Photodissociation of the Hydroxymethyl Radical from the $2^2A''(3p_z)$ State: H$_2$CO and HCOH Products†

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The photodissociation of the hydroxymethyl radical in excited vibrational levels of the Rydberg 3$p_z$ state is investigated by the core-sampling time-of-flight method and infrared-ultraviolet (IR+UV) double resonance ionization spectroscopy. Translational energy distributions of dissociation products of CH$_2$OD (3$p_z$; $\nu$) are measured for selected vibrational levels. CH$_2$OD → D + CH$_2$O (I) and CH$_2$OD → H + CHD (II) are identified as major dissociation channels. Secondary dissociation from internally excited H$_2$CO and HCOD photofragments is observed when their internal energy exceeds the threshold for H/D formation. Mechanisms for secondary H/D production include direct dissociation and dissociation following HCOD → HDCO isomerization. Several new overtone and combination bands of the $2^2A''(3p_z) \rightarrow 1^2A^+$ transition of CH$_2$OH are accessed by IR+UV double resonance spectroscopy. Initial vibrational excitation of ground-state CH$_2$OH enhances the Franck–Condon factors for subsequent electronic transitions to the $3p_z$ state. Lifetime broadening is observed for all levels in the $3p_z$ state and the linewidth increases gradually with excitation energy from 11 cm$^{-1}$ for the origin band to 65 cm$^{-1}$ for the first overtone of the OH stretch. The broadening originates in increasingly efficient nonadiabatic couplings to other states.

I. Introduction

The importance of the hydroxymethyl radical (CH$_2$OH) in atmospheric and combustion environments has motivated intensive studies of its photochemistry. 1–3 The 3$s$, 3$p$, 3$p_z$, and 3$p_y$ Rydberg states are the lowest excited states. 4–8 The 3$p$, and 3$p_z$ Rydberg states are bound, and their potential energy surfaces (PES) resemble that of the ground-state CH$_2$OH$^+$ radical ion. 4 Among these four states, only 3$p_z$ does not carry oscillator strength, and the spectroscopy involving transitions to the other states has been recently studied in molecular beams. 4,9–13

It is intriguing that in going from the highest 3$p_z$ to the 3$s$ state the spectral features are increasingly broadened. 9,13 The origin band transition to the 3$p_z$ state is the narrowest, with a 11 cm$^{-1}$ homogeneous linewidth, while the spectrum of the 3$s$ state is featureless. All of these states are predissociative with lifetimes less than a picosecond.

Previous investigations of the UV photochemistry of CH$_2$OD included measurements of translational energy and angular distributions of H and/or D photoproducst following excitation to the onset of the 3$s$ state and the origin bands of the 3$p$ and 3$p_z$ states. These studies elucidated dissocation mechanisms 14–17 and, when combined with conical intersections calculations, 18 demonstrated that the Rydberg states under investigation are coupled to lower lying states. The final dissociation step takes place on the ground state, reached through 3$s$/ground-state conical intersections along the CH and OH coordinates. 18

Several distinct vibrational levels in the 3$p_z$ state were accessed by resonance-enhanced multiphoton ionization (REMPI) spectroscopy. 4,9 These included vibrational modes $\nu_4$ and $\nu_9$ and their combination bands. However, only the origin band was investigated with respect to dissociation, and two major channels were identified: 14,17

\[
\begin{align*}
\text{CH}_2\text{OD} & \rightarrow \text{CH}_2\text{O} + \text{D} \quad \Delta H = 1.32 \pm 0.07 \text{ eV} \quad (\text{I}) \\
\text{CH}_2\text{OD} & \rightarrow \text{HCOD} + \text{H} \quad \Delta H = 3.4 \pm 0.1 \text{ eV} \quad (\text{II})
\end{align*}
\]

These channels were observed also in excitation to the 3$s$ and 3$p_z$ states, with reaction II first appearing near its energetic threshold. 16,17

In this work, we extend the previous studies to photodissociation dynamics of CH$_2$OD from selected vibronic levels of the 3$p_z$ state, e.g. 0$^1_0$, 4$^2_0$, 6$^2_0$. In addition to channels (I) and (II), secondary dissociation of CH$_2$O and HCOD fragments is observed following excitation to the 4$^2_0$ and 6$^2_0$ bands, as evidenced by the appearance of a second peak of slow D or H in the product translational energy distributions.

