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Wave Packet Methods for the Direct Calculation of Energy-Transfer Moments in Molecular Collisions

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We present a new wave packet based theory for the *direct* calculation of energy-transfer moments in molecular collision processes. This theory does not contain any explicit reference to final state information associated with the collision dynamics, thereby avoiding the need for determining vibration−rotation bound states (other than the initial state) for the molecules undergoing collision and also avoiding the calculation of state-to-state transition probabilities. The theory applies to energy-transfer moments of any order, and it generates moments for a wide range of translational energies in a single calculation. Two applications of the theory are made that demonstrate its viability; one is to collinear He + H_2 and the other to collinear He + CS_2 (with two active vibrational modes in CS_2). The results of these applications agree well with earlier results based on explicit calculation of transition probabilities.

I. Introduction

Interest in collisional energy transfer involving highly excited polyatomic molecules has grown significantly in recent years. Such energy-transfer processes, which provide a mechanism for the dissipation and accumulation of energy in excited molecules, are important in the relaxation of photoexcited molecules and in gas-phase chemical kinetics. Much of the increased interest in energy-transfer processes can be attributed to two factors: (1) the development of experimental spectroscopic techniques for the direct study of the time evolution of the excited species during relaxation[1,2] and (2) the development of theoretical methods for simulation of these experiments.[3−8]

The theoretical modeling of energy transfer in vibrationally highly excited molecules using quantum methods is difficult because of the large number of accessible quantum states. Indeed, the complete solution to such a problem, i.e., solving the quantum scattering equations to yield *all* the inelastic state-to-state collision probabilities, is clearly very challenging. As a result, most of the theoretical work done so far has involved classical trajectory calculations. However, there has been concern about the nature of the classical−quantum correspondence, which has so far only been established for model systems of low dimensionality, so quantum calculations continue to be of interest for these kinds of problems.

In most practical applications only highly averaged quantities are measured or are of interest, such as the moments of the energy-transfer rate constants and cross sections. In this paper we present a new quantum theory for the *direct* calculation of the moments of energy-transfer cross sections. This theory does not require the computation of the very large number of bound-state energies and eigenfunctions that are required in conventional coupled-channel calculations nor does it require the computation of the individual transition probabilities to these large numbers of closely spaced vibrational−rotational states. The theory is based on a time-dependent wave packet formalism and therefore yields moments over a wide range of energies in a single calculation. This is in contrast to a time-independent formalism that would require a separate computation to be carried out at each collision energy. The moments of the energy-transfer cross sections, which result from the theory, fully characterize the energy-transfer cross sections.

The theory developed here is similar in spirit to the other quantum theories that have been developed in recent years that determine averaged information about a scattering process directly from the Hamiltonian, without the need for determining fully state-resolved information. Of particular note here is the work by Miller et al.[9] for determining the cumulative reaction probability and the thermal rate constant for bimolecular chemical reactions. However, the present application to energy-transfer moments is not directly related to this work, since one cannot take advantage of the simplifying features of reactive fluxes in the present application, and there is a dependence of the moments on the initial state that complicates our evaluation.

Following a discussion of the details of the new theory (section II), the results of its application to collinear collisions of He + H_2 (section III) and of He + CS_2 (section IV) are presented and comparisons to other calculations are made. Section V summarizes our conclusions.

II. Theory and Computations

The general strategy of the time-dependent computations involves preparation of an initial wave packet on a grid in the asymptotic region where the He atom is separated from its collision partner by a large distance. This wave packet is then given momentum in the negative x direction (x being the atom−molecule scattering coordinate) through multiplication by a complex phase factor. The time-dependent Schrödinger equation is then solved by propagating the wave packet forward in time in many relatively small steps using the complex Chebychev polynomial expansion[10−13] of the evolution operator. As the

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wave packet evolves, it is reflected back along the x coordinate. An “analysis line”, corresponding to a fixed value of x, is defined to lie perpendicularly across the exit valley in its asymptotic region. At each time step, a cut is taken through the wave packet along this analysis line, and the resulting wave function is analyzed as defined for our new theory (see details below). The analysis makes use of the fast Fourier transform (FFT) technique[14,15] for conversions between the coordinate and momentum domains[16] and between the time and energy domains.

