

# String-plucking model for vibrational excitation of molecules\*

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A "string-plucking" model has been developed to describe the translational to vibrational energy transfer between an atom and a harmonic oscillator in terms of the time-dependent force constant and equilibrium distance of the molecule. The model is compared with exact classical trajectory calculations of collinear and "breathing sphere" collisions involving repulsive exponential or Lennard-Jones interaction potentials. In the adiabatic limit for simple collisions (i.e., in the absence of multiple collisions produced by a light middle atom or a deep potential well), the energy transfer predicted by the model is in good agreement with the exact trajectory results. In the case of the Lennard-Jones potential, both model and exact calculations predict that the effect of decreasing the initial kinetics energy is to increase the fractional energy transfer up to 100%. For breathing sphere collisions with a Lennard-Jones potential, the model correctly predicts a sharp decline in energy transfer at a critical impact parameter which is found in the exact trajectory calculations to equal the rainbow impact parameter. For simple collisions with either potential both model and exact calculations show that the effect of increasing the vibrational energy is equivalent to diminishing the initial radial kinetic energy by an equal amount. The model is also compared with the Landau-Teller, Nikitin, and Attermeyer-Marcus theories, and their regions of validity are explored.

## I. INTRODUCTION

In the last few years there has been much progress in the understanding of energy transfer on a microscopic scale. Exact transition probabilities are being measured experimentally by such techniques as molecular beams, laser-induced fluorescence, and microwave double resonance. In addition, exact quantum mechanical and semiclassical calculations of these quantities are being performed.<sup>1</sup> In order to provide physical insight into these results as well as numerical estimates for systems too complex for exact treatment, it is desirable to have simple, semiquantitative models of energy transfer. In this paper we develop a new, intuitive model of translation-vibration energy transfer and test this and several of the current models against exact trajectory calculations.

The intuitive basis of our model is that during a collision the local equilibrium distance  $r_e$  and force constant  $k$  of a chemical bond are temporarily distorted. For example, if the interaction potential is attractive, the bond tends to weaken and  $r_e$  tends to increase. After the collision, if the bond has not ruptured, the molecule may be found in a vibrationally excited state. In the model calculation the functions  $k(t)$  and  $r_e(t)$  are estimated and the motion of a harmonic oscillator described by these functions is calculated. Because of the brief "plucking" of  $k(t)$  and  $r_e(t)$  we call this treatment a "string-plucking" model. The idea of string plucking was recently used by Russek<sup>2</sup> in a study of vibrational excitation and dissociation induced by polarization forces. He distinguished between impulsive excitation by direct transfer of kinetic energy in a hard nuclear collision and long range, adiabatic plucking of the electrons, which allows the molecule to fall apart long after the scattering partner has left. Although we

treat both types of scattering with the same formalism, we find the distinction useful because of the different time domains involved in the two cases.

In principle, adiabatic string plucking can be applied to any interaction potential between the atom and molecule. For simplicity, however, we have limited ourselves to spherically symmetric potentials and made the impulsive approximation that the trajectory of the atom can be obtained by assuming the oscillator is frozen in its unperturbed equilibrium position. We refer to this as a one-body impulsive trajectory. Recently a number of models have been developed using similar adiabatic and impulsive approximations. In particular, Mahan,<sup>3</sup> Heidrich *et al.*,<sup>4</sup> Levine and Johnson,<sup>5</sup> Morse and Labreque,<sup>6</sup> and Nikitin<sup>7</sup> use the impulsive approximation for the atom, while Attermeyer and Marcus<sup>8</sup> and Thiele and Katz<sup>9</sup> assume that the diatom adjusts adiabatically to the presence of the atom. These authors compare their results with existing exact calculations, and for the most part report favorable agreement. We have found, however, that for a sufficiently large mass ratio (i.e., light middle atom) or deep potential well, and in some cases for a high translational energy or steep potential wall, all of these models (including our own) fail. For this reason we explore the validity of the adiabatic and impulsive approximations in some detail.

In Sec. II we discuss the details of the model. We have found that the method works well if initially the molecule is unexcited ( $E_v=0$ ), while with a simple modification the model can also handle the case with initial vibration. In Sec. III we compare the model with exact classical calculations for  $E_v=0$ , while in Sec. IV we treat the case  $E_v>0$ . In Sec. V, we compare string plucking with various other models and, in the final section, we summarize and discuss our results. Trial calculations have shown that, except near threshold or

for multiple collisions, classical trajectories provide an accurate estimate of the total energy transfer, and therefore, are suitable for the present study. In a subsequent paper we will compare exact classical and semiclassical calculations with exact quantum solutions and discuss in more detail their regions of validity.

## II. DETAILS OF THE MODEL

For simplicity, consider a collision between atom A and harmonic oscillator BC governed by a spherically symmetric intermolecular potential. We can write the potential in the form

$$V(y', x') = \frac{1}{2}k_0 y'^2 + U(y', x'), \quad (1)$$

where  $U$  is the intermolecular potential,  $y'$  is the deviation of the oscillator from its unperturbed equilibrium position  $r_0$ ,  $k_0$  is the unperturbed force constant and  $x'$  is the distance from A to the center of mass of BC. If  $V$  has a local minimum in  $y'$ , we can expand the potential about the local equilibrium position  $r_e(x')$ , giving

$$V(y', x') = \frac{1}{2}k(x') \{y' - [r_e(x') - r_0]\}^2 + \dots \quad (2)$$

If  $x'$  is known as a function of the time  $t$ ,  $V$  can be considered as a function of  $y'$  and  $t$ , and Eq. (2) can be written as

$$V(y', t) = \frac{1}{2}k(t) \{y' - [r_e(t) - r_0]\}^2 \quad (3)$$

ignoring terms in the series of order higher than 2.

The calculation is divided into two distinct parts: first the evaluation of the functions  $x'(t)$ ,  $k(t)$ , and  $r_e(t)$ , and second the solution of the oscillator equation of motion subject to the time dependent potential  $V(y', t)$ . The first part is always done classically, while the second part is done either classically or quantum mechanically.<sup>10</sup> Clearly, to solve for  $x'(t)$  exactly it is necessary to solve the full classical problem exactly. However, in order to keep the model simple we use the one-body impulsive  $x'(t)$  obtained from the potential  $V(y'=0, t)$ .

We have tested the classical version of the model with two kinds of potentials: the repulsive exponential potential

$$U(x, y) = D \exp[-(x-y)], \quad (4)$$

where  $D$  is a constant and the (12, 6) Lennard-Jones potential

$$U(x, y) = 4\epsilon[(x-y)^{-12} - (x-y)^{-6}], \quad (5)$$

where  $\epsilon$  is the well depth. We have used for both potentials the more convenient reduced coordinates

$$\begin{aligned} x &= (x' - \lambda r_0)/l \\ y &= \lambda y'/l, \end{aligned} \quad (6)$$