The OH ($\nu_1$) and CH ($\nu_2$ and $\nu_3$) stretch modes in the 3$p_z$ state of CH$_2$OH are important in the dissociation dynamics as they constitute reaction coordinates for channel (I) and (II), respectively. 18 Excited vibrational levels in the 3$p_z$ state involving these modes were not detected previously by REMPI, 4,9 because of small Franck–Condon (FC) factors in excitation from the vibrationless level in the ground state. Recently, we reported infrared spectroscopy involving OH and CH stretch modes in the ground state of CH$_2$OH. 19 By carrying out IR+UV double resonance experiments, new vibrational levels in the 3$p_z$ state were also directly observed. In these experiments, a FC-favorable transition to a selected vibrational level in the 3$p_z$ state is accessed by preparing a suitable vibrational level in the ground state prior to UV excitation. The dissociation dynamics from the new levels has been inferred from spectral analyses. For example, the transition to the first overtone of the OH stretch is broadened considerably, indicating a shorter lifetime than that of lower energy vibrational levels in the 3$p_z$ state.

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II. Experimental Details

The radical generation procedure and experimental arrangement have been described in detail previously and will be briefly summarized here.9,14 A mixture of 4% CH$_3$OD or CH$_3$OH (Aldrich, used without further purification) and ~1% Cl$_2$ (Air gas, 99.5%) in He at 2 atm total pressure in a 4 L glass bulb is prepared. This mixture is delivered to the radical generation chamber by a piezoelectrically driven pulsed nozzle operating at 10 Hz. A 355 nm laser pulse beam (Spectra Physics, GCR-11; 8 mJ, focused by a 30 cm f.l. cylindrical lens) crosses the edge of a 1-mm diameter quartz tube attached in front of the nozzle orifice. The radiation dissociates Cl$_2$, and the Cl atoms react rapidly with CH$_2$OD (CH$_3$OH), creating CH$_2$OD(CH$_2$OH).

The CH$_2$OD(CH$_3$OH) radicals undergo further cooling during the supersonic expansion. They pass through a 1.51 mm diameter skimmer (Beam Dynamics), and reach the photodissociation region vibrationally cold. A 11.0 K rotational temperature is estimated from the 1+1′ two-color REMPI spectrum obtained via the 3p$_z$ state.9

A. Photofragment Yield (PFY) Spectra of H Atoms from CH$_2$OD. In this experiment, the CH$_2$OD radical beam is intersected with a UV pump beam whose frequency is scanned over the region of interest. The pump laser radiation excites the radicals to the 3p$_r$ Rydberg states and then further ionizes them. A counterpropagating probe laser beam whose wavelength is fixed at ~121.6 nm is set to detect H atoms by 1+1′ two-color REMPI via the L-α transition. The UV pump radiation is obtained from a seeded Nd:YAG laser-pumped OPO/OPA (Continuum, PL8000/Sunlite/FX-1; 0.5 mJ, 40 cm f.l. lens) system. The VUV probe laser radiation is generated in a tripling system. The VUV probe laser beams are generated by the same laser systems used for the pumping of H atoms by the two-color REMPI spectrum via the 2 2 A$^1$-1 2 A$^1$ transition.9 IR radiation (4 mJ, 20 cm f.l. lens) is obtained from another seeded Nd:YAG pumped OPO/OPA (Continuum, PL8000/Sunlite/FX-1; 1.0 mJ, 40 cm f.l. lens) system. The spectra are recorded in both “IR on” and “IR off” conditions. In “IR on” conditions, the probe laser is fired 20 ns after the pump laser, whereas with “IR off”, the probe laser precedes the pump laser by 1 μs. The time delay is regulated by Labview controlled digital pulse/delay generators (DG 535, Stanford Research Systems, 5 ps resolution).

