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The failure of rigid shell models for rotationally inelastic LiH–He collisions

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A simple rigid-body model for rotationally inelastic LiH–He collisions has been implemented. This treatment assumes impulsive collisions between a point particle and a smooth spherical shell whose center is displaced from the center of mass of the LiH molecule. For a given collision energy the radius and displacement of the shell are adjusted for a best fit to the equipotential contour at this energy on the *ab initio* surface of D. M. Silver [J. Chem. Phys. 72, 6445 (1980)]. Cross sections for transitions from the rotationless $j=0$ state to all possible final j' states have been computed in a classical trajectory approach and have been compared to more accurate quantum coupled-states values at $E_{col}=0.3$ eV [E. F. Jendrek and M. H. Alexander, J. Chem. Phys. 72, 6452 (1980)]. The results from this simple model differ drastically both in magnitude and their j' dependence from those obtained in the more sophisticated treatment. While such rigid-body models have been used in the analysis of inelastic scattering experiments, the present study suggests that little physical significance can be attached to the size or shape of the rigid shell contour so obtained.

I. INTRODUCTION

Recent experimental advances[1–3] now allow the study of rotational energy transfer in molecular collisions in far more detail than has been hitherto possible. Our theoretical understanding of these processes is hindered by the computational difficulties of an accurate treatment of the collision dynamics and, more importantly, by the unavailability of accurate potential surfaces for many systems. For these reasons there is much interest in developing simple, computationally efficient models which could be used in the interpretation of experimental data. Various authors have suggested that rotationally inelastic atom–molecule collisions could be simulated by the purely classical impulsive scattering of a point particle by an anisotropic rigid shell.[4–6] This type of model has recently been exploited by Beck, Ross, and Schepper[7] to explain the experimentally observed[8] structure in the recoil velocity distributions of K atoms scattered inelastically from N_2 and CO at c.m. angles $\theta > \pi/2$.

Over the past several years we have been involved in an investigation of rotationally inelastic LiH–He collisions.[9–11] State-resolved experimentally derived[11] cross sections for inelastic transitions from the incident LiH $j=1$ level were found to agree well with theoretical predictions[10] from a quantum treatment of the collision dynamics based on an *ab initio* potential surface.[9] At the collision energies of our experiment (0.2–0.4 eV), only the repulsive wall of the potential plays a role, so that one might expect a rigid-shell model to provide a reasonable description of the dynamics.

The extreme asymmetry of the charge distribution in the LiH molecule suggests that an off-center spherical shell or "loaded sphere" would be a more appropriate model for LiH–He collisions than the rigid ellipsoids used by LaBudde and Bernstein[4] and Beck *et al.*[7] An off-center shell is consistent with a physical picture in which rotational inelasticity is due primarily to collisions between the He atom and the diffuse H^- charge distribution at one end of the LiH molecule. This picture is supported by an examination of the equipotential contours of the *ab initio* LiH–He surface of Silver.[9] Kolb and Elgin[6] have used off-center spherical shells to model O–NH_3 collisions. Historically, loaded spheres have been used in studies of transport phenomena in molecular gases.[12]

Beck *et al.*[7] have characterized in detail rotationally inelastic classical scattering from rigid cylindrically symmetric shells and have obtained expressions for various types of classical differential cross sections. In the next section we present a simplified treatment, in which a classical trajectory approach is employed, for the scattering from an initially rotationless off-center spherical shell. The specific application to the LiH–He system is discussed in Sec. III, and the predicted cross sections are compared with the results of our earlier quantum calculations.[10] A brief conclusion follows.