where

$$\lambda = m_c/(m_b + m_c), \quad (7)$$

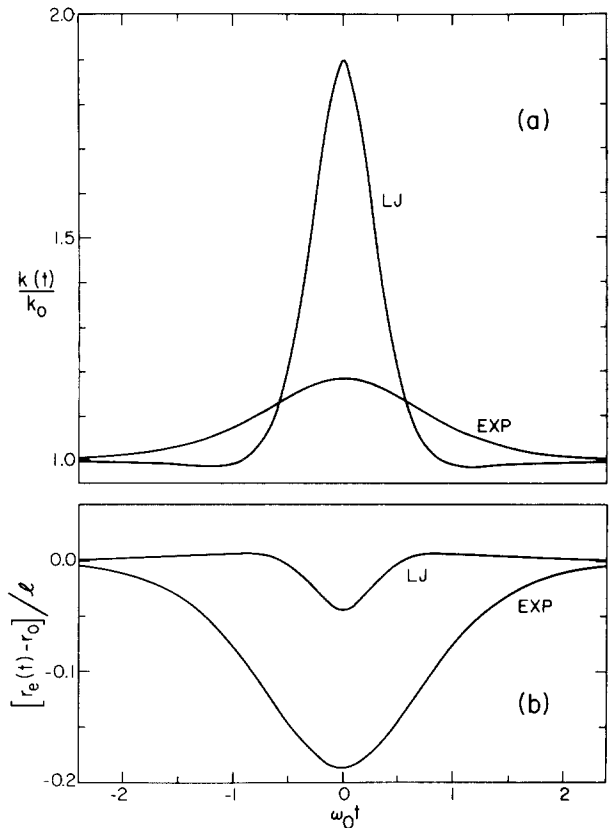


FIG. 1. Driving functions for typical collisions with exponential (EXP) and Lennard-Jones (LJ) potentials. The time-dependent force constant (a) and equilibrium distance (b) are evaluated from the impulsive trajectories with  $m=0.1$ ,  $\bar{E}_i=0.225$  for the exponential potential and  $m=1/13$ ,  $\bar{E}_i=2.5 \times 10^{-3}$ ,  $\bar{\epsilon}=1.875 \times 10^{-3}$  for the Lennard-Jones potential.  $K_0$  is the unperturbed force constant,  $r_0$  the unperturbed equilibrium distance, and  $l$  the range parameter of the potential.

$m_j$  is the mass of atom  $j$ ,  $l$  is a range parameter of the potential, and  $x-y$  is the distance between atoms A and B.

The "driving functions"  $k(t)/k_0$  and  $[r_e(t) - r_0]/l$  for typical collinear collisions with these potentials are shown in Fig. 1. These functions, derived from the approximate one-body impulsive trajectory described above, are symmetric about the turning point (at  $t=0$ ) and approach 1 and 0, respectively, at large  $|t|$ . As the atom approaches the molecule, the repulsive exponential force compresses the oscillator and stiffens the bond, as is shown by the monotonically decreasing equilibrium distance and increasing force constant along the incoming part of the trajectory. In the case of the Lennard-Jones potential, the long range attraction produces an initial increase in the equilibrium distance and decrease in the force constant at large separations, followed by the opposite, repulsive behavior at shorter distances.

Once  $k(t)$  and  $r_e(t)$  are known, the motion of the

TABLE I. Typical collision parameters.<sup>a</sup>

Parameter	Ar+N <sub>2</sub> <sup>b</sup>	He+O <sub>2</sub> <sup>c</sup>	D <sub>2</sub> +Li <sup>d</sup>
$m$	0.588	0.111	0.636
$E_0$ (EXP)	22.9	11.8	5.72
$E_0$ (LJ)	7100	3260	2040
$\epsilon$	0.011	0.0027	0.0045

<sup>a</sup> Energies are in electron volts. In evaluating  $E_0$  (Eq. (14)), the range parameter  $l$  for the exponential potential was assumed to be 0.2 Å, while for the Lennard-Jones potential it was taken from the references in footnotes b-d.

<sup>b</sup> M. Cavallini, M. G. Dondi, G. Scoles, and U. Valbusa, *Chem. Phys. Lett.* **10**, 22 (1971); K. G. Anlauf, R. W. Bickes, and R. B. Bernstein, *J. Chem. Phys.* **54**, 3647 (1971).

<sup>c</sup> H. P. Butz, R. Feltzen, H. Pauly, and H. Vehmeyer, *Abstracts of the VIIth International Conference on the Physics of Electronic and Atomic Collisions* (North-Holland, Amsterdam, 1971), p. 557.

<sup>d</sup> R. K. B. Helbing and E. W. Rothe, *J. Chem. Phys.* **48**, 3945 (1968).

oscillator can be obtained to an arbitrary degree of accuracy, either classically or quantum mechanically, by a piecewise analytical approximation technique. In both cases we represent  $k(t)$  and  $r_e(t)$  by a series of steps of width  $\Delta t$ , with constant value throughout each interval. The equations of motion are easily solved along each step, and the solutions are matched at the endpoints. The classical solution in the  $j$ th time interval  $[t_j, t_j + \Delta t]$  is just

$$y_j(t) = A_j \sin(\omega_j t + \phi_j), \quad (8)$$

where  $\omega_j = [k(t_j)/\mu]^{1/2}$ ,  $\mu$  is the reduced mass of the oscillator, and the amplitude  $A_j$  and phase  $\phi_j$  are chosen so that  $y$  and its derivative are continuous at  $t = t_j = t_{j-1} + \Delta t$ . If the molecule is initially vibrating, it is necessary to average over the initial phase  $\phi_0$ . Quantum mechanically we wish to solve the time-dependent Schrodinger equation  $H(t)\Psi = i\hbar(\partial\Psi/\partial t)$ , where the Hamiltonian is

$$H(t) = -(\hbar^2/2\mu)(\partial^2/\partial y^2) + \frac{1}{2}k_0 y^2 + U[y', x'(t)]. \quad (9)$$

This is achieved by expanding  $\Psi(t)$  for the  $j$ th time interval in the eigenfunctions  $|s_j\rangle$  of the perturbed harmonic oscillator for this step:

$$\Psi_j(t) = \sum_s a_{js} |s_j\rangle \exp[-i(s + \frac{1}{2})\omega_j t]. \quad (10)$$

The  $|s_{j+1}\rangle$  can be expressed as linear combinations of the  $|s_j\rangle$ . This, combined with the condition that  $\Psi$  and its derivative be continuous at  $t_{j+1}$ , permits us to obtain the  $a_{j+1,s}$  in terms of the  $a_{js}$  and the solution is thereby propagated from interval to interval.

The final vibrational energy for the classical case at a time  $t_f$  is

$$E_v^f(E_v, \phi_0) = \frac{1}{2}k_0 A_f^2, \quad (11)$$

where  $E_v$  and  $\phi_0$  are, respectively, the initial vibrational energy and phase of the oscillator. This result is

averaged over different values of  $\phi_0$  [using the same  $k(t)$ ,  $r_e(t)$  and  $x(t)$ ] to give the phase averaged final vibrational energy,  $\langle E_v^f \rangle$ . The quantum mechanical expectation value of the final vibrational energy is

$$\langle E_v^f \rangle = \sum_s (s + \frac{1}{2}) a_{fs}^2 \hbar \omega_0, \quad (12)$$

where at time  $t_f$  the molecule is no longer an eigenstate of the unperturbed Hamiltonian  $H(\pm\infty)$ . In the following sections the single trajectory energy transfer (calculated from either exact classical trajectories or from the string plucking model), is defined by

