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The reactions \( F + \text{CH}_3\text{OH} \rightarrow \text{HF} + \text{CH}_3\text{O} \), \( F + C_2\text{H}_5\text{OH} \rightarrow \text{HF} + C_2\text{H}_5\text{O} \), and \( F + \text{OH} \rightarrow \text{HF} + O \) are studied by photoelectron spectroscopy of the negative ions \( C_2\text{H}_5\text{OH}^- \), \( C_2\text{H}_5\text{O}^- \), and \( \text{OH}^- \). In each case, photodetachment accesses the transition-state region for direct hydrogen abstraction. The photoelectron spectra exhibit resolved vibrational structure which is sensitive to details of the potential surface in the transition-state region. To aid in the interpretation of the spectra, ab initio equilibrium structures, harmonic frequencies, and hydrogen bond dissociation energies are calculated for the ions \( C_2\text{H}_5\text{OH}^- \) and \( \text{OH}^- \). The anharmonic hydroxyl hydrogen stretching potential is also calculated for the two ions. Using the calculated ion properties and the fitted ab initio reaction surfaces of Sloan et al. (J. Chem. Phys. 1981, 75, 1190), a two-dynamical dimensional simulation of the photoelectron spectrum of O\( ^* \)H\( ^* \) is presented and modifications to the reaction surfaces are discussed. The spectra of the alcohol complexes are discussed in light of this simulation, and the role of the "bath" degrees of freedom in these spectra is considered.

### Introduction

During the past several years, considerable progress has been made toward the spectroscopic characterization of the transition state in simple chemical reactions. An array of frequency techniques has been developed which allows one to directly probe the transition-state region of the potential energy surfaces describing these reactions. These experiments are aimed at achieving a better understanding of the microscopic forces that govern the dynamics of bimolecular and unimolecular reactions.

One of the more promising approaches to this problem has been to photodetach a stable negative ion in order to form an unstable neutral complex in the vicinity of the transition state for a chemical reaction. For example, in a study of a unimolecular transition state, Lineberger and co-workers used photoelectron spectroscopy of \( C_2\text{H}_5^- \) to investigate the unstable vinylidene radical, which rapidly isomerizes to acetylene. In an experiment that serves as a precursor to the work described here, Brauman and co-workers used photoelectron spectroscopy of \( C_2\text{H}_5- \) to investigate the unstable vinylidene radical, which is sensitive to details of the potential surface in the transition-state region. To aid in the interpretation of the spectra, ab initio equilibrium structures, harmonic frequencies, and hydrogen bond dissociation energies are calculated for the ions \( C_2\text{H}_5\text{OH}^- \) and \( \text{OH}^- \). The anharmonic hydroxyl hydrogen stretching potential is also calculated for the two ions. Using the calculated ion properties and the fitted ab initio reaction surfaces of Sloan et al. (J. Chem. Phys. 1981, 75, 1190), a two-dynamical dimensional simulation of the photoelectron spectrum of \( O^* \text{H}^* \) is presented and modifications to the reaction surfaces are discussed. The spectra of the alcohol complexes are discussed in light of this simulation, and the role of the "bath" degrees of freedom in these spectra is considered.

### TABLE I: Hydrogen Abstraction Reactions of Fluorine

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H_{298}^\circ ) (kcal/mol)</th>
<th>( \Delta S_{298}^\circ ) (cal/mol K)</th>
<th>( k_{298} ) (10^-11 cm^3 s^-1)</th>
<th>( E_v ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F + H-( \text{O}^* )</td>
<td>-34.0</td>
<td>-34.0</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>F + H-OCH( _3 )</td>
<td>-32.2</td>
<td>-32.6</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>F + H-OCH( _2\text{H} )</td>
<td>-32.0</td>
<td>-32.3</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>F + H-H</td>
<td>-32.1</td>
<td>-32.1</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>F + H-( \text{OH} )</td>
<td>-17.2</td>
<td>-17.5</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>F + H-CH( _2\text{OH} )</td>
<td>-42.2</td>
<td>-42.9</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>F + H-CH( _3\text{OH} )</td>
<td>-43.2</td>
<td>-43.9</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

### Reference


The exothermicities for these reactions are given in Table 1. Both reactions 1 and 2 are very fast at room temperature: \( k_{\text{tot}} = 1 \times 10^{10} - 2 \times 10^{10} \text{ cm}^3 \text{ s}^{-1} \). There is a considerable range \( 1^{11,16} \) of reported branching ratios. \( 1^{14} \) However, there is a consensus that the reaction 2 proceeds with more than the statistical 25% of total product at room temperature, and this fraction may be as high as 80% \( 1^{13} \). For F + C2H5OH, there are three channels available. If the fluorine attack were completely non-site-specific, one would expect a branching ratio in F + C2H5OH of 18% for C2H5O formation. As with methanol, the reported branching ratios \( 1^{17} \) indicate that fluorine abstracts at the hydroxyl group faster than at the methyl or methylene groups. Khatoon’s work, \( 1^{17} \) using isotopically labeled reactants and a mass spectrometric detection scheme, indicates that the probability of abstraction of a particular hydrogen by fluorine is 5 times more likely at the hydroxyl site than at one of the alkyl sites, for both methanol and ethanol. This preference in both reactions is interesting since the CH2O and C2H5O product channels are less exoergic by 10 kcal/mol (see Table 1). As we shall see, our experimental data addresses the dynamics of the hydroxyl hydrogen abstraction channel only.

The energy disposal in both products of reaction 1 can be measured: the HF produced by infrared chemiluminescence and the CH2O product by laser-induced fluorescence. This has been used in a series of experiments \( 1^{11,15,16,19} \) to determine, in detail, how the partitioning of energy compares to results for the well-characterized triatomic F + HX reactions (X = halogen). \( 2^{10} \)
The results indicate that, for the F + CH2OH reaction, the presence of a large number of product degrees of freedom has a small but noticeable effect on overall energy disposal, in comparison to the F + HX reactions. The fraction of available energy appearing as HF vibrational excitation is slightly less than in the F + HX reactions, and about 2% of the available energy appears as vibrational excitation of the \( v_2 \) mode (C–O stretch) of the CH2OH radical. The single chemiluminescence study of F + CH2OH suggests similar behavior for this system. \( 2^{11} \) Thus, one expects the potential energy surfaces for both the F + CH2OH and F + C2H5OH reactions to share important features with the F + HX surfaces, particularly a small entrance channel barrier to reaction.

The reaction of fluorine with hydroxyl has been less well studied. Possible reactions of F with OH are

\[
\begin{align*}
F + \text{HO} &\rightarrow \text{HF} + \text{O}^0(\text{P}) \\
F + \text{OH} &\rightarrow \text{HF}^\ast + \text{HF} + \text{O}^0(\text{P}) \\
&\rightarrow \text{HF} + \text{O}^0(\text{D}) \\
F + \text{HO} &\rightarrow \text{HF} + \text{O}^0(\text{D}) \\
\end{align*}
\]

In (3) and (5) fluorine directly attacks the hydroxide end of the hydoxyl; (3) proceeds on a triplet surface and is exothermic by 34 kcal/mol, while (5), which is 11 kcal/mol endothermic, occurs on a singlet surface. This mechanism is akin to the reactions discussed so far with the alcohols. Reaction 4 involves the radical fluorine atom attacking the oxygen atom, the site of the unpaired electron on OH, and forming vibrationally hot HOF(\( \text{A}^1 \)). This radical–radical recombination should proceed with no barrier. However, a spin-forbidden nonadiabatic transition is then required for HF + O(\( \text{P} \)) production. The overall room-temperature rate constant for reaction of F + OH by all pathways has been measured to be \( 4.1 \times 10^{11} \text{ cm}^3 \text{ s}^{-1} \). \( 2^{12} \)

Sloan and co-workers \( 2^{23} \) have measured product-state distributions from the F + OH reaction. They observed infrared chemiluminescence from product HF vibrational levels up to \( v = 3 \) when reacting F with H2O. The F + H2O reaction is exoergic enough to produce only HF(\( v = 0 \)). The observation of population in higher HF vibrational levels was explained in terms of a secondary reaction, of F with OH produced by the F + H2O reaction, taking place in their chamber. The product vibrational and rotational distributions from the secondary reaction appeared to be statistical. On the basis of this and an ab initio calculation, which predicted a large barrier for (3), the authors concluded that the dominant reaction pathway is via attack of fluorine on the oxygen end of the OH molecule (4) and that HOF is a long-lived intermediate, which decays by a nonadiabatic transition. As we shall show below, the OHF\(^\ast \) photoelectron spectrum is quite sensitive to the barrier for direct abstraction (3), allowing us to test Sloan’s conclusions. This adiabatic pathway for F + OH to yield O(\( \text{P} \)) + HF by direct abstraction is entirely analogous to the alcohol reactions. Thus, we will also use the results on the F + OH system to serve as a model for understanding the CH2OH\(^\ast \) and C2H5OH\(^\ast \) photoelectron spectra.

