The Microwave Spectra and r_0, r_s, and r_m Structures of Ethylene Oxide

Chiaki Hirose

Laboratory of Molecular Spectroscopy, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152

(Received April 23, 1973)

The rotational spectra of ten isotopic species of ethylene oxide, $^{12}C_2H_4{}^{16}O$, $^{12}C^{13}CH_4{}^{16}O$, $^{12}C_2H_4{}^{18}O$, $^{12}C_2H_3D^{16}O$, *cis*- and *trans*-$^{12}C_2H_2D_2{}^{16}O$, $^{12}C^{13}CH_2D_2{}^{16}O$, and $^{12}C_2H_2D_2{}^{18}O$ were observed. A least-squares fit including centrifugal distortion effect to the first order was made to derive the effective values of the A′, B′, C′, τ'_{aaaa}, τ'_{bbbb}, τ'_{cccc}, and τ'_{aabb} parameters and their correlation factors; τ'_{bbcc} and τ'_{aacc} were found to be insignificant. The rotational constants were used to determine the r_0, r_s, and r_m structures. The structural parameters were derived as:

$$r_0(\mathrm{CC})=1.470\pm0.003,\ r_s(\mathrm{CC})=1.466\pm0.002,\ r_m(\mathrm{CC})=1.462\pm0.003,$$

$$r_0(\mathrm{CH})=1.085\pm0.004,\ r_s(\mathrm{CH})=1.085\pm0.001,\ r_m(\mathrm{CH})=1.086\pm0.004,$$

$$r_0(\mathrm{CO})=1.434\pm0.002,\ r_s(\mathrm{CO})=1.431\pm0.001,\ r_m(\mathrm{CO})=1.428\pm0.002,$$

$$\angle_0\mathrm{HCH}=116.28\pm0.69,\ \angle_s\mathrm{HCH}=116.61\pm0.09,\ \angle_m\mathrm{HCH}=116.92\pm0.69,$$

$\theta_0=22.34\pm0.46$, $\theta_s=21.99\pm0.11$, $\theta_m=21.63\pm0.48$ in units of Å and degrees; θ represents the angle of the H_2C plane to the CC bond. The indicated error limits are 2.5 times the variances.

Ethylene oxide is one of the molecules for which bent bonds can be expected.[1] Cunningham *et al.* first investigated the r_0 structure on the basis of the microwave spectra of several isotopic species and showed both C-C and C-O distances were considerably different from those in aliphatic hydrocarbons and ethers.[2] Turner and Howe carried out a computer calculation of the r_0 structure which uses the rotational constants obtained by Cunningham *et al.* to improve the structural parameters:[3]

The rotational spectra of ethylene oxide in the ground and excited vibrational states were observed in the present study in order to get further information on the molecular structure and the vibrational modes. The present paper will report on the microwave spectra of ten isotopic species in their ground vibrational states. The rotational and centrifugal distortion constants were determined by a least-squares fit. Effective parameters were obtained by assuming some of the centrifugal distortion constants.

The structural parameters, r_0, r_s, and r_m, were derived from the rotational constants by taking into account correlations among the rotational constants.

Experimental

The species studied in the present work are normal ethylene oxide, *cis*- and *trans*-dideutero ethylene oxide, monodeutero ethylene oxide, and the ^{13}C- and ^{18}O-substituted species. Normal ethylene oxide was purchased from the Matheson Co., the *cis*- and *trans*-dideutero species were provided by Mr. Masahiro Kawasaki of the Tokyo Institute of Technology, monodeutero ethylene oxide was present in the dideutero species as an impurity, and the ^{13}C- and ^{18}O-isotopic species were used in their natural abundance.

The microwave spectrum was observed using a conventional Stark modulation spectrometer with a waveguide cell cooled with dry ice. Since the vibrational frequencies are higher than 600 cm^{-1}, the rotational spectra of ^{13}C- and ^{18}O-species were assigned by comparing the change in spectral intensity at room temperature and at the temperature of dry ice. The observed frequencies and their assignments are listed in Table 1.

Analysis of Data

Since the analysis showed effects of centrifugal distortion of as much as 30 MHz for the $J=8$—8 transition of normal ethylene oxide, a least-squares fit including centrifugal distortion to the first order was carried out.

The parameters describing the transition frequencies are expressed as follows:[4]

$$\begin{aligned} A' &= A-\hbar^4(3\tau_{\mathrm{bcbc}}-2\tau_{\mathrm{acac}}-2\tau_{\mathrm{abab}})/4,\\ B' &= B-\hbar^4(3\tau_{\mathrm{acac}}-2\tau_{\mathrm{abab}}-2\tau_{\mathrm{bcbc}})/4,\\ C' &= C-\hbar^4(3\tau_{\mathrm{abab}}-2\tau_{\mathrm{bcbc}}-2\tau_{\mathrm{acac}})/4, \qquad (1)\\ \tau'_{\alpha\alpha\alpha\alpha} &= \hbar^4\tau_{\alpha\alpha\alpha\alpha},\\ \tau'_{\alpha\alpha\beta\beta} &= \hbar^4(\tau_{\alpha\alpha\beta\beta}+2\tau_{\alpha\alpha\beta\beta}),\ (\alpha\neq\beta) \end{aligned}$$

where α and β stand for a, b, or c. As has been pointed out by Watson,[5] when the centrifugal distortion is treated by the first-order perturbation, at most eight parameters (three effective rotational constants, τ'_{aaaa}, τ'_{bbbb}, τ'_{cccc}, and the two linear combinations of τ'_{aabb}, τ'_{bbcc}, and τ'_{aacc}) can be experimentally determined. A detailed analysis of the correlation among the parameters showed that the observed spectra contained sufficient information to determine only four centrifugal terms with statistical significance. Since τ'_{aacc} and τ'_{bbcc} were estimated to be indistinguishable from zero by preliminary calculations where one of the two parameters was put equal to zero to give the other the stated value, they were both tentatively set equal to zero in the present analysis. The same situations were encountered in all the isotopes. Table 2 lists the converged values of the parameters.*

---

* The listed values should be understood as effective ones which are enough to account for the frequencies listed in Table 1. Systematic errors can be introduced from the assumption that $\tau'_{aacc}=\tau'_{bbcc}=0$, the shortages in observation of high-J transitions and R-type transitions, and perhaps even from the lack of transitions of the a- or c-type. A preliminary analysis of the millimeter-wave spectrum of normal species indicates that the inclusion of high-J transitions gives τ'_{cccc} a negative value, as is expected from the theory of centrifugal distortion.

