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Quantum-Mechanical State-to-State Differential Cross Sections for the Reaction $F + H_2 \rightarrow H + HF$

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This communication presents the first nonperturbative quantum-mechanical calculation for state-resolved angular differential cross sections for a chemical rearrangement for which experimental results are available. The reaction studied, $F + H_2 \rightarrow H + HF$, is an important prototype for understanding reaction dynamics and is one of the few for which comparisons of experiment and theory are possible. The significant features of the state-to-state angular distributions for this reaction observed experimentally are reproduced by this study.

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In this communication we report quantum-mechanical calculations of state-resolved angular differential cross sections for the reaction[1]

$$F + H_2(v_i = 0, j_i = 0) \rightarrow HF(v_f = 0, 1, 2, 3) + H. \quad (1)$$
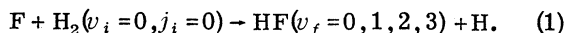
The final products are resolved so far as the final vibrational state of the HF is concerned but are degeneracy averaged and summed over final rotational states. This system is of great importance because Sparks et al.[2] have recently reported the first experimental determination of such state-resolved angular distributions for a reactive molecular collision. The system is of further importance for its role in the (F_2, H_2)

laser system and the fact that it represents one of the main prototype reactions for studying energy disposal in reactive collisions. The calculations were performed by using the so-called Muckerman-V potential surface,[3] and as will be seen, they yield results which agree with the experiments of Sparks et al.[2] These results represent the first successful computation of such phase-sensitive cross sections which can be compared with experiment.

The physical content of the approximation we employ is based on the recognition that some nuclear motion degrees of freedom in molecular collisions are slower than others. As a conse-

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quence, one can approximately solve for the faster motions as a parametric function of the slow degrees of freedom. One thereby obtains at some stage of the calculation an amplitude describing the transition from one state to another which is diagonal in the coordinate representation of the slow variables. The physical amplitudes are then obtained by a suitable transformation from the coordinate representation for the slow variables to an appropriate quantum number representation. These ideas have, of course, been used in the Born-Oppenheimer theory of electronic structure.[4] In addition, Chase's adiabatic approximation[5] in nuclear physics uses this idea for treating target rotational states. In the last few years, it was shown that for inelastic (nonreactive) atom-molecule collisions, not only the target rotation but also the orbital rotation of the projectile could be treated in this way,[6] but the details are somewhat more complicated and subtle.[5b] The combined approximation to the target rotation and projectile orbital rotation is referred to as the in-

finite-order sudden approximation (IOS).[5b,7] The present calculations have been carried out with the recently developed reactive infinite-order sudden approximation (RIOS) as formulated by Khare, Kouri, and Baer.[8,9] The IOS has been frequently applied within the context of nonreactive (inelastic) collisions where it has been found to yield good results for many systems.[10,11]

The Khare-Kouri-Baer formulation of the RIOS follows the "exact" close-coupling procedure developed by Kupperman, Schatz, and Baer[12] for reactive scattering. The approach employs the l-labeling method for treating the orbital angular momentum portion of the IOS.[8,10,11,13] The RIOS consists of computing S-matrix elements for fixed values of the angle γ_α defined by

$$\cos\gamma_\alpha = \vec{R}_\alpha \cdot \vec{r}_\alpha, \tag{2}$$

where the vector $\vec{R}_\alpha$ is from the center of mass of the diatom to the atom in arrangement α and $\vec{r}_\alpha$ is the diatom internuclear vector in arrangement α. The equation solved in each arrangement channel is[8]

$$\left[-\frac{\hbar^2}{2\mu}\left\{\frac{1}{R_\alpha^2}\frac{\partial}{\partial R_\alpha}\left(R_\alpha^2\frac{\partial}{\partial R_\alpha}\right)+\frac{1}{r_\alpha^2}\frac{\partial}{\partial r_\alpha}\left(r_\alpha^2\frac{\partial}{\partial r_\alpha}\right)-\frac{\overline{l}_\alpha(\overline{l}_\alpha+1)}{R_\alpha^2}-\frac{\overline{j}_\alpha(\overline{j}_\alpha+1)}{r_\alpha^2}\right\}\right.$$
$$\left.+V(R_\alpha,r_\alpha,\gamma_\alpha)-E\right]\psi_\alpha = 0; \quad \alpha=\lambda,\nu. \tag{3}$$

