PHYSICAL REVIEW A VOLUME 8, NUMBER 6 DECEMBER 1973

Vibrational-Rotational Excitation in Atom–Diatomic-Molecule Collisions

Juliette W. Ioup*†
Physics Department, University of Connecticut, Storrs, Connecticut, 06268
Mathematics Department, Louisiana State University in New Orleans, New Orleans, Louisiana, 70122

Arnold Russek
Physics Department, University of Connecticut, Storrs, Connecticut, 06268

(Received 15 November 1972; revised manuscript received 24 May 1973)

Differential and total cross sections are calculated for elastic scattering and also for rotational and vibrational excitation when an atom and a diatomic molecule collide at keV energies. Explicit calculations for vibrational excitation are here limited to the first vibration state only, although the method can easily be extended to higher vibrational states. The results are valid for small-angle scattering at keV energies, for which the motion of the nuclei can be treated in the Born approximation, while the electronic motion is treated in the adiabatic approximation. The cross sections are obtained as analytic expressions, the exact solutions which follow from a realistic potential form with several adjustable parameters. These parameters can be adjusted to fit the proposed potential form to the potential appropriate to the desired collision reactants. The potential form includes the long-range R^{-6} van der Waals interaction as well as the steep repulsive potential at short ranges and is a function also of the orientation angle between the molecular axis and the incident direction. Hydrogen-atom–hydrogen-molecule scattering is presented as an example. The potential for three hydrogen atoms is obtained by adjusting the parameters in the analytical expression for the potential to the *ab initio* calculation of the H_3 energy surface of Shavitt *et al.*, and numerical values for the differential and total cross sections are obtained. In the case of other collision reactants, for which no *ab initio* energy-surface calculations are available, the results of the present work conversely permit the parameters (and, therefore, the energy surface) to be determined by experimental cross-section measurements at keV energies.

I. INTRODUCTION

Any attempt to make progress toward an *ab initio* understanding of chemical processes first requires a knowledge of the so-called "energy surface." This shorthand term stands for the energy of interaction of all the systems involved as functions of their relevant spacings and orientation angles. When only two atoms are involved (i.e., the diatomic molecule), the energy of interaction is a function of only a single variable, the internuclear separation. Even in this simple case, the energy "surface" is by no means easy to obtain. Nevertheless, considerable progress has been made, both theoretically and experimentally, for many interacting pairs of atoms. However, when passing on to systems containing three or more atoms, the energy surfaces are almost completely uncharted, except for small regions around the respective equilibrium configurations. On the one hand, theoretical calculations are prohibitive and, on the other hand, low-energy-collision experiments to explore the energy surface are all but impossible.

One of the purposes of this work is to call attention to the fact that for systems consisting of three atoms, a considerably wider portion of the energy surface can be experimentally determined by atom-molecule collisions in the much more accessible keV energy range. The projectile atom beam can easily be produced by accelerating ions to the desired energy and then neutralizing them in a charge-exchange chamber. Techniques both for forming and detecting beams in this energy range are by now standard. The upper limit of useful energies for studying the energy surface would be about 2–3 keV. Above these energies the collision time becomes so short that the electronic state is unable to adiabatically adjust to the changing internuclear separations. The breakdown of adiabatic electronic behavior above the cutoff is evidenced by the onset of electronic excitation produced by the collisions. It should be pointed out that for a study of the energy surface, only the electronic state need adjust adiabatically to the changing internuclear separations. At the keV collision energies in the envisaged experiments, the collisions could not be completely adiabatic; both rotational and vibrational excitation would occur. (These latter excitations are not eliminated until the collision energy is reduced below 1 or 2 eV.) However, far from making the experiments ambiguous, the occurrence of rotational and vibrational excitation (if these cross sections are measured) actually provides more detailed information on the energy surface.

The motivation for this phase of the present work grew out of an earlier study[1,2] of dissociation induced by polarization forces when molecular ions collide on neutral-atom targets. The collisions studied involved small-angle (i.e., large-impact-parameter) scattering of H_2^+ and HeH^+ on noble gases at 10 keV. It had originally been reasoned that for large-impact-parameter scattering, the details of the shape of the potential at small internuclear separations should not have much effect, as long as the potential was devoid of unphysical singularities. The results of the theoretical study, however, proved to be surprisingly sensitive to the form of the cutoff used to make the polarization potential nonsingular at small internuclear separations. As a consequence, it became evident that such collisions could be used as a probe to study the energy surface over the entire range of internuclear separations of interest to chemical processes. In essence, an accurate and complete differential scattering experiment at a single incident energy would in principle provide a Fourier transform of the energy surface.

However, although this can be conceived in principle, it cannot be realistically accomplished in practice. Therefore, this paper takes a practical approach. A realistic functional form of the energy surface is assumed with several adjustable parameters. (Proper adjustment of these parameters can, for example, quite adequately fit what is known of the H_3 energy surface.) With this functional form, simple analytic expressions for the differential cross sections both for elastic scattering and for scattering with rotational-vibrational excitation are obtained in terms of the adjustable parameters in the potential form. Thus, an experimental measurement of the various differential cross sections can be used to determine the adjustable parameters in the potential function.

A second purpose of the present work is the calculation of several cross sections for collisions of H on H_2. In particular, the differential and total cross sections for elastic scattering and for excitation from the ground state to any permitted rotational level of the ground and first vibrational states of the molecule are calculated for H on H_2. Only certain final rotational states are allowed in the collision by the potential form chosen. The calculation of these cross sections for the case of H on H_2 has been accomplished by fitting the parameters of the potential form assumed in this work to existing calculations of the H_3 potential, which has been determined in sufficient detail to yield meaningful cross sections.

The calculation of the potential-energy surface for H_3 has had a long and a controversial history. It would disrupt the continuity to outline that history at this point, since it is not the purpose of this work either to calculate the potential-energy surface of H_3 or to present an optimum parametrization of that energy surface. Rather, a parametrization is presented which is both adequate to describe the potential and from which elastic and rotational-vibrational excitation cross sections can be calculated analytically, so that adjustable parameters might be meaningfully fitted from experimental data.

It should be borne in mind that, although there have been many calculations pertaining to the energy of interaction of three hydrogen atoms, not all the published results are useful. The potential form required to yield rotational and vibrational excitation must contain dependences on all three variables relevant to the three-body potential surface. In this work they are r_B, the internuclear separation of the two protons in the H_2 molecule; R, the distance between the third atom and the center of mass of the molecule; and θ, the angle between $\vec{R}$ and $\vec{r}_B$. Each of the potential surfaces from the literature was examined to determine its usefulness in obtaining the potential as a function of these three quantities. Most calculations were unfortunately made for the linear arrangement, and thus the dependence of the potential on the angle θ could not be deduced from them. Such calculations included those by Ellison, Huff, and Patel,[3] Hayes and Parr,[4] Pedersen and Porter,[5] Michels and Harris,[6] Schwartz and Schaad,[7] Edmiston and Krauss,[8] Salomon,[9] and Cheung and Wilson.[10] Margenau[11] and Conroy and Bruner[12] presented results for the linear configuration and one additional orientation. Calculations by Eyring and Polanyi,[13] Takayanagi,[14] Dalgarno, Henry, and Roberts,[15] and Tang[16] contain no information about the r_B dependence; the equilibrium separation of the molecule was assumed in their work. Tang and Karplus[17] considered the equilibrium case and one slightly larger separation. Since it is absolutely necessary to know the dependence of the potential on r_B in order to calculate the vibrational excitation of the molecule resulting from the collision, these potentials were also unsatisfactory. Porter and Karplus[18] give contour maps of the potential-energy surface for four different orientations of the system, thus including both internuclear separation and angular dependence. The paper by Shavitt, Stevens, Minn, and Karplus[19] (SSMK) was considered to be the most useful. It contains tables of energy values for three orientations of the system and for various internuclear separations of all three atoms.

Expressions for the differential and total cross sections are obtained in Sec. II using a hybrid[1] approximation for atom–diatomic-molecule collisions. The analytical form of the interaction potential which appears in the matrix elements is discussed in Sec. III. Evaluation of the matrix elements required for the differential cross sections is carried out in Sec. IV, and the numerical procedure to compute total cross sections is described in Sec. V. Section VI contains results obtained for hydrogen-atom–hydrogen-molecule scattering.

II. FORMALISM

For the intermediate range of incident energies, i.e., a few hundred eV up to a few keV, the electronic motion is nearly adiabatic, despite the fact that the incident energy is far above the threshold value of approximately 15 eV for electronic excitation. However, it must be understood that electronic excitation is indeed taking place, albeit with small probability relative to such other processes as elastic scattering and vibrational-rotational excitation. As a matter of fact, the upper limit of the range is determined by the increasing probability of electronic excitation. In view of the existence of nonadiabatic electronic behavior which cannot be entirely neglected, there is some question as to whether cross-section measurements in this energy range can yield meaningful information about the adiabatic energy surface which is desired.

The experimenter is now easily able, by energy analysis of the collision, to distinguish between those processes in which electronic excitation did and did not take place. Indeed, in several laboratories, the state of the art has been developed almost to the point where individual vibrational excitations can be resolved, and it is anticipated that this capability will be achieved in the near future. It would be expected, on intuitive grounds, that if the experimenter measures those cross sections which do not involve electronic excitation, then these data should yield information concerning the adiabatic energy surface. However, this intuitive insight must be placed on a firm theoretical foundation before the results thus obtained can be trusted.

The formalism in this section, which follows that of Ref. 1, was developed to describe a collision in this intermediate energy range in which the electronic motion is essentially able to follow adiabatically the changing internuclear separation while the vibrational-rotational motion is unable to do so and is treated in the Born approximation. As a consequence, this method has been termed the "hybrid" approximation. It is, however, a complete and rigorous approximation and also yields the cross sections for electronic excitation which result as a departure from completely adiabatic motion. These latter cross sections, which can be discriminated against by present experimental techniques, will not be pursued here, but will be taken up in a future paper. The intent of this work is to stress what can be learned about the adiabatic energy surface by scattering experiments in the intermediate energy range.

The coordinates used to describe the system are shown in Fig. 1. The nuclei of the diatomic molecule are separated by a distance $\vec{r}_B$, and the atom is located at a distance $\vec{R}$ from the center of mass of the molecule. The positions of the electrons are specified by $\vec{r}_{a1}$, $\vec{r}_{a2}, \ldots,$ and $\vec{r}_{b1}$, $\vec{r}_{b2}, \ldots,$ which give the location of each electron with respect to the center of mass of the system to which it belongs. The angle θ describes the relative orientation of $\vec{R}$ and $\vec{r}_B$. The electron masses are neglected with respect to the proton masses.

