Infrared Laser Stark Spectroscopy of Hydroxymethoxycarbene in ⁴He Nanodroplets

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Abstract

Hydroxymethoxycarbene, CH₃O $\ddot{\text{C}}$ OH, was produced *via* pyrolysis of monomethyl oxalate and subsequently isolated in ⁴He nanodroplets. Infrared laser spectroscopy reveals two rotationally resolved *a*,*b*- hybrid bands in the OH-stretch region, which are assigned to *trans,trans*- and *cis,trans*- rotamers. Stark spectroscopy of the *trans,trans*-OH stretch band provides the *a*-axis inertial component of the dipole moment, namely $\mu_a = 0.62(7)\text{D}$. The computed equilibrium dipole moment agrees well with the expectation value determined from experiment, consistent with a semi-rigid CH₃O $\ddot{\text{C}}$ OH backbone computed *via* a potential energy scan at the B3LYP/cc-pVTZ level of theory, which reveals substantial conformer interconversion barriers of ≈ 17 kcal/mol.

1. Introduction

Carbenes ($R''-\ddot{C}-R'$) have been implicated as intermediates in reactions relevant to atmospheric[1-3], combustion[4, 5], and interstellar chemistry[6-11]. The chemistry of these species can be heavily influenced by quantum mechanical tunneling [12-14]. For example, at 11 K, hydroxymethylene ($H\ddot{C}OH$) converts to H_2CO in solid Ar (with a half-life of only ~ 2 h) despite a 30 kcal/mol barrier [15]. Methylhydroxycarbene ($CH_3\ddot{C}OH$) exhibits tunneling-controlled rearrangement dynamics in the low-temperature regime, where branching ratios for interconversion to either vinyl alcohol or acetaldehyde are governed by barrier width, rather than barrier height [16].

Isomerization rates for this class of reactive intermediates are largely dictated by the R' - and R'' -substituent groups[17]. For example, dihydroxycarbene ($HO\ddot{C}OH$) shows no propensity for tunneling on any practical experimental timescale, as recently demonstrated in Ar matrix isolation studies [18]. Recent gas-phase and He nanodroplet spectroscopic studies with theoretical calculations have structurally characterized $HO\ddot{C}OH$ [19, 20]. The back-donated electron density from the second O atom into the empty C atom p -orbital of $HO\ddot{C}OH$ plays a significant role in its stability towards tunneling, in comparison to the analogous $H\ddot{C}OH$ and $CH_3\ddot{C}OH$ systems, which undergo relatively prompt isomerization[15, 16, 21].

Carbene systems have been probed extensively in the gas phase[22-26], and in matrix isolation[9, 17, 27, 28]. Only recently, however, have the isolated hydroxyl-substituted carbenes been probed in the gas phase. Reisler and co-workers employed sliced velocity-mapped ion imaging to probe the photodissociation dynamics of the hydroxymethyl radical (CH_2OH) and its

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4 deuterated analogue [21]. The dynamics are heavily influenced by the level of deuteration of the
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6 hydroxymethylene photoproduct, which they conclude is a result of passage through different
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8 conical intersections.[29]Using a combination of microwave rotational spectroscopy and high-
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10 level calculations, McCarthy and coworkers reported a detailed structural characterization of the
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12 *trans,cis*-HO $\ddot{\text{C}}$ OH rotamer[19].Most recently, HO $\ddot{\text{C}}$ OH was isolated and characterized in He
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14 nanodroplets using infrared (IR) laser Stark spectroscopy[20]. This technique directly probes the
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16 permanent electric dipole moment of the molecule, which provides insight into the ground
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18 vibronic wavefunction, which is related to the structural rigidity of the system, and its stability,
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20 or lack thereof, towards tunneling.
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28 Here, we employ He droplets to probe the OH stretch bands and dipole moment of the
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30 methoxy-substituted R''- $\ddot{\text{C}}$ OH carbene. A survey IR spectrum of Ar matrix-isolated CH₃O $\ddot{\text{C}}$ OH
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32 has been reported previously [18]. On the basis of previous He droplet studies of H $\ddot{\text{C}}$ OH and
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34 HO $\ddot{\text{C}}$ OH, we expect the OH stretch bands of CH₃O $\ddot{\text{C}}$ OH rotamers in solid Ar to be significantly
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36 red-shifted from band origins of the isolated species[20, 30]. In contrast, the interactions
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38 between dopant molecules and the He environment are sufficiently weak such that we expect the
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40 OH stretch bands to be centered within 1-2 cm⁻¹ of the gas-phase origins[31]. This work can
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42 thus serve as a guide for future gas-phase studies of CH₃O $\ddot{\text{C}}$ OH. Here, we present the
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44 characterization of two rotamers of CH₃O $\ddot{\text{C}}$ OH, *via* measurements in the CH and OH stretching
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46 vicinity, the latter of which gives rise to bands with rotational substructure. Permanent electric
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48 dipole moment components were obtained for the lowest-energy *trans,trans*-conformer *via* Stark
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2. Experiment

