Electronic Spectroscopy and Photodissociation Dynamics of the 1-Hydroxyethyl Radical CH₃CHOH

Boris Karpichev, Laura W. Edwards, Jie Wei, and Hanna Reisler*

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482

Received: September 7, 2007; In Final Form: October 30, 2007

The electronic spectroscopy and photodissociation dynamics of the CH₃CHOH radical in the region 19 400–37 000 cm⁻¹ (515–270 nm) were studied in a molecular beam using resonance-enhanced multiphoton ionization (REMPI), photofragment yield spectroscopy, and time-of-flight (TOF) spectra of H and D fragments. The onset of the transition to the Rydberg 3s state, the lowest excited state, is estimated at 19 600 ± 100 cm⁻¹. The 3s state dissociates fast, and no REMPI spectrum is observed. The origin band of the transition to the 3p state, identified by 2 + 2 REMPI, lies at 32 360 ± 70 cm⁻¹, and a vibrational progression in the C–O stretch is assigned. When exciting CH₃CHOH near the onset of the unstructured absorption to the 3s state, only one peak is observed in the center-of-mass (c.m.) translational energy (E_t) distribution obtained by monitoring H photofragments. The measured recoil anisotropy parameter β = −0.7 ± 0.1 is typical of a perpendicular transition. The O–H bond energy is determined to be Dₒ = 1.1 eV ± 0.1 eV. At excitation energies > 31 200 cm⁻¹ (3.87 eV) a second, low E_t peak appears in the c.m. E_t distribution with β ≈ 0. Its relative intensity increases with excitation energy, but its β value does not change. In contrast, the β value of the higher E_t peak becomes monotonically less negative at higher excitation energies, decreasing to −0.2 ± 0.1 at 35 460 cm⁻¹. By comparison of the TOF distributions of the isotopologs CH₃CHOH, CH₃CHOH, and CD₃CHOH, it is concluded that two major product channels dominate the photodissociation, one leading to acetaldehyde and the other to vinyl alcohol (enol) products. There is no indication of isomerization to ethoxy. It appears that separate conical intersections lead to the observed channels, and the dynamics at the conical intersection and the exit channel deposit much of the available energy into internal energy of the products.

I. Introduction

The chemistry of hydroxyalkyl radicals is important in atmospheric chemistry and combustion environments. For example, CH₂OH is a significant product in the reaction of O(1D) with methane and Cl atoms and OH radicals with methanol. The hydroxyalkyl radicals larger than CH₂OH, the structural isomers 1- and 2-hydroxyethyl radicals (CH₃CHOH and CH₂CH₂OH, respectively), are relevant to ethanol combustion. These isomers are also involved in the photochemistry of the ethoxy radical, as products in the reaction of halogen atoms with ethanol and as intermediates in the O + C₂H₅ and OH + C₂H₆ reactions. The role of hydroxyalkyl intermediates in combustion reactions has recently been highlighted by the discovery that the enol tautomers of aldehydes are significant combustion intermediates. For example, vinyl alcohol (ethenol, CH₂=CHOH), the less stable tautomer of acetaldehyde (CH₃=HC=O), is formed in flames of ethanol, olefins, and commercial fuels. Both tautomers can be formed in the decomposition of ground state hydroxyethyl radicals. In spite of their importance very little is known about the photophysics and photochemistry of hydroxyalkyl radicals.

An unstructured electronic absorption spectrum of CH₃CHOH recorded at 300 K in the region 230–300 nm has a maximum absorption cross section of 3.6 × 10⁻¹⁸ cm². The spectrum shows that absorption at < 300 nm rises strongly toward shorter wavelengths, but the measurements stopped at 230 nm, where the spectrum reached a plateau, and did not extend to wavelengths longer than 300 nm. A paper on the kinetics of CH₃CHOH reports a resonance-enhanced multiphoton ionization (REMPI) signal of the parent ion in the range 430–460 nm, which likely arises from 2 + 1 ionization via a Rydberg state. The adiabatic ionization energy of CH₃CHOH is 6.64 eV, much lower than the corresponding value for CH₂OH (7.56 eV). A photoelectron spectroscopy study revealed a progression of ~1600 cm⁻¹ in the CO stretch of the ion, in agreement with the expected shortening of the CO bond upon ionization.

