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Transition State Spectroscopy of the $OH + H_2 \rightarrow H_2O + H$ Reaction via Photodetachment of H_3O^- and D_3O^-

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The transition state region of the reaction $OH + H_2 \rightarrow H_2O + H$ is investigated by photoelectron spectroscopy of the H_3O^- and D_3O^- anions. The peaks observed in the spectra are from a combination of vibrational progressions and overlapping anion \rightarrow neutral electronic transitions. The photoelectron angular distributions indicate that two processes contribute to the spectra; these are assigned to photodetachment from the $H^{-}(H_2O)$ and OH⁻(H₂) forms of the anion. A comparison of experiments performed in two different laboratories shows that the two forms of the ion readily interconvert and that the relative populations are determined solely by the temperature of the ions. To interpret the spectra, a two-dimensional ab initio potential energy surface for the anion was constructed, wave functions for the first few vibrational levels were determined, and the photoelectron spectra were simulated using the Walch-Dunning-Schatz-Elgersma surface for the $OH + H_2$ reaction. A comparison of the experimental and simulated spectra showed that photodetachment from the v = 0 level of the anion, which is localized in the H⁻(H₂O) well, primarily probes the H + H₂O exit valley of the neutral surface. The v = 2 level of the anion is the first with significant amplitude in the $OH^{-}(H_{2})$ well, and photodetachment from this level probes the $OH + H_{2}$ transition state region. The simulated spectra are in qualitative agreement with the experimental spectra but do indicate that the neutral reactive surface needs to be modified.

I. Introduction

Anion photoelectron spectroscopy has proved to be a powerful tool in the study of the transition state region of bimolecular chemical reactions.¹ This technique was first used to study reactions involving the heavy + light-heavy mass combination, but there is clear interest in extending it to a wider variety of chemical reactions. For example, the recent series of photoelectron spectroscopy studies of the FH2⁻ anion^{2,3} has provided important information on the geometry of the transition state for the prototypical three-atom reaction $F + H_2 \rightarrow FH + H$. In this paper, anion photoelectron spectroscopy is applied to the four-atom reaction $OH + H_2 \rightarrow H_2O + H$. This reaction is isoelectronic with the $F + H_2$ reaction and has been the topic of detailed kinetic⁴ and molecular beam scattering studies,⁵ while the reverse reaction has been studied in a series of hot H atom experiments.⁶ The OH + H₂ reaction has also developed into a benchmark system for quantum mechanical scattering calculations.7 These calculations qualitatively reproduce most of the experimental results. However, the potential energy surface^{8,9} used in these studies is likely to require modification. In particular, the geometry of the transition state is believed to be incorrect, and there is a spurious well in the entrance valley. Calculations are currently underway to produce a more accurate surface for this reaction.¹⁰ The goal of the work presented in this paper is to provide an experimental probe of the $OH + H_2$ transition state region. This is accomplished via photoelectron spectroscopy of the H₃O⁻ anion. A preliminary account of this work has been given elsewhere.¹¹

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The H₃O⁻ anion was first observed by Paulson and Henchman¹² in 1982. Since then, several experimental^{13,14} and abinitio¹⁵⁻¹⁸ studies have been carried out to understand the structure and reactivity of this anion. Calculations indicate that there are two low-lying structures of the anion. The lowest lying configuration of the anion is believed to be a hydrated hydride structure, which we will indicate by $H^{-}(H_2O)$. A second low-lying structure corresponds to an OH⁻ anion weakly bonded to H₂, indicated by OH⁻(H₂). The barrier to interconversion between these two geometries is expected to be on the order of a few kcal/mol. Both structures are expected to be intermediates in the ion-molecule reaction $OH^- + H_2 \rightarrow H_2O$ + H⁻, the kinetics of which have been studied in several laboratories.¹⁹ In a recent mass spectrometric study by Miller et al.,¹⁴ rate constants for formation of the H_3O^- anion and its reaction with a large number of reagents have been measured. These authors determine that the dissociation energies at 298 K to form $H^- + H_2O$ and $OH^- + H_2$ are 0.62 \pm 0.04 and 0.20 \pm 0.04 eV, respectively. Photodetachment of the H₃O⁻ anion was first reported in 1985 by Miller et al.;²⁰ however, only a preliminary analysis of the spectrum was presented at that time. The experiments presented here are much more extensive than the previous study, and this paper provides the first thorough analysis of the photoelectron spectra.

The overall energetics of H₃O⁻ photodetachment are shown in Figure 1. This shows the two low-lying anion configurations and their respective dissociation limits, along with the reaction coordinate and calculated barrier, 0.27 eV,^{8.9} for the OH + H_2 reaction. The anion energetics are from our own ab initio calculations which are described in this paper. The $OH^{-}(H_2)$ configuration is 0.085 eV higher in energy than the $H^{-}(H_2O)$

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Figure 1. Overall energetics of anion and neutral surfaces involved in $\rm H_3O^-$ photodetachment.

geometry. The barrier to conversion from $H^-(H_2O)$ to $OH^-(H_2)$ is 0.165 eV. Photodetachment of $H^-(H_2O)$ and $OH^-(H_2)$ will clearly probe very different parts of the neutral potential energy surface. Detachment of the $H^-(H_2O)$ structure will probe the $H + H_2O$ product valley, while detachment of the $OH^-(H_2)$ structure probes the entrance valley and transition state region. In the present study H_3O^- anions are generated via two different mechanisms in an attempt to selectively produce the two isomers and, hence, probe different parts of the neutral surface *via* photodetachment.

In addition to the experimental work reported here, we extend the *ab initio* studies of the anion by constructing a 2-D surface for H_3O^- anion and calculating the vibrational wave functions supported by this surface. These 2-D anion wave functions are used in a dynamical wavepacket calculation to simulate the photoelectron spectra. Although these studies are carried out only in two dimensions, and can therefore not be expected to quantitatively agree with the experimental spectra, the agreement between the simulations and experimental data is encouraging but also suggests that there are some problems with the neutral surface. Thompson and Miller²¹ have recently carried out a higher dimensional quantum mechanical simulation of the $H_3O^$ photodetachment spectrum. This simulation assumes a harmonic OH⁻(H₂) well and results in poor agreement with our experimental data. While the disagreement may indicate problems with the neutral surface, it is most likely that the disagreement arises from the anion wave function used in these studies.

