

Microwave Spectrum and Structure of Ethylene Ozonide-D₄

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Rotational spectra of six isotopic species of ethylene ozonide-D₄ have been assigned. The O_p-O_p distance was calculated six independent ways using Kraitchman's substitution equations, and values between 1.458 and 1.462 Å were obtained. This is in contrast to a similar analysis for normal ethylene ozonide where the O_p-O_p distance varied between 1.455 and 1.502 Å. This difference is associated with the greater value of $I_b - I_a$ for the D₄ species which markedly decreases the effect of axes rotations upon isotopic substitution. The structural parameters derived from the D₄ data set are in excellent agreement with those extracted from the H₄ analyses after minimization of axes rotation effects.

INTRODUCTION

The O_p-O_p distance in ethylene ozonide, $\overline{\text{H}_2\text{COOCH}_2\text{O}}$, was recently shown to vary over a range of almost 0.05 Å when it was calculated six ways from an overdetermined data set using Kraitchman's equations (1, 2). This unusually large variance via the substitution method was attributed to an amplification of residual vibrational effects by large axes rotations upon isotopic substitution in a near oblate top. This effect is sensitive to the value of $I_b - I_a$. Since this quantity is 10 times greater for ethylene ozonide-D₄, axes rotation effects should be considerably reduced using substitution equations for that species. Consequently, the assignment of rotational spectra of six new isotopic species of ethylene ozonide-D₄ was undertaken in order to carry out a parallel structure analyses in the D₄ axes system. We wished to confirm that residual vibrational effects are not unduly amplified in this isotopic system and that Kraitchman's equations yield a more internally consistent O_p-O_p distance. In addition, we wanted to provide a check on the previously determined r_s structure, which was derived after identifying the large axis rotation phenomena and contingent upon the validity of that analysis.

EXPERIMENTAL DETAILS

The rotational lines assigned for six new isotopic species of ethylene ozonide-D₄ are listed in Table 1. The ¹³C species was assigned in natural abundance while the five enriched ¹⁸O species were prepared and assigned using synthetic procedures and the spectrometer previously employed (1). One attractive feature of the study was that one synthesis involving C₂D₄ (99% D) and O₃ (~60% ¹⁸O) yielded all five ¹⁸O species. The assignment was based on the frequency fit, expected isotopic shifts, Stark effects, intensities, and internal checks on the moments due to the C₂ symmetry axis in several species. The rotational constants and derived planar second moments of inertia are

Table 1. Ground State Transition Frequencies in MHz for Various Isotopic Species of D₄-Ethylene Ozonide.

Transition	¹⁸ O _e	¹⁸ O _p	¹⁸ O _e ¹⁸ O _p	¹⁸ O _F ¹⁸ O _p	¹⁸ O _e ¹⁸ O _p ¹⁸ O _p	¹³ C
1 ₁₁ -2 ₂₀	30514.72	30523.23	29875.15	29883.17	29264.33	30946.92
1 ₁₀ -2 ₂₁	26172.21	26493.85	25510.54	25771.98	-----	27107.01
2 ₁₂ -3 ₀₃	26983.05	26932.28	26430.01	26428.29	25917.53	27151.83
2 ₁₁ -3 ₂₂	34233.41	34563.00	33399.89	33678.79	-----	35260.81
2 ₀₂ -3 ₁₃	-----	27255.62	26596.71	26675.90	26028.81	27607.61
2 ₂₁ -3 ₁₂	30841.26	-----	30421.89	29929.27	30180.87	29810.45
3 ₁₃ -4 ₀₄	35130.15	-----	34389.79	34437.33	33693.02	35487.14
3 ₀₃ -4 ₁₄	35157.78	35187.18	34410.21	34474.11	33704.41	35576.17

listed in Table 2. These rotational constants fit the observed spectra with deviations no larger than ± 0.08 MHz.

RESULTS AND ANALYSIS

The structure analysis closely paralleled the procedure followed in the previous study of the C₂O₃H₄ isotopic species. The most direct way to determine if residual vibrational effects have been attenuated is to compute $d(O_pO_p)$ from the overdetermined C₂O₃D₄ data set using Kraitchman's equations. The results are listed in Table 3. For C₂O₃D₄ the computed values range over only 0.004 Å, while for C₂O₃H₄ the range was 0.047 Å. The smaller range for C₂O₃D₄ is probably typical of the agreement that can be obtained from Kraitchman's equations when applied in favorable cases to asymmetric tops (3). The contrast in consistency between C₂O₃D₄ and C₂O₃H₄ arises from the ten fold increase in $I_b - I_a$ for C₂O₃D₄ (see Table 4). This quantity appears in Kraitchman's equa-

Table 2. Rotational Constants and Planar Moments of Inertia.

