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Transition Probabilities and Differential Cross Sections for Vibrational Excitation in Collisions of H^+ with H_2, HD, and D_2†

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The angle and energy dependence of the differential cross sections are reported for resolved vibrational transitions in low-energy collisions of H^+ with H_2, HD, and D_2. The specific transition probabilities for the different isotopic molecules scale in the order $D_2 > HD > H_2$ at the same initial kinetic energy and scattering angle, but when compared at the same reduced kinetic energy, $E_r = E/\hbar\omega$, are approximately equal, suggesting that the interaction leading to vibrational excitation in this system is primarily the dilution of the molecular bond as the proton passes. We discuss the results in terms of a semiclassical model for vibrational excitation based on an oscillator driven by a time-dependent force.

INTRODUCTION

Until very recently, experimental investigations of translational-vibrational energy transfer in bimolecular collisions were confined to various relaxation techniques.[1] These methods have yielded valuable information on vibrational relaxation at thermal energies and even on the rate of vibrational relaxation as a function of vibrational state in the case of highly sophisticated laser-excited fluorescence experiments.[2] Because a thermal distribution of collision energies is present, however, detailed information on the translational energy dependence of the transition probability is not obtained by relaxation measurements and these methods are confined to the low-energy regime, where the transition probabilities are usually very small. For a more complete description of the process one would like to have information which is more microscopic, such as the cross section or differential cross section for vibrational energy transfer as a function of both kinetic energy and the internal quantum states of the colliding molecules initially and finally. In principle, molecular beam methods are uniquely suitable for such studies, however the practical constraints are considerable. Ideally, one should have a focusing vibrational state selector to allow selection of the primary beam vibrational state and direct determination of the scattered product state distribution. Inhomogeneous field selection for rotational states has been used with success, but there appears to be little hope of applying analogous methods to the selection of vibrational states.[3] The use of bolometers to measure vibrational energy has been suggested,[4] but this method is sensitive only to the average energy of a molecule and would require knowledge of the translational and rotational contributions. The laser-induced fluorescence method recently described by Zare *et al.*[5] may eventually permit direct observation of the final state distribution in products of both reactive and nonreactive collisions, but is now in a very early stage of development. In the absence of a detector specific for a given vibrational state, one can still determine the state of a product molecule from the translational energy defect of the collision Q, if sufficiently high translational energy resolution for both the primary and secondary beams is available and if the initial state is well defined. It is, of course, the difference in translational energies in center-of-mass (c.m.) coordinates, not laboratory (lab) coordinates which defines the change in internal energy, and the transformation between lab and c.m. energy is unique only if the lab angle of the scattered molecule as well as the lab energy is measured.

Recently several groups have undertaken the study of vibrational excitation in ion-neutral collisions by the energy-loss technique. The method is not limited to collisions involving ions, but the problems associated with velocity analyzing and detecting neutrals at translational energies where vibrational excitation probabilities are large seem to be more severe. The first studies of heavy particle collisions in which vibrational transitions were resolved were made by Moore and Doering.[6] Their apparatus has high-energy resolution but detects only those ions which are scattered very near 0°. These measurements have since been extended to a wide variety of systems,[7] including $H^+ + H_2$ at 100–1500 eV (lab).[8] By time-of-flight analysis, Held, Schöttler, and Toennies[9] succeeded in resolving the vibrational transitions in $Li^+ + H_2$ collisions for scattering near 180° c.m.

Early studies of the dependence of collision inelasticity on angle[10,11] showed that the total inelasticity in the systems studied increased with increasing scattering angle, but the resolution was not sufficient to distinguish between vibrational and rotational excitation or to identify the final vibrational states. The first measurements of the dependence of vibrational transition probabilities on scattering angle were reported by Cosby and Moran[12] for the system $O_2^+ + Ar$. Later, similar results[13] were presented for $CO^+ + Ar$. Since both of these studies involved molecular ions formed by electron bombardment with a distribution of vibrational and rotational states, it was not possible to identify unambiguously the initial and final states responsible for the observed energy-loss spectra.

In an earlier paper[14] we reported differential cross sections for resolved vibrational transitions in $H^+ + H_2$ collisions. Here we present further data on the energy and angle dependence of the transition probabilities in this system and on the isotope effect. Because the collisions involve a structureless ion and a low-temperature neutral molecule, the initial and final vibrational states are well defined. Although rotational transitions cannot be resolved with the present instrument, evidence is presented that rotational excitation is not important in this range of energy and scattering angle. The reported differential cross sections and transition probabilities may therefore be taken to be state-to-state quantities directly comparable to results of quantum-mechanical treatments of the vibrational-excitation problem.

Many quantum-mechanical calculations of vibrational excitation in linear triatomic systems have been reported, as well as several for three-dimensional systems.[15] However, none of these was done with a potential form suitable for the H_3^+ system. Here we confine our interpretation to a semiclassical model which provides a particularly simple description of the collisional excitation process.

EXPERIMENTAL

Apparatus

The apparatus used for this work was constructed from an instrument built earlier by Giese and Maier[16] and used for the measurement of total cross sections for ion-molecule reactions. The modifications have been so extensive, however, that the present instrument bears only a general morphological resemblance to the earlier one.

Ions are formed in an electron-bombardment source, focused into a magnetic analyzer which provides both mass and energy selection, then refocused into the collision cell. Product ions emerging from the cell are energy analyzed, accelerated into a magnetic mass spectrometer, and finally detected by an ion counter. Several instruments similar in principle but differing markedly in various design details have been built by others.[17]

The heart of the apparatus is shown in Fig. 1. The ion source is particularly simple yet it produces an ion beam of nearly space-charge-limited intensity at very low energies. The source gas flows through a 1.0-mm-i.d. stainless-steel tube positioned vertically above a horizontal tungsten mesh strip, which serves as both an extraction grid and filament. The mesh is heated by a dc current and is typically held at −120 V with respect to the tube. The emitted electrons are thus accelerated toward the tube orifice while the ions formed are accelerated away. A simple lens system consisting of a double-aperture lens followed by X-Y steering plates then focuses the beam into the primary analyzer. This is a 90° deflection 2.54-cm radius Permalloy magnet with a 3-mm gap. A lens similar to that described by Lindholm[18] follows the magnet. This lens can be used for either retarding or accelerating the beam between the analysis magnet and the collision cell, but in all the experiments described here the beam was analyzed at a low energy (typically 1.5 eV), then accelerated to the desired final energy in order to obtain the best possible resolution. The collision cell consists of a bronze block containing two superimposed chambers 1.5 mm high, 8 mm wide, and 5 mm deep. The ion beam enters the lower chamber through a 0.75-mm-diam hole. By means of a two-way valve located inside the vacuum system, the target gas can be admitted to either the lower or upper chamber. Corrections to the product-ion signal for events occurring outside the collision cell can then be made by subtracting the signal measured with gas in the upper (dummy) chamber from that measured with the target gas in the lower chamber under identical leak-rate conditions.