III. Results

A. REMPI and H-Atom PFY Spectra of CH$_2$OD. Several vibrational levels in the 3p$_z$ state of CH$_2$OD have been previously characterized by REMPI spectroscopy in a flow reactor and molecular beam.4,9 We have reproduced the 1+1′ REMPI spectrum via the 2 2 A$^1$-1 2 A$^1$ transition, and our results are shown in the top panel of Figure 1. The two strong progressions have been assigned as 60$_n$ (CO stretch) and 40$_n$ (CH$_2$ scissors), n = 0 and 1, by Johnson and Hudgens4 and Arisgov et al.9 A PFY spectrum of H atoms is recorded in the same energy region of the REMPI spectrum of CH$_2$OD and shown in Figure 1. In this experiment, the frequency of the pump laser is scanned, whereas that of the probe laser is fixed at the peak of the detection line of the H atom. The clear correspondence between the H—PFY and CH$_2$OD REMPI spectral features indicates that H atom is a product of the dissociation of CH$_2$OD (3p$_r$). Combined with the D photofragment yield spectrum reported previously by Conroy et al. in the same energy region,14 we conclude that both H and D are produced in dissociation from the vibrational levels of 3p$_z$ examined here.

B. Translational Energy Distributions of D and H Channels of CH$_2$OD. Figure 2, panels b and c, shows translational energy distributions, P(E$_T$)’s, of the D (top panel) and H (bottom panel) channels [reactions I and II, respectively] obtained from core-sampling TOF distributions of H and D photofragments from CH$_2$OD. Each set of spectra are recorded with the pump laser polarization parallel and perpendicular to the TOF axis. The alteration of the polarization is accomplished by controlling the time delay between the trigger of the pump laser pulse and a photoelastic modulator (PEM-80, HINDS International, Inc.). The pump and probe laser beams are generated by the same laser systems used in H atom PFY experiment. The procedure of transforming the measured TOF profile into kinetic energy distribution P(E$_T$) has been described in detail elsewhere.14,20

Figure 1. 1+1′ REMPI spectrum (upper panel) and H photofragment yield spectrum (lower panel) of CH$_2$OD. Assignments are from ref 9.

C. IR+UV Double Resonance Ionization of CH$_3$OH. In these experiments, the IR laser beam frequency is fixed at the center of a transition to a selected rovibrational level of the OH− or CH− stretch mode in the ground state, whereas the UV frequency is scanned in the energy region around 41 062 cm$^{-1}$, i.e., the peak of the origin band of the CH$_3$OH 2 2 A$^1$-1 2 A$^1$ transition.9 IR radiation (4 mJ, 20 cm f.l. lens) is obtained from a seeded Nd:YAG pumped OPO/OPA (LaserVision) and UV radiation is obtained from another seeded Nd:YAG pumped OPO/OPA (Continuum, PL8000/Sunlite/FX-1; 1.0 mJ, 40 cm f.l. lens) system. The spectra are recorded in both “IR on” and “IR off” conditions. In “IR on” conditions, the probe laser is fired 20 ns after the pump laser, whereas with “IR off”, the probe laser precedes the pump laser by 1 μs. The time delay is regulated by Labview controlled digital pulse/delay generators (DG 535, Stanford Research Systems, 5 ps resolution).
The center of the Doppler profile of the D and H photofragment. Each result is shown after background subtraction taken by tuning the pump laser frequency off resonance. Through this subtraction procedure, the contributions of D and H background from the radical generation process are minimized.