The photodissociation of the hydroxyethyl radical has not been studied before. However, following UV excitation of the ethoxy isomer (CH₃CHOH), Neumark and co-workers observed the unexpected C₂H₃ + H₂O channel, which they suggested evolved via isomerization on the excited-state to hydroxyethyl.

There are no theoretical papers on the excited states of the hydroxyethyl radical. However, there are several ab initio calculations of the geometry of the ground state and the ion as well as barriers to isomerization and dissociation on the ground-state potential energy surface (PES). The lowest barrier channels calculated for the ground state PES are:

\[ CH₃CHOH → CH₂CHO + H \quad \Delta H = 1.04 \text{ eV} \]  
\[ → CH₂CHOH + H \quad \Delta H = 1.46 \text{ eV} \]  
\[ → CH₃ + CHOH \quad \Delta H = 3.13 \text{ eV} \]  

where \( \Delta H \) is the thermochemical dissociation threshold.

* To whom correspondence should be addressed. E-mail: reisler@usc.edu.
Radicals generated in the quartz tube undergo cooling during the supersonic expansion. The rotational temperature is estimated at 10–15 K, as shown in our work with CH₂OH.³⁰ The detection chamber is separated from the source chamber by a skimmer (Beam Dynamics, 1.51 mm diameter). In the detection chamber, the pump and probe laser beams are counterpropagating and cross the molecular beam at a right angle.

The pump (dissociation) radiation is generated by a Nd:YAG-pumped OPO/OPA laser system (Continuum, PL8000/Sunlite/FX-1; 0.5–2 mJ at 250–400 nm, 14–20 mJ at 470–520 nm; 25 cm f.l. lens). The probe laser detects H and D fragments by 1+1 REMPI via the Lyman-α transition. The doubled output (365 nm, 2 mJ) of a Nd:YAG-pumped dye laser system (Continuum, NY81/NDE6000, LDS 751) is focused (20 cm f.l. lens) into a 1000 Torr mixture of Kr (25%) and Ar (75%). The tripled 121.6-nm radiation is focused in the detection chamber (MgF₂ 7.5 cm f.l. lens) along with the residual 356-nm light.

Ions generated in the experiment are accelerated perpendicularly to the laser and molecular beams by a static electric field. A system of two electrostatic lenses provides space-focusing conditions for a range of acceleration voltages. After traversing an 18-cm field-free drift region, the ions reach a multichannel plate detector (MCP, Galileo, 25 nm) installed at the top of the TOF tube.

The polarization of the pump laser is controlled by a photoelastic modulator (PEM-80, HINDS International, Inc.). All TOF distributions are recorded with two polarizations (parallel and perpendicular to the TOF axis), which allows calculation of the recoil anisotropy parameter β.³⁸

Because the ion signals are low, proper core sampling of the ion velocity distribution is impossible to achieve. Instead, the voltages applied to the extractor and repeller plates are gradually decreased while preserving space-focusing conditions. At the lowest possible voltage with an acceptable signal-to-noise ratio the conversion of the TOF spectra to an energy distribution (Eₜ distributions) is done. In order to find the position and width of the peak in the region of low Eₜ distributions, a convolution of two Gaussian-like distributions is performed. This method is described in more detail by Syage.³⁸ The conversion of the TOF spectra to an Eₜ scale is calibrated using Eₜ distributions obtained in our previous experiments on CH₂OH photodissociation.²⁸

III. Results

Two types of experiments were carried out. First, REMPI and photofragment yield spectra of H or D were recorded in regions where transitions to Rydberg states were expected in
order to assign the electronic transitions. To elucidate the photodissociation dynamics, TOF spectra were obtained at selected energies, and the recoil anisotropy parameters were determined.

