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The Simplest Criegee Intermediate ($\text{H}_2\text{C}=\text{O}-\text{O}$): Isotopic Spectroscopy, Equilibrium Structure, and Possible Formation from Atmospheric Lightning

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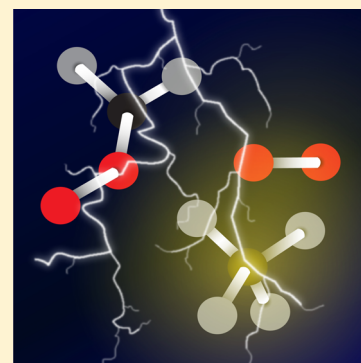
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S Supporting Information

ABSTRACT: A number of research groups have recently succeeded in producing the simple carbonyl oxides H_2COO and CH_3CHOO in sufficient quantity to observe them spectroscopically and to probe the kinetics of their reactions with NO_2 and SO_2 . These latter studies provide evidence that the carbonyl oxides play an important role in the atmosphere, likely contributing to pollutant removal, aerosol formation, and planetary cooling. In this work, Fourier transform microwave and double-resonance spectroscopy are combined with theory to study five isotopic species of $\text{H}_2\text{C}=\text{O}-\text{O}$, and a precise equilibrium structure is reported for this ephemeral yet crucial reactive intermediate. In contrast to the other investigations, which have exclusively produced $\text{H}_2\text{C}=\text{O}-\text{O}$ by halogen chemistry, passing a mixture of methane and excess molecular oxygen through an electrical discharge generates this isomer of H_2CO_2 with high selectivity, thereby suggesting that the molecule is produced in the direct vicinity of atmospheric lightning.



SECTION: Spectroscopy, Photochemistry, and Excited States

The class of molecules known as Criegee intermediates ($\text{RR}'\text{C}=\text{O}-\text{O}$), first postulated 40 years ago¹ to participate in the ozonolysis of alkenes, resisted direct experimental observation until quite recently. In the past few years, several groups have prepared the simplest Criegee species, $\text{H}_2\text{C}=\text{O}-\text{O}$ (formaldehyde oxide or, more generically, carbonyl oxide; see Figure 1), and characterized it by synchrotron photoionization,^{2,3} as well as ultraviolet,⁴ infrared,⁵ and rotational⁶ spectroscopy. This long-sought biradical, which has an electronic structure similar to that of ozone, has exclusively been generated with halogen chemistry, most commonly by the reaction between CH_2I (formed by photolysis of diiodomethane (CH_2I_2) with 248 nm radiation) and O_2 ,^{2,4,5} or by attack of a chlorine atom on dimethyl sulfoxide (DMSO).³ In the study by Nakajima and Endo,⁶ it was produced in an electrical discharge source using a $\text{CH}_2\text{Br}_2/\text{O}_2$ gas mixture. Preparation of the simplest Criegee intermediate by means of halogenated precursors is motivated by extensive kinetic studies of the $\text{CH}_2\text{I} + \text{O}_2$ reaction, which conclude that a non-negligible fraction of chemically excited CH_2IOO complexes yield $\text{H}_2\text{C}=\text{O}-\text{O} + \text{I}$.

A recent and important kinetic study by Welz et al.² revealed that the rates of reaction of $\text{H}_2\text{C}=\text{O}-\text{O}$ with SO_2 and NO_2 are roughly 2 to 4 orders of magnitude greater than those assumed in standard atmospheric models for removal of SO_2 and NO_2 via Criegee chemistry. The former reaction may have

substantial implications for the formation of sulfuric acid, and consequently for aerosol formation.⁷ In the case of NO_2 , it was suggested²—and since confirmed⁸—that the fast reaction between $\text{H}_2\text{C}=\text{O}-\text{O}$ and NO_2 forms the nitrate (NO_3) radical, a potent oxidant in the nighttime troposphere,^{9–11} and that this process might raise the NO_3 concentration significantly in atmospheric models. Taken together, these findings suggest that the role of this elusive and fascinating class of molecules in atmospheric chemistry is much more significant than had already been believed (ozonolysis is known to be a major source of the highly reactive OH radical in the troposphere,^{12,13} and also thought to participate in the formation of heavily oxidized organics such as carboxylic acids¹⁴ and peroxy radicals¹⁵).