C. IR+UV Double Resonance Spectroscopy. An example of an IR + UV double resonance spectrum is shown in Figure 3. This spectrum is obtained by fixing the IR frequency at 3674.3 cm^{-1} [vP(0)(2)] to pump CH2OH to a single rovibrational level of the fundamental OH stretch (v1) in the ground state, while scanning the UV frequency. The assignment of the rovibrational level in the ground state is based on ref 19. The solid and dot dashed lines represent “IR-on” and “IR-off” spectra, respectively. The 0^0_0 transition, slightly saturated in our spectrum, is the dominant feature. It is observed in both “IR-off” and “IR-on” spectra, with the intensity in the “IR-on” spectrum reduced by depletion of ground-state population by IR absorption. A new vibrational level to the red of the origin band (0^0_0) is evident in the “IR-on” spectrum. The absence of this peak in the “IR-off” spectrum suggests that it is associated with the rovibrational level excited in the IR. Similar spectra, shown in ref 19, are obtained by varying the IR frequency and accessing selected rovibrational levels of the fundamental CH symmetric stretch (v3) at 3048.9 cm^{-1} [vR(2)], CH asymmetric stretch (v2) at 3170.5 cm^{-1} [vR(1)], and the first OH-stretch overtone (2v1) at 7159.7 cm^{-1} [vP(2)].^19 The additional transitions and their assignments are shown in Figure 4.

IV. Discussion

A. CH2O and HCOD Products from CH2OD (3p). As shown in Figure 2, the translational energy distributions of the D and H channels obtained by exciting the 0^0_0, 4^0_0, and 6^0_0 bands are similar in shape in the region of high translational energy. It has been previously shown that excitation in the origin band gives rise to D and H products from channels (I) CH2OD → D + CH2O and (II) CH2OD → H + CHOD, respectively. The measured H/D ratio was 1.0 ± 0.2 for the origin band. Its value increases smoothly in the energy region covering absorption to the 3s, 3p, and 3p states. No sharp change was detected when the band origins of the transitions to the 3p and 3p states were reached, indicating the existence of a common final step in the dissociation following excitation to the 3s, 3p, and 3p states. The translational energy limits associated with production of CH2O and CHOD are marked by arrows in Figure 2. The consistency of these limits with the observations indicates that channels (I) and (II) are major pathways in the dissociation from the 4^0_0 and 6^0_0 bands as well.

Unlike the results from the 0^0_0 band, however, a second peak at low translational energy begins to develop in the P(E_T)’s of the D and H channels obtained via excitation to the 4^0_0 band (Figure 2b), and its intensity increases with increasing excitation energy. An example is shown in Figure 2c obtained via excitation to the 6^0_0 band. Caution has been exercised in ascertaining that these peaks do not represent artifacts of the core sampling technique in the region of small recoil. It is well-known that the core-sampling assumption breaks down when v ≤ rcore/τ, where rcore is the core radius and τ is the time-of-flight of ions reaching the core region. This breakdown leads to a large increase in collection efficiency at low E_T, and thus enhancement of signal intensity. In our experimental arrangement, the translational energy corresponding to the breakdown of core-sampling is 0.02 eV, a value that is almost an order of magnitude smaller than the translational energy of the peaks of the slow features. In addition, even though the experimental conditions are the same for all the measured vibrational levels shown in Figure 2, the slow peak is observed only following 4^0_0 and 6^0_0 excitations and its width increases with the increase in excitation energy. This confirms that the slow peak represents a change in mechanism rather than an experimental artifact.
Although quantitative evaluations of \( P(E_f) \) are not secure in the low \( E_T \) region, qualitative conclusions can still be drawn by comparing distributions from different vibrational levels in the 3pz state.

We believe that the slow peaks arise from secondary dissociation of “hot” \( \mathrm{H}_2\mathrm{CO} \) and HCOD generated by reactions I and II, respectively. The \( P(E_f) \)'s of products from the 000 band (Figure 2a) indicate that \( \mathrm{CH}_2\mathrm{O} \) and HCOD fragments with large amounts of internal excitation are produced. These fragments further dissociate when their internal energy exceeds the dissociation thresholds to \( \mathrm{H(D)} + \mathrm{D(H)CO} \), i.e., the radical channel of formaldehyde and hydroxymethylene dissociation.