The following discussion presents the details of the new theory and how it can be implemented in the time-dependent quantum mechanical calculations. We begin by writing down an equation for the cross section for inelastic collision from initial state i to final state f:[17]

$$\sigma_{\mathrm{i}\to f}(E) = \frac{\pi}{k_{\mathrm{i}}^{2}} \sum_{J} (2J+1)|S^{J}_{\mathrm{i}\to f} - \delta_{\mathrm{i}f}|^{2} \tag{1}$$

where $k_{\mathrm{i}} = p_{\mathrm{i}}/\hbar$, J is the total angular momentum of the system, and $S^{J}_{\mathrm{i}\to f}$ are the elements of the **S** matrix. We then define the quantity of interest, which is the cross section for the moments of energy transfer:

$$\sigma^{n}_{\mathrm{i}}(\Delta E,E) = \sum_{f} \sigma_{\mathrm{i}\to f}(E)(\Delta E)^{n} \tag{2}$$

where E is the collision energy and ΔE is the difference in energy between the initial and final vibrational states of the collision partner, $\Delta E = E_{\mathrm{f}} - E_{\mathrm{i}}$. The quantity in eq 2 is the cross section for the nth moment of the energy transfer at energy E. For $n = 1$ this is just the cross section for energy transfer, and the average energy transfer $\langle \Delta E \rangle$ equals $\sigma_{\mathrm{i}}{}^{1}/\sigma_{\mathrm{i}}{}^{0}$. Note that although we have developed the theory for scattering in three dimensions, the corresponding one-dimensional theory is easily developed by restricting the sum over J to $J = 0$ and omitting the factor of π/k^{2} in eq 1. Note also that the quantity being calculated has been summed over all final states and therefore depends only on the initial state. Substituting eq 1 into eq 2 and assuming i ≠ f, we have

$$\sigma^{n}_{\mathrm{i}}(\Delta E,E) = \sum_{f} \frac{\pi}{k_{\mathrm{i}}^{2}} \sum_{J} (2J+1)|S^{J}_{\mathrm{i}\to f}|^{2}(E_{f} - E_{\mathrm{i}})^{n} \tag{3}$$

The quantity $|S^{J}_{\mathrm{i}\to f}|^{2}$ can be obtained from the wave packet. The Fourier grid Hamiltonian (FGH) method[18] is used to compute the one-dimensional vibrational eigenfunctions, and these in turn are used to define a potential-optimized discrete variable representation (DVR) with its associated grid points and basis functions.[19−21] The eigenfunction of the initial state of the collision partner, $\phi_{\mathrm{i}}(y)$, is computed in this DVR basis. This wave function is then multiplied by a Gaussian function in the x (scattering) coordinate $[\exp(-\beta(x - x_{0})^{2})]$, and the product of these two functions is multiplied by an incoming traveling wave in the x coordinate. Therefore, the initial wave packet can be written as

$$\Psi(x,y) = \mathrm{e}^{-\beta(x-x_{0})^{2}}\mathrm{e}^{-\mathrm{i}k(x-x_{0})}\phi_{\mathrm{i}}(y) = g(x)\phi_{\mathrm{i}}(y) \tag{4}$$

We must then analyze $g(x)$ to determine how much of it corresponds to a momentum “k” (i.e., we find the amplitude of the component of the wave packet with magnitude of the momentum k that is in the appropriate direction to simulate a He atom approaching its collision partner). This is done by Fourier transforming the initial wave packet to obtain[22]

$$f(k_{\mathrm{i}}) = \frac{1}{2\pi} \int_{x=0}^{\infty} \mathrm{e}^{-\mathrm{i}k_{\mathrm{i}}x} g(x)\,\mathrm{d}x \tag{5}$$