II. Experimental Section

The experiments described in this paper were carried out at the University of California in Berkeley and at the Joint Institute of Laboratory Astrophysics (JILA) in Boulder. The JILA photoelectron spectrometer is based on a continuous laser system and hemispherical electron analyzer, whereas the Berkeley instrument is based on a pulsed laser system and time-of-flight detection techniques. The most important difference between the experiments described in this paper lies in the production method of the anions. Two different production methods were used in attempt to generate different H_3O^- isomers, $OH^-(H_2)$ and $H^-(H_2O)$. In this section both experimental setups and anion production methods will be discussed briefly.

The dual time-of-flight photoelectron spectrometer used in the Berkeley study has been described in detail elsewhere.²² Briefly, negative ions are formed by crossing a pulsed molecular beam with a continuous 1 keV electron beam close to the orifice, in the continuum flow region of the free jet expansion. The ions are mass separated using time-of-flight. Ions of the desired mass are photodetached with a pulsed laser, and the energy distribution of the ejected electrons is determined by a second time-of-flight system.

 H_3O^- (D_3O^-) ions were generated by expanding a mixture of 2% N_2O , 48% CH_4 (CD₄), and 50% H_2 (D₂) through the pulsed beam value at a pressure of 40 psig. The likely mechanism for H_2O^- formation is

$$N_2 O + e^- \rightarrow O^- + N_2 \tag{1}$$

$$O^- + CH_4 \rightarrow OH^- + CH_3$$
 (2)

$$OH^- + H_2 + M \rightarrow H_3O^- + M$$
(3)

This production mechanism was chosen to attempt to maximize the OH⁻(H₂) isomer relative to H⁻(H₂O). The negative ions are injected into a Wiley-McLaren type mass spectrometer. Ions separate according to their masses, and the ions of interest are photodetached by a pulsed laser beam at a photon energy of 2.98 eV (416 nm, third harmonic of a Nd:YAG laser Raman shifted in H₂). A small fraction of the photoelectrons are detected at the end of a 1 m long flight tube, orthogonal to the laser and ion beams. The electron energy resolution is 8–10 meV at eKE = 0.65 eV and degrades as (eKE)^{3/2} for higher electron kinetic energies.

The negative ion photoelectron spectrometer used in the Boulder laboratory has been described in detail previously²³ and in a recent review article.²⁴ Only a brief description is given here, with emphasis on ion production. The H_3O^- and D_3O^- ions were synthesized in a microwave flowing afterglow ion source using an ion-molecule reaction discovered by Nibbering *et al.*¹³

$$OH^{-} + H_2CO \Leftrightarrow [HOH \cdots HCO^{-}] \rightarrow HOH \cdots H^{-} + CO$$
 (4)

The final step in this reaction is a hydride transfer, so this reaction should favor the production of $H^-(H_2O)$ over $OH^-(H_2)$.

The reaction is a three-step process conducted within the flowing afterglow. First, O^- was produced by passing 0.1%O₂ with approximately 7 standard liters per minute of He gas directly through the microwave discharge cavity. The total gas pressure was 0.6 Torr. Next, CH₄ was put through an inlet downstream of the discharge and allowed to react with the O⁻ to produce OH⁻. In the third step, formaldehyde was titrated through an inlet further downstream to optimize the H_3O^- ion beam intensity. D_3O^- was produced by using OD^- (from CD_4) and D_2CO . Under optimum conditions, a mass-analyzed beam of 50 pA of H_3O^- or D_3O^- could be obtained. Ions were produced at vibrational and rotational temperatures of about 300 K under normal circumstances; alternatively, the ions could be cooled using a liquid nitrogen Dewar which surrounds the last 20 cm of the flowing afterglow tube. The cooling performance of the liquid nitrogen jacket has been characterized by remeasuring the photoelectron spectra of ions previously studied in the same spectrometer at room temperature.²⁵ Franck-Condon analyses of the photoelectron spectra collected from cooled anions indicate that vibrational and rotational temperatures are less than 200 K.

Negative ions were extracted from the flowing plasma through an aperture into a high-vacuum region, formed into a beam, and mass selected with a Wien velocity filter. The mass selected ion beam was crossed with approximately 100 W of 351 nm (3.531 eV) radiation, obtained from an intracavity CW argon ion laser. Photodetached electrons ejected into a small solid



Figure 2. Photoelectron spectra for H_3O^- at $\Theta = 0^\circ$, taken at (a) Berkeley and (b) Boulder. Assignments to H_2O vibrations (ν_1 , ν_2 , ν_3) are indicated in the bottom frame.

angle perpendicular to the ion and laser beams were energy analyzed in a hemispherical electron kinetic energy analyzer and imaged onto a position-sensitive detector at an electron energy resolution of 6 meV. The absolute energy scale was calibrated to an accuracy of ± 0.004 eV by photodetaching O⁻, for which the electron affinity is well-known.²⁶ A small correction for compression of the energy scale was obtained by photodetaching W⁻ and calibrating the atomic energy level spacings to those listed by Moore.²⁷

In both experiments the angle Θ between the laser polarization vector and the direction of electron detection was varied. At a given electron kinetic energy, the photoelectron angular distribution is given by²⁸

$$I(\Theta) \propto 1 + \beta P_2(\cos \Theta) \tag{5}$$

where P_2 is the second-order Legendre polynomial and β is the anisotropy parameter, which has limiting values +2 and -1. Spectra were taken at $\Theta = 0^\circ$ and 90° and at the "magic angle" $\Theta = 54.7^\circ$, where $P_2(\cos \Theta) = 0$. If only one anion \rightarrow neutral electronic transition contributes to the photoelectron spectrum, then β should be approximately constant for all the features in the spectrum. On the other hand, a noticeable variation of relative peak intensities with Θ is a good indication that more than one electronic transition is contributing to the spectrum.