II. FORMULATION OF THE CLASSICAL DYNAMICS

We consider the collision of a point particle of reduced mass μ with a smooth rigid spherical shell of radius r whose center lies at a displacement $d(\beta, \alpha)$ from the origin of the center-of-mass coordinate system, as shown in Fig. 1. The magnitude of the displacement d is a property of the potential and is hence fixed. The angles β and α are the polar and azimuthal angles, respectively, which describe the orientation of the molecular axis in space. The molecule has moment of inertia I and is further assumed to be initially rotationless. The point particle is taken to be initially in the xz plane with relative velocity v directed along the posi-

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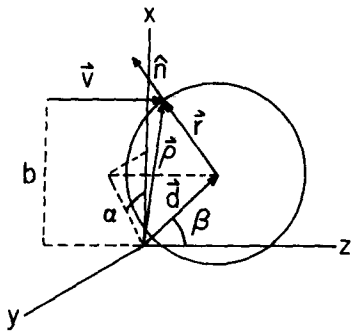

FIG. 1. Coordinate system used to describe the scattering of a point particle by a rigid spherical shell of radius r centered at a distance $\mathbf{d}(d, \rho, \alpha)$ from the origin. The quantities b, v, $\hat{\rho}$, and $\hat{n}$ denote, respectively, the impact parameter, the initial relative velocity vector, the point of impact between the point particle and the spherical shell, and the normal to the surface of the sphere at the point of impact.

tive z axis and impact parameter b (measured along the positive x axis).

For a given velocity, an encounter is fully described by ascribing values to the parameters b, β, and α. In this model, energy transfer occurs only if the point particle strikes the spherical shell. This implies that the impact parameter must lie in the range

$$\max(b_{\min}, 0) \leq b \leq b_{\max} , \tag{1}$$

where $b_{\min}$ and $b_{\max}$ are the smaller and larger of the (real) roots of the equation

$$b^2 - 2bd\sin\beta\cos\alpha + (d^2\sin^2\beta - r^2) = 0 . \tag{2}$$

The point of impact on the surface of the sphere, denoted $\rho(x, y, z)$, has Cartesian components

$$x = b , \tag{3a}$$

$$y = 0 , \tag{3b}$$

$$z = \zeta + d\cos\beta , \tag{3c}$$

where

$$\zeta = -(r^2 - d^2\sin^2\beta - b^2 + 2bd\sin\beta\cos\alpha)^{1/2} . \tag{4}$$

Since the scattering is assumed to be an impulsive collision with a smooth sphere, only the component of relative velocity normal to the sphere at the point of impact is altered by the collision. In a notation where underlining denotes quantities after collision, we have

$$\underline{\mathbf{v}} = \mathbf{v} + \Delta\mathbf{v}\hat{n} , \tag{5}$$

where $\hat{n}$, the unit normal to the sphere at the point of impact, is

$$\hat{n} = (\xi\hat{i} + \eta\hat{j} + \zeta\hat{k})/r . \tag{6}$$

Here

$$\xi = b - d\sin\beta\cos\alpha , \tag{7a}$$

$$\eta = -d\sin\beta\sin\alpha , \tag{7b}$$

and ζ is given by Eq. (4).

Since the molecule is assumed to be initially rotationless, the initial total angular momentum is entirely orbital:

$$\mathbf{J} = \mu\boldsymbol{\rho}\times\mathbf{v} . \tag{8}$$

Note that since the initial x coordinate of the particle is positive (Fig. 1), the orbital angular momentum will be directed along the negative y axis. After collision, there is an additional component due to the molecular rotation, $\underline{\mathbf{j}}$, so that the final angular momentum is

$$\underline{\mathbf{J}} = \mu\boldsymbol{\rho}\times\underline{\mathbf{v}} + \underline{\mathbf{j}} . \tag{9}$$

Invoking angular momentum conservation, we set Eqs. (8) and (9) equal and obtain

$$\underline{\mathbf{j}} = -\mu\Delta v\boldsymbol{\rho}\times\hat{n} . \tag{10}$$

Since the normal to the surface of a sphere at any point is directed along the radius of the sphere, the vectors ρ and $\hat{n}$ are related by

$$\rho = \mathbf{d} + r\hat{n} . \tag{11}$$

As noted previously, the vector displacement d of the sphere lies along the internuclear axis of the molecule. The cross product in Eq. (10) implies that $\underline{\mathbf{j}}$ will be perpendicular to ρ, $\hat{n}$, and, from Eq. (11), d. In other words, in this rigid-shell model, collisions excite only rotations whose angular momentum vector is perpendicular to the bond axis, as would occur for real diatomic molecules.