The Hamiltonian for the entire system may be written in the form

$$H = T_R + H_A + H_B + V_{AB} \ , \tag{1}$$

where T_R is the translational kinetic-energy operator of relative motion of the two systems, H_A is the internal Hamiltonian operator for system A, which is taken to be the atom, H_B is similarly the operator for system B, the molecule, and V_{AB} is the interaction potential between A and B.

In the adiabatic approximation the Hamiltonian is decomposed into a nuclear term h and an electronic term $\mathcal{H}$ such that

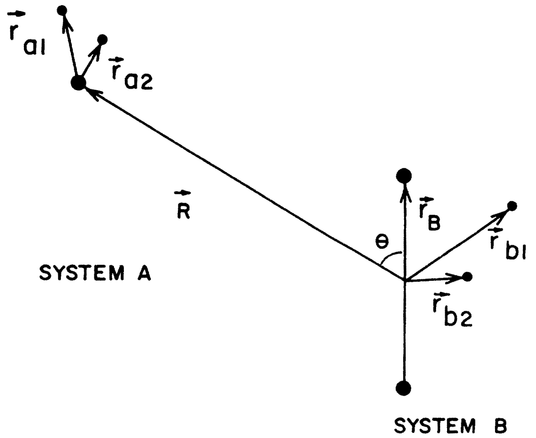

FIG. 1. Scattering system consisting of an atom and a homonuclear diatomic molecule at a separation $\vec{R}$. The distance between the nuclei in the molecule is $\vec{r}_B$ and the positions of the electrons are given by $\vec{r}_{a1}$, $\vec{r}_{a2}, \ldots,$ $\vec{r}_{b1}$, $\vec{r}_{b2}, \ldots,$

$$H = h + \mathcal{H} \,, \tag{2}$$

where $\mathcal{H}$ is the sum of the kinetic-energy operators for each electron plus the potential energy between each electron and either a proton or another electron, and h is the sum of the kinetic-energy operators for each proton plus the potential energy between the protons. The eigenstates and eigenenergies for the electrons are obtained for fixed interproton separations by

$$\mathcal{H}\varphi_n(\vec{r}_{a1}, \vec{r}_{a2}, \ldots, \vec{r}_{b1}, \vec{r}_{b2}, \ldots; \vec{R}, \vec{r}_B) = \mathcal{E}_n(\vec{R}, \vec{r}_B)\varphi_n(\vec{r}_{a1}, \vec{r}_{a2}, \ldots, \vec{r}_{b1}, \vec{r}_{b2}, \ldots; \vec{R}, \vec{r}_B) \,. \tag{3}$$

$\mathcal{E}_n(\vec{R}, \vec{r}_B)$ is next used as the electron contribution to the internuclear potential energy in solving for the eigenstates and eigenenergies of the nuclei:

$$[h + \mathcal{E}_n(\vec{R}, \vec{r}_B)]\chi_m(\vec{R}, \vec{r}_B) = E_{nm}\chi_m(\vec{R}, \vec{r}_B) \,, \tag{4}$$

where n refers to electronic quantum numbers and m refers to protonic quantum numbers. The wave function for the complete system is then the product of φ_n for the electrons and χ_m for the nuclei.

In the hybrid approximation, the electrons are treated in the adiabatic approximation, but the nuclei in the Born approximation. Thus the adiabatic electronic eigenstates φ_n are not multiplied by the protonic wave functions described above, but instead by a wave function calculated on the basic of no interaction between systems A and B. The complete orthonormal basis set which defines the hybrid approximation is thus

$$\psi_{Knv}(\vec{r}_{a1}, \vec{r}_{a2}, \ldots, \vec{r}_{b1}, \vec{r}_{b2}, \ldots; \vec{R}, \vec{r}_B) = e^{i\vec{K}\cdot\vec{R}}\chi_v(\vec{r}_B)\varphi_n(\vec{r}_{a1}, \vec{r}_{a2}, \ldots, \vec{r}_{b1}, \vec{r}_{b2}, \ldots; \vec{R}, \vec{r}_B) \,. \tag{5}$$

The relative motion of A and B is described by the plane wave $e^{i\vec{K}\cdot\vec{R}}$, just as in the usual Born approximation. The eigenfunction $\chi_v(\vec{r}_B)$ for the molecule is the vibrational-rotational state for a diatomic mulecule, where v stands for all quantum numbers describing the vibrational-rotational state of the molecule. This wave function is calculated for an isolated molecule, when the atom and molecule are at infinite separation. The protons are too slow in the intermediate energy range to be able to adjust in the short collision time. The eigenfunctions can be seen to be truly hybrid: The first two factors, which describe the nuclear motion, are from the Born approximation; the last factor, which describes the electronic motion, is from the adiabatic approximation.

Time dependence is included by multiplying the eigenfunctions above by the time-dependent factor $e^{-E_{Knv}t/\hbar}$, where

$$E_{Knv} = \frac{K^2}{2\mathfrak{M}_{AB}} + \epsilon_n(A) + \epsilon_{n,v}(B) \,. \tag{6}$$

$\mathfrak{M}_{AB}$ is the reduced mass of the entire system and $\epsilon_n(A)$ and $\epsilon_{n,v}(B)$ are the internal energies of the two isolated systems.

The basis functions given above form a complete orthonormal set, so that any function may be expanded in terms of them:

$$\Psi(\vec{r}_{a1}, \vec{r}_{a2}, \ldots, \vec{r}_{b1}, \vec{r}_{b2}, \ldots; \vec{R}, \vec{r}_B) = \sum_{Knv} a_{Knv}(t)\psi_{Knv}e^{-iE_{Knv}t/\hbar} \,. \tag{7}$$

Schrödinger's equation for the system is

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t} \,. \tag{8}$$

Following the usual procedure, the expansion for Ψ is substituted into the Schrödinger equation and inner products with each basis element taken, resulting in the first-order equations

$$[-i\hbar\,\dot{a}_{Knv} - a_{Knv}E_{Knv}]e^{-iE_{Knv}t/\hbar} + \sum_{K'n'v'}\langle\psi_{Knv}|H|\psi_{K'n'v'}\rangle a_{k'n'v'}e^{-iE_{K'n'v'}t/\hbar} = 0 \,. \tag{9}$$

The term H_A in the Hamiltonian is the internal-energy operator for the atom, and thus is purely electronic in nature, consisting of the kinetic-energy operator for the electron plus the potential between it and its nucleus. The internal-energy operator for the molecule, H_B, may be broken up into an electronic part $\mathcal{H}_B$ and a nuclear part h_B. The interaction potential V_{AB} is the sum of three potential terms: V_{e-e}, the sum of the potentials between those pairs of electrons having one of the pair in the atom and the other in the molecule; V_{e-p}, the sum of the interaction potentials between each electron of either the atom or molecule and each proton of the other; and V_{p-p}, the sum of the interaction potentials between those pairs of protons having one of the pair in the atom and the other in the molecule. Then the Hamiltonian may be written

$$\begin{aligned} H &= T_R + H_A + \mathcal{H}_B + h_B + V_{e-e} + V_{e-p} + V_{p-p} \\ &= T_R + \mathcal{H} + \mathcal{V} \,. \end{aligned} \tag{10}$$

where $\mathcal{H}$ is the electronic component,

$$\mathcal{H} = H_A + \mathcal{H}_B + V_{e-e} + V_{e-p} \,, \tag{11}$$

and $\mathcal{V}$ is the term involving just the nuclei,

$$\mathcal{V} = h_B + V_{p-p} \,. \tag{12}$$

Then the action of the Hamiltonian on ψ_{Knv} may be written

$$H\psi_{Knv}=\left(\frac{K^2}{2\mathfrak{M}_{AB}}+\mathcal{E}_n(\vec{R},\vec{r}_B)+\mathcal{V}\right)\psi_{Knv} -\frac{1}{2\mathfrak{M}_{AB}}e^{i\vec{K}\cdot\vec{R}}\chi_v[2i\vec{K}\cdot\vec{\nabla}_R\varphi_n+\nabla_R^2\varphi_n]. \tag{13}$$

The second term on the right-hand side of Eq. (13) represents cross terms due to the action of T_R on φ_n, which is also a function of $\vec{R}$. This term is responsible for electronic excitation. If electronic excitation is found to be negligible in the energy range considered, this term must also be negligible.

The electronic energy of the total system when the two atoms of the molecule are at a separation $\vec{r}_B$ and the third atom is located at a distance $\vec{R}$ from the center of mass of the molecule is $\mathcal{E}_n(\vec{R},\vec{r}_B)$. When the atom and molecule are infinitely separated the total electronic energy is

$$\mathcal{E}_n(\infty,r_B)=\epsilon_n(A)+\epsilon_n(B). \tag{14}$$

Also, for the molecule,

$$[h_B+\epsilon_n(B)]\chi_v=\epsilon_{nv}(B)\chi_v. \tag{15}$$

Using Eqs. (6), (14), and (15), Eq. (13) may be written

$$H\psi_{Knv}=[E_{Knv}+\mathcal{E}_n(\vec{R},\vec{r}_B)-\mathcal{E}_n(\infty,r_B)+V_{p-p}]\psi_{Knv} -\frac{1}{2\mathfrak{M}_{AB}}e^{i\vec{K}\cdot\vec{R}}\chi_v[2i\vec{K}\cdot\vec{\nabla}_R\varphi_n+\nabla_R{}^2\varphi_n]. \tag{16}$$

In obtaining this result, the Born-Oppenheimer approximation has been used for the molecule so that the operator h_B applied to the total wave function ψ_{Knv} acts only on the molecular vibrational-rotational eigenfunction χ_v and not on the electronic wave function φ_n.