The electrostatic energy analyzer is a 4.75-cm-radius 45°-deflection cylindrical condenser. The object point is the center of the collision cell and no object aperture is used. A 0.75-mm-diam aperture in the analyzer end plate, 5.4 cm from the object point, defines the solid angle of acceptance. Ions exiting through the vertical 1.5-mm-wide slit at the image point of the analyzer are accelerated in a constant field gradient to 5000 eV for mass analysis in the product mass spectrometer. This is accomplished by floating the entire ion-source–collision-cell–energy analyzer system at +5000 V. A quadrupole doublet lens[19] is used to optimize ion transmission through the secondary mass spectrometer, which is a 30.5-cm-radius 60°-sector instrument.

The data reported here were obtained using an EMI-9603 particle multiplier for ion counting. This has since been superseded by a detector of the Daly type.[20] With the pulse-height discriminator level optimized, the new detector has an efficiency of about 70% for H_2^+ and a background counting rate of less than 0.1 counts/sec.

For experiments with low-energy ion beams it is essential that surface charge variations on the focusing elements be minimized. This is accomplished by spray coating all the metal surfaces close to the low-energy beam path with colloidal graphite.

The ion-source–collision-cell assembly rotates with respect to the energy analyzer and product mass spectrometer to permit measurement of the angular distribution of scattered ions. A range of −5° to +50° with respect to the primary ion beam is accessible.

The basic instrumental energy resolution, taken to be the convolution of the ion-beam energy distribution and the energy-analyzer transmission functions, was 1 to 2% full width at half-maximum (FWHM) of the ion energy in these experiments. The actual resolution obtained in a scattering experiment, however, also depends on the velocity distribution of the target gas. For this reason the collision cell was cooled with liquid nitrogen. Even so, the target velocity spread contributed about half of the total energy spread in the scattered ions. The laboratory angular resolution was about 1.5° FWHM.

With the exception of the large product mass spectrometer and detector, the experiment is housed in a 76×46-cm-diam glass bell jar pumped by an Edwards 15-cm mercury diffusion pump with Freon-cooled and liquid-nitrogen-cooled baffles. The flight tube of the product mass spectrometer is pumped by an Ultek 100-liter/sec ion pump. The operating pressure in the main chamber is about 2×10^{-6} Torr.

Technique

In almost any scattering experiment, data taken in the laboratory coordinate system must be transformed into c.m. coordinates for convenient interpretation. If the velocity vectors of particles in a binary collision are known before the collision and the velocity vector of one of the particles is measured afterward, the transformation is simple and unique. In general, the entire product velocity vector distribution function can be generated by a series of scans of product flux as a function of lab angle at constant lab speed or of lab speed at constant lab angle. These data can then be transformed to c.m. coordinates and plotted in the form of a contour map of the appropriate differential cross section.[21] In order to make it possible to determine profiles of the product distribution in c.m. coordinates without the necessity of first producing the entire product velocity distribution in lab coordinates, we have developed a technique for scanning simultaneously both the lab energy and lab angle in such a way as to keep either the c.m. angle or c.m. energy constant. Both the energy analyzer potential and the angle setting are governed by servomechanisms digitally controlled by a 20-character-block paper-tape reader through *D* to *R* converters. The paper tape which controls the experiment is generated using a shared-time computer system with a terminal in the laboratory. The input parameters are the reactant and product masses, the initial c.m. collision energy, the product c.m. energy and

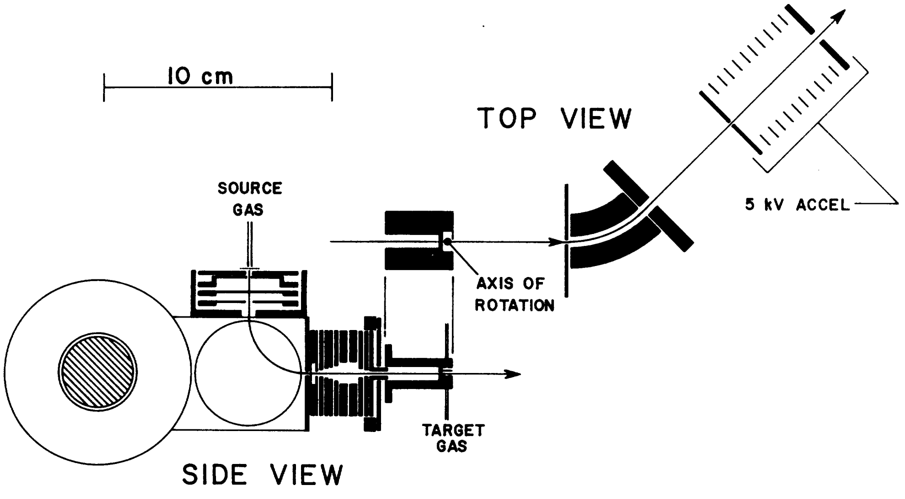

FIG. 1. Schematic diagram of the apparatus showing the ion-source–collision-cell assembly and the product energy analyzer. Apertures are not to scale.

angle ranges to be scanned, and the number of points to be taken. From this information the computer produces a tape with codes for the energy and angle in lab coordinates corresponding to each desired point in c.m. coordinates. The scan is timed and the data accumulated using a Nuclear Data model 110 pulse-height analyzer as a multiscaler. The accuracy of the energy settings obtained from the transformation was checked by observing the energy loss of H^+ scattered elastically from Ar and He and was found to be about 0.03 eV.

Reduction of Data

From an experiment in which vibrational states of the products are resolved, one wishes to know (a) what is the probability that molecules scattered into a given angle will be in quantum state ν, and (b) what is the angular distribution of those molecules scattered into final state ν. Thus the clearest way to present the data is in the form of the differential cross section I_ν for scattering of products into the element $d\Omega\, d\nu$, where $d\Omega = \sin\chi\, d\chi\, d\phi$ is the element of solid angle in c.m. coordinates. $I_\nu(\chi, \nu)$ can then be plotted as a function of χ for a specific ν or as a function of ν at constant χ.

