Quantum reactive scattering calculations of Franck–Condon factors for the photodetachment of $H_2F^-$ and $D_2F^-$ and comparisons with experiment

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Received 15 April 1991; in final form 8 May 1991

The nuclear Franck–Condon factor for the photodetachment processes $H(D)F^+ + h\nu \rightarrow H(D)F + e^-$, $H(D)F + H(D) + e^-$ for $J=0$ has been calculated using the $S$-matrix Kohn variational method for reactive scattering on the T5a potential energy surface. The positions of peaks in the spectra of our theoretical calculations are in excellent agreement with those found in the recent experiment of Weaver and Neumark. The width of the main peak in the spectrum of $H_2F^-$ matches perfectly with the experimental one, but the width of the main peak for the $D_2F^-$ is narrower than the experiment.

1. Introduction

Photodissociation and other half-collision experiments, such as photodetachment of negative ions that produce unstable neutral species, provide an attractive means to investigate reaction dynamics of molecular systems. The primary advantage of studying these processes, from a dynamical point of view, is that one eliminates the need of averaging over partial waves (impact parameters) which is inherent in a full-collision experiment that measures reaction cross sections. As a result of this unfolding of partial waves, one can often obtain some detailed dynamical information which would otherwise be difficult to obtain from a collision experiment. For example, dynamical resonances are usually difficult to detect by measuring the energy dependence of integral cross sections because the resonance energy depends on total angular momentum, with the result that the sum over partial waves (i.e. angular momentum) tends to average out the resonance structure (cf. inhomogeneous broadening) [1]. Another major difference between a half-collision experiment and a full-collision experiment is that dynamics in the former are mainly determined by the Franck–Condon overlap which is restricted in a small region, while the dynamics in the latter are determined by the global features of the potential surface. Thus we can roughly classify the former as the local detection method, and the latter as the global detection method, although global features of the potential surface can also be assessed in the half-collision experiment by examining the product state distribution of the fragments.

However, in molecular photodissociation, reaction occurs on excited electronic potential energy surface(s), while most bimolecular reactions in which we are interested occur primarily on the ground potential energy surfaces. Recent photodetachment experiments by Neumark and co-workers [2–4], in which photodetachment of negative ions such as $\text{CHCl}^-$, $\text{IHI}^-$, and $\text{H}_2\text{F}^-$, produces unstable neutral complexes which subsequently dissociate, provide a useful method to investigate the bimolecular reac-
tion dynamics in the vicinity of the transition state region on the ground potential energy surface. As in photodissociation processes, the photodetachment process is essentially governed by the nuclear Franck-Condon overlap integral between the bound state wavefunction of the anion and the reactive scattering wavefunction of the neutral system. Such experiments directly probe the transition state region and are thus expected to be sensitive to the features of the potential energy surface and the dynamics in the vicinity of this region. The comparison between experiment and theoretical calculation can therefore provide some detailed insight into the nature of dynamics in the transition state region, such as dynamical resonances. The primary theoretical task is computation of the reactive scattering wavefunction. However, because the bound state wavefunction has well-defined total angular momentum (usually \(J=0\) or very small), one needs to carry out the reactive scattering calculation only for \(J=0\) or possibly a few values of total angular momenta \(J\). Thus the amount of computing is greatly reduced compared to the computation of reaction cross sections which normally requires scattering calculations up to very high \(J\). Theoretical calculations of photoelectron spectra of \(\text{ClHCl}^-\) have been carried out by Schatz [5], and of \(\text{IHI}^-\) by Schatz [6] and Gazdy and Bowman [7], and useful insights have been gained by comparisons of these calculations with the corresponding experiments [2,3].