III. Experimental Results

Figure 2 shows the Berkeley and JILA H₂O⁻ photoelectron spectra taken with an incident photon energy $h\nu = 2.98$ and 3.53 eV, respectively, at $\Theta = 0^{\circ}$ laser polarization. To facilitate comparison between the two data sets, the spectra are plotted as a function of the electron binding energy, eBE. This is given by eBE = $h\nu - eKE$, where eKE is the electron kinetic energy. The spectra are very similar and are dominated by a broad peak (fwhm 175 meV) centered at an electron binding energy of 1.53 eV with smaller, equally broad peaks at 2.00 and 2.38 eV.

In Figure 3 we show $\Theta = 0^{\circ}$ spectra for D₃O⁻. The top frame, Figure 3a, shows the Berkeley spectrum, taken at a



Figure 3. Photoelectron spectra for D_3O^- at $\Theta = 0^\circ$, taken at (a) Berkeley, (b) Boulder at room temperature, and (c) Boulder with ions cooled to 200 K. Assignments to D_2O vibrations (ν_1 , ν_2 , ν_3) are indicated in the bottom frame.

photon energy of 2.98 eV. Figure 3b,c shows data taken at JILA at a photon energy of 3.53 eV. The two sets of JILA data were taken with the ion source at two different temperatures. Figure 3b shows the room temperature spectrum while Figure 3c shows the spectrum obtained when the ion drift tube was cooled by liquid N₂ leading to an estimated temperature of the ions of 200 K. The three spectra are very similar, showing peaks at 1.53, 1.88, and 2.17 eV. The width of the peaks is 160 meV at fwhm. The binding energy of the main feature at 1.53 eV is not shifted upon deuteration, whereas the binding energy of the smaller features shifted to lower energies. This suggests that the three peaks are members of a single vibrational progression with its origin at 1.53 eV. Despite the different mechanisms for generating the negative ions, the spectra obtained by the Berkeley group and the JILA group show remarkable similarity. Neither the relative intensity nor the width of the peaks seems to depend on the mechanism of ion formation. Moreover, the JILA spectra at $\Theta = 0^{\circ}$ appear independent of source temperature.

Figure 4 shows the Berkeley and JILA H₃O⁻ photoelectron spectra taken with incident photon energies of 2.98 and 3.53 eV, respectively, at $\Theta = 90^{\circ}$ laser polarization. The $\Theta = 0^{\circ}$ spectra are clearly quite different from the $\Theta = 90^{\circ}$ spectra. The spectra in Figure 4 consist of broad peaks centered at eBE = 1.53 and 2.05 eV, and there is a sharp and very intense peak at eBE = 1.83 eV in both spectra which is absent in the Θ = 0° spectra. Compared to the $\Theta = 0^{\circ}$ spectra, the peak at 2.05 eV is considerably larger relative to the peak at 1.53 eV. The peak at 2.05 eV is also is shifted somewhat toward higher eBE relative to the peak seen at 2.00 eV in the $\Theta = 0^{\circ}$ spectra. Both of these effects are more noticeable in the JILA data. It appears that at $\Theta = 90^{\circ}$ a new feature has emerged at just slightly higher energy than the 2.00 eV peak in the $\Theta = 0^{\circ}$ spectra. The sharp peak at eBE = 1.83 eV in the Θ = 90° spectra is due to OH⁻. In the mass spectra on both instruments,



Figure 4. Photoelectron spectra for H_3O^- at $\Theta = 90^\circ$, taken at (a) Berkeley and (b) Boulder.



Figure 5. Photoelectron spectra for D_3O^- at $\Theta = 90^\circ$, taken at (a) Berkeley, (b) Boulder at room temperature, and (c) Boulder at 200 K.

the OH⁻ peak is 2 orders of magnitude more intense than the H_3O^- peak, and the tail of the OH⁻ mass peak overlaps the H_3O^- peak giving rise to the peak at eBE = 1.83 eV. Some of the intensity of this peak comes from ¹⁸OH⁻, which has the same mass as $H_3^{16}O^-$.

In Figure 5 we show $\Theta = 90^{\circ}$ spectra for D_3O^- . The top frame, Figure 5a, shows the Berkeley spectrum. Figure 5, b and c, shows JILA data for room temperature and cooled ions, respectively. Photodetachment due the tail of the OD⁻ mass channel is observed at 1.83 eV in the Berkeley spectrum. All

three spectra show peaks at 1.53 and 2.05 eV, and the spectrum in Figure 5c shows a small peak at 1.88 eV. The peaks at 1.53 and 1.88 eV were part of the progression in the $\Theta = 0^{\circ}$ spectrum of D₃O⁻, but the 2.05 eV feature only appears in the $\Theta = 90^{\circ}$ spectra. This peak occurs at the same energy as the 2.05 eV feature in the H₃O⁻ spectra and is therefore insensitive to isotopic substitution. The deuterated spectra further support our claim that the peak at 2.05 eV is a new feature that is observed only at $\Theta = 90^{\circ}$. Its intensity is strongly temperature dependent; a comparison between parts b and c of Figure 5 shows that the intensity of this feature is dramatically reduced upon cooling. A similar effect was observed when the H₃O⁻ ions were cooled (not shown).

Spectra of H_3O^- and D_3O^- were also taken in both laboratories at the magic angle, $\Theta = 54.7^\circ$. The spectra were intermediate in appearance between the $\Theta = 0^\circ$ and $\Theta = 90^\circ$ spectra and are therefore not shown.

The differences between the $\Theta = 0^{\circ}$ and $\Theta = 90^{\circ}$ spectra show that two detachment processes with different polarization dependences contribute to the spectra, with the most intense peaks from these two processes occurring at eBE = 1.53 and 2.05 eV. The absolute intensity of the 1.53 eV peak drops considerably when the laser polarization is rotated from 0° to 90°. We determined that the anisotropy parameter β for this peak is ~ 1.8 . The anisotropy parameter for the 2.05 eV peak is more difficult to characterize, but this peak does appear to have maximum intensity at $\Theta = 90^{\circ}$. Hence, the two peaks appear to result from different anion \rightarrow neutral electronic transitions. This preliminary interpretation of the spectra is supported by the isotope effects. These imply that the $\Theta = 0^{\circ}$ spectrum represents a single vibrational progression but that two distinct electronic transitions with origins at 1.53 and 2.05 eV contribute to the $\Theta = 90^{\circ}$ spectrum.

