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UV absorption spectrum of the C2 Criegee intermediate CH3CHOO

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The UV spectrum of CH3CHOO was measured by transient absorption in a flow cell at 295 K. The absolute absorption cross sections of CH3CHOO were measured by laser depletion in a molecular beam to be \((1.06 \pm 0.09) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}\) at 308 nm and \((9.7 \pm 0.6) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}\) at 352 nm. After scaling the UV spectrum of CH3CHOO to the absolute cross section at 308 nm, the peak UV cross section is \((1.27 \pm 0.11) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}\) at 328 nm. Compared to the simplest Criegee intermediate CH2OO, the UV absorption band of CH3CHOO is similar in intensity but blue shifted by 14 nm, resulting in a 20% slower photolysis rate estimated for CH3CHOO in the atmosphere. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4892582]

INTRODUCTION

Carbonyl oxides, or Criegee intermediates, have been studied extensively with the aim of understanding their chemical properties and their role as oxidizers in the troposphere.1,2 Criegee proposed the formation of such intermediates in the reaction of ozone with unsaturated hydrocarbons.3,4 An example is shown in (R1) for ethene. The carbonyl oxide formed (e.g., CH2OO) may subsequently decompose, undergo photolysis, or react with other species. Because the formation of Criegee intermediates during ozone-alkene reactions is much slower than their decomposition,5,6 these species typically have low steady-state concentrations, which have hindered efforts to directly detect Criegee intermediates in the laboratory until recently.7

\[
\text{CH}_2 = \text{CH}_2 + \text{O}_3 \rightarrow \text{CH}_2\text{OO} + \text{CH}_2\text{O} \rightarrow \text{products. (R1)}
\]

The simplest Criegee intermediate, CH2OO, was directly observed by Welz et al.8 using tunable vacuum UV photoionization mass spectrometry (PIMS), a sensitive technique that allowed separation of CH2OO from its various isomers on the basis of ionization energies. Remarkably, their work introduced an efficient method for producing CH2OO and other Criegee intermediates, by preparing CH2I2 (or a corresponding diiodoalkane) in O2 and irradiating the mixture with UV light. CH2OO is then produced by the reaction of the resulting CH2I with O2. Subsequent studies have adapted this synthesis scheme to characterize vibrational,9 rotational,10 and electronic states11–14 of CH2OO, as well as its reactivity with atmospheric species such as SO2, NO2, and volatile organic compounds.8,15–20 Notably, an unexpectedly large rate coefficient was determined for the reaction of CH2OO with SO2.8 This result could dramatically alter estimates of sulfuric acid concentrations and aerosol formation rates in the atmosphere.21

Most work has focused on the simplest Criegee intermediate CH2OO. Only a handful of studies have investigated other carbonyl oxides such as CH3CHOO, the “next simplest” Criegee intermediate. Taatjes et al.22 probed the syn- and anti-conformers of CH3CHOO with PIMS and estimated the relative thermal population of the syn-conformer over the anti-conformer to be 90:10 at 298 K, assuming similar photoionization cross sections for both conformers. They also determined conformer-specific rate constants for reaction with SO2 and H2O.22 Beames et al. measured the UV absorption spectrum of CH3CHOO by laser depletion of the ground electronic state of CH3CHOO in a jet-cooled molecular beam, which was detected with PIMS at 10.5 eV.23

Direct measurement of the UV absorption spectrum of CH3CHOO has not been reported. Furthermore, considerable discrepancies in the reported UV spectra of CH2OO11–13 suggest that additional studies may also be necessary for CH3CHOO. In this work, the UV absorption spectrum of CH3CHOO is measured by transient absorption spectroscopy, and is scaled to the absolute absorption cross section at 308 nm measured by laser depletion in a molecular beam.

