COMMUNICATIONS

Rotationally resolved differential scattering cross sections for the reaction \( \text{F} + \text{para-} \text{H}_2 (v=0, j=0) \rightarrow \text{HF} (v' = 2,3, j') + \text{H} \)

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Time-of-flight spectra of HF products in the \( v' = 2 \) vibrational state from reactive scattering of F atoms from para-H\(_2\) exhibit at least four smaller peaks which are assigned to the rotational states \( j' = 7,8,9, \) and \( 10. \) The center-of-mass rotational distributions are in good agreement with accurate quantum mechanical and approximate coupled states calculations. © 1999 American Institute of Physics. [S0021-9606(99)01221-0]

The \( \text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H} \) reaction and its isotopic variants have become a benchmark system in the field of reaction dynamics.\(^1\) The reaction is a prototype for many low barrier exoergic bimolecular reactions and has only 11 electrons. It is also readily accessible to accurate \textit{ab initio} calculations of its potential hypersurface.\(^2\) In addition, since light partners (e.g., H\(_2\) and H) are involved, it provides an excellent testing ground for quantum mechanical theories of reactive scattering. As opposed to the other benchmark reaction, H+H\(_2\), which is determined by a single potential energy surface (PES), at least two PES corresponding to different nearby electronic states may be involved in the \( \text{F} + \text{H}_2 \) reaction.\(^3\) Since presently one of the biggest challenges in the field is understanding the role of multiple potential surfaces, this system provides an excellent testing ground for new concepts in this direction.

Earlier experimental work included rate constant measurements\(^4\) which provided information on activation energies. Then followed a series of spectroscopic and laser studies on the overall product vibrational distributions.\(^5\) Subsequently, important new insight into the structure of the transition state has come from photoelectron spectroscopy of \( \text{FH}^- \).\(^6\) As long ago as 1970\(^7\) a long series of crossed molecular beam scattering experiments have been reported which had sufficient resolution to determine the product vibrational state distributions. One of the most fascinating findings was the 1985 discovery by Neumark \textit{et al.}\(^8\) of a sharp peaking in the forward scattering direction for certain time-of-flight (TOF) resolved final vibrational states. This led to conjectures concerning the possibility of resonances and in turn stimulated a large number of theoretical studies.\(^9,10\) Starting in about 1993 our group in Göttlingen further improved the scattering signal sensitivity and resolution in order to obtain more accurate and detailed product rotational state distributions.\(^11\) These experiments, which were limited to the \( \text{F} + \text{D}_2 \) reaction for experimental reasons, led, together with a dedicated quantum mechanical (QM) treatment, to the discovery of bimodal rotational distributions.\(^12\) These appeared only at the lowest collision energy of 90 meV (≈2.1 kcal/mol) and then only for certain final vibrational states. A recent more accurate QM treatment, based on hyperspherical coordinates, has confirmed the bimodality\(^13\) and reopens the question of the possible role of complexes.

Because of the large infrared (IR) transition moment of the HF (DF) molecule, this system is also ideally suited for spectroscopic studies. Polanyi and co-workers\(^7\) were the first to exploit these possibilities and were able to probe the HF (\( v',j' \)) rotational distribution in low pressure arrested relaxation chemiluminescence experiments using a sensitive Fourier transform IR spectrometer. Very recently two independent groups have succeeded in using different IR based techniques to explore the rotational distributions in scattering experiments. In experiments by Keil’s group\(^14\) the scattered HF product beam is crossed by an intense IR beam produced by a line tunable continuous-wave HF chemical laser. The absorption or the stimulated emission by the scattered product molecules leads to a corresponding increase or decrease in the bolometer signal. These results are then compared with simulations based on QM calculations\(^9\) on the Stark–Werner PES.\(^2\) Good agreement was found between the QM simulated and the measured laboratory angular distributions for the HF product states \( v' = 1, j' = 5,6,7, \) and \( v' = 2, j' = 4,5,6 \) at a collision energy of \( E_{cm} \approx 160 \text{ meV}. \) The QM calculation, however, understimates the \( v' = 1 \) scattering into the forward hemisphere observed by Keil and co-workers.\(^15\) Since this experiment is most sensitive to sideways scattering, the center-of-mass angular resolution is rather limited. In another very recent experiment Nesbitt and collaborators\(^16\) were able to directly observe IR absorption in the region where the two beams cross each other. From this the rotational state distributions for \( v' = 1,2, \) and 3 products integrated over all scattering directions were determined.