After substitution, Eq. (9) for the coefficients becomes

$$i\hbar\dot{a}_{Knv}=\sum_{K'n'v'}\left\{\left[\langle\psi_{Knv}|\mathcal{E}_n(\vec{R},\vec{r}_B)-\mathcal{E}_n(\infty,r_B)+V_{p-p}|\psi_{K'n'v'}\rangle -\frac{1}{2\mathfrak{M}_{AB}}\langle\psi_{Knv}|e^{i\vec{K}'\cdot\vec{R}}\chi_{v'}[2i\vec{K}'\cdot\vec{\nabla}_R\varphi_{n'}+\nabla_R^2\varphi_{n'}]\rangle\right]a_{K'n'v'}e^{i(E_{Knv}-E_{K'n'v'})t/\hbar}\right\} \tag{17}$$

The first matrix element in the expression above refers to the vibrational-rotational excitation. The interaction potential between the atom and the diatomic molecule, otherwise termed the "energy surface," is

$$V(R,r_B,\theta)=\mathcal{E}_n(\vec{R},\vec{r}_B)-\mathcal{E}_n(\infty,r_B)+V_{p-p}. \tag{18}$$

Its form will be discussed below. The second matrix element describes the electronic excitation (that is, departure from adiabatic behavior) and is not investigated further in this work. The results for electronic excitation for collisions which occur at relatively large impact parameters can be shown to be identical to the corresponding Born cross sections for the systems involved.[1]

The differential cross section is obtained using time-dependent perturbation theory[20] to derive the transition rates which are then converted into differential cross sections. The differential cross section is

$$\frac{d\sigma_{FI}}{d\Omega}=\left(\frac{\mathfrak{M}_{AB}}{2\pi\hbar^2}\right)^2\frac{K_F}{K_I}|M_{FI}|^2, \tag{19}$$

where the matrix element M_{FI} is given by

$$M_{FI}=\langle\psi_{Knv}|V(R,r_B,\theta)|\psi_{K'n'v'}\rangle. \tag{20}$$

This matrix element involves the potential $V(R,r_B,\theta)$, which describes the interaction between the atom and the molecule: It is the energy surface and contains no terms involving the electronic coordinates. Since the adiabatic electronic wave functions φ_n are orthonormal for fixed $\vec{R}$ and $\vec{r}_B$, integration over all electronic coordinates yields the Kronecker $\delta_{nn'}$, so that

$$M_{FI}=\int d^3R\,e^{i\vec{K}\cdot\vec{R}}\int d^3r_B\,\chi_v(\vec{r}_B)^* \times V(R,r_B,\theta)\chi_{v'}(\vec{r}_B)\delta_{nn'}, \tag{21}$$

where

$$K=K_F-K_I. \tag{22}$$

The total cross section is obtained by integrating the differential:

$$\sigma_{FI}=\int\frac{d\sigma_{FI}}{d\Omega}d\Omega. \tag{23}$$

Assuming that $|M_{FI}|^2$ is azimuthally symmetric, as will be the case after averaging over all initial and summing over all final orientations, then the total cross section becomes

$$\sigma_{FI}=\left(\frac{\mathfrak{M}_{AB}}{2\pi\hbar^2}\right)^2\frac{K_F}{K_I}2\pi\int_0^\pi|M_{FI}|^2\sin\theta\,d\theta \tag{24}$$

or

$$\sigma_{FI} = \left(\frac{\mathfrak{M}_{AB}}{2\pi\hbar^2}\right)^2 \frac{2\pi}{K_I^2} \int_{K_{\min}}^{K_{\max}} |M_{FI}|^2 \, K dK . \tag{25}$$

The result which has been achieved is, as might have been expected on intuitive grounds, just the golden-rule approximation to the cross sections for elastic scattering and scattering with vibrational-rotational excitation using the adiabatic energy surface $V(R, r_B, \theta)$ as the perturbation Hamiltonian. What has been demonstrated is not, however, trivial. In fact, it is not even precisely true. This approximation is valid despite the occurrence of electronic excitation and other nonadiabatic effects, only because the nonadiabatic electronic effects, which are contained in the second matrix element in Eq. (17), are small. However, they do in principle contribute to cross sections which do not involve electronic excitation. Indeed, it is these terms which determine the upper limit of the energy range in which the adiabatic energy surface may be extracted from experimental scattering data.

The terms in the nonadiabatic component of Eq. (17) which contribute to scattering without electronic excitation are those in the second matrix element on the right-hand side for which the final electronic state $\varphi_{n'}$ is the same as the initial electronic state φ_n. There are two such terms. One of them is of the form $(\varphi, i\vec{K}\cdot\vec{\nabla}_R\varphi)/\mathfrak{M}_{AB}$; the other is a $(\varphi, \nabla_R{}^2\varphi)/2\mathfrak{M}_{AB}$ term. The inner products are here indicated over electronic coordinates only, yielding the nonadiabatic corrections to the scattering potential $V(R, r_B, \theta)$. Now $K = P_{\text{inc}} = (2\mathfrak{M}_{AB}E_{\text{inc}})^{1/2}$, while $\vec{\nabla}_R\varphi$ is of the order of $\vec{\nabla}_r\varphi$ and is thus of the order of $p_{\text{el}} \approx (2m\,|E_{\text{el}}|)^{1/2}$. Here m stands for the electronic mass, E_{inc} the incident beam energy, and E_{el} the electronic contribution to the scattering potential V. The reduced mass $\mathfrak{M}_{AB}$ can be taken to be approximately the proton mass M. Thus, the two nonadiabatic corrections to the matrix element for scattering without electronic excitation are of the order $(mE_{\text{inc}}/M|E_{\text{el}}|)^{1/2} E_{\text{el}}$ and $p^2/2M \approx (m/M)E_{\text{el}}$. The former is a velocity-dependent contribution to the scattering potential. In order that it be comparable with the adiabatic contribution to the scattering potential, the incident energy would have to be roughly equal to $(M/m)E_{\text{el}}$. Taking the electronic energy to be of the order of a rydberg, the incident energy would have to be 2000 Ry for velocity-dependent forces to be comparable with the adiabatic contribution to the potential. It was for this reason that the upper limit of incident beam energy was placed in the vicinity of a few keV for the experimental probe of the adiabatic energy surface for H_3. The second term, $(m/M)E_{\text{el}}$, is always negligible, unless very high accuracy is desired.

III. POTENTIAL

The interaction potential is expanded in a Legendre polynomial series:

$$V(R, r_B, \theta) = \sum_n f_n(R, r_B) P_n(\cos\theta) . \tag{26}$$

Only even Legendre polynomials appear in the expansion because the diatomic molecule is assumed to be homonuclear. Terms higher than second order are neglected. The functions f_0 and f_2 are approximated by the expressions

$$f_0(R, r_B) = a_1 e^{-a_2 R} - [a_3/(R^6 + a_4^6)] \tag{27}$$

and

$$f_2(R, r_B) = a_5 e^{-a_6 R} - [a_7/(R^6 + a_8^6)] , \tag{28}$$

where the odd-numbered coefficients a_i are functions of r_B:

$$a_i = a_{i1} + a_{i2}(r_B - r_0) + a_{i3}(r_B - r_0)^2 ,$$
$$i = 1, 3, 5, 7 . \tag{29}$$

The equilibrium separation of the diatomic molecule is r_0.

The potential may be considered as a short-range part plus a long-range part. The short-range part describes the nuclear repulsion and depends on R exponentially as $e^{(-aR)}$. The long-range part is the van der Waals potential, proportional to R^{-6}. The denominators of the van der Waals terms are chosen to be of the form $R^6 + a^6$ so that these terms would approach a finite limit when R approaches zero. The value of the constant a in the denominator gives the range of the exchange effect for the electrons. When R is greater than a the probability that the electrons in the two systems may be exchanged is very small and therefore they may be treated as distinct; when R is less than a, the electron exchange probability is significant. However, polarization forces are still important in the region $R > a$, for, although the electrons are distinguishable for the two systems, they are not isolated, and they do interact with each other.

The four coefficients a_i which are functions of r_B reflect the dependence of the potential on the internuclear separation in the molecule. In this work the molecule is approximated by a harmonic oscillator and therefore terms up to $(r_B - r_0)^2$ were included.

The even-numbered coefficients were assumed to be constant in r_B. The two in the exponents, a_2 and a_6, give the strength of the internuclear repulsion between the atom and the molecule. The two in the denominators of the van der Waals terms, a_4 and a_6, give the range of the electron-exchange region between the atom and the molecule as described above. The potential is well behaved at large and small R.

The unspecified parameters a_i in the expressions for the potential have been included to facilitate comparison with experiment. They will be carried through the calculations to appear in the final forms for the collision cross sections. Comparison of these expressions with experimental collision data would allow numerical determination of these coefficients to obtain a specific potential for each atomic-diatomic system studied. In addition, the larger number of parameters allows better agreement with a previously determined potential surface; this procedure was used in the example of hydrogen-atom–hydrogen-molecule scattering.

Since the many coefficients of this form of the H_3 potential were adjusted to give a close fit to the SSMK potential, a comparison of this potential with various semiempirical potential surfaces would parallel a similar comparison of the surface of SSMK to the semiempirical surfaces. Such a discussion may be found in Sec. IV of the SSMK paper, in which their potential surface is compared to the semiempirical surfaces of Eyring and Polanyi,[13] Sato,[21] and Porter and Karplus.[18]

IV. DIFFERENTIAL CROSS SECTIONS

The integration for the matrix element of Eq. (21) requires evaluation of integrals over both d^3R and d^3r_B. The integration over $\vec{R}$ is carried out first. A coordinate system is chosen which has the momentum-transfer vector $\vec{K}$ along the z axis. The orientation of $\vec{R}$ in this system is specified by the angles θ_R and φ_R. The orientation of $\vec{r}_B$ is similarly given by θ_B and φ_B.