We may solve for the change Δv in the velocity by imposing energy conservation:

$$\tfrac{1}{2}\mu v^2 = \tfrac{1}{2}\mu\underline{v}^2 + \tfrac{1}{2}\underline{j}^2/I . \tag{12}$$

From Eqs. (5), (10), and (12) we obtain the following expression for the final rotational angular momentum:

$$\underline{\mathbf{j}} = 2\mu(\mathbf{v}\cdot\hat{n})(\boldsymbol{\rho}\times\hat{n})/D , \tag{13}$$

where D is given by

$$D = 1 + \mu|\boldsymbol{\rho}\times\hat{n}|^2/I . \tag{14}$$

The scattering angle in the center-of-mass frame is given by

$$\cos\theta = \underline{\mathbf{v}}\cdot\mathbf{v}/(|\underline{\mathbf{v}}|\,|\mathbf{v}|) , \tag{15}$$

which from Eqs. (5), (10), and (12) becomes

$$\cos\theta = \frac{D - 2(\mathbf{v}\cdot\hat{n})^2/v^2}{\{D[D - 4(\mathbf{v}\cdot\hat{n})^2/v^2]\}^{1/2}} . \tag{16}$$

Expressions analogous to Eqs. (13) and (16) for the final rotational angular momentum and c.m. scattering angles have been derived previously.[4,7]

To obtain $\underline{j}$ and θ for given values of b, β, and α, one first determines ρ and $\hat{n}$ from Eqs. (3), (4), (6), and (7) and then substitutes into Eqs. (13) and (16). As in conventional classical trajectory calculations the continuous distribution of final rotational angular momentum can be quantized. We use here the "smooth sampling" algorithm.[13] For each integer value j' of the final angular momentum, we define a binning function

$$N(b, \beta, \alpha; j') = 0 \quad \text{if} \quad \delta > 1 \tag{17a}$$

$$= 1 - \delta \quad \text{if} \quad \delta < 1 , \tag{17b}$$

where

$$\delta = \text{abs}[j' - |\underline{\mathbf{j}}(b, \beta, \alpha)|/\hbar]. \tag{18}$$

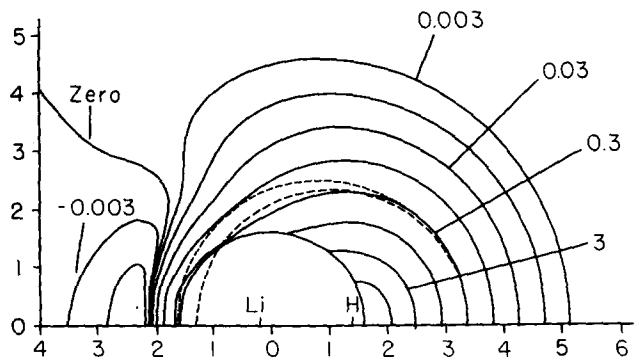

FIG. 2. Equipotential contours (eV) of the LiH–He rigid-rotor potential surface of Silver (Ref. 9). The distances (Å) refer to the separation between the He atom and the center of mass of the LiH molecule. Inside of the small circle of radius 1.6 Å centered about the origin the expansion of the potential given in Ref. 9 is no longer valid. The off-center spherical shells used in the present study are indicated by the two dashed circles. The inner corresponds to the parameters $d=1.03$ Å, $r=2.3$ Å; the outer, to the parameters $d=0.88$ Å, $r=2.45$ Å.