$$\Delta E = E_v^f - E_v \quad (13a)$$

and the phase averaged energy transfer by

$$\langle \Delta E \rangle = \langle E_v^f \rangle - E_v. \quad (13b)$$

### III. COMPARISON WITH EXACT CALCULATION FOR COLLISIONS OF A MOLECULE WITH NO INITIAL VIBRATIONAL ENERGY

In order to study the effects of different potentials, mass combinations, energies and impact parameters, it is especially convenient to use reduced variables. Secret<sup>11</sup> has shown that by proper scaling it is possible to reduce by one the number of independent parameters in the classical problem.<sup>12</sup> Since we utilize this fact in much of what follows, we will first briefly summarize and slightly extend his results. We express length in units of the potential range parameter  $l$  [see Eq. (6)], time in units of the unperturbed reciprocal angular frequency  $\omega_0^{-1}$ , and energy in units of the quantity

$$E_0 = k_0 l^2 / \lambda^2. \quad (14)$$

We define the mass ratio

$$m = m_a m_c / m_b (m_a + m_b + m_c). \quad (15)$$

The reduced equations of motion are

$$\begin{aligned} m\ddot{x} &= F(x-y) + \bar{E} \bar{b}^2 / x^2 \\ \ddot{y} &= -y - F(x-y), \end{aligned} \quad (16)$$

where  $F$  is the force between  $A$  and  $B$ ,  $\bar{b} = b/l$  is the reduced impact parameter, and  $\bar{E} = E/E_0$  is the total reduced energy.

If the molecule is not initially vibrating, the collinear problem is completely defined by specifying the reduced mass  $m$  and the initial reduced translational energy  $\bar{E}_t$ , plus any additional parameters contained in  $U$  such as the reduced well depth  $\bar{\epsilon}$ . If the molecule is initially vibrating, it is also necessary to specify the initial reduced vibrational energy  $\bar{E}_v$  and phase  $\phi_0$ . The single parameter  $\bar{E}_t$  relates the force constant, initial kinetic energy, and the range of the potential. Classically<sup>12</sup> this means that an energetic collision on a "soft" potential (large  $l$ ) is equivalent to a weak collision on a "hard" potential. It is simple to prove that in the high energy

or hard sphere limit, the amount of energy transferred  $\Delta\bar{E}$  in a "simple" collision (as opposed to a "sticky" or multiple collision) is just the laboratory kinetic energy transferred in the collision of a moving hard sphere and a stationary one with a mass ratio of  $m$ , i.e.,

$$\lim_{\bar{E}_t \rightarrow \infty} (\Delta\bar{E}/\bar{E}_t) = 4m/(m+1)^2. \quad (17)$$

To facilitate the use of reduced variable plots, we have listed in Table I the parameters for several systems illustrating the range of values normally encountered.

The results of both model and exact collinear calculations for the exponentially repulsive potential [Eq. (4)] with  $\bar{E}_v=0$  are shown in Figs. 2-4. Note that for collinear collisions with this potential, the energy transfer is independent of  $D$ . For small  $m$ , the fraction of energy transferred (for the exact calculations) increases with both  $\bar{E}_t$  and  $m$ , and approaches the hard sphere limit [Eq. (17)] at large  $\bar{E}_t$ . However, for  $m \gtrsim 0.5$  the light middle atom strikes the heavy incoming atom two or more times,<sup>11</sup> reducing the net energy transfer and producing extrema in  $\Delta\bar{E}/\bar{E}_t$ . The

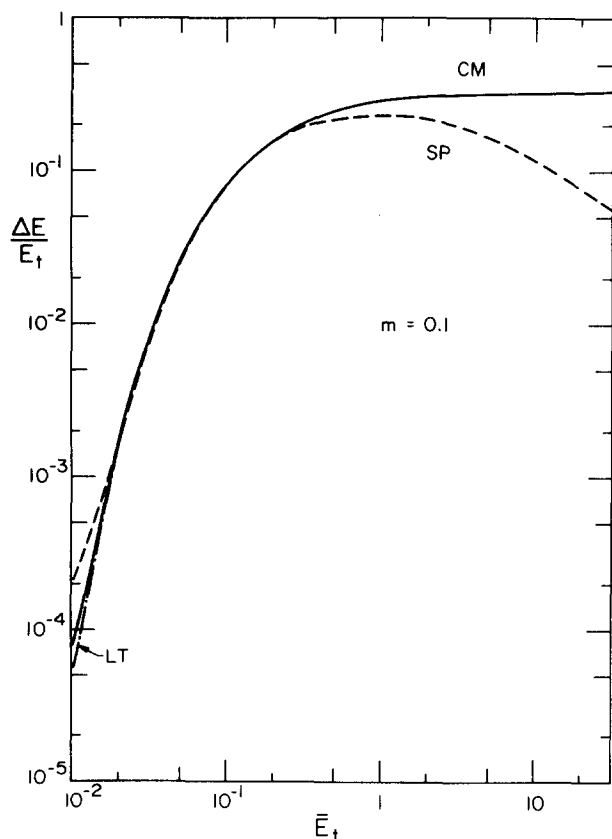


FIG. 2. Classical fractional energy transfer as a function of reduced initial translational energy for collinear collisions between an atom and an initially unexcited ( $E_v=0$ ) harmonic oscillator with an exponential interaction potential. The solid curve corresponds to exact trajectories, the dashed curve to the string-plucking model, and the dot-dashed curve to the Landau-Teller theory. The mass ratio  $m=0.1$  corresponds to a light atom hitting the heavy end of the molecule.

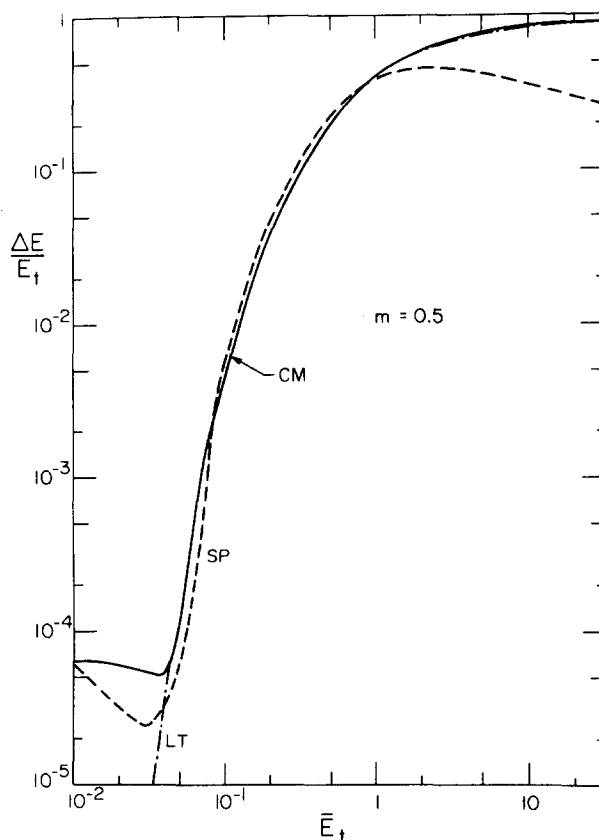


FIG. 3. The same as Fig. 2, but with a mass ratio  $m=0.5$ .

