An experimental and theoretical study on rotational constants of vibrationally excited CH₂OO

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Abstract:

Pure rotational transitions of the simplest Criegee intermediate, CH₂OO, were observed for several excited vibrational levels by Fourier-transform microwave spectroscopy combined with a double-resonance technique, and precise rotational constants of vibrationally excited CH₂OO were determined. Comparing the experimentally determined vibration-rotation constants with those derived from a high-level *ab initio* potential energy surface, vibrational assignments were made for the observed levels. The observed intensities of the $1_{01}-0_{00}$ rotational lines suggested that the COO bending mode is significantly excited.

Keywords:

Criegee intermediate, vibrationally excited levels, rotational constants, Fourier-transform microwave spectroscopy, potential energy surface, multimode calculations

1. Introduction

After the first gas-phase identification of the simplest Criegee intermediate (CI), CH_2OO [1], CIs have drawn much attention of many researchers because of their atmospheric importance. CIs are considered to be a primary product of ozonolysis [2,3] which is an important removal process for alkenes in the troposphere [4-6]. Nascent CIs from the ozonolysis of alkenes have large internal energy, undergoing intramolecular rearrangements and promptly releasing the hydroxyl (OH) radical [7-9], the most important oxidant in the troposphere. The OH release from the nascent CIs competes with collisional relaxation, producing stabilized CIs (sCIs). Direct kinetic experiments of sCIs [10-15] have proven that their reactions with several atmospheric trace constituents are very rapid, and they are potentially important initiators for atmospheric oxidation.

Many spectroscopic studies on CIs have been reported so far. Ultraviolet spectra of CH_2OO [16-18], CH_3CHOO [19,20], and larger alkyl-substituted CIs [21] are dominated by broad features reflecting their strongly repulsive nature of the upper electronic state, $\tilde{B}$, in the Franck-Condon region. Although the latest high-level *ab initio* calculations have identified a shallow well on the $\tilde{B}$ state away from the Franck-Condon region [22], detailed information about the molecules is still difficult to obtain. Several fundamental frequencies of CH_2OO have been experimentally determined by infrared absorption spectroscopy [23]. Recently, infrared absorption of CH_3CHOO was also reported by action spectroscopy detecting the OH radical emitted by infrared driven dissociation to $\text{C}_2\text{H}_3\text{O} + \text{OH}$ [9]. Precise rotational constants of CH_2OO [24-26] and CH_3CHOO [27,28] have been experimentally determined by pure rotational spectroscopy. In particular, the molecular geometry of CH_2OO has been derived from the experimental rotational constants of several isotopologues [24,25]. However, all the reported

pure rotational transitions of CIs are those for the ground vibrational levels, and no rotational constants in excited vibrational levels have been reported. In this Letter, we report pure rotational spectroscopy on vibrationally excited CH_2OO . Precise rotational constants in the excited vibrational levels are determined. Assignments for the observed vibrational levels are made based on quantum calculations on an accurate theoretical potential energy surface (PES) of CH_2OO . The new information provided here helps to determine the rotation-vibration coupling in this system, which is important for establishing an accurate spectroscopic model for the molecule.

2. Experimental

2.1. Method

The transient species CH_2OO was produced in a supersonic jet by an electric discharge of a gas mixture of diiodomethane and O_2 diluted in neon buffer gas. The premix gas of 2% O_2 and 98% Ne with a total pressure of 2.5 atm was passed through a liquid container filled with diiodomethane in order to introduce the precursor with sufficient partial pressure. The gas mixture was expanded into a vacuum chamber through a pulsed-solenoid valve, and pulsed voltage of 900 V was applied between electrodes attached in front of the nozzle of the pulsed valve [29], synchronized with the gas expansion. When argon was employed as buffer gas, rotational transitions of vibrationally excited CH_2OO became weaker, probably because of the higher efficiency of collisional cooling by Ar atoms. When we used helium as buffer gas, the production of CH_2OO became unstable and the observed line intensities became weaker. Neon was thus employed as buffer gas throughout the present experiment.