The interaction potential has been expanded in a Legendre-polynomial series so that the integrals over d^3R necessary for the cross section are of the form

$$I_L = \int d^3R\, f_L(R, r_B) e^{i\vec{K}\cdot\vec{R}} P_L(\hat{R}\cdot\hat{r}_B)\,, \tag{30}$$

where the $f_L(R, r_B)$ are given by Eqs. (27) and (28), and $\hat{R}\cdot\hat{r}_B = \cos\theta$, where θ is the angle between $\hat{R}$ and $\hat{r}_B$. Now

$$\vec{K}\cdot\vec{R} = KR\cos\theta_R = KR\mu\,, \tag{31}$$

so that

$$I_L = \int d^3R\, f_L(R, r_B) e^{ikR\mu} P_L(\hat{R}\cdot\hat{r}_B)\,. \tag{32}$$

Legendre polynomials involving $\cos\theta$ may be expanded in terms of spherical harmonics involving θ_R, φ_R, θ_B, and φ_B by using the addition theorem so that

$$I_L = \frac{4\pi}{2L+1} \sum_M Y_L^M(\theta_B, \varphi_B) \int_0^\infty R^2\, dR\, f_L(R, r_B) \times \int_{-1}^{+1} d\mu\, e^{iKR\mu} \int_0^{2\pi} d\varphi_R\, Y_L^M(\theta_R, \varphi_R)^*\,. \tag{33}$$

The integration over φ_R gives no contribution when $M \neq 0$ and is 2π when $M = 0$, so that I_L is

$$I_L = 2\pi P_L(\cos\theta_B) \int_0^\infty R^2\, dR\, f_L(R, r_B) \times \int_{-1}^{+1} d\mu\, e^{iKR\mu} P_L(\mu)\,. \tag{34}$$

Now $P_L(\mu)$ is a polynomial in μ, so I_L will contain terms of the form

$$J_m(r_B) = \int_0^\infty R^2\, dR\, f_L(R, r_B) \int_{-1}^{+1} d\mu\, e^{iKR\mu} \mu^m\,, \tag{35}$$

which may also be written as

$$J_m(r_B) = \int_0^\infty R^2\, dR\, f_L(R, r_B) \frac{d^m}{dK^m} \frac{1}{(iR)^m} \times \int_{-1}^{+1} d\mu\, e^{iKR\mu}\,. \tag{36}$$

The integration over μ can now be carried out, resulting in

$$J_m(r_B) = \frac{2}{i^m} \frac{d^m}{dK^m} \frac{1}{K} \int_0^\infty dR\, f_L(R, r_B) R^{1-m} \sin KR\,. \tag{37}$$

The expansion of the interaction potential contained only the first two even Legendre polynomials, so that m is either zero or two. The two integrals to be evaluated are then

$$I_0(r_B) = 2\pi P_0(\cos\theta_B) J_0(r_B) = \frac{4\pi}{K} \int_0^\infty dR\, f_0(R, r_B) R \sin KR \tag{38}$$

and

$$I_2(r_B) = 2\pi P_2(\cos\theta_B)\left[\tfrac{3}{2} J_2(r_B) - \tfrac{1}{2} J_0(r_B)\right] = \pi P_2(\cos\theta_B)\left[\frac{d^2}{dK^2}\left(-\frac{6}{K}\int_0^\infty dR\, f_2(R, r_B) \frac{\sin KR}{R}\right) - \frac{2}{K}\int_0^\infty dR\, f_2(R, r_B) R \sin KR\right]. \tag{39}$$

Using standard integral tables and contour integration, these become

$$I_0(r_B)=\frac{4\pi}{K}\left\{\frac{2a_1a_2K}{(a_2^2+K^2)^2}+\frac{\pi a_3}{6a_4^4}\left[2e^{-Ka_4/2}\cos\left(\frac{Ka_4\sqrt{3}}{2}+\frac{\pi}{3}\right)-e^{-Ka_4}\right]\right\} \tag{40}$$

and

$$\begin{aligned}I_2(r_B')=\pi P_2(\cos\theta_B)\Bigg\{&\frac{8a_5a_6}{(a_6^2+K^2)^2}+\frac{12a_5a_6}{K^2(a_6^2+K^2)}-\frac{12a_5}{K^3}\tan^{-1}\frac{K}{a_6}+\frac{2a_7\pi}{3Ka_8^4}\left[2e^{-Ka_8/2}\cos\left(\frac{Ka_8\sqrt{3}}{2}+\frac{\pi}{3}\right)-e^{-Ka_8}\right]\\&-\frac{2a_7\pi}{K^2a_8^5}\left[2e^{-Ka_8/2}\cos\left(\frac{Ka_8\sqrt{3}}{2}-\frac{\pi}{3}\right)+e^{-Ka_8}\right]-\frac{2a_7\pi}{K^3a_8^6}\left[2e^{-Ka_8/2}\cos\left(\frac{Ka_8\sqrt{3}}{2}\right)+e^{-Ka_8}-3\right]\Bigg\}.\end{aligned} \tag{41}$$

These expressions are well behaved when K approaches zero. With the integration over d^3R performed, the matrix element is now given by

$$M_{FI}=\int d^3r_B\,\chi_v^*(\vec{r}_B)\,[I_0(r_B)+I_2(r_B)]\times\chi_{v'}(\vec{r}_B)\,. \tag{42}$$

For the integration over d^3r_B the vibrational-rotational wave functions must be explicitly written out. They may be expressed in separated form as

$$\chi_v(\vec{r}_B)=F_v(r_B)\,Y_L^M(\hat{r}_B)\,, \tag{43}$$

where $Y_L^M(\hat{r}_B)$ is a spherical harmonic. In the function $F_v(r_B)$ the quantum number v refers to the vibrational state of the molecule.

The absolute value squared of the matrix element must be summed over all projections of the final angular momentum and averaged over all initial projections. The required quantity is

$$|M_{FI}|^2=\frac{1}{2L+1}\sum_M\sum_{M'}|\langle F_v(r_B)\,Y_L^M(\hat{r}_B)|\,I_0+I_2\,|\times F_{v'}(r_B)\,Y_{L'}^{M'}(\hat{r}_B)\rangle|^2\,. \tag{44}$$

The integration over the angles θ_B and φ_B will be carried out first. Writing $I_L(r_B)$ in the form

$$I_L(r_B)=\mathcal{U}_L(r_B)P_L(\cos\theta_B)\,, \tag{45}$$

$\mathcal{U}_0(r_B)$ and $\mathcal{U}_2(r_B)$ are real quantities which depend only on r_B and not on θ_B or φ_B. Equation (45) may be substituted into Eq. (44) and the result expanded to give (after using the orthonormality property of the spherical harmonics and the fact that $P_0=1$)

$$\begin{aligned}|M_{FI}|^2=\frac{1}{2L+1}\sum_M\sum_{M'}\Big|&|Q_1|^2\delta_{LL'}\delta_{MM'}+|Q_1||Q_2|\,\delta_{LL'}\delta_{MM'}\int Y_L^M(\hat{r}_B)^*P_2(\cos\theta_B)\,Y_{L'}^{M'}(\hat{r}_B)\,d\varphi_B\,d(\cos\theta_B)\\&+|Q_1||Q_2|\,\delta_{LL'}\delta_{MM'}\int Y_L^M(\hat{r}_B)P_2(\cos\theta_B)\,Y_{L'}^{M'}(\hat{r}_B)^*\,d\varphi_B\,d(\cos\theta_B)\\&+|Q_2|^2\int Y_L^M(\hat{r}_B)^*P_2(\cos\theta_B)\,Y_{L'}^{M'}(\hat{r}_B)\,d\varphi_B\,d(\cos\theta_B)\Big|^2\,.\end{aligned} \tag{46}$$

Q_1 and Q_2 are the radial integrals which are functions only of K:

$$Q_1=\int_0^\infty F_v(r_B)^*\mathcal{U}_0(r_B)F_{v'}(r_B)r_B^2\,dr_B\,, \tag{47}$$

$$Q_2=\int_0^\infty F_v(r_B)^*\mathcal{U}_2(r_B)F_{v'}(r_B)r_B^2\,dr_B\,. \tag{48}$$

When the first term is summed over M and M', all but one term (when $M=M'$) vanish, as indicated by the δ function. The second and third terms (the cross terms) vanish after summation over M and M' and use of the addition theorem and the orthogonality of the Legendre polynomials. Similarly, using the addition theorem and the orthonormality of the spherical harmonics, the last term can be simplified so that $|M_{FI}|^2$ becomes

TABLE I. Numerical values in atomic units for the coefficients in the analytical expansion of the potential for H_3. These values were obtained by a least-squares fit to the SSMK surface.

Coef.	Value	Coef.	Value
a_{11}	0.169 199	a_{51}	0.002 578
a_{12}	0.052 106	a_{52}	−0.018 677
a_{13}	−0.189 842	a_{53}	0.101 318
a_2	0.595 382	a_6	0.101 367
a_{31}	306.871	a_{71}	29.1367
a_{32}	−444.553	a_{72}	409.222
a_{33}	−172.712	a_{73}	1955.31
a_4	5.290 97	a_8	5.348 79

$$|M_{FI}|^2 = |Q_1|^2 \delta_{LL'} + |Q_2|^2 \frac{2L'+1}{10} \times \int_{-1}^{+1} P_2(\mu) P_L(\mu) P_{L'}(\mu)\, d\mu$$

$$= |Q_1|^2 \delta_{LL'} + |Q_2|^2 (2L'+1) \frac{C(L, L', 2; 0, 0, 0)^2}{25} . \tag{49}$$

The initial state of the molecule is most probably the ground vibrational state ($v = 0$). For heuristic purposes we will also take it to be in the lowest rotational state ($L = 0$). In practical applications, the distribution of rotational states will have to be folded in. The molecule may be excited into any of the higher vibrational states by the collision; the calculation only requires that the correct molecular vibrational states be substituted into the radial integrals Q_1 and Q_2. However, only the even-numbered excited rotational states are allowed when the initial state is the ground state. This is a result of the presence of the integral of three Legendre polynomials in Eq. (49). The restriction to even-numbered rotational states is a consequence of the fact that the diatomic molecule is taken to be homonuclear and therefore only even terms appear in the Legendre-polynomial expansion of the potential. The second term in the potential leads to the Legendre polynomial of order 2 in the integral of Eq. (49). This integral is nonzero only for even values of L', i.e., only even-numbered excited rotational states.

Cross sections will be calculated in this work for four different final states of the molecule: the ground state (elastic scattering), the first allowed excited rotational state in the ground vibrational state, the ground rotational state in the first excited vibrational state, and the first rotational state allowed by the collision in the first excited vibrational state. Cross sections for higher-order states may be calculated in a similar manner.

In order to calculate the radial integrals Q_1 and Q_2 in the square of the matrix element, it is necessary to know the form of the vibrational wave functions $F_v(r_B)$ for the target molecule. There are several approximations for the diatomic molecule which may be used to obtain these eigenfunctions. For example, the molecule may be represented by a Morse oscillator[22] or a harmonic oscillator.[23] In the interest of having the vibrational wave functions as simple as possible, the harmonic-oscillator approximation was used in this work. If the separation of the two atoms is r_B, then the potential energy of such an oscillator is given by

$$E_{\text{pot}} = k(r_B - r_0)^2 \tag{50}$$

TABLE II. Comparison of potentials for various R, r_B, and θ values. Interaction-potential-energy values from SSMK are in the column V_{SSMK} and corresponding energies computed from the analytical form of the potential are those under V.

