Two Photon Energy, (cm⁻¹)

FIG. 2. A region near the band origin of the REMPI spectrum of Fig. 1, shown on an expanded scale.

\[ \omega = 57 \, 719 \, \text{cm}^{-1} \]  

is consistent with estimated upper bounds provided by \textit{ab initio} calculations for the lowest lying \( ^1\Delta_g \) state.\(^{(2a-2c),2(e)} \) This state correlates with the separated atom \( \text{C}(^1D) + \text{C}(^1D) \) states; the dissociation energy \( D_0 = 13 \, 000 \pm 2 \, \text{cm}^{-1} \) conforms well with the measured values of \( \omega_x \) and \( \omega_x x_e \) given in Table I.

\begin{table}[h]
\begin{center}
\begin{tabular}{ll}
\hline
D & 13 000 ± 2 cm⁻¹ \\
B & 1.364 ± 0.005 cm⁻¹ \\
\hline
T & 57 719 ± 2 cm⁻¹ \\
\hline
\hline
\omega_x & 1 151 ± 2 cm⁻¹ \\
D & 7.7 \times 10^{-6} \text{ cm}^{-1} \\
\omega_x x_e & 21.5 ± 1 \text{ cm}⁻¹ \\
\hline
r_e & 1.435 ± 0.003 Å \\
v_0 & 47 061 ± 2 \text{ cm}^{-1} (1 \, ^1\Delta_g - ^1\Pi_u) \\
\hline
\end{tabular}
\end{center}
\end{table}

\(^{1}\) Supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Grant No. DE-FG02-86-ER13508.

\(^{2}\) K. P. Huber and G. Herzberg, \textit{Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules} (Van Nostrand Reinhold, New York, 1979); contains a tabulation of the spectroscopic constants for the known electronic states of \( \text{C}_2 \).


Accurate three-dimensional quantum scattering calculations for \( \text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H} \)

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This Communication reports the successful application of a powerful new approach for carrying out quantum scattering calculations to the important \( \text{F} + \text{H}_2 \) reaction. We believe that these are the first accurate quantum scattering calculations for the three-dimensional version of this reaction. The approach is based on Miller's formulation\(^{4}\) of reactive scattering (i.e., a coupled channel expansion simultaneously in the Jacobi coordinates of all arrangements) and uses the \( S \)-matrix version of the Kohn variational principle.\(^{2}\) This is superior to other basis set methods\(^{3,4}\) that adopt this formulation in that it requires matrix elements only of the Hamiltonian operator itself, and not those involving the Green’s function of a reference problem. Previous test calculations\(^{2(b)}\) for the three-dimensional \( \text{H} + \text{H}_2 \) reaction have shown the approach to be accurate, stable, and efficient.

The \( \text{F} + \text{H}_2 \rightarrow \text{H} + \text{HF} \) reaction is much more demanding computationally than \( \text{H} + \text{H}_2 \) because of its large exoergicity and thus the large number of HF rotational/ vibrational states that are energetically accessible. It is thus crucial in this case to exploit the fact that two of the three atoms are identical. If \( a(\text{F} + \text{H}_2) \), \( b(\text{H}^\ast + \text{HF}) \), and \( c(\text{H} + \text{HF}) \) denote the three distinguishable atom arrangements, then it was shown in Ref. 1 that linear combinations (the sum and difference) of the states of the symmetrically equivalent arrangements, \( b \) and \( c \), can be made such that the states of arrangement \( a \) couple only to one of these linear combinations. That is, states of arrangement \( a \) (\( \text{F} + \text{H}_2 \)) that are even (odd) on exchange of the two \( \text{H} \) atoms couple only to the linear combination of states of arrangements \( b \) and \( c \) that are even (odd) on this exchange. Thus, all the relevant matrices in the expression for the \( S \) matrix in Ref. 2(b) have the dimension of the number of basis functions of the \( \text{F} + \text{H}_2 \) arrangement plus the number of basis functions of the \( \text{H} + \text{HF} \) arrangement, but not twice the number of \( \text{H} + \text{HF} \) basis functions as would be the case without symmetry decoupling. Since the number of HF states is much
greater than the number of H\textsubscript{2} states, the dimension of all the matrices is about half of what it would be without this symmetry decoupling. All other aspects of the calculation are identical to those in Ref. 2(b).

Figure 1 shows the reaction probabilities for total angular momentum \( J = 0 \), as a function of total energy \( E \) (relative to the bottom of the reactant potential energy surface). The initial state of H\textsubscript{2} is \( \nu = j = 0 \), and the final vibrational states of HF are indicated in the figure; the reaction probabilities are summed over final rotational states of HF. The corresponding numerical values are given in Table I. The dominance of \( \nu_{HF} = \nu_{j} = 2 \) in the low energy region is well known experimentally.\textsuperscript{5}

The present calculations used the Muckerman\textsuperscript{6} 5 potential energy surface. The basis set\textsuperscript{7} was (12, 10, 8, 6, 4) for H\textsubscript{2}, and (22, 18, 14, 10, 7, 4, 3) for HF, for a total of 110 rovibrational states. The number of distributed Gaussians\textsuperscript{7} for the translational basis was 31 for the F + H\textsubscript{2} arrangement and 32 for the H + HF arrangement. Smaller basis sets were used in various convergence tests, and indications are that the larger reaction probabilities are converged to at least a few percent and the smaller ones to at least the fourth decimal place. More specifics of this will be described in a fuller publication.