A Balle-Flygare type Fourier-transform microwave (FTMW) spectrometer [30] operated in the

frequency region of 4–40 GHz was used for the observation of pure rotational transitions below 40 GHz. An FTMW-millimeter wave double-resonance technique [31] was used for observing pure rotational transitions located above 40 GHz and confirming the assignments of those observed by FTMW spectroscopy.

2.2. Observed transitions

The $1_{01}-0_{00}$ transitions of vibrationally excited CH_2OO were surveyed by FTMW spectroscopy in the region of 22800–23280 MHz, corresponding to the frequency region from –380 MHz to +100 MHz relative to the $1_{01}-0_{00}$ transition of the ground vibrational level, 23186.5 MHz [24]. Among many diamagnetic lines observed in the survey scan, we picked up transitions originating from discharge products. The strong *a*-type transition $2_{02}-1_{01}$, which is located at almost twice the $1_{01}-0_{00}$ transition frequency, was surveyed by double-resonance spectroscopy using each of the transitions picked up in the 23 GHz region as the monitor of the double-resonance signal. After such a screening procedure, a total of nine $1_{01}-0_{00}$ lines of vibrationally excited CH_2OO were identified. The observed transition frequencies of $1_{01}-0_{00}$ and $2_{02}-1_{01}$ are listed in Table 1, where capital letters A–I are given to the observed vibrational levels for convenience.

The *b*-type transition $1_{10}-1_{01}$ was then surveyed by double-resonance spectroscopy monitoring each of the nine $1_{01}-0_{00}$ transitions. Because the permanent electric dipole moment of CH_2OO lies almost along the principal *a*-axis, its *b*-type rotational transitions are much weaker than those of *a*-type. Therefore, the double-resonance scans for the $1_{10}-1_{01}$ transitions require the monitor transition $1_{01}-0_{00}$ to be observed with a moderate intensity by FTMW spectroscopy. Since the observed intensities of $1_{01}-0_{00}$ of the vibrational levels B and E were too weak to employ them as the monitor transitions in such double resonance spectroscopy, the $1_{10}-1_{01}$ transitions of these vibrational levels could not be observed. Finally, we observed the $1_{11}-2_{02}$ transitions using ν_6

FTMW spectroscopy, with the population of the lower 2_{02} level pumped up by applying the extra microwave radiation resonant with the known $2_{02}-1_{01}$ transition. All the observed transitions in the present study are listed in Table 1.

Rotational analyses were made by least-squares fits using the Watson's A-reduced Hamiltonian [32]. The centrifugal distortion constants for all the observed vibrational levels are assumed to be the same as those of the ground vibrational level reported by Daly *et al.* [26]. The determined rotational constants for each vibrational level are listed in Table 1. Shifts of the rotational constants from those of the ground vibrational level are summarized in Table 2, together with the observed intensities of the $1_{01}-0_{00}$ transitions.

A stick diagram of the observed $1_{01}-0_{00}$ transitions is given in Figure 1, where two series of vibrational satellites having almost the same frequency gap are recognized. One of them consists of those of 0_0 , C, F, H, and I, and the other A, D, and G. Rotational constants for each vibrational level are customarily expressed such as

$$X_v = X_e - \sum \alpha_i^X (\nu_i + d_i / 2),$$

where X indicates a specific rotational constant ($X = A, B, C$), d_i is the degeneracy of the i -th mode, and α is the first-order vibration-rotation constant. Since the energy of the 1_{01} rotational level is given by the sum of the rotational constants of B and C , vibrational satellites of the $1_{01}-0_{00}$ rotational line show progression-like structures. The vibrational levels C, F, H, and I can thus be assigned to the $\nu = 1, 2, 3$, and 4 levels of a certain vibrational mode, and the levels A, D, G must be combinations of these vibrational levels and one quantum of a different mode. The vibrational dependences of the rotational constants given in Table 2 support these assignments.