R (a.u.)	r_B (a.u.)	θ (deg)	V_{SSMK} (hartree)	V (hartree)
2.6475	1.765	0.0000	0.017 517	0.016 880
2.7195	1.679	0.0000	0.017 230	0.017 504
2.7650	1.640	0.0000	0.016 798	0.017 368
2.8245	1.609	0.0000	0.016 231	0.016 763
2.8960	1.582	0.0000	0.015 491	0.015 864
2.9775	1.559	0.0000	0.014 584	0.014 761
3.0695	1.539	0.0000	0.013 495	0.013 505
3.1750	1.522	0.0000	0.012 268	0.012 098
3.3065	1.507	0.0000	0.010 792	0.010 439
3.4405	1.493	0.0000	0.009 304	0.008 913
3.5785	1.481	0.0000	0.007 876	0.007 502
3.7190	1.470	0.0000	0.006 554	0.006 238
3.9205	1.457	0.0000	0.004 954	0.004 710
4.1295	1.445	0.0000	0.003 609	0.003 466
4.3555	1.435	0.0000	0.002 505	0.002 465
4.5855	1.427	0.0000	0.001 680	0.001 770
4.8595	1.419	0.0000	0.001 010	0.001 290
5.0370	1.412	0.0000	0.000 791	0.001 155
2.5849	1.777	20.104	0.020 122	0.019 901
2.6804	1.667	21.056	0.019 464	0.020 061
2.7979	1.605	21.755	0.018 093	0.018 524
2.9138	1.571	22.254	0.016 578	0.016 707
3.0650	1.542	22.775	0.014 556	0.014 380
3.2068	1.518	23.204	0.012 544	0.012 364
3.3400	1.503	23.541	0.010 838	0.010 624
3.5016	1.489	23.898	0.008 937	0.008 735
3.6488	1.476	24.196	0.007 369	0.007 226
4.1475	1.443	25.010	0.003 510	0.003 496
4.6378	1.423	25.601	0.001 520	0.001 602
5.1306	1.412	26.055	0.000 582	0.000 917
5.6432	1.407	26.426	0.000 169	0.000 862
3.1001	1.560	22.773	0.014 630	0.013 763
2.3931	1.809	40.892	0.029 043	0.029 272
2.4771	1.716	42.543	0.028 279	0.028 382
2.5910	1.650	43.991	0.026 230	0.026 048
2.7074	1.609	45.086	0.023 796	0.023 515
2.8448	1.578	46.100	0.020 964	0.020 683
2.9953	1.549	47.058	0.017 785	0.017 769
3.1424	1.525	47.868	0.014 882	0.015 151
3.2650	1.514	48.415	0.012 888	0.013 259
3.4268	1.496	49.102	0.010 374	0.010 919
3.8848	1.457	50.652	0.005 290	0.005 775
4.3590	1.434	51.808	0.002 464	0.002 576
4.8578	1.419	52.731	0.001 012	0.000 920
5.4164	1.408	53.535	0.000 326	0.000 319
2.8844	1.600	46.100	0.021 050	0.020 226
5.3842	1.400	53.533	0.000 340	0.000 237

and the eigenfunctions are given by

$$F_v(r_B)=N_v H_v[\alpha(r_B-r_0)]\,e^{-\alpha^2(r_B-r_0)^2/2}, \tag{51}$$

where N_v is the normalization factor, the $H_v[\alpha(r_B-r_0)]$ are Hermite polynomials of order v,

$$\alpha=(2\mu k/\hbar^2)^{1/4}, \tag{52}$$

and the reduced mass of the molecule is

$$\mu=m/2, \tag{53}$$

where m is the mass of one atom.

The radial wave functions for the diatomic molecule are thus given by Eq. (51) with normalization factors

$$N_0=\left(\frac{r_0e^{-\alpha^2r_0^2}}{2\alpha^2}+\frac{\sqrt{\pi}}{4\alpha^3}(2\alpha^2r_0^2+1)\times[1-\operatorname{erf}(-\alpha r_0)]\right)^{-1/2} \tag{54}$$

and

$$N_1=\left(\frac{r_0e^{-\alpha^2r_0^2}}{\alpha^2}+\frac{\sqrt{\pi}}{\alpha^3}(\alpha^2r_0^2+1.5)\times[1-\operatorname{erf}(-\alpha r_0)]\right)^{-1/2}, \tag{55}$$

where

$$\operatorname{erf}(z)=\frac{2}{\sqrt{\pi}}\int_0^z e^{-t^2}\,dt\,. \tag{56}$$

The quantized vibrational energy levels of the harmonic oscillator are[24]

$$E_v=(v+\tfrac{1}{2})h\nu, \tag{57}$$

where ν is the frequency of oscillation given by

$$\nu=\frac{1}{2\pi}\left(\frac{2k}{\mu}\right)^{1/2}. \tag{58}$$

The zero-point energy of the oscillator is $\frac{1}{2}h\nu$.

The rotational energy levels for the molecule rotating about its center of mass are

$$E_L=L(L+1)\hbar^2/2\mathcal{I}, \tag{59}$$

where $\mathcal{I}$ is the moment of inertia for the molecule.

In elastic scattering there is no transfer of energy to the internal states of the molecule, and both the initial and final vibrational and rotational states of the molecule are the ground state. The quantum numbers do not change during the collision, so $L'=L=0$ and $v'=v=0$. Then the differential cross section is given by

$$\frac{d\sigma_{00,00}}{d\Omega}=\left(\frac{\mathfrak{M}_{AB}}{2\pi\hbar^2}\right)^2|Q_1|^2, \tag{60}$$

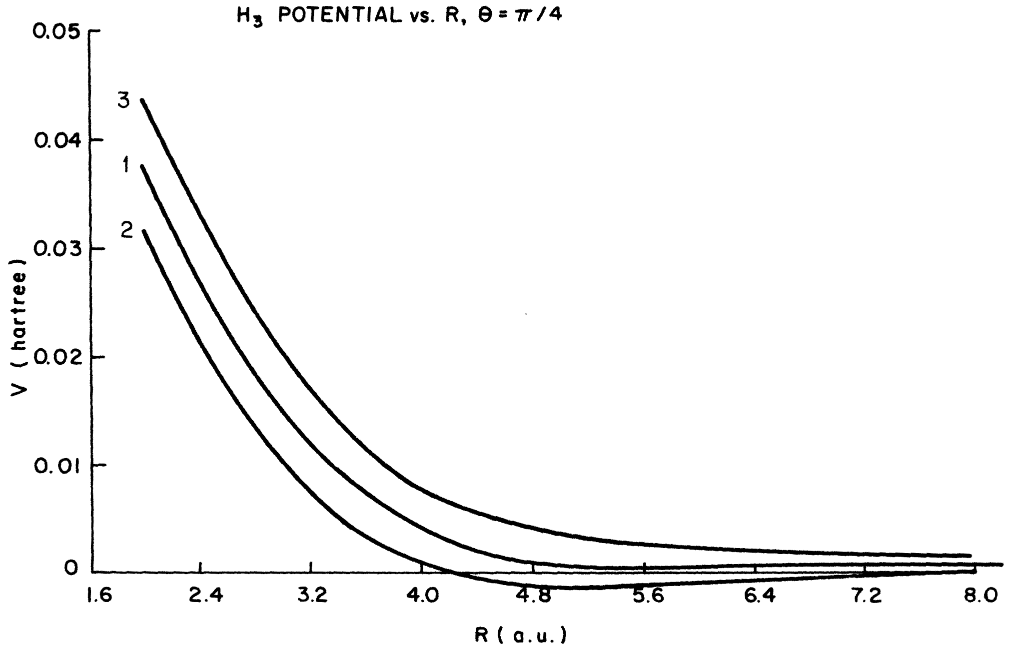

FIG. 2. Potential for the H_3 system as a function of R, the distance between the atom and the center of mass of the molecule, for $\theta=\frac{1}{4}\pi$ rad and $r_B=r_0$. Curve 1 is the best fit to the SSMK calculation. Curves 2 and 3 result when a_2 is increased and decreased, respectively, by 10% from the best-fit value.

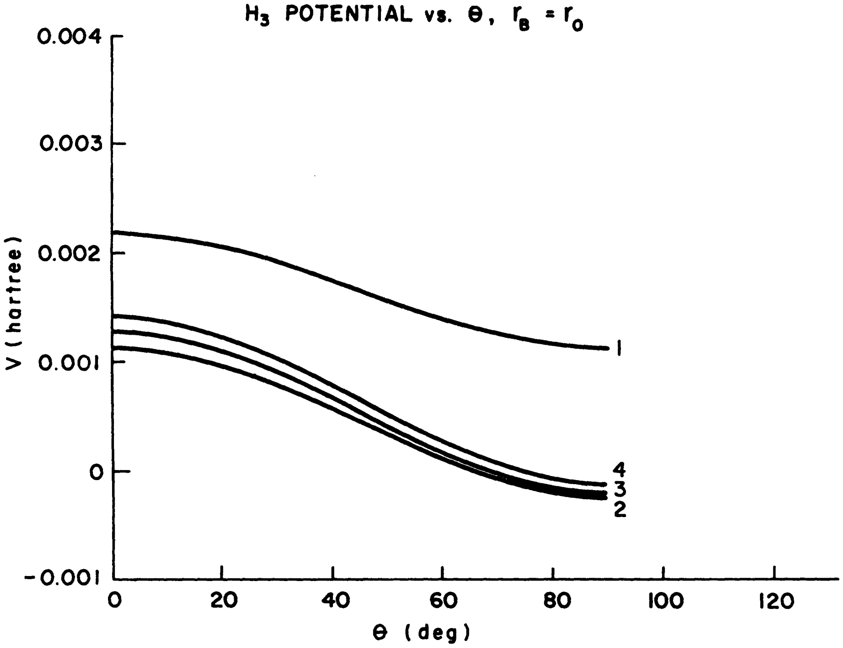

FIG. 3. Potential for the H_3 system as a function of θ for $r_B = r_0$. Curve 1 for $R = 4.5$ a.u.; curve 2 for $R = 5.5$ a.u.; curve 3 for $R = 6.0$ a.u.; and curve 4 for $R = 6.5$ a.u.

where

$$Q_1 = \int_0^\infty F_0(r_B)^* \mathfrak{U}_0(r_B) F_0(r_B) r_B^2 \, dr_B \tag{61}$$

and

$$\mathfrak{U}_0(r_B) = \frac{4\pi}{K}\left\{\frac{2a_1a_2K}{(a_2^2+K^2)^2} + \frac{a_3\pi}{6a_4^4}\left[2e^{-Ka_4/2}\cos\left(\frac{Ka_4\sqrt{3}}{2} + \frac{\pi}{3}\right) - e^{-Ka_4}\right]\right\}. \tag{62}$$

$\mathfrak{U}_0(r_B)$ may be written

$$\mathfrak{U}_0(r_B) = c_1 + c_2(r_B - r_0) + c_3(r_B - r_0)^2, \tag{63}$$

where the c_i are given by

$$c_i = \frac{8\pi a_{1i} a_2}{(a_2^2+K^2)^2} + \frac{2\pi^2 a_{3i}}{3Ka_4^4}\left[2e^{-Ka_4/2}\cos\left(\frac{Ka_4\sqrt{3}}{2} + \frac{\pi}{3}\right) - e^{-Ka_4}\right], \quad i = 1, 2, 3. \tag{64}$$