In order to compensate for overlap of adjacent peaks in the energy spectra, we first converted the product flux into the relative differential cross section I for scattering into the element $d\Omega\, dE$ in c.m. coordinates by multiplying the measured signal by a factor proportional to the Jacobian

$$J = g/v^3, \tag{1}$$

where g is the relative speed of the products and v the laboratory speed of the detected ion. The data in this form were then fitted to a superposition of Gaussian functions by an iterative least-squares method. Taking the relative differential cross sections for the discrete transitions $(0 \rightarrow \nu)$ to be the areas of the resolved Gaussians, we then transformed these to I_ν, using the Jacobian

$$J_\nu = \frac{dE}{d\nu} \tag{2}$$

and data on the spacing of vibrational levels from Herzberg.[22] J_ν differs from a constant only because of the anharmonicity of the vibrational motion and in these calculations varied over a range of only 26%. Transition probabilities for a given scattering angle are defined as

$$P_\nu = I_\nu \Big/ \sum I_\nu . \tag{3}$$

RESULTS

Most of the data presented here were acquired in the form of energy distributions of the scattered protons measured at constant c.m. angle. These experiments ranged in energy from 4 to 21 eV and in angle from 6° to 36°. Figure 2 shows a set of typical energy profiles for the $H^+ + H_2$ system, in this case for a fixed c.m. scattering angle of 11° and for initial kinetic energies of 4–16 eV. Though the vibrational structure is visible in the data, overlap of adjacent peaks clearly requires unfolding of the distribution in order to obtain transition probabilities for

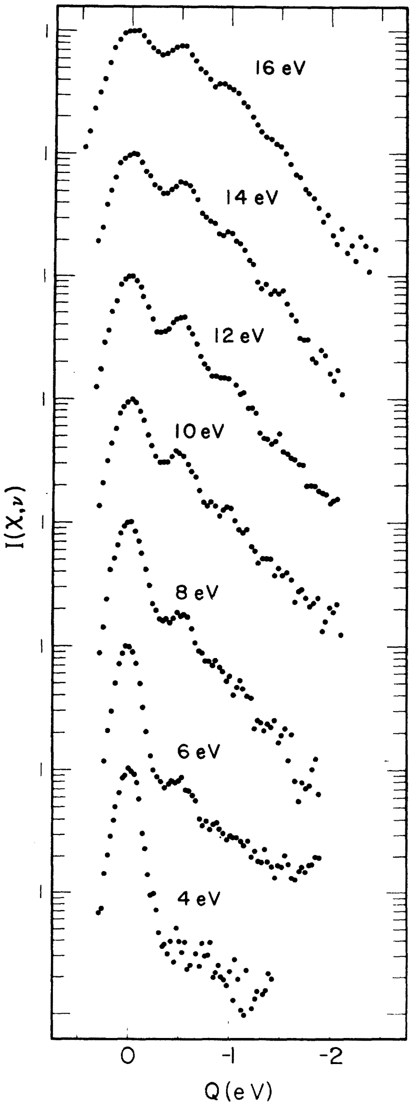

FIG. 2. Differential cross sections for scattering of H^+ from H_2 at a c.m. scattering angle of 11° and primary c.m. kinetic energies from 4 to 16 eV. Each curve is normalized to unity at the peak.

specific states. Transition probabilities obtained by fitting each of the measured energy distributions as described are given in Table I. As expected, the probability of vibrational excitation increases with increasing kinetic energy and with increasing scattering angle. An example of the angle dependence of the transition probabilities is given in Fig. 3.

In comparing results for the different hydrogen isotopes at the same energy and scattering angle, we find that the vibrational transition probabilities scale in the order $D_2 > HD > H_2$, or inversely as the order of the transition energies. If, however, the transition probabilities are weighted by the energies of the transitions, the isotopic differences largely disappear. Figure 4 shows the average energy transfer for $H^+ + H_2$, HD, and D_2 as a function of energy for $\chi = 11°$. The individual probabilities at fixed scattering angle for the three isotopic molecules also approximately coincide when compared at the same value of initial kinetic energy measured in units of the respective vibrational quanta. Figure 5 shows the transition probabilities as a function of this reduced energy $E_r = E/\hbar\omega$ for all three isotopes at $\chi = 11°$.

For the system $H^+ + H_2$ at 10-eV c.m. kinetic energy, we also measured the angular dependence of the differential cross section for scattering into the elastic and the first two vibrationally inelastic channels. These curves are shown in Fig. 6. At this energy good separation between adjacent peaks in the energy-loss spectrum is achieved and the excitation probability is sufficiently high to permit measurements over a wide range of angle for these three final states. The data were acquired by scanning the c.m. angle at fixed c.m. energies corresponding to each final state. After normalization and transformation of the measured intensities to yield I_ν, the differen-

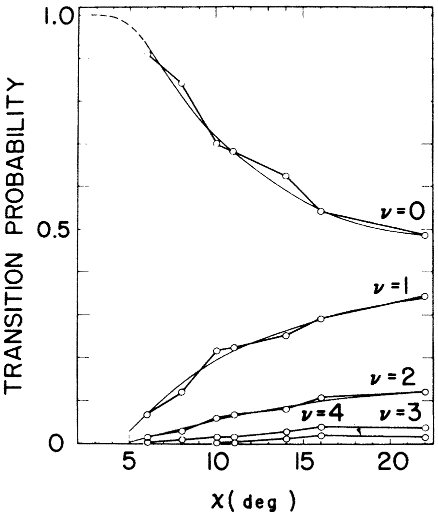

FIG. 3. Vibrational transition probabilities as a function of c.m. scattering angle for 10-eV $H^+ + H_2$ collisions.

TABLE I. Vibrational transition probabilities for collisions of H^+ with H_2, HD, and D_2 in their ground vibrational states.