3. Theoretical computations

Recently, a full-dimensional near-equilibrium PES of CH₂OO has been developed using the permutation invariant polynomial-neural network (PIP-NN) method [33,34] based on ~50,000 points calculated at the level of CCSD(T)-F12a/aug-cc-pVTZ [35]. The calculated rotational constants, vibrational frequencies, and IR spectrum are in excellent agreement with experiment, which shows the excellent performance of the PES. In order to help the vibrational assignment, we employed the MULTIMODE approach [36] to compute the rotational constants of each specific vibrational level. Since the theory has been discussed extensively in the literature, few details are given here. Briefly, the Hamiltonian was defined in mass-scaled normal mode coordinates and the potential is expressed in a hierarchical n -mode representation. The $J = 0$ vibrational levels were first determined using the vibrational self-consistent field (VSCF) approach [37,38]. The vibrational wavefunction was further expanded in terms of the eigenfunctions of the VSCF Hamiltonian in order to account for coupling among the nine vibrational modes (virtual configuration interaction (VCI) method [39,40]). For rotationally excited states, the VCI basis is a direct product of the VSCF basis and symmetric top wavefunctions $|J, K, 0\rangle$. The Hamiltonian matrix is diagonalized to obtain the ro-vibrational levels [39]. Only $J = 0$ and 1 VCI calculations are needed for the determination of the rotational constants of each specific vibrational state by using the relation [41] between the calculated ro-vibrational states and the rotational constants: $E(1_{01}) = B + C$, $E(1_{11}) = A + C$, $E(1_{10}) = A + B$, with respect to each specific vibrational state $E(0_{00}) = 0$. The calculated results for the fundamental vibrational levels are listed in Table 3.

4. Discussion

The two vibrational modes observed in the present experiment may be identified by comparing the shifts of rotational constants (Table 2) in the fundamental vibrational levels, A and C, to the theoretical values listed in Table 3. Since the theoretical shifts of the ν_7 mode, $\Delta A_7 = -845$ MHz, $\Delta B_7 = -39$ MHz, and $\Delta C_7 = -36$ MHz, reproduce the shifts of the rotational constants observed for the vibrational level C ($\bullet 879.6$, $\bullet 40.7$, $\bullet 38.8$ MHz) very well, the vibrational level was assigned to $1\nu_7$. Similarly, the vibrational level A was assigned to $1\nu_8$. No conclusive assignments have been made for the vibrational levels B and E of which rotational constants are not experimentally determined due to the lack of observations of the b -type transitions. However, the level B is temporally assigned to $2\nu_8$, and E to $1\nu_7 2\nu_8$ or $1\nu_6$, based on their $\Delta(B+C)$ values. Vibrational assignments for the observed levels in the present study are summarized in Table 2. The feature of the COO bending mode, ν_7 , was observed for the first time in this study. The fundamental band of ν_7 has escaped from the measurement in the previous IR study [23] of this molecule due to instrument limits.

The observed intensities of the $1_{01}-0_{00}$ transitions are considered to be approximately proportional to the population of CH_2OO in each vibrational level. The intensities listed in Table 2 therefore indicate a remarkable excitation of the ν_7 vibration (COO bend). Sanz *et al.* [42] have reported a systematic study on relaxation of vibrationally excited states in discharged supersonic jets, using a similar experimental setup to that of the present study. Interestingly, they shows that collisional relaxations in a supersonic jet of Ne carrier gas are inefficient for vibrational modes with the frequencies of slightly larger than 500 cm^{-1} , such as the ν_7 mode of CH_2OO . This may also be the case for the ν_9 mode, of which the fundamental frequency is only $\sim 100\text{ cm}^{-1}$ higher than that of ν_7 . However, since the feature of the $1\nu_9$ level of CH_2OO was not observed in the

present experiment, the population in this level is estimated to be less than 10^{-3} of that at $1\nu_7$, from the detection limit of the present experiment. Although the small energy gap between the $1\nu_7$ and $1\nu_9$ levels may enhance the collisional relaxation from $1\nu_9$ to $1\nu_7$, a full explanation for the present observation seems to be difficult only with the relaxation dynamics in the jet expansion.