Overall, the comparison of the Berkeley and JILA data shows that the photoelectron spectrum is rather insensitive to the mechanism by which H_3O^- is generated. This implies that the two forms of the anion are readily interconvertible. The nature of the anion is explored further in the next two sections.

IV. Calculations

In order to interpret the experimental spectra, the H₃O⁻ anion must be better characterized. There are a large number of ab initio studies on the H₃O⁻ anion. Early calculations debated whether the anion is stable at all; a calculation²⁹ published just prior to the first experimental observation of H₃O⁻ concluded that the ion is not stable by as much as 3 eV. These early calculations are highly unreliable as large basis sets, and high levels of electron correlation are required to describe the electronic binding in this anion. Although there are still significant differences between results of recent calculations,¹⁵⁻¹⁸ the general picture has now converged. The anion is now predicted to be stable with respect to dissociation and detachment and to exist in two forms. The H⁻(H₂O) structure is considered to be the most stable structure, with the $OH^{-}(H_2)$ structure being a few kcal/mol higher in energy. The barrier to interconversion is calculated to be on the order of a few kcal/ mol.

An important issue that has not been addressed is the nature of the vibrational levels in the H_3O^- anion. In particular, are $H^-(H_2O)$ and $OH^-(H_2)$ two distinct isomers, each with its own sets of vibrational levels, or do even the lowest vibrational wave functions sample both geometries? To address this question, we have carried out *ab initio* calculations to generate a 2-D potential energy surface for the H_3O^- anion. We then calculate the first few vibrational wave functions supported by this Transition State of the $OH + H_2 \rightarrow H_2O + H$ Reaction

$$\begin{array}{c} O \xrightarrow{R_{OH1}} H1 \xrightarrow{R_{H1H2}} H2 \\ H3 \xrightarrow{H_{3}OH1} OH1H2 \xrightarrow{H1} H2 \end{array}$$

Figure 6. Labeling of the bond distances and angles in H_3O^- .

TABLE 1: *Ab Initio* Geometries for H_3O^- (Distances in Å and Angles in deg)

geometry	<i>R</i> (OH1)	<i>R</i> (OH3)	<i>R</i> (H1H2)	∠H3OH1	∠OH1H2
$H^{-}(H_2O)^a$	1.015	0.963	1.485	99.0	169.8
OH ⁻ (H ₂) ^a	1.957	0.968	0.770	133.8	172.5
trans state ^b	1.346	0.964	0.930	98.4	177.8

^a MP4/6-311++G**. ^b MP4//MP2/6-311++G**.

TABLE 2: Ab Initio Energetics for Stationary Points and Asymptoes of H_3O^-

	energy (
geometry	MP2 ^a	MP4	rel energy ^d (eV)
$H^{-}(H_2O)$	-76.811 297	-76.829 925 ^b	0.000
$OH^{-}(H_2)$	-76.809 259	-76.826 808 ^b	0.085
trans state	-76.806 425	-76.823 842 ^c	0.165
$H^- + H_2O$	-76.781 304	-76.800 865 ^b	0.787
$OH^- + H_2$	-76.800545	-76.817 927 ^b	0.325

^a MP2/6-311++G**. ^b MP4/6-311++G**. ^c MP4//MP2/6-311++G**. ^d Determined from MP4 energies.

surface. Finally, these anion wave functions will be used in dynamical wavepacket calculations in which the photoelectron spectra are simulated. This section describes the three aspects of our analysis.

A. Ab Initio Calculations. As a starting point in our calculations, we have optimized the geometries of both anion structures, while constraining them to planar geometries, at the MP2/6-311++G** and MP4/6-31++G** level. The transition state geometry was optimized at the MP2 level, and the MP4 energy was calculated at this geometry. The labeling of the atoms and bond distances and angles is shown in Figure 6. The optimized geometries for the two minima and the transition state are presented in Table 1, and the MP2 and MP4 energies are presented in Table 2. The $H^-(H_2O)$ structure is the global minimum, while the $OH^{-}(H_2)$ structure is 0.085 eV higher in energy at the MP4/6-311++G** level. The barrier to interconvert from $H^{-}(H_2O)$ to $OH^{-}(H_2)$ is 0.165 eV. Our results are in good agreement with previous studies. The only discrepancy between our calculations and calculations of Kraka,¹⁵ Simons,¹⁶ and Dunning¹⁸ is that we find a bent $OH^{-}(H_2)$ structure, in contrast to the linear structure found by the other authors. This bent structure is also found by Ortiz.¹⁷ We have investigated the bend potential and found that our minimum energy geometry lies only $\sim 0.02 \text{ eV}$ below the linear structure.

From the relative energies given in Table 2, one obtains the dissociation energies of the anion, D_e , with respect to the OH⁻ + H₂ and H⁻ + H₂O channels. Our values are in good agreement with previous experimental^{12,14} and theoretical results.¹⁵⁻¹⁸ From Table 2, we find $\Delta E = -0.462 \text{ eV}$ for the reaction H⁻ + H₂O \rightarrow OH⁻ + H₂, excluding zero point energies. Adding the zero point energies (0.490 eV for OH⁻ + H₂ and 0.559 eV for H₂O) yields $\Delta E = -0.531 \text{ eV}$, in excellent agreement with the experimental value of -0.568 eV based on known heats of formation for the anion and neutral species involved in the reaction.^{30,31}

Given that our MP4 results for the stationary points are reasonable, we have constructed a two-dimensional potential energy surface in the most relevant degrees of freedom which are necessary to describe the double well and the dissociation



Figure 7. Ab initio two-dimensional surface for H_3O^- . See Figure 6 for explanation of coordinates. The contours are spaced by 0.10 eV.

coordinates. In our calculations both R(O-H1) and R(O-H2)are varied (see Figure 6). The other degrees of freedom are fixed at suitable values. The H3OH1 angle is fixed at 99°, close to the angle found for both the $H^{-}(H_2O)$ and transition state geometry. This value is quite different from the optimum geometry found for OH⁻(H₂), for which \angle H3OH1 = 134°. However, this bend potential is very flat in the $OH^{-}(H_2)$ well; the potential energy difference between 99° and of 134° is only 0.017 eV. The OH3 bond length is fixed at 0.965 Å, very close to the values obtained for both wells and the transition state. The OH1H2 angle is fixed at 180°. The MP4/6-311++G** energy was calculated on a rectangular grid consisting of 33 values of R(O-H1) between 0.77 and 2.42 Å and 23 values for R(O-H2) between 1.95 and 3.1 Å. The resultant potential energy surface is shown in Figure 7. The locations of the two minima and the transition state are clearly visible, as are the dissociation channels leading to $H^- + H_2O$ and $OH^- + H_2$.