The \(\text{F} + \text{H}_2\) reaction has been extensively studied both experimentally and theoretically for many years, but rigorous three-dimensional reactive scattering calculations for this reaction have only occurred during the past few years [8–16]. Most recently, converged integral cross sections have been reported [17–19] for this reaction using the T5a potential energy surface of Truhlar and co-workers [20]. The T5a potential surface is a rather elaborate surface based on high-level ab initio calculations, and approximate quantum dynamics calculations using the bending corrected rotating linear model (BCRLM) on this surface reproduce some features of the experimental angular distribution [21]. Nevertheless, both reaction probabilities for total angular momentum \(J=0\) [9,10,12,13–16] and cross sections [17,19] obtained from exact quantum calculations predict \(\text{HF}(\nu=3)\) to be the dominant product while experiments [22] have shown that \(\text{HF}(\nu=2)\) dominates. It thus appears that the T5a potential surface needs modification in order to produce the correct vibrational branching ratio.

Our earlier calculations of the Franck-Condon factor for \(\text{H}_2\text{F}^-\) photodetachment [9] were in reasonable agreement with the experiment of Neumark and co-workers [4] but the experimental spectrum was much broader. Since then, Weaver and Neumark [23] have obtained new experimental spectra for \(\text{H}_2\text{F}^-\), \(\text{D}_2\text{F}^-\) and \(\text{HDF}^-\) using a different polarization for the photodetachment laser. The new experimental photoelectron spectrum of \(\text{I}_2\text{F}^-\), in which the contribution from transitions to excited \(\text{F} + \text{H}_2\) surfaces is largely eliminated, is in much better agreement with our previous calculation. In this paper, we report new calculations for the \(\text{H}_2\text{F}^-\), extending the energy to below the threshold of the \(\text{F} + \text{H}_2\) arrangement and to higher energies where a fourth peak was identified in the experimental spectrum. Reactive scattering calculations have also been carried out for the \(\text{F} + \text{D}_2\) system for total scattering energies up to 0.68 eV. Transition probabilities for the reaction \(\text{F} + \text{D}_2 \rightarrow \text{DF} + \text{D}\) are shown and are compared to a previous calculation by D'Mello et al. [24,25]. The Franck-Condon factor for the photodetachment of \(\text{D}_2\text{F}^- + h\nu \rightarrow \text{F} + \text{D} + e^-\). \(\text{D} + \text{DF} + e^-\) is presented and compared with experiment. All the calculations we report in this paper are for total angular momentum \(J=0\) for both the \(\text{H}_2\text{F}^-\) and \(\text{D}_2\text{F}^-\) systems.

2. Methods and calculations

The nuclear Franck-Condon factor for the photodetachment process of an anion yielding a specific final state \(n\) is given by

\[ P_n(E) = |\langle \chi | \psi_{Fn} \rangle|^2, \tag{1} \]

where \(|\chi\rangle\) is the bound state wavefunction of the anion and \(|\psi_{Fn}\rangle\) is the full reactive scattering wavefunction whose asymptotic internal state is labeled by \(n\) (which also includes rearrangement channel labels). The total Frank-Condon factor, regardless of the final state \(n\), is given by summing over the channel index \(n\),

284
\[ P(E) = \sum \langle \chi | \psi_{En} \rangle \langle \psi_{En} | \chi \rangle \]
\[ = -\frac{1}{\pi} \text{Im} \langle \chi | G^+(E) | \chi \rangle, \]  
(2)

where \( G^+(E) \) is the full Green function for the neutral system. The bound state wavefunction \( \chi \) is chosen to be the same as we used in ref. [9] and the equilibrium parameters are those from Simons' calculation [26]. The reactive scattering calculations are carried out using the \( S \)-matrix Kohn variational method [27]. The reader is referred to ref. [9] for details regarding the evaluation of eq. (2). For the \( F^+H_2 \) reaction, all the parameters in our current calculation are essentially the same as those used in a recent calculation of cross sections by one of the authors [19]. However, the current calculation extends the energy from 0.02 eV (below the threshold for the \( F^+H_2 \) arrangement) to 0.88 eV in order to cover the entire spectrum from the experiment. A slightly larger basis set has been used in the \( F^+H_2 \) calculation for energies between 0.60 and 0.88 eV.