Our experiment starts with the negative ion analogue of the reaction transition state which we wish to study. It is useful for that ion to be well-characterized. The CH2OH\(^\ast \) anion has been fairly well-studied and was first observed by Riveros in an ion cyclotron resonance (ICR) cell. \( 2^{24} \) In this anion, F\(^\ast \) binds to the hydroxyl hydrogen of CH2OH, since this hydrogen is considerably more acidic than the methyl hydrogens. Larson and McMahon determined the CH2OH\(^{\ast} \) binding energy to be 29.6 kcal/mol. \( 2^{25} \) The proton affinity of CH2O (or the gas-phase acidity of CH2OH) is slightly higher than that of F\(^{28}\) (381.2 versus 371.4 kcal/mol). \( 2^{26} \) This means that F + CH2OH is the lowest dissociation channel for CH2OH\(^\ast \); Jasinski et al. \( 2^{27} \) have experimentally confirmed this by infrared multiphoton dissociation of the ion in an ICR cell. In addition, the relative proton affinities lead one to expect the shared proton in CH2OH\(^\ast \) to lie closer to the O atom than to the F atom in the ion equilibrium structure.

The proton affinity of CH2O (378.1 kcal/mol) \( 2^{28} \) is nearer to, but still higher than, that of F\(^{28}\). Thus, it would be expected that the shared proton in CH2OH\(^\ast \), though still closer to the O than the F atom, would be more evenly shared than in CH2OH\(^\ast \). In agreement with this, the measured binding energy of CH2OH\(^\ast \), 31.5 kcal/mol, \( 2^{29} \) is higher than that of CH2OH. The OHF\(^\ast \) ion has not been observed previously, but since the proton affinity of O\(^{28}\) (382.2 kcal/mol) \( 2^{30} \) is comparable to that of CH2O, one expects binding and structure similar to that of the alcohol complexes, namely OH\(^{\ast} \)F\(^\ast \).

The position of the shared proton in the anion is critical to our photoelectron spectroscopy experiment, since the region of the A + HB potential energy surface accessible via photodetachment
is determined by the ion geometry. For example, we have reported studies of the Br + HI, Cl + HI, and F + HI reactions by photoelectron spectroscopy of BrHF, ClHF, and HF. The proton affinities of Br, Cl, and F are at least 10 kcal/mol greater than that of F. Therefore, we expect R_{OHF} < R_{HF} in the XHF ions. The ions consequently have better geometric overlap with the I + HX product valleys on their respective neutral potential energy surfaces, and this is indeed the region that is probed in the reported photoelectron spectra. This turns out to be the case for all the asymmetric X + HY reactions, where X and Y are halogen atoms.

On the other hand, photodetachment of CH$_3$OF, C$_2$H$_5$OF, and OHF$^-$ should result in considerably better overlap with the F + CH$_3$OH, F + C$_2$H$_5$OH, or F + OH reactant valleys, respectively. This is arguably the most important region of the surface since it includes the barrier along the minimum-energy path. Thus, the significance of the results presented here is twofold. The photoelectron spectra of the ROHF$^-$ and OHF$^-$ ions represent an extension of our "transition-state spectroscopy" method to more complex reactions. Furthermore, the spectra of all three systems allow us to probe a more interesting part of the potential energy surface for the corresponding neutral reaction in comparison to the XHY$^+$ spectra.

In addition to the experimental results, we present ab initio calculations that describe the equilibrium structure, harmonic frequencies, and binding energies of the CH$_3$OF$^-$ and OHF$^-$ ions. A two-dimensional dynamical simulation of the OHF$^-$ photoelectron spectrum is then described, which is used as a starting point for considering modifications to the F + OH reaction potential surfaces. The spectra of the polyatomic systems are discussed, with reference to the OHF$^-$ simulation, and finally the role of the extra degrees of freedom is evaluated.

Experimental Section

The time-of-flight photoelectron spectrometer used in this study has been described in detail elsewhere. Briefly, negative ions are formed by crossing the expansion of a pulsed molecular beam valve with a 1-keV continuous electron beam close to the valve orifice. For production of OHF$^-$, the gas mixture expanded through the valve was N$_2$O with a trace concentration of HF. The OHF$^-$ formation mechanism is probably via dissociative attachment of N$_2$O by slow secondary electrons, N$_2$O + e$^-$ → NO + N$_2$, followed by the clustering process O$^+$ + HF + M → OHF$^-$ + M. The best way we found to make a stable beam of CH$_3$OF$^-$ (or C$_2$H$_5$OF$^-$) was to put a few drops of CH$_3$OH (or C$_2$H$_5$OH) into the pulsed beam valve, which hangs vertically in the source chamber, and pass a 5% N$_2$/He mixture through the valve. Dissociative attachment to N$_2$ gives NO, which then clusters to the alcohol. Under the same expansion conditions, we have obtained vibrational temperatures of 150-300 K for CH$_3$CN$^-$ and rotational temperatures of less than 100 K for SH$^-$ prepared in a similar source.

The ions formed in the source chamber are extracted perpendicular to the molecular beam and injected into a Wiley-McLaren type time-of-flight mass spectrometer. Ions separate according to their masses, and the ion of interest is photodetached by the fifth harmonic of a pulsed Nd:YAG laser (213 nm, 5.825 eV). The photoelectrons produced by this process are ejected into all solid angles, and a small fraction (10$^{-4}$) is collected by a detector at the end of a 1-m field-free flight tube. The flight time of the electrons is recorded and converted into center-of-mass kinetic energy. The energy resolution function of the instrument is given in ref 5; essentially the apparatus' electron energy resolution is 8 meV at 0.65 eV and degrades as $E^{1/2}$ at higher electron kinetic energies.

Results and Analysis

1. Experimental Results. The CH$_3$OH$^-$ and C$_2$H$_5$OH$^-$ photoelectron spectra are shown in Figure 1. The spectra are considerably more complex than the spectra of the triatomic anions we have previously studied. The clearest structural pattern in both spectra are the four regularly spaced steps between 1.2 and 2.8 eV. The labeled arrows (A-D), at 2.69, 2.24, 1.85, and 1.54 eV in Figure 1a and 2.58, 2.18, 1.83, and 1.50 eV in Figure 1b, mark the onset of each step. There are two sharper features, E at 1.15 eV, and F at 1.03 eV, in the CH$_3$OF$^-$ spectrum.

The peaks are labeled in order of increasing internal energy of the neutral complex. The electron kinetic energies (eKEs) are related to the internal energies of the neutral species ($E_i^{(0)}$) by

$$eKE = hv - D_i(ROHF) - EA(F) - \Delta E_i^{(0)} - E_i^{(0)} + E_i^{-}$$

Thus, peaks with highest electron kinetic energy correspond to neutral states with lowest internal energy. In (6), hv is the laser photon energy, 5.825 eV, EA(F) is the electron affinity of fluorine, 3.399 eV, and $D_i(ROHF)$ is the bond dissociation energy of ground-state ROHF$^-$ to form ground-state ROH + F. For $D_i(CH$_3$OHF$^-$), we use the experimental bond dissociation enthalpy, DH$_{298}$, and correct to 0 K using a set of ab initio calculated frequencies (see below); this yields 1.244 eV. For $D_i(C$_2$H$_5$OHF$^-$), we use the experimental bond dissociation enthalpy for this ion, and the same correction to 0 K as calculated for CH$_3$OF$^-$, yielding 1.327 eV. $\Delta E_i^{(0)}$ is the exoergicity for the reaction F + ROH → RO + HF and is given in Table 1. $E_i^{(0)}$ is the energy of the [ROHF] complex relative to ground-state RO + HF. $E_i^{-}$ is the internal energy of the precursor ion ROHF above zero point. As all the anions studied here are expected to be prepared cold, this quantity is assumed throughout to be zero.