An integral cross section for a transition from the initially rotationless $j=0$ state to any given final state can be obtained by summing and averaging the binning function over all values of b, β, α. Explicitly we have

$$\sigma_{j=0\to j'} = (4\pi)^{-1} \int_0^\infty 2\pi b\, db \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta\, d\beta\, N(b, \beta, \alpha; j') \ . \tag{19}$$

The factor of $(4\pi)^{-1}$ is the normalization constant for the average over initial molecular orientations (β and α integrations).

In fact, the upper limit in the b integration is $d+r$ since there will never be any collisions beyond this value, regardless of the initial molecular orientation. In actual practice, the integral in Eq. (19) is evaluated numerically by a trivariate quadrature, which gives

$$\sigma_{0\to j'} = \frac{\pi}{8}(d+r)^2 \sum_{i,j,k=1}^{N} (x_i+1)\, w_i w_j w_k N(b_i, \beta_j, \alpha_k; j') \ , \tag{20}$$

where the (x_i, w_i) denote the abscissas and weights for an N-point quadrature over the interval $(-1, +1)$ and

$$b_i = \tfrac{1}{2}(d+r)(x_i+1) \ , \tag{21a}$$

$$\beta_j = \cos^{-1}(x_j) \ , \tag{21b}$$

$$\alpha_k = \pi(x_k+1) \ . \tag{21c}$$

A differential cross section may be obtained by adding to the integrand in Eq. (19) some angular resolution function which goes to zero except when the scattering angle $\theta(b, \beta, \alpha)$ [Eq. (16)] lies sufficiently close to a given value. It is also convenient to define a weighted partial inelastic opacity, $bP_{j\to j'}(b)$, in terms of which the $j\to j'$ integral cross section may be expressed:

$$\sigma_{j\to j'} = 2\pi \int_0^\infty bP_{j\to j'}(b)\, db \ . \tag{22}$$

With the trajectory approach, $bP_{j\to j'}(b)$ can be defined from Eq. (19) as

$$bP_{j=0\to j'}(b) \simeq (8\pi\epsilon)^{-1} \int_{b-\epsilon}^{b+\epsilon} b\, db \times \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta\, d\beta\, N(b, \beta, \alpha; j') \ . \tag{23}$$

This integral can then be evaluated numerically as in Eq. (20), by summing over many individual trajectories.

III. NUMERICAL CALCULATIONS AND COMPARISON WITH QUANTUM RESULTS

Figure 2 displays an equipotential contour plot of the *ab initio* LiH–He surface reported by Silver.[9] Superimposed are two off-center spherical shells with parameters $d=1.03$ Å, $r=2.3$ Å and $d=0.88$ Å, $r=2.45$ Å, respectively. As can be seen, both fit the 0.3 eV contour reasonably well and should therefore provide reasonable rigid-body models for the scattering of He by LiH($j=0$) at a collision energy of 0.3 eV. For both sets of parameters integral cross were computed using the procedure described in the previous section. The integral in Eq. (20) was evaluated using a 67th order repeated Simpson's rule, which required ~300 000 collision trajectories.

The resulting cross sections are listed in Table I and compared there and in Fig. 3 with our previous[10] quantum coupled-states[14] (CS) cross sections for the same system. Clearly, the rigid-body model gives a completely inaccurate representation of the dependence on final rotational quantum number. For the small values of j' the cross sections are far too small and then become too large for large j'. More insight into this disagreement can be gained from the comparison, shown in Fig. 4, of the rigid-body and quantum[15] partial opacities for the $j=0\to 3$, 6, and 9 transitions. In all three cases the peak in the quantum partial opacity curves occurs at impact parameters of 3.5–4 Å, which lie beyond the range of the off-center rigid sphere (see Fig. 2).

TABLE I. Integral cross sections for the rotationally inelastic scattering of He by LiH($j=0$) at $E_{col}=0.3$ eV.