Species	A/MHz	B/MHz	C/MHz	I_{aa} , uÅ ²	I_{bb} , uÅ ²	I_{cc} , uÅ ²
¹⁶ O ₂ ¹⁶ O ₂ ¹⁶ O ₂ (a)	7689.05 (2) ^(b)	6534.36 (2)	4120.83 (1)	62.1270	55.5124	10.2143
¹⁸ O ₂ ¹⁶ O ₂	7380.51 (2)	6534.59 (2)	4010.64 (1)	67.1249	58.2596	10.2146
¹⁸ O ₂ ¹⁸ O ₂	7486.41 (1)	6436.31 (2)	4034.00 (1)	68.1372	57.1245	10.3823
¹⁸ O ₂ ¹⁸ O ₂ ¹⁶ O ₂	7188.61 (2)	6431.49 (2)	3944.70 (1)	68.1956	59.9195	10.3626
¹⁸ O ₂ ¹⁸ O ₂ ¹⁸ O ₂	7272.88 (2)	6358.60 (2)	3953.07 (1)	68.9129	58.9219	10.5663
¹⁸ O ₂ ¹⁸ O ₂ ¹⁸ O ₂	6975.42 (1)	6358.86 (2)	3863.88 (1)	68.9049	61.8851	10.5659
¹³ C	7676.72 (3)	6410.32 (3)	4076.90 (2)	68.3606	55.6002	10.2321

(a) The constants from this species were taken from Ref. 1.

(b) The uncertainty is twice the standard deviation from the frequency fit.

Table 3. Peroxide Bond Distance Calculated by Kraitchman's Equations for Different Isotopic Species.

	Parent $O_e O_p O_p$	Subst. $O_e O_p O_p$	Distance O_p-O_p
I	16 16 16	16 16 18	1.462 $\overset{\circ}{\text{A}}$
II	18 16 16	18 16 18	1.462
III	18 18 18	18 16 18	1.458
IV	16 18 18	16 16 18	1.459
V	16 16 16	16 18 18	1.461
VI	18 18 18	18 16 16	1.460

tions in the denominator of axes rotation factors. This change effectively reduces about tenfold the residual vibrational effects that remain when taking differences of effective moments in the substitution calculation. It is interesting to note that although

Table 4. The r_s and the Estimated r_s^* Peroxide Oxygen Coordinates and Bond Distances for Different Isotopic Species.

	$O_e O_p O_p$	$O_e O_p O_p$	$O_e O_p O_p$	$O_e O_p O_p$
Parent	16 16 16	18 16 16	18 18 18	16 18 18
Substituted	16 16 18	18 16 18	18 16 18	16 16 18
a_s	0.6661 $\overset{\circ}{\text{A}}$	0.6663 $\overset{\circ}{\text{A}}$	0.6685 $\overset{\circ}{\text{A}}$	0.6687 $\overset{\circ}{\text{A}}$
b_s	0.9446	0.9735	0.9293	0.9004
c_s	0.3009	0.3009	0.2912	0.2918
$ a_s^* - a_s $ (a)	0.0018	0.0016	0.0031	0.0028
$ b_s^* - b_s $	0.0020	0.0021	0.00095	0.0012
$ c_s^* - c_s $	-0.0017	-0.0017	-0.0017	-0.0017
$r_s : d(O_p-O_p)$	1.462	1.462	1.458	1.459
$r_s^* : d^*(O_p-O_p)$	1.464	1.464	1.463	1.463
$I_{bb} - I_{aa}$ (b)	11.6146	8.8642	7.0249	9.9914
K_1^a, K_2^a, K_3^a	0.33, -0.033, -0.01	0.311, -0.046, -0.01	-0.468, -0.037, +0.01	-0.430, -0.028, -0.01
K_2^b, K_3^b, K_1^b	0.293, -0.010, 0.04	0.293, -0.010, 0.05	-0.236, -0.009, 0.08	-0.250, -0.009, 0.05
K_3^c, K_1^c, K_2^c	0.895, 0.013, 0.00	0.895, 0.017, 0.00	-0.795, 0.021, 0.00	-0.793, 0.015, 0.00

(a) Estimated using Eq. 2 in Ref. 1, the values of K_i^x in this table and the values of δx discussed in the text. Note that the values of K_i^x in Table 7 of Ref. 1 require the following corrections to be consistent with Eq. 2: (1) All values must be doubled; (2) the labels for the 2nd and 3rd last rows should be respectively, K_3^c, K_1^c, K_2^c and K_2^b, K_3^b, K_1^b .

(b) In $u\text{A}^2$ for parent species.

Table 5. Preferred r_s Coordinates and Structural Parameters for Ethylene Ozonide-D₄.