Starting with the initial wave packet given in eq 4, the time-dependent Schrödinger equation is solved by propagating in discrete time intervals using the complex Chebychev polynomial expansion.[10−13] After each time interval, the wave packet is evaluated along an analysis line in the asymptotic region such that $x = x_{\infty}$. If we represent a cut through the wave packet along this analysis line at time t as $\Psi(x_{\infty},y,t)$ and expand it in terms of the eigenfunctions of the final state of the collision partner, $\phi_{f}(y)$, we can compute the time-dependent coefficients, $C_{f}(t)$:[22,23]

$$C_{f}(t) = \int_{y=0}^{\infty} \phi_{f}(y)\Psi(x_{\infty},y,t)\,\mathrm{d}y \tag{6}$$

The Fourier transform of these time-dependent coefficients is[22,23]

$$A_{f}(E) = \frac{1}{2\pi} \int_{t=0}^{\infty} \mathrm{e}^{\mathrm{i}Et/\hbar} C_{f}(t)\,\mathrm{d}t \tag{7}$$

where $A_{f}(t)$ are the corresponding energy-dependent coefficients. The **S** matrix element is then given by[22−24]

$$S^{J}_{\mathrm{i}\to f}(E) = \frac{\hbar}{\mu} \sqrt{k_{\mathrm{i}}k_{f}}\, \frac{A_{f}(E)}{f(-k_{\mathrm{i}})}\, \mathrm{e}^{\mathrm{i}k_{\mathrm{f}}x}. \tag{8}$$

and therefore

$$|S^{J}{}_{\mathrm{i}\to f}(E)|^{2} = \frac{\hbar^{2}}{\mu^{2}} k_{\mathrm{i}}k_{f} \left|\frac{A_{f}(E)}{f(-k_{\mathrm{i}})}\right|^{2} \tag{9}$$

Thus, the cross section is given by eqs 3 and 9. Substitution of eq 9 into eq 3 gives

$$\begin{aligned}
\sigma^{n}_{\mathrm{i}}(\Delta E,E) &= \frac{h^{2}}{4\pi\mu^{2}} \left(\frac{1}{k_{\mathrm{i}}}\right) \sum_{J} (2J+1) \sum_{f} k_{f} \left|\frac{A_{f}(E)}{f(-k_{\mathrm{i}})}\right|^{2} (E_{f} - E_{\mathrm{i}})^{n} \\
&= \frac{h^{2}}{4\pi\mu^{2}k_{\mathrm{i}}|f(-k_{\mathrm{i}})|^{2}} \sum_{J} (2J+1) \sum_{f} \frac{k_{f}(E_{f} - E_{\mathrm{i}})^{n}}{4\pi^{2}} \times \\
&\qquad \int_{t'}\int_{t} \mathrm{e}^{-\mathrm{i}Et/\hbar}\langle \Psi^{J}(x_{\infty},y,t)|\phi_{f}(y)\rangle\langle\phi_{f}(y)| \times \\
&\qquad \Psi^{J}(x_{\infty},y,t')\rangle \mathrm{e}^{\mathrm{i}Et'/\hbar}\,\mathrm{d}t\,\mathrm{d}t' \\
&= \frac{h^{2}}{16\pi^{3}\mu^{2}k_{\mathrm{i}}|f(-k_{\mathrm{i}})|^{2}} \sum_{J} (2J+1) \int_{t'}\int_{t} \mathrm{e}^{-\mathrm{i}Et/\hbar} \times \\
&\qquad \langle \Psi^{J}(x_{\infty},y,t)|[\sum_{f} (E_{f} - E_{\mathrm{i}})^{n}|\phi_{f}(y)\rangle\langle\phi_{f}(y)|k_{f}] \times \\
&\qquad |\Psi^{J}(x_{\infty},y,t')\rangle \mathrm{e}^{\mathrm{i}Et'/\hbar}\,\mathrm{d}t\,\mathrm{d}t'
\end{aligned} \tag{10}$$