ratio of the unperturbed vibrational period to the collision time is approximately equal to  $\pi\bar{v}$  where the reduced velocity<sup>13</sup>  $\bar{v}$  is defined by

$$\frac{1}{2}m\bar{v}^2 = \bar{E}_t. \quad (18)$$

At low energy ( $\bar{v} \lesssim 1$ ) the model calculation agrees fairly well with the exact result. At higher energies ( $\bar{v} \gtrsim 1$ ) the model oscillator does not have time to react to the rapid perturbation in  $k(t)$  and  $r_s(t)$ , and this produces a falloff in the string plucking value of  $\Delta\bar{E}/\bar{E}_t$ . For many systems the model breaks down only at energies above several electron volts. Focusing attention on the low energy parts of Figs. 3 and 4, we note that the model predicts the minimum which appears in the  $m=0.5$  and  $m=1.0$  cases. However, for larger  $m$ , which corresponds to an even lighter middle atom, we do not expect the model to work as well because of enhanced multiple collisions. These multiple encounters resemble Polanyi's<sup>14</sup> clouting collisions associated with reactive interactions and also the nonreactive multiple collisions of an atom with a rapidly rotating molecule investigated by Kelley and Wolfsberg.<sup>15</sup>

When the potential surface has an attractive well the scattering is very different. The long range attraction accelerates the atom, which then transfers a substantial part of its energy to the oscillator. This effect is especially important at low energies, and causes

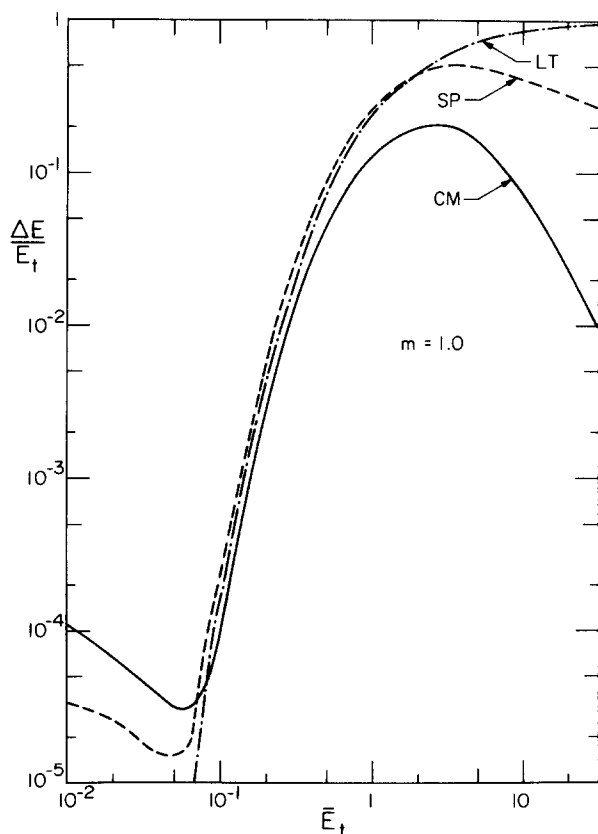


FIG. 4. The same as Fig. 2, but with a mass ratio  $m=1.0$ , corresponding to a heavy atom hitting the light end of the molecule. The falloff in the exact energy transfer at large reduced energy is due to multiple collisions.

$\Delta\bar{E}/\bar{E}_t$  to approach the hard sphere limit from above. (See Fig. 5.) The model correctly predicts this trend, but with a high energy falloff for  $\bar{v} \gtrsim 0.1$ . For an initial kinetic energy smaller than the magnitude of the well depth, both model and exact calculations predict a fractional energy transfer as large as 100%. At still lower values of  $\bar{E}_t$ , the model breaks down and predicts  $\Delta\bar{E}/\bar{E}_t > 100\%$ , while the exact calculation shows a sudden decrease in  $\Delta\bar{E}/\bar{E}_t$  [Fig. 5(b)]. Examination of the exact trajectories shows that this decline in energy transfer is due to the occurrence of "sticky" collisions or Feshbach-type resonances resembling Polanyi's clutching collisions in reactive scattering.<sup>14</sup> The critical value of  $\bar{E}_t$  below which clutching occurs is a sensitive function of  $\bar{\epsilon}$ . For collinear collisions with  $m=1/13$ ,  $\bar{E}_v=0$  and  $\bar{\epsilon}=0.001, 0.01$ , and  $0.1$ , the critical values of  $\bar{E}_t$  for clutching are  $0.00049, 0.0021$ , and  $0.0048$ , respectively. For  $\bar{E}_v > 0$  trial calculations showed that the critical value of  $\bar{E}_t$  is greater than for  $\bar{E}_v=0$  because certain initial vibrational phases are especially favorable for vibrational excitation, thereby reducing the translational energy available to the atom and trapping it in a complex. Eastes and Secrest<sup>16</sup> considered the case of a Morse interaction potential between the atom and the diatom at low energies and a narrower

energy range for quantum collinear collisions. They found no major influence of the presence of the well.

The clutching trajectories are generally complicated and differ qualitatively from the multiple collisions due to large  $m$  described above. In the latter case, the incoming atom has a simple trajectory with a single turning point, while the light middle atom clouts it several times. In the case of the deep well, the incoming atom can bounce many times and the detailed trajectory is very sensitive to the initial phase of the oscillator and the accuracy of the calculation. In the equivalent quantum mechanical calculation it is necessary to include many closed channels to obtain convergence. It is not surprising that the model, which assumes an impulsive trajectory for the atom, cannot reproduce this phenomenon.

So far we have considered results of calculations for the collinear case. For three-dimensional collisions it is necessary also to include rotation of the molecule. To avoid this additional complication, we have treated the molecule as a "breathing sphere" with a spherically symmetric potential. Wagner and McKoy<sup>17</sup> did an exact quantum mechanical calculation of inelastic scattering of an atom and a harmonic oscillator, using both asymmetric and breathing sphere Lennard-Jones interaction potentials. They found for moderate energies that the exact transition probabilities differed from the breathing sphere approximation by at most 10%. Wartell and Cross<sup>18</sup> reached the same conclusion from a model calculation. However, classical trajectory calculations by Razner<sup>19</sup> suggest that for large  $J$ , if the vibrational-rotational coupling energy exceeds the vibrational spacing,<sup>20</sup> the breathing sphere approximation might not be valid. Nevertheless, for smaller  $J$ , the results above<sup>17,18</sup> justify the use of the breathing sphere approximation in our calculations.

We performed a series of exact classical trajectory calculations and the equivalent string-plucking calculations for both the exponential and Lennard-Jones breathing sphere potentials. Figure 6 shows the fraction of energy transferred as a function of reduced impact parameter for fixed masses, energy and potential parameters. We found that whenever the string-plucking model is applicable to the collinear case, it also works well for noncollinear collisions. The quantity  $\Delta\bar{E}/E_t$  for the Lennard-Jones potential exhibits a precipitous falloff when  $\bar{b}$  exceeds some critical value  $\bar{b}_{\max}$ . Here is a case where the model provides a physical interpretation that is not readily apparent from the exact trajectory calculations. As was pointed out in connection with Fig. 1 for collinear collisions ( $t=0$ , at large distances the long range attraction causes the local equilibrium distance to increase  $\{[r_e(t)-r_0]/l > 0\}$  and the force constant to decrease  $[k(t)/k_0 < 1]$  with respect to their unperturbed values, whereas repulsion at the turning point ( $t=0$ ) produces the opposite effect. As the impact parameter is increased, however, the atom feels less of the repulsive part of the potential.