	$\sigma_{0\to j'}$ (Å^2)		
	Rigid shell		
j'	$d=1.03$ Å $r=2.3$ Å	$d=0.88$ Å $r=2.45$ Å	Quantum[a]
1	0.16	0.20	12.15
2	0.29	0.40	7.14
3	0.45	0.53	5.67
4	0.56	0.68	3.81
5	0.64	0.81	4.14
6	0.79	0.95	3.63
7	0.87	1.04	2.42
8	0.97	1.16	3.31
9	1.07	1.25	3.74
10	1.15	1.35	2.43
11	1.23	1.41	1.44
12	1.29	1.50	0.88
13	1.37	1.53	0.56
14	1.40	1.57	0.36
15	1.45	1.56	0.23
16	1.44	1.50	0.14
17	1.23	1.17	0.01
18	0.22	0.19	<0.01

[a]Reference 10.

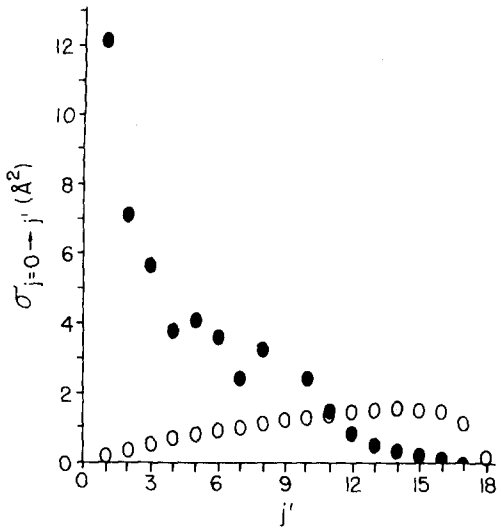

FIG. 3. Integral cross sections for rotationally inelastic LiH ($j=0$) + He collisions at $E=0.3$ eV. The open circles indicate the predictions of the off-center spherical shell model developed here and the filled circles are the quantum coupled-states values from Ref. 10. The differences corresponding to the two different sets of shell parameters (Table I) would be virtually unresolvable on this graph.

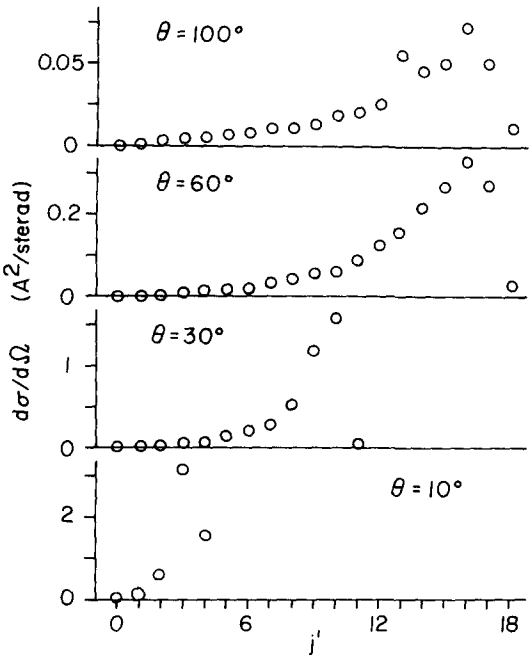

FIG. 5. Differential cross sections for $j=0\to j'$ versus c.m. scattering angle θ for the off-center spherical shell with $d=1.03$ Å, $r=2.3$ Å. These have been calculated using a step function of width 1° as the angular resolution function in Eq. (19).