Now let $\hat{H}_{y}$ be the internal Hamiltonian such that

$$\hat{H}_{y}|\phi_{f}(y)\rangle = E_{f}|\phi_{f}(y)\rangle \tag{11}$$

and

$$\sum_{f} |\phi_{f}(y)\rangle\langle\phi_{f}(y)| = \hat{\mathrm{I}}$$

We also must evaluate (see eq 10)

$$\langle \phi_f(y)|k_f|\Psi^J(x_\infty,y,t')\rangle = [\langle \phi_f(y)|\hat{k}_x|\Psi^J(x,y,t')\rangle]_{x=\infty} \quad (12)$$

where $\hat{k}_x$ is the momentum operator for the x coordinate. Equation 12 follows from the fact that in the limit $x \rightarrow \infty$, Ψ^J becomes a plane wave $e^{ik_f x}$ when projected onto the eigenfunction $\phi_f(y)$ for $f \neq i$. To evaluate this expression, we define the function Φ_x^J by

$$\hat{k}_x|\Psi^J(x,y,t')\rangle = |\Phi_x^J(x,y,t)\rangle \quad (13)$$

This equation is evaluated by Fourier transforming $\Psi^J(x,y,t)$ along x and multiplying by k_x, then back Fourier transforming. Equation 10 can now be rewritten in the form

$$\sigma_i^n(\Delta E,E) = \frac{h^2}{16\pi^3\mu^2 k_i|f(-k_i)|^2}\sum_J (2J+1)\int_{t'}\int_t e^{-iEt/\hbar}e^{iEt'/\hbar} \times \langle\Psi^J(x_\infty,y,t)|(\hat{H}_y - E_i)^n|\Phi_x^J(x_\infty,y,t')\rangle \, dt\, dt' \quad (14)$$

If we now define

$$X^{Jn}(y,E) = \int_{t'} e^{iEt'/\hbar}(\hat{H}_y - E_i)^n\Phi_x^J(x_\infty,y,t')\, dt'$$

and

$$\Psi^J(y,E) = \int_t e^{iEt/\hbar}\Psi^J(x_\infty,y,t)\, dt$$

then eq 14 can be rewritten as

$$\sigma_i^n(\Delta E,E) = \frac{\hbar^2}{4\pi\mu^2 k_i|f(-k_i)|^2}\sum_J (2J+1)\langle\Psi^J(y,E)|X^{Jn}(y,E)\rangle \quad (15)$$

Equation 15 shows the primary result of the new theory, which is that the cross sections for the moments of energy transfer can be obtained directly, without first obtaining the state-to-state inelastic collision cross sections. Although the initial energy E_i appears in eq 14 and the eigenfunction $\phi_i(y)$ is needed to define the initial wave packet in eq 4, these can be determined with significantly less effort than is needed to determine the entire spectrum of energy levels for a full state-resolved scattering calculation. In addition, if one only wishes to calculate moments for a statistical ensemble of states (such as a microcanonical ensemble), the sampling of initial conditions can be performed in many ways that do not require eigenvalues and eigenfunctions.

Note what is involved in the evaluation of X^{Jn}. One first needs to evaluate Φ_x^J as described above. Then the application of H_y is performed using highly efficient potential optimized discrete variable representation techniques.[17−19] The symbol "y" represents all the internal coordinates of the collision partners. The internal Hamiltonian is divided into a separable (kinetic energy plus potential) and a nonseparable (potential) part. The potential optimized discrete variable representation technique provides us with a compact grid based matrix representation of the separable part of the Hamiltonian, while the nonseparable potential part is handled by direct multiplication. A time Fourier transform is then used to determine X^{Jn}.

Because the theory is formulated within a time-dependent framework, the energy dependence of these cross sections is also immediately obtained. The corresponding one-dimensional theory is obtained from eq 15 by setting $J = 0$ and multiplying by k_i^2/π.

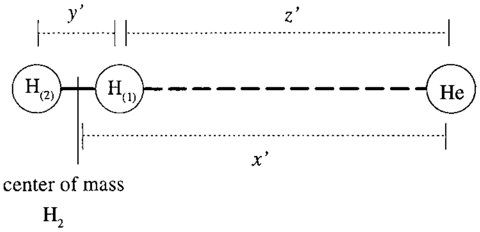

Figure 1. Definition of coordinates for the collinear He + H$_2$ collision.