Helium nanodroplet isolation and its application to IR laser Stark spectroscopy have been previously described in detail elsewhere[31-34]. Droplets with an average size of 4000 He atoms are formed in a cryogenic nozzle expansion (17K) of high-purity He gas (30 bar) through a 5 μm diameter pinhole nozzle. The droplets evaporatively cool to ≈ 0.4 K, and the droplet expansion is skimmed into a beam before entering into a differentially pumped chamber, containing an effusive pyrolysis source previously described in detail [20]. $\text{CH}_3\text{O}\ddot{\text{C}}\text{OH}$ is produced *via* the pyrolytic decomposition of monomethyl oxalate (**1a**, **1b**), which was synthesized by mixing equimolar amounts of anhydrous oxalic acid and anhydrous methanol under vacuum for 24 h in a fashion similar to that described by Schreiner and coworkers [18].

The products resulting from the thermal decomposition of (**1**) at 1000 K are picked up by the droplet beam and subsequently cooled to ≈ 0.4 K through evaporation of He atoms[35]. The flow rate through the pyrolysis tube under these conditions is sufficiently low such that we expect an average pick-up of less than one $\text{CH}_3\text{O}\ddot{\text{C}}\text{OH}$ molecule per droplet. The doped droplet beam passes through a Stark/multipass cell, which is used to apply an electric field to the laser-droplet beam interaction region. Finally, the doped droplet beam enters an electron-impact ionization quadrupole mass spectrometer.

Tunable IR radiation from a continuous-wave, optical parametric oscillator (OPO) system (Lockheed-Martin Aculight) is directed either counter-propagating to the droplet beam (Zero-field spectra) or into the multipass cell (Stark spectra), and is used to vibrationally excite the He-solvated molecules[36]. All droplets irradiated by the IR beam are exposed to a uniform Stark field in the multipass region, which is calibrated by measuring the known Stark spectrum of He-

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4 solvated HCN [37]. A Fresnel rhomb is used to rotate the laser polarization with respect to the
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12 tuned with ≈ 10 MHz resolution [36]. The IR spectrum is detected as a depletion in $m/z=29$ u ion
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solvated HCN [37]. A Fresnel rhomb is used to rotate the laser polarization with respect to the static Stark field. Vibrational excitation results in the evaporation of several hundred He atoms from each droplet and a reduced cross section for ionization. The OPO is chopped at 80 Hz and tuned with ≈ 10 MHz resolution [36]. The IR spectrum is detected as a depletion in $m/z=29$ u ion signal. The 29 u channel (HCO^+) was determined here to be a major fragmentation channel of $\text{CH}_3\text{O}\ddot{\text{C}}\text{OH}$ following the ionization of doped He droplets. All spectra are normalized to the laser power.