1. Photofragment Yield and REMPI Spectra. As stated in section I, our search for electronic absorption was guided by results obtained for CH$_2$OH$^{30,33-35}$ In analogy with CH$_2$OH, we assumed that the lowest absorption bands involved Rydberg states and that the quantum defects did not change much relative to those in CH$_2$OH. As described in section IV, this was indeed found to be true, and therefore in the material that follows we use spectroscopic assignments of the upper electronic states that correspond to those in CH$_2$OH.

3$s$ Region. This is the lowest excited state, and as in CH$_2$OH, no ions of CH$_3$CHOH (CH$_3$CHOD) were detected upon excitation in this region. Therefore, H(D) photofragment yield spectroscopy was used to monitor absorption. The onset of H (or D from CH$_3$CHOD) fragment signal was determined at 19 600 ± 100 cm$^{-1}$ (2.43 ± 0.01 eV). Figure 1 displays a background-subtracted D-photofragment yield spectrum in the region where the transition to the 3$s$ Rydberg state was predicted to be located. A similar spectrum was obtained by monitoring H-fragments from CH$_3$CHOH, but the signal-to-noise ratio was slightly better with CH$_3$CHOD due to lower D background. No H signal from CH$_3$CHOD was observed in this region.

3$p$ Region. A distinct feature of the 3$p$ state in CH$_2$OH was a longer lifetime than the 3$s$ state, which has made REMPI detection possible.$^{34}$ In contrast, in CH$_3$CHOH, no REMPI signal was observed up to the origin band of the 3$p$ state (see below). Photofragment yield spectra of H atoms taken in the wavelength region where absorption to 3$p$ was expected did not show features that could distinguish it from absorption to the 3$s$ state. Therefore, this transition remains unassigned.

3$p$ Region. A distinct 2 + 2 REMPI spectrum was observed in the 32 000–38 000 cm$^{-1}$ region expected for the transition to the 3$p$ state. The lowest energy peak in Figure 2 is assigned as the origin band of the transition, which is located at 32 360 ± 70 cm$^{-1}$ (4.01 ± 0.01 eV). Similar to the corresponding CH$_2$OH spectrum shown in the top panel of Figure 2,$^{30}$ the two other peaks, located at 1560 ± 100 cm$^{-1}$ intervals, form a vibrational progression in the C–O stretch excitation. The scan was taken with a step size of 5 cm$^{-1}$, but no additional structure was observed with a finer step size. The REMPI spectrum extends to shorter wavelengths than displayed in Figure 2, but no further structure is observed, probably due to a combination of spectral congestion and lifetime broadening.

2. Time-of-Flight (TOF) of H(D) Photofragments. Figure 3 displays a typical background-subtracted TOF spectrum of H atoms recorded following excitation at 21 276 cm$^{-1}$ (2.63 eV; 470 nm) with laser polarization parallel and perpendicular to the ion TOF axis. The background is subtracted. Zero time indicates fragment with no recoil.

3. Time-of-Flight (TOF) of H(D) Photofragments. Figure 4 displays a typical background-subtracted TOF spectrum of H atoms recorded following excitation at 21 276 cm$^{-1}$ (2.63 eV; 470 nm) with laser polarization parallel and perpendicular to the ion TOF axis. The background is subtracted. Zero time indicates fragment with no recoil.
state. The photofragment $E_t$ distribution exhibits a single anisotropic peak with $\beta = -0.7 \pm 0.1$