		Final vibrational state					
E (eV)	χ (deg)	0	1	2	3	4	5
				H_2			
4	11	0.956	0.044	···	···	···	···
6	11	0.879	0.087	0.033	···	···	···
8	11	0.781	0.151	0.051	0.017	···	···
10	11	0.656	0.230	0.077	0.025	0.012	···
12	11	0.624	0.267	0.082	0.026	···	···
14	11	0.556	0.298	0.104	0.032	0.010	···
16	11	0.489	0.330	0.131	0.039	0.010	···
10	6	0.911	0.069	0.015	0.005	···	···
10	8	0.841	0.120	0.030	0.009	···	···
10	10	0.700	0.218	0.061	0.017	0.004	···
10	11	0.683	0.225	0.067	0.017	0.007	···
10	14	0.625	0.253	0.080	0.030	0.012	···
10	16	0.542	0.291	0.108	0.039	0.020	···
10	22	0.487	0.342	0.119	0.037	0.015	···
6	28	0.799	0.173	0.028	···	···	···
6	36	0.726	0.227	0.047	···	···	···
				HD			
9	11	0.745	0.206	0.049	···	···	···
10	11	0.696	0.218	0.066	0.020	···	···
12	11	0.586	0.259	0.112	0.044	···	···
15	11	0.512	0.297	0.139	0.053	···	···
18	11	0.418	0.346	0.162	0.058	0.017	···
21	11	0.327	0.353	0.219	0.066	0.034	···
10	22	0.412	0.345	0.191	0.052	···	···
				D_2			
4	11	0.950	0.050	···	···	···	···
6	11	0.849	0.114	0.036	···	···	···
10	11	0.550	0.275	0.108	0.044	0.016	0.008
4	12	0.934	0.066	···	···	···	···
10	22	0.253	0.323	0.230	0.118	0.048	0.028

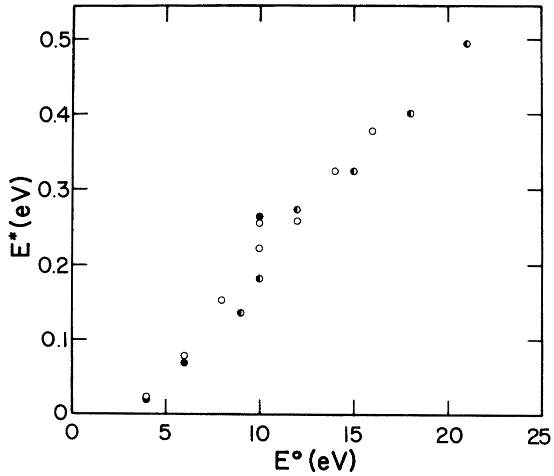

FIG. 4. Average vibrational energy transfer as a function of initial c.m. kinetic energy for $H^+ + H_2$ (○), HD (◑), and D_2 (●), and a c.m. scattering angle of 11°.

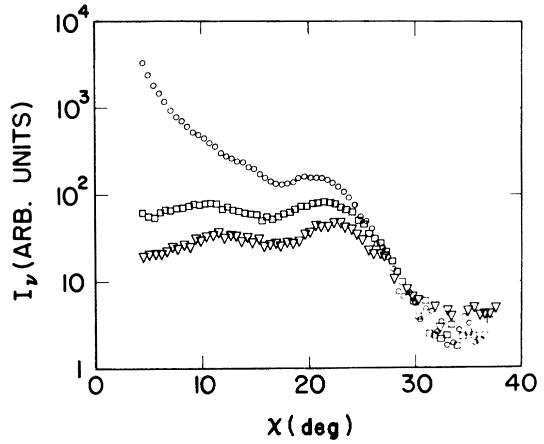

FIG. 6. Differential cross sections I_ν as a function of angle for 10-eV $H^+ + H_2$ and final H_2 vibrational states $\nu = 0$ (○), $\nu = 1$ (□), and $\nu = 2$ (▽).

tial cross sections were corrected for overlap of adjacent peaks by multiplying the cross section at each point by a correction function, forcing the relative differential cross-section ratios to coincide with the transition probabilities obtained from the fitted energy-loss spectra at constant angle. The corrections were small at large angles but were as large as a factor of 5 at the smallest angle of the experiment, where overlap of the $\nu = 0$ and $\nu = 1$ peaks were, respectively, major contributions to the measured intensities at energies corresponding to $\nu = 1$ and $\nu = 2$. The angle distributions reported in our previous paper[14] did not include this correction and therefore exaggerated the relative importance of vibrational excitation at small angles. Despite the influence of the inelastic channels and the anisotropy of the $H^+ + H_2$ potential,[23-25] the elastic differential cross section exhibits both a rainbow maximum and additional small-angle undulations due to quantum-mechanical interferences. The angular distribution at 6 eV (Fig. 7) shows no enhancement of these quantum undulations even though the probability of vibrational excitation at this energy is small. We thus attribute the small amplitude of the quantum undulations compared with those observed for proton scattering from spherically symmetric potentials[26] primarily to averaging of the interference structure over the orientation of the target molecules,[27] rather than to the influence of inelastic channels.

Since the effect of potential anisotropy on the elastic differential cross section is so apparent, one might also expect a high probability for rotational excitation. Because the measured energy lost from translation must include energy going into both rotational and vibrational degrees of freedom, rotational excitation will result in a shift of the peaks for the various final vibrational states to more negative values of Q than would be observed for pure vibrational transitions. In every experiment reported here the location of the peaks in the energy-loss spectra are consistent within experimental error with the assumption of no rotational excitation. Figure 8 illustrates this observation. Shown are the energy-loss spectra for $H^+ + H_2$, HD, and D_2 at 10-eV c.m. kinetic energy and $\chi = 22°$. The data and the individual and superimposed fitted functions are compared with the Q values expected for pure vibrational excitation and vibrational excitation accompanied by the lowest-energy rotational excitation possible

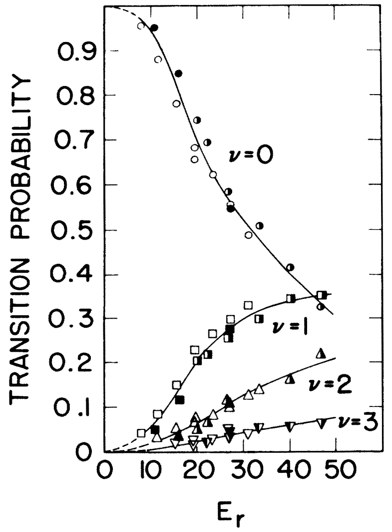

FIG. 5. Vibrational transition probabilities as a function of reduced energy $E/\hbar\omega$ for 10-eV $H^+ + H_2$ (○), HD (◑), and D_2 (●) collisions and a scattering angle of 11°.