III. Test Cases: He + H2 Inelastic Collisions

For testing purposes, we have applied the one-dimensional version of the new theory to the collinear He + H$_2$ system, considering both harmonic and Morse binding potentials for H$_2$. The calculations are set up following the formalism discussed by Clark and Dickinson.[25]

The collision problem is illustrated in Figure 1. All three atoms are constrained to move along the line defined by the molecular axis, H(1)−H(2). The distance between the He atom and the center of mass of H$_2$ is represented by x', and y' and z' are the H(1)−H(2) and He−H(1) distances, respectively. The incident He atom encounters the repulsive core of the intermolecular potential, $V'(z')$, between He and H(1), and H(1) and H(2) are bound by the intramolecular potential, $V'(y')$.

We consider both the harmonic and Morse binding potentials, which take the form

$$V'(y') = {}^1\!/_2 f\,(y' - y'_{eq})^2 \quad (16)$$

$$V'(y') = D_e[\exp\{-a(y' - y'_{eq})\} - 1]^2 \quad (17)$$

where f is the harmonic oscillator force constant, y'_{eq} is the H(1)−H(2) equilibrium distance, and D_e and a are the Morse potential well depth and steepness parameter, respectively.

It is then useful to transform to dimensionless coordinates (x,y,z) where the collision problem is most conveniently expressed. Therefore, we have

$$x = \eta[(1/\gamma)x' - \gamma y'_{eq}]$$

$$y = \eta(y' - y'_{eq})$$

$$z = x - y$$

$$\eta = [(\mu f)^{1/2}/\hbar]^{1/2}$$

$$\mu = (m_{H(1)}m_{H(2)})/(m_{H(1)} + m_{H(2)})$$

$$g = m_{H(2)}/(m_{H(1)} + m_{H(2)})$$

The Schrödinger equation may then be written[26]

$$\left[\frac{-1}{2m}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + V(y) + V(z)\right]\Psi = \frac{1}{2}E\Psi$$

where $m = (m_{He}m_{H(2)})/[m_{H(1)}(m_{He} + m_{H(1)} + m_{H(2)})]$, $V(y \text{ or } z) = V'(y \text{ or } z)/({}^1\!/_2\hbar\omega_e)$, and E is the total energy of the system in units of $1/_2\hbar\omega_e$ ($\omega_e = 2\pi c$ times the vibrational constant as defined in Herzberg[27]). In these coordinates, eqs 16 and 17 become

$$V(y) = {}^1/_2 y^2$$

$$V(y) = D_e[\exp\{-y/(2D_e)^{1/2}\} - 1]^2$$

respectively, where $D_e = D_e/({}^1/_2\hbar\omega_e)$. The interaction potential, $V(z)$, is chosen to be

$$V(z) = V_0 \exp(-\alpha z)$$

where V_0 and α are constants. Since the Hamiltonian is invariant under the transformation $x \rightarrow x + \delta$, $V_0 \rightarrow V_0 \exp(\alpha\delta)$, where δ is a constant, V_0 may be chosen arbitrarily, and thus, we set it to 1 hartree divided by ${}^1/_2\hbar\omega_e$. Now the model systems are completely specified by the dimensionless constants $m = {}^2/_3$, $\alpha = 0.314$, and $D_e = 9.3$, values that are realistic for He$-$H$_2$ collisions.[25,26,28,29]

For later reference we note that the quantized vibrational energies are (in units of $\hbar\omega_e$)

$$E_n = 2(n + {}^1/_2) \qquad (18)$$

$$E_n = 2[(n + {}^1/_2) - (n + {}^1/_2)^2/(4D_e)] \qquad (19)$$

for the harmonic and Morse cases, respectively.