Figure 5 displays the c.m. $E_t$ distribution obtained by monitoring H fragments from photodissociation of CH$_3$CHOH at 31,250 cm$^{-1}$ (3.87 eV) excitation energy with parallel and perpendicular polarizations of the pump laser. For high $E_t$, the recoil distribution is anisotropic but with a lower anisotropy parameter than was observed at lower excitation energies (near the onset of absorption to the 3s state), and $\beta = -0.4 \pm 0.1$ is obtained for both CH$_3$CHOH and CH$_3$CHOD. In addition, a small isotropic peak ($\beta = -0.0 \pm 0.1$) appears in the low $E_t$ region. The peak of slow photofragments is absent in Figure 6, which shows an $E_t$ distribution for CH$_3$CHOD dissociation obtained at the same excitation energy by recording the D fragment TOF spectrum. A notable feature of this distribution is the difference between $E_{t,max}$ and the available energy: $E_{avail} = E_{diss} - D_0 = 3.87 - 1.2 = 2.67 \pm 0.1$ eV (where $D_0$ is adjusted for zero-point energy), whereas $E_{t,max} = 2.2 \pm 0.1$ eV, giving, $E_{avail} - E_{t,max} = 0.47 \pm 0.14$ eV as the minimum internal energy in the molecular cofragment. In contrast, in the case of CH$_3$CHOH, $E_{t,max}$ and $E_{avail}$ are equal within the error bars. H and D fragment TOF spectra in the 21,000−31,300 cm$^{-1}$ excitation range show similar trends.

Figures 7 and 8 show typical c.m. $E_t$ distributions obtained following excitation of CH$_3$CHOH (CH$_3$CHOD) at 35,460 cm$^{-1}$ (the third peak in Figure 2). The two peaks in Figure 7 become broader than those at lower excitation energy, and the recoil anisotropy parameters of the high $E_t$ peaks are lower ($\beta = -0.2 \pm 0.1$). The low $E_t$ peak grows in relative intensity but remains isotropic. The gap between $E_{t,max}$ and $E_{avail}$ increases to 0.39 eV (0.79 eV) for CH$_3$CHOH (CH$_3$CHOD). The $E_{t,max} - E_{avail}$ gap increases gradually with excitation energy up to the highest measured excitation energy of 35,460 cm$^{-1}$, while the $\beta$ parameter decreases with increasing excitation energy. The dependence of $\beta$ on excitation energy is shown in Figure 9. A TOF distribution was also recorded by monitoring D atoms from the CD$_3$CHOH isotopolog. It showed only a slow peak comparable to the low $E_t$ peak in Figure 7, in contrast to the D fragment TOF spectrum from CH$_3$CHOD, which displayed only the high $E_t$ peak.

IV. Discussion

1. Assignment of the 3s and 3p States. The low ionization energy of CH$_2$OH results in electronic Rydberg states that are lower in energy than the lowest valence states. The ionization energy of CH$_3$CHOH is almost 1 eV lower than that of CH$_2$OH (6.64 eV vs 7.56 eV), the lowest-lying electronic
states of the former are also expected to be of Rydberg nature and lie at even lower excitation energy. The valence states, however, should not vary much in energy in going from CH$_2$OH to CH$_3$CHOH. The positions of the Rydberg states can be estimated by the Rydberg formula: $E = 4E - R(n - \delta)^2$ where $R = 109,737.316$ cm$^{-1}$, $n$ is the principal quantum number, and $\delta$ is the quantum defect obtained experimentally from the energies of the corresponding Rydberg states of CH$_2$OH (see Table 1).

The first excited electronic state is the 3s state. The onset of the H photofragment yield spectrum is at 19,600 ± 100 cm$^{-1}$, which is close to the predicted value of 18,530 cm$^{-1}$. Our inability to observe a CH$_3$CHOH$^+$ REMPI signal despite the stability of the ion$^{12,14}$ suggests that internal conversion from the 3s to the ground state with subsequent dissociation is faster than ionization from the Rydberg state. A similar conclusion was reached with regard to CH$_2$OH in the 3s state.$^{29,34}$ Notice that CH$_3$CHOH starts absorbing at 510 nm, which makes it unstable in visible light.