EXPERIMENTAL AND THEORETICAL METHODS

Transient absorption spectroscopy

The transient absorption measurements of CH3CHOO were carried out in a flow apparatus, modified slightly from previous descriptions.13,24 For the CH3CHOO absorption experiments, a mixture of O2 and N2 was bubbled through liquid CH3CHI2 (Aldrich, ≥98.0%). The CH3CHI2 liquid was slightly heated (311 K) to ensure saturation of its vapor above the liquid, resulting in a stable concentration of CH3CHI2 in the gas flow. For SO2 scavenging experiments, SO2 (99.98%)
was also introduced from a cylinder maintained at 273 K to achieve a low vapor pressure for easier flow control. The mixing ratio of each gas (CH$_3$CHI$_2$, O$_2$, and SO$_2$) was controlled by four mass flow controllers (Brooks Instruments, 5850E). A fifth mass flow controller was used to maintain a small flow of the N$_2$/O$_2$ carrier gas (1%–2% of the total N$_2$/O$_2$ flow rate) near the photolysis cell windows to avoid contamination. All gases were mixed in Teflon tubes and passed through a smaller cell (201 mm long) upstream of the photolysis cell. The absorption of CH$_3$CHI$_2$ and SO$_2$ in this small cell was monitored continuously throughout the experiment with a D$_2$ lamp (Ocean Optics, D-2000) and a spectrometer (Ocean Optics, USB2000+UV-VIS-ES).

Transient absorption in the photolysis cell (750 mm long, 20 mm inner diameter) was detected with a continuous light source (Energetiq, EQ-99) and a gated iCCD spectrometer (Spectrometer: Andor SR303i; iCCD: Andor iStar DH320T-18F-E3). The wavelength scale of the spectrometer was calibrated with the emission spectrum from a mercury lamp (1.5 nm resolution, calibration accuracy 0.25 nm) before each experiment. The pressure and flow rate in the photolysis cell were controlled with mass flow controllers and an outlet valve to a mechanical pump. A linear flow velocity faster than 0.8 m/s was maintained to allow complete refreshment of gases between laser pulses (1 Hz repetition rate).

CH$_3$CHOO was produced from photolysis of CH$_3$CHI$_2$ by a 248 nm KrF excimer laser (Coherent Compx Pro 205 F) and subsequent reaction of CH$_3$CHI with O$_2$. The change in absorption by CH$_3$CHOO and SO$_2$ and CH$_3$CHOO were ionized by electron impact at 45 eV, and the ions traveled through a quadrapole mass filter to a Daly detector. Arrival time profiles of CH$_3$CHOO (at $m/z = 60$, C$_2$H$_4$O$_2^+$) were recorded using a multichannel scaler (Ortec, Turbo-MCS).

Another excimer laser beam operating at 25 Hz (at either 352 nm or 308 nm) intersected the CH$_3$CHOO molecular beam directly after it passed the defining slit at a point 25 cm upstream of the mass spectrometer, resulting in depletion of the signal at $m/z = 60$. The laser beam was attenuated homogeneously by a variable attenuator (Laseroptik, IVA351nm or IVA308nm) to the desired pulse energy, which was measured with a power meter (Gentec-EO, UP25N + Solo 2 controller).

Under the molecular beam conditions in these experiments, the photodepletion signal can be related to the absorption cross section $\sigma$, the photodissociation quantum yield $\phi$, and the laser fluence $I$ using Eq. (1), where $N_0$ and $N$ are the numbers of molecules before and after laser irradiation,

$$\frac{N}{N_0} = e^{-\sigma \phi} \cdot \frac{\Delta N}{N_0} = \frac{N_0 - N}{N_0} = 1 - e^{-\sigma \phi} \cdot (1)$$

Absorption at the wavelengths studied here excites CH$_3$CHOO and CH$_3$CHI$_2$ to repulsive states or states higher than their dissociation thresholds, resulting in rapid and complete dissociation ($\phi = 1$). Because of inhomogeneity in the laser beam profile, however, the absolute laser fluence $I$ may be difficult to quantify with sufficient accuracy to yield accurate cross sections $\sigma$ for CH$_3$CHOO using Eq. (1). Two additional methods of determining absolute CH$_3$CHOO cross sections were therefore used.