The eKE corresponding to $E_i^{(0)} = 0$ is shown by arrows against the axis at 2.60 eV (Figure 1a) and 2.50 eV (Figure 1b).

References

The Journal of Physical Chemistry, Vol. 95, No. 21, 1991 8069

Spectroscopy of the Transition State

Figure 2. Photoelectron spectrum of CH₃ODF⁻ recorded at 213 nm. Arrows as for Figure 1.

Figure 3. Photoelectron spectrum of OHF⁻ recorded at 213 nm. Arrows against the axis indicate energies corresponding to asymptotes for formation of O(³P) + HF, F + OH, and O(⁴D) + HF, in order of decreasing electron kinetic energy.

Arrows indicate the electron kinetic energy corresponding to photodetaching ground-state CH₃OHF⁻ (C₂H₅OH⁻) and forming ground-state HF + CH₃O (C₂H₅O). We refer to these energies henceforth as product asymptotes. The reactant asymptotes, indicated by arrows at 1.18 eV (Figure 1a) and 1.10 eV (Figure 1b), correspond to ground-state F + CH₃OH (C₂H₅OH) formation for which \( E^{ex} = -\Delta E^0 \). All the structure in each spectrum occurs at lower eKE than the product asymptote and is therefore due to states of the neutral complex that can dissociate to HF + CH₃O (C₂H₅O) products. In addition, features in the spectra at lower eKE than the reactant asymptote correspond to states of the complex that can also dissociate to F + CH₃OH (C₂H₅OH) reactants.

The photoelectron spectrum of CH₃ODF⁻ (Figure 2) shows a clear isotope effect. The spectrum shows six steps more closely spaced than those in the CH₃OH⁻ spectrum. This isotope effect suggests that the step structure is due to a vibrational mode of the neutral complex analogous to the \( \nu_4 \) mode seen in the triatomic bialdehyde spectra. The spacing between the steps in Figure 1a,b is less than that between the first few vibrational levels of HF, and the spacing between the second, third, and fourth steps is less than the corresponding levels of the OH stretch in CH₃OH. This "red shift" occurs because the experiment probes the transition-state region where the reacting species are interacting strongly. The H atom vibrates in a shallower potential than in isolated HF or CH₃OH.

The intensity in the CH₃OH⁻ spectrum builds as one moves from the HF + CH₃O product asymptote to the F + CH₃OH reactant asymptote at lower electron kinetic energy. The intensity distribution in the CH₃OH⁻ spectrum is similar, although there is relatively more signal near the HF + CH₃O asymptote. The breadth of all the features in the photoelectron spectra is considerably larger than the experimental resolution. Spectra recorded at 266 nm (4.66 eV, not shown) show the right-most steps in each of the 213-nm spectra with lower electron kinetic energy and therefore higher resolution. Despite this higher resolution, there is no additional structure observed; the step profiles are unchanged.

The photoelectron spectrum of OHF⁻ is shown in Figure 3. The peak positions and widths are listed in Table II. The electron kinetic energies corresponding to the dissociation asymptotes O(³P) + HF (2.43 eV), F(²P⁳/²) + OH(²S₂) (0.95 eV), and O(⁴D) + HF (0.46 eV) are shown in Figure 3, as before, with arrows against the energy axis. These energies are calculated from a relationship similar to eq 6, along with our best ab initio ion binding energy estimate (see below), the exoergicity for reaction 3 in Table I, and the experimental oxygen atomic energy level splittings. Again, all structure observed in the spectrum corresponds to states of the neutral unstable with respect to dissociation to the lowest energy product channel (O(³P) + HF). Moreover, peaks A-D correspond to neutral states which can only dissociate to O(³P) + HF products.

The overall appearance of the OHF⁻ spectrum is clearly very similar to both of the ROHF⁻ spectra. This is an interesting result considering the far fewer vibrational degrees of freedom in the [OHF] complex as well as its different electronic character (see below). However, there are several differences between the OHF⁻ and ROHF⁻ spectra. The onset of structure occurs at almost 0.3 eV lower electron kinetic energy in the OHF⁻ spectrum. Between the product and reactant asymptotes, the OHF⁻ spectrum looks more like a set of broad peaks, in contrast to the step structure seen in the CH₃OH⁻ and C₂H₅OH⁻ spectra. The feature below the reactant asymptote in the OHF⁻ spectrum (labeled E) is much more distinct than any corresponding structure in the other spectra. Finally, the intensity in the OHF⁻ spectrum builds in the same way as the other spectra, but in this spectrum, there is even less intensity at the O + HF product asymptote than at the product asymptote in the CH₃OH⁻ spectrum.

The photoelectron spectra of OHF⁻, CH₃OH⁻, and C₂H₅OH⁻ all show maximum intensity near the asymptote for dissociation into reactants F + OH, F + CH₃OH, and F + CH₃OH rather than the energetically lower product asymptote. This is in sharp contrast to the asymmetric bialytic ions, all of which show maximum intensity at the product asymptote. We can understand the intensity distributions in terms of the qualitative discussion of the ion geometries in the Introduction. Because the proton affinities of O²⁻, CH₃O⁻, and C₂H₅O⁻ are 0.47, 0.42, and 0.29 eV higher than that of F⁻, the hydrogen should lie closer to the O atom than the F atom in all three anions. We therefore expect good Franck-Condon overlap with OH-F or ROH-F configurations of the neutral complex localized in the entrance valley of the reactive potential energy surface. The overall intensity envelope seen in the spectra are in accord with this reasoning. In particular, the observation that the CH₃OH⁻ spectrum has more intensity at the product asymptote than the C₂H₅OH⁻ spectrum is consistent with the higher proton affinity of CH₃O⁻.

It is clear from this discussion that the anion geometry has a significant effect on the photoelectron spectrum. In contrast to

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TABLE II: Estimated Peak Centers and Widths from the Photoelectron Spectra of OHF⁻<sup>b</sup>

<table>
<thead>
<tr>
<th>peak</th>
<th>onset&lt;sup&gt;b&lt;/sup&gt;</th>
<th>center&lt;sup&gt;b&lt;/sup&gt;</th>
<th>width&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.46 (0.01)</td>
<td>2.25 (0.02)</td>
<td>0.35 (0.03)</td>
</tr>
<tr>
<td>B</td>
<td>1.95 (0.02)</td>
<td>1.82 (0.03)</td>
<td>0.31 (0.03)</td>
</tr>
<tr>
<td>C</td>
<td>1.51 (0.02)</td>
<td>1.38 (0.04)</td>
<td>0.30 (0.04)</td>
</tr>
<tr>
<td>D</td>
<td>1.16 (0.02)</td>
<td>1.01 (0.02)</td>
<td>0.30 (0.04)</td>
</tr>
<tr>
<td>E</td>
<td>0.80 (0.01)</td>
<td>0.15 (0.03)</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>0.45 (0.03)</td>
<td></td>
<td>~0.4</td>
</tr>
</tbody>
</table>

<sup>b</sup>Onsets of four highest energy steps are also given. All energies in eV; approximate uncertainties shown in parentheses. Steps are measured at 50% of rising edge. Centers and widths are estimated by a six-Gaussian fit to the photoelectron spectrum. Because bands overlap, the estimated uncertainties are large.

