State-to-state reaction probabilities for $\text{H}^- + \text{H}_2$, D_2 collisions

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The potential energy surfaces for the ground and low-lying excited states of the H_3^- system are calculated by means of the diatomics-in-molecule (DIM) method. State-to-state reaction probabilities for rearrangement in $\text{H}^- + \text{H}_2$, D_2 collisions are calculated by the S matrix Kohn variational method in the discrete variable representation for the collinear configuration, and the results for $\text{H}^- + \text{D}_2$ collisions compared with recent experimental data.

1. Introduction

Considerable progress has been made in the quantum scattering theory of chemical reactions in the past few years, using a variety of time-independent and time-dependent approaches (for recent reviews, see ref. [1])^{#1}. Among the former, the S -matrix version of the Kohn variational principle (SKVP) [3] is one especially general and straightforward approach, and the variant of this which employs a discrete variable representation as the square-integrable (L^2) basis set (DVR-SKVP) [4] is particularly attractive and is the approach used in the present Letter.

Recent experiments [5,6], as well as increasing interest in the unique chemical dynamics occurring on more than a single Born–Oppenheimer potential en-

ergy surface, have attracted our attention to the reaction $\text{H}^- + \text{D}_2$. Although this reaction is from the $\text{H} + \text{H}_2$ family, we share the view of Zimmer and Linder [5] that theoretical investigations of $\text{H}^- + \text{H}_2$, D_2 collisions are highly desirable and will stimulate further experimental work. To date, however, rigorous quantum mechanical calculations have not yet been performed for these reactions.

The ground potential energy surface for the H_3^- system has been calculated using a variety of approaches [7–14]. The general behavior of the surface for the collinear and T-shaped configurations was presented by Keil and Ahlrichs [8]. Recent ab initio calculations [11,12] mainly concerned the stability of the H_3^- anion. In these articles it was shown that the H_3^- anion has a shallow well about 1.2 kcal/mol deep in the collinear configuration near $R=6$ au and $r=r_e$. (R is the Jacobi scattering coordinate, connecting one atom to the center of mass

^{#1} See papers in ref. [2] and references to earlier work of the respective authors therein.

of the other two, r is the diatomic stretch, and r_e the equilibrium diatomic stretch distance.) The potential energy surface for the bent and T-shaped configurations was also presented in ref. [12]. It was determined that at small internuclear distances the ground state surface of H_3^- crosses the ground surface of H_3 , which could explain the experimentally observed [15] detachment of electrons in collisions of H^- with hydrogen molecules in the ground and low-lying excited vibrational states. The model for detachment of H^- in collisions with high vibrationally-excited hydrogen molecules was proposed in ref. [14], where the ground and first excited potential energy surfaces of H_3^- were calculated by means of the diatomics-in-molecules (DIM) method, using a minimal basis set. The DIM calculation gives a fairly good approximation to the ground potential energy surface. The first excited potential energy surface, as well as the ground surface, has also been calculated by the molecular orbital (MO) method [13]; these results may be understood as the surface of neutral H_3 with an additional electron.

Although the ab initio surface is assumed to be more accurate than the DIM surface, we have chosen an improved DIM surface with which to perform our 2D (and in general 3D) variational scattering calculations since the DIM method is simpler than ab initio, and allows one to obtain 3D potential energy surfaces not only for the ground state, but also for the excited states correlated at infinite reaction coordinate to the correct $H+H_2^-$ limit, which the MO surfaces do not do. We therefore expect that the present scattering calculations will have only qualitative accuracy, and that discrepancies with experiment will motivate further work on the potential energy surfaces.

2. Potential energy surfaces

We refer to ref. [16] and references therein for background on the DIM method. The crucial element in a DIM calculation is the choice of diatomic potentials. The potentials for the $H_2(^1,3\Sigma_{g,u})$ states are well known (see, for example, ref. [17]), while those for $H_2^-(^2\Sigma_{g,u})$ states are still not known very

accurately (see, for example, the discussion in refs. [18,19]). Using the results of ref. [19] for $H_2^-(^2\Sigma_u)$ in DIM calculations of the ground PES for H_3^- leads to a deep well, in conflict with ab initio calculations [11,12], while using those of ref. [20] yields a more realistic ground PES of H_3^- . Thus, the results of ref. [20] were chosen for our DIM calculations.