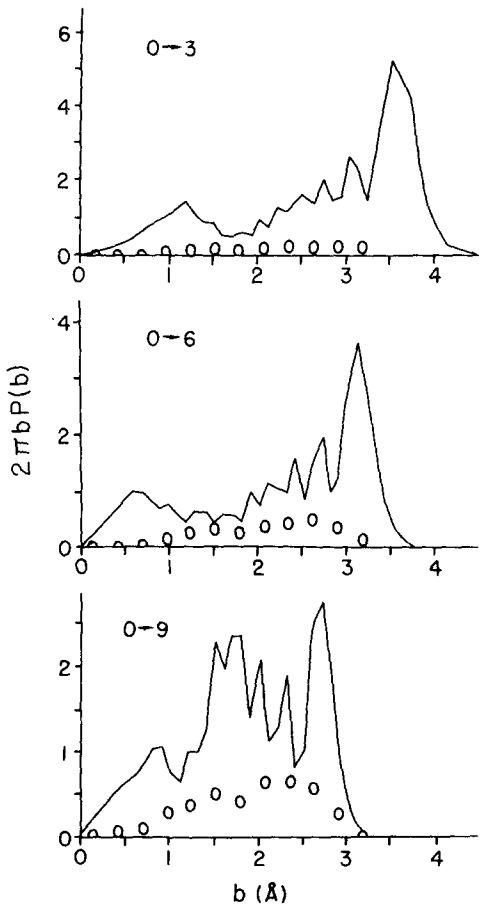

FIG. 4. Weighted partial opacities for the $j=0\to 3$, 6, 9 transitions. The solid curves designate the quantum coupled-states values (Ref. 15). The open circles denote the predictions of the off-center spherical shell model with $d=1.03$ Å, $r=2.3$ Å determined using Eq. (23).

The implication is that even for LiH–He, where the interaction potential is almost entirely repulsive,[9] a significant fraction of the inelasticity is due to collisions which never fully penetrate to the repulsive wall. This is especially true for the low Δj transitions, which explains why the corresponding cross sections are so underestimated in the rigid-body model. Also, even at smaller impact parameter the quantum partial opacities are larger. This is not a quantum effect since recent classical trajectory calculations[16] based on the *ab initio* potential surface yield partial opacity curves and integral cross sections which agree extremely well, even in fine detail, with the quantum values. Rather, the difference in magnitude between the quantum and classical rigid-body partial opacities indicates that a more effective torque is exerted on the LiH molecule by an interaction which gradually increases in strength than by a purely impulsive interaction. It is possible, of course, that free variation of the parameters d and r, which define the loaded sphere, would lead to better agreement with the quantum cross sections. In our opinion, such a procedure would tend to conceal the physical inadequacies of the rigid sphere model, since, to judge from Fig. 2, the "optimal" rigid contour would bear little relation to the appropriate hard sphere equipotential of the *ab initio* surface.

We turn now to an examination of the differential cross sections. Figure 5 displays these as a function of j' at four different scattering angles. The classical rotational rainbow[8,17–20] is clearly apparent. As predicted by the methods of Beck *et al.*,[7] the off-center rigid potential exhibits an extremal value of j' which moves rapidly to

large j' as θ increases and is near j'_{max}, the largest energetically allowed value, for $\theta > \pi/2$. The singularity in the classical differential cross section at the limiting values of j' arises because of the large number of initial conditions (b, β, α) which all lead to the maximal torque applied to the molecule. This is reminiscent of rainbow scattering in atom–atom collisions,[21] in which collisions over a broad range of impact parameters b lead to the same scattering angle.

Unfortunately, a direct comparison between the quantum and classical rigid-body differential cross sections for the LiH–He system is not possible since we did not determine a sufficient number of S-matrix elements in our earlier CS study. However, to judge from the accuracy of the rigid-body integral cross sections (Fig. 3 and Table I), it is virtually certain that the corresponding rigid-body differential cross sections will be substantially in error.