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TABLE III: Ab Initio Geometries and Zero-Point Energies for CH$_3$OHF$^*$ and CH$_3$OH$^*$

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$OHF$^*$</th>
<th>CH$_3$OH$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHF/ RHF</td>
<td>1.004 1.059</td>
<td>0.942 0.964</td>
</tr>
<tr>
<td>MP2/ MP2</td>
<td>1.462 1.373</td>
<td>1.401 1.427</td>
</tr>
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</table>

TABLE IV: Harmonic Frequencies (in cm$^{-1}$), Calculated with 6-31++G** Basis Set, for CH$_3$OHF$^*$

<table>
<thead>
<tr>
<th>Mode</th>
<th>RHF</th>
<th>MP2</th>
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<tbody>
<tr>
<td>$\omega (\alpha')$</td>
<td>3133</td>
<td>3102</td>
</tr>
<tr>
<td>$\omega (\beta')$</td>
<td>3106</td>
<td>3106</td>
</tr>
<tr>
<td>$\omega (\alpha')$</td>
<td>2901</td>
<td>2215</td>
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<tr>
<td>$\omega (\beta')$</td>
<td>1731</td>
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<td>$\omega (\alpha')$</td>
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<td>1156</td>
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<tr>
<td>$\omega (\beta')$</td>
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<td>1178</td>
</tr>
<tr>
<td>$\omega (\alpha')$</td>
<td>1230</td>
<td>1132</td>
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</table>

* Bond lengths are in angstroms and bond angles in degrees.

the bialide ions, no spectroscopic data exist for ROHF$^*$ and OHF$^*$. Therefore, in order to obtain a more quantitative picture of the anions, we have performed ab initio calculations on OHF$^*$ and CH$_3$OHF$^*$ to determine their structure and properties.

2. Ab Initio Calculations: Method and Results. Fully optimized geometries, frequencies, and dissociation energies were calculated for the hydrogen-bonded anions OHF$^*$ and CH$_3$OHF$^*$ at both the Hartree–Fock (HF) and second-order Møller–Plesset (MP2) level of theory. In addition, MP4 level calculations were employed to estimate hydrogen bond dissociation energies. The calculations reported here were performed with the GAUSSIAN 98,29 GAUSSIAN 86,30 and CADDAC41 ab initio packages available at the San Diego Supercomputer Center. The standard 6-31++G** basis set was used throughout; the incorporation of diffuse functions (+) is mandatory for a proper description of these anions. For OHF$^*$, a spin-unrestricted wave function was used to describe both the $^1$I ground and $^2$Σ excited states.

The results of these calculations are summarized in Tables III–VII. For the purposes of analyzing our photoelectron spectra, the most important results are the ion equilibrium geometries, the shape of their potential surfaces along the hydroxyl hydrogen stretching coordinate, and the ab initio estimate of their dissociation energy into F$^*$ and OH or CH$_3$OH. For the last of these, an estimate of the zero-point energy correction is required, so frequencies were calculated for the hydrogen-bonded ions and the product fragments at both the HF and MP2 level of theory. All energies quoted ($E_0$) include this zero-point energy correction, which is applied at the same level of theory as the calculated energy (except for the MP4 energies where the MP2 zero-point energies are used). MP4 electronic energies include all single, double, triple, and quadruple excitations while maintaining a frozen core (MP4SDTQ-FC); the MP2 energies have all electrons considered for correlation (MP2-FULL). The calculation of the ion force field, apart from providing zero-point energies, was also useful for (a) obtaining a reasonable form for each anion's vibrational normal coordinates and (b) providing an estimate for the hydrogen bond stretching frequencies in the ions. Both of these will be used in the dynamical calculations described below.

The dissociation fragments of OHF$^*$ and CH$_3$OHF$^*$ that we need to consider are F$^*$, CH$_3$OH$^*$, HF, OH, and O$. Computations of fully optimized geometries and frequencies for these fragments were made using literature values for calculations using similar sized basis sets. The MP2 geometries and frequencies agree well with experimental values for CH$_3$OH$^*$, HF, and OH, and the fluorine electron affinity is well reproduced at the MP2 level. The oxygen electron affinity, calculated at the same level of theory, 1.09 eV, is in poorer agreement with the experimental value of 1.46 eV.30 By calculating the MP2/6-31++G** equilibrium geometry of the Jahn–Teller distorted ground state of CH$_3$OH$^*$ using scaled46 harmonic frequencies from the HF/6-31++G** force fields for ion and neutral, we computed a zero-point-corrected adiabatic electron affinity of 1.47 eV for CH$_3$OH. This is to be compared with the experimental value of 1.57 eV.44

Geometries and Frequencies. Our qualitative expectations for the hydrogen-bonded ion geometries and dissociation energies are based on the proton affinity scale and have been outlined above. We expect that the closer the proton affinity of the bases A$^#$ and B$, the larger the degree of sharing of the proton and the stronger the hydrogen bond in AHB$^-$. From comparison of the proton affinities of the methoxide, hydroxide, and fluoride ions, we expect the hydrogen to be closer to the oxygen than fluorine in both CH$_3$OHF$^*$ and OHF$^*$. The quantitative ab initio results shown in Tables III and VI show that indeed the hydrogen sits closer to the oxygen than the fluorine for both ions. In fact, the equilibrium parameters for the two ions are very similar; the difference in O–F separation is smaller than 0.01 Å, and the hydrogen position is different by only 0.02 Å. However, the ab initio calculations suggest that OHF$^*$ has the hydrogen more centrally located. This last result is contrary to the proton affinity argument, but CH$_3$OH is only slightly more acidic than OH.

The equilibrium geometry for CH$_3$OHF$^*$, which has C$_3$ symmetry, is shown in Figure 4. The F$^-$/CH$_3$OH isomer is expected to lie considerably higher in energy than CH$_3$OH$^*$–F$^-$. The hydrogen bond is slightly bent, as found for F(H$_2$O)$^*$5 and using scaled46 harmonic frequencies from the HF/6-31++G** force fields for ion and neutral, we expect the hydrogen to be closer to the oxygen than fluorine in both CH$_3$OHF$^*$ and OHF$^*$. The qualitative ab initio results shown in Tables III and VI show that indeed the hydrogen sits closer to the oxygen than the fluorine for both ions. In fact, the equilibrium parameters for the two ions are very similar; the difference in O–F separation is smaller than 0.01 Å, and the hydrogen position is different by only 0.02 Å. However, the ab initio calculations suggest that OHF$^*$ has the hydrogen more centrally located. This last result is contrary to the proton affinity argument, but CH$_3$OH is only slightly more acidic than OH.

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qualitative agreement with those shown here, but the earlier treatments were limited to small basis sets without a complete set of diffuse functions and neglected electron correlation.

For AHB species, a pertinent question to ask is whether there are two minima on the potential energy surface, corresponding to AH-B and A'-HB, or whether the two coalesce to form one broad, fairly flat-bottomed minimum. In the case of the symmetric bhalide ions of AHA-, this is extremely important as it determines whether the equilibrium structure is centrosymmetric or not. For example, calculations for CICHCl and BrHBr reveal that a Hartree–Fock description predicts a double-minimum potential for these anions, whereas the inclusion of other electronic configurations in the ground-state wave function leads to a significant lowering of the energy for centrosymmetric geometries compared to the AH-A- geometries. Even using Möller–Plesset perturbation theory to second order (MP2) causes the double-minimum potentials for the AHA- ions to coalesce into a single flat-bottomed minimum. High-resolution spectroscopy studies indicate these anions do, in fact, have centrosymmetric equilibrium structures. For an asymmetric ion such as CH$_3$OH$,^*$ we might expect to find local minima, CH$_3$O$.^-$.^-OHF, as well as the global one described by Figure 4 and Table III. Figure 5 shows a plot of the potential energy as a function of the position of the hydrogen atom between the O and F atoms which are assumed, along with all other degrees of freedom, to be fixed. The plot shows that at the Hartree–Fock level there is evidence of a plateau in the potential corresponding to the CH$_3$O$.^-$.^-HF structure but that it disappears at the MP2 level. The MP2 correction clearly stabilizes geometries with the hydrogen more evenly shared between F and O; the potential shape is distinctly different. This has a large effect on the vibrational level spacings for the "O–H stretch" and the shape of the ground vibrational wave function along this coordinate. This will, in turn, have a profound effect on the intensity

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**TABLE V: Ab Initio Energies for CH$_3$OH$^*$, Including Zero-Point Energies**

<table>
<thead>
<tr>
<th>Method</th>
<th>Total Energy ($E_t$)</th>
<th>ZPE</th>
<th>Frequency ($v$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHF/6-31+G** // RHF/6-31+G**</td>
<td>214.485</td>
<td>1.031</td>
<td>1.286</td>
</tr>
<tr>
<td>MP2/6-31+G**</td>
<td>214.482</td>
<td>1.031</td>
<td>1.286</td>
</tr>
<tr>
<td>MP4/6-31+G** // MP4/6-31+G**</td>
<td>214.480</td>
<td>1.031</td>
<td>1.286</td>
</tr>
</tbody>
</table>

*Zero-point energies calculated from force field evaluated at same level of theory as energy, except for MP4 where MP2 zero-point energies are used.