Because Criegee intermediates are now widely believed to be crucial players in the troposphere, mechanisms for formation of these (formal) singlet biradical species—distinct from their involvement as putative transients, chemically activated (and indeed, never observed) intermediates in the reaction of O_3 with alkenes—are an important field of inquiry. Perhaps motivated by the fact that present strategies for forming the simplest Criegee species have relied solely on halogen

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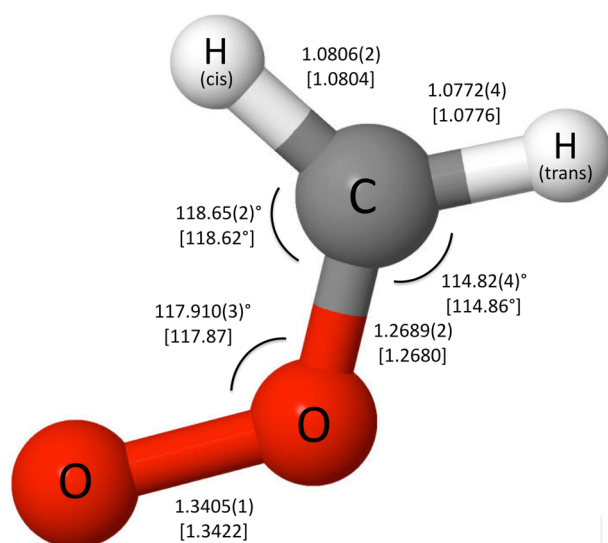


Figure 1. The empirical (“semi-experimental”) equilibrium (r_e^{emp}) structure of $\text{H}_2\text{C}=\text{O}-\text{O}$, derived from rotational constants of nine isotopic species and zero-point vibrational corrections calculated at the CCSD(T) level of theory. Numbers in parentheses are 1σ uncertainties in units of the last digit. The computed equilibrium structure parameters are included in the brackets. The bond lengths are given in Å.

chemistry, it has been suggested that—apart from the unknown fraction of Criegee intermediates that are collisionally stabilized products of ozonolysis—processes occurring in the marine boundary layer (where halogens are found naturally and DMSO is an important sulfur-containing species) might lead to additional production of $\text{H}_2\text{C}=\text{O}-\text{O}$.^{16,17}

In addition to their significance in mechanistic organic chemistry and atmospheric chemistry, Criegee intermediates have an unusual electronic structure that has long been known to pose problems for various quantum-chemical approaches.^{18–26} For these reasons, precise determinations of their geometrical structures are desirable. A significant recent step in this direction was taken by Nakajima and Endo,⁶ who recorded the microwave spectrum of four isotopic forms of the parent compound: $\text{H}_2\text{C}=\text{O}-\text{O}$, $\text{H}_2\text{C}=\text{O}-^{18}\text{O}$ and the corresponding d_2 species, using Fourier transform (FT) microwave spectroscopy in combination with a molecular beam discharge source. With rotational constants derived from the isotopic analysis, a molecular structure was determined. The C–O and O–O bond lengths are consistent with the idea that $\text{H}_2\text{C}=\text{O}-\text{O}$ has more zwitterion than biradical character, in agreement with the infrared study.⁵ Owing to correlations between geometrical parameters which arise from use of doubly substituted isotopic species (e.g., $^{18}\text{O}^{18}\text{O}$), however, some ambiguities are present in the purely experimental structure, i.e., there are large uncertainties in the two OCH bond angles. Nevertheless, the structure that they report is in good agreement with a very high-level *ab initio* computation done as part of the same work.