The remarkable excitation of the ν_7 mode may reflect the nascent vibrational distribution of CH_2OO produced in the present experiment, even though it must be substantially relaxed under the jet expansion of the neon buffer gas. In the case of the photolysis production of CH_2OO in the $\text{CH}_2\text{I}_2 + \text{O}_2$ system, it has been suggested that the photolysis product iodomethyl radical, CH_2I , associates with O_2 , producing the “hot” iodomethylperoxy radical, $\text{CH}_2\text{IOO}^\#$, which rapidly dissociates to $\text{CH}_2\text{OO} + \text{I}$ [10,43-45]. A similar mechanism can be postulated for the present CH_2OO production in the electric discharge. The change of the COO angle between CH_2IOO and CH_2OO is thus one of the possible explanations for the significant excitation of the COO bending vibration. To check this point, geometry optimization and harmonic frequency calculation of CH_2IOO was performed by the density functional theory with the B3LYP functional using the MOLPRO program package [46]. The cc-pVTZ basis set was used for the C, H, and O atoms, and the ECP-based basis set, cc-pVTZ-PP, for the I atom. Two potential minima with different configurations of the CH_2I - moiety were found in the geometry optimization, as shown in Figure 2. The I atom lies out of the COO plane for the more stable conformer (I), and it lies in the COO plane at the *trans* position to the terminal oxygen atom for the less stable conformer (II). Although the current results are obtained at the B3LYP level, the COO angle for both of the two conformers is not much different from the angles between the sp^3 hybrid orbitals, 109° , which is smaller by 10° than that of the COO angle of CH_2OO , 118° [24,25,35]. Such a change in the

COO angle seems too small to explain the observed significant excitation of the ν_7 mode. However, the repulsive force working between the C and I atoms during the C-I dissociation process may result in the excitation of the CH_2 wagging motion of CH_2OO for the conformer (I), and the COO bending motion for the conformer (II), as observed in the present study. Another possible explanation is that the $\text{CH}_2\text{I} + \text{O}_2$ association induces the excitation of the COO bending motion in the intermediate product CH_2IOO , and the bending excitation is carried over to CH_2OO . Although no detailed discussion is possible in the present study, dynamics experiments or theoretical approaches on the $\text{CH}_2\text{I} + \text{O}_2$ reaction may provide more information to explain the present experimental observation, the significant excitation of the COO bending mode in CH_2OO .

In summary, we observed pure rotational transitions of vibrationally excited CH_2OO , and the precise rotational constants were determined for several vibrational levels where two vibrational modes, ν_7 (COO bend) and ν_8 (CH_2 wag), are excited. Theoretical vibration-rotation constants of CH_2OO derived from a nine-dimensional PES computed with the CCSD(T)-F12a/aug-cc-pVTZ level of theory reproduce the experimental values very well. They must be useful for further spectroscopic studies on vibrationally excited levels of CH_2OO .

Acknowledgements

The present study was supported by JSPS KAKENHI Grant Numbers 25410004 (M.N. & Y.E.), 19205002 (Y.E.), the US Department of Energy Grant Number DE-FG02-05ER15694 (H.G.) and the Hundred-Talent Foundation of Chongqing University Project No. 0220001104420 (J.L.).