---

**TABLE VI: Ab Initio Geometry and Frequencies for OHF$^-*$**

<table>
<thead>
<tr>
<th>Method</th>
<th>R(O-H) Å</th>
<th>R(O-HF) Å</th>
<th>ZPE</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHF/6-31+G**</td>
<td>1.031</td>
<td>1.400</td>
<td>180.0</td>
<td>379, (1070, 1227), 2514</td>
</tr>
<tr>
<td>MP2/6-31+G**</td>
<td>1.078</td>
<td>1.346</td>
<td>180.0</td>
<td>433, (1064, 1225), 2015</td>
</tr>
</tbody>
</table>

*R$_O$ (O-H) in the free hydroxyl radical is 0.955 Å (UHF/6-31+G**), 0.973 Å (UMP2/6-31+G**), and 0.970 Å (experimental, ref 37).**

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**TABLE VII: Ab Initio Energies for OHF$^*$, Including Zero-Point Energies**

<table>
<thead>
<tr>
<th>Method</th>
<th>Total Energy ($E_t$)</th>
<th>ZPE</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHF/6-31+G** // UHF/6-31+G**</td>
<td>214.849</td>
<td>0.000</td>
<td>175.212</td>
</tr>
<tr>
<td>MP2/6-31+G** // MP2/6-31+G**</td>
<td>214.842</td>
<td>0.000</td>
<td>175.212</td>
</tr>
<tr>
<td>MP4/6-31+G** // MP4/6-31+G**</td>
<td>214.840</td>
<td>0.000</td>
<td>175.212</td>
</tr>
</tbody>
</table>

*Zero-point energies calculated from force field evaluated at same level of theory as energy, except for MP4 where MP2 zero-point energies are used.

**Figure 4. Calculated geometry for CH$_3$OH$^*$ (top) and OHF$^*$ (bottom). Bond lengths (Å) and angles (deg) are those calculated by full geometry optimization at MP2/6-31+G**.**

---

**Figure 5. Potential energy profile along the hydroxyl hydrogen stretching coordinate in CH$_3$OH$^*$. Cuts are calculated by fixing geometry parameters at the MP2/6-31+G** equilibrium values and varying $R_{OH}$. To simplify calculations, the F–H–O angle is treated as linear (this increases the electronic energy by 2 × 10^{-4} au) and the $R_{OF}$ is fixed at the sum of MP2 equilibrium $R_{OH}$ and $R_{HF}$. CH$_3$OH$^*$ potential variation shown at the HF/6-31+G** level (dashed, for absolute HF energy subtract 214.527 au) and at MP2/6-31+G** (solid, for absolute MP2 energy subtract 215.077 au).**
distribution seen in the photoelectron spectrum.

The calculated harmonic vibrational frequencies for the CH$_3$OHF$^-$ ion are shown in Table IV; $\omega_0$ is the O-H stretching mode which corresponds to the potential function we have been discussing. The harmonic frequency for this mode (2215 cm$^{-1}$) is strongly perturbed from its value in CH$_3$OH (MP2/6-31+G** value 3900 cm$^{-1}$). The F-HOR stretching mode, $\omega_9$, is analogous to $\omega_0$ in the halide ions and OHF$^-$ (see below). These two stretching modes, the O-H stretch and the O-F stretch, are the two modes most important to understanding the photoelectron spectra.

The ab initio results for the ground $^1\Sigma$ state of the OHF$^-$ anion are shown in Table VI and Figure 4. It is clear from the similarity in the equilibrium geometry of this ion and the OHF mobility in CH$_3$OHF$^-$ that the CH$_3$ group has little effect on the hydrogen bond, except to slightly bend it. It is worth noting that, in contrast to CH$_3$:OHF$^-$, OHF$^-$ is open shelled but the spin remains localized on the oxygen atom, as in OH. The spin–orbit splitting in this state is expected to be smaller than the 139 cm$^{-1}$ of OH(2$^1\Sigma$).37

The bending vibration has two components for the linear molecule in a degenerate electronic state. The O-H stretching frequency, 2015 cm$^{-1}$, is significantly higher than that for OHF$^-$ (3900 cm$^{-1}$). Using the MP2 harmonic frequencies of CH$_3$OHF$^-$ (Table IV) and CH$_3$:OHF$^-$, and assuming that the change in the average rotational energy on dissociation is zero, we calculate $\Delta^2P_{O}(2^1\Sigma \rightarrow 1^2\Pi)$ = 1.32 eV (30.4 kcal/mol) at MP2 and 1.29 eV (29.8 kcal/mol) at MP4 compared to the experimental value of 1.28 $\pm$ 0.04 eV (29.6 $\pm$ 1 kcal/mol). It appears that the ab initio estimate is in good accord with the experimental data, placing confidence in the MP4 $D_0^2$ estimate, 1.48 eV (34.0 kcal/mol), for OHF$^-$.

Figure 6. Schematic molecular orbital diagram for OHF$^-$.

3. Simulation of the OHF$^-$ Photoelectron Spectrum. In this section, we simulate the OHF$^-$ photoelectron spectrum using our ab initio results for OHF$^-$ along with the ab initio potential energy surfaces developed for the F + OH reaction by Sloan and co-
It assumes of a linear triatomic AHB. This method, which is based on the all nuclear motion takes place on a collinear potential energy wave packet propagation technique of Kosloff and Kosloff, treats approximation, is the anion ground vibrational wave function, is defines the time autocorrelation function \( C(t) \)
\[
C(t) = \langle \phi(0) \phi(t) \rangle
\]
and the Fourier transform of this complex function yields the photoelectron spectrum.\(^{57,58}\)

The simulation makes use of the collinear ab initio surfaces that have been developed for the lowest triplet and singlet channels of the F + OH system. Sloan and co-workers evaluated energy points across the two surfaces using a multireference configuration interaction (MRCI) scheme, employing the multireference analogue of Davidson’s correction\(^{59}\) to extrapolate energies to full configuration interaction (FCI). To calculate the entire collinear surfaces, the authors were constrained to use of the relatively small 4-31G basis set. The surfaces were each fitted to a rotated Morse oscillator spline (RMOS) function.\(^{60}\) The authors went on to show that the barrier height on the lowest triplet surface remained virtually unchanged when the basis set was improved to double-\(\tilde{Z}\) plus polarization (DZP) quality. We shall first consider only the lowest surface for the collinear reaction \( F(3P) + OH(2\Pi) \rightarrow HF(\Sigma^+) + O(3P) \) for our simulation. This surface has \( \Pi \) electronic symmetry, and a classical barrier of 12 kcal/mol at \( R_{OH} = 1.08 \text{ Å} \) and \( R_{HF} = 1.32 \text{ Å} \).

Together with the neutral potential surface, we also require the wave function for the ground vibrational state of the anion. The wave function is assumed to be separable along the two normal coordinates, \( Q_1 \) and \( Q_2 \). To construct this vibrational wave function, we use our MP2 values for the anion equilibrium geometry (\( R_{HF} \) and \( R_{OH} \)) and frequencies (\( \omega_1 \) and \( \omega_2 \)) for the two stretching vibrations. The following transformation from internal coordinates (in Å) to normal coordinates (in amu\(^{1/2}\), Å) is derived from the ab initio Cartesian force constant matrix:
\[
Q_1 = 2.989(R_{HF} - R^*_{HF}) + 2.747(R_{OH} - R^*_{OH})
\]
\[
Q_2 = 0.198(R_{HF} - R^*_{HF}) + 1.158(R_{OH} - R^*_{OH})
\]
Note that \( Q_1 \approx 3(R_{HF} - R^*_{HF}) \) and \( Q_2 \approx (R_{OH} - R^*_{OH}) \).