In this equation, R_α and r_α are mass-scaled coordinates and the symmetric mass μ is given by[12]

$$\mu = \left(\frac{M_\lambda M_\nu M_\kappa}{M_\lambda+M_\nu+M_\kappa}\right)^{1/2}; \tag{4}$$

the M_α, $\alpha=\lambda,\nu,\kappa$, are the masses of the three atoms in the system. Here λ and ν are the initial and final arrangement labels, and $\overline{l}_\alpha$ and $\overline{j}_\alpha$ are the IOS orbital and rotor "effective quantum numbers.[8,10,11]" For the present study, $\overline{j}_\lambda$ and $\overline{j}_\nu$ are taken to be equal to zero and $\overline{l}_\lambda$ and $\overline{l}_\nu$ are chosen in such a way as to ensure that the proper asymptotic orbital angular momentum boundary conditions are correctly satisfied. The calculations produce a primitive S matrix which depends on the internal angle γ_λ and orbital angular momentum $\overline{l}$. The explicit expression used for the differential scattering cross section is

$$\frac{d\sigma}{d\omega}(v_\lambda,j_\lambda=0,m_\lambda=0|v_\nu) = \sum_{m_\nu j_\nu}|f(v_\nu j_\nu m_\nu|v_\lambda,0,0|\theta\Psi)|^2, \tag{5}$$

where the state-to-state helicity scattering amplitude is

$$f(v_\nu j_\nu m_\nu|v_\lambda j_\lambda m_\lambda|\theta\Psi) = \frac{i^{j_\lambda-j_\lambda+1}}{2k_{v_\lambda j_\lambda}}\sum_J(2J+1)d_{m_\lambda m_\nu}{}^J(\theta)S^J(v_\nu j_\nu m_\nu|v_\lambda j_\lambda m_\lambda). \tag{6}$$

The angle θ is that between the final and initial relative linear momenta. Here ω is the solid angle, v_α, j_α, and m_α are, respectively, the vibrational, rotational, and p-helicity quantum numbers in arrangement α, $d_{m_\lambda m_\nu}{}^J(\theta)$ is the Wigner rotation matrix,[14] and $S^J(v_\nu j_\nu m_\nu|v_\lambda j_\lambda m_\lambda)$ is the scattering matrix in the helicity representation. It is related to the Arthurs-Dalgarno S matrix by[15]

$$S^J(v_\nu j_\nu m_\nu|v_\lambda j_\lambda m_\lambda) = \sum_{l_\nu l_\lambda} i^{l_\lambda-l_\nu}\left(\frac{[l_\lambda][l_\nu]}{[J]^2}\right)^{1/2}\langle l_\lambda 0 j_\lambda m_\lambda|Jm_\lambda\rangle\langle l_\nu 0 j_\nu m_\nu|Jm_\nu\rangle S^J(v_\nu j_\nu l_\nu|v_\lambda j_\lambda l_\lambda), \tag{7}$$

where $[x]$ stands for $2x + 1$. The $S^J(v_\nu j_\nu l_\nu | v_\lambda j_\lambda l_\lambda)$ are given in terms of the primitive fixed-γ_λ S matrix by

$$S^J(v_\nu j_\nu l_\nu | v_\lambda j_\lambda l_\lambda) = i^{l_\lambda + l_\nu - 2\bar{l}} \sum_{\Omega_\lambda \Omega_\nu} \frac{([l_\lambda][l_\nu])^{1/2}}{[J]} \langle l_\lambda 0 j_\lambda \Omega_\lambda | J\Omega_\lambda \rangle \langle l_\nu 0 j_\nu \Omega_\nu | J\Omega_\nu \rangle (-)^{j_\nu - \Omega_\nu}$$