In this paper, the isotopic spectroscopy of $\text{H}_2\text{C}=\text{O}-\text{O}$ has been extended significantly and an extremely precise and accurate equilibrium structure is obtained, with $\text{H}_2\text{C}=\text{O}-\text{O}$ generated by a means entirely distinct from the halogen chemistry reported previously. We report the rotational spectrum of all five singly substituted (with ^{13}C , ^{18}O and ^2H) isotopic species: $d_1\text{-cis}$ and $d_1\text{-trans}$ $\text{HDC}=\text{O}-\text{O}$, $\text{H}_2\text{C}=\text{O}-^{18}\text{O}$

O , $\text{H}_2\text{C}=\text{O}-^{18}\text{O}$, and $\text{H}_2^{13}\text{C}=\text{O}-\text{O}$. This information has been combined with that of Nakajima and Endo and high-level coupled-cluster calculations to determine the equilibrium structure of the molecule using a well-established procedure. Perhaps the most significant finding of our research is the discovery that $\text{H}_2\text{C}=\text{O}-\text{O}$ is readily produced with high selectivity by simply passing methane and molecular oxygen through an electrical discharge. This finding suggests that atmospheric lightning could be a potential source of Criegee intermediates, a possibility that has apparently not been considered previously, and one which may have important implications for tropospheric chemistry.

The same type of microwave spectrometer and double resonance techniques used in the original investigation⁶ of $\text{H}_2\text{C}=\text{O}-\text{O}$ were employed here to measure rotational spectra of its singly substituted isotopologues.^{27,28} We quickly established that an electrical discharge through a dilute mixture of CH_4/O_2 gives rise to a rotational line at exactly the frequency of the $1_{0,1} \rightarrow 0_{0,0}$ line reported by Nakajima and Endo, and that the carrier of this line behaves in the same way as that expected for $\text{H}_2\text{C}=\text{O}-\text{O}$ (i.e., discharge dependent, nonmagnetic, etc.). This line was readily observed with good signal-to-noise ratio (>10) with minimal integration time (3 s). Because isotopic samples of methane fully enriched in ^{13}C or partially enriched in deuterium (e.g., CH_3D_2) are commercially available, and statistical mixtures of $^{16}\text{O}/^{18}\text{O}$ O_2 are easily generated, searches for the five new isotopologues were then undertaken, guided by the coupled-cluster calculations performed here. Ultimately, at least three lines (two *a*-type and one *b*-type) were found for all five species, the minimum number required to determine all three rotational constants of each to high precision. Owing to the high spectral resolution of the measurement (0.1 ppm), well-resolved deuterium quadrupole hyperfine structure was apparent in the fundamental rotational line of the two d_1 species, from which it is then possible to derive the quadrupole tensor element $\chi_{aa}(\text{D})$ for both. From these constants, assignment of the complex hyperfine pattern for the same rotational line of $\text{D}_2\text{C}=\text{O}-\text{O}$ is straightforward (see Figure 2). The new laboratory measurements are given in Tables S1 and S2; spectroscopic constants for all nine isotopic species are summarized in Table 1.

An empirical (sometimes called “semi-experimental”²⁹) structure was derived for $\text{H}_2\text{C}=\text{O}-\text{O}$, in which the rotational constants for all nine isotopic species were corrected for effects of zero-point vibrational motion, as calculated theoretically using second-order vibrational perturbation theory.³⁰ When these contributions, calculated at the CCSD(T)³¹ level of theory with an atomic natural orbital basis set,³² are applied (Table S3), the derived inertial defects for all species are uniform and nearly zero (ranging from -0.008 to $+0.003$ amu Å²; see Table S3), a clear indication that both the electronic structure method used and second-order vibrational perturbation theory provide accurate treatments of the electronic and vibrational structure, respectively, of this small carbonyl oxide. Using a standard nonlinear least-squares minimization procedure, the seven unique structural parameters (four bond lengths and three bond angles) were then optimized to simultaneously reproduce the three moments of inertia of the nine isotopic species. The resulting structure is remarkably precise, reproducing all 27 rotational constants to an rms error of only 0.45 MHz, and yielding bond lengths with a statistical uncertainty of sub-mÅ, and bond angles to better than $\pm 0.04^\circ$