References

- [1] C.A. Taatjes, G. Meloni, T.M. Selby, A.J. Trevitt, D.L. Osborn, C.J. Percival, D.E. Shallcross, J. Am. Chem. Soc. 130 (2008) 11883.
- [2] R. Criegee, G. Wenner, Justus Liebig Ann. Chem. 564 (1949) 9.
- [3] R. Criegee, Angew. Chem. Int. Ed. Engl. 14 (1975) 745.
- [4] R. Atkinson, J. Phys. Chem. Ref. Data 26 (1997) 215.
- [5] J.G. Calvert, R. Atkinson, J.A. Kerr, S. Madronich, G.K. Moortgat, T.J. Wallington, G. Yarwood, *The Mechanisms of Atmospheric Oxidation of the Alkenes*; Oxford University Press, Oxford, U.K., 2000.
- [6] R. Atkinson, J. Arey, Chem. Rev. 103 (2003) 4605.
- [7] J. H. Kroll, J.S. Clarke, N.M. Donahue, J.G. Anderson, K.L. Demerjian, J. Phys. Chem. A 105 (2001) 1554.
- [8] J.H. Kroll, S.R. Sahay, J.G. Anderson, K.L. Demerjian, N.M. Donahue, J. Phys. Chem. A 105 (2001) 4446.
- [9] F. Liu, J.M. Beames, A.S. Petit, A.B. McCoy, M.I. Lester, Science 345 (2014) 1596.
- [10] O. Welz, J.D. Savee, D.L. Osborn, S.S. Vasu, C.J. Percival, D.E. Shallcross, C.A. Taatjes, Science 335 (2014) 204.
- [11] C.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, C.J. Percival, Phys. Chem. Chem. Phys. 14 (2012) 10391.
- [12] C.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.K.W. Mok, D.L. Osborn, C.J. Percival, Science 340 (2013) 177.
- [13] D. Stone, M. Blitz, L. Daubney, N.U.M. Howes, P. Seakins, Phys. Chem. Chem. Phys. 16 (2014) 1139.

- [14] O. Welz, A.J. Eskola, L. Sheps, B. Rotavera, J.D. Savee, A.M. Scheer, D.L. Osborn, D. Lowe, A.M. Booth, P. Xiao, M.A.H. Khan, C.J. Percival, D.E. Shallcross, C.A. Taatjes, *Angew. Chem. Int. Ed.* 53 (2014) 4547.
- [15] Z.J. Buras, R.M.I. Elsamra, A. Jalan, J.E. Middaugh, W.H. Green, *J. Phys. Chem. A* 118 (2014) 1997.
- [16] J.M. Beames, F. Liu, L. Lu, M.I. Lester, *J. Am. Chem. Soc.* 134 (2012) 20045.
- [17] L. Sheps, *J. Phys. Chem. Lett.* 4 (2013) 4201.
- [18] W.-L. Ting, Y.-H. Chen, W. Chao, M.C. Smith, J.J.-M. Lin, *Phys. Chem. Chem. Phys.* 16 (2014) 10438.
- [19] J.M. Beames, F. Liu, L. Lu, M.I. Lester, *J. Chem. Phys.* 138 (2013) 244307.
- [20] M.C. Smith, W.-L. Ting, C.-H. Chang, K. Takahashi, K.A. Boering, J.J.-M. Lin, *J. Chem. Phys.* 141 (2014) 074302.
- [21] F. Liu, J.M. Beames, A.M. Green, M.I. Lester, *J. Phys. Chem. A* 118 (2014) 2298.
- [22] R. Dawes, B. Jiang, H. Guo, *J. Am. Chem. Soc.*, in press, DOI: 10.1021/ja510736d.
- [23] Y.-T. Su, Y.-H. Huang, H.A. Witek, Y.-P. Lee, *Science* 340 (2013) 174.
- [24] M. Nakajima, Y. Endo, *J. Chem. Phys.* 139 (2013) 101103.
- [25] M.C. McCarthy, L. Cheng, K.N. Crabtree, O. Martinez, T.L. Nguyen, C.C. Womack, J.F. Stanton, *J. Phys. Chem. Lett.* 4 (2013) 4133.
- [26] A.M. Daly, B.J. Drouin, S. Yu, *J. Mol. Spectrosc.* 297 (2014) 16.
- [27] M. Nakajima, Y. Endo, *J. Chem. Phys.* 140 (2014) 011101.
- [28] M. Nakajima, Q. Yue, Y. Endo, *J. Mol. Spectrosc.*, in press, DOI: 10.1016/j.jms.2014.11.004.