In the simulations carried out for the BrHI\(^+\) photoelectron spectrum,\(^{7}\) the experimental intensity distribution was impossible to model without including anharmonicity along the \( Q_1 \) coordinate for the anion. The anion potential surface was therefore described by the sum of a Morse potential for the \( \nu_1 \) mode and a harmonic potential for the heavy atom \( \nu_1 \) stretching mode. For OHF, the MP2 potential energy cut along the \( R_{OH} \) coordinate can be fit to a Morse function; this is shown in Figure 7. The \( R_{HF} \) coordinate is an extremely good approximation to \( Q_2 \) if \( R_{HF} \) is kept fixed, as seen in eqs 10 and 11, so the Morse potential in Figure 7 is assumed to be the potential energy along the \( Q_2 \) coordinate. The one-dimensional fit to this function yields \( \omega = 2015 \text{ cm}^{-1} \) (as expected from Table VI) and \( \omega_X = 350 \text{ cm}^{-1} \). A harmonic potential is constructed along \( Q_1 \) by using the MP2 frequency (433 cm\(^{-1}\)) from Table VI. The required initial wave packet, \( \phi(0) \), is then set equal to the ground vibrational wave function of this anion potential surface.

The simulation is performed by propagating the initial wave packet on a grid in two dimensions, under the influence of the neutral collinear potential surface. The propagation is continued until all flux has left the grid. Absorbing boundaries are imposed at the edges of the grid;\(^{51}\) this device greatly reduces the configuration space the grid must span and, thus, the calculation time. All computational details of the method are contained in ref 7, and the relevant parameters are listed in the figure captions for each simulation. Figure 8 shows the simulated photoelectron spectrum of OHF\(^+\) resulting from wave packet propagation on

\[\text{Intensity}\]
\[\text{Electron Kinetic Energy (eV)}\]

\[\begin{array}{l}
5 \\
4 \\
3 \\
2 \\
1 \\
0
\end{array}\]

Figure 8. Simulated OHF\(^+\) photoelectron spectrum from two-dimensional wave packet propagation on the \( ^{1}\text{II} \) RMOS surface (dashed) superimposed on experimental spectrum (solid). Also shown is the result of a one-dimensional simulation (sticks) described in text. Labels above sticks refer to \( \nu_3 \) quantum numbers (see Figure 11). Both simulations have been shifted by 0.22 eV to higher electron kinetic energy (see text).
the $^3\Pi$ ab initio surface. The result is exact within the collinear approximation.

Figure 9 shows the wave packet dynamics that give rise to this simulation. The potential surface is plotted in the mass-scaled coordinates defined in ref 7; essentially $x = 3R_{OH}$ and $y = R_{OH}$. These coordinates almost exactly parallel the normal coordinates of the ion $Q_2$ and $Q_3$. The first frame (Figure 9a) shows the initial wave packet, corresponding to the anion wave function. The asymmetric shape of the wave packet derives from the pronounced anharmonicity along $Q_2$. The wave packet sits right over the saddle point of the reaction surface (marked in the Figure with a cross), underlying the sensitivity of the photoelectron spectrum to features of the surface at the saddle point and to the magnitude of the barrier height. The initial wave packet also extends into both the reactant valley and around the reaction "corner" into the product valley.

The following frames of Figure 9 show the bifurcation of the wave packet into both valleys; the subsequent disappearance of the wave packet out to fragments is very swift. The component of the wave packet exiting out to $Q(3P) + HF$ has a faster rate of disappearance from the Franck–Condon region than the component traveling down to the entrance valley. The latter component, moving parallel to the $x$ axis and out to $F + OH$, shows little vibrational excitation as compared to that moving in the $Q(3P) + HF$ exit valley, where considerable nodal structure, corresponding to HF vibrational excitation, is seen perpendicular to the direction of motion. In Figure 9d the last component of the wave packet is seen leaving the grid; the shape of the wave packet is distorted here because of the absorbing boundary.

In accord with the extremely fast movement of the wave packet away from its nascent position on the neutral potential energy surface, the autocorrelation function shows very fast decay and evidence of only a weak recurrence. The absolute value of the autocorrelation function, $|C(T)|$, is plotted in Figure 10. The fast fall time is in strong contrast with the long-lived recurrences in the autocorrelation functions calculated for bimolecular photodetachment.7,62,63 The Fourier transform of this autocorrelation function yields a broad, but structured, simulated photoelectron spectrum, and it is this that is shown with the dashed line in Figure 8.

In this simulation, the two low-intensity peaks between the product and reactant asymptotes are from transitions to states of the complex that correlate to different product HF vibrational levels. The single, more intense feature near the reactant asymptote is narrower than the other peaks (fwhm $< 200$ meV versus $\approx 300$ meV). This peak is most likely due to the component of the wave packet moving out along the entrance valley to $F + OH$, which, as noted above, leaves the Franck–Condon region more slowly than that departing along the exit valley.

To confirm these "assignments", we have performed a one-dimensional simulation that treats only the potential along the $y$ or $R_{OH}$ coordinate with the mass-weighted coordinate $x$ fixed at its value for the ion equilibrium geometry, $x_p$. This, to a good approximation, is the effective potential for the hydrogen stretching $r_3$ mode.7 In Figure 11 these one-dimensional potentials for the anion and neutral are shown along with the first few eigenvalues and eigenfunctions supported by each potential. The anion potential is the $^3\Pi$ Morse potential shown in Figure 7; neutral effective potential (upper) is a cut through the $^3\Pi$ RMOS surface at constant $x = x_p$ (see text). Calculated eigenstates are labeled by their $r_3$ quantum numbers.

The two-dimensional peak widths and the spacings in the two-dimensional simulation have $\approx 200$ meV versus $\approx 300$ meV. This, to a good approximation, is the effective potential for the hydrogen stretching $r_3$ mode.7 In Figure 11 these one-dimensional potentials for the anion and neutral are shown along with the first few eigenvalues and eigenfunctions supported by each potential. The anion potential is the $^3\Pi$ Morse potential shown in Figure 7; neutral effective potential (upper) is a cut through the $^3\Pi$ RMOS surface at constant $x = x_p$ (see text). Calculated eigenstates are labeled by their $r_3$ quantum numbers.

The one-dimensional stick spectrum consists of a progression in the $r_3$ mode of the [OHF] complex; the peak labels in Figure 8 correspond to the energy levels in Figure 11. Peaks 0, 1, and 2 result from transitions to the $O + HF$ product (exit) valley, while an inspection of the one-dimensional neutral wave functions (Figure 11) shows that the $v_3 = 3$ level is localized in the $F + OH$ reactant (entrance) valley. Peak 3 in the one-dimensional simulation lines up with the intense peak in the two-dimensional simulation, indicating that the latter is indeed due to a state of the complex localized in the reactant valley. Peaks 0 and 1 apparently correspond to the two peaks in the two-dimensional simulation between the reactant and product asymptotes, although the one-dimensional peaks occur at slightly higher electron kinetic energy. The comparison between the simulations suggests that peak 2 is hidden as a shoulder in the two-dimensional simulation.

The intense peak in the two-dimensional simulation has a definite asymmetry, and it can be readily confirmed that there is an intensity contribution, corresponding to the $v_3 = 2$ stick, on the high electron energy side of this peak. The one-dimensional treatment is approximate in that it does not consider overlap at different values of $y$, and the time scale separation of $x$ and $y$ is strictly only appropriate for extreme heavy–light–heavy systems.5 It is these inadequacies that are presumably responsible for the one-dimensional sticks not coinciding with the centers of the two-dimensional peaks. However, this analysis does provide some insight into the appearance of the two-dimensional simulation.

Let us now compare the simulated and experimental spectra (Figure 8). The two-dimensional peak widths and the spacings of the product progression agree reasonably well with experiment, and the intensity distribution is in qualitative agreement with the experimental profile. The overall agreement between experimental and simulated peak widths is particularly striking as it indicates
that rapid dissociation on a collinear surface can explain the broad experimental peaks. On energetic grounds we assign peaks A–D to states of the [OHF] complex that dissociate to O + HF products. On the basis of one- and two-dimensional simulations, we assign the intense experimental peak at 0.80 eV (E, Figure 3) as a reactant peak: a state of the [OHF] complex that dissociates to F + OH reactants.

However, in Figure 8, the one- and two-dimensional simulations have been shifted by 0.22 eV to higher electron kinetic energy so that the experimental peak E lines up with the most intense simulated peak. An even larger shift would be expected if the simulation had been performed on a comparable three-dimensional potential energy surface rather than the collinear surface used here; this additional shift will be approximately equal to the bending zero-point energy near the saddle point on the three-dimensional surface.6 This bending zero-point energy is estimated to be ~0.05 eV.6 Thus, simulations on a comparable three-dimensional surface would need to be shifted by about 0.27 eV to higher electron kinetic energy. The significance of this shift is discussed in the following section.