B. Anion Vibrational Wave Functions. As the barrier to interconversion between the two forms of the anion is only 0.165 eV, it is clear that the anion vibrational wave functions will not be accurately described in the harmonic oscillator approximation. More sophisticated methods are required to describe the strongly anharmonic nature of the wave functions. We have calculated the first few vibrational wave functions for H_3O^- and D_3O^- on our two-dimensional potential energy surface using the discrete variable representation (DVR) method.³² The wave functions are calculated in the Jacobi coordinates (R,r), where R is the distance of the O atom to the center of mass of H1H2 and r = R(H1H2). We used 25 harmonic oscillator basis functions in each coordinate, with $1.3 \le R \le$ 2.9 and $0.5 \le r \le 2.1$. The potential energy at the DVR points is obtained by interpolation on the 2-D ab initio grid. Since the potential energy is diagonal in the DVR coordinate representation, it is not necessary to obtain an analytical fit to the *ab initio* potential energy points.

The lowest three vibrational wave functions for H_3O^- , together with the anion surface in Jacobi coordinates, are shown in Figure 8. For both H_3O^- and D_3O^- (not shown) the v = 0and v = 1 levels are localized in the $H^-(H_2O)/(D^-(D_2O))$ well. The v = 2 level is the first with significant amplitude in the $OH^-(H_2)$ well. It is important to note, however, the v = 2 wave function is not localized within this well but rather is delocalized with considerable amplitude near both minima. The accuracy of the constructed potential energy surface is at best 0.05 eV, which is only slightly smaller than the calculated barrier height and energy difference between the two minima. The true wave functions may therefore be somewhat different from those we obtained. Our wave functions are, however, very helpful in interpreting the photoelectron spectra and understanding the energetics of the anion.



Figure 8. Calculated anion surface in Jacobi coordinates (a) and H₃O⁻ wave functions: (b) v = 0, (c) v = 1, and (d) v = 2.

C. Dynamical Wavepacket Simulations. Given an initial anion wave function and a model potential energy surface for the neutral reaction, one can simulate a photoelectron spectrum and compare the results to experiment. The simulation can be performed using either time-independent or time-dependent methods.¹ Thompson and Miller²¹ have performed an exact quantum simulation of the H₂O⁻ spectrum treating the anion as a harmonic oscillator localized in the $OH^{-}(H_2)$ well and using the six-dimensional $OH + H_2$ surface developed by Schatz and Elgersma⁹ as a fit to the *ab initio* points calculated by Walch and Dunning⁸ (WDSE surface). However, the results of the last section show that the harmonic oscillator approximation for the anion is inadequate, particularly when simulating photodetachment from the $OH^-(H_2)$ well. We have therefore carried out two-dimensional simulations of the H₃O⁻ photoelectron spectra using the anion wave functions obtained in the previous section.

In order to simulate the spectra, we use the dynamical wavepacket formalism developed by Heller³³ and the wavepacket propagation scheme of Kosloff and Kosloff.³⁴ Our implementation of this method has been discussed previously.³⁵ The principles are as follows. Upon photodetachment the anion wave function is projected onto the neutral potential energy surface, forming the starting point for the propagation. The initial wavepacket $|\phi(0)\rangle$ is propagated according to

$$|\phi(t)\rangle = \exp(-i\hat{H}t/\hbar)|\phi(0)\rangle \tag{6}$$

where $\exp(-i\hat{H}t/\hbar)$ is the time evolution operator and \hat{H} is the nuclear Hamiltonian for the neutral surface. The overlap of $\phi(t)$ with $\phi(0)$ defines the time autocorrelation function C(t):

$$C(t) = \langle \phi(0) | \phi(t) \rangle \tag{7}$$

and the Fourier transform of the autocorrelation function yields the photoelectron spectrum:

$$\sigma(E) \propto \int_{-\infty}^{\infty} \exp(iEt/\hbar) C(t) \, \mathrm{d}t \tag{8}$$

We restrict our wavepacket analysis to two dimensions. The two-dimensional neutral surface is obtained by fixing all but two parameters of the full dimensionality WDSE surface.^{8,9} Specifically, the HOH bend angle is fixed at the free H_2O bend

angle (104.5°) in these simulations, and all other parameters are fixed at the same values we used in constructing the 2-D anion surface and wave functions. The simulated spectra for a HOH bend angle of 99°, which is the angle used in the anion calculations, were qualitatively the same. The simulated photoelectron spectra will be presented and discussed in section V.

V. Discussion

The strong effect of laser polarization on the relative intensities of the photoelectron peaks suggests that there are two distinct photodetachment processes occurring for which the photoelectron angular distributions are quite different. On the basis of the *ab initio* H_3O^- surface described above, it is reasonable to expect that one process corresponds to photodetachment from the $H^-(H_2O)$ well, while the other corresponds to photodetachment from the $OH^-(H_2)$ well. However, our calculated vibrational wave functions indicate that there are no strongly localized $OH^-(H_2)$ levels and that the latter contribution is more accurately described as coming from ions with sufficient vibrational excitation (i.e., $v \ge 2$; see Figure 8) to have considerable amplitude in the $OH^-(H_2)$ well.