First, in addition to measuring the depletion of CH$_3$CHOO, the relative depletion of CH$_3$CHI$_2$ at 308 nm was measured in the molecular beam. By analyzing the experimental data using Eq. (1), the value of $\sigma \phi$ was obtained for both CH$_3$CHOO and CH$_3$CHI$_2$, assuming $\phi = 1$. From this, the ratio $\sigma$ (CH$_3$CHOO)/$\sigma$ (CH$_3$CHI$_2$) can then be deduced. As discussed below, if $\sigma$ (CH$_3$CHI$_2$) is known and reliable, the absolute value of $\sigma$ (CH$_3$CHOO) can then be obtained.

Second, a method was developed to estimate the absolute fluence of the excimer laser beam. The profile of the laser beam was recorded using a laser beam profiling digital camera (WinCamD, model UCD23, 8.8 mm × 6.6 mm image area, 6.45 $\mu$m × 6.45 $\mu$m pixel area, 14-bit ADC) and DataRay imaging software. A rectangular slit (2 mm high, 19 mm wide) in the laser beam path, 15 mm ahead of the laser beam-molecular beam crossing point, removed the “wings” of the laser beam vertical profile so that only the most intense and uniform portion of the laser beam was used. Using the measured laser pulse energy and the intensity profile, the absolute laser fluence can be deduced. See the supplementary material for further experimental details.
Theoretical calculations

Detection of the Criegee intermediate in the experiments described above may be subject to interference from isomers of CH₃CHOO. To investigate the possible isomers of CH₃CHOO, geometry optimization was performed using density functional theory with Becke’s three parameter hybrid functional (B3LYP), coupled cluster singles and doubles with perturbative triples (CCSD(T)), and multireference complete active space self-consistent field (MC CASSCF) methods. The two single reference methods were employed using Dunning’s aug-cc-pVTZ basis set, and the CASSCF calculation was performed using the aug-cc-pVDZ basis set. For the CASSCF method, all core electrons and the 2s electrons on carbon and oxygen were frozen. Furthermore, due to computational limitations, two high energy orbitals were removed from the full valence active space, thus giving an active space of 16 electrons in 14 orbitals. Additional CASSCF optimization was performed using an active space of 10 electrons in 10 orbitals, which corresponds to the 5 important bonds for the description of the different isomers of CH₃CHO.

The single reference methods yielded 7 stable molecular minima and 2 OH radical complexes, while one extra molecular minimum was obtained using the CASSCF method. B3LYP and CASSCF(10,10), frequency calculations were performed to confirm that the calculated geometries are minima. Using these optimized geometries, the electronic transition energies and oscillator strengths were calculated for the first four excited states by performing single-point CCSD equation-of-motion (CCSD-EOM) calculations with the aug-cc-pVTZ basis set. The B3LYP calculations were performed using the Gaussian 09 program, while all other calculations were performed using the MOLPRO program.

RESULTS AND DISCUSSION

Figure 1 (top) shows examples of transient absorbance measured at different photolysis delay times. Depletion of the broad CH₃CHI₂ absorption due to photolysis in (R2) below results in the negative absorbance peaked near 290 nm, and absorption of CH₃CHO (the peak labeled as band A) appears in the first few μs due to (R3) below and decreases as the delay time is increased. Formation of IO is likely due to (R4), and its distinct vibrational peaks at 412, 420, 428, and 436 nm appear at longer delay times. Absorption spectra for CH₃CHI and IO, along with further details of data analysis, are available in the supplementary material.

\[
\begin{align*}
\text{CH}_3\text{CHI}_2 + h\nu \rightarrow \text{CH}_3\text{CHI} + \text{I}, \\
\text{CH}_3\text{CHI} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{I}, \\
\text{CH}_3\text{CHO} + \text{I} \rightarrow \text{CH}_3\text{CHO} + \text{IO}, \\
\text{CH}_3\text{CHO} + \text{SO}_2 \rightarrow \text{products}, \\
\text{CH}_3\text{CHOO} + \text{CH}_3\text{CHO} \rightarrow \text{products}.
\end{align*}
\]