3. Results

3.1 Pyrolysis of monomethyl oxalate

Thermal decomposition of monomethyl oxalate (**1**) can, in principle, produce CO_2 and four carbene conformers; specifically, *trans,trans*- (**2**); *cis,trans*- (**3**); *trans,cis*- (**4**); and *cis,cis*- (**5**) [18]. Moreover, precursor decomposition may lead to methyl formate and CO_2 . Schematic structures and energetics computed at the B3LYP/cc-pVTZ level of theory are shown in Fig. 1. The relative energetics of each in conjunction with computed barrier heights between the lowest-energy carbene species can be used to estimate the most probable outcomes of the thermal decomposition of (**1**). At 1000 K, the pyrolysis of (**1**) is expected to generate carbenes *via* H-atom migration and subsequent loss of CO_2 . Given the orientation of the hydroxyl and methoxy groups, we expect the *trans,trans*- $\text{CH}_3\text{O}\ddot{\text{C}}\text{OH}$ (**2**) and *cis,trans*- $\text{CH}_3\text{O}\ddot{\text{C}}\text{OH}$ (**3**) rotamers to originate from the *cTc*- (**1a**) and *cTt*- (**1b**) precursors, respectively. The *cTc*- and *cTt*- are computed to be the lowest energy conformers of the monomethyl oxalate precursor (see Supplementary Material). Once (**2**)/(**3**) are produced from the unimolecular decomposition of

(1a)/(1b), these carbene rotamers can transform among themselves and into (4)/(5) via torsional motion about either the OCOH or COCO dihedral angles. The barrier heights between the lowest-energy carbene conformers were computed at the B3LYP/cc-pVTZ level to provide further insight into the expected outcome of the pyrolysis of (1). As shown in Fig. 2, the *trans,trans*- species is the lowest-energy conformer. A 180° rotation about the COCO dihedral (θ_1) yields the *cis,trans*- conformer, which lies 1.7 kcal/mol higher in energy than the *trans,trans*- species, with a calculated rotational barrier height of 17.4 kcal/mol. Rotation about the OCOH dihedral (θ_2) from the *trans,trans*- geometry yields the nearly isoenergetic *trans,cis*- conformer, with a calculated barrier of 16.5 kcal/mol.

To determine whether the energy remaining in the carbene after it is produced via the thermal decomposition of (1) is sufficient to overcome these computed rotational barriers, a survey of the (1a) to (2) reaction coordinate was performed. A transition state structure (TS) lying ≈ 21 kcal/mol above the *cTc*- monomethyl oxalate equilibrium geometry was identified at the B3LYP/cc-pVTZ level of theory using the QST3 method in Gaussian09[38] (details can be found in the Supplementary Material). Although qualitatively similar to the TS structure identified by Huang and coworkers[39] in their study of the thermal decomposition of *cTc*- oxalic acid to yield *trans,trans*-HO $\ddot{C}$ OH, the barrier computed for *cTc*- monomethyl oxalate decomposition is slightly lower, likely a consequence of the repulsive methyl group, resulting in more favorable loss of CO₂. The TS structure is nearly isoenergetic with (2), suggesting that the *trans,trans*- carbene species can be produced with low internal vibrational energy, thereby prohibiting its facile rotational interconversion to one of the other carbene rotamers. On the basis of this admittedly low-level computational analysis, we expect to observe the *trans,trans*-

(2) and *cis,trans*-(3) conformers exclusively, consistent with earlier analogous work on the thermal decomposition of oxalic acid to yield two different conformers of HO $\ddot{C}$ OH[20].

3.2 OH-Survey Spectrum

The IR spectra reported here represent the laser-induced depletion signal in a single mass channel. Based upon previous work on H $\ddot{C}$ OH and HO $\ddot{C}$ OH in He droplets [20, 30], we found that mass 29 u, corresponding to (HCO⁺), was a major fragmentation product of the electron-impact ionization process for the hydroxycarbene doped He droplets. Moreover, significant laser-induced depletion signal was observed in the 29 u mass channel when the laser was tuned into resonance with the OH or CH stretching bands of these species. The IR spectra resulting from the thermal decomposition of monomethyl oxalate(1) were therefore similarly acquired on the m/z=29 u channel.