Table 1. Observed frequencies and their deviations from calculated frequencies (in MHz)

Transition	$^{12}C_2H_4{}^{16}O$			$^{12}C^{13}CH_4{}^{16}O$		
	Obsd^{a}	Δ(cent)$^{b)}$	$\Delta^{c)}$	Obsd$^{a)}$	Δ(cent)$^{b)}$	$\Delta^{c)}$
$1_{11}\leftarrow 0_{00}$	39581.64*	−0.05	+0.18	39117.71*	−0.07	+0.14
$1_{10}\leftarrow 1_{01}$	11386.05	−0.14	+0.11	11466.11	−0.12	+0.09
$2_{12}\leftarrow 1_{01}$	67777.40	−0.02	−0.09	66768.56	−0.31	−0.27
$2_{02}\leftarrow 1_{11}$	63558.67	+0.07	+0.00	—	—	—
$2_{11}\leftarrow 2_{02}$	24923.69*	−0.67	−0.01	24351.97*	−0.39	+0.18
$2_{20}\leftarrow 2_{11}$	15603.90	−0.73	+0.30	16195.69	−0.76	+0.07
$2_{21}\leftarrow 2_{12}$	34157.04*	−1.16	−0.02	34397.53*	−0.91	+0.02
$3_{21}\leftarrow 3_{12}$	23610.42*	−1.64	+0.00	23278.44*	−1.41	+0.10
$3_{30}\leftarrow 3_{21}$	23134.16*	−2.52	−0.10	24667.66	−2.67	−0.09
$3_{31}\leftarrow 3_{22}$	39680.05*	−3.43	−0.11	40513.89	−3.33	+0.11
$4_{22}\leftarrow 4_{13}$	41579.46*	−3.75	−0.04	40166.73	−2.61	−0.17
$4_{31}\leftarrow 4_{22}$	24834.30*	−3.56	+0.00	25247.76*	−3.48	−0.05
$4_{40}\leftarrow 4_{31}$	34147.76*	−6.64	−0.01	36859.03	−7.06	−0.04
$5_{23}\leftarrow 5_{14}$	63538.10	−8.22	+0.04	—	—	—
$5_{32}\leftarrow 5_{23}$	37780.74*	−5.64	+0.01	36462.89	−4.76	−0.13
$5_{41}\leftarrow 5_{32}$	29687.08*	−7.78	+0.02	31407.24	−8.02	−0.17
$6_{42}\leftarrow 6_{33}$	35790.57*	−8.99	+0.01	35337.94	−8.66	−0.13
$6_{51}\leftarrow 6_{42}$	38701.05*	−16.15	−0.01	42134.12	−16.84	+0.03
$6_{61}\leftarrow 6_{52}$	66648.16	−25.16	+0.06	—	—	—
$7_{52}\leftarrow 7_{43}$	37328.78*	−16.05	−0.01	38541.78	−16.65	+0.12
$8_{62}\leftarrow 8_{53}$	43398.00*	−29.67	+0.65	—	—	—
$9_{54}\leftarrow 9_{45}$	—	—	—	67840.89	−20.52	+0.11

Transition	$^{12}C_2H_4{}^{18}O$			$^{12}C_2H_3D^{16}O$		
	Obsd$^{a)}$	Δ(cent)$^{b)}$	$\Delta^{c)}$	Obsd$^{a)}$	Δ(cent)$^{b)}$	$\Delta^{c)}$
$1_{11}\leftarrow 0_{00}$	37620.59	−0.02	−0.78	37580.17	−0.04	+0.34
$1_{10}\leftarrow 1_{01}$	10364.10	−0.14	−0.03	10925.00	−0.11	+0.04
$2_{02}\leftarrow 1_{11}$	62732.60	+0.31	+1.53	58336.18	+0.12	−0.67
$2_{11}\leftarrow 2_{02}$	25754.59	−0.87	−0.10	21284.05	−0.53	−0.05
$2_{20}\leftarrow 2_{11}$	12511.59	−0.62	+0.19	16822.39	−0.61	−0.01
$2_{21}\leftarrow 2_{12}$	31091.52	−1.26	−0.03	32774.05	−0.98	−0.18
$3_{12}\leftarrow 3_{03}$	—	—	—	38190.67	−1.72	+0.17
$3_{21}\leftarrow 3_{12}$	24202.90	−1.67	+0.09	21212.88	−1.26	−0.02
$3_{30}\leftarrow 3_{21}$	—	—	—	27356.03	−2.21	+0.04
$3_{31}\leftarrow 3_{22}$	34058.27	−3.13	+0.02	40137.71	−2.88	+0.02
$4_{22}\leftarrow 4_{13}$	—	—	—	33890.10	−2.88	+0.09
$4_{23}\rightarrow 4_{14}$	—	—	—	59363.97	−4.38	−0.93
$4_{31}\leftarrow 4_{22}$	23342.08	−2.99	−0.03	25443.48	−2.92	−0.01
$4_{40}\leftarrow 4_{31}$	21764.68	−5.16	+0.09	41664.47	−5.89	−0.03
$4_{41}\leftarrow 4_{32}$	38064.99	−6.48	−0.04	—	—	—
$5_{32}\leftarrow 5_{23}$	41912.03	−6.03	+0.21	31522.22	−4.48	−0.01
$5_{41}\leftarrow 5_{32}$	23839.29	−5.73	−0.14	35048.15	−6.79	+0.05
$5_{50}\leftarrow 5_{41}$	29262.73	−11.30	+0.11	—	—	—
$6_{42}\leftarrow 6_{33}$	39058.16	−7.31	−0.03	33776.67	−7.82	+0.02
$6_{51}\leftarrow 6_{42}$	26191.58	−11.37	+0.01	—	—	—
$6_{60}\leftarrow 6_{51}$	38315.34	−21.22	−0.20	—	—	—
$7_{43}\leftarrow 7_{34}$	—	—	—	42232.50	−10.63	+0.07
$7_{52}\leftarrow 7_{43}$	36599.93	−9.89	−0.04	42052.25	−14.89	−0.08
$7_{61}\leftarrow 7_{52}$	30733.70	−21.87	−0.26	—	—	—
$8_{53}\leftarrow 8_{44}$	—	—	—	42246.24	−15.96	−0.09
$8_{71}\leftarrow 8_{62}$	37573.58	−39.10	−0.02	—	—	—
$8_{62}\leftarrow 8_{53}$	35395.60	−16.15	−0.01	—	—	—
$9_{72}\leftarrow 9_{63}$	36144.65	−29.11	+0.10	—	—	—