Referring to Figure 2, we notice that slow components appear in the \( P(E_f) \)'s of both D and H atoms. Secondary D fragments can be generated only via dissociation of HCOD products, either directly or following isomerization, whereas slow H atoms can originate in dissociation of both \( \mathrm{CH}_2\mathrm{O} \) and HCOD. Secondary dissociation is not observed in the dissociation via the 000 band of \( \mathrm{CH}_2\mathrm{OD} \), in accordance with energy conservation: no \( \mathrm{CH}_2\mathrm{O} \) and CHOD fragments carrying sufficient internal energy for dissociation to H/D can be produced at this excitation energy. The exact position of the slow peak in the bottom panels is hard to discern, because this feature is partially overlapped by the primary feature of the H channel, which is centered at low translational energies. Nevertheless, all of the slow peaks can be associated energetically with secondary dissociation of \( \mathrm{CH}_2\mathrm{O} \) or HCOD/CHDO products. The solid line in each panel in Figure 2 indicates the value of the translational energy below which \( \mathrm{CH}_2\mathrm{O} \) fragments carry sufficient internal energy to dissociate to H + HCO.21 The consistency of these values with the onsets of the slow H/D peaks in all the panels suggests that secondary dissociation of \( \mathrm{CH}_2\mathrm{O} \) and CHOD takes place, giving rise to slow H and D atoms.

To further assess the sources of slow H and D products, as well as the role of \( \mathrm{H}_2\mathrm{CO} \leftrightarrow \mathrm{HCOH} \) isomerization, we discuss here briefly additional information relevant to the unimolecular reactions of these two isomers. Features of the \( \mathrm{H}_2\mathrm{CO} \) PES have been extensively explored previously, revealing that \( \mathrm{H}_2 + \mathrm{CO} \) and \( \mathrm{H} + \mathrm{HCO} \) are the main dissociation pathways on the S1 PES.22-24 The barrier to \( \mathrm{H}_2 + \mathrm{CO} \) has been calculated by various methods,23,24,26-31 and experimental work by Polik et al. places it at 3.41 eV,36 whereas the \( \mathrm{H} + \mathrm{HCO} \) pathway is barrierless and its dissociation threshold is 3.75 eV.27,39 Because of the loose transition state of the radical channel, its importance relative to the \( \mathrm{H}_2 + \mathrm{CO} \) channel increases with increasing excitation energy.

To the best of our knowledge, experimental studies of the dissociation of HCOH have not been reported. Previous theoretical calculations by Goddard and Schaefer show that the trans conformer of hydroxycarbene lies slightly below the cis form, and the isomerization barrier from \( \text{trans-} \)hydroxycarbene to formaldehyde is \( \sim1.56 \) eV.24 This corresponds to a barrier of \( \sim3.68 \) eV relative to \( \mathrm{CH}_2\mathrm{O} \), a value close to the dissociation threshold of \( \mathrm{CH}_2\mathrm{O} \rightarrow \mathrm{H} + \mathrm{HCO} \) (3.75 eV). In more recent studies,35,39-42 the relevant energies were recalculated, and it was found that (i) the barrier to isomerization is comparable to but slightly lower than the energy threshold to direct \( \mathrm{H}_2\mathrm{CO} \) dissociation (e.g., 1.3 vs 1.5 eV),35,41 and (ii) \( \mathrm{H}_2\mathrm{CO} \) lies much lower in energy than \( \text{cis,trans-} \)HCOH (by 2.2–2.4 eV).25,39,40 Therefore, dissociation of HCOH(D) via isomerization is a possible pathway for H(D) formation:

\[
\text{cis,trans-} \text{HCOH} \xrightleftharpoons[k_{-1}]{k_1} \mathrm{H}_2\mathrm{CO} \rightarrow \mathrm{H} + \mathrm{CHO}
\]