The contributions from these two processes can be partially unraveled by considering the energetics shown in Figure 1. It clearly takes more energy to photodetach OH⁻(H₂) than $H^{-}(H_2O)$. Moreover, the electron binding energy of $OH^{-}(H_2)$ will be greater than that of OH^- , $eBE(OH^-) = 1.83 \text{ eV}$. Hence, any signal at lower eBE than this, namely, the peak at 1.53 eV, must be due to photodetachment of $H^{-}(H_2O)$, and the vibrational progression in the $\Theta = 0^\circ$ spectra should also be assigned to H⁻(H₂O) photodetachment. These same energetic considerations imply that the broad feature at 2.05 eV can be at least partially due to photodetachment from $OH^{-}(H_2)$. The temperature effects seen in the JILA spectra are consistent with these assignments. The $\Theta = 0^{\circ}$ spectra are insensitive to temperature. However, the peak at 2.05 eV decreases in intensity as the temperature is lowered (see Figure 5b,c), so it is likely due to vibrationally excited anions.

Further information on the origin of the photoelectron peaks can be derived by considering the polarization dependences in more detail. Consider the photoelectron anisotropy parameters likely to arise from photodetachment from the H⁻(H₂O) and OH⁻(H₂) wells. To zero order, we would expect these values of β to resemble those for H⁻ and OH⁻, respectively. In the case of H⁻, the electron is being removed from an atomic s-orbital, so p-wave photodetachment should occur, leading to $\beta = 2$ and a cos²(Θ) angular distribution. Recall that β was 1.8 for the peak at eBE = 1.53 eV. This supports our assignment of this peak and the associated vibrational progression to H⁻(H₂O) photodetachment.

On the other hand, the extra electron in OH⁻ occupies a p-orbital on the oxygen atom. Photodetachment very close to the threshold should result in an s-wave with an isotropic angular distribution ($\beta = 0$), but d-wave photodetachment will begin to contribute significantly not too far above the detachment threshold, leading to a negative value of β and photoelectron angular distribution that peaks at $\Theta = 90^{\circ}.^{36}$ This strong anisotropy is clearly illustrated in the contribution to the spectra from OH⁻; we observe a strong peak at eBE 1.83 eV in the Θ = 90° spectra, while this feature is absent at the opposite polarization. The anisotropy of the feature at 2.05 eV follows that of the background OH⁻, supporting the above arguments based on energetics and temperature that it is largely due to photodetachment of OH⁻(H₂).

Overall, then, it appears that the $\Theta = 0^{\circ}$ spectra are entirely due to H⁻(H₂O) photodetachment, while both forms of the ion

contribute to the $\Theta = 90^{\circ}$ spectra. These strong polarization effects make it possible to analyze both contributions to the spectra in detail.

A. $\Theta = 0^{\circ}$ Spectra. A qualitative interpretation of the Θ = 0° spectra is relatively straightforward. The main feature at 1.53(2) eV in the deuterated $\Theta = 0^{\circ}$ spectrum occurs at the same binding energy as in the H₃O⁻ spectrum. Since this 1.53 eV peak is largely (or even entirely) due to H⁻(H₂O)/D⁻(D₂O), the difference between the electron binding energy of this ion measured from the onset of the peak (1.40 eV) and that of H⁻ (0.75 eV) puts an upper limit on the H⁻···H₂O bond dissociation energy of 0.65 eV. This is in good agreement with the previously determined value of the H⁻···H₂O bond dissociation energy at 298 K of 0.62 ± 0.05 eV. The vertical electron binding energy of 1.53(2) eV is in excellent agreement with the value of 1.5 eV calculated by Ortiz.¹⁷

The second peak in the $\Theta = 0^{\circ} H_3 O^-$ spectrum is separated from the main peak by the antisymmetric stretch frequency of H_2O . The small feature at 2.38 eV is not exactly at the energy expected for two quanta in the antisymmetric stretch mode but occurs at ~90 meV lower eBE. Upon closer inspection, all of the peaks show distinctly asymmetric peak shapes. These shapes can be rationalized by assuming there is some H₂O bend excitation. In Figure 2, the assignment to H₂O vibrations (labeled as $(\nu_1 \ \nu_2 \ \nu_3)$, where ν_1 is the symmetric stretch, ν_2 is the bend, and v_3 is the antisymmetric stretch mode) is indicated by arrows. In the D_3O^- spectrum the peaks show the appropriate isotopic shift for the bend and antisymmetric stretch frequencies. The arrows in Figure 4 indicate the vibrational frequencies of the D₂O molecule. As in the H₃O⁻ spectrum, the small feature at 2.17 eV is shifted from the energy expected for (002) and occurs at \sim 50 meV lower binding energy. From our ab initio calculations it is clear that the H₂O moiety in the H⁻(H₂O) well is significantly distorted from the free H₂O structure: in the anion the HOH angle is tightened by 5°, and the OH bond lengths are asymmetric. We calculated that the lowest vibrational level is localized in this well. Therefore, excitation in both the bend and stretch modes is expected for photodetachment from the v = 0 level of the H₃O⁻ anion.

In summary, the main features in our $\Theta = 0^{\circ}$ photoelectron spectra can be interpreted in terms of Franck-Condon transitions to a free H₂O molecule, confirming our assignment of this spectrum to photodetachment from the H⁻(H₂O) well. However, the widths of the peaks and the energy shift of the (002) excitation cannot be explained in such a "static" Franck-Condon model. The peak widths arise from two effects. We are accessing a dissociative neutral potential energy surface, so there is a homogeneous width associated with the decay dynamics of the neutral species. Unresolved vibrational structure from bound coordinates on the neutral surface can also contribute; these coordinates are perpendicular to the reaction coordinate and might include, for example, bending motion of the departing H atom with respect to the H₂O moiety. Similarly, the energy shift of the (002) peak is most likely due to a perturbation of the H₂O by the departing H atom.

By performing the two-dimensional simulations of the photoelectron spectrum discussed in the previous section, these effects can be investigated in more detail. Specifically, simulations assuming that the anion is in its v = 0 level will yield the photoelectron spectrum expected from H⁻(H₂O) photodetachment. Figure 9 shows the projection of the H₃O⁻ v = 0 anion wave function on the 2-D neutral surface, obtained by fixing the other variables at the values described in section IV.C. The simulated photoelectron spectrum obtained by propagation of



Figure 9. 2-D potential energy surface for the OH + H₂ \rightarrow H₂O + H reaction in mass-weighted Jacobi coordinates: r = R(H1-H2) and $R' = (\mu_{OH,H_2}/\mu_{H_2})^{1/2}R(O - c.m.[H1H2])$. The contours are spaced by 0.20 eV. The Franck–Condon region for the H₃O⁻ v = 0 wave function is shaded.