Our calculations for the He + H$_2$ system are based on grids consisting of 256 evenly spaced points in the x coordinate and 10 points of a potentially optimized grid[17−19] in the y coordinate. The step size in time for the calculations is taken to be 0.10, and we propagate for 500 time steps. The β parameter, which determines the width of the initial wave packet, is set to 1.0. For the harmonic case, the kinetic energy is chosen to be 6.0, and the strength of the quartic complex damping function used in the absorbing potential (as defined by Vibók and Balint-Kurti[30]) is -33.0. For the Morse case, the kinetic energy is 4.0, and the strength of the damping function is -16.5.

Figures 2 and 3 present the cross sections for the moments of the energy transfer, $\sigma_i^n(\Delta E,E)$, versus total energy, E, for the He + H$_2$ system with H$_2$ represented as a harmonic and as a Morse oscillator, respectively. Included in these figures are the results from our new theory (for $n = 0-3$) as well as the results of time-independent quantum calculations for $n = 2$ by Clark and Dickinson.[25] They calculated exact quantum mechanical vibrational energy transition probabilities, which can be converted into energy-transfer moments using eq 2 and either eq 18 or eq 19. All results in both figures refer to the initial state being equal to the ground state of H$_2$. These figures show excellent agreement between the results from the new theory and the results of Clark and Dickinson for both test cases. Another test of the theory is provided by the zeroth moment, which should be unity, independent of E. Here, the figures indicate that this moment is indeed very close to unity. Overall then, this application demonstrates a successful first application of the new theory for the direct calculation of the energy-transfer moments.

IV. Collinear He + CS$_2$

In this section we apply the new theory to a collinear model of He + CS$_2$ in which both the intermolecular and intramolecular potentials are chosen to be realistic. This collinear model has been studied in the past by both classical and quantum methods, with particular emphasis on the classical$-$quantum correspondence for the energy-transfer moments. The early classical dynamics work[3] included comparisons of the energy-transfer properties associated with the collinear model to those of full-dimensional classical simulations. These studies determined that although the collinear model is missing the low-frequency bend mode of CS$_2$, the energy-transfer moments from the collinear model are very similar to those from the full-dimensional calculations. Later, additional classical dynamics calculations were done in conjunction with quantum calculations in studies by Schatz and co-workers.[31,32] The quantum dynamics calculations were performed using coupled-channel calculations with basis sets of 500 (for energies up to 75 kcal/mol (ref 29)) and 1000 (for energies up to 92 kcal/mol (ref 30)) vibrational states from a discrete variable representation calculation. These studies demonstrated very good classical$-$quantum agreement of the energy-averaged first moments over a wide range of molecular vibrational energies, provided that the translational energy is not too low (translational temperatures below 300 K).

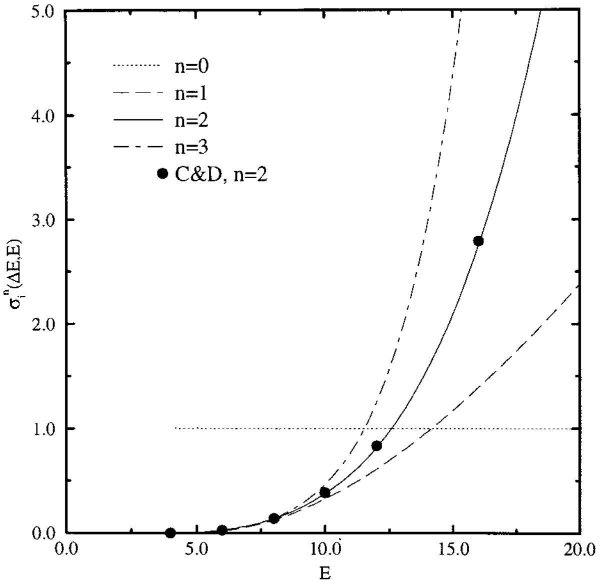

Figure 2. Energy-transfer moments for collinear He + H$_2$ collisions, with H$_2$ modeled as a harmonic oscillator and initially in the ground state. Filled circles indicate results for the second moment from time-independent calculations of Clark and Dickinson.[25]

