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Dynamical Resonances in Collinear, Coplanar, and Three-Dimensional Quantum Mechanical Reactive Scattering*

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We present results of one-, two-, and three-dimensional calculations for the H + H_2 exchange reaction which provide the first evidence for dynamical internal excitation (Feshbach) resonances in chemical reactions using noncollinear calculations. The change of the resonance energy and width with collision dimensionality and with total angular momentum is analyzed and indicates the existence of observable effects on certain reactive cross sections.

Internal excitation resonances have been observed in a large number of diverse collision phenomena including π-p scattering,[1] electron-atom and electron-molecule scattering,[2] and (theoretically) rotationally inelastic atom-molecule scattering,[3] but they have yet to be detected in atom-diatom reactive scattering experiments. Their existence has previously been established theoretically only in collinear models of these simple chemical reactions.[4-8] The results of those collinear calculations indicate that these resonances are responsible for oscillations in the reaction probabilities near the resonance energies through their interference[8] with the direct mechanisms. However, because of partial-wave averaging, it was not known whether such resonances would exist in the three-dimensional (3-D) world. We present here the results of accurate quantum mechanical calculations for 1-D, 2-D, and 3-D collisions for the historically important $H+H_2$ exchange reaction which provide the first evidence for dynamical resonances in chemical reactions for noncollinear systems. An understanding of the relation between the characteristics of such resonances and the nature of the potential surfaces which give rise to them may prove a sensitive probe in the experimental characterization of these surfaces and in the development and testing of approximate reaction-dynamic theories.

The methods used for solving the Schrödinger equation for the collinear, coplanar, and three-dimensional $H+H_2$ collisions are the same as those we developed and used previously.[8-11] In order to obtain accurate results in the 2-D and 3-D calculations at the relatively high energies at which the resonances were found, quite large vibration-rotation basis sets were required, involving five or six vibrations and rotational quantum numbers $j=0-6$ to $j=0-9$ for each vibration for a total of sixty coplanar channels (for all values of total angular momentum quantum number J), and 40 to 90 ($J=0, 1$) 3-D channels. For most of these noncollinear calculations, tests of conservation of flux, microscopic reversibility, and invariance with respect to number and choice of expansion functions indicated convergence of 5 to 10% although a few poorer results (20%) were included. The collinear results, for which ten vibrational basis functions were used, are accurate to 0.5% or better. The Porter-Karplus[12] potential energy surface was used for all calculations.

The resulting 1-D,[13] 2-D, and 3-D reaction probabilities P^R, defined in the figure caption, are plotted as a function of the total energy E in Fig. 1. It can be seen that all vibrationally elastic probabilities in Fig. 1(a) show a similar behavior, rising from an effective threshold energy E_{thres} (the value of E for which $P^R = 0.01$) to a relatively flat plateau, and dipping later to a minimum at an energy E_r. The values of E_{thres} are 0.420, 0.470, and 0.525 eV and of E_r are 0.873, 0.922, and 0.975 eV for the 1-D, 2-D, and 3-D systems, respectively. The vibrationally inelastic P^R of Fig. 1(b) are also analogous to one another and display maxima at the same energies E_r for which the vibrationally elastic ones show minima. In a previous study,[8] we used a delay-time analysis (for a slightly different H + H_2 potential energy surface[4]) to show that the minima and maxima in the 1-D $P_{0\to0}{}^R$ curves are the result of resonances. Since there are no attractive wells in the H + H_2 potential surface, it is inferred that these are internal excitation (Feschbach) resonances. This inference is confirmed for the 1-D case by a vibrationally adiabatic analysis[14] in which the scattering wave function from the $v = 0$ reagent state is expanded in terms of the bound-state eigenfunctions of cuts of the potential surface transverse to the reaction coordinate. In the region of the saddle point this analysis indicates that at the resonance energy the system has a 90% probability of being found in the $v = 1$ state of this transverse (symmetric stretch) internally excited mode of motion (i.e., that the energy is "trapped" in this mode). The physical situation in the 2-D and 3-D systems is analogous to the 1-D one, and since the reaction probabilities in Fig. 1 for all these systems show similar dips and peaks, we conclude that all three correspond to a Feshbach resonance centered at the values of E_r given above, and with approximate widths of 0.022, 0.045, and 0.035 eV for the 1-D, 2-D, and 3-D cases, respectively. The $P_{00\to1}{}^R(3\text{-D}, J=0)$ reaction probability is dominated by this resonance at energies within 0.1 eV of the effective threshold, in spite of the sum over all product rotational states.