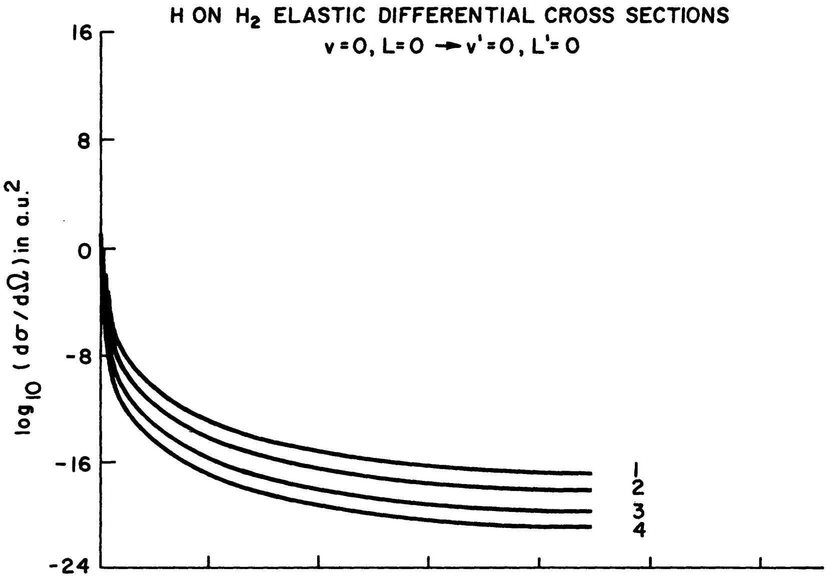

FIG. 4. H on H_2 elastic differential cross sections as a function of θ. Curve 1 for an incident energy of 1 keV; curve 2 for 2 keV; curve 3 for 5 keV; and curve 4 for 10 keV.

The radial integration may be carried out using integration by parts so that Q_1 becomes

$$Q_1 = N_0^2\left[c_1\left(\frac{r_0 e^{-\alpha^2 r_0^2}}{2\alpha^2} + \frac{\sqrt{\pi}}{4\alpha^3}\,(2\alpha^2 r_0^2 + 1)[1 - \operatorname{erf}(-\alpha r_0)]\right) + c_2\left(\frac{e^{-\alpha^2 r_0^2}}{2\alpha^4} + \frac{r_0\sqrt{\pi}}{2\alpha^3}[1 - \operatorname{erf}(-\alpha r_0)]\right)\right.$$
$$\left. + c_3\left(\frac{r_0 e^{-\alpha^2 r_0^2}}{4\alpha^4} + \frac{\sqrt{\pi}}{4\alpha^5}\,(\alpha^2 r_0^2 + 1.5)[1 - \operatorname{erf}(-\alpha r_0)]\right)\right]. \tag{65}$$

Inelastic scattering was considered when the final state of the molecule was the first excited rotational state allowed by the collision in the ground vibrational state. (The initial state is here always assumed to be the ground state. In applications where this is not the case, the only change occurs in the integral of three Legendre polynomials. These are tabulated so that only a small amount of additional work is required once the distribution of rotational states is known.) The quantum numbers are $v' = v = 0$, $L' = 2$, $L = 0$; and the differential cross section is given by

$$\frac{d\sigma_{02,00}}{d\Omega} = \left(\frac{\mathfrak{M}_{AB}}{2\pi\hbar^2}\right)^2 \frac{1}{5}|Q_2|^2, \tag{66}$$

where

$$Q_2 = \int_0^\infty F_0(r_B)^* \mathcal{U}_2(r_B) F_0(r_B) r_B^2\, dr_B \tag{67}$$

and

$$\mathcal{U}_2 = c_4 + c_5(r_B - r_0) + c_6(r_B - r_0)^2. \tag{68}$$

Here the c_i are given by

$$c_{i+3} = \frac{8\pi a_{5i} a_6}{(a_6^2 + K^2)^2} + \frac{12\pi a_{5i} a_6}{K^2(a_6^2 + K^2)} - \frac{12\pi a_{5i}}{K^3}\tan^{-1}\left(\frac{K}{a_6}\right) + \frac{2a_{7i}\pi^2}{3Ka_8^4}\left[2e^{-Ka_8/2}\cos\left(\frac{Ka_8\sqrt{3}}{2} + \frac{\pi}{3}\right) - e^{-Ka_8}\right]$$
$$+ \frac{2a_{7i}\pi^2}{K^2 a_8^5}\left[2e^{-Ka_8/2}\cos\left(\frac{Ka_8\sqrt{3}}{2} - \frac{\pi}{3}\right) + e^{-Ka_8}\right] - \frac{2a_{7i}\pi^2}{K^3 a_8^6}\left[2e^{-Ka_8/2}\cos\left(\frac{Ka_8\sqrt{3}}{2}\right) + e^{-Ka_8} - 3\right], \quad i = 1, 2, 3 \tag{69}$$

so that

$$Q_2 = N_0^2\left[c_4\left(\frac{r_0 e^{-\alpha^2 r_0^2}}{2\alpha^2} + \frac{\sqrt{\pi}}{4\alpha^3}\,(2\alpha^2 r_0^2 + 1)[1 - \operatorname{erf}(-\alpha r_0)]\right) + c_5\left(\frac{e^{-\alpha^2 r_0^2}}{2\alpha^4} + \frac{r_0\sqrt{\pi}}{2\alpha^3}[1 - \operatorname{erf}(-\alpha r_0)]\right)\right.$$
$$\left. + c_6\left(\frac{r_0 e^{-\alpha^2 r_0^2}}{4\alpha^4} + \frac{\sqrt{\pi}}{4\alpha^5}\,(\alpha^2 r_0^2 + 1.5)[1 - \operatorname{erf}(-\alpha r_0)]\right)\right]. \tag{70}$$

Inelastic scattering was also considered when the final state was the ground rotational state in the first excited vibrational state. The quantum numbers are then $v' = 1$, $v = 0$, $L' = L = 0$; the differential cross section is

$$\frac{d\sigma_{10,00}}{d\Omega} = \left(\frac{\mathfrak{M}_{AB}}{2\pi\hbar^2}\right)^2 \frac{K_F}{K_I}|Q_1|^2, \tag{71}$$

where now

$$Q_1 = \int_0^\infty F_0(r_B)^* \mathcal{U}_0(r_B) F_1(r_B) r_B^2\, dr_B. \tag{72}$$

The c_i are the same as those given in Eq. (64) for elastic scattering. Integrating by parts results in

$$Q_1 = 2\alpha N_0 N_1\left[c_1\left(\frac{e^{-\alpha^2 r_0^2}}{2\alpha^4} + \frac{r_0\sqrt{\pi}}{2\alpha^3}[1 - \operatorname{erf}(-\alpha r_0)]\right) + c_2\left(\frac{r_0 e^{-\alpha^2 r_0^2}}{4\alpha^4} + \frac{\sqrt{\pi}}{4\alpha^5}\,(\alpha^2 {r_0}^2 + 1.5)[1 - \operatorname{erf}(-\alpha r_0)]\right)\right.$$
$$\left. + c_3\left(\frac{e^{-\alpha^2 r_0^2}}{\alpha^6} + \frac{3r_0\sqrt{\pi}}{4\alpha^5}[1 - \operatorname{erf}(-\alpha r_0)]\right)\right]. \tag{73}$$

The third case of inelastic scattering treated was for the final molecular state to be the first excited rotational state allowed by the collision in the first excited vibrational state. The quantum numbers are correspondingly $v' = 1$, $v = 0$, $L' = 2$, $L = 0$; the differential cross section is

$$\frac{d\sigma_{12,00}}{d\Omega} = \left(\frac{\mathfrak{M}_{AB}}{2\pi\hbar^2}\right)^2 \left(\frac{K_F}{K_I}\right)\frac{1}{5}|Q_2|^2, \tag{74}$$

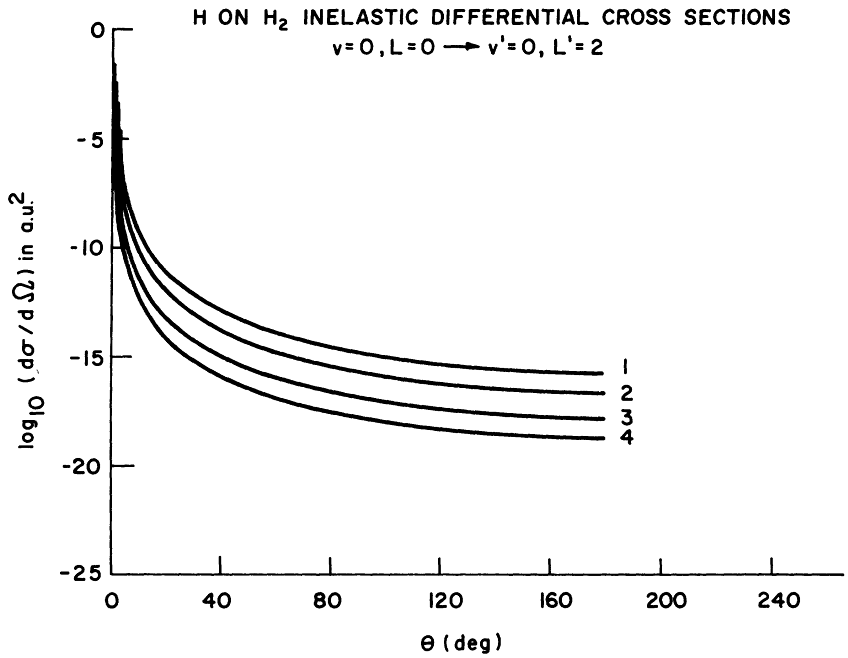

FIG. 5. H on H_2 inelastic differential cross sections as a function of θ. The final state of the H_2 molecule is the first excited rotational state allowed by the collision in the ground vibrational state. Curve 1 for an incident energy of 1 keV; curve 2 for 2 keV; curve 3 for 5 keV; and curve 4 for 10 keV.

where now

$$Q_2=\int_0^\infty F_0(r_B)^*\mathfrak{U}_2(r_B)\,F_1(r_B)r_B^2\,dr_B\,. \tag{75}$$

Again integrating by parts to obtain Q_2,

$$\begin{aligned}Q_2=2\alpha N_0N_1\Bigg[c_4\left(\frac{e^{-\alpha^2r_0^2}}{2\alpha^4}+\frac{r_0\sqrt{\pi}}{2\alpha^3}\left[1-\mathrm{erf}(-\alpha r_0)\right]\right)\\+c_5\left(\frac{r_0e^{-\alpha^2r_0^2}}{4\alpha^4}+\frac{\sqrt{\pi}}{4\alpha^5}(\alpha^2r_0^2+1.5)\right.\\\left.\times\left[1-\mathrm{erf}(-\alpha r_0)\right]\right)\\+c_6\left(\frac{e^{-\alpha^2r_0^2}}{\alpha^6}+\frac{3r_0\sqrt{\pi}}{4\alpha^5}\left[1-\mathrm{erf}(-\alpha r_0)\right]\right)\Bigg]\,.\end{aligned} \tag{76}$$

Here, the c_ξ are those given in Eq. (69).