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In this communication we report on new angle resolved TOF spectra for the F+para-H₂ (v = 0, j = 0) reaction at a collision energy of 81 meV (1.87 kcal/mol) for a wide range of center-of-mass scattering angles θ. As a result of further improvements in the apparatus, it has now become possible to resolve maxima due to higher rotational states (j = 7, 8, 9, and 10) for the final vibrational state v = 2. From deconvolution of the TOF spectra rotational distributions for all final rotational states v = 2, j = 0–11 are obtained for θ = 90° and θ = 150°–175° and, additionally, for v = 3, j = 0–3 at θ = 135°–155°. For comparison with the experiments new QM coupled states calculations are also presented.

The crossed molecular beam apparatus with capabilities for both in-plane and out-of-plane detection has been described in Ref. 11(a). The following modifications were made to facilitate these new experiments. (1) The F atom oven source was further optimized by fabricating it out of a single crystal of CaF₂, which was mounted in a special way to avoid fracturing it at high temperatures. The source could be operated for more than 300 h at source temperatures of 1400–1450 K, compared to 1150 K in the previous experiments. Thus, despite the increased source pressure of 15 bar (previously 10 bar), the degree of dissociation remained at about 50%. (2) The disturbing mass spectrometer background at 20 amu (HF) resulting from Ar⁺ arising from the use of argon as the seed gas in the F+D₂ experiments was eliminated by seeding it with krypton. (3) This also reduced the F-atom beam energy to compensate for the greater velocity of H₂ compared to D₂. The factor four loss in the F-atom signal, compared to using the Ar seeded beam, was more than compensated for by the improved F-atom source. (4) The secondary H₂ beam was converted to para-H₂ with an estimated j = 0 concentration of >95%. The important beam parameters are listed in Table I.

The overall energetic resolution of the HF products under optimal kinematic conditions is about 5 meV [full width at half maximum (FWHM)]. However, the actual resolution in a given TOF spectrum varies considerably depending on the final scattering angles, the product vibrational states, and kinematic factors. Because of the wide spacing of the HF rotational levels at 4.8, 14.4, 28.8, 48.0, and 72.0 meV for j = 1, 2, 3, 4, and 5, respectively, only rotational states with j > 2 can, in principle, be completely resolved, but the population of the low lying states can be reliably fitted by the simulation.

Figure 1 shows representative TOF spectra for four different laboratory scattering angles (θ, Φ) at a collision energy of 81 meV. The TOF spectrum in Fig. 1(a) is measured under kinematic conditions where all three final vibrational states appear. The broad peak at a flight time of t = 2.25 ms corresponds to the same v' = 3 as the peak at t = 1.7 ms but, because it arises from CM angles close to 180°, it is kinematically broadened compared to the faster v' = 3 peak.
From the vertical bars, which indicate the expected peak locations, it is apparent that in this spectrum individual rotational states are not resolved for \( \nu' = 3 \), although the asymmetric tails clearly indicate considerable rotational populations. The resolution is increased by going to laboratory scattering angles at which the \( \nu' = 3 \) peak no longer appears [Figs. 1(b)–1(d)]. In these spectra the \( j' = 8, 9, 10, \) and 11 peaks in the \( \nu' = 2 \) maximum are clearly separated and shoulders due to \( j' = 7 \) can also be discerned. To extract the experimental CM state-to-state differential cross sections the TOF distributions were simulated numerically with all the experimental averaging effects included using procedures described earlier. 11