Table 1. (continued)

Transition	*trans*-$^{12}C_2H_2D_2{}^{16}O$			*trans*-$^{12}C^{13}CH_2D_2{}^{16}O$		
	Obsd$^{a)}$	Δ(cent)$^{b)}$	$\Delta^{c)}$	Obsd$^{a)}$	Δ(cent)$^{b)}$	$\Delta^{c)}$
$1_{11}\leftarrow 0_{00}$	35528.55^{+}	−0.04	+0.13	35164.55	−0.04	+0.25
$1_{10}\leftarrow 1_{01}$	10357.87	−0.09	+0.04	10409.28	−0.09	+0.03
$2_{12}\leftarrow 1_{01}$	60698.73	+0.01	−0.28	59918.84	−0.01	−0.49
$2_{11}\leftarrow 2_{02}$	18829.50^{+}	−0.38	−0.06	18577.22	−0.37	−0.12
$2_{20}\leftarrow 2_{11}$	17092.35^{+}	−0.57	−0.05	17499.89	−0.55	−0.03
$2_{21}\leftarrow 2_{12}$	31072.93^{+}	−0.84	+0.01	31227.11	−0.81	−0.10
$3_{12}\leftarrow 3_{03}$	33196.82^{+}	−1.21	+0.05	32549.29	−1.17	+0.16
$3_{21}\leftarrow 3_{12}$	19742.85^{+}	−0.98	−0.04	19794.69	−0.99	−0.06
$3_{22}\leftarrow 3_{13}$	40992.29^{+}	−1.68	+0.04	40857.24	−1.61	−0.09
$3_{30}\leftarrow 3_{21}$	28947.35^{+}	−2.20	+0.01	29903.69	−2.09	+0.03
$3_{31}\leftarrow 3_{22}$	39254.25^{+}	−2.67	−0.05	39776.08	−2.56	−0.05
$4_{22}\leftarrow 4_{13}$	29191.80^{+}	−2.06	−0.03	28623.67	−2.10	−0.05
$4_{31}\leftarrow 4_{22}$	25859.61	−2.60	−0.02	—	—	—
$5_{32}\leftarrow 5_{23}$	28611.88^{+}	−3.49	+0.08	28592.74	−3.54	−0.01
$5_{41}\leftarrow 5_{32}$	37879.62^{+}	−6.51	+0.11	39386.60	−6.20	+0.04
$5_{50}\leftarrow 5_{41}$	59941.84	−12.51	+0.08	—	—	—
$6_{33}\leftarrow 6_{24}$	39274.01^{+}	−5.80	−0.03	38268.18	−5.99	+0.08
$6_{42}\leftarrow 6_{33}$	34017.64^{+}	−6.93	+0.00	34985.04	−6.81	+0.02
$6_{43}\leftarrow 6_{34}$	58775.94	−10.63	−0.31	58987.79	−10·47	−0.62
$7_{43}\leftarrow 7_{34}$	37235.33^{+}	−8.27	−0.03	37060.07	−8.51	−0.03
$8_{53}\leftarrow 8_{44}$	41800.99	−14.28	+0.04	—	—	—