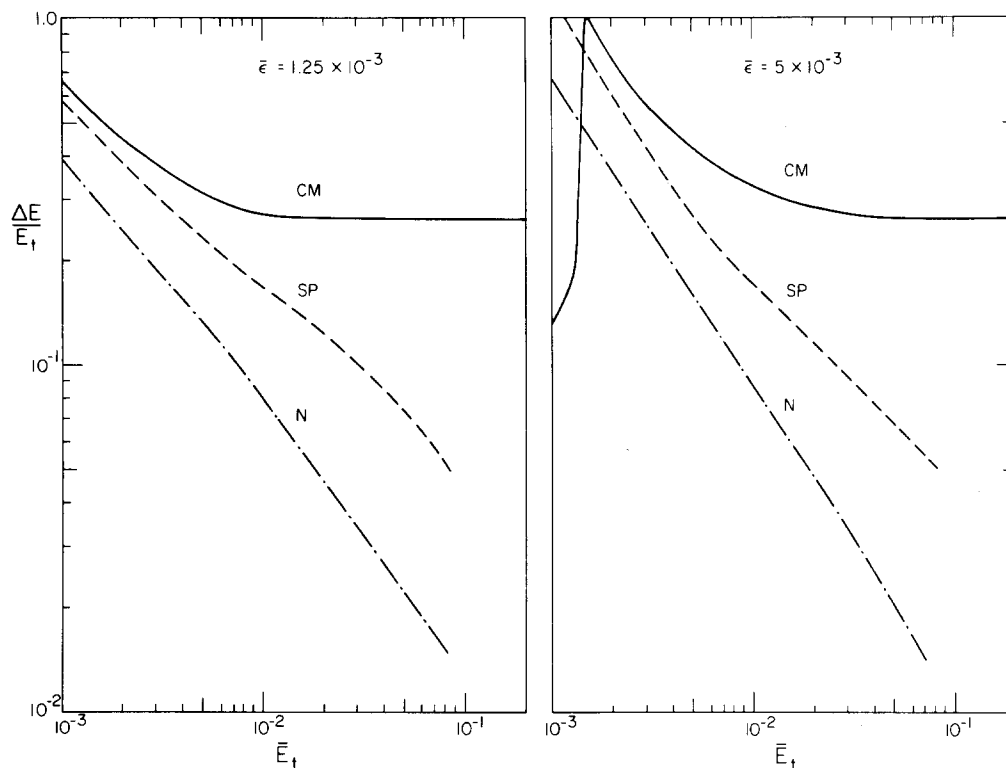


FIG. 5. Classical fraction energy transfer as a function of reduced initial translational energy for collinear collisions between an atom and an initially unexcited harmonic oscillator with a Lennard-Jones interaction potential. The solid curves correspond to exact trajectories, the dashed curves to the string-plucking model, and the dot-dashed curves to the Nikitin model. The mass ratio is 1/13 and the reduced well depth is (a) 0.00125 and (b) 0.005.

Consequently, the driving function  $[r_e(t=0) - r_0]/l$  increases with  $\bar{b}$  (see Fig. 7), and for  $\bar{b} = \bar{b}_{\max}$  this quantity reaches a maximum positive value. At still larger  $\bar{b}$ ,  $r_e(t=0)$  decreases and approaches zero. Similarly,  $k(t=0)/k_0$  decreases with  $\bar{b}$ , and reaches a minimum value slightly less than one at  $\bar{b} \approx \bar{b}_{\max}$ . The sharp decrease in  $\langle \Delta \bar{E} \rangle / \bar{E}_t$  as  $\bar{b}$  approaches  $\bar{b}_{\max}$  from below indicates that vibrational excitation is caused almost entirely by the repulsive (short range) part of the potential.

The maximum in  $[r_e(t=0) - r_0]/l$  vs  $\bar{b}$  is suggestive of the conditions for rainbow scattering. At large impact parameters the attractive part of the potential causes the scattering angle  $\chi$  to be negative. As  $\bar{b}$  is decreased, the repulsive part of the potential produces a minimum in  $\chi$  at  $\bar{b} = \bar{b}_R$ . Since the extrema in both the deflection function ( $\chi$  vs  $\bar{b}$ ) and the driving functions are caused by competition between attractive and repulsive forces, it seems plausible that there might be a simple relation between  $\bar{b}_{\max}$  and  $\bar{b}_R$ . In Fig. 7 the deflection functions for the impulsive trajectories [using the potential  $V(y=0, x)$ ] as well as for the exact trajectories are plotted. In both cases  $\bar{b}_R = 1.55$ , which is the same as  $\bar{b}_{\max}$  within the accuracy of its determination. The fact that  $\bar{b}_{\max} = \bar{b}_R$  provides an interesting link between energy transfer and differential cross sections, with the

rainbow impact parameter providing an upper limit to the  $\bar{b}$  contributing to vibrational excitation cross sections.<sup>21</sup>

#### IV. MODIFICATION FOR MOLECULES WITH INITIAL VIBRATIONAL ENERGY

In the previous section we showed that the model in its classical mechanical version works reasonably well for a molecule which is initially not vibrating ( $\bar{E}_v = 0$ ). To be of practical value, however, the model must also include zero point vibrational energy. Its application for  $\bar{E}_v > 0$  is straightforward, as described at the end of Sec. II. We performed such calculations for the classical case with the exponential potential and found that  $\langle \Delta \bar{E} \rangle$  increases with increasing  $E_v$ . We have also performed the corresponding exact classical trajectory calculations and obtained for simple collisions (i.e., those not involving multiple encounters) the opposite behavior.

Various modifications of the model were attempted to predict correctly the effect of initial vibration. It seemed possible that the difficulty might be caused by use of the approximate potential  $U(y=0, x)$  in calculating the impulsive trajectory of the atom  $x(t)$ . Two attempts were made to improve the potential. In the

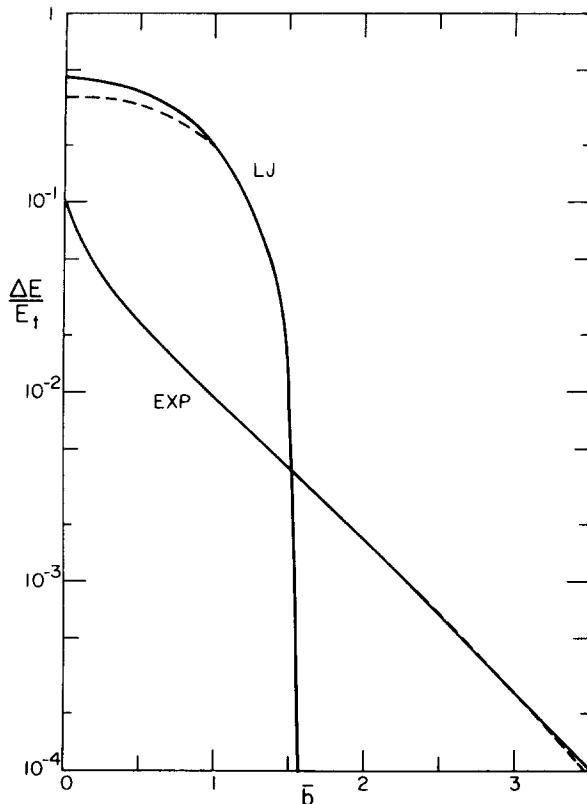


FIG. 6. Classical fractional energy transfer for three dimensional collisions between an atom and an initially unexcited harmonic oscillator with a breathing sphere potential, as a function of reduced impact parameter,  $\bar{b}$ . Solid curves are for exact classical trajectories and dashed curves are for the string-plucking model. Parameters for the exponential potential are  $m=0.1$ , and  $\bar{D}=\bar{E}_t=0.124$ ; for the Lennard-Jones potential they are  $m=1/13$ ,  $\bar{E}_t=2.5 \times 10^{-3}$ , and  $\bar{\epsilon}=1.875 \times 10^{-3}$ .

