DIFFERENTIAL CROSS SECTION (ANGULAR DISTRIBUTION)
FOR THE REACTION \( H + H_2(v = j = 0) \rightarrow H_2(v', \text{odd } j') + H \)
IN THE ENERGY RANGE 0.90-1.35 eV

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Calculations are reported of the differential cross section for the reaction \( H + H_2(v = j = 0) \rightarrow H_2(v', \text{odd } j') + H \) for total energy \( E \) from 0.9 to 1.35 eV. Total angular momentum values up to \( J = 24 \) are included in the partial wave summations, and in all respects these results should be the essentially exact (i.e. to a few percent) values for this (LSTH) potential energy surface. Complete differential cross sections are reported at several energies for final vibrational states \( v' = 0 \) and 1, and for various final rotational states \( j' \). Of particular interest is the energy dependence of the differential cross section for back-scattering. Specifically, it is seen that the energy dependence of the \( J = 0 \) reaction probability is qualitatively similar to that of the differential cross section for back-scattering, so that resonance structure which is quite apparent in the former shows up to some extent in the latter. Even this structure, though, is not as pronounced as that reported in recent experimental results for the integral cross section. The lack of agreement between theory and experiment with regard to resonance structure in the energy dependence of these cross sections thus remains unaccounted for.

1. Introduction

We recently reported [1] the calculation of integral cross sections for the fundamental reaction
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H + H_2(v = j = 0) \rightarrow H_2(v' = 1, j' = \text{odd}) + H
\] (1)
in the range of energies relevant to recent experiments by Nieh and Valentini [2]. These experiments have attracted considerable attention because they showed resonance-like structure in the energy dependence of the integral cross sections for reaction (1), presumably due to a short-lived collision complex. It was surprising, therefore, that our calculations – which used the supposedly accurate Liu-Siegbahn [3] potential energy surface (fit to a useful analytic form by Truhlar and Horowitz [4]), and which should be the rigorous result for a given potential surface – showed no such resonance-like features.

Our calculations [1] did, however, show resonance structure in reaction probabilities for individual small values of \( J \) (the total angular momentum quantum number); it is the sum over \( J \) which is involved in constructing the integral cross section that averages out the resonance structure. On the basis of semiclassical ideas [5], however, one knows that observation of the angular distribution (i.e. differential cross section) to some extent unfolds the partial wave sum, and in particular that scattering in the backward direction (\( \theta = 180^\circ \)) has its major contribution from small \( J \). We therefore speculated that the energy dependence of the differential cross section for back-scattering might show resonance structure and that perhaps this (or something related to it) was what was actually observed experimentally. Recent calculations [6] by us for the related \( D + H_2 \rightarrow HD + H \) reaction have indeed shown such structure in the energy dependence of the differential cross section for back-scattering.

The purpose of this paper is thus to present the results of calculations for the differential cross section of reaction (1) and, in particular, to consider the energy dependence of the cross section for scattering at \( \theta = 180^\circ \) (and also other fixed angles). Specific comparisons show that there is indeed a qualitative correspondence between the energy...
dependence of the reaction probability for \( J=0 \) and that of the differential cross section for back scattering. For completeness we also show the dependence of the full angular distribution on energy and on the final rotational and vibrational state.

The methodology that we use, namely the S-matrix version [7] of the Kohn variational principle [8] applied to Miller's formulation [9] of reactive scattering, has been summarized quite completely in our recent paper [6] on the \( \text{D}+\text{H}_2 \rightarrow \text{HD}+\text{H} \) reaction, so here we give only the results. Total angular momentum values up to \( J=24 \) were included in the partial wave sums, and all other aspects of the calculation are the same as our earlier ones [1] for the integral cross section; here the S-matrix elements are simply assembled to produce differential rather than the integral cross sections.