The fast rate of (R5) \((2.4 - 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1})\) reported by Taatjes et al. allows SO₂ to be used as an efficient scavenger for CH₃CHO. Figure 1 (bottom) shows absorbance traces for different concentrations of SO₂ scavenger. The rapid depletion in absorbance upon addition of SO₂ is expected to originate solely from CH₃CHO depletion (since the absorption change due to other species consumed or produced, such as SO₂, CH₃CHO, and SO₃, is much weaker). When all experimental conditions except the SO₂ concentrations are kept constant, subtracting the absorbance in the presence of SO₂ from the absorbance without SO₂ yields an absorption spectrum containing contributions from CH₃CHO and SO₂ at a 1:1 ratio. After scaling the UV absorption spectrum to the absolute cross sections obtained by laser depletion (discussed below), the contribution of SO₂ absorption to the spectrum can be easily removed.

As shown in the supplementary material, the SO₂ scavenging experiments allowed us to measure the decay rate of CH₃CHO in the presence of SO₂ under pseudo first-order conditions. We determined the rate constant for (R5)
to be \((2.0 \pm 0.3) \times 10^{-11}\) \(\text{cm}^2\) \(\text{molecule}^{-1}\) \(\text{s}^{-1}\), which agrees with a value of \((2.4 \pm 0.3) \times 10^{-11} \) \(\text{cm}^2\) \(\text{molecule}^{-1}\) \(\text{s}^{-1}\) reported for the dominant \textit{syn}-conformer of CH$_3$CHOH.$^{22}$

Under our experimental conditions, we did not observe the kinetics of the \textit{anti}-conformer, which is reasonable if its thermal population is only 10%.$^{22}$ The \textit{anti}-conformer was reported to react with SO$_2$ at a faster rate of \((6.7 \pm 1.0) \times 10^{-11} \) \(\text{cm}^3\) \(\text{molecule}^{-1}\) \(\text{s}^{-1}\).$^{22}$

Without SO$_2$ in the photolysis cell, decay of CH$_3$CHOH is due primarily to (R6), the self-reaction of the Criegee intermediate, and to (R4), the reaction of CH$_3$CHOH with O atoms. Because (i) CH$_3$CHI is consumed by excess O$_2$ within the first few μs, (ii) CH$_3$CHOH is relatively short-lived in comparison with CH$_3$CHI$_2$ and IO, and (iii) the shapes of the CH$_3$CHI$_2$ and IO spectra are quite distinct, the contributions of CH$_3$CHI$_2$ and IO to the absorbance can be easily subtracted. The resulting spectrum is consistent with the spectrum obtained using SO$_2$ scavenger (see Figure 2), although slight discrepancies at wavelengths longer than 400 nm suggest contributions from other absorbing species (possibly CH$_3$CHIOO, an adduct of CH$_3$CHI and O$_2$). The SO$_2$ scavenging method used in this work to extract the CH$_3$CHOH spectrum provides species selectivity based on the chemical reactivity of CH$_3$CHOH. The “self-reaction” method has somewhat lower selectivity. Hence, the small discrepancies between the SO$_2$-scavenging spectrum and the self-reaction spectrum in Figure 2 likely originate from contaminants that have weaker absorption.