$$\times 2\pi \int_0^1 y_{j_\nu \Omega_\nu}{}^*(\gamma_\nu(\gamma_\lambda), 0) d_{\Omega_\nu \Omega_\lambda}{}^J(\Delta(\gamma_\lambda)) S_{\bar{l}\nu_\lambda}{}^{v\nu}(\gamma_\lambda) y_{j_\lambda \Omega_\lambda}(\gamma_\lambda, 0) d(\cos\gamma_\lambda). \tag{8}$$

The numerical value of $\bar{l}$ chosen for a particular l_λ, l_ν matrix element is equal to $(l_\lambda + l_\nu)/2$. [This is the average-l labeling choice of $\bar{l}$.[11]] The angle $\Delta(\gamma_\lambda)$ is the angle between $\vec{R}_\lambda$ and $\vec{R}_\nu$, the scattering vectors in arrangements λ and ν. In the above expression, γ_ν and Δ are uniquely determined, once γ_λ is given, by a matching surface which separates the λ and ν arrangements.[8,12,16] We now turn to discuss the computational results for the $F + H_2$ system.

In Figs. 1-4 we give the state-to-state angular reactive differential cross sections (degeneracy averaged over m_λ, and summed over m_ν and j_ν but resolved with respect to final vibrational state v_ν). In each figure, we give the cross sections into the $v_f = 1$, 2, and 3 vibrational states for a given total energy. These energies correspond to translational energies $E_k = 0.073$ eV (1.68 kcal/ mole); 0.093 eV (2.14 kcal/mole); 0.156 eV (3.54 kcal/mole); and 0.233 eV (5.37 kcal/mole). The results are all scaled to equal 1 at $\theta = \pi$, and they display the following features: (a) The differential cross section for the $v_f = 3$ product is backwards peaked at $\theta = \pi$ for all four energies. (b) The differential cross section for $v_f = 1$ is

backwards peaked ($\theta = \pi$) for the first three energies but sideways peaked ($\theta \simeq 90°$) at the highest energy. (c) The differential cross section for $v_f = 2$ is backwards peaked ($\theta = \pi$) only for the lowest two energies. At $E_k = 0.156$ eV (3.54 kcal/mole) it is sideways peaked ($\theta \simeq 100°$) and at $E_k = 0.233$ eV (5.37 kcal/mole) the peak is at $\theta \simeq 60°$.

These results can be compared at least qualitatively with the recent experimental results of Sparks et al.[2] They have measured these same reactive state-to-state cross sections at two energies, namely $E_k = 2$ kcal/mole and $E_k = 3.17$ kcal/mole. They found that at $E_k = 2$ kcal/mole, all three products ($v_f = 1, 2, 3$) are backwards peaked ($\theta = \pi$), just like our results for $E_k = 1.68$ and 2.14 kcal/mole. However, at $E_k = 3.17$ kcal/mole, only the $v_f = 1$ and 3 are backwards peaked while the $v_f = 2$ is sideways peaked at an angle $\theta \simeq 120°$.[17] Thus, the present theoretical results are in complete agreement with the available experimental results and constitute the first such phase-sensitive quantities which have been successfully calculated for a system which is also experimentally accessible.