first calculation the function

$$\tilde{U}(x) = \int_{-A_0}^{A_0} P(y) U(y, x) dy \quad (19)$$

was used instead, where  $P(y)$  is the classical probability distribution of  $y$  for the unperturbed oscillator. We found for the exponential potential that this modification produced the proper trend in  $\langle \Delta \bar{E} \rangle$  vs  $\bar{E}_v$ , but the effect was only about one-third of that of the exact result. In the second calculation we used the original potential  $U(y, x)$  and calculated the exact  $x(t)$  in order to obtain the "best possible" driving functions. These "best" functions were then used in the usual manner to obtain the string-plucking  $\langle \Delta \bar{E} \rangle$ . In this case, we found that  $\langle \Delta \bar{E} \rangle$  increases with  $\bar{E}_v$ , the opposite of the exact result. It thus appears that vibrational energy transfer is very sensitive to the incoming part of the trajectory and it is not possible to uncouple the motion of the atom and oscillator unless  $\bar{E}_v=0$ . The difficulty in uncoupling the equations of motion appears to be borne out by the failure of the exact semiclassical

calculations of Locker and Wilson<sup>22</sup> to agree with their exact classical results.

While improving the driving functions did not improve the model, a different kind of modification was found which did succeed. We noticed that for simple collisions the exact classical trajectory value for  $\langle \Delta \bar{E} \rangle$  with  $\bar{E}_v > 0$  could be well approximated by the result obtained from a single exact trajectory with modified initial conditions<sup>23</sup>:

$$\begin{aligned} \bar{E}_v' &= 0, \\ \bar{E}_t' &= \bar{E}_t - \bar{E}_v. \end{aligned} \quad (20)$$

Table II shows the accuracy of this modification for several typical exact trajectories. For  $\bar{E}_v \lesssim 0.1 \bar{E}_t$ ,  $\Delta \bar{E}' / \bar{E}_t$  agrees with the exact value within 1%, while ignoring  $\bar{E}_v$  entirely produces an error of  $\sim 20\%$ . The approximation becomes poorer as  $\bar{E}_v / \bar{E}_t$  increases. For example, for collinear collisions and the exponential potential with  $m=0.1$  and  $\bar{E}_t=0.225=3\bar{E}_v$ , the modification produces an error of 17% as compared with a 42% error if  $\bar{E}_v$  is ignored.

It appears that for head-on collisions the effect of the initial vibrational energy on the average energy transfer is to "quench" (i.e., decrease the availability of) the translational energy by  $\bar{E}_v$ . For noncollinear collisions we found that  $\bar{E}_v$  does not effectively quench the radial translational energy. An improved modification is obtained by considering the system at the point of closest approach, with coordinates  $(x_c, y_c)$ . We

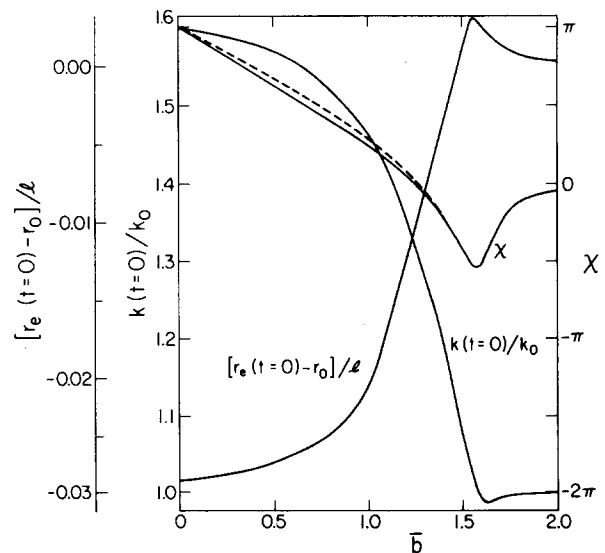


FIG. 7. Deflection function and driving functions for a Lennard-Jones potential. Mass ratio, initial energies, and well depth are the same as in Fig. 6. The driving functions are evaluated at the point of closest approach ( $t=0$ ). The scattering angle  $\chi$  is calculated for both exact (solid curve) and impulsive [dashed curve, calculated from the potential  $V(y=0, x)$ ] trajectories. Note the different ordinate scales for the driving functions (left side) and deflection function (right side).

TABLE II. Quenching of translational energy.

Potential	$m$	$\bar{b}$	$\bar{E}_t$	$\bar{E}_v$	$\langle \Delta \bar{E} / \bar{E}_t \rangle^a$	$\Delta E' / E_t^b$
Exponential	0.1	0	0.225	0.1020	0.0226	0.0471
				0.0750	0.0727	0.0847
				0.0450	0.1133	0.1186
				0.0321	0.1314	0.1339
				0.0250	0.1413	0.1425
				0.0107	0.1598	0.1602
				0.0	0.1736	0.1736
Exponential	1.0	0	0.5	0.25	-0.0221	0.0034
				0.125	0.0115	0.0169
				0.05	0.0309	0.0312
				0.0	0.0434	0.0434
Lennard-Jones $\bar{\epsilon}=0.00125$	0.0769	0	0.01	0.005	0.163	0.154
				0.0025	0.221	0.218
				0.001	0.256	0.255
				0.	0.280	0.280
Exponential $\bar{D}=0.225$	0.1	1	0.225	0.045	0.0133	0.0137
				0.	0.0151	0.0151

<sup>a</sup> Phase averaged over exact classical trajectories. Four trajectories were found sufficient for this average.

<sup>b</sup> Results of classical trajectories with initial conditions given by Eqs. (20) and (22).

generalize Eq. (20) by making

$$\bar{E}'_t = \bar{E}_k(y_c, x_c) + V(y_c, x_c) [1 - (\bar{E}_v / \bar{E}_t)].$$

For  $\bar{b}=0$ , the kinetic energy term  $\bar{E}_k(y_c, x_c)$  vanishes and  $V(y_c, x_c)$  equals  $E_t$ , reducing this equation to Eq. (20). We make the further approximation  $V(y_c, x_c) \approx V(0, \bar{x}_c)$  where  $\bar{x}_c$  is defined by

$$\bar{E}_t(\bar{b}^2/\bar{x}_c^2) + V(y=0, \bar{x}_c) = \bar{E}_t \quad (21)$$

and obtain for arbitrary  $\bar{b}$

$$\begin{aligned} \bar{E}'_t &= \bar{E}_t - \gamma \bar{E}_v \\ \bar{E}'_v &= 0, \end{aligned} \quad (22)$$

where

$$\gamma = V(y=0, \bar{x}_c) / \bar{E}_t. \quad (23)$$

For  $\bar{b}>0$  this modification is less accurate than for collinear collisions. Also, since for noncollinear collisions quenching is less efficient, the error introduced by ignoring initial vibration is smaller than in the collinear case. For a typical collision shown at the bottom of Table II,  $\Delta \bar{E}' / \bar{E}_t$  is 3% larger than the exact value. If in this calculation we had used  $\gamma=1$ , the error would have been -20% and, if we had ignored initial vibration, the error would have been 14%.