Another feature common to CH$_2$OH and CH$_3$CHOH is the strong negative recoil anisotropy of the photofragment distribution in excitation to the 3s state ($\beta_{3s} = -0.7 ± 0.1$ for both radicals near the onset of the transition). The ground-state equilibrium geometry of both CH$_2$OH and CH$_3$CHOH is nonplanar.$^{12,14}$ In CH$_2$OH, a low barrier to CH$_3$ inversion (140 cm$^{-1}$) allows the two mirror image equilibrium structures of C$_s$ symmetry to rapidly interconvert.$^{31-43}$ As a result, the electronic wavefunction of CH$_2$OH complies with the C$_s$ point group. This gives the transition from the ground state (A$_0^+$) to the 3s and 3p$_x$ states, which are of A symme- try, a perpendicular moment. The observation of similar anisotropy in the transition to 3s for both radicals suggests similar orientation of the transition dipole moment relative to the O–H bond (the only bond fission channel observed near the onset of 3s state excitation) as well as similar symmetry of the electronic wavefunctions. By use of C$_v$ symmetry for the electronic transitions of CH$_3$CHOH, we assign the first two Rydberg states as $1^2A'(3s)$ and $2^2A'(3p)$. For CH$_2$OH, the transition to 3p$_x$ was calculated to be very weak and was not observed.$^{31,40}$ Likewise, we do not see any evidence for a transition to this state in CH$_3$CHOH.

The 3p$_x$ state of CH$_3$CHOH could not be identified in our experiment. No REMPI of CH$_3$CHOH was seen around the predicted onset of the transition (about 27 700 cm$^{-1}$), and no discernible change in the H-photofragment spectrum was detected. In the hydroxymethyl radical, fast predissociation of the 3p$_x$ state caused considerable broadening of the peaks in the REMPI spectrum.$^{34}$ Since CH$_3$CHOH has twice as many vibrational degrees of freedom as CH$_2$OH, it is likely that the 3p$_x$ state predissociates even faster, reducing its ionization efficiency and broadening the peaks beyond the sensitivity of our measurements. Apparently, H-photofragment spectra in this excitation region are dominated by 3s state absorption and show no special features that indicate the onset of additional absorption to another state.

The first REMPI signal of CH$_3$CHOH appears at 32,360 cm$^{-1}$ near the predicted origin of absorption to the 3p$_x$ (2$^2A'$) state at 33,684 cm$^{-1}$. In keeping with a model of faster predissociation than in CH$_3$OH, the peaks are much broader than for the 3p$_x$ state of CH$_2$OH (Figure 2). As in hydroxymethyl, they form a vibrational progression with peaks separated by 1560 ± 100 cm$^{-1}$, close to the frequency of the C–O stretch vibration in the ion.$^{25}$ The progression can be rationalized by the promotion of an electron from the C–O antibonding $\pi^*$ orbital to a nonbonding Rydberg orbital in excitation to the 3p$_x$ state, which leads to a shortening of the C–O bond length. In contrast to the H photofragment yield spectrum of CH$_2$OH in the region of the 3p$_x$ state, which shows the same vibronic bands as the REMPI spectrum, there was no discernible structure in the H(D) yield spectra of CH$_3$CHOH(D) above the onset of the transition to 3p$_x$, indicating that absorption to the 3s state still dominates the absorption spectrum in this region.

It is noteworthy that a 2 + 1 REMPI spectrum of CH$_3$CHOH was reported in the region around 430–460 nm ($2\nu = 46,510–43,480$ cm$^{-1}$),$^{24}$ which corresponds according to the Rydberg formula to one of the 4p states. Higher Rydberg states usually couple less efficiently to other Rydberg and valence states, and their dissociation is less rapid, which allows observation of the 2 + 1 REMPI signal.

2. Photodissociation Dynamics. The conclusion from the spectroscopic studies is that, throughout the examined region, which encompasses absorptions to the 3s, 3p$_x$, and 3p$_y$ Rydberg states, the predominant absorption is to the 3s state. Therefore, in the discussion below, we assume that dissociation is initiated from 3s, although contributions from 3p$_x$ excitation are likely at shorter wavelengths.