The results give a strong indication that the RIOS method is capable of providing vibrational-state−resolved angular distributions of sufficient quality to aid both in guiding experimentalists as
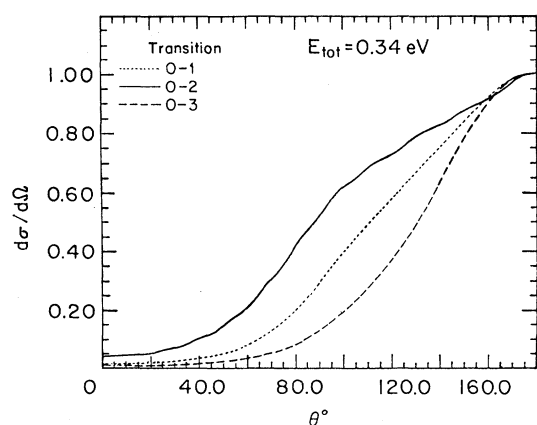

FIG. 1. Vibrational-state−resolved degeneracy-averaged differential cross sections for the reaction $F + H_2 \rightarrow H + HF$. The $v_f = 1$ are given by the dotted curve, $v_f = 2$ by the solid curve, and $v_f = 3$ by the dashed curve. The cross sections are all normalized to 1 at $\theta = 180°$. The incident relative kinetic energy is $E_k = 0.073$ eV $= 1.68$ kcal mole^{-1}.
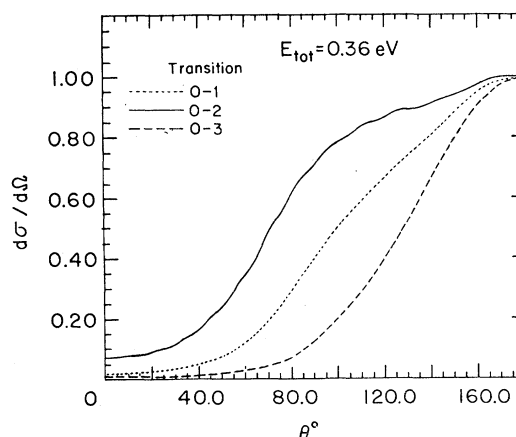

FIG. 2. Same as Fig. 1 except for $E_k = 0.093$ eV $= 2.14$ kcal mole^{-1}.

FIG. 3. Same as Fig. 1 except for E_k = 0.156 eV
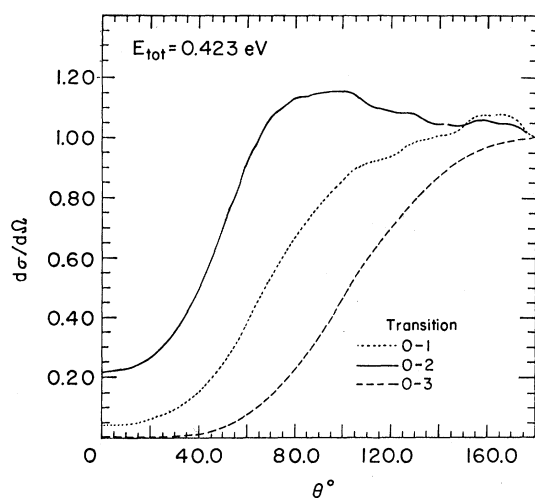= 3.54 kcal mole^{-1}.

FIG. 4. Same as Fig. 1 except for E_k = 0.233 eV
= 5.37 kcal mole^{-1}.

to where the most intense signals may be expect-
ed and also in using such experimental measure-
ments to gain information about intermolecular
interactions and reaction mechanisms. Unlike the
more exact but extremely costly and difficult
close-coupling procedure, the RIOS method can
be applied to other reactions and should be ex-
tremely useful in probing molecular reaction dy-
namics. The widely used quasiclassical trajec-
tory procedure, by contrast, does not yield the
sideways peaking of the HF $(v_f = 2)$ product at the
energy $E_k = 3.17$ kcal/mole.[3c] Thus, for the same
Muckerman-V potential, the quasiclassical trajec-
tory method predicts backwards scattering of all
the HF products for these energies.[3c] The suc-
cess of the RIOS approximation in predicting the
sideways peaking of the $v_f = 2$ HF product also in-
dicates that the decoupling of faster and slower
degrees of freedom does provide a useful physical
basis for understanding the reactive dynamics
in this system.