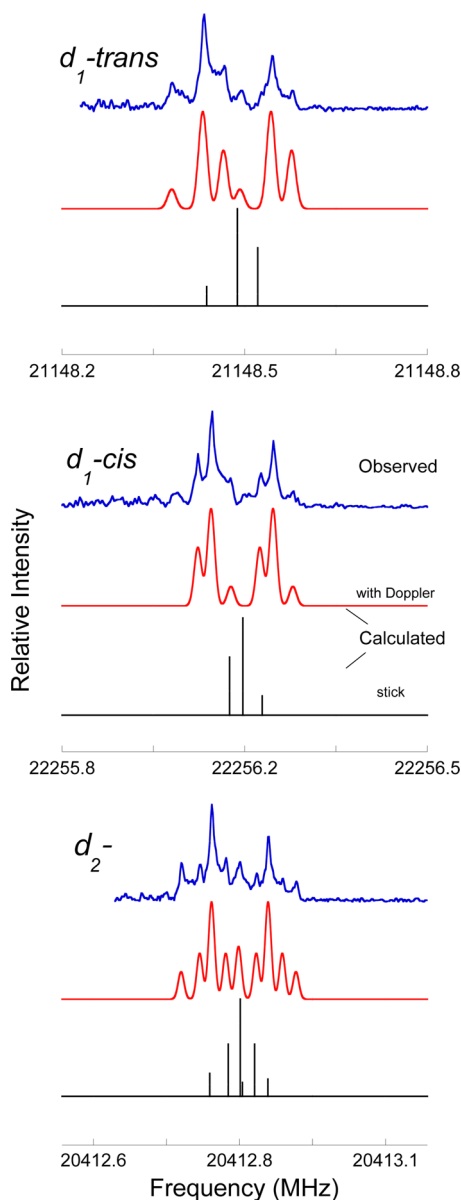


Figure 2. The fundamental rotational transitions of d_2 - and the two d_1 -isotopic species of $\text{H}_2\text{C}=\text{O}-\text{O}$, showing well-resolved hyperfine structure from the deuterons. The double-peaked line profile is instrumental in origin, arising from the Doppler effect. Each best-fit stick spectrum (bottom) is convoluted with the instrument response function (10 kHz FWHM line widths; ~ 800 m/s for the speed of the molecular beam; middle) for comparison with the observed spectrum (top). The integration time for each spectrum was approximately 45 min.

(Figure 1). In parallel, a high-level equilibrium structure was also computed by theory. The calculations, which employ large one-particle basis sets, and include corrections for very high levels of electron correlation (“quadruple excitation” effects), are the most advanced yet carried out for the structure of $\text{H}_2\text{C}=\text{O}-\text{O}$, and yield the structural parameters also documented in Table 2.

The r_e^{emp} structure is in near perfect agreement with the equilibrium structure calculated with theory (Table 2). We note that the two C–H bonds are predicted to systematically differ in length by ~ 0.003 Å at different levels of theory, and that is what is also found using our combined structural analysis. The

largest difference between the four bond lengths in the calculated r_e and the present r_e^{emp} structures is ~ 0.002 Å; for the angles, the largest deviation is less than 0.1° . In light of the extensive isotopic spectroscopy and high-level quantum-chemical calculations that have now been undertaken, $\text{H}_2\text{C}=\text{O}-\text{O}$, a molecule whose rotational spectrum was only detected a short time ago, can now be considered as one of better characterized reactive species from the perspective of molecular structure. Indeed, there are few stable molecules for which the equilibrium structure is known as precisely and confidently as that determined here for the simplest Criegee intermediate.