Our DIM calculations of the ground surface for H_3^- confirm the result of ab initio calculations [11,12] that the collinear surface has a minimum with respect to angular deformation. This strong steric effect justifies the restriction of the system in this initial study to the collinear configuration. As an example of the DIM PES, the ground and first excited states for the collinear configuration are presented in fig. 1. The ground PES which correlates to $H^-+H_2(^1\Sigma_g)^{#2}$ (fig. 1a), has two valleys with a shallow well of 0.054 eV; this agrees well with the results of ab initio calculations [11,12]. There is also a saddle point of 0.62 eV at $r_{ab}=r_{bc}=1.61$ au. This value for the saddle point falls comfortably within the range of the previous calculations [8,9,13]. The ground state surface of H_3^- calculated in the present work lies below the ground surface of H_3 calculated by DMBE [17], while the surface of H_3^- in ref. [12] crosses the ground surface of H_3 at small distances. This disagreement could be due to errors in the potentials of H_2^- at small distances, although this crossing was found only in ref. [12] while other ab initio calculations did not show it (see, for example, the discussion in ref. [15]).

The first excited surface correlates to $H+H_2^-(^2\Sigma_u)$, and is shown in fig. 1b. It has two shallow valleys and a relatively deep well of 2.4 eV below dissociation at $r_{ab}=r_{bc}=2.1$ au. This well was not found by molecular orbital (MO) calculations [13], where it was pointed out that the physical significance of those calculations for the excited state is questionable. The first excited surface calculated in the present work has the same physical meaning as the potentials of $H_2^-(^2\Sigma_{g,u})$ with respect to H_2 , while the first excited surface in ref. [13] was understood by those authors as corresponding to "the surface of neutral

^{#2} It is good to emphasize that the ground PES of H_3^- at large reactional and vibrational coordinates correlates to $H+H_2^-(^2\Sigma_u)$, due to the stronger attractive behavior of the potential in $H_2^-(^2\Sigma_u)$ than in $H_2(^1\Sigma_g)$ at large internuclear distances.

Fig. 1. The plots of the calculated ground (a) and first excited (b) potential energy surfaces of the H_3^- anion. For (a), the contour spacing is 0.02 H, with minimum and maximum contour values of -0.18 H and -0.02 H, respectively. For (b), the contour spacing is 0.005 H, with minimum and maximum contour values of -0.12 H and 0.0 H, respectively.

H_3 with an additional electron in a diffuse molecular orbital", i.e. a Rydberg state. In some regions the first excited surface of H_3^- in our calculations is above the surface of neutral H_3 and hence is quasi-stationary. This surface is responsible for detachment of H^- in collisions with H_2 in excited vibrational states [14] due to the nonadiabatic region along the line $r_{ab} = r_{bc}$.

Thus, DIM calculations of the H_3^- system presented in this Letter provide reasonably reliable ground and low-lying excited potential energy surfaces, and allow us to perform scattering calculations for collisions of H^- , D^- with H_2 , D_2 , DH and determine the state-to-state reaction probabilities.

3. Dynamics

In this section we present exact quantum scattering results for the title reactions in the collinear configuration. The calculations are carried out via the DVR-SKVP method [4,21]. We review the method very briefly before presenting the results and comparing them to the experimental observations.