For the \( F^+D_2 \) reaction, we employed a primitive basis set \(^{31}\) of \((14, 12, 10, 8, 6, 4) \times 19\) for the \( \Gamma I D_2 \) arrangement and \((26, 26, 24, 19, 14, 9, 6) \times 23\) for the \( D+DF \) arrangement in our production runs. These primitive basis functions are then contracted quasidiabatically to generate new basis functions that are selected by an energy cutoff using the scheme presented in ref. [28]. The standard energy cutoff \( E_{\text{cut}} = \alpha E \) is not very effective for energies close to zero (or negative), however, so we used a modified form \( E_{\text{cut}} = \alpha (E + E_0) \). The parameter \( \alpha = 1 \) and \( E_0 = 0.45 \) eV were used for the production runs, which produces overqualified quasidiabatic basis sets for calculations at low energies. The actual number of quasidiabatic basis functions used in scattering calculation differs for each scattering energy and ranges from about 2200 to 3100 for energies ranging from 0.02 to 0.68 eV. The bound state wavefunction \( \chi \) must of course be modified for the \( D_2F^- \) system because normal mode frequencies are different due to isotope effects. We used the same (linear) equilibrium geometry as for \( H_2F^- \) and scaled the frequencies appropriately for the masses of \( D_2F^- \).

3. Results and discussion

The results for the \( H_2F^- \) system are shown in fig. 1 in which the top figure (fig. 1a) shows the energy dependence of the reaction probabilities \( P_{v=00} \) from the ground state of \( H_2 \) to vibrational state \( v \) of the product \( HF \) for \( v=2, 3, 4 \) (summed over final rotational states), while the bottom figure (fig. 1b) shows the total Franck–Condon factor as a function of scattering energy. We can basically identify four peaks at energy of 0.285, 0.33, 0.44, and 0.80 eV. Our earlier calculation for this system included energies up to 0.53 eV and enabled us to identify the first three peaks [9]. As is shown in ref. [9], the first peak at 0.285 eV is associated with \( v=2 \) state of the HF fragment in the \( H^+F \) arrangement, while at high energies the dominant contribution to the Franck–Condon factor is from the \( F^+H_2 \) arrangement channels. It is also clear from fig. 1 that the peak at 0.285 eV in fig. 1b correlates perfectly with the small resonance peak in the \( P_{v=2-00}(E) \) transition probability. It is very interesting to note that a small resonance peak in the transition probability can produce a prominent peak in the Franck–Condon factor. The fourth peak at about 0.80 eV, which was outside the energy range of our earlier calculation [9], is evident in our current calculation even though the intensity is very weak.

For the \( F^+D_2 \) reaction, D'Mello et al. [24] have recently calculated reaction probabilities for \( J=0 \) in the energy range 0.1925–0.4 eV. We carried out reactive scattering calculations for \( J=0 \) in the energy range 0.02–0.68 eV. Fig. 2a shows a comparison of our results to those of ref. [24] for reaction probabilities from the ground state of \( D_2 \) to the two final vibrational states \( v=3 \) and 4 of DF. The two calculations are in excellent agreement with each other, which provides some assurance that our calculations are correct.

The Franck–Condon factor for the photodetachment of \( D_2F^- \) is shown in fig. 2b together with the reaction probabilities \( P_{v=00} \) in fig. 2a for the three dominant final vibrational states of \( v=2, 3, 4 \). As with \( H_2F^- \), we can basically identify four peaks at 0.18,
0.235, 0.295 and 0.57 eV, although the peaks at 0.18 and 0.57 eV are very weak. By examining the state-specific Franck-Condon factor in the vicinity of 0.18 eV, we find that this first small peak comes from the contribution of the \( v=3 \) state of the fragment \( \text{DF} (v=3) + \text{D} \); it lies just below the threshold energy of \( \text{DF} (v=4) \) and also below the opening of the \( \text{F}+\text{D}_2 \) arrangement. The overall FC factors at energies above 0.20 eV are dominated by the \( \text{F}+\text{D}_2 \) fragment states. This is very similar to the \( \text{H}_2\text{F}^- \) situation in which the first peak corresponds to the fragment \( \text{HF} (v=2) + \text{H} \) and lies just below the threshold energy of \( \text{HF} (v=3) \). However, in the \( \text{F}+\text{H}_2 \) system, the resonance energy corresponding to this peak is above the threshold of the \( \text{F}+\text{H}_2 \) arrangement and thus it shows up in the energy dependence of reaction probabilities for \( \text{F}+\text{H}_2 (00) \rightarrow \text{HF} (v=2) + \text{H} \).