There is qualitative agreement of the present results with earlier calculations by Redmon and Wyatt,\textsuperscript{8} but it is far from quantitative; the squares and circles in Fig. 1 show their results for \( \nu_{HF} = 2 \) and 3, respectively. Though based on the Muckerman 5 potential energy surface, the calculations of Ref. 9 actually incorporated a variety of approximations to make them tractable; the most serious of these is probably the neglect of even-\( j \)-odd \( j \) rotational coupling in HF product channel. Agreement with collinear calculations\textsuperscript{10} on this same potential surface is only very qualitative, casting serious doubt on the usefulness of collinear calculations for this reaction.

The present calculations are intended to provide benchmark results for the three-dimensional version of this important reaction, with a simple but reasonable potential energy surface. It is important at this early stage to demonstrate that theory can in fact produce quantitative reactive scattering results for a given potential energy surface. Once this is clear, it will be more worthwhile to concentrate future calculations, e. g., for \( J > 0 \), on more realistic potential surfaces.\textsuperscript{11}

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\textsuperscript{7}This notation means inclusion of H\textsubscript{2} rotational states up to \( j = 12 \), 10, 8, 6, 4 for H\textsubscript{2} vibrational states \( \nu = 0, 1, 2, 3, 4 \), respectively, and inclusion of HF rotational states up to \( j = 22, 18, \ldots \), 3 for HF vibrational states \( \nu = 0, 1, \ldots, 6 \), respectively.
\textsuperscript{9}(a) M. J. Redmon and R. E. Wyatt, Int. J. Quantum Chem. 58, 403 (1975); (b) 118, 343 (1977); (c) Chem. Phys. Lett. 63, 209 (1979).

Table I. Three-dimensional F + H\textsubscript{2} \rightarrow H + FH reaction probabilities for \( J = 0 \), from \( \nu_{HF} = 0 \) \( \rightarrow \nu_{j} \) summed over \( j \).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\( E_{\text{rel}} \) (eV)* & \( \nu_{j} = 0 \) & \( \nu_{j} = 1 \) & \( \nu_{j} = 2 \) & \( \nu_{j} = 3 \) \\
\hline
0.28 & 8.9 (–7)* & 7.1 (–6) & 1.2 (–4) & 8.9 (–6) \\
0.29 & 1.1 (–5) & 7.2 (–5) & 1.2 (–3) & 8.9 (–6) \\
0.30 & 6.9 (–5) & 4.1 (–4) & 6.7 (–3) & 2.3 (–4) \\
0.31 & 3.1 (–4) & 1.7 (–3) & 2.8 (–2) & 2.0 (–3) \\
0.32 & 1.3 (–3) & 5.7 (–3) & 9.5 (–2) & 9.3 (–3) \\
0.33 & 4.9 (–3) & 1.5 (–2) & 2.7 (–1) & 4.0 (–2) \\
0.34 & 1.2 (–2) & 2.8 (–2) & 5.3 (–1) & 8.6 (–2) \\
0.35 & 1.6 (–2) & 3.4 (–2) & 6.2 (–1) & 1.3 (–1) \\
0.36 & 1.9 (–2) & 3.2 (–2) & 5.6 (–1) & 1.5 (–1) \\
0.37 & 1.7 (–2) & 3.0 (–2) & 4.9 (–1) & 1.4 (–1) \\
0.38 & 1.4 (–2) & 2.7 (–2) & 4.0 (–1) & 2.4 (–1) \\
0.39 & 1.4 (–2) & 2.5 (–2) & 3.4 (–1) & 2.6 (–1) \\
0.40 & 1.5 (–2) & 2.4 (–2) & 3.0 (–1) & 2.6 (–1) \\
0.41 & 1.5 (–2) & 2.5 (–2) & 2.5 (–1) & 2.8 (–1) \\
0.42 & 1.7 (–2) & 2.7 (–2) & 2.2 (–1) & 2.8 (–1) \\
0.43 & 1.9 (–2) & 3.0 (–2) & 2.1 (–1) & 2.8 (–1) \\
0.44 & 2.3 (–2) & 3.5 (–2) & 2.3 (–1) & 2.9 (–1) \\
0.45 & 2.9 (–2) & 4.3 (–2) & 2.6 (–1) & 3.0 (–1) \\
0.46 & 3.5 (–2) & 5.0 (–2) & 3.3 (–1) & 3.0 (–1) \\
0.47 & 4.0 (–2) & 5.6 (–2) & 4.1 (–1) & 3.0 (–1) \\
0.48 & 4.1 (–2) & 5.4 (–2) & 4.6 (–1) & 3.0 (–1) \\
0.49 & 4.1 (–2) & 5.0 (–2) & 4.7 (–1) & 2.8 (–1) \\
0.51 & 4.1 (–2) & 4.6 (–2) & 4.5 (–1) & 2.1 (–1) \\
0.52 & 3.8 (–2) & 5.1 (–2) & 4.3 (–1) & 2.0 (–1) \\
\hline
\end{tabular}
\caption{Three-dimensional F + H\textsubscript{2} \rightarrow H + FH reaction probabilities for \( J = 0 \), from \( \nu_{HF} = 0 \) \( \rightarrow \nu_{j} \) summed over \( j \).}
\end{table}

\*\( E_{\text{rel}} \) is measured relative to the F + H\textsubscript{2} potential asymptote.
\*\textsuperscript{b}The number in parentheses is the power of 10 that the preceding number should be multiplied by.