In addition to the exact classical calculations, we also performed some trial collinear quantum mechanical calculations<sup>24</sup> for the exponential potential with  $m=1/13$  and found the same kind of quenching effect. Except near the threshold for vibration excitation, we found that the two sets of initial conditions, (a)  $E_t, E_v = (n + \frac{1}{2})\hbar\omega_0$  and (b)  $E'_t = E_t - s\hbar\omega_0, E'_v = (m + s + \frac{1}{2})\hbar\omega_0$ , where  $s$  and  $n$  are arbitrary integers, yield the same

total energy transfer to within 3%. Finally, trial exact classical calculations were done for  $\bar{E}_v > \bar{E}_t$  to see if there is a similar effect for net de-excitation of the molecule. We found indeed that  $\Delta \bar{E}$  is negative and its absolute value increases with  $\bar{E}_v$ , but no simple relation akin to Eq. (20) was observed.

## V. COMPARISON WITH OTHER MODELS

The Landau-Teller model,<sup>25</sup> as modified by Mahan<sup>3</sup> and Heidrich *et al.*,<sup>4</sup> predicts

$$\langle \Delta \bar{E} \rangle_{LT} / \bar{E}_t = [4m / (m+1)^2] (\pi/\bar{v})^2 \text{csch}^2(\pi/\bar{v}), \quad (24)$$

where  $\bar{v}$  is defined by Eq. (18).

As shown in Figs. 2-4, for small  $m$  and large  $\bar{E}_t$ , the LT model is in excellent agreement with exact classical calculations. At large  $m$ , the theory fails to account for multiple collisions and, at very small  $\bar{E}_t$ , the impulsive approximation breaks down. The string-plucking model, on the other hand, is valid at low energies but fails at high energies where the oscillator does not have sufficient time to respond, as discussed after Eq. (18). There is a useful region of intermediate energy where both models agree with the exact classical calculations.

The usual Landau-Teller theory, which is an approximate first-order perturbation solution of the classical equation of motion, does not take into account the initial vibrational energy of the oscillator. Yao and Yao<sup>26</sup> have extended the theory to second order and obtained a correction term that is a function of  $m, E_t$ , and  $\bar{E}_v$ . For  $m=0.05405, E_t=0.0189$ , and  $E_v/\bar{E}_t=0.105$  their approximate  $\langle \Delta \bar{E} \rangle$  is 12% less than the exact result, while for  $\bar{E}_v/\bar{E}_t=0.05$  their quoted error is only



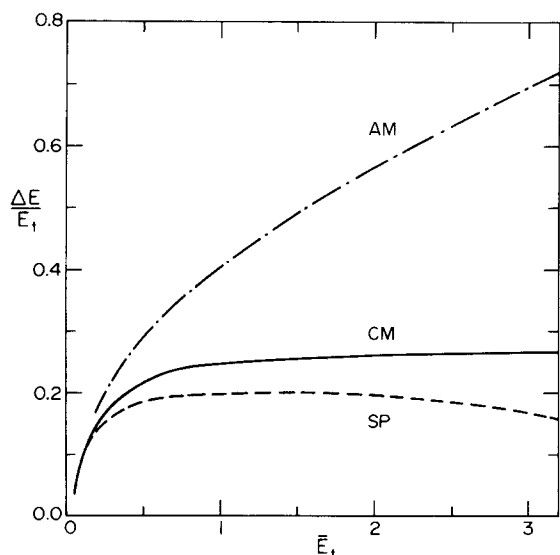


FIG. 8. Classical fractional energy transfer as a function of reduced initial translational energy for collinear collisions between an atom and an initially unexcited harmonic oscillator with an exponential interaction potential and a mass ratio  $m=1/13$ . The solid curve corresponds to exact trajectories, the dashed curve to the string-plucking model, and the dot-dashed curve to the adiabatic theory of Attermeyer and Marcus.

1%. A simpler and more accurate improvement of the Landau-Teller theory is the energy quenching model, as considered in Eq. (20) and the paragraph following it.

Another limitation of the Landau-Teller theory is that it requires that either  $U(y, x)^1$  or  $\ln U(y, x)^2$  be linear in  $y$  in order that the force be expressed purely as a function of time. If this condition is not met, further analytical approximations are required. In the case of the Lennard-Jones potential, Nikitin<sup>7</sup> introduced an adiabatic approximation, which gives in reduced units

$$\langle \Delta E / \bar{E}_i \rangle_N = \frac{1}{2} (12\pi/49)^2 [m/(m+1)]^2 \bar{E}_i^{-1} \exp(-2\omega_0\tau), \quad (25)$$

where

$$\omega_0\tau = \bar{v}^{-1} \int_0^{\bar{x}_0} \left( \frac{V(y=0, \xi)}{\bar{E}_i} - \frac{\bar{v}^2}{\xi^2} - 1 \right)^{1/2} d\xi. \quad (26)$$

In Eq. (25) the  $1/(m+1)^2$  factor of Mahan<sup>3</sup> and Heidrich *et al.*<sup>4</sup> has been included. A typical collinear result that we have calculated is shown in Fig. 5. The proper qualitative dependence on  $\bar{E}_i$  and  $\bar{v}$  is predicted, with a high energy falloff somewhat worse than in the string-plucking model.<sup>27</sup>

The models considered so far may be contrasted with purely adiabatic theories in which the oscillator adjusts continuously to the presence of the atom, following a trajectory along the "valley floor" of the potential

surface. Attermeyer and Marcus<sup>8</sup> have done calculations with a classical model of this type. Some of their results with corresponding string-plucking and exact classical calculations are shown in Fig. 8. We note that at high energies the purely adiabatic model and the hybrid string-plucking model break down.<sup>28</sup> A possible explanation of why the former exceeds the hard sphere limit is that the requirement of following the adiabatic trajectory leads to an overestimation of the oscillator distortion. In the string-plucking model this distortion seems to be underestimated because, as pointed out after Eq. (18), the oscillator does not adjust sufficiently to the rapidly changing driving functions.

## VI. CONCLUSION

We have found that for simple one-dimensional and breathing sphere collisions with no initial vibrational energy the string-plucking model correctly predicts the dependence of total energy transfer on mass, force constant, translational energy, potential strength, and impact parameter, and somewhat less accurately the dependence on long range attraction. With a slight modification it also predicts correctly the effect of initial vibrational energy for  $\bar{E}_i \gtrsim 3\bar{E}_v$ . The chief value of the model is as a heuristic tool in that it provides a simple intuitive description of energy transfer utilizing the chemical concepts of bond length and stiffness. This description may perhaps be most revealing for chemically reactive surfaces. As the reactants approach, the bond in question stretches and begins to break. If a chemical rearrangement does not occur, the effect of the driving functions may be (a) to return the system to the reagent part of the potential surface with increased vibrational energy or (b) to force the system up onto the dissociative plateau. Such processes may occur in H+K<sub>2</sub> collisions.<sup>29</sup> Although reactive scattering occurs, it is hard to understand how KH can form before the energetic H atom is reflected back into the entrance valley of the potential surface. A possible explanation is that a breakup reaction occurs. The strong, though brief, perturbation leaves the diatom in a highly excited state and the K atoms may slowly separate after the H atom has departed.

Another possible application of string-plucking is to collisions involving more than one potential energy surface,<sup>30</sup> such as  $K+O_2 \rightleftharpoons K^++O_2^-$ . The driving functions for the two potential surfaces are substantially different, and even a temporary switch from one to the other may result in large amounts of energy transfer.