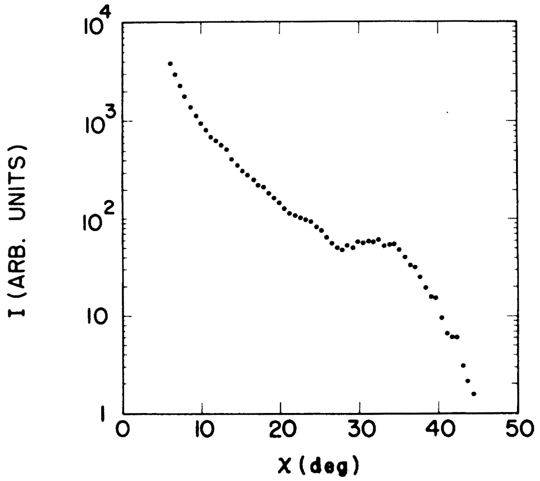

FIG. 7. Angle dependence of the vibrationally elastic differential cross section for 6-eV $H^+ + H_2$ collisions.

for the predominant symmetry state of the target molecule.

The energies of the expected rotational transitions are given in Table II. Only the HD ($J=0 \rightarrow J=1$) rotational transition requires too little energy for the shift to be observed experimentally if the transition occurs with high probability. Particularly in the case of H_2, moderate probabilities for rotational excitation should be detectable, since 75% of the target molecules are initially in the $J=1$ state and, if we assume the probability of nuclear spin flip to be negligible, must be excited to at least $J=3$, requiring 0.075 eV. For an energy of 10 eV and $\chi=22°$ the data place an upper limit on the probability of this process of about 20%.

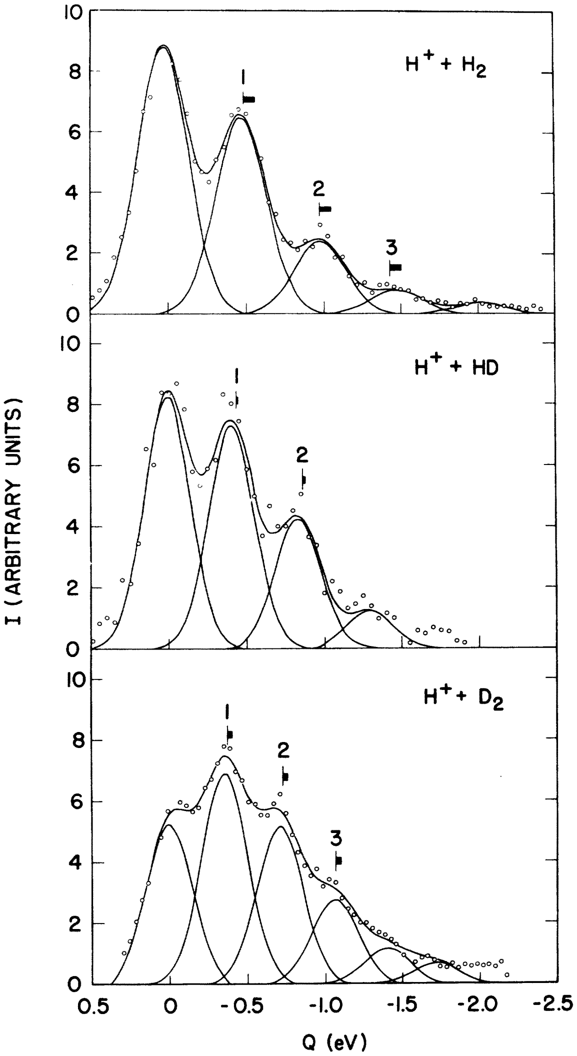

FIG. 8. Differential cross section I as a function of Q for 10-eV $H^+ + H_2$, HD, and D_2 collisions and a c.m. scattering angle of 22°. The solid lines are the individual and superimposed Gaussians obtained from the least-squares fit. The flags show the theoretical locations of those peaks whose location the computer was allowed to adjust, relative to the elastic peak ($Q=0$). The horizontal bars on the flags give the energy increment associated with the ($1 \rightarrow 3$) rotational transition of H_2, the ($0 \rightarrow 1$) transition of HD, and the ($0 \rightarrow 2$) transition of D_2.

Despite the higher transition energy the vibrational excitation probabilities for $H^+ + H_2$ collisions are much larger than those observed for $H^+ + N_2$ or $H^+ + CO$ when compared at the same initial relative kinetic energy and scattering angle.[28] The total cross section for vibrational excitation in the high-energy small-angle regime is also unusually high for $H^+ + H_2$.[8]

DISCUSSION

The gross features of many hydrogen-atom transfer reactions in this energy range have been interpreted using the stripping model,[29] in which the ion transfers momentum only to the atom which is abstracted. For this reason it is worthwhile giving passing consideration to a classical model for the vibrational energy transfer in which the ion collides with only one of the atoms of the molecule. Simple dynamical analysis[11] gives the energy transfer as a function of scattering angle and the masses of the three atoms. Because of conservation of momentum, the energy transfer is less effective as the difference between the masses of the colliding atoms becomes larger; hence the excitation of H_2 should be greater than that of D_2. This model is therefore ruled out on the basis of the observed isotope effect alone. It has also failed to predict the magnitude of the energy-loss dependence on kinetic energy for collisions of molecular ions with atomic neutrals.[11]

Vibrational energy transfer in collisions is a very old problem and one which has inspired a large number of theoretical papers.[15] Most of these report quantum-mechanical treatments and indeed, the scattering of a proton by a molecule at an energy of a few eV clearly requires quantum mechanics for a complete description. The angular distributions of scattered protons in Fig. 7, for example, show damped undulations due to

TABLE II. Rotational transition energies for H_2, HD, and D_2.

Transition ($J \rightarrow J'$)	Energy (eV) H_2	HD	D_2
$0 \rightarrow 1$	...	0.011	...
$0 \rightarrow 2$	0.045	0.068	0.030
$1 \rightarrow 3$	0.075	...	0.050

scattered wave interference. Even though steady progress has been made in formulation of the problem and in developing computational techniques, a complete three-dimensional quantum-mechanical treatment using a realistic potential appears at present to be difficult and extremely expensive. In the following discussion we therefore consider a semiclassical model.

The literature on vibrational excitation of a diatomic molecule by an atom has placed emphasis on the interaction between the projectile atom and the individual atoms of the molecule.[15] In the course of the collision the integrated response of each molecular atom is in general different, so the molecule becomes excited. It would appear that any treatment so formulated will fail to account for the unusual degree of vibrational excitation found for $H^+ + H_2$ in comparison with other systems or even the most gross feature of the observed isotope effect in this system, namely, that the total excitation energy in D_2 is about equal to that in H_2. Another important effect the collision can have, however, is the alteration of the electronic structure of the target molecule by the presence of a third atom. In this case vibrational excitation occurs because, as the third atom passes, the bond length of the molecule is changed and the nuclei are accelerated toward the new potential minimum.[30] This process will result in vibrational excitation unless the collision occurs over a time much longer than a vibrational period. In the rather large impact parameter $H^+ + H_2$ collisions of this study, the second feature of the interaction is probably much more important than the first.