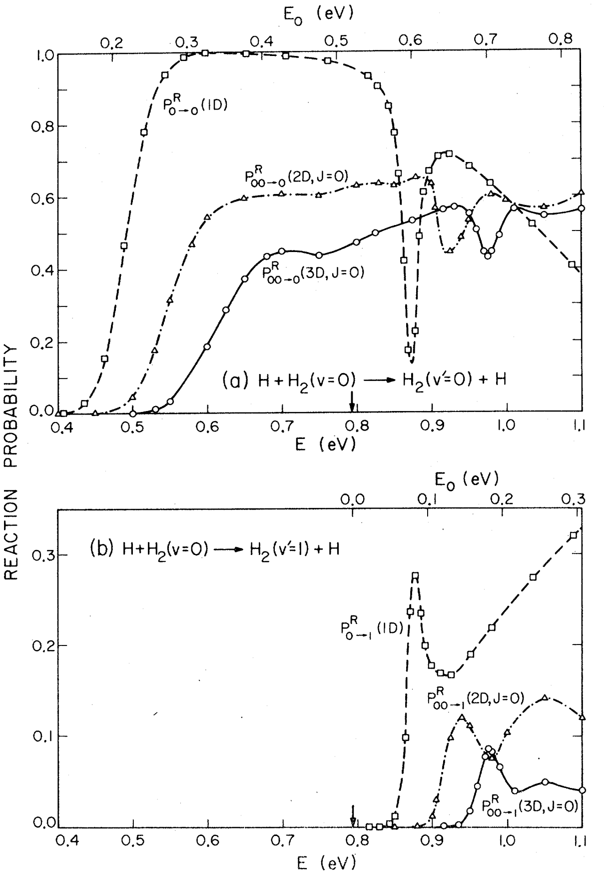

FIG. 1. Collinear (1-D), coplanar (2-D), and three-dimensional (3-D) reaction probabilities for the H + H_2 exchange reaction as a function of the total energy E and relative translational energy E_0. $P_{0\to0}{}^R$ and $P_{0\to1}{}^R$ are the collinear reaction probabilities from $v=0$ of the reagent H_2 to $v'=0$ and $v'=1$, respectively, of the product H_2. $P_{00\to0}{}^R$ and $P_{00\to1}{}^R$ are the 2-D or 3-D (as specified) reaction probabilities for the total angular momentum $J=0$ partial wave from $v=0$, $j=0$ of the reagent H_2 to $v'=0$ and $v'=1$, respectively, of the product H_2 summed over all product rotational states within a given vibrational manifold. (a) The vibrationally elastic reation probabilities, (b) the vibrationally inelastic ones. The points actually computed are indicated by geometrical symbols. Arrow in abscissa indicates the energy at which the $v=1$ state of H_2 becomes accessible.

The change in resonance energy with dimensionality is almost identical to the corresponding change in the effective threshold energies and is in the range 0.050 to 0.055 eV for both the 1-D to 2-D and 2-D to 3-D shifts. These shifts agree with previous estimates[15] of the additional zero-point "bending" energy which must be put into the triatomic motions of the coplanar and 3-D transition states. This indicates that these resonances are influenced by the potential energy surface in the strong interaction region. Both coplanar and 3-D calculations indicate that the resonance has a significant effect only on the $J = 0$–7 partial waves (which appears to coincide with the range of J for which $P_{00\to1}{}^R$ is significant), whereas nonnegligible reaction probabilities $P_{00\to0}{}^R$ are found for the wider J range 0–17. *No significant change of either resonance energy or width with the quantum number J was detected for the 2-D system.*[16] This very important result is probably due to the dominant character of potential (rather than angular momentum) coupling in the region of strong interaction, and suggests that the partial-wave sum present in the expressions for the reaction cross sections will not eliminate the effect of the individual partial-wave resonances. From the width of the 3-D resonance we estimate a lifetime of 3.8×10^{-14} sec (corresponding approximately to 2–3 transition-state symmetric stretch vibrations), about $\frac{2}{3}$ of the 1-D lifetime. A crude estimate of the effect of the resonance on the integral cross section $\sigma_{00\to1}{}^R$ for the reaction between distinguishable atoms in three dimensions can readily be obtained by a simple interpolation procedure. The shape of the coplanar $P_{00\to1}{}^R(J)$ curve both on and off resonance as a function of J has a very simple monotonically decreasing form which is quite similar in appearance to the shape of $P_{00\to0}{}^R(J)$ at lower collision energies. Incomplete 3-D calculations for the 3-D $P_{00\to1}{}^R(J)$ curve indicate that an analogous comparison with the lower energy $P_{00\to0}{}^R$ curves is valid. We have therefore used these 3-D $P_{00\to0}{}^R(J)$ curves along with the accurately known $J=0,1$ values of $P_{00\to1}{}^R(J)$ and its $J=7$ cutoff to interpolate the remaining $P_{00\to1}{}^R(J)$ needed for a cross-section calculation. The reactive cross section obtained in this manner shows an energy dependence similar to that of $P_{00\to1}{}^R(J=0)$ of Fig. 1(b), with a peak value of 0.014 Å^2 at the resonance energy.[17, 18] To estimate the effect of the resonance on the angular dependence of the differential reactive cross sections ($\sigma_{00\to0}{}^R$ and $\sigma_{00\to1}{}^R$), we note that below the resonance energy, this dependence shows no oscillations and is backward peaked.[11] At the resonance energy, one should expect oscillations to develop as a result of the interference between direct and resonance mechanisms.[19, 20]