Transition	*trans*-$^{12}C_2H_2D_2{}^{18}O$			*cis*-$^{12}C_2H_2D_2{}^{16}O$		
	Obsd$^{a)}$	Δ(cent)$^{b)}$	$\Delta^{c)}$	Obsd$^{a)}$	Δ(cent)$^{b)}$	$\Delta^{c)}$
$1_{11}\leftarrow 0_{00}$	33833.37	−0.03	−0.00	35350.40^{+}	−0.04	−0.05
$1_{10}\leftarrow 1_{01}$	9459.80	−0.08	−0.20	10050.36	−0.08	+0.11
$2_{12}\leftarrow 1_{01}$	—	—	—	60650.68	−0.06	+0.09
$2_{11}\leftarrow 2_{02}$	19157.03	−0.37	−0.02	18741.21^{+}	−0.31	+0.09
$2_{20}\leftarrow 2_{11}$	—	—	—	16168.23^{+}	−0.58	−0.04
$2_{21}\leftarrow 2_{12}$	28379.49	−0.72	−0.03	30150.23^{+}	−0.80	+0.04
$3_{12}\leftarrow 3_{03}$	34581.47	−1.19	−0.02	33290.15^{+}	−0.95	+0.11
$3_{21}\leftarrow 3_{12}$	18684.45	−0.93	+0.05	19252.90^{+}	−0.92	+0.03
$3_{22}\leftarrow 3_{13}$	39298.85	−1.54	+0.00	40230.90^{+}	−1.38	−0.01
$3_{30}\leftarrow 3_{21}$	22176.30	−1.68	+0.18	27008.93^{+}	−2.27	+0.21
$3_{31}\leftarrow 3_{22}$	—	—	—	37656.90^{+}	−2.72	−0.10
$4_{22}\leftarrow 4_{13}$	30996.24	−2.10	+0.35	29325.75^{+}	−1.88	−0.24
$4_{31}\leftarrow 4_{22}$	21381.52	−2.16	−0.25	24407.96	−2.49	−0.11
$4_{40}\leftarrow 4_{31}$	33574.31	−4.51	−0.03	41241.83	−6.20	+0.12
$5_{32}\leftarrow 5_{23}$	28366.27	−3.25	−0.09	28096.93^{+}	−3.25	−0.01
$5_{41}\leftarrow 5_{32}$	28218.20	−5.02	+0.13	35040.32^{+}	−6.33	−0.27
$5_{50}\leftarrow 5_{41}$	—	—	—	—	—	—
$6_{33}\leftarrow 6_{24}$	—	—	—	39828.92^{+}	−5.46	+0.06
$6_{42}\leftarrow 6_{33}$	—	—	—	32116.27^{+}	−6.44	+0.09
$6_{43}\leftarrow 6_{34}$	—	—	—	—	—	—
$6_{52}\leftarrow 6_{43}$	—	—	—	59627.63	−14.77	−0.05
$6_{51}\leftarrow 6_{42}$	39123.20	−10.61	+0.00	—	—	—
$7_{43}\leftarrow 7_{34}$	38859.46	−7.65	−0.09	36874.07^{+}	−7.70	−0.06
$7_{52}\leftarrow 7_{43}$	33947.92	−10.71	−0.11	42337.10	−13.38	−0.00
$8_{53}\leftarrow 8_{44}$	37039.15	−11.16	+0.25	39567.17^{+}	−13.01	+0.08

Table 1. (continued)

Transition	cis-$^{12}C^{13}CH_2D_2{}^{16}O$			cis-$^{12}C_2H_2D_2{}^{18}O$		
	Obsd[a]	Δ(cent)[b]	Δ[c]	Obsd[a]	Δ(cent)[b]	Δ[c]
$1_{11}\leftarrow 0_{00}$	34994.35	−0.04	−0.07	33667.52	−0.03	+0.07
$1_{10}\leftarrow 1_{01}$	10116.74	−0.08	+0.06	—	—	—
$2_{12}\leftarrow 1_{01}$	59872.17	−0.11	+0.12	58154.31	+0.05	−0.12
$2_{11}\leftarrow 2_{02}$	18479.78	−0.28	+0.15	19142.06	−0.41	−0.10
$2_{20}\leftarrow 2_{11}$	16614.63	−0.54	+0.02	13208.26	−0.44	−0.03
$2_{21}\leftarrow 2_{12}$	30349.66	−0.71	+0.09	—	—	—
$3_{12}\leftarrow 3_{03}$	32629.38	−0.78	+0.07	34650.75	−1.40	−0.08
$3_{21}\leftarrow 3_{12}$	19298.48	−0.91	+0.06	18425.51	−0.93	−0.03
$3_{22}\leftarrow 3_{13}$	40124.32	−1.18	−0.02	38645.13	−1.69	+0.09
$3_{30}\leftarrow 3_{21}$	28068.41	−2.04	−0.02	20429.47	−1.59	−0.19
$3_{31}\leftarrow 3_{22}$	38258.30	−2.48	+0.02	32710.84	−2.16	+0.12
$4_{22}\leftarrow 4_{13}$	28697.60	−1.83	−0.19	31344.38	−2.31	+0.20
$4_{31}\leftarrow 4_{22}$	25122.36	−2.39	−0.01	20389.44	−2.03	−0.03
$4_{32}\leftarrow 4_{23}$	—	—	—	40801.46	−3.60	−0.04
$4_{40}\leftarrow 4_{31}$	—	—	—	30707.86	−4.29	+0.19
$4_{41}\leftarrow 4_{32}$	—	—	—	39615.30	−4.87	−0.02
$5_{41}\leftarrow 5_{32}$	36668.79	−5.82	+0.03	25968.08	−4.59	+0.14
$5_{50}\leftarrow 5_{41}$	58187.61	−11.58	−0.04	—	—	—
$6_{33}\leftarrow 6_{24}$	38676.12	−5.43	+0.10	—	—	—
$6_{42}\leftarrow 6_{33}$	33041.21	−6.30	−0.12	—	—	—
$7_{43}\leftarrow 7_{34}$	36486.33	−7.90	+0.03	39728.02	−8.11	−0.17
$8_{53}\leftarrow 8_{44}$	40608.35	−12.95	+0.13	36911.87	−10.68	+0.07
$8_{62}\leftarrow 8_{53}$	—	—	—	39371.86	−17.83	+0.21
$5_{32}\leftarrow 5_{23}$	27998.56	−3.28	−0.09	—	—	—

a) Values marked by * and + agree essentially with previous measurements in Ref. 2 and in R. J. Myers and W. D. Gwinn, cited in NBS Monograph 70 "Microwave Spectral Tables", Vol. IV, p. 197 (1968) issued by U. S. Department of Commerce respectively. One of the latter values for 8_{53}—8_{44} of cis-$^{12}C_2H_2D_2{}^{16}O$ seems to be a typographical error. b) Correction due to centrifugal distortion. c) $\Delta=\nu(\text{obsd})-\nu(\text{calcd})$, where ν(calc)'s are obtained by use of the parameters given in Table 2.