In Fig. 2 the CM rotational distributions are compared with calculated QM differential cross sections for electronically adiabatic scattering on the same \textit{ab initio} potential hypersurface\(^2\) based on two different approaches. (1) The calculations based on hyperspherical (HS) coordinates are considered to be nearly “exact” since they do not involve any fundamental approximations, \(^9\) whereas (2) the coupled states (CS) calculations use negative imaginary potentials (NIPs)\(^8\) to decouple arrangements. \(^12\)\(^,\)\(^19\) Frames (a)–(c) in Fig. 2 display comparisons of the experimental with the CS-NIP distributions and frames (d)–(f) show comparisons with the HS distributions. It is important to emphasize that each of the distributions corresponds to a single set of laboratory angles but not always to a single center-of-mass angle. Thus, the final rotational states in the experimental distributions correspond to different CM angles: \( j' = 0 \) to \( \theta = 150^\circ \); \( j' = 4 \) to \( \theta = 151^\circ \); \( j' = 5 \) to \( \theta = 153^\circ \); \( j' = 6 \) to \( \theta = 155^\circ \); \( j' = 7 \) to \( \theta = 158^\circ \); \( j' = 8 \) to \( \theta = 160^\circ \); \( j' = 9 \) to \( \theta = 164^\circ \); \( j' = 10 \) to \( \theta = 170^\circ \) and, finally, \( j' = 11 \) to \( \theta = 172^\circ \). A similar situation is encountered in Figs. 2(c) and 2(f) which show rotational distributions for \( \nu' = 3 \). Here, \( j' = 0 \) corresponds to \( \theta = 135^\circ \), \( j' = 2 \) to \( \theta = 142^\circ \), and \( j' = 3 \) to \( \theta = 152^\circ \). The curves in Figs. 2(b) and 2(e), however, refer to a single center-of-mass angle, namely, \( \theta = 90^\circ \). For the comparisons the relevant theoretical cross sections have all been normalized with a single scaling parameter that was chosen to provide the same cross section as the experiment at the corresponding maxima of the \( j' \) distribution of \( \nu' = 2 \) in Figs. 2(a) and 2(d). In general the two theoretical distributions are in reasonable agreement and very similar to the experimental rotational distributions. The curves do not always peak at the same \( j' \) value but the shift is equal to or less than \( \Delta j' = 2 \).

None of the distributions show any bimodality as was found previously for the F + D\(_2\)→DF + D reaction.\(^12\) Compared to the rotational distributions of Neumark et al.\(^{11(a)}\) the present rotational distributions are narrower and peak at about 30% smaller rotational states, in better agreement with the theory.

As a further test of the CS-NIP method, calculated vibrational state selected integral and total integral reactive cross sections with accurate theoretical HS and approximate CS-NIP calculations.

<table>
<thead>
<tr>
<th>( \nu' = 0 )</th>
<th>( \nu' = 1 )</th>
<th>( \nu' = 2 )</th>
<th>( \nu' = 3 )</th>
<th>Total reactive cross section (( \AA^2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt (beam)(^a)</td>
<td>...</td>
<td>0.20</td>
<td>1.0</td>
<td>0.68</td>
</tr>
<tr>
<td>Expt (IR)(^b)</td>
<td>...</td>
<td>0.31</td>
<td>1.0</td>
<td>0.47</td>
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<tr>
<td>Expt (IR)(^c)</td>
<td>&lt;0.04</td>
<td>0.35</td>
<td>1.0</td>
<td>0.50</td>
</tr>
<tr>
<td>CS-NIP(^d)</td>
<td>0.02</td>
<td>0.19</td>
<td>1.0</td>
<td>0.43</td>
</tr>
<tr>
<td>HS(^f)</td>
<td>...</td>
<td>0.18</td>
<td>1.0</td>
<td>0.39</td>
</tr>
</tbody>
</table>

\(^a\)Reference 8(a).
\(^b\)Reference 5(a).
\(^c\)Reference 16.
\(^d\)Present calculations.
\(^e\)Result obtained for an inelastic calculation presented in Ref. 22.
\(^f\)Reference 9.

FIG. 2. Comparison of experimental and theoretical rotational state-to-state differential cross sections in the center-of-mass system. The solid curves show the experimental distributions. Frames (a)–(c) show in addition the approximate QM coupled states results (CS-NIP) and frames (d)–(f) show the exact QM HS calculations. The cross sections in (a) and (d) are for \( \nu' = 2 \) states at different center-of-mass angles as follows: \( j' = 0 \) for \( \theta = 150^\circ \); \( j' = 4 \) for \( \theta = 151^\circ \); \( j' = 5 \) for \( \theta = 153^\circ \); \( j' = 6 \) for \( \theta = 155^\circ \); \( j' = 7 \) for \( \theta = 158^\circ \); \( j' = 8 \) for \( \theta = 160^\circ \); \( j' = 9 \) for \( \theta = 164^\circ \); \( j' = 10 \) for \( \theta = 170^\circ \); and \( j' = 11 \) for \( \theta = 172^\circ \).
less elaborate CS-NIP numerically calculated integral total as well as the integral state-to-state vibrational cross sections in Table II. The success of the CS-NIP approximation for these two rather complicated systems suggests that it can be successfully used for the QM treatment of polyatomic systems.20 It is likely that the agreement with experiment can be further improved by matching wave functions further out in the asymptotic region rather than employing the perturbative approach as done here.

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