We conclude, in summary, that dynamical resonances do indeed exist in noncollinear $H+H_2$ and can cause nonnegligible effects on observable reaction cross sections. Such resonances are bound to exist in other reactions also, as they have already been detected in collinear calculations for $F+H_2$ (D_2, HD)[21] and $Cl+H_2$,[22] whose potential energy surfaces also do not have attractive wells. An understanding of the circumstances that give rise to Feshbach resonances can play an important role in the improvement of our knowledge of reactive collision dynamics. Since classical trajectory methods do not include the interference effects associated with the resonances, nor do most semiclassical[21, 23] and approximate quantum methods,[24] a theoretical 3-D treatment of resonances for most other chemical reactions will require the development of better approximate techniques, and the results presented here should be valuable in this endeavor. In addition, accurate quantum mechanical results (be they 1-D, 2-D, or 3-D) can serve as a useful predictive guide in the experimental search for dynamical resonances, and it is hoped that the present paper will stimulate such a search.

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[17] Since the distinguishable-atom nonreactive probability $P_{00\to1}{}^{N}(J)$ is very similar in both energy and J dependence to $P_{00\to1}{}^{R}(J)$, we expect that the nonreactive integral cross section $\sigma_{00\to1}{}^{N}$ should also have a peak at the resonance energy. This implies that the effect of atom indistinguishability should not appreciably alter the conclusions of this analysis.

[18] The smallness of this cross section may lead to experimental detection difficulties, and other reactive systems may be more favorable candidates for experimental investigation. The point we are making is nevertheless of significant conceptual importance, namely that resonances can exist and play an important role in chemically reactive collisions for which the corresponding potential energy surface does not have an attractive well.

[19] The individual partial-wave contributions to the differential cross sections are highly oscillatory in nature, and fairly slight calculational inaccuracies in the elements of the scattering matrix element for one partial wave are usually enough to upset the delicate balance between partial waves which leads to nonoscillatory differential cross sections, thereby resulting in strong spurious oscillations. It is reasonable to expect that the presence of resonances in some of the partial waves which contribute significantly to the cross sections should have a similar effect, as is experimentally observed for inelastic electron scattering. (See H. Ehrhardt, in *Physics of the One and Two Electron Atoms*, edited by F. Bopp and H. Kleinpoppen (North-Holland, Amsterdam, 1969), p. 598.

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Laboratory Microwave Spectrum of HCO^{+}†

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The $J=0\to1$ rotational transition of the HCO^{+} ion has been observed with the same apparatus used earlier for detection of CO^{+}. A discharge in various mixtures of hydrogen and carbon monoxide cooled to near liquid-nitrogen temperature was employed in a slow-flow system. The frequency we have obtained is 89 188.545 ± 0.020 MHz, but because of the ion drift velocity in the dc discharge this exceeds, by an unknown but small amount, the true rest frequency. This observation confirms the long-standing contention that the radio astronomical X-ogen line is in fact due to HCO^{+}.

In 1970 Buhl and Snyder[1] discovered a new molecular transition at 89190 MHz in several interstellar sources. Since they could not identify with certainty the species responsible for this emission they named it X-ogen. Later that year Klemperer[2] postulated that this mysterious line was actually due to the molecular ion HCO^{+}, whose theoretically predicted rotational constant agreed very well with that corresponding to the X-ogen frequency and which was expected to be a fairly stable and abundant species under the conditions prevailing in the interstellar clouds. Since that time this identification of X-ogen as HCO^{+} has become fairly generally accepted, although it has not been definitely proven. Strong support for it has come recently from Snyder *et al.*,[3] who have reported observation of an interstellar line at 86 754 MHz which they identify as $H^{13}CO^{+}$. More recent theories[4,5] of the processes involved in forming interstellar molecules involve ion-molecule reactions in a crucial way, and HCO^{+} is a cornerstone species in this modeling of interstellar kinetics. In fact it is so important that the whole picture would be tarnished if