Although the transition state for the radical channel of \( \mathrm{H}_2\mathrm{CO} \) is loose (located at \( \sim3 \) Å), Reid et al. find in their ab initio calculations that the transition state for \( \text{cis,trans-} \)HCOH \( \rightarrow \mathrm{H} + \mathrm{HCO} \) is much tighter (\( \sim2 \) Å).42 In fact, their calculations indicate a distinct barrier for dissociation of the trans isomer. Reid et al. argue convincingly that the tightness of the transition state and the existence of the barrier result from avoided crossings of electronic states that lead to the adiabatic \( S_0 \) and \( S_1 \) states of HCOH. Therefore, at energies close to the dissociation threshold the direct dissociation rate of HCOH may be sufficiently slow to allow isomerization to \( \mathrm{H}_2\mathrm{CO} \), which has a deep well. Bauerfeld et al. calculated the microcanonical rate coefficients \( k(EJ) \) for the \( \mathrm{H}_2\mathrm{CO} \rightarrow \mathrm{H}_2 + \mathrm{CO} \), \( \mathrm{H}_2\mathrm{CO} \rightarrow \mathrm{H} + \mathrm{HCO} \), and \( \mathrm{H}_2\mathrm{CO} \rightarrow \text{trans-} \)HCOH paths in a range of energy from 0 to 0.7 eV above the barrier of formaldehyde isomerization,23 which covers the energy region examined here. The calculations show that the three unimolecular paths compete at these energies. The rate constants calculated by classical trajectories and Rice-Ramsperger-Kassel-Marcus (RRKM) theory show that the rate constant of the forward reaction \( (k_1) \) is larger than the reverse one \( (k_{-1}) \) by nearly an order of magnitude at low excess energies, as expected by the energetics.30 Thus, we argue that near the dissociation threshold HCOH isomerization to CHDO is an additional source of slow H and D products. A more complete experimental and theoretical study of the dissociation of CHOH will help in further clarifying the roles of direct dissociation and dissociation via isomerization.

Additional evidence for the production of “hot” formaldehyde in dissociation of \( \mathrm{CH}_2\mathrm{OD} \) (3p) is provided by the observation of secondary CO products. Previously, we reported that CO products in \( \nu = 0 \) and 1 were observed in photodissociation of \( \mathrm{CH}_2\mathrm{OD} \) at 230.1 nm (5.37 eV).16 In this one-color experiment, we used (2+1) REMPI via the CO \((\mathrm{B}^1\Sigma^+ \rightarrow \mathrm{X}^1\Sigma^+)\) state to detect CO, and we interpreted the observed CO \((\nu = 0,1) \) signals as arising from secondary dissociation of \( \mathrm{CH}_2\mathrm{O} \).

We cannot exclude some contribution to the slow D and H peaks from isomerization of the \( \mathrm{CH}_2\mathrm{OD} \) precursor followed by dissociation. The isomerization of \( \mathrm{CH}_2\mathrm{OD} \) to \( \mathrm{CH}_2\mathrm{DO} \) may give rise to “hot” \( \mathrm{CH}_2\mathrm{O} \) and CHDO fragments. No evidence for such isomerization was found experimentally in dissociation from the 3s and 3p states of \( \mathrm{CH}_2\mathrm{OD} \).16,17 However, a small contribution (~10%) from the isomerization pathway has been estimated by Harding in the \( \mathrm{H}_2 + \mathrm{OD} \) reaction that evolves via a \( \mathrm{CH}_2\mathrm{OD} \) intermediate.41 The initial energy of 5.4 eV used in the calculations is close to the energies of the vibrational levels in 3p, reported here.

In summary, the photodissociation of \( \mathrm{CH}_2\mathrm{OD} \) via the 000, 400, and 600 levels of the 3p state gives rise to highly internally excited \( \mathrm{CH}_2\mathrm{O} \) and HCOD. Secondary dissociation of these fragments is the likely source of the slow peaks in the H and D translational energy distributions. Based on previous results, the predissociation mechanism from the 3p state probably involves conical intersections along the OH and CH coordinates.17,18 Sequential conical intersections with lower Rydberg states may explain why products generated via the 3p state are internally hot, whereas dissociation following excitation to the lower 3s and 3p states gives rise to products with a larger fraction of energy disposed in translation.16,17 Symmetry considerations dictate that in the initial coupling between the 2A"(3p) state and lower Rydberg states of A' symmetry, out-of-plane modes must be involved. Such modes may propagate through the sequence of internal conversions that precede the final 3s/
ground-state conical intersections located in the repulsive part of the PES. The radicals undergoing such multiple intersections may carry a large amount of internal energy in out-of-plane modes (torsion and CH\textsubscript{2} wag) as they reach the final dissociation step on the ground PES, leading finally to "hot" products.