Let us call the vector location of one of the H_2 nuclei with respect to the other $\vec{r}$, the vector between the proton and the H_2 c.m. $\vec{R}$, and the angle between these vectors θ. For the $H_3{}^+$ ground state, the equilibrium value of r for $\theta = 90°$ is 1.66 bohr and for $\theta = 0°$ is 1.54 bohr, compared with 1.40 bohr for H_2.[24] These large changes in equilibrium distance are unlikely to be matched by any molecule with more than two electrons. For example, the changes in molecular internuclear distances in N_2 and CO upon protonation are probably only 1–2%, depending on the geometry.[31] This implies that the stretching force applied to the molecule in the field of the proton is much smaller for N_2 and CO than for H_2, accounting for the large difference in excitation probability.

The very low degree of rotational excitation compared to vibrational excitation suggests that the potential energy in the region of coordinate space explored by these experiments is not a strong function of θ. Let us therefore consider the interaction to be composed of two parts—a force acting along $\vec{R}$, which determines the angular deflection, and a force acting along $\vec{r}$, which is responsible for vibrational excitation. This picture of the interaction lends itself well to semiclassical treatment, since the high-energy translational motion can be calculated classically while the low-energy vibrational motion is evaluated quantum mechanically. The formalism for a similar semiclassical model which also includes a description of rotational excitation was developed by Wartell and Cross.[32] Ritchie[33] performed a semiclassical calculation of vibrational excitation for $H^+ + H_2$ at higher energies, making the additional assumption that the potential governing the two-body trajectories is independent of the vibrational coordinate. For kinetic energies sufficiently high that the total interaction time is much shorter than a vibrational period, this approximation is expected to be good, while at lower energies the vibrational motion of the diatomic may alter the intermolecular potential substantially during the collision, requiring a calculation of the classical trajectory using the full potential hypersurface.

At the energies and scattering angles of these experiments classical mechanics is expected to provide a reasonably accurate description of the translational motion,[34] which can be obtained by integrating the three atom classical equations of motion in three spatial dimensions. At each instant along the trajectory the diatomic potential energy V, as a function of the vibrational coordinate x, is given by the cut through the potential energy hypersurface at fixed R and θ. $V(x,t)$ then defines the diatomic vibrational eigenfunctions at every point in the trajectory. Evaluation of the transition probabilities between asymptotic vibrational states would in general require solution of the Schrödinger equation for an oscillator having a different time-dependent anharmonic potential for each set of initial conditions. A rather simple solution is obtained, however, for a harmonic oscillator in which the original potential is perturbed only slightly by the collision. In this case, the potential can be written as the sum of the harmonic-oscillator potential and a time-dependent perturbation $U(x,t)$:

$$V(x,t) = \tfrac{1}{2}kx^2 + U(x,t). \qquad (4)$$

Expanding $U(x,t)$ in a Taylor series around $x = 0$ and neglecting second-order and higher terms gives

$$V(x,t) = \tfrac{1}{2}kx^2 + U(0,t) + xF(t), \qquad (5)$$

where $F(t)$ is the force applied externally to the oscillator as a result of the interaction and is given by the gradient of U at $x=0$. The potential V which is thus obtained differs from the unperturbed harmonic-oscillator potential only in having its minimum shifted. The force constant remains unchanged. For this special case of the force-driven harmonic oscillator there exists a well-known correspondence between the classical and quantum-mechanical equations of motion.[35] Solving the time-dependent Schrödinger equation gives for P_ν, the probability of excitation from the ground state to state ν, a Poisson distribution[36]:

$$P_\nu = e^{-\epsilon}\epsilon^\nu/\nu!\,, \tag{6}$$

where ϵ is obtained by dividing $\mathcal{E}$, the energy transferred classically to the same harmonic oscillator driven by the same force $F(t)$, by the quantum vibrational energy-level spacing $\hbar\omega$. The average energy transferred quantum mechanically, $\hbar\omega\sum\nu P_\nu$, is exactly $\mathcal{E}$, and the classical energy transfer to a force-driven harmonic oscillator initally at rest is simply[37]

$$\mathcal{E}=(1/2\mu)\left|\int_{-\infty}^{\infty}F(t)e^{-i\omega t}\,dt\right|^2. \tag{7}$$

Thus in the approximation of the collisional excitation process in terms of a harmonic oscillator driven by a force independent of x, the semiclassical solution is given exactly by a classical calculation. There is, however, reason to question the validity of a perturbation potential linear in x for the $H^+ + H_2$ system. In particular, electron exchange between the proton and the H_2 molecule can be expected to decrease the force constant for vibration,[30] necessitating the inclusion of higher-order terms in x. Fortunately, the difference in the classical and quantum-mechanical average excitation energies due to higher-order terms in the perturbation potential has been shown by Treanor to be small[38]; therefore the classical calculation can still be expected to be a good approximation to the quantum-mechanical one.

Pending a calculation of ϵ from the classical trajectories, we have normalized our data by dividing P_ν by P_0, the probability for no excitation, and have plotted this ratio versus $-\ln P_0$ in Fig. 9. The curves are calculated from Eq. (6) with no adjustable parameters and the data points correspond to the complete set of transition probabilities given in Table I. The good agreement between the theoretical and experimental relative transition probabilities suggests that classical three-dimensional trajectory calculations of the vibrational excitation are likely to be successful. These calculations are under way and will be reported later. Early results indicate that the excitation energy is roughly correct, the classical rainbow angles are close to those observed,[39] and the rotational excitation is very small, in agreement with our experimental results.

Whether the collision is viewed classically or quantum mechanically it is clear that our experiments are more sensitive to certain regions of the potential energy hypersurface than other regions. For the collisions involved here, the interaction time is typically less than half of an H_2 vibrational period. Therefore the force between the H_2 nuclei will usually be repulsive throughout the duration of the interaction with the proton. Because of the rapid falloff of the differential cross section at angles beyond the rainbow maximum, all of the energy scans in this study were made at c.m. angles smaller than or approximately equal to the rainbow angle. In terms of a cut through the hypersurface corresponding to fixed r and θ, the experiments are therefore most sensitive to the attractive branch of the potential as a function of R. The charge-induced dipole contribution to the potential is primarily responsible for the long-range attraction between the H^+ and H_2 and, because the polarizability of the H_2 molecule is an increasing function of r,[23] it also contributes to the repulsion between the H_2 nuclei.