V. TOTAL CROSS SECTIONS

The total cross sections for the collision of an atom with a homonuclear diatomic molecule are given by Eqs. (24) and (25). The integration over the angle θ is from 0 to π rad; the integration over the momentum K is from the minimum value to the maximum value. These momenta minima and maxima will be numerically different for each of the collision cases. In all cases, however, as K increases the integrand becomes vanishingly small when K is much less than the maximum value.

For elastic scattering, the minimum momentum transferred is obviously zero for the collision in which the incoming particle is forward scattered and undeviated from its original path. The maximum momentum is transferred for backscattering: After the collision the incident particle travels back in the opposite direction along its original trajectory with equal and opposite momentum. The maximum momentum transferred is thus twice the incident momentum K_I.

For each inelastic case, the minimum momentum transferred is that which corresponds to the energy used to raise the target molecule into that particular excited state. Energies above the ground state of the molecule are given by Eqs. (57) and (59). The minimum values for K can be obtained from these energies since

$$K_{\min}=\hbar^{-1}(2\mathfrak{M}_{AB}E_{v\,L})^{1/2}\,. \tag{77}$$

The maximum momentum transferred for each inelastic case again occurs for backscattering. The incident atom recoils back along the original path but with a momentum less than the incident momentum by the amount corresponding to the energy which was used to excite the target molecule. Thus the final momentum is

$$K_F=K_I-K_{\min}\,, \tag{78}$$

so that for inelastic scattering

$$K_{\max}=2K_I-K_{\min}\,. \tag{79}$$

Total cross sections may then be calculated by numerical integration of Eq. (24) or (25).

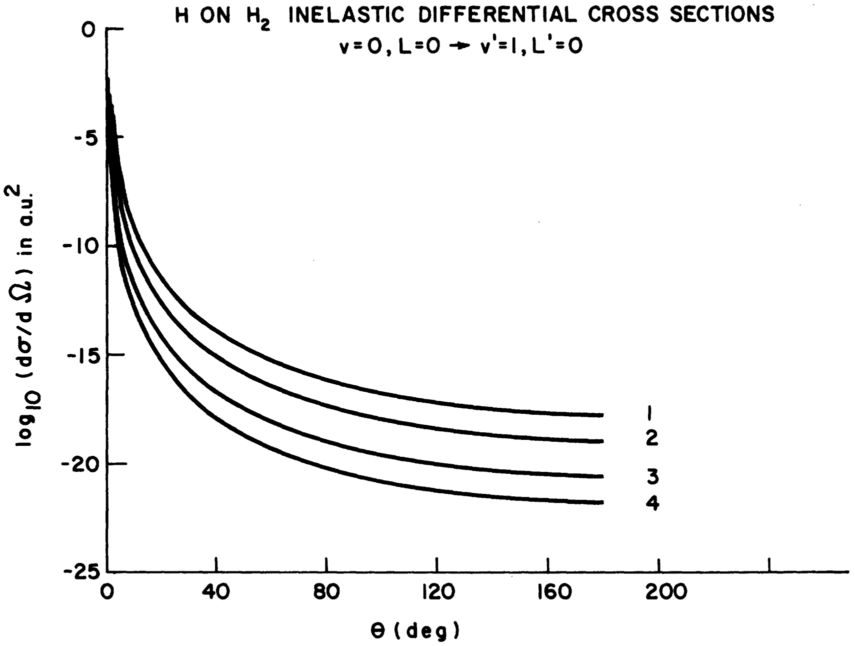

FIG. 6. H on H_2 inelastic differential cross sections as a function of θ. The final state of the H_2 molecule is the ground rotational state in the first excited vibrational state. Curve 1 for an incident energy of 1 keV; curve 2 for 2 keV; curve 3 for 5 keV; and curve 4 for 10 keV.

VI. APPLICATION TO HYDROGEN

For hydrogen-atom–hydrogen-molecule scattering, the interaction potential for three hydrogen atoms is needed. The calculation of such a potential energy surface has a long history as it is the simplest atom-molecule system which may be studied.[3-19] The potential form required here to calculate vibrational and rotational excitation has dependences on r_B, the internuclear separation in the molecule; R, the distance between the atom and the center of mass of the molecule; and θ, the angle between R and r_B. The paper by SSMK[19] was found to be the most useful in obtaining numerical values for the coefficients a_i in the analytical form of the potential.[25] A nonlinear least-squares fitting program[26] was used on a PDP-10 time-sharing computer to obtain the coefficients. The equilibrium separation of the hydrogen molecule is that given by SSMK, i.e.,

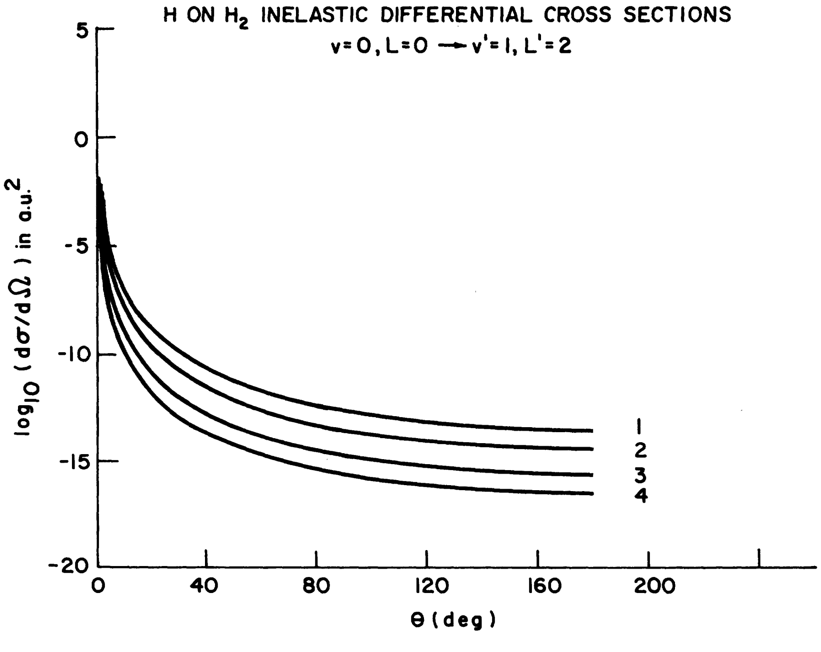

FIG. 7. H on H_2 inelastic differential cross sections as a function of θ. The final state of the H_2 molecule is the first excited rotational state allowed by the collision in the first excited vibrational state. Curve 1 for an incident energy of 1 keV; curve 2 for 2 keV; curve 3 for 5 keV; and curve 4 for 10 keV.

$r_0 = 1.4018$ a.u. The numerical values of the coefficients which reproduce the SSMK surface the most accurately are given in Table I.

Values of the interaction energy computed from the analytical expression for the potential are compared with the data of SSMK in Table II for various R, r_B, and θ values. This table contains the data points from Tables VIII and IX of the SSMK paper. (The variables of SSMK are not the same as those used in this paper; however, the entries in Table II are the same points as in SSMK Tables VIII and IX, expressed in the present notation.) The values given in the column labeled V_{SSMK} were obtained from the total-energy data given in SSMK by subtracting the rest energy of the H atom and the energy of the H_2 molecule for that particular internuclear separation, leaving only the interaction energy of the system. The interaction energies in the column labeled V were computed from the Legendre polynomial expansion of the potential for the given R, r_B, and θ values.

The H_3 potential as a function of the distance between the atom and the center of mass of the molecule which best fits the SSMK values is given as curve 1 in Fig. 2, with the H_2 interatomic separation at the equilibrium value r_0, and the angle between R and r_B fixed at $\frac{1}{4}\pi$ rad. The van der Waals minimum occurs when R is 5.500 a.u. and the well depth is about 0.0024 hartree. It rises slightly after this minimum and then approaches zero as the distance between the atom and molecule increases. The energy in this region represents an extrapolation from the SSMK values, which are themselves unreliable at 5 a.u. Therefore no particular significance should be attached to the particular behavior shown. Indeed, the minimum would be expected to have a negative value, corresponding to attractive polarization forces. Curves 2 and 3 in Fig. 2 show the potentials which result when a_2 is, increased and decreased, respectively, by 10% from the values which best fit the SSMK calculations. This illustrates that the analytic potential form given by Eqs. (26)–(28) is adequate to represent the true potential. It also illustrates how experimental scattering data good enough to fix a_2 to within 10% could provide an experimental test for calculated energy surfaces.

Figures 2 and 3 show only the interaction-potential energy. The total energy of the system is, of course, equal to the sum of this energy plus the energies of an isolated hydrogen atom and an isolated hydrogen molecule at equilibrium separation. Figure 3 shows the potential as a function of the angle when r_B is held at the equilibrium separation r_0. The four curves on this graph were plotted with four different values of the separation R near the van der Waals minimum. Curve 2 has the minimum energy, and the van der Waals minimum occurs for this value of R, as shown in Fig. 2. It may also be seen from Fig. 3 that the minimum energy configuration with r_B at the equilibrium separation is the arrangement when the atom is on the perpendicular bisector of the molecule, i.e., when $\theta = \frac{1}{2}\pi$ rad.