While the absorbance due to CH$_3$CHOH can be extracted from the transient absorption, it is difficult to know the absolute number density of CH$_3$CHOH in the photolysis cell. Therefore, to convert the spectrum of CH$_3$CHOH to absorption cross sections, the absolute cross sections at 308 nm and 352 nm were measured by mass spectrometric detection of the laser depletion of CH$_3$CHOH in a molecular beam. This method has been used previously to selectively detect species with short lifetimes and at low concentrations.$^{13,42,43}$ Figure 3 (top solid symbols) shows the CH$_3$CHOH depletion signal \((\Delta N/N_0)\) at 308 nm at a variety of laser pulse energies and the fit to Eq. (1). The good fit indicates that a single species is being measured (or multiple species that have similar cross sections). At high laser energy the CH$_3$CHOH signal approaches 100% depletion, consistent with \(\phi = 1\). The relative depletion of CH$_3$CHI$_2$ was also measured under similar conditions, shown in Figure 3 (top open symbols) with the fit to Eq. (1). Saturation of the CH$_3$CHOH depletion signal occurs at a lower laser pulse energy than that for CH$_3$CHI$_2$, indicating the cross section of CH$_3$CHOH is larger.

Because the temperature in a molecular beam (e.g., \(T_{\text{rot}} \approx 10\) K) is much lower than room temperature, we must consider the effect of temperature on the absorption cross section. 308 nm is near the peak of the CH$_3$CHI$_2$ UV absorption band$^{41}$ and is therefore likely to have a negligible temperature dependence, as observed for CH$_3$I.$^{41,44}$ Assuming the low temperature cross section at 308 nm is the same as that at 298 K for CH$_3$CHI$_2$, we may use the laser depletion of CH$_3$CHI$_2$ to calibrate the laser fluence. In other words, since we know the relative laser fluence for both the CH$_3$CHOH and CH$_3$CHI$_2$ experiments, we can deduce the cross section ratio \(\sigma(\text{CH}_3\text{CHOH})/\sigma(\text{CH}_3\text{CHI}_2)\), and, subsequently, \(\sigma(\text{CH}_3\text{CHOH})\) based on the literature value of \(\sigma(\text{CH}_3\text{CHI}_2)\) at 298 K.$^{41}$

![Comparison of CH$_3$CHOH and CH$_2$OO absorption spectra](image-url)
consistent with the absolute cross sections measured in the jet-cooled molecular beams (see Figure 2), further supporting the validity of our assumption that temperature has little effect near the absorption peaks. The peak cross section for CH3CHO is \((1.27 \pm 0.11) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}\) at 328 nm. Numerical values for the CH3CHO absorption cross sections as a function of wavelength can be found in the supplementary material.

The CH3CHO spectra obtained in this work are compared in Figure 2 with the CH2OO spectrum reported by Ting et al. The peak wavelength for CH3CHO at 328 nm is blue shifted by 14 nm from the CH2OO peak at 342 nm. Previous theoretical calculations attributed this wavelength shift to stabilization of the ground electronic state and destabilization of the excited electronic state of the syn-conformer of CH3CHO, which dominates CH3CHO populations over the anti-conformer at 298 K. This blue shifted spectrum has also been demonstrated by Beames et al. for syn-CH3CHO in comparison with CH2OO under jet-cooled conditions, although (as discussed below) their uncertainty may be larger.

While clear vibronic structure on the long wavelength side was observed for CH2OO by Ting et al. and by Sheps, the CH3CHO absorption shows a similar but much weaker structure (i.e., a step-like oscillation). This smearing of the vibronic structure may be expected for a molecule with more degrees of freedom. There are two possible reasons why the oscillatory structure in the CH3CHO spectra (Figure 2, 330–380 nm) appears stronger in the SO2-scavenging spectrum than in the self-reaction spectrum. We think there are two possible reasons. First, because the SO2-scavenging spectrum is of CH3CHO. These two conformers may have anti(CH3CHO) and syn(CH3CHO) are assumed to be unity. See the supplementary material for error estimation.

