

Communication: Determination of the molecular structure of the simplest Criegee intermediate CH₂OO

Masakazu Nakajima and Yasuki Endo

Citation: *The Journal of Chemical Physics* **139**, 101103 (2013); doi: 10.1063/1.4821165

View online: <http://dx.doi.org/10.1063/1.4821165>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/139/10?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

Observation of hydroxymethyl hydroperoxide in a reaction system containing CH₂OO and water vapor through pure rotational spectroscopy

J. Chem. Phys. **143**, 164307 (2015); 10.1063/1.4933433

Communication: Spectroscopic characterization of an alkyl substituted Criegee intermediate syn-CH₃CHOO through pure rotational transitions

J. Chem. Phys. **140**, 011101 (2014); 10.1063/1.4861494

Fourier transform microwave spectroscopy and molecular structure of the 1,1-difluoroethylene-hydrogen fluoride complex

J. Chem. Phys. **131**, 204301 (2009); 10.1063/1.3250865

Rotational spectroscopy and molecular structure of the 1,1,2-trifluoroethylene-acetylene complex

J. Chem. Phys. **128**, 064315 (2008); 10.1063/1.2828503

Fourier transform microwave spectroscopy of the 2 Σ + ground states of YbX (X=F, Cl, Br): Characterization of hyperfine effects and determination of the molecular geometries

J. Chem. Phys. **115**, 6979 (2001); 10.1063/1.1404146



NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP Applied Physics Reviews

Communication: Determination of the molecular structure of the simplest Criegee intermediate CH₂OO

Masakazu Nakajima and Yasuki Endo^{a)}

Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan

(Received 12 August 2013; accepted 29 August 2013; published online 13 September 2013)

The simplest Criegee intermediate CH₂OO was detected in a discharged supersonic jet of a CH₂Br₂ and O₂ gas mixture by Fourier-transform microwave spectroscopy. The experimentally determined rotational constants of CH₂OO and its isotopologues enabled us to derive the geometrical structure. The determined OO and CO bond lengths, which are relevant to a discussion on its electronic structure, are 1.345(3) and 1.272(3) Å, respectively. The CO bond length is close to that of a typical double bond and is shorter than that of the OO bond by 0.07 Å, indicating that CH₂OO has a more zwitterionic character H₂C=O⁺–O[–] than biradical H₂Ċ–O–Ċ. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4821165>]

The generally accepted mechanism of ozonolysis of alkenes was first proposed by Criegee.^{1,2} In the ozonolysis processes, a primary organic ozonide decomposes to a carbonyl compound and a carbonyl oxide, R₁R₂COO, which is known as a Criegee intermediate (CI). Since ozonolysis is considered to be a major removal process of alkenes in the troposphere,³ atmospheric significance of its product, CI, has been discussed for decades. So far, oxidation of atmospheric trace gases has been considered to be dominantly initiated by ozone, the hydroxyl and nitrate radicals, and the chlorine atom.^{3,4} Thermally stabilized CIs are now postulated as another important initiator of oxidation.^{5,6} The first direct detection of CIs in the gas phase was reported for the simplest CI, CH₂OO, in 2008 by Taatjes *et al.*⁷ They used a tunable vacuum ultraviolet synchrotron radiation source, and photoionized CH₂OO was selectively detected by mass spectrometry. By means of the photoionization detection method, direct kinetic measurements of CH₂OO and CH₃CHOO with several atmospherically relevant reactants were carried out,^{8–10} and atmospheric roles of CIs have become possible to be discussed based on the experimentally determined rate constants.

CIs may have two types of canonical structures, biradical and zwitterion as illustrated in Fig. 1. Criegee originally postulated them as zwitterions,^{1,2} which adequately account for the observed chemistry.¹¹ The CO and OO bond lengths of CIs draw attention in discussions on their electronic structures. The two bond lengths must be almost same when a CI is described as a biradical. On the other hand, in the zwitterionic picture, the CO bond length becomes significantly shorter than that of OO, because they have more double and single bond characters, respectively. Thus, experimental determinations of geometrical structures of CIs provide essential information relevant to their chemistry. Gas-phase spectroscopy is a straightforward approach to determine molec-

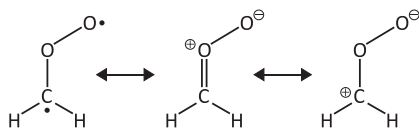
ular structure experimentally. Recently, gas-phase spectra of CH₂OO have been reported in ultraviolet¹² and infrared¹³ regions. Although the reported spectra are not rotationally resolved, the rotational contours observed for the IR bands have been used to infer the molecular structure.¹³ In the present study, we applied pure rotational spectroscopy to this important intermediate, and very accurate sets of the rotational constants were obtained for CH₂OO and its isotopologues to determine the molecular structure experimentally.