Examining dissociation from vibrations along the OH (\nu\textsubscript{1})- or CH (\nu\textsubscript{2} and \nu\textsubscript{3})- stretch modes may provide additional insight into surface couplings and dissociation mechanisms. Unfortunately, these modes in the 3p\textsubscript{z} state are not easily accessed because of unfavorable FC factors with the vibrationally unexcited ground state. This encouraged us to search for these levels by vibrationally mediated IR+UV double resonance spectroscopy.

**B. Lifetimes and Vibrationally Mediated Spectroscopy of CH\textsubscript{2}OH.** No vibronic bands involving \nu\textsubscript{1}-\nu\textsubscript{3} modes were observed in the REMPI spectrum shown in Figure 1. This can be explained by comparing the geometries of the radical’s ground and 3p\textsubscript{z} states. The equilibrium geometries of the ground-state radical and cation were calculated ab initio.\textsuperscript{4,7,8} Since Rydberg orbitals are large and diffuse, the geometries of the cation and neutral Rydberg states are similar to a good approximation. The calculations show that the main geometry change in going from the neutral to the cation involves a 0.12 Å decrease in CO bond distance, consistent with a progression in the CO stretch (\nu\textsubscript{3}) observed in the REMPI spectrum. The OH bond distance changes by only 0.02 Å and the two C-H bond distances change by less than 0.01 Å.

Considering the small OH and CH bond distance changes, \Delta v = 0 sequences are expected in excitation of the \nu\textsubscript{1}-\nu\textsubscript{3} modes to Rydberg states, explaining the absence of these modes in the REMPI spectrum obtained in the molecular beam. Vibrational levels of these modes in the 3p\textsubscript{z} state are not easily accessed by prior vibrational excitation in the ground state. To this end, we exploited the method developed for studying IR transitions to the OH and CH stretch vibrations in the ground state of CH\textsubscript{2}OH.\textsuperscript{19} By first preparing CH\textsubscript{2}OH in vibrationally excited levels on the ground state, FC factors for selected transition to the 3p\textsubscript{z} state could be enhanced. The vibrational frequencies in 3p\textsubscript{z} are derived from the IR+UV double resonance transition frequencies by using the relation

\[
\nu(3p_z) = \nu_{IR} + \nu_{UV} - \nu(3p_z(0^0_0))
\]

The corresponding assignments and band center frequencies for the peaks shown in Figure 4 are listed in Table 1 and compared with calculated values. The frequencies of \nu\textsubscript{2} and \nu\textsubscript{3} calculated for the ground electronic states of the neutral and the cation differ by only \sim 50 cm\textsuperscript{-1}. Since the observed bandwidth (FWHM) of the 0^0_0 transition is greater than 50 cm\textsuperscript{-1}, the 2^1_1 and 3^1_1 peaks are obscured by the 0^0_0 peak. We did, however, observe a slight enhancement in signal to the red of the 0^0_0 peak following excitation to \nu\textsubscript{2} or \nu\textsubscript{3} on the ground state in positions corresponding to the 2^1_1 and 3^1_1 transitions.\textsuperscript{19} These overlapped bands are not considered further.

The 3^1_2, 2^1_2, 1^1_2, and 1^1_2 bands, however, are well separated from the 0^0_0 band and can be investigated. The 1^1_1 band is considerably broader than the 3^1_2, 2^1_2, and 1^1_2 transitions as evident from Figure 4. The homogeneous linewidths were estimated by simulating the spectra with a Lorentzian width as a fit parameter. The fit results are shown in Figure 4 as solid lines and the homogeneous linewidths that give the best fits are listed in Table 1.

We varied the IR and UV laser energies used in the IR + UV double resonance experiments. The broadness of the bands was independent of IR laser energy in the range 3–5 mJ and UV laser energy of 0.8–1.2 mJ. In addition, the 3^1_2 band had the same total energy as the 6^1_2 band observed in the REMPI spectrum reported in ref 9, in which 0.2 mJ UV laser energy (focused with 100 cm f.l. lens) was used. The 6^1_2 band is best fit with a 20 ± 2 cm\textsuperscript{-1} linewidth, in good agreement with the value shown in Table 1. The similar linewidths obtained in the IR + UV double resonance and REMPI spectra suggests that power broadening is negligible.