3.1. Discrete variable representation implementation of the *S*-matrix version of the Kohn variational principle

The working equations of the *S*-matrix version of the Kohn variational principle are

$$\mathbf{S} = \frac{i}{\hbar} (\mathbf{B} - \mathbf{C}^\dagger \mathbf{B}^* {}^{-1} \mathbf{C}), \quad (1)$$

where

$$\mathbf{B} = \mathbf{M}_{00} - \mathbf{M}_0^\dagger \mathbf{M}^{-1} \mathbf{M}_0, \quad (2)$$

and

$$\mathbf{C} = \mathbf{M}_{10} - \mathbf{M}_0^\dagger \mathbf{M}^{-1} \mathbf{M}_0. \quad (3)$$

Here, $\mathbf{M}_{00}$ and $\mathbf{M}_{10}$ are matrix elements of $\hat{H} - E$ over the free, or unbound basis functions, each one of which corresponds to an open channel at energy E , and is a solution of the "asymptotic" Hamiltonian, i.e. at infinite separation of the atom and diatom. Thus, they are square matrices whose dimension is the number of open channels. $\mathbf{M}$ is a matrix of $\hat{H} - E$ in a square-integrable basis used to describe

the scattering wavefunction in the "interaction region", i.e. the active region of the potential energy surface where exchange occurs. The order of $\mathbf{M}$ is the number of square-integrable basis functions used. Finally, $\mathbf{M}_0$ is a rectangular matrix of $\hat{H}-E$ with the free functions on one side and the square-integrable basis functions on the other. In the DVR version of the SKVP, the square-integrable basis is a set of DVR grid points, laid down over the interaction region. The main computational effort of the SKVP is in solving the linear system $\mathbf{M}\mathbf{x}=\mathbf{M}_0$ in order to determine $\mathbf{x}\equiv\mathbf{M}^{-1}\mathbf{M}_0$.

There are several advantages of constructing the $\mathbf{M}$ matrix in a DVR: first, since DVRs require no quadratures, because the potential energy matrix is diagonal, the matrix elements are trivial to evaluate. Further, for the same reason, the DVR matrix is extremely sparse, becoming sparser as the number of degrees of freedom increases. This sparsity can be exploited with great thrift by employing iterative methods for solving the above linear system. These methods, such as those based on the Lanczos procedure to produce a tridiagonal representation, have at their core the need to multiply successively the matrix, $\mathbf{M}$, into a vector. The fewer non-zero elements of $\mathbf{M}$, the more efficient this procedure is.

There are many different types of DVR that one may choose. Most are based on Gaussian quadrature points and weights that are associated with a set of orthogonal polynomials. However, two of us recently introduced [4] a new type of DVR, based on shifted sinc function, where $\text{sinc}(x)=\sin(x)/x$. The grid points are evenly spaced and have uniform weights. We have found this DVR to be especially useful for many scattering systems, including the ones studied here.

The calculations performed here are essentially the same as those reported earlier [4], the main difference being, of course, the potential energy surfaces used. One other difference is that whereas previously the DVR grid was laid down in the interaction region using normal coordinates of the transition state, here we use Jacobi coordinates of the second, unseen arrangement. Thus, for the distinguishable particle collinear reaction $\text{AB}+\text{C}\rightarrow\text{A}+\text{BC}$, Jacobi coordinates corresponding to the (unseen) arrangement $\text{B}+\text{AC}$ have been used.

Another point of departure from the calculations

of ref. [4] is that, whereas in that paper the collinear calculations were small enough that direct methods could be used for solving the linear system of eqs. (2) and (3), here iterative, Lanczos-based methods were used to carry this out. In particular, the SYMMLQ algorithm [22] has been used. The details of this procedure will be presented in a forthcoming article [21].

3.2. Results and comparison with experiment

In this section we present the results of calculations via the DVR-SKVP for state-to-state transition probabilities in collinear $\text{H}^- + \text{H}_2$, D_2 collisions, i.e. for the following reactions:

The reactions (4) and (6) are ones with rearrangement and simultaneous charge transfer, while the reactions (5) and (7) are ones without rearrangement, i.e. inelastic collisions. The state-to-state reaction probabilities for reactions (4), (5) are shown in fig. 2a and for inelastic reactions (6), (7), in fig. 2b. We can understand the figures in the following way: the reactions have energy thresholds, which shift to higher energy with increasing vibrational excitation from the state with $v=0$; the energies of the maxima of the reaction probabilities are also increased, while the maximum values themselves are decreased. We note that the threshold energies are substantially above the barrier or endothermic energy defects. For example, at an energy equal to the saddle point barrier, the reaction probabilities are less than 0.01, but rapidly increase with increasing energy; the endothermic energy defect for $v=0\rightarrow v'=1$ in eq. (4) is 0.51 eV, but the reaction threshold is at about 0.7 eV; the endothermic energy defect for $v=0\rightarrow v'=1$ in eq. (6) is 0.49 eV, and the reaction threshold is at about 0.7 eV, and so on.

We now compare the calculated probabilities with experimental data. The calculated threshold energy for $\text{H}^- + \text{D}_2$ collisions is in excellent agreement with

Fig. 2. Calculated state-to-state transition probabilities in collinear (a) $\text{H}^- + \text{H}_2$ and (b) $\text{H}^- + \text{D}_2$ collisions as a function of relative translational energy. The solid lines denote reactive probabilities (eqs. (4) and (6) respectively), and the dotted lines denote inelastic probabilities (eqs. (5) and (7) respectively). Curve 1 denotes $v=0 \rightarrow v'=0$, curve 2 denotes $v=0 \rightarrow v'=1$ and curve 3 denotes $v=0 \rightarrow v'=2$.

that observed experimentally for the total cross section 0.42 ± 0.12 eV [5,6]. This threshold is to be compared with the value of the saddle point barrier (0.62 eV) calculated in the present work (the vibrational energy for $\text{D}_2(v=0)$ is 0.19 eV). It should be mentioned that the threshold in ref. [9] was found to be 1.5 eV, while our calculations confirm the result of refs. [5,6]. Furthermore, at low energies qualitative agreement with experiment [23] is obtained, not only for $v=0 \rightarrow v'=0$ but for all the calculated reactions. This is presumably a consequence of the fact that the lowest PES has a collinear reaction path, and that at relatively low energy there is little rotational excitation. However, the maximum in the experi-

mental partial cross section [23] (summing over rotational states) is shifted in comparison with our 2D calculations for reaction probability. For example, in $\text{H}^- + \text{D}_2$, the relative translational energy at the maximum of the $v=0 \rightarrow v'=0$ peak is 1.0 eV; for $v=0 \rightarrow v'=1$, it is 1.5 eV; for $v=0 \rightarrow v'=2$, it is 1.8 eV. In our calculations, these are 0.61 eV for $v=0 \rightarrow v'=0$, 0.96 eV for $v=0 \rightarrow v'=1$, and 1.21 eV for $v=0 \rightarrow v'=2$. These shifts are probably due to rotational excitations which were experimentally observed [5], but of course absent from our collinear calculations. A difference of 0.4 eV (the shift of our calculated maximum for $v=0 \rightarrow v'=0$ from the experimental cross section maximum) corresponds to a rotational excitation for D_2 of about $j=10$, a level of excitation consistent with that seen experimentally [23]. Furthermore, we have performed some preliminary three-dimensional ($J=0$, but including nonzero rotational angular momentum of the fragments) calculations for these reactions, and the results indicate a shift in the maximum of the reaction probabilities (summed over rotational states) toward higher energies.

4. Conclusion

The calculated transition probabilities for collinear collisions agree well with experimental data [5,6,23]. Our calculations essentially confirm the conclusions of refs. [5,23] about the reaction thresholds with excitation of different vibrational states and about rotational excitation. To compare theoretical with experimental results more fully, three-dimensional calculations with $J>0$ are required, which we plan to do. We also plan to extend the current approach to other reactions in H^- , $\text{D}^- + \text{H}_2$, HD , D_2 collisions, especially those involving more than a single potential energy surface. Above about 1.8 eV, the PES correlating to $\text{H} + \text{H}_2^-$ becomes important. The calculated PES of H_3^- and DVR-SKVP scattering calculations will allow such investigations.

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