2. Results

Fig. 1 shows the results of primary interest for present purposes, namely the differential cross section in the backward direction, \( \theta=180^\circ \) (and also at some other fixed angles), as a function of total energy. The initial state in all cases is the ground state \( v=j=0 \), and the final state is \( (v', j') = (1, 1) \) and \( (1, 3) \) for figs. 1a and 1b, respectively. (These are the two final states for which the experimental integral cross sections were reported in ref. [2].) For final state \( (v', j') = (1, 1) \) there is no dramatic resonance structure, though there is a well-defined shoulder at \( E \approx 1.0 \text{ eV} \) for the back-scattering \( \theta=180^\circ \) cross section; this resembles very much the structure obtained before [6] for the \( \text{D}+\text{H}_2 \) reaction. For final state \( (v', j') = (1, 3) \) (fig. 1b), however, there is a prominent peak (0.12 eV half width) at \( E \approx 1.15 \text{ eV} \), and a less noticeable shoulder at \( E \approx 1.0 \text{ eV} \). For angles less than \( 180^\circ \) all of these structures become less pronounced.

The energy dependence in fig. 1 is certainly not identical to that seen in the experiments of Nieh and Valentini [2], but it does show enough resemblance (for \( \theta=180^\circ \)) to lend some support to our earlier [1] suggestion that the experiments may be preferentially observing back-scattered products rather than an integral cross section. At present, though, one must still say that experiment and theory are not in agreement with respect to the structure in the energy dependence of these ortho–para reactive cross sections.

To examine in more detail the relation between the energy dependence of the \( J=0 \) reaction probability and the differential cross section for back-scattering, fig. 2 compares these quantities directly. Figs. 2a and 2b are for final states \( (v', j') = (1, 1) \) and \( (1, 3) \), respectively. There is qualitative agreement between these quantities, but it is of course not quantitative. The exact value of the differential cross section at \( \theta=180^\circ \) involves a sum over all values of \( J \); it is only in the classical limit [10] \( \theta=180^\circ \) implies \( J \approx 0 \).

For completeness, fig. 3 shows the full angular distribution for three different values of the total en-

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Fig. 1. Differential cross section, at several fixed center-of-mass scattering angles \( \theta \) for the reaction \( \text{H}+\text{H}_2(v=j=0) \rightarrow \text{H}_2(v', j')+\text{H} \), as a function of total \( E \). (a) and (b) are for the final states \( (v', j') = (1, 1) \) and \( (1, 3) \), respectively.
Fig. 2. Comparison of the energy dependence of the J=0 reaction probability, P_{j=\infty}^{v,j}(E=180^\circ)$, and the differential cross section for back-scattering, $\sigma_{\text{back}}(E=180^\circ)$. The units for the abscissa are (a) for $\sigma$ and unitless for $P$. (a) and (b) are for final states $(v', j')=(1, 1)$, and $(1, 3)$, respectively.

Fig. 3. Differential cross section for $\text{H}+\text{H}_2(v'=j'=0) \rightarrow \text{H}_2(v', j') + \text{H}$, summed over all odd values of $j'$. At low energies the distributions are all peaked in the backward direction, and the peak in the angular distribution moves progressively to smaller angles with increasing rotational excitation of the product molecule.

3. Concluding remarks

The energy dependence of the differential cross section for back-scattering is indeed seen to be qualitatively similar to that of the reaction probability for $J=0$. This suggests that observation of the energy dependence of the back-scattering cross section is a good way to see resonance features that are due to short-lived collision complexes.

For the present example, however, the energy dependence of the back-scattering cross section does not show as much structure as that reported by Nieh.
and Valentini [2]. Therefore, even if our suggestion that the experiments may be observing preferentially back-scattered products were correct, it does not appear that this would provide a complete resolution of the experimental-theoretical discrepancy.

We also wish to make special note of the paper by Manolopoulos and Wyatt [11] (preceding paper) in which calculations very similar to ours have been carried out. It is quite impressive that these two sets of calculations - carried out with significantly different variations in methodology, totally different Fortran codes, and in different parts of the country - are in essentially complete agreement for the integral and differential cross sections over a wide range of energy. It is a significant illustration of the extent to which the fledgling field of ab initio quantum chemistry calculations for the potential surface in order to remove completely this source of uncertainty.

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