Within the quoted uncertainties, we can assert that the values of A', B', and C' are equal to those of A, B, and C respectively. The B values for the ^{16}O- and ^{18}O-species have appreciable differences both in the normal and the *trans*-dideutero species. Since the oxygen atom is on the b axis, this is due to the effect of zero-point vibration. The correlation matrix for the rotational constants has appreciable off-diagonal elements.** These correlations were taken into account when these rotational constants were used in the calculation of the structural parameters.[6]

Calculation of Structurel Parameters

By the use of the rotational constants of the ten isotopic molecules, it was possible to apply the method of r_s(Costain)[7] and r_m(Watson).[8] Since the rotational constants are indirect observations,[6,9] nondiagonal weight matrices, which took correlations into account, were used in the calculation.

Equation (1) shows that the values of $\tau_{\alpha\beta\alpha\beta}$'s are needed to obtain the rotational constants, whereas only a combination of $\tau_{\alpha\alpha\beta\beta}$ and $\tau_{\alpha\beta\alpha\beta}$ is determined when the centrifugal distortion is treated to the first order. However, as the $\tau_{\alpha\beta\alpha\beta}$'s are expected to be small and as their isotopic differences are even smaller, the effective rotational constants, A', B', and C', were used without corrections for the calculation of the structural parameters.***

Because of the C_{2v} symmetry, there are four independent structural parameters to be determined.

The r_0 Structure. The r_0 structure was derived by a least-squares fitting of all the observed rotational constants. The weight matrix, **W**, was calculated as:

$$\mathbf{W}=\begin{pmatrix}\mathbf{D}_1^{-1} & & & \mathbf{0}\\ & \mathbf{D}_2^{-1} & & \\ & & \ddots & \\ \mathbf{0} & & & \mathbf{D}_{10}^{-1}\end{pmatrix} \qquad (2)$$

where the suffixes are for each isotopic species and where

** For example, suppose that 1_{10}—1_{01}, 1_{11}—0_{00}, and 2_{12}—1_{01} transitions are observed with equal accuracy. In the rigid rotor approximation, their frequencies are $A-C$, $A+C$, and $A+3C$ respectively. The correlation factor between A and C is calculated to be −0.5222.

*** The rotational constants corrected for $\tau_{\alpha\beta\alpha\beta}$ and their isotopic differences should be used for the calculation of the r_0 and r_s structures respectively, if we were to be in strict accordance with the original definitions. Thus, the structures derived in the present study contain systematic errors introduced by the neglect of the corrections, but they may be assumed to be within the reliability intervals of the structural parameters.

TABLE 2. CONVERGED VALUES AND THEIR VARIANCES OF EFFECTIVE PARAMETERS (in MHz)[a)]

	$^{12}C_2H_4{}^{16}O$	v_i [b)]	$^{12}C^{13}CH_4{}^{16}$	v_i [b)]	$^{12}C_2H_4{}^{18}O$	v_i [b)]
A'	25483.79	0.028	25291.89	0.055	23992.83	0.112
B'	22120.76	0.031	21597.77	0.058	22121.58	0.117
C'	14097.71	0.026	13825.75	0.056	13628.56	0.126
τ'_{aaaa}	−0.2186	0.002	−0.2301	0.013	−0.1843	0.009
τ'_{bbbb}	−0.0730	0.002	−0.0750	0.006	−0.0700	0.005
τ'_{cccc}	+0.0294	0.008	−0.0483	0.032	0.0952	0.064
τ'_{aabb}	−0.1534	0.002	−0.1520	0.004	−0.1407	0.004
σ^2 [c)]	0.0129		0.0205		0.0916	

	t-$^{12}C_2H_2D_2{}^{16}O$	v_i [b)]	t-$^{12}C^{13}CH_2D_2{}^{16}O$	v_i [b)]	t-$^{12}C_2H_2D_2{}^{18}O$	v_i [b)]
A'	22943.19	0.030	22786.84	0.061	21646.74	0.092
B'	18198.47	0.032	17852.32	0.072	18202.46	0.099
C'	12585.27	0.030	12377.50	0.060	12186.66	0.093
τ'_{aaaa}	−0.1667	0.003	−0.1617	0.015	−0.1377	0.009
τ'_{bbbb}	−0.0358	0.001	−0.0379	0.004	−0.0385	0.003
τ'_{cccc}	0.0251	0.007	0.0201	0.017	0.0214	0.022
τ'_{aabb}	−0.0815	0.001	−0.0842	0.003	−0.0817	0.002
σ^2 [c)]	0.0064		0.0261		0.0321	

	c-$^{12}C_2H_2D_2{}^{16}O$	v_i [b)]	c-$^{12}C^{13}CH_2D_2{}^{16}O$	v_i [b)]	c-$^{12}C_2H_2D_2{}^{18}O$	v_i [b)]
A'	22700.41	0.050	22555.61	0.037	21424.03	0.047
B'	18318.39	0.054	17963.42	0.040	18317.20	0.050
C'	12650.08	0.051	12438.85	0.038	12243.45	0.048
τ'_{aaaa}	−0.1754	0.006	−0.1627	0.004	−0.1336	0.005
τ'_{bbbb}	−0.0401	0.002	−0.0432	0.002	−0.0413	0.002
τ'_{cccc}	0.0061	0.013	−0.0067	0.010	0.0334	0.013
τ'_{aabb}	−0.0768	0.002	−0.0817	0.002	−0.0776	0.002
σ^2 [c)]	0.0184		0.0100		0.0157	

	$^{12}C_2H_3D^{16}O$	v_i [b)]
A'	24252.47	0.058
B'	19905.34	0.057
C'	13327.40	0.056
τ'_{aaaa}	−0.1791	0.008
τ'_{bbbb}	−0.0486	0.002
τ'_{cccc}	0.0390	0.010
τ'_{aabb}	−0.1095	0.002
σ^2 [c)]	0.0229	

a) Both τ'_{bbcc} and τ'_{aacc} are assumed to be zero. b) Variance of parameter. 2.5 times v_i indicates a reliability intervals of the corresponding parameter. c) The standard deviation of transition frequencies is represented by σ.