Prior to a spectral survey, geometrical optimizations of CH₂OO were carried out on the ground ¹A' potential surface assuming a planar C_s geometry using the Molpro 2012.1 program package,¹⁴ in order to predict the rotational transition frequencies. Geometrical parameters to be optimized are shown in Fig. 2 and those optimized with the CCSD(T)-F12/aug-cc-pV5Z level of theory are listed in Table I. Rotational constants calculated from the optimized geometry are 78 377, 12 550, 10 817 MHz for A_e, B_e, and C_e of the normal species, respectively. Equilibrium geometries obtained with several other levels of theory are also given in Table S-I of the supplementary material.¹⁵

The reactive transient species, CH₂OO, was produced in a supersonic jet by a pulsed electric discharge¹⁶ of a gas mixture of CH₂Br₂ and O₂ diluted in Ar. Typical concentrations of CH₂Br₂ and O₂ were 0.15% and 1.0%, respectively. The CH₂OO isotopologues, CD₂OO, CH₂¹⁸O¹⁸O, and CD₂¹⁸O¹⁸O, were produced using the isotope-enriched precursors, CD₂Br₂ and/or ¹⁸O₂. A Balle-Flygare type Fourier-transform microwave (FTMW) spectrometer¹⁷ operated in the frequency region of 4–40 GHz was used for the observation of pure rotational transitions of CH₂OO. An FTMW-millimeter wave (mmW) double-resonance technique¹⁸ was used for observing pure rotational transitions at higher frequencies than 40 GHz.

At first, we surveyed an *a*-type transition, 1₀₁–0₀₀, corresponding to the frequency of *B* + *C*, predicted at 23.4 GHz. Since CH₂OO is a singlet molecule without *I* ≥ 1 nuclei, a rotational transition without fine and hyperfine structures

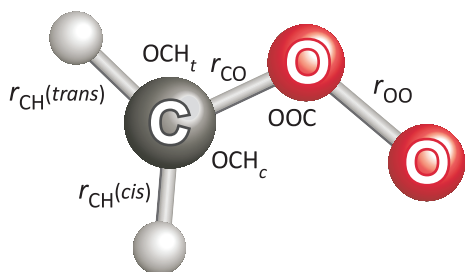
^{a)} Author to whom correspondence should be addressed. Electronic mail: endo@bunshi.c.u-tokyo.ac.jp

FIG. 1. Lewis structures of CH₂OO.

and showing no Zeeman effect was surveyed. An FTMW spectrum of the observed $1_{01}-0_{00}$ transition of CH₂OO is shown in Fig. 3(a). The intensity of the CH₂OO signal was not affected by changing the O₂ concentration in the precursor gas mixture from 1% to 10%, indicating that CH₂OO is quickly produced by the O₂ addition to the discharge products of CH₂Br₂ and the produced CH₂OO is not consumed by collisions with O₂. On the other hand, the CH₂OO signal became weaker when the CH₂Br₂ concentration was increased up to 0.4%. It is considered that CH₂OO is consumed by reactions with CH₂Br₂ or its discharge products.

To confirm the assignment of the observed $1_{01}-0_{00}$ transition of CH₂OO, we observed the $2_{02}-1_{01}$ transition with the FTMW-mmW double-resonance technique by monitoring the $1_{01}-0_{00}$ signal. Since the double-resonance signal was observed at quite close to the expected frequency, it is evident that the two observed transitions are originating from the same molecular species and have a common rotational level, 1_{01} . A b -type transition, $1_{10}-1_{01}$, was also observed with the same double-resonance technique. Another b -type transition, $1_{11}-2_{02}$, was predicted to be located at 18.9 GHz, which is accessible by the FTMW spectrometer. However, population in the lower level, 2_{02} , was very small due to the unfavorable Boltzmann distribution under the jet cooled condition where molecules are typically cooled to ~ 3 K in our apparatus. Thus, we pumped the population of CH₂OO up to the rotational level 2_{02} from 1_{01} by irradiating a MW radiation corresponding to the known $2_{02}-1_{01}$ transition. The FTMW signal of $1_{11}-2_{02}$ was greatly enhanced by the MW irradiation. We thus confirmed that the observed transition is originating from CH₂OO, and the lower level is 2_{02} . A total of four rotational transitions were observed for CH₂OO.