Coordinates		Bond Lengths		Bond Angles		Dihedral Angles		
O _e	b	1.1852 ^o Å	CH _{eq}	1.090 ^o Å	C-C	104.6°	C ₁ O _e C ₂ O _p	-16.23°
	a	0.6654	CH _{ax}	1.100	C=O	99.2	C ₁ C _p O _e C ₂	-49.39
O _p	b	0.9451	CO _e	1.415	O=O	105.7	C _e C _p O _p	40.79
	a	0.3011	CO _p	1.410	HCH	112.7	C ₁ O _e C ₂ H _{eq}	-131.85
C	b	0.3195	OO	1.461	C _e CH _{eq}	110.5	C ₁ O _e C ₂ H _{ax}	102.96
	a	0.1354			C _e CH _{ax}	109.7		
H _{ax}	b	1.4214			C _p CH _{eq}	107.5		
	a	0.2764			C _p CH _{ax}	110.7		
H _{eq}	b	1.1896						
	a	1.9210						
H _{eq}	b	0.6191						
	c	0.5302						

the range for $d(O_pO_p)$ is small, some residual vibrational effects still apparently remain. This is consistent with Watson's recent analysis that an r_s structure is not necessarily isotopically invariant (4).

A further estimate on the extent of these residual vibrational effects for C₂O₃D₄ was made by calculating $|x_s^*| - |x_s|$ using Eq. (2) in Ref. (1). $|x_s^*|$ is a corrected substitution coordinate after an estimate is made for the magnitude of the remaining vibrational effects that do not cancel by the Kraitchman procedure. Values for these residual effects were assumed equal to those for the H₄ analysis (≤ 0.006 amu Å²). The quantities $|x_s^*| - |x_s|$ and r_s^* , the corrected substitution value of $d(O_pO_p)$ are listed in Table 4. The average value of r_s^* of 1.4635 Å is close to the average value of 1.4647 Å estimated from the H₄ data, where much larger corrections occurred (see Table 7 of Ref. (1)). Also the corrections for C₂O₃D₄ are comparable to those estimated using Costain's formula (5, 6); this again underscores the attenuation of axes rotation effects in the D₄ system, since the Costain formula ignores that contribution.

As a final check,¹ the r_s structure was calculated in the principal axes of ¹²C₂¹⁶O₃D₄ following an identical procedure to that outlined previously for ¹²C₂¹⁶O₃H₄ (1). That procedure was selected as the best method to obtain an r_s structure which should minimize vibrational effects and contain the fewest assumptions. The coordinates and structural parameters obtained from this procedure are listed in Table 5. It is indeed striking that the derived structural parameters agree within 0.003 Å and 0.5° for the two data sets. Error estimates for the structural parameters are similar to those discussed for C₂O₃H₄ and Ref. (1) can be consulted.

¹ Another check employing the Pierce double substitution method to calculate the O_p coordinates (See Ref. (1) for details) was inconclusive. The second difference $\Delta\Delta P_B$ was only 0.0487 $\mu\text{Å}^2$ and the results were extremely sensitive to changes in this value within its experimental uncertainty.

DISCUSSION

The excellent agreement with the preferred r_s structure previously reported, the good consistency for $d(O_pO_p)$ from Kraitchman's equations and the reduced effect from vibrations are the most noteworthy results of this study.

Regarding the detailed structural parameters obtained in the two studies, the excellent agreement supports the comments made in the previous paper (1) regarding the significance of the small difference between the CO_e and CO_p bond distances and the slightly shorter value for $d(O_pO_p)$ compared to the often estimated value of 1.47–1.48 Å in other systems. Also, it is interesting that $d(CH_{ax})$ is larger than $d(CH_{eq})$ in both calculations, suggesting that the difference is not an artifact.

The consistency in $d(O_pO_p)$ when computed several ways (Tables 3, 4) and the reduction of vibrational effects in $C_2O_3D_4$ confirm that the major difficulty in using Kraitchman's equations for $C_2O_3H_4$ was correctly identified, viz., amplification of vibrational effects of a typical magnitude due to large axes rotations. This effect is a sensitive function of I_b-I_a in near oblate tops and changes in this quantity readily account for the differences between the two isotopic species. Therefore, the possibility of the effect arising in an r_s structure analysis can be readily evaluated and some estimate of its magnitude can be made guided by the studies on ethylene ozonide and the work of Nygaard (7).

Regarding the broader question of the significance of r_s structure (3, 4, 8–11), it is interesting to note that ethylene ozonide is the largest asymmetric top for which the consistency of the substitution structure has been tested for so many different isotopic species. Although the r_s structure is not necessarily isotopically invariant (4), the divergence has been small for a number of linear and symmetric tops (3). The consistency for $C_2O_3H_4$ and $C_2O_3D_4$ is not quite as high as in these simpler systems, nevertheless the agreement is very satisfactory (provided one eliminates the r_s calculations which emphasize axes rotation effects). The agreement might be fortuitous considering the complexity of the molecule, the smallness of several coordinates and the four H atoms in the molecule. However, we are disinclined to this opinion in view of the pervasiveness and large number of cross checks. Perhaps, the relative isotopic invariance indicates that in this case, as suggested by others (3, 7, 11), the preferred r_s structure is close to the r_e structure. Some error approximations support this (1). However, it will require either a detailed vibrational analysis (9) to more rigorously establish this or the rotational constants of an additional number of isotopic species with subsequent application of the Watson r_m analysis (4).

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