The ground-state H_3^+ hypersurface has been accurately calculated for more than 200 points,[24] making this system one of the best cases for detailed comparison of theory and experiment. An

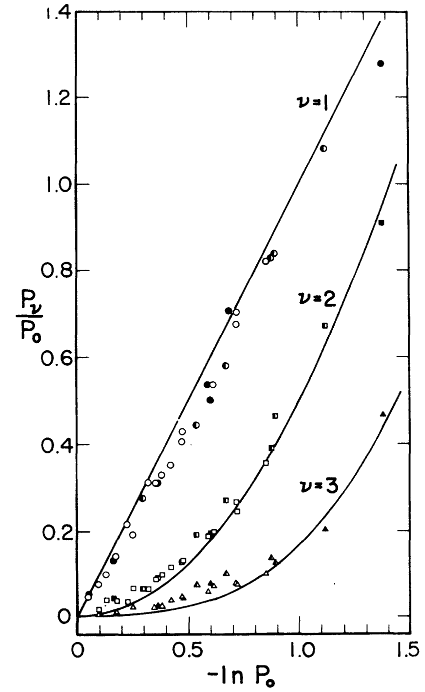

FIG. 9. P_ν/P_0 vs $-\ln P_0$ for the complete set of experimental transition probabilities given in Table I. The solid lines are the theoretical ratios determined from Eq. (6).

important complication, however, is that a second electronic surface must, in general, also be considered.[25] The higher-energy surface corresponds at large R to the electronic configuration $H_2^+ + H$, having an energy 1.835 eV above $H^+ + H_2$. The two diabatic singlet surfaces have a seam of crossing which is avoided for the adiabatic surfaces. Preston and Tully[25] have calculated the diabatic coupling terms and have concluded that the probability of transitions between the two surfaces is negligible outside regions of coordinate space localized at the seam of avoided crossing. The only seam of interest for low-energy collisions is located at $r \sim 2.5$ bohr. This seam is evidently reached in many reactive collisions at energies above threshold for the formation of H_2^+, as evidenced by the fact that the cross section for this channel is comparable to the cross section for the thermoneutral channel.[40] In order to reach the crossing seam the H_2 internuclear distance must be stretched far beyond its minimum energy value, leading Preston and Tully to surmise that electronic transitions occur principally while the reaction products are receding. For the peripheral nonreactive collisions involved in these vibrational excitation experiments, however, the H_2 molecule, even if it is excited to a high enough vibrational level ($\nu = 4$) to reach the crossing seam, in general does not have sufficient time to reach the required separation during the collision. Therefore we believe that the vibrational excitation process can be accurately described using only the adiabatic potential surface for the ground electronic state.

Some features of the data obviously require additional theoretical framework for adequate interpretation. The quenching of the rainbow structure and quantum undulations in the elastic differential cross section for anisotropic potentials is understood qualitatively,[41] but the presence of inelastic channels complicates the problem substantially. Considering the peripheral nature of the trajectories leading to vibrational excitation in this system it is perhaps not too surprising that a rainbowlike structure is observed in the angle dependence of the differential cross sections for the inelastic channels as well as for the elastic channel. The maximum shifts to larger scattering angles for increasing product vibrational quantum number. Truhlar[42] has estimated the shift semiclassically, obtaining values close to the experimental ones. Qualitatively, if it is assumed that the (spherical) scattering potential is not a function of the vibrational quantum number of the molecule, then the effect of vibrational excitation on the trajectory of the proton is to remove translational energy equal to the vibrational quantum. The rainbow angle is inversely dependent on energy and therefore shifts to a larger value. The smaller angle structure in the inelastic differential cross sections is not understood at present. It may, of course, be due to simple quantum-mechanical interference between partial waves corresponding to the two negative branches of the classical inelastic deflection function. The period of the undulations, more than twice that of the undulations in the elastic differential cross section, is puzzling. Presumably the trajectory calculations in progress will answer the question as to whether this structure is classical, like the rainbow maximum, or quantum mechanical.

SUMMARY

Differential cross sections have been measured for the scattering of protons from H_2, HD, and D_2 at c.m. energies between 4 and 21 eV and at c.m. angles between 6° and 36°. Scans of proton energy loss at a fixed c.m. scattering angle show resolved vibrational excitation peaks while rotational excitation appears to be improbable. The vibrational structure has been unfolded to give specific quantum transition probabilities. At the same initial energy and scattering angle the transition probabilities for the different isotopes increase with decreasing transition energy, but the *average* energy transfer at a given collision energy and scattering angle seems to be approximately independent of the isotopic composition of the molecule. Angular distributions have been measured for resolved elastic and vibrationally inelastic scattering in this system. The distributions show rainbow maxima and severely damped quantum undulations.

The high probability of vibrational excitation and the isotope effects are probably inconsistent with any model of vibrational excitation that involves only the interactions between the proton and the individual atoms of the molecule. Instead, the dominant mode of excitation appears to be the perturbation of the electronic structure of the molecule by the proton, which results in a force tending to stretch the molecule.

The system studied here is particularly simple from a theoretical point of view, involving the collision of a structureless particle with a molecule in a well-defined quantum state, $(\nu = 0, J = 0)$ or $(\nu = 0, J = 1)$, interacting via an accurately known potential, and leading to scattering at a specific angle into a resolved vibrational state with the rotational state of the molecule probably unchanged. The measured transition probabilities can be expected to provide an unusually direct and meaningful test for theories of vibrational excitation.

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[1] G. M. Burnett and A. M. North, *Transfer and Storage of Energy by Molecules* (Interscience, London, 1969), Vol. 2.

[2] R. B. Kurzel, E. O. Degenkold, and J. I. Steinfeld, J. Chem. Phys. 56, 1784 (1972), and references cited therein.

[3] H. Pauly and J. P. Toennies, *Advances in Atomic and Molecular Physics* (Academic, New York, 1965), Vol. 1, p. 251.

[4] G. A. Fisk (private communication).

[5] A. Schultz, H. W. Cruse, and R. N. Zare, J. Chem. Phys. 57, 1354 (1972); J. L. Gole and R. N. Zare, J. Chem. Phys. 57, 5331 (1972).

[6] J. H. Moore, Jr. and J. P. Doering, Phys. Rev. Lett. 23, 584 (1969).