- [29] Y. Endo, H. Kohguchi, Y. Ohshima, Faraday Discuss. 97 (1994) 341.
- [30] T.J. Balle, W.H. Flygare, Rev. Sci. Instrum. 52 (1981) 33.
- [31] Y. Sumiyoshi, H. Katsunuma, K. Suma, Y. Endo, J. Chem. Phys. 123 (2005) 054324.
- [32] J.K.G. Watson, J. Chem. Phys. 46 (1967) 1935.
- [33] B. Jiang, H. Guo, J. Chem. Phys. 139 (2013) 054112.
- [34] J. Li, B. Jiang, H. Guo, J. Chem. Phys. 139 (2013) 204103.
- [35] J. Li, S. Carter, J.M. Bowman, R. Dawes, D. Xie, H. Guo, J. Phys. Chem. Lett. 5 (2014) 2364.
- [36] J.M. Bowman, S. Carter, X. Huang, Int. Rev. Phys. Chem. 22 (2003) 533.
- [37] J.M. Bowman, Acc. Chem. Res. 19 (1986) 202.
- [38] M.A. Ratner, R.B. Gerber, J. Phys. Chem. 90 (1986) 20.
- [39] S. Carter, J.M. Bowman, J. Chem. Phys. 108 (1998) 4397.
- [40] S. Carter, J.M. Bowman, N.C. Handy, Theo. Chem. Acc. 100 (1998) 191.
- [41] R.N. Zare, *Angular Momentum*; John Wiley & Sons, Inc., New York, 1988.
- [42] M.E. Sanz, M.C. McCarthy, P. Thaddeus, J. Chem. Phys. 122 (2005) 194319.
- [43] H. Huang, A.J. Eskola, C.A. Taatjes, J. Phys. Chem. Lett. 3 (2012) 3399.
- [44] D. Stone, M. Blitz, L. Daubney, T. Ingham, P. Seakins, Phys. Chem. Chem. Phys. 15 (2013) 19119.
- [45] W.-L.Ting, C.-H. Chang, Y.-F. Lee, H. Matsui, Y.-P. Lee, J.J.-M. Lin, J. Chem. Phys. 141 (2014) 104308.
- [46] MOLPRO, version 2012.1, a package of ab initio programs, H.-J. Werner, P.J. Knowles,

G. Knizia, F.R. Manby, M. Schütz, and others, see <http://www.molpro.net>.

Table 1. Observed rotational transitions and rotational constants of CH₂OO (in MHz).

vib. level	observed transitions				rotational constants ^a		
	$1_{01}-0_{00}^b$	$2_{02}-1_{01}^c$	$1_{10}-1_{01}^c$	$1_{11}-2_{02}^b$	<i>A</i>	<i>B</i>	<i>C</i>
0 ₀ ^d	23186.490	46338.238	67024.906	18943.145	77748.9415(46)	12465.1742(36)	10721.3577(46)
A	23157.523	46281.800	66487.122	18506.278	77218.9160(29)	12428.4556(22)	10729.1167(29)
B ^e	23131.146	46230.229					
C	23107.029	46178.963	66184.061	18263.518	76869.33911(11)	12424.475800(83)	10682.60034(10)
D	23075.139	46116.789	65463.200	17654.668	76157.45104(99)	12383.61137(76)	10691.57285(99)
E ^e	23044.233	46053.774					
F	23029.342	46023.145	65420.762	17655.476	76066.9149(34)	12385.9103(27)	10643.4749(34)
G	22994.174	45954.547	64494.641		75150.775 ^f	12340.765 ^f	10653.456 ^f
H	22953.379	45870.706	64729.179	17113.333	75335.8503(66)	12349.4259(52)	10603.9931(66)
I	22879.132	45721.634	64103.963	16631.787	74670.8101(69)	12315.0036(54)	10564.1689(69)

^a Centrifugal distortion constants are fixed to those reported in ref. 26 for the A-reduced form. In parentheses, 1σ errors applied to the last digits.