Figure 3 shows a survey spectrum of the OH-stretch region, recorded under high temperature pyrolysis source conditions. Four distinct features are evident in the 3630 cm⁻¹ to 3700 cm⁻¹ frequency range. The bands marked with * are assigned to residual methanol, which was incompletely removed in the synthesis of the precursor. These assignments are based upon previous experiments in He droplets [40]. The anharmonic frequencies and harmonic intensities of the OH stretching vibrations for both expected carbene conformers were computed at the MP2/cc-pVTZ level of theory. The band origin for the *cis,trans*- species is predicted to be 3661.0 cm⁻¹ (137 km/mol), and the *trans,trans*- band origin is predicted to be 3669.7 cm⁻¹ (138 km/mol). The frequency predictions suggest an assignment of the 3655.3 and 3659.2 cm⁻¹ bands, as shown in Fig. 3. On the basis of harmonic frequency calculations, Schreiner and coworkers

assigned two bands in the OH stretch region to two separate carbene conformers [18]. They reported experimental band origins at 3629.4 cm^{-1} and 3631.8 cm^{-1} for the *cis,trans*- and *trans,trans*- species, respectively. We now expect the OH stretch bands of matrix-isolated hydroxycarbene systems to be red-shifted from the He droplet band origins by $\approx 30\text{ cm}^{-1}$. Indeed, similar band origin differences were observed for both hydroxymethylene and dihydroxycarbene [20, 30]. Apparently, the solid Ar matrix environment exerts a significant perturbation to the OH oscillators in these systems. Although the assignment of the droplet spectrum is consistent with calculations and matrix isolation results, an unambiguous assignment can be made on the basis of transition dipole moment projections, rotational constants, and permanent electric dipole moments obtained from IR laser Stark spectroscopy.

A survey spectrum through the CH-stretching vicinity and a discussion of its assignment is provided in the Supplementary Material. This region is more ambiguous than the OH-stretch region, as the CH-vibrational bands do not exhibit rotationally resolved structure, analysis of which would enable spectral assignment. In addition, the predicted band intensities are much weaker than those in the OH-stretch region, and there is a substantial contribution from methyl formate, which is also formed *via* the thermal decomposition of **(1)**.

3.3 Zero-field spectra

Higher-resolution, zero-field spectra of the bands in the OH-stretch region are given in Fig. 4. Both the *cis,trans*- and *trans,trans*-carbene conformers have C_s symmetry equilibrium geometries. The OH-vibrations are of a' symmetry and have transition dipole moment projections along both the a - and b - inertial axes. The high-resolution spectra given in Fig. 4