IV. CONCLUSION

We have implemented here a rigid-body classical model for rotationally inelastic LiH–He collisions, which involves implusive collisions between a point particle and a smooth spherical shell displaced in origin from the center of mass of the LiH molecule. For a given collision energy the radius and displacement of the shell are adjusted for a best fit of the "hard sphere" equipotential contour of the *ab initio* surface determined by Silver.[9] The resulting collision dynamics can be treated analytically so that it is extremely easy to calculate cross sections for transitions from the rotationless $j = 0$ state to any final rotational state. Unfortunately, the values so obtained differ tremendously from more accurate quantum coupled-states values, both in absolute magnitude as well as in their dependence on the final rotational quantum number.

We must then conclude that the off-center rigid shell model does not provide a sufficiently accurate description of the dynamics of rotationally inelastic LiH–He collisions. It should be noted that the present model does not allow for "multiple encounter" collisions where the rigid shell would undergo a second or third encounter with the point particle. In addition, we have not considered the case where the LiH molecule is initially rotating. Although these features could be introduced, a significant improvement in the accuracy of the predicted partial opacities and integral cross sections does not seem likely.

Due to the ease of the calculations, it is tempting to use a rigid-body model in the analysis of experimental integral cross section data. Indeed, this type of model[7] has been extremely helpful in understanding the physical origin of the observed structures, the rotational rainbows, in doubly differential cross sections.[2,8,18] Unfortunately, to judge from the present results, it is likely that quantitative agreement with experimental integral cross sections could be obtained only with rigid shells which would have little physical relation to the relevant hard sphere contours of the true potential surface.

ACKNOWLEDGMENTS

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[1]Recent reviews include J. P. Toennies, Ann. Rev. Phys. Chem. 27, 225 (1976); M. Faubel and J. P. Toennies, Adv. At. Mol. Phys. 13, 229 (1977).
[2]K. Bergmann, R. Engelhardt, V. Hefter, and J. Witt, J. Chem. Phys. 71, 2726 (1979).
[3]P. J. Dagdigian, B. E. Wilcomb, and M. H. Alexander, J. Chem. Phys. 71, 1670 (1979).
[4]R. A. LaBudde and R. B. Bernstein, J. Chem. Phys. 55, 5499 (1971).
[5]W. L. Dimpfl and B. H. Mahan, J. Chem. Phys. 60, 3238 (1974).
[6]C. E. Kolb and J. B. Elgin, J. Chem. Phys. 66, 119 (1977).
[7]D. Beck, U. Ross, and W. Schepper, Z. Phys. A 293, 107 (1979).
[8]W. Schepper, U. Ross, and D. Beck, Z. Phys. A 290, 131 (1979); D. Beck, U. Ross, and W. Schepper, Phys. Rev. A 19, 2173 (1979).
[9]D. M. Silver, J. Chem. Phys. 72, 6445 (1980).
[10]E. F. Jendrek and M. H. Alexander, J. Chem. Phys. 72, 6452 (1980).
[11]P. J. Dagdigian and B. E. Wilcomb, J. Chem. Phys. 72, 6462 (1980).
[12]J. H. Jeans, *Dynamical Theory of Gases* (Cambridge U. P., London, 1904), pp. 92, 192; J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 509.
[13]R. G. Gordon and R. P. McGinnis, J. Chem. Phys. 55, 4898 (1971); N. C. Blais and D. G. Truhlar, *ibid.* 65, 5335 (1976).
[14]P. McGuire and D. J. Kouri, J. Chem. Phys. 60, 2488 (1974); R. T Pack, *ibid.* 60, 633 (1974).
[15]E. F. Jendrek (unpublished).
[16]A. Metropolous and D. M. Silver (to be published).
[17]L. D. Thomas, J. Chem. Phys. 67, 5224 (1977).
[18]W. Eastes, U. Ross, and J. P. Toennies, Chem. Phys. 39, 407 (1979).
[19]J. M. Bowman, Chem. Phys. Lett. 62, 309 (1979).
[20]R. Schinke, J. Chem. Phys. 72, 1120 (1980).
[21]See, for example, M. S. Child, *Molecular Collision Theory* (Academic, New York, 1974), Chap. 2.