[7] J. H. Moore, Jr. and J. P. Doering, Phys. Rev. 182, 176 (1969); J. Chem. Phys. 52, 1692 (1970).

[8] F. A. Herrero and J. P. Doering, Phys. Rev. A 5, 702, (1972).

[9] W. D. Held, J. Schöttler, and J. P. Toennies, Chem. Phys. Lett. 6, 304 (1970).

[10] W. R. Gentry, E. A. Gislason, B. H. Mahan, and C. W. Tsao, J. Chem. Phys. 47, 1856 (1967).

[11] M. H. Cheng, M. H. Chiang, E. A. Gislason, B. H. Mahan, C. W. Tsao, and A. S. Werner, J. Chem. Phys. 52, 6150 (1970).

[12] P. C. Cosby and T. F. Moran, J. Chem. Phys. 52, 6157 (1970).

[13] F. Petty and T. F. Moran, Phys. Rev. A 5, 266 (1972).

[14] H. Udseth, C. F. Giese, and W. R. Gentry, J. Chem. Phys. 54, 3642 (1971).

[15] For a review of early work, see K. Takayanagi, Prog. Theor. Phys. Suppl. 25, 1 (1963); later work is reviewed by D. Rapp and T. Kassal, Chem. Rev. 69, 61 (1969). A brief review of recent work is given by D. J. Wilson and D. J. Locker [J. Chem. Phys. 57, 5393 (1972)]. A very extensive list of references on molecular excitation has been collected by R. A. LaBudde and R. B. Bernstein [J. Chem. Phys. 55, 5499 (1971)].

[16] C. F. Giese and W. B. Maier, II, J. Chem. Phys. 39, 739 (1963).

[17] W. R. Gentry, E. A. Gislason, B. H. Mahan, and C. W. Tsao, J. Chem. Phys. 49, 3058 (1968); R. L. Champion, L. D. Doverspike, and T. L. Bailey, J. Chem. Phys. 45, 4377 (1966); Z. Herman, J. Kerstetter, T. Rose, and R. W. Wolfgang, Discuss. Faraday Soc. 44, 123 (1967); C. R. Iden, R. Liardon, and W. S. Koski, J. Chem. Phys. 56, 851 (1972).

[18] E. Gustafsson and E. Lindholm, Ark. Fys. 18, 219 (1960); H. von Koch and E. Lindholm, Ark. Fys. 19, 123 (1961).

[19] C. F. Giese, Rev. Sci. Instrum. 30, 260 (1959).

[20] N. R. Daly, Rev. Sci. Instrum. 31, 264 (1960).

[21] R. W. Wolfgang and R. J. Cross, Jr., J. Phys. Chem. 73, 743 (1969).

[22] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, London, 1950), p. 532.

[23] W. Kolos and L. Wolniewicz, J. Chem. Phys. 46, 1426 (1967).

[24] I. G. Csizmadia, R. E. Kari, J. C. Polanyi, A. C. Roach, and M. A. Robb, J. Chem. Phys. 52, 6205 (1970), also J. C. Polanyi (private communication).

[25] R. K. Preston and J. C. Tully, J. Chem. Phys. 54, 4297 (1971).

[26] R. L. Champion, L. D. Doverspike, W. G. Rich, and S. M. Bobbio, Phys. Rev. A 2, 2327 (1970).

[27] H. Udseth, C. F. Giese, and W. R. Gentry, in *Proceedings of the Seventh International Conference on the Physics of Electronic and Atomic Collisions*, Amsterdam, 1971, edited by L. M. Branscomb *et al.* (North-Holland, Amsterdam, 1972), p. 264.

[28] H. Udseth, C. F. Giese, and W. R. Gentry, in *Proceedings of the Eighth International Conference on the Physics of Electronic and Atomic Collisions*, Belgrade, 1973, edited by B. C. Čobić and M. V. Kurepa (Institute of Physics, Beograd, 1973), p. 93.

[29] A. Henglein, Adv. Chem. Ser. 58, 63 (1966).

[30] J. Korobkin and Z. I. Slawsky, J. Chem. Phys. 37, 226 (1962), have made a similar suggestion.

[31] H. B. Jansen and P. Ros, Theor. Chim. Acta 21, 199 (1971).

[32] M. A. Wartell and R. J. Cross, J. Chem. Phys. 55, 4983 (1971).

[33] Burke Ritchie, Phys. Rev. A 6, 1902 (1972).

[34] A criterion for the validity of a classical description of particle motion is that the potential change over a distance equal to the wavelength of the particle be small. This criterion is well satisfied for the translational motion in this experiment. The criterion is $d(\lambdabar)/dx \ll 1$; $\lambdabar = \hbar/P$ or $dV/dx \ll P^3/\mu\hbar$. For $H^+ + H_2$ at 10 eV c.m., $P^3/\mu\hbar = 621$ eV/Bohr and $dV/dx \sim 2$ eV/Bohr. A somewhat more restrictive criterion for the validity of a classically defined impact parameter and scattering angle χ is $\chi b/\lambdabar \gg 1$. For the experiments here $\chi b/\lambdabar \sim 20$.

[35] Donald Rapp, J. Chem. Phys. 40, 2813 (1964).

[36] M. S. Bartlett and J. E. Moyal, Proc. Camb. Philos. Soc. 45, 545 (1949), a calculation in momentum space. E. Kerner [Can. J. Phys. 36, 371 (1958)], obtained the same result in configuration space.

[37] L. D. Landau and E. M. Lifshitz, *Mechanics*, 2nd ed., (Pergamon, New York, 1969).

[38] C. S. Treanor, J. Chem. Phys. 43, 532 (1965).

[39] A discussion of the relationship between the classical rainbow angle and the quantum angular distribution may be found in H. Pauly and J. P. Toennies, *Advances in Atomic and Molecular Physics* (Academic, New York, 1965), Vol. I, p. 281.

[40] J. Krenos and R. Wolfgang, J. Chem. Phys. 52, 5961 (1970); M. G. Holliday, J. T. Muckerman, and L. Friedman, J. Chem. Phys. 54, 1058 (1971).

[41] R. E. Olson and R. B. Bernstein, J. Chem. Phys. 49, 162 (1968); R. J. Cross, J. Chem. 49, 1976 (1968); W. H. Miller, J. Chem. Phys. 50, 3124 (1969); R. F. Cross, J. Chem. Phys. 52, 5703 (1970).

[42] D. G. Truhlar, J. Chem. Phys. 58, 3109 (1973).