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4 reveal two distinctly different bands. Most notably, the lower-frequency feature is nearly a pure
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6 *a*-type band, whereas the higher-frequency band clearly has both *a*- and *b*-type components, the
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8 latter of which appears on the high-frequency side of the band contour. The lower frequency
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10 band is also much weaker than the higher frequency band, by about a factor of 4, and the feature
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12 to the blue of the lower frequency band (marked by *) is due to an impurity.
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16 The red traces shown in Fig. 4 are the simulated spectra generated in PGOPHER[41] with
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18 a 0.4 K rotational temperature. Rotational constants obtained from calculations at the MP2/cc-
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20 pVTZ level of theory were reduced by a factor of 3 and utilized in the initial simulations. The
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22 rotational constant renormalization is necessary to account for the well-established solvent-
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24 induced increase in the rotor's moment of inertia[31, 33, 34]. Each rotational constant is expected
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26 to be affected by the He solvent in a unique way that depends sensitively on the molecule-helium
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28 interaction potential. Nevertheless, when comparisons to gas-phase values are available, it is
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30 typical to observe rotational constants reduced by a factor of 2 to 3 for heavier rotors such as
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32 CH₃O $\ddot{\text{C}}$ OH. With these initial conditions, a contour fitting analysis was performed to determine
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34 the experimental rotational constants and transition dipole moment projections along each
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45 component for a satisfactory simulation. The $(B+C)/2$ constant extracted from the simulation is
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47 2.8 and 2.0 times smaller than the computed equilibrium values for the *cis,trans*- and *trans,trans*-
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49 conformers, respectively, and both of these values are within range of the typical reduction
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51 factors observed for helium-solvated molecules. An *A* rotational constant equal to 0.3 cm⁻¹ is
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53 required in the simulation to reproduce the *Q*-branch feature at the band origin. The *A* constant
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55 is a factor of 2.1 smaller than the *ab initio* value for the higher energy *cis,trans*- conformer,
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4 whereas it is 5.8 times smaller than the predicted value for the lowest energy *trans,trans*-
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6 conformer. Taken together, these rotational constant reduction factors are consistent with an
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8 assignment of the lower frequency band to the OH stretch of the *cis,trans*- conformer.
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11 A rotational fine structure analysis was similarly performed on the higher-frequency *a,b*-
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13 hybrid band centered at 3659.232(1) cm⁻¹, and the resulting simulation is shown in Fig. 4. A
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15 satisfactory simulation now requires transition dipole components along both inertial axes. A
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17 ratio($d\mu_a/dq$):($d\mu_b/dq$) $\approx$ 3 is necessary to reproduce the intensity of the *b*-type feature on the
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19 high-frequency side of the hybrid band. Moreover, a rotational constant equal to 0.73 cm⁻¹ is
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21 necessary to reproduce the spacing between *a*- and *b*-type components, which is 2.4 times
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23 smaller than obtained from computations of the *trans,trans*- conformer. Collectively, these
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25 rotational constants and transition moment components are consistent with an assignment of the
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27 higher frequency band to the OH stretch of the *trans,trans*- conformer.
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34 This fine structure analysis, summarized in Table I, provides a basis for an initial
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36 assignment of the lower-frequency band to *cis,trans*-CH₃O $\ddot{C}$ OH and the higher-frequency band to
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38 the *trans,trans*-conformer. Permanent electric dipole moments obtained through IR laser Stark
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40 spectroscopy, as discussed below, confirm these assignments.
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48 49 **3.4 Stark Spectroscopy**

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51 Stark spectroscopy was performed on the most intense high-frequency band in the OH
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53 stretch region. Unfortunately, the signal was too weak to perform a similar measurement on the
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55 lower frequency band. Permanent electric dipole moments of helium-solvated
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4 molecules, extracted from Stark spectra, have been observed to be in good agreement with dipole
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6 moments obtained from gas-phase spectra, when comparisons are available[37].
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10 Spectra of the high-frequency *a,b*-hybrid band were acquired at various field strengths
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12 with both parallel and perpendicular laser polarization configurations, as shown in Figs. 5 and 6,
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14 respectively. The red traces are simulated spectra generated in PGOPHER [41] using the
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16 rotational constants previously derived from the zero-field spectrum. Optimized simulations
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18 reveal the *a*-axis component of the dipole moment to be 0.62(7) D, where the uncertainty is
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20 estimated on the basis of the sensitivity of the rotational contour to changes in the dipole
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22 moment. The *b*-axis component of the dipole moment is fixed to 0.45 D, which is the *ab initio*
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24 value at the MP2/cc-pVTZ level of theory. The *b*-type component is too weak to derive a
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26 definitive *b*-axis dipole moment component and uncertainty from the spectra. Nevertheless, we
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28 note that the experimental Stark spectra are qualitatively consistent with the simulations in the *b*-
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30 type region of the spectrum. The experimental *a*-axis component of the dipole moment agrees
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32 with the *ab initio* prediction for the *trans,trans*-rotamer ($\mu_a = 0.60$ D), thereby firmly
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34 establishing our initial assignment. In comparison, the computed *a*-axis component for the
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36 *cis,trans*-rotamer is 0.31 D. Given this rather firm assignment of the 3659.23 cm⁻¹ band to the
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38 OH stretch of *trans,trans*-CH₃O $\ddot{C}$ OH, it is reasonable to assign the lower-frequency band to the
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40 *cis,trans*- species.
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50 We note that the harmonic intensities for the observed *trans,trans*- and *cis,trans*- species
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52 are predicted to be roughly equivalent (Table I). However, we observe the *trans,trans*-
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54 conformer in significantly greater abundance in He droplets, as is evident in Fig. 2. Analysis of
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56 the two normalized features yields a relative abundance of 1:4.5 for the *cis,trans* and *trans,trans*
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58 species, respectively.
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4. Discussion