The $1_{01}-0_{00}$ transition of CD₂OO was observed by replacing CH₂Br₂ with CD₂Br₂ in the precursor sample gas, as shown in Fig. 3(b). The observed spectrum shows a complex hyperfine splitting caused by the nuclear quadrupole interactions due to the nuclear spin of deuterium. Since the splitting is too small to resolve each hyperfine component completely in our spectrum, we took the position of the most intense hyperfine component as the center frequency of the

FIG. 2. Structure of CH₂OO.TABLE I. Theoretically and experimentally determined structures of CH₂OO.

	Theory ^a	Fit 1 ^b	Fit 2 ^b
r_{OO} (Å)	1.3409	1.344(1)	1.345(3)
r_{CO} (Å)	1.2683	1.274(1)	1.272(3)
$r_{CH(cis)}$ (Å)	1.0820	1.147(15)	1.094(1)
$r_{CH(trans)}$ (Å)	1.0790	1.118(7)	1.088(4)
OOC (deg)	117.950	118.06(2)	118.02(3)
OCH(cis) (deg)	118.623	108.24(221)	117.96(56)
OCH(trans) (deg)	114.862	120.80(129)	114.862(fixed) ^a
σ^c (MHz)	...	1.11	2.83

^aValues optimized with CCSD(T)-F12/aug-cc-pV5Z.

^bValues in parentheses denote 1σ errors, applied to last digits.

^cStandard deviation of the fit.

pure rotational transition of CD₂OO. We also observed pure rotational transitions for the ¹⁸O isotopologues CH₂¹⁸O¹⁸O and CD₂¹⁸O¹⁸O using the ¹⁸O₂ sample gas. Although we attempted to observe singly ¹⁸O-substituted CH₂OO using the 1:1 mixture gas of ¹⁶O₂ and ¹⁸O₂ for producing the molecules, no spectrum positively assigned to that of the isotopologue was observed at least with the intensity of 1/100 of that of the normal species. Since no enhancement of singly ¹⁸O-substituted CH₂OO signal was observed using the mixture gas of ¹⁶O₂ and ¹⁸O₂, it is considered that no atomic oxygen is involved in the production mechanism of CH₂OO under the present experimental condition. For all the three isotopologues, CH₂¹⁸O¹⁸O, CD₂OO, and CD₂¹⁸O¹⁸O, the $1_{01}-0_{00}$ transition was observed by FTMW spectroscopy, and the, $2_{02}-1_{01}$, $1_{10}-1_{01}$, and $1_{11}-0_{00}$ transitions were observed by FTMW-mmW double-resonance spectroscopy monitoring the $1_{01}-0_{00}$ transition with the FTMW spectrometer. Frequencies of all the observed transitions are listed in Table II. Rotational constants of CH₂OO and its isotopologues were determined with Watson's A -reduced Hamiltonian,¹⁹ assuming the centrifugal distortion constants of ozone²⁰ for all the isotopologues. The determined rotational constants are listed in Table III. The inertial defects of all the isotopic species, about 0.1 uÅ², clearly indicate that CH₂OO is a planar molecule.

Assuming CH₂OO as a planar molecule, its effective molecular structure was determined by a least-squares fitting

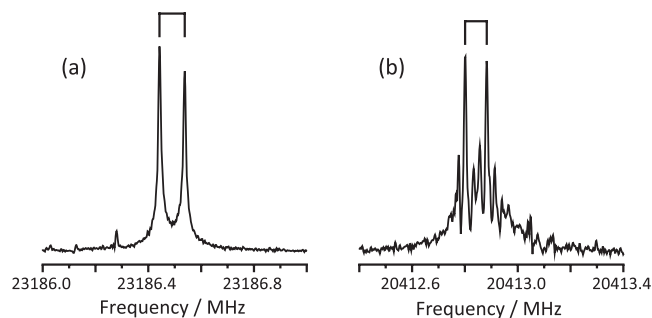


FIG. 3. Fourier-transform microwave spectra of the $1_{01}-0_{00}$ transitions of (a) CH₂OO and (b) CD₂OO. The observed line is split into two Doppler components because the direction of the supersonic jet expansion is parallel to the standing wave in the Fabry-Pérot cavity of the spectrometer. The CD₂OO spectrum shows a complicated splitting due to quadrupole moments of the deuterium nuclei.