By comparing line intensities with those of a stable gas at known concentration (i.e., 0.1% OCS in Ne), taking into account differences in the rotational partition functions, dipole moments, and the instrument response function with frequency, we estimate that on the order of $\sim 10^{10-11}$ $\text{H}_2\text{C}=\text{O}-\text{O}$ molecules are produced per gas pulse using CH_4 as a precursor gas. At this abundance, it should be possible to undertake follow-up investigations, including microwave-IR double resonance spectroscopy to better map out the vibrational spectrum of this simple carbonyl oxide. The CH_4/O_2 gas mixture has the added advantage that it is also fairly clean, producing few larger carbon-chain molecules and avoiding strong background lines that might arise from halogenated species, factors that could complicate spectroscopic identification and analysis at other wavelengths.

The mechanism by which $\text{H}_2\text{C}=\text{O}-\text{O}$ is formed in our molecular beam discharge source is unknown, but some inferences can be drawn. Since the O_2 unit is also conserved⁶ during molecule formation when starting with CH_4 and O_2 , the pathway would appear to be fairly simple, and, for example, mechanisms involving ozone can be ruled out. The direct reaction $\text{CH}_2 + \text{O}_2$ is quite exothermic³³ (since a C=O bond is formed), and the chemically activated product of the reaction would quickly revert to reactants or go on to form other products. Furthermore, the apparent barriers to isomerization are sufficiently low that other isomers—cyclic dioxirane and dihydroxycarbene ($\text{HO}-\ddot{\text{C}}-\text{OH}$)—would be expected to form. Consequently, it is significant in this regard that no rotational lines of dioxirane (which has a well-documented microwave spectrum³⁴) or the *cis*-, *trans*- conformer of $\text{HO}-\ddot{\text{C}}-\text{OH}$ (the rotational spectrum of which has recently been identified by our groups³⁵) are observed in our experiments, indicating that $\text{H}_2\text{C}=\text{O}-\text{O}$ is formed rather selectively. Even for the most stable isomers of CO_2H_2 , *trans*- and *cis*-formic acid $\text{HOC}(\text{O})\text{H}$, lying more than 80 kcal mol^{−1} below the other structures on the potential energy surface, lines are observed only at threshold levels. One species that is observed, however, is the methyl peroxy radical CH_3O_2 ,³⁶ which is likely formed with considerable excess energy and unlikely to be stabilized to an appreciable extent under the conditions of the discharge. As the barriers to further reaction of CH_3O_2 via decomposition and/or isomerization are rather significant,³⁷ however, an approximate microcanonical equilibrium will be set up between hot CH_3O_2 and the reactants. Because the O_2 concentration in the discharge is relatively high, vibrationally excited O_2 can then react with CH_3O_2 molecules (many of which will have at least 32 kcal/mol of internal energy, the exothermicity of the CH_3+O_2 reaction) to form HO_2 and $\text{H}_2\text{C}=\text{O}-\text{O}$. Preliminary calculations indicate that this reaction is endothermic by 26 kcal/mol, but faces a barrier of 44 kcal/mol. Hence CH_3O_2 molecules with vibrational excitation of about 10 kcal/mol with respect to the entrance channel could form $\text{H}_2\text{C}=\text{O}-\text{O}$, or