$\mathbf{D}_i{}^{-1}$ are the 3×3 submatrices corresponding to the rotational constants A, B, and C. The method for estimating this weight matrix has been described in a separate paper.[6)]

The bond length, $r_0(CH)$, was assumed to be longer than $r_0(CD)$ by about 0.002 Å.[10)] In order to verify this difference, four parameter sets were investigated; besides $r(CO)$ and $r(CC)$ and the angle, θ, between H_2C plane and CC bond, which were taken as variables, the following assumptions were made for $r(CD)$, ∠HCH, and ∠DCH:

Set 1) $r(CH)=r(CD)$, ∠HCH = ∠DCH,
Set 2) $r(CH)\neq r(CD)$, ∠HCH = ∠DCH,
Set 3) $r(CH)=r(CD)$, ∠HCH ≠ ∠DCH, and
Set 4) $r(CH)\neq r(CD)$, ∠HCH ≠ ∠DCH.

The analysis led to the following conclusions: a) The most proper set of parameters in the r_0 structure is set 1, since higher correlations emerge among the parameters in the other sets, and b) the isotope effects on $r_0(CH)$ and ∠HCH cannot be detected. The resulting parameters, summarized in Table 4, agree with those reported in previous papers.[2,3)]

The r_s Structure Obtained from Kraitchman's Formula. The structure of ethylene oxide was derived from the conventional Kraitchman method;[11)] the coordinates of each atom were first calculated by solving an equation in a matrix form as:

$$\begin{bmatrix} p_{aa}p_{ab}p_{ac} \\ p_{ba}p_{bb}p_{bc} \\ p_{ca}p_{cb}p_{cc} \end{bmatrix} = \mu \begin{bmatrix} p_{ab}p_{ac} & p_{ac}p_{aa} & p_{aa}p_{ab} \\ p_{bb}p_{dc} & p_{bc}p_{ba} & p_{ca}p_{bb} \\ p_{cb}p_{cc} & p_{cc}p_{ca} & p_{ca}p_{cb} \end{bmatrix} \cdot \begin{bmatrix} a_s^2 \\ b_s^2 \\ c_s^2 \end{bmatrix} \qquad (3)$$

where:

$$p_{\alpha\beta} = P_\alpha' - P_\beta, \qquad (4)$$

$$P_\alpha = (-I_\alpha + I_\beta + I_\gamma)/2, \qquad (5a)$$

$$P_\alpha' = (-I_\alpha' + I_\beta' + I_\gamma')/2, \qquad (5b)$$

$$(\alpha,\ \beta,\ \gamma = \text{a, b, or c})$$

and

$$\mu = M\Delta m/(M + \Delta m).$$

The I_a, I_b, I_c quatities are the principal moments of inertia of one of the reference species (normal, *trans*-D_2 and *cis*-D_2- ethylene oxide), and the primed quantities, I_a''s, are the principal moments of inertia of one of the species in which one of the atoms in the reference molecule is replaced by an isotope. M is the molecular weight of the reference species, Δm is the change in the molecular weight caused by the isotopic substitution, and a_s, b_s, and c_s are the coordinates of the substituted atom referred to the principal axis system of the reference species.

A direct substitution of the observed values into Eq. (3) gave imaginary values to those coordinates which are expected to be equal to or close to zero. Hence, the following conditions were imposed: 1) The values of P_a' for the ^{18}O species of normal, *trans*-D_2-, and *cis*-D_2- ethylene oxides were set equal to P_a. The observed values of $P_a' - P_a$ were taken into account in the error analysis of the results by the use of the law of the propagation of errors.[6] 2) The values of P_c' for the ^{18}O species of the normal and the *trans*-D_2-ethylene oxide were set equal to P_c, with the observed values of $P_c' - P_c$ treated in the same manner as $P_a' - P_a$.

The calculations were carried out for the sets of isotopic species (the normal ^{18}O-, ^{13}C-, and D_1-ethylene oxides), *trans*-D_2-, *trans*-D_2-^{18}O-, *trans*-D_2-^{13}C-, and D_1-ethylene oxides), and (*cis*-D_2-, *cis*-D_2-^{18}O-, *cis*-D_2-^{13}C-, and D_1-ethylene oxides), taking the first species in each set as the reference molecule. The principal axis coordinates of the O, C, and H atoms for the normal *trans*-D_2-, and *cis*-D_2- species thus calculated are shown in Table 3. The coordinates of the H atoms in the deuteroethylene oxides which are not replaced by D could not be determined by the present method; even the use of the first-moment equation provided only the b and c coordinates of the hydrogen atoms in the *cis*-D_2 molecule. The values thus derived are shown in parentheses in Table 3. The remaining coordinates, the a and c coordinates of the *trans*-D_2 and the c coordinates of the *cis*-D_2 species, could not be obtained by the first-moment equation or by setting the cross products of inertia at zero. The structural parameters calculated from the coordinates are also summarized in Table 3, along with their estimated error limits. The r_s(CH) derived for the normal species is longer than that for the dideutero species by about 0.003 Å, but they overlap in their reliability intervals.