It should be noted that these figures have been

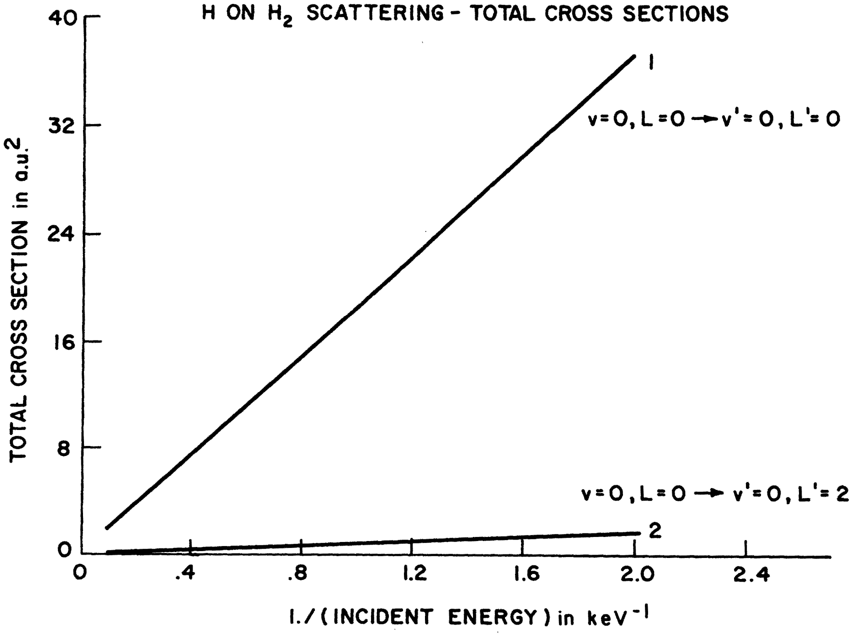

FIG. 8. H on H_2 total cross sections as a function of the inverse of the energy of the incident particle. Curve 1 for elastic scattering and curve 2 for inelastic scattering, where the final state of the H_2 molecule is the first excited rotational state allowed by the collision in the ground vibrational state.

plotted using the analytical form of the potential computed with the coefficients of Table I. These coefficients were obtained by a least-squares fit to the data of SSMK. These data were somewhat limited in scope, and a more accurate representation of the potential could be obtained if, for example, interaction-potential energies were known for more internuclear separations of the three atoms and more orientations of the system. A possibly important source of error here, however, arises from the fit of the analytical form of the potential to the SSMK data. Increasing round-off error limited the accuracy such that the potential was fitted to within 10% accuracy for most, but not all, points (see Table II). Increased accuracy might be obtained by using additional Legendre polynomials in the expansion or with a completely different analytical form. The potential form chosen here is a relatively simple one which makes the integrals tractable in order to test the scattering calculation. As long as these limitations are kept in mind as well as those of the SSMK calculation itself, then this is a reasonable description of the H_3 interaction potential.

Elastic- and inelastic-scattering differential cross sections for hydrogen-atom–hydrogen-molecule scattering were computed. In order to obtain numerical values in the differential cross-section calculation, it is necessary to know the various parameters in the expressions for the c_i. The coefficients in the expression for the interaction potential of the system, the a_l, are given in Table I. The parameter α may be calculated using Eqs. (52) and (58). The vibration frequency of a hydrogen molecule was obtained from H_2 spectra by Stoicheff,[27] and α was computed to be 2.8670 a.u.$^{-1}$ using his results. The equilibrium separation of the atoms in the H_2 molecule is that given by SSMK. For these values of α and r_0, the exponential terms in the expressions for the differential cross sections are approximately zero, and the error functions are very close to -1. The elastic and inelastic differential cross sections may be computed from the corresponding equations. The results for hydrogen are shown in Figs. 4–7. Each figure contains curves for incident energies of 1, 2, 5, and 10 keV. The log of the elastic differential cross section drops off more rapidly as a function of angle than the logs of the inelastic differential cross sections, especially for the case where the molecule is both vibrationally and rotationally excited. The products of an elastic collision are scattered primarily in the forward direction, while those which are vibrationally and rotationally excited, though fewer in number, show a greater proportion at larger angles.

The minimum values of the momentum transfer K used in calculating the inelastic total cross sections were obtained from the vibrational and rotational energy levels for a hydrogen molecule. Several calculations and measurements have been made of the energies of these vibrational and

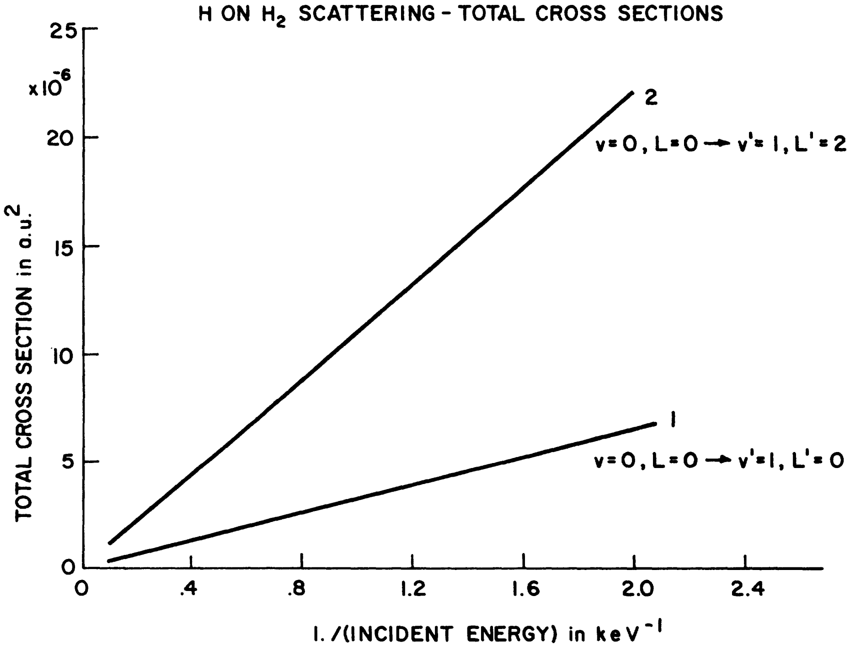

FIG. 9. H on H_2 total cross sections as a function of the inverse of the energy of the incident particle. Curve 1 for inelastic scattering where the final state of the H_2 molecule is the ground rotational state in the first excited vibrational state, and curve 2 when the final state of the molecule is the first excited rotational state allowed by the collision in the first excited vibrational state.

rotational states and are reported in the literature.[27,28] Evaluation of both forms of the expression for the total cross section, i.e., integration over θ as well as K, was carried out numerically on a PDP-10 computer; identical results were obtained. A Gaussian integration program[29] with up to 96 points of quadrature was used. Figure 8 shows the total cross section versus the inverse of the energy of the incident particle for elastic scattering and inelastic scattering, where the final state of the molecule is the first rotational state allowed by the collision in the ground vibrational state. Inelastic scattering when the final state of the molecule is the ground or the first excited rotational state in the first excited vibrational state is shown in Fig. 9. In both figures the graphs are straight lines, indicating that the total cross section is a function of the inverse of the incident energy, a result similar to that obtained by the Born approximation.

ACKNOWLEDGMENTS

Thanks are due to the Computing Center at the Louisiana State University in New Orleans for providing computer time and consultation.

---

*Present address: Physics Department, Xavier University, New Orleans, La. 70125.

†Taken in part from a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree at the University of Connecticut.

[1] A. Russek, Physica 48, 165 (1970).

[2] J. Schopman and J. Los, Physica 48, 190 (1970).

[3] F. O. Ellison, N. T. Huff, and J. C. Patel, J. Am. Chem. Soc. 85, 3544 (1963).

[4] E. F. Hayes and R. G. Parr, J. Chem. Phys. 47, 3961 (1967).

[5] L. Pedersen and R. N. Porter, J. Chem. Phys. 47, 4751 (1967).

[6] H. H. Michels and F. E. Harris, J. Chem. Phys. 48, 2371 (1968).

[7] M. E. Schwartz and L. J. Schaad, J. Chem. Phys. 48, 4709 (1968).

[8] C. Edmiston and M. Krauss, J. Chem. Phys. 49, 192 (1968).

[9] M. Salomon, J. Chem. Phys. 51, 2406 (1969).

[10] A. S. Cheung and D. J. Wilson, J. Chem. Phys. 51, 4733 (1969).

[11] H. Margenau, Phys. Rev. 64, 131 (1943); Phys. Rev. 66, 303 (1944).

[12] H. Conroy and B. L. Bruner, J. Chem. Phys. 47, 921 (1967).

[13] H. Eyring and M. Polanyi, Z. Phys. Chem. B 12, 279 (1931).

[14] K. Takayanagi, Proc. Phys. Soc. Lond. A 70, 348 (1957).

[15] A. Dalgarno, R. J. W. Henry, and C. S. Roberts, Proc. Phys. Soc. Lond. 88, 611 (1966).

[16] K. T. Tang, Phys. Rev. 187, 122 (1969).

[17] K. T. Tang and M. Karplus, J. Chem. Phys. 49, 1676 (1968).

[18] R. N. Porter and M. Karplus, J. Chem. Phys. 40, 1105 (1964).

[19] I. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, J. Chem. Phys. 48, 2700 (1968).

[20] L. I. Schiff, *Quantum Mechanics*, 2nd ed. (McGraw-Hill, New York, 1955), p. 196.

[21] S. Sato, J. Chem. Phys. 23, 592 (1955); J. Chem. Phys. 23, 2465 (1955).

[22] P. M. Morse, Phys. Rev. 34, 57 (1929).

[23] L. I. Schiff, Ref. 20, p. 60.

[24] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Vol. I, p. 16.

[25] R. P. Saxon and J. C. Light [J. Chem. Phys. 56, 3874, (1972); J. Chem. Phys. 56, 3885 (1972)] have recently used the SSMK results to obtain a potential for a reactive scattering calculation. The analytical form which they used was a linear potential times a rotation barrier with a Morse oscillator added for molecular vibration.

[26] James Clark (private communication).

[27] B. P. Stoicheff, Can. J. Phys. 35, 730 (1957).

[28] L. Wolniewicz, J. Chem. Phys. 45, 515 (1966); T. G. Waech and R. B. Bernstein, J. Chem. Phys. 46, 4905 (1967); J. P. Poll and G. Karl, Can. J. Phys. 44, 1467 (1966); D. F. Zetick and F. A. Matsen, J. Mol. Spectry. 24, 122 (1967); J. K. Cashion, J. Chem. Phys. 45, 1037 (1966); J. V. Foltz, D. H. Rank, and T. A. Wiggins, J. Mol. Spectry. 21, 203 (1966); G. Herzberg and L. L. Howe, Can. J. Phys. 37, 636 (1959); R. G. Parr and R. F. Borkman, J. Chem. Phys. 49, 1055 (1968); C. L. Beckel and J. P. Sattler, J. Mol. Spectry. 20, 153 (1966).

[29] G. E. Ioup, Ph.D. dissertation (University of Florida, 1968) (unpublished).