TABLE II. Pure rotational transition frequencies of CH₂OO and its isotopologues (in MHz).

	CH ₂ OO	o.-c. ^a	CH ₂ ¹⁸ O ¹⁸ O	o.-c. ^a	CD ₂ OO	o.-c. ^a	CD ₂ ¹⁸ O ¹⁸ O	o.-c. ^a
1 ₀₁ –0 ₀₀ ^b	23186.490	– 15	21877.537	– 27	20412.842 ^c	– 44	19292.188 ^c	– 57
2 ₀₂ –1 ₀₁ ^d	46338.238	7	43721.075	14	40780.978	23	38541.760	29
1 ₁₀ –1 ₀₁ ^d	67024.906	0	62382.127	1	51186.417	1	48210.785	2
1 ₁₁ –2 ₀₂ ^b	18943.145	0						
1 ₁₁ –0 ₀₀ ^d			82595.395	– 1	69871.255	– 1	65865.308	– 2

^aResidues in the least-squares fits. Applied to the last digits.^bObserved by FTMW spectroscopy.^cPosition of the most intense hyperfine component.^dObserved by FTMW-mmW double-resonance spectroscopy.

using the experimentally determined rotational constants A and B of the four isotopologues. The CH bond lengths were assumed to be shortened by 0.004 Å by the deuterium substitution as the effect of the zero-point vibration.²¹ Since eight independent experimental rotational constants are available for the determination of the CH₂OO structure, all of the seven geometrical parameters of planar CH₂OO were able to be determined in the least-squares fitting. The determined parameters are listed in Table I as fit 1. As seen in the table, the determined OCH angles largely deviate from the theoretical values, which are roughly 119° and 115° for the *cis* and *trans* bond angles, respectively. Furthermore, the 1σ errors of the determined OCH angles are much larger than that of the OOC angle. We, therefore, concluded that the two OCH angles are difficult to be determined at the same time from the available experimental data, and at least one of the angles should be fixed to the theoretical value. The fitted parameters obtained by fixing the OCH(*trans*) angle to that optimized with the CCSD(T)-F12/aug-cc-pV5Z level of theory are listed in Table I as fit 2. Although we made least-squares fittings by fixing the OCH(*cis*) angle or both of the OCH angles to those of the *ab initio* values, all the three results are essentially same and the determined parameters agree with each other within 1σ errors. The standard deviation of the least-squares fit is ~3 MHz, which seems reasonable as an error caused by variation of the r_0 structure among the isotopologues. The determined structure in fit 2 must thus properly represent the r_0 structure of CH₂OO. Theoretical r_0 values based on vibrational perturbation treatments would be useful for further discussions on the validity of the present experimental values. The experimentally determined CO bond length 1.272(3) Å, that is significantly shorter than the OO bond

length 1.345(3) Å, indicates that the ground electronic state of CH₂OO is better described as a zwitterion, H₂C=O[⊕]–O[⊖]. Energized CH₂OO is considered to be a possible source of the OH radical by the decomposition through a four-membered transition state. Therefore, the OCH angles, one of which is assumed to be the *ab initio* value in the present fitting procedure, attract our attention in terms of the interaction between the H atoms and the terminal O atom. Experimental rotational constants of singly deuterated CH₂OO must be helpful for unambiguous determination of the OCH angles.

FTMW and FTMW-mmW double-resonance spectroscopy combined with the discharged jet expansion was successfully adopted for observations of the pure rotational transitions, and subsequent experimental determination of the molecular structure of the simplest Criegee intermediate, CH₂OO. This experimental technique is considered to be a powerful tool to investigate the molecular structures of more complicated CIs. A large amount of alkenes including relatively complex biogenic compounds such as terpenes is emitted into the atmosphere, and ozonolysis of such compounds produces alkyl-substituted CIs with several conformers. Knowledge of chemistry on individual conformers of substituted CIs would be necessary for discussing their atmospheric impact. Although conformer-specific detections have been reported for CH₃CHOO utilizing the difference of the photoionization threshold energy or the UV absorption wavelength,^{10,22} such conformer-selective techniques seem to be difficult for larger CIs. Since rotational energy levels are highly sensitive to the molecular structure, conformers of substituted CIs may be unambiguously distinguished from each other with spectroscopic detections through their pure rotational transitions. Pure rotational spectroscopy of a series of