The agreement between the experimental dipole moment and the computed non-vibrationally averaged dipole moment was surprising given our initial expectation of a non-rigid backbone in the structure of $\text{CH}_3\text{O}\ddot{\text{C}}\text{OH}$. A potential energy and dipole moment scan was carried out to further explore the rigidity of this system. Relative energies and the magnitude of the dipole moment are reported as functions of two different dihedral angles in Fig. 2. The scan reveals a nearly flat dipole moment function in the vicinity of the equilibrium geometry. Near the *trans,trans*- minimum, the largest change in the dipole moment is observed for motion about $\theta_2(\text{OCOH dihedral})$, and a rotation by $\sim 20^\circ$ is required to change $|\mu|$ by $+0.1$ D. This relative insensitivity of $|\mu|$ to torsion is consistent with the observed agreement between theoretical (equilibrium) and experimental Stark spectra, the latter of which necessarily probe the expectation value of the permanent dipole moment.

The band origins for the *trans,trans*- and *cis,trans*-rotamers are determined to be 3659.23 cm^{-1} and 3655.20 cm^{-1} , respectively, which differ quite substantially from the band origins reported by Schreiner and coworkers in their Ar matrix isolation study (*trans,trans*: 3631.8 cm^{-1} , *cis,trans*: 3629.4 cm^{-1})[18]. A red shift of $\sim 26\text{ cm}^{-1}$ is observed for the OH stretch vibrations, which is consistent with shifts observed for two other hydroxycarbene species that have been isolated in both Ar matrices and He droplets[15, 18, 20, 30]. For all three of the hydroxycarbene species studied thus far in He droplets, $\text{H}\ddot{\text{C}}\text{OH}$ [17], $\text{HO}\ddot{\text{C}}\text{OH}$ [15], and $\text{CH}_3\text{O}\ddot{\text{C}}\text{OH}$, we expect a frequency shift less than 2 cm^{-1} from the gas-phase band origin. These results should therefore serve as a guide for future high-resolution jet-cooled studies of these species.

5. Conclusion

$\text{CH}_3\text{O}\ddot{\text{C}}\text{OH}$ was isolated and characterized in ^4He nanodroplets. Survey scans through the OH- and CH- stretching vicinities were obtained, and two conformers produced from the pyrolysis of (**1**) were observed, assignment of which was based upon anharmonic frequency calculations, rovibrational analysis of each band, comparison with earlier work in an Ar matrix [18], and ultimately, the permanent electric dipole moment obtained through IR laser Stark spectroscopy. The excellent agreement between the experimental dipole moment and non-vibrationally averaged computed dipole moments is due to the weak dependence of the dipole moment function to torsion in the vicinity of the equilibrium *trans,trans*- structure. Barrier heights computed as a function of rotation about two different dihedrals between the three lowest-energy carbene conformers reveal that rotational interconversion between them is unlikely given the relatively low energy remaining in the carbene upon fragmentation of the monomethyl oxalate precursor. This work reiterates the ideal means for producing these important reactive intermediates through pyrolysis of α -keto carboxylic acids, and He droplets are again shown to be a suitable medium for which to isolate these species and probe their structure with rotationally resolved IR spectroscopy. Perhaps most notably, insight into the ground state electronic structure of this species is obtained through the dipole moment analysis performed here. We expect these results to motivate future jet-cooled, gas-phase studies of these elusive species.