^b Observed by FTMW spectroscopy.

^c Observed by double-resonance spectroscopy.

^d Transition frequencies are cited from ref. 24. The rotational constants are re-determined in the present study.

^e Only two transitions were observed.

^f The constants are determined from three transition data.

Table 2. Observed shifts of rotational constants from those of the ground vibrational level, intensities, and assignments.

vib. level	ΔA / MHz	ΔB / MHz	ΔC / MHz	$\Delta(B+C)$ / MHz	intensity ^a	assignment
0 ₀	0	0	0	0	100	0 ₀
A	• 530.026	• 36.719	7.759	• 28.960	0.77	1v ₈
B				• 55.344 ^b	0.03	2v ₈ ?
C	• 879.602	• 40.698	• 38.757	• 79.456	11.00	1v ₇
D	• 1591.490	• 81.563	• 29.785	• 111.348	0.43	1v ₇ 1v ₈
E				• 142.257 ^b	0.06	1v ₇ 2v ₈ or 1v ₆ ?
F	• 1682.027	• 79.264	• 77.883	• 157.147	2.40	2v ₇
G	• 2598.167	• 124.409	• 67.902	• 192.311	0.06	2v ₇ 1v ₈
H	• 2413.091	• 115.748	• 117.365	• 233.113	0.53	3v ₇
I	• 3078.131	• 150.171	• 157.189	• 307.359	0.32	4v ₇

^a Observed intensity of the 1₀₁–0₀₀ line (in arbitrary unit).

^b Shift of the 1₀₁–0₀₀ transition frequency.

Table 3. Theoretical rotational constants of the ground and excited vibrational levels of CH₂OO, and shifts of them from the ground vibrational level.

level	description ^c	freq. ^d	rotational constants ^a			shifts ^{a,b}		
			<i>A</i>	<i>B</i>	<i>C</i>	ΔA	ΔB	ΔC
0 ₀	Ground	0	77460	12444	10700	---	---	---
ν_1	C-H anti-sym. str.	3150	77357	12431	10689	• 103	• 13	• 10
ν_2	C-H sym. str.	3013	77378	12440	10692	• 82	• 5	• 7
ν_3	CH ₂ scissor	1434	77976	12444	10679	516	0	• 21
ν_4	CO str. / CH ₂ scissor	1285	77276	12416	10710	• 184	• 28	10
ν_5	CH ₂ rock	1212	77912	11473	10596	451	28	• 103
ν_6	O-O str.	927	77233	12378	10640	• 228	• 66	• 60
ν_7	COO bend	526	76615	12405	10664	• 845	• 39	• 36
ν_8	CH ₂ wag	859	76909	12411	10712	• 552	• 33	12
ν_9	CH ₂ twist	622	78247	12458	10713	787	13	13

^a in MHz.

^b Given as the difference in rotational constant between the ground and $\nu = 1$ levels.

^c Vibrational mode specification.

^d Fundamental frequency in cm⁻¹.

Figure Captions

Figure. 1 Stick diagram of the observed $1_{01}-0_{00}$ lines.

Figure. 2 Two conformers of CH_2IOO obtained with the B3LYP/cc-pVTZ (cc-pVTZ-PP for I atom) level of theory. The conformer (I) is more stable than the conformer (II) by 1.1 kcal/mol with zero-point energy correction.

Figure1

conformer I
($\Delta E = 0$)

conformer II
($\Delta E \sim +1.1$ kcal /mol)