TABLE III. Experimentally determined rotational constants.^a

	CH ₂ OO	CH ₂ ¹⁸ O ¹⁸ O	CD ₂ OO	CD ₂ ¹⁸ O ¹⁸ O
A (MHz)	77 752.655(16)	72 495.023(22)	60 535.097(35)	57 044.307(45)
B (MHz)	12 465.247(13)	11 771.158(26)	11 070.696(43)	10 465.211(55)
C (MHz)	10 721.313(16)	10 106.460(22)	9342.245(35)	8827.088(45)
σ^b (MHz)	0.017	0.030	0.050	0.063
ΔI (uÅ ²)	0.0949	0.1006	0.0974	0.1024

^aAssuming the centrifugal distortion constants of ozone in Ref. 20. Values in parentheses denote 1σ errors, applied to the last digits.^bStandard deviation of the fit. Residues of the fits are listed in Table II.

CIs would, thus, be not only a tool for determinations of their molecular structures, but also provide fundamental data for conformer-selective laboratory and field detections of CIs.

The present study was supported by JSPS KAKENHI Grant Nos. 25410004 and 19205002.

- ¹R. Criegee and G. Wenner, *Justus Liebig Ann. Chem.* **564**, 9 (1949).
²R. Criegee, *Angew. Chem., Int. Ed. Engl.* **14**, 745 (1975).
³R. Atkinson and J. Arey, *Chem. Rev.* **103**, 4605 (2003).
⁴L. Vereecken and J. S. Francisco, *Chem. Soc. Rev.* **41**, 6259 (2012).
⁵R. L. Mauldin III, T. Berndt, M. Sipilä, P. Paasonen, T. Petäjä, S. Kim, T. Kurtén, F. Stratmann, V.-M. Kerminen, and M. Kulmala, *Nature (London)* **488**, 193 (2012).
⁶M. Boy, D. Mogensen, S. Smolander, L. Zhou, T. Nieminen, P. Paasonen, C. Plass-Dülmer, M. Sipilä, T. Petäjä, L. Mauldin, H. Berresheim, and M. Kulmala, *Atmos. Chem. Phys.* **13**, 3865 (2013).
⁷C. A. Taatjes, G. Meloni, T. M. Selby, A. J. Trevitt, D. L. Osborn, C. J. Percival, and D. E. Shallcross, *J. Am. Chem. Soc.* **130**, 11883 (2008).
⁸O. Welz, J. D. Savee, D. L. Osborn, S. S. Vasu, C. J. Percival, D. E. Shallcross, and C. A. Taatjes, *Science* **335**, 204 (2012).
⁹C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, D. L. Osborn, E. P. F. Lee, J. M. Dyke, D. W. K. Mok, D. E. Shallcross, and C. J. Percival, *Phys. Chem. Chem. Phys.* **14**, 10391 (2012).
¹⁰C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke, D. W. K. Mok, D. L. Osborn, and C. J. Percival, *Science* **340**, 177 (2013).
¹¹W. H. Bunelle, *Chem. Rev.* **91**, 335 (1991).
¹²J. M. Beames, F. Liu, L. Lu, and M. I. Lester, *J. Am. Chem. Soc.* **134**, 20045 (2012).
¹³Y.-T. Su, Y.-H. Huang, H. A. Witek, and Y.-P. Lee, *Science* **340**, 174 (2013).
¹⁴H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2012.1, a package of *ab initio* programs, 2012, see <http://www.molpro.net>.
¹⁵See supplementary material at <http://dx.doi.org/10.1063/1.4821165> for theoretically obtained equilibrium geometries.
¹⁶Y. Endo, H. Kohguchi, and Y. Ohshima, *Faraday Discuss.* **97**, 341 (1994).
¹⁷T. J. Balle and W. H. Flygare, *Rev. Sci. Instrum.* **52**, 33 (1981).
¹⁸Y. Sumiyoshi, H. Katsunuma, K. Suma, and Y. Endo, *J. Chem. Phys.* **123**, 054324 (2005).
¹⁹J. K. G. Watson, *J. Chem. Phys.* **46**, 1935 (1967).
²⁰M. Bellini, P. DeNatale, G. DiLorenzo, L. Fusina, M. Inguscio, and M. Prevedelli, *J. Mol. Spectrosc.* **152**, 256 (1992).
²¹W. Gordy and R. L. Cook, *Microwave Molecular Spectra* (John Wiley and Sons, New York, 1984).
²²J. M. Beames, F. Liu, L. Lu, and M. I. Lester, *J. Chem. Phys.* **138**, 244307 (2013).