TABLE 3. ATOMIC COORDINATES AND STRUCTURAL PARAMETERS[a)]

	Nomal	*trans*-D_2	*cis*-D_2
a_s(O)	0.00000(363)	0.00000(322)	0.00000(286)
b_s(O)	0.80226(204)	0.82883(108)	0.83079(88)
c_s(O)	0.00000(337)	0.00000(313)	0.01945(197)
a_s(C)	0.73239(79)	0.72581(65)	0.73202(62)
b_s(C)	0.42741(113)	0.39915(102)	0.39348(98)
c_s(C)	0.00000(271)	0.09115(391)	0.07163(470)
a_s(H)[b)]	1.26235(81)	—	—
b_s(H)	0.64112(117)	0.61247(78)	(0.5251)[c)]
c_s(H)	0.92344(64)	—	(0.9458)[c)]
a_s(D)[c)]	—	1.37277(60)	1.26203(76)
b_s(D)	—	0.61247(78)	0.69174(91)
c_s(D)	—	0.74997(56)	0.82280(66)
r(CO)	1.4313(31)	1.4294(24)	1.4293(38)
r(CC)	1.4648(16)	1.4630(23)	1.4640(12)
r(CH)	1.0859(18)	1.0824(34)	1.0816(56)
∠HCH	116.50(43)	—	—
θ[b)]	21.59(28)	—	—
∠OCC	59.21(13)	59.21(13)	59.18(11)

a) Coordinates and bond lengths are in Å and angles are in degreees with reliability intervals indicated in parentheses. b) Rotational constants of the D_1 species species were used to derive the coordinates of the H or D atoms. c) Calculated by the first moment equation. d) Angle of the C–C bond to the H_2C plane.

The value of c_s(C) of the *trans*-D_2 species combined with the r(CC) indicates that the principal axis system of the species is obtained by the rotation of 7.15° around the b-axis, following the displacement of the origin of that of the normal species. For the *cis*-D_2-species, the rotation angle of 4.25° around the a-aixs is derived from the c_s(C), c_s(O), r(CC), and r(CO) values. A μ_s value of 0.14 D can be expected for the latter species if one assumes that the total dipole moment of 1.88 D of the normal species is unchanged and lies along the symmetry axis of the ring.

The r_s Structure Derived by a Least-squares Fit. The r_s parameters were also derived from a least-squares fit of the changes caused by isotope substitutions in the principal moments of inertia. The analysis was based on either a diagonal or a nondiagonal weight matrix.[6] The converged parameters were not significantly different, but the correlation factors obtained for a nondiagonal weight matrix were somewhat smaller. This tendency is contrary to that observed for the r_0 structure. The parameters derived from the non-diagonal weight matrix are shown in Table 4. Strong correlations were observed between r_s(CH) and r_s(CD) and between $\angle_s$HCH and $\angle_s$DCH, but the other parameters were not affected. No significant differences were observed between r_s(CH) and r_s(CD) or between $\angle_s$HCH and $\angle_s$DCH.

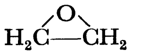
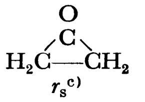
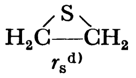
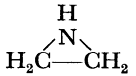
The r_m Structure. The r_m structure was derived from an approximate equation: $I_e = 2I_s - I_0$ as proposed by Watson for estimating the equilibrium structure.[8] He pointed out that one of the disadvantages of the r_m structure is that the equation is not sufficiently

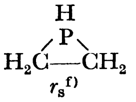
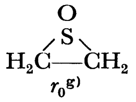
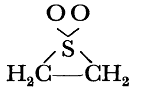
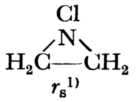
Table 4. Structural parameters of ethylene oxide a),e)

	r_0	r_s	r_m	r_0 b)	r_0 c)
r(CC)	1.470(3)	1.466(2)	1.462(3)	1.472	1.470(3)
r(CH)	1.085(4)	1.085(1)	1.086(4)	1.082	1.084(5)
r(CO)	1.434(2)	1.431(1)	1.428(2)	1.436	1.435(3)
∠HCH	116.3(7)	116.6(1)	116.9(7)	116.7	116.3(11)
θ d)	22.3(5)	22.0(1)	21.6(5)	21.9	21.9(11)
∠COC	61.67	61.64	61.62	61.24	61.61
φ f)	7.24	7.60	7.97	7.66	7.70

a) Bond lengths are in Å and bond angles are in degrees. b) Ref. 2. No error limits are given in the reference. c) Ref. 3. Error limits indicated in the original paper are multiplied by 2.5 to make them consistent with others. d) Angle of the C-C bond to the H_2C plane. e) Values in parentheses indicate the reliability intervals. f) $\varphi = \angle OCC/2 - \theta$.

Table 5. Comparison of structures of three-membered rings a)

	 r_m b)	 r_s c)	 r_s d)	 r_s e)
r(CC)	1.462(3)	1.575(12)	1.484(6)	1.481
r(CH)	1.086(4)	1.086(25)	1.083(10)	1.084
r(CX)	1.428(2)	1.475(17)	1.815(14)	1.475
∠HCH	116.9(7)	114.1(20)	115.8	115.72
θ i)	21.6(5)	29.1(20)	28.2	—
∠CXC	61.62	64.60	48.27	60.25
φ j)	7.97	−0.26	5.28	—

	 r_s f)	 r_0 g)	 r_0 h)	 r_s l)
r(CC)	1.502	1.504(3)	1.590(11)	1.484
r(CH)	1.093	(1.078) k)	(1.078) k)	1.093
r(CX)	1.867	1.822(3)	1.731(6)	1.488
∠HCH	114.4	(116.0) k)	(116.0) k)	117.1
θ i)	30.5	(28.3) k)	(28.3) k)	—
∠CXC	47.4	48.77(16)	54.40(25)	59.80
φ j)	2.65	4.5	3.1	—

a) Bond lengths are in Å and bond angles are in degrees. Reliability intervals are shown in parentheses. Note that r(CC) for propane, $(CH_3)_2CH_2$, is 1.526±0.002 Å (Ref. 13). b) Present study. c) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 1896 (1969). d) K. Okiye, C. Hirose, D. Lister, and J. Sheridan, *Chem. Phys. Lett.*, **24**, 111 (1974). e) B. Bak and S. Skaarup, *J. Mol. Struct.* **10**, 385 (1971). f) M. T. Bowers, R. A. Beaudet, H. Goldwhite, and R. Tang, *J. Amer. Chem. Soc.*, **91**, 17 (1969). g) S. Saito, This Bulletin, **42**, 663 (1969). h) Y. Nakano, S. Saito, and Y. Morino, *ibid.*, **43**, 368 (1970). i) Dihedral angle of the C-C bond and the H_2C plane. j) $\varphi = \angle OCC/2 - \theta$, the positive value of φ corresponds to the case when the H_2C plane is pushed toward another H_2C plane from the plane bisecting the OCC angle. k) assumed values. l) B. Bak and S. Skaarup, *J. Mol. Struct.* **12**, 259 (1972). The CH_2 groups are reported to be twisted.