\(1\sigma\) uncertainty.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Wavelength (nm)</th>
<th>Method</th>
<th>Cross section ((\text{cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3CHO</td>
<td>308.4</td>
<td>CH3CHI reference</td>
<td>((10.9^{+0.9}_{-0.9}) \times 10^{-18})</td>
</tr>
<tr>
<td></td>
<td>Absolute laser fluence</td>
<td>((10.3^{+0.9}_{-0.9}) \times 10^{-18})</td>
<td></td>
</tr>
<tr>
<td>CH2OO</td>
<td>351.8</td>
<td>Absolute laser fluence</td>
<td>((9.7^{+0.6}_{-0.6}) \times 10^{-18})</td>
</tr>
<tr>
<td></td>
<td>Absolute laser fluence</td>
<td>((11.0^{+0.8}_{-0.8}) \times 10^{-18})</td>
<td></td>
</tr>
</tbody>
</table>

*Calculated using the measured value of 3.85 ± 0.19 for the ratio \(\sigma_\text{CH3CHI2}/\sigma_\text{CH3CHI1}\) and \(\sigma_\text{CH3CHI1} = (2.83 \pm 0.20) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}\). The CH3CHI and CH3CHI2 are assumed to be unity. See the supplementary material for error estimation.

Table I summarizes the laser depletion results for CH3CHO at 308 and 352 nm as well as for CH2OO at 352 nm. These absolute cross sections are also plotted in Figure 2. The CH3CHO spectra obtained with the methods outlined above were scaled to the average cross section at 308 nm obtained from laser depletion. Here, we assume the temperature effect on the cross sections of CH3CHO is negligible at 308 nm. This assumption is reasonable since 308 and 352 nm are near the peak of the UV absorption band, as in the case of CH2OO. For both CH3CHO and CH2OO, the scaled room-temperature cross sections at 352 nm are consistent with the absolute cross sections measured in the jet-cooled molecular beams (see Figure 2), further supporting the validity of our assumption that temperature has little effect near the absorption peaks. The peak cross section for CH3CHO is \((1.27 \pm 0.11) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}\) at 328 nm. Numerical values for the CH3CHO absorption cross sections as a function of wavelength can be found in the supplementary material.

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While clear vibronic structure on the long wavelength side was observed for CH2OO by Ting et al. and by Sheps, the CH3CHO absorption shows a similar but much weaker structure (i.e., a step-like oscillation). This smearing of the vibronic structure may be expected for a molecule with more degrees of freedom. There are two possible reasons why the oscillatory structure in the CH3CHO spectra (Figure 2, 330–380 nm) appears stronger in the SO2-scavenging spectrum than in the self-reaction spectrum. We think there are two possible reasons. First, because the SO2-scavenging spectrum is obtained from the difference between two spectra (with and without SO2), the noise level in the SO2-scavenging spectrum is much higher than that in the self-reaction spectrum. Some structure may appear more “oscillatory” when the noise is higher. Second, we cannot rule out the possibility that the oscillatory structure belongs to one of the two stable conformers (syn and anti) of CH3CHO. These two conformers may have different reactivity towards SO2 and towards themselves, such that the SO2-scavenging and self-reaction spectra are different in the relative conformer populations.

Measurements of the CH3CHO spectrum by Beames et al. are also plotted in Figure 2, scaled by a factor of 0.25 to roughly match the 308 nm cross section reported

\[ \text{FIG. 3. (Top)} \text{ Saturation curves for laser depletion of CH3CHO (m/z = 60) and CH3CHI (m/z = 155, CH3CHI), a daughter ion of CH3CHI, at 308.4 nm. The x-axis is the laser pulse energy, which is proportional to the laser fluence. The lines are fits to Eq. (1). (Top inset)} \text{ Arrival time profiles of CH3CHO at different laser fluences at 308.4 nm. (Bottom)} \text{ Saturation curve for laser depletion of CH3CHO (m/z = 60) at 351.8 nm. The x-axis is the absolute laser fluence, deduced from the laser pulse energy and the measured laser beam profile. The line is the fit to Eq. (1).} \]
here for easier comparison. The discrepancies are surprising, especially since both studies used laser depletion in a molecular beam to determine the cross sections. In particular, their scaled cross section value at 352 nm is significantly smaller or, alternatively, their unscaled cross section is significantly larger than our data from 300 to 350 nm. For the earlier CH2OO studies, the inconsistencies between the CH2OO laser depletion data from Beames et al." and from our group were primarily at wavelengths longer than 352 nm and might therefore be explained by a possible temperature effect around 380 nm. However, such a possibility is ruled out for CH3CHO in this work by the use of the absolute laser fluence to determine the cross section of CH3CHO in the molecular beam at 352 nm directly. One possible cause of the discrepancies may be that Beames et al. only used the beam spot size, not a beam profiler measurement, to deduce their laser fluence, which may have larger uncertainty due to the inhomogeneity in the laser beam.

