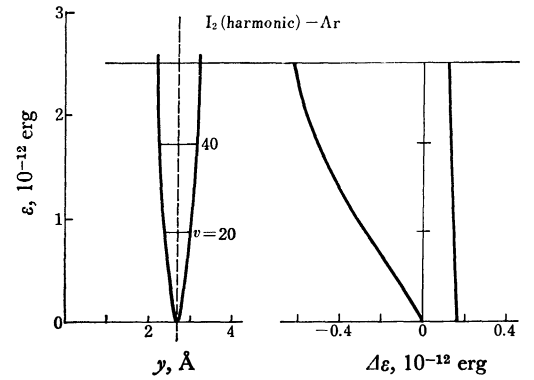

Fig. 11. The average energy change of a harmonic I_2 molecule in collision with an Ar atom as a function of initial vibrational energy. The incident energy is fixed at 0.87×10^{-12} erg.

The effects of the variation of the Morse parameter a on the energy transfer were also examined for a fixed collision energy of $E=0.87\times10^{-12}$erg. The results are shown in Fig. 12. The a values chosen were 1.0 and 3.0 which should be compared with the most plausible value 1.546 for the I_2–Ar system. A larger a corresponds to a greater anharmonicity.[21] The main feature of the results for a large a is the decrease in efficiency of the upward transitions for molecules of low vibrational energy together with the uniform diminution in efficiency of the downward transitions. The former would act to retard the activation of stable molecules, while the latter would accelerate the dissociation of vibrationally excited molecules to continuum. The net result is

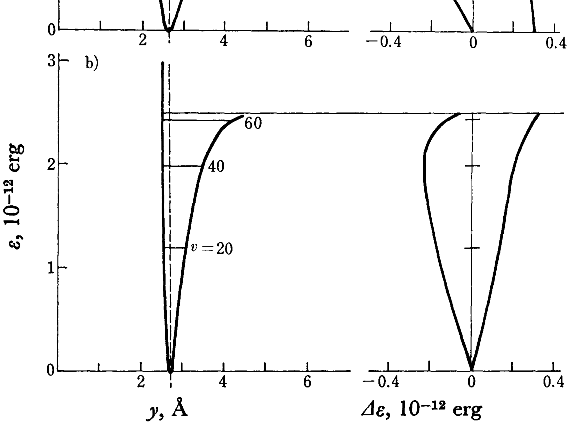

Fig. 12. Effects of the vibrational anharmonicity on the energy change of I_2 in collision with Ar.
a) $a=1.0$ Å; b) $a=3.0$ Å

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[21] This can be readily verified by expanding the Morse potential function with respect to $(y-y_e)$:

$$D\{\exp[-a(y-y_e)]-1\}^2 = Da^2(y-y_e)^2 \times[1-a(y-y_e)+(7/12)a^2(y-y_e)^2+\cdots]$$

that the depopulation of energized molecules will be more conspicuous for diatoms of greater vibrational anharmonicity.

Discussion

From the results we conclude that Morse oscillators are subjected to a maximal extent of vibrational deactivation in the region just beneath the dissociation threshold. The conclusion has an important bearing on the dissociation-recombination kinetics of diatomic molecules in inert gas.

In dissociation, the molecules energized up to the threshold would tend to get excited still more or dissociated on a collision with a heat-bath molecule, whereas the molecules of low internal energy would be provided with far less opportunity of getting excited. As a result, the energized molecules would be kept depopulated below their thermal distribution, thus effecting a considerable lowering in dissociation rate. This is exactly what we have as an image for the nonequilibrium kinetics of dissociation processes.3) The region of the maximal deactivation efficiency can then be taken as a "bottleneck" to a normal upward flow of vibrational energy.

By the same token, the highly energized molecules formed by recombination of atoms would be overpopulated on one hand, and would still retain a good deal of chance to get redissociated on the other. Once the energized molecules have passed through the bottleneck, they are all subjected to deactivation to stable molecules. The net effect is again a lowering in the rate of downward flow because of the presence of the bottleneck, if it is not too narrow. This could be regarded as a physical basis of the steady-flow assumption5) which was invoked in order to account for the kinetics of the molecular recombinations of iodine and bromine atoms. However, if the bottleneck is very narrow because of a great anharmonicity of the molecule formed, it will play a critical role in controlling the rate of energy flow. The steady-state assumption will then be considerably in error, and the net rate will be decreased anomalously as in the case of fluorine.22)

We have not attempted to consider the energy increments averaged over the thermal distribution of collision energies, E. Neither was the energy flow considered explicitly in relation with the reaction rates. Nevertheless, the $\Delta\varepsilon(E, \varepsilon)$ calculated for energized molecules is useful for understanding the kinetic feature of dissociation and recombination. The presence of a bottleneck in these reactions (viewed as energy flow phenomena) can be visualized more clearly than ever before, from an inspection of $\Delta\varepsilon(E, \varepsilon)$ calculated for anharmonic diatomic molecules.

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22) D. J. Seery, *J. Phys. Chem.*, **70**, 1684 (1966).