Table 1. Spectroscopic Constants of Isotopic CH₃OO (in MHz)

constant ^a	H ₂ COO ^b	H ₂ ¹³ COO ^b	H ₂ C ¹⁸ OO ^b	H ₂ CO ¹⁸ O ^b	D ₂ COO ^c	<i>d</i> _{1,trans} -HDCOO ^b	<i>d</i> _{1,cis} -HDCOO ^b	D ₂ C ¹⁸ O ¹⁸ O ^b	H ₂ C ¹⁸ O ¹⁸ O ^b
A ₀	77748.8661(122)	77072.9452(51)	73393.85724(42)	76885.08447(206)	60529.6337(141)	76636.5023(74)	61770.577(171)	57038.981(53)	72490.994(68)
B ₀	12465.2577(127)	12089.4617(51)	12464.44267(42)	11776.82999(208)	11070.4320(141)	11310.0224(74)	12135.131(170)	10465.1416523(51)	11771.168(69)
C ₀	10721.2765(131)	10429.6523(51)	10632.74067(42)	10192.67475(206)	9342.4422(141)	9838.5050(73)	10121.056(170)	8827.064(50)	10106.393(66)
Δ _J	0.01129	0.01067	0.01114	0.01024	0.00806	0.00839	0.01148	0.00759	0.01009
Δ _K	2.56597	2.55006	2.38128	2.51923	0.99238	2.19776	1.21167	0.9459	2.32966
Δ _{JK}	−0.06802	−0.07032	−0.06166	−0.06462	−0.09541	−0.04564	−0.03116	−0.01293	−0.05806
δ _J	0.00226	0.00211	0.00234	0.00197	−0.00177	0.00153	0.0026	0.0016	0.00204
δ _K	0.06068	0.05701	0.0583	0.05666	−0.0002	0.04826	0.0591	0.04302	0.05459
χ _{aa} (<i>d</i> _{1,cis})					−0.0845(72)		−0.0851(72)		
χ _{bb} (<i>d</i> _{1,cis})					0.19214		0.1925		
χ _{cc} (<i>d</i> _{1,cis})					−0.1014		−0.1014		
χ _{aa} (<i>d</i> _{1,trans})					0.1003(66)	0.1074(23)			
χ _{bb} (<i>d</i> _{1,trans})					−0.00693	−0.01588			
χ _{cc} (<i>d</i> _{1,trans})					−0.10818	−0.10818			
σ (MHz)		0.007	0.001	0.003	0.007	0.012	...	0.025	0.026
Δ ₀ ^d	0.023	0.0948	0.0990	0.0964	0.0944	0.0888	0.1059	0.1015	0.1006

^aNote: Units are MHz. Uncertainties (1σ) are in units of the last significant digit. Centrifugal distortion parameters were constrained to values calculated at the CCSD(T)/ANO1 level of theory. Deuterium quadrupole-coupling parameters with no uncertainties were constrained to values calculated at the CCSD(T)/cc-pCVQZ level of theory. ^bDerived from line frequencies in Table S1 or from ref 6. ^cDerived from line frequencies in Table S2 and from ref 6. ^dInertial defect in amu Å².

Table 2. Geometrical Parameters of $\text{H}_2\text{C}=\text{O}-\text{O}$ (Bond Lengths in Å and Bond Angles in Degree) Calculated at Various Levels of Theory

theory	$r_{\text{O}-\text{O}}$	$r_{\text{C}-\text{O}}$	$r_{\text{C}-\text{H}}$ (trans)	$r_{\text{C}-\text{H}}$ (cis)	\angle_{OOC}	\angle_{OCH} (trans)	\angle_{OCH} (cis)
CCSD(T)/aug-cc-pCVQZ	1.3406	1.2676	1.0780	1.0810	118.00	114.91	118.66
CCSD(T)/aug-cc-pCVSZ	1.3394	1.2665	1.0777	1.0806	118.02	114.90	118.64
$\Delta T/\text{cc-pVTZ}(\text{fc})^{a,b}$	0.0038	−0.0036	0.0002	0.0001	−0.11	0.11	0.01
$\Delta Q/\text{cc-pVDZ}(\text{fc})^{a,c}$	−0.0010	0.0051	−0.0003	−0.0003	−0.03	−0.15	−0.04
total ^d	1.3422	1.2680	1.0776	1.0804	117.87	114.86	118.62
exper. ^e	1.3405(1)	1.2689(2)	1.0772(4)	1.0806(2)	117.910(3)	114.82(4)	118.65(2)