In the simulations, the rotational constants of the lower state are fixed at the values determined in ref 19. Because we have no information on the change in geometry upon vibrational excitation in the 3p\textsubscript{z} state, a rigid rotor approximation is used, and rotational constants of the upper state are calculated using the equilibrium geometry of the radical ion. The radical is treated as a prolate-top undergoing a parallel transition,\textsuperscript{6,8,9} and the rotational constant B is taken as the average of the calculated asymmetric rotor rotational constants B and C. Note that only a singlerovibrational level in the ground state is involved in the IR+UV double resonance spectra, while the 0^0_0 and 6^1_2 bands should be simulated with \( T = 10 \) K rotational temperature.

Comparing with the 11 cm\textsuperscript{-1} homogeneous linewidth of the 0^0_0 band (obtained under unsaturated conditions),\textsuperscript{9} incremental increases in linewidth are observed with increasing vibrational energy in 3p\textsubscript{z}, with a 6-fold increase relative to 0^0_0 for the first overtone transition at 6639 cm\textsuperscript{-1}. This implies a large decrease in lifetime for the \nu\textsubscript{1} = 2 vibronic level in the 3p\textsubscript{z} state (see Table 1).

Several factors can contribute to the shorter lifetime of the 2^1_1 level. As discussed above, we believe that dissociation from the 3p\textsubscript{z} state involves multiple surface crossings.\textsuperscript{17} The lifetime dependence on excitation energy in the 3p\textsubscript{z} state is probably due to stronger overall coupling to modes that promote nonadiabatic transitions via conical intersections. The increase in the density of states with increasing vibrational energy may also lead to significant intramolecular vibrational redistribution (IVR) in 3p\textsubscript{z}, making crossing seams between 3p\textsubscript{z} and lower Rydberg states more accessible. A similar behavior has been observed in the photodissociation of formaldehyde via \( T_1\textsuperscript{22} \). Mode-selective effects have not been found; they may be distinguished from merely energy effects in cases when nearly isoenergetic vibrational levels in the 3p\textsubscript{z} state can be observed. It also remains for electronic structure calculations to further explore the 3p\textsubscript{z} PES and especially its nonadiabatic couplings to other states.

**V. Conclusions**

The dissociation dynamics from several vibrational levels in the 3p\textsubscript{z} states have been examined using both P(E\textsubscript{1}) measure-
ments and spectroscopy analysis. Translational energy distributions of the D and H channels are obtained for dissociation from the $0_0^0$, $4_0^4$, and $6_0^6$ levels in the $3p_z$ state of CH$_2$O. In addition to the two major dissociation channels, CH$_2$OD $\rightarrow$ D + CH$_2$O and CH$_2$OD $\rightarrow$ H + CHOD, observed for all the vibrational levels, secondary dissociation of CH$_2$O and CHOD takes place following excitation to the $4_0^4$ and $6_0^6$ bands. CH$_2$O and CHOD products carrying internal energy sufficient for dissociation give rise to H(D) + D(H)CO fragments. Isomerization of CHOD to CHD is found to be a possible pathway for dissociation of CHOD, in addition to direct dissociation to D + HCO.

$1_1^1$, $1_2^2$, and two combination bands ($3^3 6_0^6$ and $2^2 4_0^4$) in CH$_2$OH are identified in IR+UV double resonance spectra. A decrease in lifetime with increasing excitation energy is deduced from the homogenized linewidth of these bands. This increase in predissociation rate is most likely a consequence of increasing coupling matrix elements to lower lying electronic states. The out-of-plane modes that promote the sequential surface couplings required for dissociation are probably also responsible for the large internal energy of the formaldehyde and hydroxymethylene products.

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References and Notes

(21) The corresponding value for HCOD has been calculated by taking into account the isotope replacement. This difference is ignored in Figure 2, which is justified considering the low resolution of the core-sampling method at low $E_R$ and the overlap of the fast and slow peaks.
(39) Klippenstein, S. private communication.
(41) Harding, L. B. private communication.