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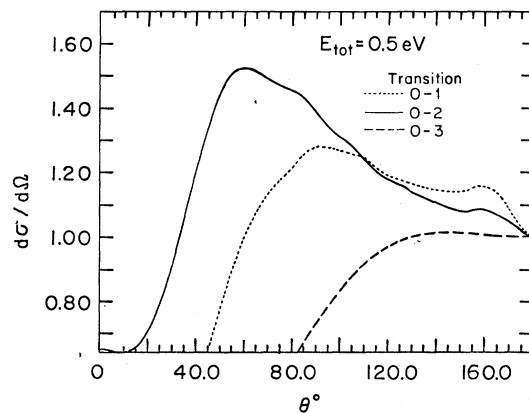[2]R. K. Sparks, C. C. Hayden, K. Shobatake, D. M.

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Inhibited Absorption of Blackbody Radiation

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A cutoff with wavelength is observed in the absorption of blackbody radiation by free atoms. The cutoff arises from a discontinuity in the density of modes between parallel conducting plates. Absorption at a wavelength of $\frac{2}{3}$ cm by atoms between planes $\frac{1}{3}$ cm apart is measured at a temperature of 180 K. The discontinuity in the absorption rate occurs when the absorption wavelength is varied across the cutoff of one of the parallel plate modes.

The effect of conducting surfaces on the radiation rate of elementary atomic systems has been studied theoretically by a number of investigators,[1-4] but experimental evidence is scarce. The principal experimental work is an elegant series of studies by Drexhage on fluorescence of a thin dye film near a mirror.[5] Drexhage observed an alteration in the fluorescence lifetime, arising from the interference of the molecular radiation with its surface image. The radiation rate in such an experiment is sensitive to the optical properties of the surface, and quenching-rate data on surface-deposited molecules can yield detailed information on molecule-surface interactions.[6] We have undertaken a study of the radiative properties of atoms in the proximity of conductors with a somewhat different goal: to alter the coupling of atoms with the vacuum by manipulating the mode structure of the system. We report here the results of a study of blackbody radiative transfer of free atoms between conducting planes at a wavelength so long that the conductor is, to good approximation, ideal. The transfer rate undergoes a discontinuity with frequency which can be explained in terms of the effect of the elementary mode structure on the spontaneous decay rate. The experiment serves as a step toward the achievement of conditions in which spontaneous emission can be effectively eliminated.[4]

The experiment involves radiative transfer between two Rydberg states of sodium by absorption of thermal radiation at a wavelength of $\frac{2}{3}$ cm. Absorption occurs midway between parallel conducting plates $\frac{1}{3}$ cm apart. A small dc field is applied between the plates to vary the absorption wavelength by the Stark effect. The field is slowly increased, and as the wavelength drops below the cutoff value for one of the parallel plate modes, the absorption rate is seen to increase abruptly.

The rate for radiative absorption between two states is $A\bar{n}$, where A is the spontaneous transition rate and $\bar{n}$ is the photon occupation number. For a thermal field, $\bar{n} = [\exp(h\nu/kT) - 1]^{-1}$. A is proportional to the mode density $\rho(\nu)$ for photons at the transition frequency ν.[3,4] In free space, $\rho(\nu) = 4\pi\nu^2/c^3$. Between parallel conducting planes there are families of modes for the electric field parallel and perpendicular to a normal to the planes, $\rho_\parallel$ and $\rho_\perp$, respectively. The characteristic cutoff frequency is $\nu = c/2d$, where d is the plate separation. In the frequency region $0 < \nu < 2\nu_c$, the mode densities are

$$\rho_\parallel = 4\pi\frac{\nu_c\nu}{c^3},$$

$$\rho_\perp = \begin{cases} 4\pi\dfrac{\nu_c\nu}{c^3}, & \nu > \nu_c, \\ 0, & \nu < \nu_c. \end{cases}$$