In our analysis of the bihalide spectra,6,7 we commented extensively on the role of excited electronic states of the neutral in our photoelectron spectra, and contributions from excited states are likely in the spectra presented here as well. Fitted to the model the contribution of one excited state, the \( \Delta \) state, to the photoelectron spectrum, because a potential energy surface is available for this state.23 We shall defer a full discussion of the electronic structure of this and other excited states until later, but here we show the results of performing an identical simulation, using the RMOS \( \Delta \) surface of Sloan and co-workers, to that described above for the \( ^3 \)II surface. The wave packet dynamics should be quite different on the \( \Delta \) surface, which adiabatically connects F + OH(\( ^3 \)II) to HF(\( ^2 \Sigma^+ \)) + O(\( ^1 \)D). This is an endergonic process for which the barrier is expected to lie on the O(\( ^1 \)D) + HF side of the potential energy surface, and this is borne out by the ab initio calculated surface. Thus, photodetachment to the \( \Delta \) surface should result in less overlap with the saddle point region than photodetachment to the \( ^3 \)II surface.

Figure 12 shows the contribution of the \( \Delta \) simulation to the overall photoelectron spectrum. Both the \( ^3 \)II and \( \Delta \) simulations have been shifted to higher electron kinetic energy by the same 0.22 eV discussed above. The electronic transition dipole moments for transition from ion ground state to the neutral \( ^3 \)II and \( \Delta \) states have been set in the ratio 1:5 to best reproduce experiment, in the absence of any other data. By including the \( \Delta \) state, the simulation now reproduces the broad experimental peak (F) at 0.45 eV. The overall agreement between the simulated and experimental spectra is quite remarkable considering that all potential parameters are the "raw" ab initio ones, including the energy separation between the two electronic-state progressions. This would seem to be strong evidence for the overlapping contribution of excited states in the experimental photoelectron spectrum.

Discussion

1. OHF Photoelectron Spectrum. Let us return to consider the neutral reaction surface that dominates the OHF photoelectron spectrum, the \( ^3 \)II surface. We wish to assess how realistic this surface is and apply what we learn to the fluorine + alcohol reaction surfaces. Although there is qualitative agreement between the simulated and experimental profiles, there are some serious deficiencies. We shall discuss these discrepancies, and some possible causes, in the hope of obtaining a more detailed picture of the neutral potential energy surface in the transition-state region.

The three major areas in which the theoretical fit differs from the experimental spectrum are (i) the number of peaks in the product vibrational progression and their positions relative to the reactant peak, (ii) the large shift required for the entire simulation, and (iii) the intensity distribution of peaks corresponding to product states. These deviations are almost certainly due to deficiencies in the neutral potential energy surface and/or the equilibrium properties of the anion. Because ab initio descriptions of potential minima are known to be predicted to a higher degree of accuracy than points on a global surface far away from minima, we shall make the assumption in the following discussion that the anion structure and dissociation energy have been correctly described and that all changes need to be made to the neutral surface. This is not likely to be completely true but merely reflects the likely relative error bars on the calculations.

One obvious problem is that the reaction exoergicity on the RMOS \( ^3 \)II surface is incorrect. The RMOS fit to the FCI/4-31G exoergicity is 1.198 eV as compared to the experimental value, 1.502 eV. (These figures reflect bottom of the well energies for the diatomic molecules.) Sloan et al. have shown that this problem stems mainly from the basis set used in the ab initio calculation.23 This gross defect is certainly contributing to the absence of any structure in the simulation at electron kinetic energies higher than 2.0 eV (Figure 8). With the surface as is, it is energetically impossible for a state to exist with an energy corresponding to the step at highest eKE in the experimental spectrum. Clearly, in any attempt to improve the simulation by changing the neutral potential energy surface, we shall seek a larger exoergicity and smaller barrier.

The other feature of the F + OH \( ^3 \)II surface that calls for some adjustment is the barrier height. A major discrepancy between the simulation on the RMOS surface and the experimental spectrum was that the simulated band origins had to be displaced to higher electron kinetic energy to get the largest feature (assigned to the reactant channel) to match the experimental peak. For the \( ^3 \)II surface, the saddle point lies in the center of the Franck-Condon region, so lowering the barrier height will shift the spectrum in the required direction. As the shift required, 0.27 eV, is considerably larger than the expected error in the ion binding energy (<0.15 eV), it seems probable that the barrier on the reaction surface is indeed too high.

To show the effect of using a smaller barrier, we have performed two further simulations. We first scaled6 the RMOS surface so as to reproduce the experimental exoergicity; this yielded a surface we shall call RMOS-A. A further round of scaling6 was per-

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(66) This estimate is based on the bending frequency calculated at the saddle point of several three-dimensional LEPS model surfaces that describe the F + HO system and have similar barrier heights to the collinear surface used in the present simulation.
formed on RMOS-A in order to approximately halve the barrier to 0.24 eV (5.5 kcal/mol). This surface we denote RMOS-B. These surfaces are not suggested as optimized potential functions that reproduce our data, but they do demonstrate the result of some very simple improvements over the pure ab initio surface. The simulated photoelectron spectra calculated on each of these surfaces, while ignoring the $^1\Delta$ state, are shown in Figure 13. The changes are significant. The RMOS-A simulation shows three, rather than two, resolved members of the product vibrational progression. In particular, a feature corresponding to experimental peak D now appears. However, the entire simulated spectrum must still be shifted, again to higher electron kinetic energy, to align the simulated reactant peak with the experimental peak E; for this surface the shift is 0.23 eV, or 0.28 eV including the zero point bend correction.

In the RMOS-B simulation (Figure 13b), when including the zero point bend correction, no shift is required to line up experimental peak E with the intense peak in the simulation. Decreasing the barrier height has thus removed the discrepancy between the energetics in the simulated and experimental spectra. The simulated peaks are still quite broad, in agreement with experiment. However, only two product peaks are discernible in the RMOS-B simulation, just as in the first simulation in Figure 8. As in that simulation, the third peak in the product progression is hidden under the intense reactant peak. Essentially, in comparison to the RMOS-A simulation, lowering the barrier has shifted the intense reactant peak to higher electron kinetic energy while not affecting the product peaks, thereby obscuring the third product peak that appeared in the RMOS-A simulation.

One important feature we have not attempted to change is the location of the saddle point on the F + OH surface. This is likely to have a major effect in a simulation. In particular, if the barrier occurred earlier in the F + OH reactant valley, the anion would have better overlap with states of the [OHF] complex that dissociate to O + HF products, and these states would be shifted in energy closer toward the product asymptote.

In any case, the simulation on the RMOS-B surface has shown that a lower barrier can eliminate the need to shift the spectrum. Considering the errors in the calculated ion binding energy and the approximate treatment of the zero point bending energy, we conclude that a realistic barrier height for the $^3\Sigma^+$ surface is in the range 0.09–0.39 eV (2–9 kcal/mol). This result is significant as it implies that even at room temperature direct hydrogen abstraction may compete with the nonadiabatic pathway suggested by Sloan et al.

Is this proposed barrier height reasonable? By comparison to other reactions of fluorine, the original ab initio barrier, 12 kcal/mol, might be considered unreasonably large for an abstraction reaction of this type. In general, ab initio reaction barriers reported are consistently too high, even with what must be considered current state-of-the-art methods. It is very likely that problems of incomplete basis set, and thus errors resulting from basis set superposition error, will be manifested in the raw fitted ab initio surface used here.

The Evans–Polanyi relationship between reaction exoergicity and barrier height states that the larger the exoergicity, the lower and earlier the classical barrier is on the reaction potential surface. This postulate has been well tested for hydrogen abstraction reactions. From this postulate, it would be expected that the reactions studied here would occur on surfaces with barriers comparable with that for F + H$_2$ and smaller than that for F + H$_2$O (see exoergicities in Table 1). Stevens et al. have estimated a 4 kcal/mol barrier for F + H$_2$O; the classical barrier height for F + H$_2$, although subject to some controversy, is currently considered to be 1.4–2.5 kcal/mol. The larger exoergicity for F + OH and F + HOR would seem to indicate that the barriers for direct abstraction for both reactions should be in the range 1–2 kcal/mol. The result of our simulations, while in agreement with a substantially lower barrier than that calculated ab initio for F + OH, seem to suggest a barrier somewhat higher than that predicted by the Evans–Polanyi relationship.