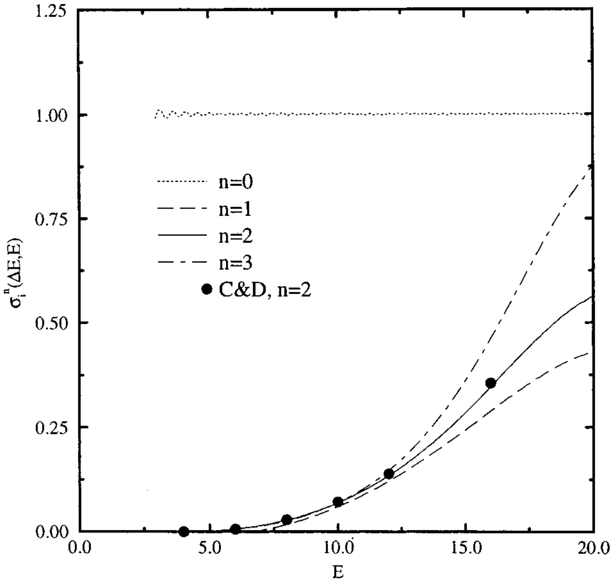

Figure 3. Energy-transfer moments for collinear He + H$_2$ collisions as in Figure 2 but with H$_2$ modeled as a Morse oscillator.

To calculate the moments of energy transfer for He + CS$_2$ using the new theory, we define X to be the coordinate between the He and the center of mass of CS$_2$, Y_1 to be the coordinate representing the C−S(2) distance, and Y_2 to be the coordinate between S(1) and the center of mass of C−S(2). Then the Hamiltonian for the complete system is

$$\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial Y_1^{\,2}} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial Y_2^{\,2}} + V(Y_1,Y_2) + V(X,Y_1,Y_2)$$

where

$$\mu = \frac{m_{\mathrm{He}}(m_{\mathrm{S(1)}} + m_{\mathrm{C}} + m_{\mathrm{S(2)}})}{m_{\mathrm{He}} + m_{\mathrm{S(1)}} + m_{\mathrm{C}} + m_{\mathrm{S(2)}}}$$

$$\mu_1 = \frac{m_{\mathrm{C}} m_{\mathrm{S(2)}}}{m_{\mathrm{C}} + m_{\mathrm{S(2)}}}$$

$$\mu_2 = \frac{m_{\mathrm{S(1)}}(m_{\mathrm{C}} + m_{\mathrm{S(2)}})}{m_{\mathrm{S(1)}} + m_{\mathrm{C}} + m_{\mathrm{S(2)}}}$$

and where $V(Y_1,Y_2)$ is the intramolecular potential for CS_2 and $V(X,Y_1,Y_2)$ is the intermolecular potential. We use the CS_2 potential surface of Carter and Murrell,[33] which is derived from a spectroscopic force field at low energies and which dissociates correctly. On this potential, the dissociation energy to CS + S is 129 kcal/mol and the harmonic stretch frequencies are 674 and 1532 cm^{-1}. We also use the He-2 intermolecular potential of Bruehl and Schatz.[3] These potentials have been used in previous studies of collisional energy transfer in the He + CS_2 system by Schatz and co-workers.[3−6,31,32] We present results for the $n = 2$ ($E_{\mathrm{i}} = 5.1$ kcal/mol) and $n = 15$ ($E_{\mathrm{i}} = 15.6$ kcal/mol) eigenstates of CS_2, for which our calculated energies match those of Schatz[34] to four significant figures.

Our calculations for the He + CS_2 system are based on grids consisting of 256 points in the X coordinate and 10 points in the Y_1 and Y_2 coordinates for $n = 2$ or 20 points in the Y_1 and Y_2 coordinates for $n = 15$. The step size in time is taken to be 100.0, and we propagate for 700 time steps. The β parameter is set to 10.0, and the kinetic energy is 0.005 au (3.14 kcal/mol) for $n = 2$ and 0.010 au (6.28 kcal/mol) for $n = 15$. In both cases, the strength of the quartic complex damping function used in the absorbing potential is −0.055.