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TABLE I. Experimental and computed molecular properties of hydroxymethoxycarbene rotamers in the OH stretching region. ^a

	<i>trans-trans</i> (<i>a'</i>)		<i>cis,trans</i> (<i>a'</i>)	
	Helium	Theory ^b	Helium	Theory ^b
μ_a'' (D)	0.62(7)	0.60	-	0.3124
μ_b'' (D)	0.45	0.45	-	2.5946
μ_a' (D)	0.62(7)	—	-	—
μ_b' (D)	0.45	—	-	—
A''	0.73	1.7386	0.3	0.6326
A'	0.74	—	0.3	—
$\bar{B}''$	0.068	0.1506	0.074	0.2090
$\bar{B}'$	0.065	—	0.072	—
$(B - C)''$	0.01	0.0087	0	0.0596
$(B - C)'$	0.01	—	0	—
ν_0 ^c	3659.232(1)	3669.7 (138.0)	3655.20(1)	3661.0 (136.9)
$\dot{\mu}_a / \dot{\mu}_b$ ^d	3	2.32	<i>a</i> -type	5.65

^a Units in cm⁻¹ unless otherwise specified. Numbers in parentheses are 2 σ uncertainties unless otherwise noted.

^bEquilibrium *ab initio* rotational constants at the MP2/cc-pVTZ level of theory.

^c Theoretical band origins are obtained *via* anharmonic frequency computations at the MP2/cc-pVTZ level of theory. Numbers in parentheses next to theoretical values are harmonic intensities in units of km/mol. For comparison, Argon matrix band origins of the *trans,trans*, and *cis,trans*- vibrations are 3631.8 and 3629.4 cm⁻¹, respectively [18].

^d Ratio of transition dipole moment components along the *a* and *b* inertial axes.

Figure Captions:

Figure 1. Relative energies of species produced via the thermal decomposition of the two lowest-energy monomethyl oxalate conformers *cTc*(**1a**) and *cTt*(**1b**) via C-C bond cleavage and subsequent H-atom migration, as computed in this work at the B3LYP/cc-pVTZ level of theory. The relative energies of the two precursor conformers *cTc* and *cTt* are 2.5 and 0 kcal/mol, respectively. Computed rotational barriers between the carbene species are sufficiently high to prevent interconversion between them, as indicated atop interconversion arrows, and as shown in Fig. 2.

Figure 2. Potential energy and permanent electric dipole moment scan as a function of rotation about two different dihedrals at the B3LYP/cc-pVTZ level of theory. Rotational barriers of 17.4 kcal/mol and 16.5 kcal/mol were obtained for the *cis,trans*- and *trans,cis*- species, respectively, from the lowest-energy *trans,trans* conformer upon rotation about θ_1 and θ_2 . The magnitude of the permanent electric dipole moment (blue) was also computed as a function of these two coordinates.

Figure 3. Survey spectra of the pyrolysis products of monomethyl oxalate(**1**) through the OH stretching region. Laser induced ion signal depletion is measured on mass channel 29, which corresponds to HCO^+ . The bands marked with * correspond to the OH-vibrations of residual methanol from the synthesized precursor based upon earlier work of methanol embedded in ^4He droplets. The lowest-frequency band is assigned to the *cis,trans*- $\text{CH}_3\text{O}\ddot{\text{C}}\text{OH}$ conformer, whereas the higher-frequency band is assigned to the *trans,trans*-conformer.

Figure 4. Higher-resolution scan of transitions associated with the OH-stretching bands of the *trans,cis*- and *trans,trans*- conformers of CH₃O[•]COH. The feature marked by an * is due to an impurity. The lower traces shown in red were obtained in PGOPHER based upon C_s symmetry utilizing the molecular constants given in Table I.

Figure 5. Stark spectra of the *trans,trans*- conformer of CH₃O[•]COH acquired with the laser polarization aligned parallel to the static DC electric field. The simulations shown in red are generated in PGOPHER utilizing the molecular constants given in Table I.

Figure 6. Stark spectra of the *trans,trans*- conformer of CH₃O[•]COH acquired with laser polarization aligned perpendicular to the static DC electric field. The simulations shown in red are generated in PGOPHER utilizing the molecular constants given in Table I.

Figure 1
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