It is to be hoped that an ab initio reaction potential surface of improved quality can be generated which will confirm the lower barrier height for the direct abstraction process. In order to fully model the spectrum, it may be necessary to develop excited-state potential energy surfaces as well. The role of low-lying excited surfaces is explored in section 3 below.

2. CH$_3$OHF and C$_2$H$_5$O HF Photoelectron Spectra. The above discussion and simulations on the F + OH $^3\Sigma^+$ surface serve as a model for understanding the photoelectron spectra of the alcohol complexes. The similarity of the OHF spectrum to those of the polyatomic systems encourages one to think that the effect of the alkyl group is small and that the ROHF spectra can be largely explained by the analysis of the OHF spectrum. In particular, the basic structure of the peak widths observed can be understood in terms of the two-dimensional model above, the differences in intensity distributions in the three spectra are explained by the differing position of the bridging hydrogen in the ion, and the missing low electron energy peak in the ROHF spectra (peak F in the OHF spectrum, Figure 3) is attributable to the differing electronic structure in the [ROHF] and [OHF] complexes (see below).

However, as pointed out above, the features in the ROHF spectra are, in general, broader than those in the OHF spectrum. One could plausibly attribute this to the presence of additional vibrational modes in the polyatomic systems. We would like to examine this more quantitatively to ascertain which, if any, of these vibrational modes play a major role in the appearance of the ROHF photoelectron spectra. We do this by attempting to determine which of the additional modes in the polyatomic ROH and RO fragments are excited subsequent to ROHF photode-
attachment. These are referred to as "bath" modes; in the case of 
CH$_3$OHF photodetachment, these include all the CH$_3$O vibrations 
and all the CH$_3$OH vibrations except the O–H stretch.

We consider which fragment modes are excited solely on the 
basis of the differences between the geometry of the neutral 
complex created by photodetachment and the equilibrium geo-
metric of the fragments. This is a variation of the "Franck-Condon
picture" which has been shown to provide a reasonable zero-order
description of fragment excitation in photodissociation experi-
ments. In the classical picture of photodetachment, the nuclear
configuration of the neutral complex formed is the same as the 
equilibrium geometry of the ion. The displacement of the C, H, 
and O atoms in the [CH$_3$OHF] complex from the equilibrium 
geometry of free CH$_3$OH and CH$_3$O will then lead to vibrations 
in the bath modes of these species. Mapping these displacements 
into changes along each of the normal coordinates of the free
fragment, we can estimate the degree of vibrational excitation 
in each of the fragment modes. As a guide, we shall use the ab
initio changes in bond lengths and angles in the methoxy frame
from CH$_3$OHF to CH$_3$OH and CH$_3$O.

The ab initio calculations (Table III) show that the changes 
in geometry in the CH$_3$O frame between CH$_3$OHF and CH$_3$OH, 
while small, are principally in the C–O bond length and the bond
angles about the carbon atom; the C=OH angle is not dramatically
altered. Further, the calculated MP2 force field of CH$_3$OH gives 
us the normal coordinates for this molecule. By performing the 
transformation of the MP2 internal-coordinate changes into 
CH$_3$OH normal coordinates displacements, we determine which
bath modes receive excitation in this simplified photodetachment
process. The only mode appreciably excited is $r_8$ (CH$_3$ rock), 
whose observed fundamental frequency is 1060 cm$^{-1}$. The degree
of vibrational excitation is, however, still small; if we compute
Franck–Condon factors assuming two harmonic oscillators of the
same frequency modes (Table IV): the frequency 
from CH$_3$OHF to CH$_3$OH and CH$_3$O.

We have already looked at two of these potential energy surfaces
in press.

and some degree of vibrational excitation will be present. In
OHF, the O–F vibration is calculated to have the lowest frequency
($\omega_0 = 433$ cm$^{-1}$), whereas in CH$_3$OHF there are three low-fre-

frequency modes (Table IV): $\omega_0 = 391$ cm$^{-1}$ (O–F stretch), $\omega_1 = 
167$ cm$^{-1}$ (FOC bend), and $\omega_2 = 77$ cm$^{-1}$ (hindered rotation).
Assuming the two anions are formed at the same temperature, the
excitation of the additional low-frequency modes in CH$_3$OHF could
lead to broader features in the photoelectron spectrum.

### Table VIII: Possible Low-Lying Electronic States of [OHF]
Accessed in the Photoelectron Spectrum of OHF

<table>
<thead>
<tr>
<th>State</th>
<th>$\Pi_1$</th>
<th>$\Pi_2$</th>
<th>$\Pi_3$</th>
<th>$\Pi_4$</th>
<th>$\Pi_5$</th>
<th>$\Pi_6$</th>
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<tr>
<td>Energy</td>
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<td>0.0</td>
<td>0.6</td>
<td>2.8</td>
<td>3.3</td>
<td></td>
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<tr>
<td>Intensity</td>
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<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contributions</td>
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<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Spin projected UMP4 energies (see ref 76). 2 MP2/6-31++G**

anion geometry used; see Table VI.
channel hyperspherical (CCH) simulations for the CHCl+ and IHF+ photoelectron spectra. He finds good agreement in the qualitative features. For the bimolecular systems, the assumption of a collinear transition state is more reasonable than it is here. There is considerable evidence that the O(3P) + HCl → OH + Cl reaction proceeds via a bent transition state; Gordon et al. have calculated the saddle point geometry and find αOHCl = 138°. The question then arises whether the collinear IT interaction O(3P) + HF is also unstable with respect to bending and whether a bent transition state is preferred for this reaction also. However, a major difference between the two reactions is that O + HCl is approximately thermonuclear whereas O + HF is endothermic by 34 kcal/mol.

The similarity in the OHF+, CH3OHF+, and C2H5OHF+ spectra indicates that the pseudotriatomic model fairly successfully describes the polyatomic systems' spectra. However, development of theoretical methods of treating polyatomic reaction systems is clearly desirable. Further experiments from this laboratory will be forthcoming on transition-state spectra for tetratomic systems, the results of which should be able to test theoretical methods for such systems.

Acknowledgment. Support from the Air Force Office of Scientific Research under Contract AFOSR-91-0084 is gratefully acknowledged. We thank Professor J. Wright for discussions on the rotated Morse potential surfaces. We thank the San Diego Supercomputer Center for a grant to undertake the ab initio calculations. S. E. B. acknowledges fellowship support from the University of California during the course of the research presented here.

Registry No. Hg, 1333-74-0; F, 14762-94-8; MeOH, 67-56-1; EtOH, 64-17-5; OH+, 3352-57-6; MeOH-F+, 80396-05-0; EtOH-F+, 135147-62-5; OH-F+, 36505-07-4.


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Translational Energy Distribution from C2H2 + hν(193.3 nm) → C2H + H↑

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(Received: March 26, 1991)

We report the center-of-mass translational energy distribution for 193.3-nm photolysis of expansion-cooled C2H2, using high-n Rydberg-level excitation of nascent H atoms to facilitate high-resolution time-of-flight measurements. The observed resolution of ∼200 cm⁻¹ is presently limited by the ArF photolysis laser, whose band width is approximately 200 cm⁻¹. The reported distribution clearly resolves a C2H bending progression (νb ∼ 400 cm⁻¹), which reflects the trans-bent C2H excited state. A definitive assignment of all features is still not possible on the basis of currently available information on C2H. These measurements yield an upper bound to D0 of 131.8 ± 0.5 kcal mol⁻¹.

Introduction

The spectroscopy and photochemistry of acetylene have been studied extensively, both experimentally and theoretically. Early spectroscopic investigations showed a prominent bending progression in the A→X 2Σ⁺ absorption spectrum, indicating that the first electronically excited state is trans bent. Photophysical studies showed that photolysis at wavelenghts shorter than ∼200 nm yields the ethynyl radical, C2H, and an H atom. Wodtke and Lee reported the center-of-mass (CM) translational energy distribution following 193.3-nm photolysis using the angle-resolved time-of-flight (TOF) method, and gave an upper

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