Isomer interference could also cause the observed discrepancies. Beames et al. detected CH3CHO with photoionization at 10.5 eV. This method provides isomer selectivity because the ionization energies of syn- and anti-CH3CHO are about 9.4 and 9.3 eV, respectively, and other isomers have higher ionization energies. In this work we used electron impact ionization at 45 eV to detect CH3CHO and CH3CH=. Electron impact ionization at 45 eV would not discriminate isomers. To determine the potential impact of isomer interference, we calculated the oscillator strengths of relevant UV transitions for the possible isomers of CH3CHO with the CCSD-EOM method.

The results are shown in Table II. The syn- and anti-CH3CHO Criegee intermediates absorb very strongly in the near UV range, while the other isomers acetic acid, dioxirane, bisoxo, etc. absorb either rather weakly or at much shorter wavelengths. Two radical-radical complexes (CH3CO···OH complex 1 and 2) involving an acetyl radical and an OH radical were also considered. Complex 1 has an absorption peak at 307 nm, but its intensity is much weaker than that for CH3CHO. Furthermore, its energy is calculated to be ~12 kcal/mol higher than that for syn-CH3CHO. Thus, this isomer is not expected to contribute to the measured spectrum. Complex 2 absorbs strongly in the near UV range (345 nm) and is calculated to be 11 kcal mol\(^{-1}\) more stable than syn-CH3CHO. However, our preliminary calculation using B3LYP/aug-cc-pVTZ shows that the isomerization barrier of complex 2 is only 1.55 kcal mol\(^{-1}\) (see Figure S11 of the supplementary material). We therefore predict that this complex is highly unstable and would isomerize to more stable isomers before being detected in our experiments (which have a time scale on the order of 1 ms).

From the above theoretical results, we can conclude that syn- and anti-CH3CHO are the main carriers of the observed absorption spectrum, with anti-CH3CHO absorbing at longer wavelengths. Taatjes et al. inferred from their PIMS investigation that syn-CH3CHO is dominant (90\% in population) at 298 K, which is also consistent with our theoretical calculation. Considering the above discussion, the temperature effect should be minor at 308 and 352 nm wavelengths, which are near the absorption peak at 328 nm. Still, there may be subtle differences between the absorption of CH3CHO at room temperature and in a jet-cooled molecular beam. First, in the jet-cooled molecular beam of CH3CHO, it might be expected that the anti-conformer has an even smaller population than in room temperature CH3CHO. However, the barrier to interconversion of these conformers is about 38 kcal mol\(^{-1}\). Because of this high barrier, the rapid cooling process in the supersonic expansion would not reach thermal equilibrium, resulting in similar conformer populations as before expansion. Second, CH3CHO has low frequency vibrational modes which could be effectively cooled by the supersonic expansion in a molecular beam. As a result, there would be more hot bands in a room-temperature spectrum than in a jet-cooled spectrum. This may partly explain the longer wavelength tail in our UV spectrum at 295 K as compared to the jet-cooled spectrum reported by Beames et al.