But in the \( \text{F}+\text{D}_2 \) system, the resonance energy at 0.18 eV is below the energy threshold of the \( \text{F}+\text{D}_2 \) arrangement and thus does not show up in the \( \text{F}+\text{D}_2 (00) \rightarrow \text{DF} (v=3) + \text{D} \) reaction probability. One might expect that it would show up in the \( \text{D}+\text{DF} \rightarrow \text{DF} (v=3) + \text{D} \) transition probability. This observation also presumably explains why the intensity of this lowest energy peak in the Franck-Condon factor is much weaker for \( \text{D}_2\text{F}^- \) than for \( \text{H}_2\text{F}^- \); since the scattering wavefunction for the \( \text{D}_2\text{F}^- \) case is restricted primarily to the \( \text{D}_2 \text{F} \) arrangement, it has poor overlap with the anion wavefunction \( \chi \) which is located in the \( \text{D}_2 + \text{F} \) arrangement.

Finally, in fig. 3 we compare our theoretical calculations with experimental results of Weaver and Neumark [23] for the photodetachment of \( \text{H}_2\text{F}^- \) and \( \text{D}_2\text{F}^- \). We used the relation \( \epsilon = 1.272 \text{ eV} - E \) for the
Fig. 2. Same as fig. 1 except for D$_2$F$^-$ system. The plus signs and the stars in (a) are the results from ref. [24].

H$_2$F$^-$, and $\varepsilon = 1.14$ eV $- E$ for the D$_2$F$^-$, where $\varepsilon$ is the electron kinetic energy, such that the main peaks in both systems from theoretical calculations match exactly with experimental ones. For the H$_2$F$^-$ spectrum in fig. 3a, the positions of the four peaks from our theoretical calculation match very well with the four experimental peaks identified by A, B, C, and D. The width of the main peak (peak B) is in excellent agreement with experiment. The only significant discrepancy is in the region of high electron energies in which the theoretical peak A is very narrow and the FC factor decays to zero rapidly as electron energy $\varepsilon$ increases beyond 1.0 eV, while the decay of the experimental intensity occurs at an electron energy about 0.05 eV higher. The fast decay at high $\varepsilon$ is understood theoretically because the F+H$_2$ arrangement becomes closed at about 1.0 eV, so that the only open channels are in the H+HF arrangement, the scattering wavefunctions of which have very poor overlap with the anion wavefunction $\chi$ (which is localized in the H$_2$+F arrangement). It is plausible that the discrepancy with experiment may arise from internal excitation of the anion which is not included in the theoretical calculation.

Similarly for the D$_2$F$^-$ system in fig. 3b, the positions of the three peaks are in excellent agreement with the experimental ones. Of course the additional small peak at $\varepsilon = 1.14$ eV is very difficult to detect experimentally (if it exists). The largest discrepancy in the D$_2$F$^-$ spectrum is that the width of the main peak from the theoretical calculation is much narrower than the experimental one.

The overall good agreement between theory and experiment for H$_2$F$^-$ and D$_2$F$^-$ photoelectron spec-
Fig. 3. Comparison of theoretically calculated Franck-Condon factor to experimentally measured intensity of Weaver and Neumark [23], for the photodetachment processes of (a) H$_2$F$^-$ and (b) D$_2$F$^-$. 

tra provides a plausible suggestion that the T5a potential surface may be correct in the vicinity of the saddle point, particularly in the region of F + H$_2$ arrangement, and modifications are mainly needed in the region of H + HF arrangement in which energy distribution among various rovibrational states of HF occurs in order to produce the correct vibrational branching ratio of the product HF.

Acknowledgement

This work has been supported by the Camille and Henry Dreyfus Foundation, the National Science Foundation under Grant CFE89-20690, and the Air Force Office of Scientific Research under Grant No. AFOSR-91-0084. Numerical calculations were performed on an IBM RISC system/6000-540 at the Chemistry Department of New York University.

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