Figure 10. Simulated photoelectron spectra for (a) $H_3O^-(v=0)$ and (b) $D_3O^-(v=0)$.

the v = 0 anion wave function is shown in Figure 10. The corresponding spectrum for $D_3O^-(v=0)$ is also shown in Figure 10.

The simulated spectra show several features which are associated with vibrations of the nascent H₂O products. The observed vibrational progressions are associated with the local OH1 stretch mode; as the HOH angle is frozen, the 2-D wavepacket propagations cannot reproduce excitation in the bend coordinate. The frequency of the local OH stretch mode (3706 cm⁻¹ to 0.466 eV) is only slightly different from that of the antisymmetric stretch mode (3756 cm⁻¹). In the H₃O⁻ and D_3O^- experimental spectra the (001)–(000) spacing matches the free H_2O/D_2O frequency exactly, but the (002) frequency is smaller by 0.09 and 0.05 eV, respectively. Qualitatively, the same effect is found in our simulation. For both H₃O⁻ and D_3O^- , the (000)-(001) spacing matches the local stretch frequency, while the (001)-(002) spacing is smaller by 0.14 and 0.12 eV, respectively. In the deuterated complex the (002) excitation represents less internal energy than in the hydrogenated system; thus, the shifts in D₃O⁻ should be smaller than in H₃O⁻, as is observed. These shifts are indicative of the fact that the neutral surface is a reactive surface where the frequency of the antisymmetric stretch mode decreases near the transition state. The fact that the reduction in peak spacings is larger in

the simulated vs experimental spectrum suggests that the barrier on the neutral surface is too close to the Franck–Condon region. If the barrier were further out in the $OH + H_2$ valley, its effect on the peak spacings would be reduced.

In addition to comparing the vibrational structure in the simulated and experimental spectra, the absolute energy scale is also of interest. In the simulated photoelectron spectra, this is obtained from the calculated binding energy of the anion, $D_{\rm e}({\rm H}^{-}\cdots{\rm H}_2{\rm O})$, the zero point energy for the two dimensions considered in the simulation, and the known electron affinity of OH. The zero point energies for vibrations not considered in the simulation are assumed to be the same in the anion and neutral, thereby canceling out in the photoelectron spectrum. In the simulated spectrum, the onset of the photoelectron peak occurs at 1.70 eV, compared to 1.40 eV in the experimental spectra. This large difference of 0.30 eV can be either due to an error in the calculated bond dissociation energy of the anion or due to problems with the neutral surface. The calculated bond dissociation energy is $D_e(H^- \cdot \cdot \cdot H_2O) = 0.79 \text{ eV}$, while $D_{\rm e}$ from the best experimental result is 0.62 \pm 0.04 eV. This accounts for 0.17 eV, and the remaining discrepancy, 0.13 eV, is probably related to the neutral surface. Moreover, simulated spectra obtained for $\angle HOH = 104.5^{\circ}$ (Figure 10) and $\angle HOH$ = 99° (not shown) are very similar (the onset of the peak changes by only $\sim 0.06 \text{ eV}$) from which we conclude that the discrepancy does not arise solely from restricting the simulations to only two dimensions.

Upon photodetachment, the anion wavepacket accesses the neutral surface at a potential energy that is about 0.3 eV higher than the energy of dissociated $H + H_2O$ products. This is energetically halfway between the energy of the transition state and asymptotic products. If the OH + H₂ surface were to have an earlier barrier, photodetachment of H⁻(H₂O) would access the neutral surface further away from the transition state on a much flatter part of the surface, resulting in a lower electron binding energy for all of the features in the spectrum. Hence, an earlier barrier would bring the peak *energies* of the simulated spectra in better agreement with our photoelectron spectra. Such a modification is also consistent with the discrepancies between the experimental and simulated peak *spacings* as discussed above.

The peak widths are directly related to the dynamics occurring on the neutral surface. In the simulated spectra, the (000) peak is significantly broader than the (001) peak. A similar effect was observed in 2-D simulations of the BrHI- photoelectron spectrum³⁵ where the peaks corresponding to vibrationally excited states of the neutral complex are narrower than the peak corresponding to the vibrationless complex. This effect arises because the vibrationally adiabatic curves correlating the various product states become less repulsive with increasing vibrational excitation. This is the same effect that results in a reduced spacing between the (001) and (002) peaks in the $H^{-}(H_2O)$ simulated (and experimental) spectra, again indicating the effects of accessing the transition state region of the neutral surface. However, in the experimental spectra, the peak widths do not vary. This is an indication that translational and vibrational motion along coordinates neglected in the two-dimensional simulations is contributing to the peak widths and that a higher dimensionality simulation will ultimately be required to accurately simulate the $\Theta = 0^{\circ}$ spectra.

Overall, our two-dimensional simulations assuming the ion to be in its vibrational ground state do a reasonable job at simulating the $\Theta = 0^{\circ}$ spectra. Even though one might expect to probe only the repulsive exit valley of the OH + H₂ surface by photodetachment of H⁻(H₂O), the proximity of the transition



Figure 11. Photoelectron spectra for (a) H_3O^- and (b) D_3O^- obtained by subtracting the appropriately scaled $\Theta = 90^\circ$ and $\Theta = 0^\circ$ spectra.



Figure 12. 2-D potential energy surface (from refs 8 and 9) for the OH + $H_2 \rightarrow H_2O$ + H reaction in mass-weighted Jacobi coordinates. The Franck-Condon region for the $H_3O^- v = 2$ wave function is shaded.

state to the Franck-Condon region does affect the peak spacings and energies in the photoelectron spectrum. Discrepancies between the experimental and simulated spectra regarding both of these attributes suggest that the barrier should be "earlier" on the true potential energy surface.