Figures 4 and 5 present the energy-transfer moment, $\sigma_{\mathrm{i}}^{1}(\Delta E,E)$, versus total energy, E, for the collinear He + CS_2 system. Results from the new theory in these figures are in excellent agreement with the results of coupled-channel calculations by Schatz.[34]

The excellent comparisons shown in Figures 2−5 provide encouraging evidence for the utility of the new theory. Clearly, it works well for the collinear models with modest excitation of the collision partner. Future studies of this theory could include preparing the collision partner in substantially higher excited states to simulate situations involving photoexcited molecules, as discussed in the Introduction. In addition, the theory could be applied to three-dimensional collisions, as opposed to being limited to collinear collisions.

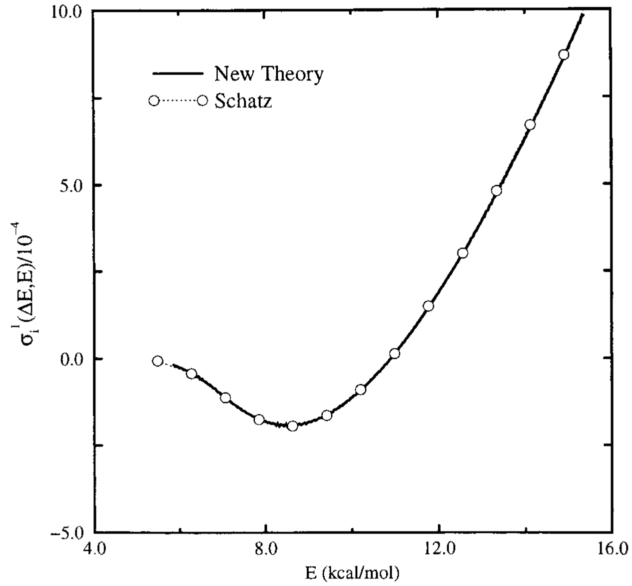

Figure 4. Energy-transfer first moment versus total energy for collinear He + CS_2 ($n = 2$, $E_{\mathrm{vib}} = 5.1$ kcal/mol) collisions. Open circles indicate results from coupled-channel calculations by Schatz.[34]

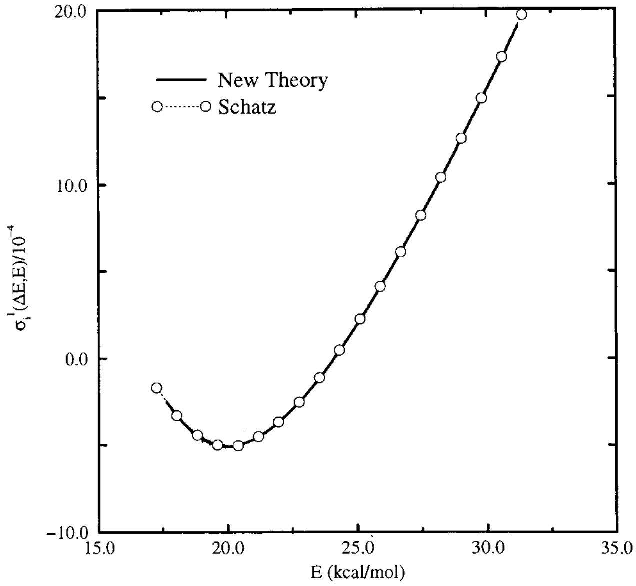

Figure 5. Energy-transfer first moment versus total energy for collinear He + CS_2 ($n = 15$, $E_{\mathrm{vib}} = 15.6$ kcal/mol) collisions. Open circles indicate results from coupled-channel calculations by Schatz.[34]

V. Conclusion

This paper has presented a new theory in which the moments of energy transfer are obtained directly, without first calculating the state-to-state inelastic collision cross sections. The theory is based on a time-dependent wave packet formalism and therefore yields the energy dependence of the calculated quantities in a single calculation. Results from application of the new theory to collinear He + H_2 and He + CS_2 systems are in excellent agreement with previous time-independent calculations. These results demonstrate the success of the new theory for collinear collision models where the collision partner has modest excitation, and they encourage future applications of the new theory to three-dimensional models as well as models with highly excited collision partners.

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