The ground state of the CH$_3$CHOH$^+$ ion is bound, and therefore so are the Rydberg states of the neutral, provided they do not interact with other states. As Rydberg states correlate with excited-state products, the 3s Rydberg state, which is the lowest electronic state, must couple to the ground state in order to predissociate to ground-state products. Near the onset of the 3s state, dissociation channels (1) and (2) are energetically accessible; i.e., both the O–H ($D_0 = 1.04$ eV) and the C$^{2-}$(H) ($D_0 = 1.46$ eV) bond fission channels,$^{21}$ where C$^{2-}$ is the terminal carbon atom, are allowed. Both channels have similar barrier heights on the ground state PES (calculated at 1.52 and 1.58 eV, respectively).$^{21}$

Had internal conversion from 3s to the ground state been followed by statistical redistribution of energy among the vibrational modes on the ground PES, one would expect close competition between these two simple bond fission channels above the barrier. However, the $E_t$ distribution near the onset of the absorption to 3s is clearly nonstatistical as most of $E_{avail}$ is deposited in translation. Also, only the O–H bond fission channel (1) is detected, even though channel (2) is energetically accessible. This follows from a comparison of the $E_t$ distributions obtained by monitoring H and D fragments from dissociation of CH$_3$CHOH and CH$_3$CHOD, respectively: each exhibits a single peak of the same shape, with $E_{t,\text{max}} = E_{\text{avail}}$ corresponding to $D_0 = 1.1 ± 0.1$ eV.

At 3.87 eV ($31,250$ cm$^{-1}$) excitation, however, a second dissociation channel is open, as seen in the H-fragment $E_t$ distribution of Figure 5. It exhibits an additional peak in the region of low $E_t$, which is not present in the corresponding D fragment $E_t$ distribution (Figure 6). Deconvolution of the H fragment TOF spectrum obtained by assuming two Gaussian shape-distributions of $E_t$ (section II) shows that the channel represented by the slow peak must have $D_0 < 2.7 ± 0.1$ eV. This value is larger than the calculated $D_0$ value of the C$^{2-}$(H) bond fission (1.46 eV) but smaller than $D_0$ for the C$^{2-}$(H) bond fission (calculated at 3.37 eV).$^{21,22}$ The interpretation that the low $E_t$ peak arises from channel (2) giving rise to CH$_3$CHOH product agrees with the result of the D fragment TOF spectrum of CD$_3$CHOH, which showed only the low $E_t$ peak. Unfortunately, the core-sampling assumption breaks at low $E_t$, so the slow peak in the TOF spectrum cannot be analyzed quantita- tively. We can say, however, that the C$^{2-}$(H) bond fission
channel opens >1 eV higher than the O–H bond fission channel, despite the similar barrier heights of the two reactions on the ground state PES. We conclude, therefore, that the dynamics on the 3s state PES must be responsible for this difference.

In CH₂OH, calculations identified an efficient (vertical) conical intersection between the 3s and the ground state, which was located in the PES region of elongated O–H bond.⁶,³⁷ This geometry favors fast and efficient dissociation of the O–H bond. A second conical intersection, located at much higher energies, led to C–H bond fission.⁶,³⁷ It is reasonable to assume that in CH₃CHOH there are at least two conical intersections between the 3s and the ground state, each favoring one of the two exit channels. Thus, after the radical goes through the conical intersection it dissociates predominantly through the corresponding channel. Accessibility to the dissociation channel in each case is controlled by the nuclear geometry and minimum energy of the intersection on the 3s PES.