Table 6. Comparison of C-X bond lengths in three-membered rings and dimethyl compounds (in Å)

	X=O	X=CO	X=NH	X=PH	X=S	X=SO	X=SO_2
$(CH_2)_2X$ a)	1.428(2)	1.475(17)	1.475	1.867	1.815(14)	1.822(3)	1.731(6)
$(CH_3)_2X$	1.410(3) b)	1.507(3) c)	1.462(5) d)	1.848(3) e)	1.802(2) f)	1.799(5) g)	1.777(6) h)

a) As for the references on structures of the ring compounds, see footnotes of Table 5. b) U. Blukis, P. H. Kasai and R. J. Myers, *J. Chem. Phys.*, **38**, 2753 (1963). c) R. Nelson and L. Pierce, *J. Mol. Spectrosc.*, **18**, 344 (1965). d) J. E. Wollab and V. W. Laurie, *J. Chem. Phys.*, **48**, 5058 (1968). e) R. Nelson, *ibid.*, **39**, 2382 (1963). f) L. Pierce and M. Hayashi, *ibid.*, **35**, 479 (1961). g) W. Feder, H. Dreizler, H. D. Rudolph, and V. Typke, *Z. Naturforsch.*, **24A**, 266 (1969). h) S. Saito and F. Makino, This Bulletin, **45**, 92 (1972).

accurate for the hydrogen-deuterium isotope effects.

The calculation of the r_m structure followed the derivation of the r_0 structure, with I_0 replaced by $I_m = 2I_s - I_0$. The weight matrix used in the derivation of the r_0 structure was used. Typical r_m parameters obtained with a nondiagonal weight matrix are listed in Table 4.

Discussion

In calculating the structural parameters, the rotational constants were treated as indirect observations. In other words, the rotational constants were derived by a least-squares fit of directly-observed transition frequencies. The correlations found among the rotational constants were accounted for by the use of nondiagonal weight matrices. The use of a nondiagonal weight matrix for the analysis of mutually-correlated data was first done by Morino *et al.* in their study of gas-phase electron diffraction.9) As Kirchhoff suggested,12) similar situations are often encountered in microwave spectroscopy. The present study is an application of this method with a slight modification (see Ref. 6 for details). A comparison of the present results with those derived assuming a mutual independence of rotational constants led to the following conclusions:

a) The parameters converged to slightly different values, although the reliability intervals estimated from a 2.5-fold variance covered the differences.

b) The correlation factors among the parameters were also different.

c) No general statement can be made as to whether a conventional use of a diagonal weight in the calculation gives smaller variances and less correlations than that of a nondiagonal weight.

The r_s structure derived from Kraitchman's method is consistent with that derived statistically within the estimated error limits (Tables 3 and 4). Therefore, the apparent isotopic differences in the parameters obtained by Kraitchman's formula (Table 3) are artifacts, as has been indicated by the present statistical analysis.

A comparison of the structural parameters of three-membered ring compounds is presented in Table 5. The CX bond lengths of these compounds are compared with those of $(CH_3)_2X$ in Table 6. The CC bond length in $(CH_3)_2CH_2$ is reported to be 1.526 ± 0.002 Å.13) An inspection of Tables 5 and 6 shows that, in three-membered rings of the H_2C-X-CH_2 type, the CC length is shortened for X=O, S, NH, PH, and SO, whereas the CX lengths are longer than their typical values by about 0.02 Å. The angles, φ, of the H_2C plane to the line bisecting the CCX plane are significantly different from zero. Since φ is expected to be equal or very close to zero in normal chemical bonds, the departure from zero in the three-membered rings is an indication of strain in the bonding.

The author is grateful to Professor Kunio Kozima for his help and encouragement and to Mr. Masahiro Kawasaki, whose sample of dideuteroethylene oxides were vital in the present study. Grateful acknowledgements also go to Professor Yonezo Morino, Professor Kozo Kuchitsu, Dr. Takeshi Oka, and Dr. Charles D. LeCroix for their helpful comments on the manuscript.

References

1) C. A. Coulson, "Valence," Oxford University Press, New York, 2nd Ed. (1961), Chap. viii.

2) G. L. Cunningham, A. W. Boyd, R. J. Myers, W. D. Gwinn, and W. J. LeVan, *J. Chem. Phys.*, **19**, 676 (1951).

3) T. E. Turner and J. A. Howe, *ibid.*, **24**, 924 (1956).

4) D. Kivelson and E. B. Wilson, Jr., *ibid.*, **20**, 1575 (1952).

5) J. K. G. Watson, *ibid*, **48**, 181 (1968).

6) C. Hirose, This Bulletin, **47**. 976 (1974).

7) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

8) J. K. G. Watson, *J. Mol. Spectrosc.*, **48**, 479 (1973).

9) Y. Morino, K. Kuchitsu, and Y. Murata, *Acta Cryst.*, **18**, 549 (1965).

10) V. W. Laurie and D. R. Herschbach, *J. Chem. Phys.*, **37**, 1687 (1962).

11) J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1966).

12) W. H. Kirchhoff, *J. Mol. Spectrosc.*, **41**, 333 (1972).

13) D. R. Lide, *J. Chem. Phys.*, **33**, 514 (1960).