^aCarbon and oxygen 1s orbitals frozen. ^bDifference between CCSDT and CCSD(T) results using cc-pVTZ basis. ^cDifference between CCSDT(Q)_A and CCSDT results using cc-pVDZ basis. ^dCCSD(T)/aug-cc-pCVSZ results augmented with ΔT and ΔQ corrections. ^eNumbers in parentheses are 1 σ uncertainties in units of the last digit.

possibly the hydrogen abstraction step is assisted by tunneling through the barrier. This scheme could plausibly produce relatively cold Criegee biradicals, as seems to be the case in our experiments. Other possible scenarios involve the self (disproportionation) reaction of methyl peroxy or reaction between HO_2 and CH_3O_2 . However, it is clear that further work aimed toward the identification of key species in the discharge is desirable and necessary before any firm conclusions can be drawn.

Irrespective of the mechanism, it is clear that molecules of methane in the presence of excess molecular oxygen and a strong electric discharge readily form $\text{H}_2\text{C}=\text{O}-\text{O}$, the simplest Criegee intermediate. It seems plausible then that a similar process occurs in the troposphere (where the concentration of methane is approximately 2 ppm and on the rise) in the immediate vicinity of lightning flashes, which occur some 1.4 billion times per year globally. Lightning is known to be an important source of the NO radical,³⁸ which is formed from the two major constituents of the atmosphere, but also more complex molecules such as peroxyacetylnitrate (PAN) and nitric acid,³⁹ which contain atoms (C and H) from less abundant molecules (presumably dominated by CO_2 , H_2 and H_2O). Moreover, the fact that a spark discharge (i.e., lightning) initiates chemistry of methane is implicit in the findings of Miller–Urey experiments done a half century ago.^{40,41} The results of our discharge experiments here are consistent with lightning flashes being an additional (and apparently remarkably selective with regard to isomers of H_2CO_2) source of Criegee intermediates, adding to ozonolysis and the sources from halogen-initiated chemistry discovered recently.

METHODS

Rotational lines of normal and isotopic $\text{H}_2\text{C}=\text{O}-\text{O}$ were detected using a combination of Balle–Flygare FT cavity microwave spectroscopy²⁷ and millimeter-microwave double-resonance techniques.²⁸ This short-lived intermediate was produced in the throat of a small electrical discharge source by applying a low-current dc potential across two copper electrodes as a dilute gas mixture, consisting of methane (0.5%) and oxygen (1.5%) heavily diluted in neon gas, passes through the nozzle source prior to supersonic expansion in the large vacuum. The singly substituted isotopologues were produced using commercially available samples enriched in ^2H , ^{13}C , or ^{18}O at the same concentration. Best-fit spectroscopic constants and structural parameters were derived using well-tested, nonlinear least-squares fitting programs. Quantum-chemical calculations were performed at the CCSD(T)³¹ and CCSDT⁴² levels of theory using the CFOUR package⁴³ and CCSDT-(Q)_A⁴⁴ with the MRCC code.⁴⁵ The geometry of $\text{H}_2\text{C}=\text{O}-\text{O}$

was optimized using analytical gradients, except that numerical gradients were used in the CCSDT(Q)_A calculations. Zero-point vibrational corrections³⁰ for each isotopic species were calculated from the CCSD(T) harmonic force field and the cubic constants;⁴⁶ the vibrational corrections as well as fourth-order centrifugal distortion terms were evaluated at the same level of theory. A more complete description of the experimental and theoretical methods is provided in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Includes additional details of methods and materials, tables of the measured rotational lines of isotopic H_2COO , along with the semi-experimental spectroscopic constants, theoretical calculations of zero-point vibrational corrections, and associated references. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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