In reference to the properties of the conical intersection, it appears that certain vibrations must be active for efficient surface coupling to take place. As the excitation energy increases in the ground-state PES following internal conversion, an increasing fraction of the parent vibrational energy is deposited into modes that appear finally as internal modes (vibration and rotation) of the acetaldehyde fragments. This is manifested in the broadening of the high-energy peak in the Eᵣ distributions and the increasing value of Eᵣ,full − Eᵣ,max. The latter is especially pronounced in CH₃CHOD. The slow vinyl alcohol product from channel (2) also has a broad internal energy distribution.

It appears that some of the excited parent vibrational levels involve out-of-plane motions, which reduce the recoil anisotropy in the perpendicular transition. Indeed, the recoil anisotropy parameter β becomes less negative as the excitation energy increases (Figure 9), concomitant with the internal energy buildup in the products. This effect is much less noticeable in CH₂OH(D) where the β parameter is nearly constant over the entire range of perpendicular transitions to 3s and 3pₓ, and a sudden change in anisotropy occurs only at the onset of the parallel transition to the Rydberg 3p state.⁵⁻¹₀,³³,³⁵,³⁶ The observation of an isotropic energy distribution for channel (2) may also reflect the favored geometries that lead to nonadiabatic transitions. The C–H bond fission channel in CH₂OH was also isotropic.²⁹

V. Conclusions

Electronic transitions to low-lying Rydberg states and photodissociation dynamics of the CH₂CHOH(D) radical in the region 19 600–37 000 cm⁻¹ were studied for the first time in a molecular beam. On the basis of the REMPI and H(D) photofragment yield spectra, we conclude that the predominant absorption in the observed region is to the lowest excited state—the Rydberg 3s state—whose onset is at 19 600 cm⁻¹. The origin band of the transition to the 3pₓ state lies at 32 360 cm⁻¹. The onsets of the observed absorptions agree well with predictions obtained by using the Rydberg formula with quantum defects similar to those obtained for the corresponding transitions in CH₂OH.

To identify the photodissociation channels, TOF spectra of D and H photofragments were recorded for CH₂CHOH, CH₃CHOH, and CD₃CHOH. At dissociation energies near the onset of absorption to the 3s state, c.m. fragment Eᵣ distributions from CH₂CHOH show only one peak at high Eᵣ, close to the maximum allowed by energy, with a recoil anisotropy parameter β typical of a perpendicular transition. At higher excitation energies, a second, low Eᵣ peak appears, which is isotropic; its relative intensity increases at higher excitation energies.

The TOF spectra obtained with the three isotopologues allow us to identify two independent dissociation channels, one leading to acetaldehyde and the other to vinyl alcohol (enol): (1) CH₃CHO + H; and (2) CH₂CHOH + H. There is no indication of isomerization to ethoxy. The former channel appears at the onset of the 3s absorption, whereas the latter first appears only ~1 eV above its thermochemical threshold. We suggest that conical intersections with the ground state lead to O–H bond fission [channel (1)] from the onset of absorption to 3s, but the conical intersection leading to the enol product [channel (2)] has a minimum energy much above the thermochemical threshold for this channel.

Another notable feature of the dissociation is the increasing amount of internal energy in acetaldehyde [channel (1)] as the excitation energy increases. The less negative β of the fast peak at higher excitation energies may result from out-of-plane motions during dissociation of vibrationally excited molecules generated in the nonadiabatic transition with the ground electronic state. These results reflect the dynamics in the region of the conical intersections as well as dynamics in the exit channel.

From experiment and theory we conclude that the Rydberg formula should hold rather well in the homologous series of CH₂OH, serving as a guide to the absorption spectra of higher hydroxyalkyl radicals whose radical center is located on the C adjacent to OH (1-position). The structureless electronic absorption extends from the visible to the UV, making these radicals unstable to visible light. Also, nonadiabatic transitions coupling the Rydberg states to the ground state are expected to be efficient, resulting in fast dissociation to several product channels.

Acknowledgment. Support by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, U.S. Department of Energy, is gratefully acknowledged. The authors wish to thank Stephen Klippenstein for unpublished results and Mikhail Ryznov for help in carrying out some of the experiments.

References and Notes