With regard to the role of CH3CHO in atmospheric photochemistry, we can calculate its photolysis rate coefficients (J-values) based on the absorption spectrum obtained in this work and its convolution with the solar flux. A comparison of photolysis lifetimes (i.e., \(\tau = J^{-1}\)) in the supplementary material shows that a somewhat longer photolysis lifetime is expected for CH3CHO relative to CH2OO (~7 and ~6 s, respectively, at a solar zenith angle (SZA) of 0°; 169 and 132 s, respectively, at 86° SZA). The difference results from the fact that, although the peak cross section for CH3CHO of 1.27 × 10\(^{-17}\) cm\(^2\) is similar to that for CH2OO (1.23 × 10\(^{-17}\) cm\(^2\) reported by Ting et al.), the blue shift of the CH3CHO spectrum reduces overlap with the solar flux at earth’s surface. Although the blue shifted spectrum and reduced overlap with the solar flux for CH3CHO versus CH2OO have been reported previously in Ref. 23 for jet-cooled CH3CHO, the quantitative cross sections and spectral shapes are different for this work versus those reported in Ref. 23, resulting in significantly different photolysis lifetimes. As shown in the supplementary material, the more intense but narrower absorption band of CH3CHO reported by Beames et al. results in shorter photolysis lifetimes (65%–91% of our values, 

<table>
<thead>
<tr>
<th>isomer</th>
<th>(E_{\text{rel}}) (kcal mol(^{-1}))</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(f)</th>
</tr>
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<tbody>
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<td>syn-CH3CHO</td>
<td>0.00</td>
<td>294</td>
<td>1.55 × 10(^{-4})</td>
</tr>
<tr>
<td>anti-CH3CHO</td>
<td>3.71</td>
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<td>1.73 × 10(^{-4})</td>
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<td>Dioxirane</td>
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<td>291</td>
<td>9.88 × 10(^{-4})</td>
</tr>
<tr>
<td>bisoxo</td>
<td>-5.46a</td>
<td>281</td>
<td>1.57 × 10(^{-3})</td>
</tr>
<tr>
<td>anti-CH2COOH</td>
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<td>208</td>
<td>3.57 × 10(^{-4})</td>
</tr>
<tr>
<td>syn-CH2COOH</td>
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<td>212</td>
<td>5.46 × 10(^{-4})</td>
</tr>
<tr>
<td>anti-CH2OOH</td>
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<tr>
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<td>2.99 × 10(^{-2})</td>
</tr>
<tr>
<td>CH3CO···OH complex 1</td>
<td>12.17</td>
<td>307</td>
<td>1.23 × 10(^{-2})</td>
</tr>
<tr>
<td>CH3CO···OH complex 2</td>
<td>-10.72</td>
<td>345</td>
<td>6.03 × 10(^{-1})</td>
</tr>
</tbody>
</table>

\*Since multireference character is important for this isomer, we were not able to optimize the geometry with the single reference CCSD(T) method. Instead, we used the geometry and energy obtained with CASSCF(6,14)/aug-cc-pVTZ. The listed energy is with respect to the syn-CH3CHO conformer calculated at the same CASSCF level.
depending on the solar zenith angle). Similarly, the cross sections of CH$_2$OO reported by the same group$^{11}$ results in a photolysis lifetime of 2.5 s at 0° SZA which is shorter than the corresponding value of 6 s based on the cross sections of our group.$^{13}$

CH$_3$CHO reacts quickly with atmospheric gases like SO$_2$, NO$_2$, and H$_2$O.$^{22}$ Based on the reported rate constants,$^{22}$ the reactive lifetime is shorter than its photolysis lifetime in typical atmospheric conditions, making its photolysis a minor process in the atmosphere.

**SUMMARY**

The CH$_3$CHO UV absorption spectrum was measured by transient absorption spectroscopy, and absolute absorption cross sections were determined at 308 and 352 nm by laser depletion. In the transient absorption measurements, SO$_2$ scavenging and self-reaction of CH$_3$CHO were used to extract the spectrum of CH$_3$CHO. In the laser depletion experiments, two methods were used to calibrate the laser fluence: CH$_2$O as a reference molecule and a laser beam profiler measurement. The cross sections presented here may facilitate analysis of the impact of CH$_3$CHO photolysis in the atmosphere, and may also provide a useful spectral signature for detection of this Criegee intermediate in laboratory investigations.

**ACKNOWLEDGMENTS**

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