B. $\Theta = 90^{\circ}$ Spectra. As discussed above, the $\Theta = 0^{\circ}$ spectra are dominated by H⁻(H₂O) photodetachment, while photodetachment from both wells contribute to the $\Theta = 90^{\circ}$ spectra. We can therefore obtain the contribution of the OH⁻(H₂) isomer to each $\Theta = 90^{\circ}$ spectrum by subtracting the appropriately scaled $\Theta = 0^{\circ}$ spectrum. The subtracted spectra obtained from the room temperature JILA data for H₃O⁻ and D₃O⁻ are shown in Figure 11. As expected, the peak due to OH⁻ contamination and the broad feature at 2.05 eV are all that survives this subtraction procedure. The broad peak is assigned to photodetachment from ions with amplitude in the OH⁻(H₂) well. The v = 2 vibrational level of the anion is the lowest level that has significant probability in the OH⁻(H₂) well. Hence, simulations originating from this state are useful to further investigate the OH⁻(H₂) contribution to the spectra.

Figure 12 illustrates the outline of the $H_3O^- v = 2$ anion wave function projected onto the neutral surface, showing its overlap with the exit valley, entrance valley, and transition state. As the wavepacket evolves in time it splits up into two components, leading to both products and reactants on the neutral surface. The photoelectron spectrum that results from



Figure 13. Simulated photoelectron spectrum for $H_3O^-(v=2)$.

propagating the v = 2 wave function is shown in Figure 13. The spectrum contains features that are related to both the product and reactant side of the neutral surface. The most prominent features of the simulation are the peaks at 1.98 and 2.09 eV, which are both associated with the transition state and reactant valley. It is these features that should be compared to the 2.05 eV feature in the difference spectrum in Figure 11.

The sharp feature at 1.98 eV arises from population being trapped in a shallow well just to the reactant side of the barrier on the WDSE surface surface. The width of this peak is the Fourier transform of the propagation time (200 fs) used in the wavepacket simulation. This sharp peak is not observed experimentally. We therefore conclude (as already has been suggested by several authors) that the well in the neutral surface is an artifact. The much broader feature centered at 2.09 eV primarily results from overlap of the anion wave function with the region of the neutral surface near the barrier. Hence, this is the feature in the spectra most closely associated with probing the reaction transition state. As illustrated in Figure 12, the wavepacket probes the entrance valley almost all the way up to top of the barrier, leading to a significant spread in binding energy. This feature in the simulated spectra clearly corresponds to the broad peak at 2.05 eV in the experimental spectra. The widths of both the simulated and experimental peaks are the same, about 0.2 eV, and the peak maxima differ by only 0.04 eV. The analysis of the $\Theta = 0^{\circ}$ spectra implied that the barrier should lie further out in the $OH + H_2$ valley than it does on the WDSE surface, and as new surfaces become available for this reaction, it will be extremely interesting to see the effect that the barrier location has on this feature of the simulation.

Of the remaining small peaks in the v = 2 simulation, those at 1.8 and 1.5 eV are associated with the portion of the anion wave function with H⁻(H₂O) character. As such, they will have a cos²(Θ) angular distribution and, hence, be absent in the Θ = 90° spectra. These features should show up in the Θ = 0° spectra, although one expects them to be much smaller than the main progression in that spectrum from photodetachment of H₃O⁻(v=0). The peak at 2.5 eV in the simulation most likely results from levels of the transition state complex that correlate to OH + H₂(v=1); no corresponding peak is seen in the experimental spectra.

Our v = 2 simulation is very different from the 5-D simulation by Thompson and Miller,²¹ who used a harmonic OH⁻(H₂) anion wave function based upon calculations of Xantheas and Dunning.¹⁸ The OH1 bond length (see Figure 6) in their simulation is 2.03 Å, probing the neutral surface far from the transition state and well into the OH + H₂ valley where the potential is quite flat. These authors find a sharp feature corresponding to formation of ground state OH + H₂ products and several much smaller peaks corresponding to products in low rotationally excited states. They find no evidence for vibrationally excited products. The agreement between Miller's results and our experimental data is poor. This is not surprising since our analysis of the anion surface shows that the harmonic oscillator approximation is not appropriate for describing the $OH^-(H_2)$ form of the anion. Nonetheless, it would clearly be very desirable to perform higher dimensionality simulations of this type using more accurate anion vibrational wave functions.

VI. Conclusions

In this paper we present an experimental and theoretical study of the H₃O⁻/D₃O⁻ photoelectron spectra. Photodetachment of H₃O⁻ probes the potential energy surface for the prototypical four-atom reaction $OH + H_2 \rightarrow H + H_2O$. Experimental spectra are discussed, along with a two-dimensional ab initio potential energy surface for the anion and the vibrational wave functions supported by this surface. Experiments on two different instruments were performed in an attempt to isolate the $H^{-}(H_2O)$ and $OH^{-}(H_2)$ forms of the anion. However, the photoelectron spectra are found to be independent of the mechanism used to synthesize the anion and indicate instead that the two isomers are in thermal equilibrium with the $H^{-}(H_2O)$ form lying slightly lower in energy. This is consistent with our calculations, which show that the v = 0 level of the anion is localized in the $H^{-}(H_2O)$ on the anion surface, whereas the v = 2 level is the lowest level with significant amplitude in the $OH^{-}(H_2)$ well.

The photoelectron angular distributions from the two forms of the ion were found to be very different, enabling us to separate the contributions of each to the photoelectron spectrum. Photodetachment of $H^{-}(H_2O)$ probes the $H + H_2O$ exit valley of the neutral surface, and the photoelectron spectrum consists of a progression in vibrational levels of H₂O that are slightly perturbed by the departing H atom. Photodetachment from the OH⁻(H₂) well probes the transition state and entrance valley of the $OH + H_2$ reaction. The resulting photoelectron spectrum is a broad peak. The experimental spectra are compared with two-dimensional simulations in which the appropriate anion wave functions are propagated on a potential energy surface proposed for the $OH + H_2$ reaction, the WDSE surface. Although the simulations reproduce some features of the experimental spectra, there are numerous discrepancies which suggest that the barrier on the neutral surface should lie further out in the reactant valley. Moreover, the neutral surface has a small well near the transition state which results in a sharp peak in the simulations. This is not observed in the experiment, indicating that the well should not be present.

These experiments represent a detailed probe of the transition state region for what is currently regarded as the prototypical four-atom reaction. We hope they stimulate the development of more accurate potential energy surfaces for both the anion and neutral, along with higher dimensional simulations of the photoelectron spectra that would result from these surfaces.

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