Recently Loesch and Herschbach<sup>31</sup> have observed close to 100% transfer of translational to internal energy in collisions of Ar+CsI. They suggest that this anomalously large fractional energy transfer, in considerable excess of the hard sphere limit of 40%, might be caused by clutching collisions and a mechanism analogous to string-plucking. However, the arguments

presented in connection with Fig. 5 suggest that the large fractional energy transfer associated with the presence of attractive wells occurs at energies above those for which clutching occurs. This result is based on the assumption that the interaction occurs on a single potential energy surface. If, on the other hand, surface crossing effects are present, as the proposed charge

transfer mechanism implies,<sup>31</sup> the effect of an attractive well on energy transfer may be different.

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We wish to thank Dr. A. Wagner for helpful discussions and for use of his quantum mechanical scattering program.

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<sup>1</sup>Contribution No. 4476

<sup>1</sup>For a recent review, see D. Rapp and T. Kassal, *Chem. Rev.* **69**, 61 (1969).

<sup>2</sup>A. Russek, *Physica (Utr.)* **48**, 165 (1970).

<sup>3</sup>B. H. Mahan, *J. Chem. Phys.* **52**, 5221 (1970).

<sup>4</sup>F. H. Heidrich, K. R. Wilson, and D. Rapp, *J. Chem. Phys.* **54**, 3885 (1971).

<sup>5</sup>R. D. Levine and B. R. Johnson, *Chem. Phys. Lett.* **8**, 501 (1971).

<sup>6</sup>R. I. Morse and R. J. Labreque, *J. Chem. Phys.* **55**, 1552 (1971).

<sup>7</sup>E. E. Nikitin, *Opt. Spectrosc.* **6**, 93 (1959).

<sup>8</sup>M. Attermeyer and R. A. Marcus, *J. Chem. Phys.* **52**, 393 (1970).

<sup>9</sup>E. Thiele and R. Katz, *J. Chem. Phys.* **55**, 3195 (1971).

<sup>10</sup>We refer to the latter as a quantum mechanical model, even though it is semiclassical in nature with the motion of the atom treated classically.

<sup>11</sup>D. Secrest, *J. Chem. Phys.* **51**, 421 (1969).

<sup>12</sup>Quantum mechanically this is not true. The time independent Schrödinger equation is  $[-(\alpha^2/2m)(\partial^2/\partial x^2 - (\alpha^2/2)(\partial^2/\partial y^2) + (1/2)(y^2/\alpha^2)]\hbar\omega_0 + U(y,x)\Psi(y,x) = E\Psi(y,x)$  where  $\alpha = (\lambda/l)(\hbar\omega_0/K_0)^{1/2}$  and  $E = \alpha^2 E/\hbar\omega_0$ . The quantum solution depends on  $\alpha^2$  and  $E/\hbar\omega_0$  independently, while the classical result depends only on their product. The quantum result has an extra degree of freedom because for  $E < (3/2)\hbar\omega_0$  vibrational excitation is impossible quantum mechanically.

<sup>13</sup>The reduced velocity is one-half of the  $\beta$  parameter in Ref. 9.

<sup>14</sup>P. J. Kuntz, M. H. Mok, and J. C. Polanyi, *J. Chem. Phys.* **50**, 4623 (1969).

<sup>15</sup>J. D. Kelley and M. Wolfsberg, *J. Chem. Phys.* **53**, 2967 (1970).

<sup>16</sup>D. Secrest and W. Eastes, *J. Chem. Phys.* **56**, 2502 (1972).

<sup>17</sup>A. F. Wagner and V. McKoy, *J. Chem. Phys.* **58**, 2604 (1973).

<sup>18</sup>M. A. Wartell and R. J. Cross, Jr., *J. Chem. Phys.* **55**, 4983 (1971).

<sup>19</sup>Ronald Razner, *J. Chem. Phys.* **51**, 5602 (1969).

<sup>20</sup>For Ar + Br<sub>2</sub> this condition is typically satisfied by a rotational angular momentum of 50  $\hbar$  and a vibrational energy of 1 eV ( $4.5 \times 10^{-3}$  in reduced units), with the minimum necessary vibrational energy inversely proportional to the rotational angular momentum.

<sup>21</sup>It is possible that this correlation is due to the central field nature of the breathing sphere model.

<sup>22</sup>D. J. Locker and D. J. Wilson, *J. Chem. Phys.* **52**, 271 (1970). They calculate the exact classical trajectories to obtain the time dependent potential  $V(y,t)$ , which is then used to solve Eq. (14) exactly.

<sup>23</sup>Similar modifications have been used previously in the calculations of vibrational energy transfer. In the modified wavenumber approximation [K. Takayanagi, *Prog. Theor. Phys. Suppl.* **25**, 1 (1963)] noncollinear collisions are compared with corresponding collinear collisions by subtracting from  $\bar{E}_t$  the centrifugal kinetic energy. Also, Benson and Berend [J. Chem. Phys. **44**, 4247 (1966)] have found that the vibrational energy transfer for collision with initial rotational energy  $E_r$  can be approximated by  $\Delta E$  for collisions with initial conditions  $E_t' = E_t + E_r$  and  $E_r' = 0$ . However, Kelley and Wolfsberg<sup>15</sup> have shown that both of these approximations are inaccurate.

<sup>24</sup>The quantum calculations were performed using the method of R. G. Gordon, *J. Chem. Phys.* **51**, 14 (1969).

<sup>25</sup>L. Landau and E. Teller, *Phys. Z. Sowjetunion* **10**, 34 (1936).

<sup>26</sup>S. J. Yao and H. Y. Yao, *J. Chem. Phys.* **54**, 4424 (1971).

<sup>27</sup>The discrepancy in Fig. 5 between Nikitin's result and our own can be partly explained as follows. One step in Nikitin's derivation is to approximate the factor  $[(l/14\nu)(E_t/\epsilon)^{1/2}]^{13/7}$  by  $[(l/14\nu)(E_t/\epsilon)^{1/2}]^2$ . While this approximation is not needed mathematically, if it is not introduced the resulting energy transfer has more degrees of freedom than allowed by the exact classical equation's of motion. That is, without changing the exponent to 2, the energy transfer cannot be expressed in terms of the minimum set of reduced parameters  $m$ ,  $\bar{E}_t$ , and  $\epsilon\bar{\epsilon}$ . Nikitin's energy transfer can be brought into better harmony with the string-plucking result by using instead the factor  $(1/14)^{13/7} [(l/\nu)(E_t/\epsilon)^{1/2}]^2$ , which increases his  $\Delta E/E_t$  by a factor of 2.1.

<sup>28</sup>Attermeyer and Marcus<sup>8</sup> suggest that at lower energy the adiabatic approximation is more accurate. Thiele and Katz<sup>9</sup> verified this prediction for an adiabatic quantum mechanical calculation. They found that adiabatic transition probabilities smaller than 0.1 are within 10% of exact calculations.

<sup>29</sup>Y. T. Lee, R. J. Gordon, and D. R. Herschbach, *J. Chem. Phys.* **54**, 2410 (1971).

<sup>30</sup>A. P. M. Baede and J. Los, *Physica (Utr.)* **52**, 422 (1971); K. Lachmann and D. R. Herschbach, *Chem. Phys. Lett.* **6**, 106 (1970).

<sup>31</sup>H. J. Loesch and D. R. Herschbach, *J. Chem. Phys.* **57**, 2038 (1972).