Microwave Spectrum of Ethylene Oxide in Excited Vibrational States

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In the rotational spectrum of ethylene oxide, the five lowest-lying vibrational states are assigned and the vibration-rotation constants and the centrifugal distortion constants are derived. The vibrational frequencies are estimated from relative intensity measurements at $\nu_a=803\pm18$ cm^{-1} and $\nu_b=814\pm23$ cm^{-1} for the anti-symmetric species (with respect to the C_2 operation) and at $\nu_c=872\pm34$ cm^{-1}, $\nu_d=1020\pm33$ cm^{-1}, and $\nu_e=1109\pm42$ cm^{-1} for the symmetric species. The intensity measurements of the remaining spectral lines showed that these lines belong to vibrational states at frequencies above about 1000 cm^{-1}. The ν_a, ν_b, and ν_c states are tentatively assigned to ν_{15}, ν_{12}, and ν_5, respectively, by taking into account the Coriolis interactions.

With a considerable number of infrared and Raman investigations carried out so far,[1–13] the assignments of certain fundamental frequencies of ethylene oxide are still subject to controversy. Namely, as shown by some examples in Table 1, different authors have proposed considerably different frequencies for ν_7 (A_2, CH_2-twisting), ν_8 (A_2, CH_2-rocking), and ν_{12} (B_1, ring deformation), for which no direct spectral evidence has been obtained. Under these circumstances, further infrared and Raman studies would seem to be ineffective in improving the situation significantly, and rather somewhat different approach is required.

Now, it is known that the intensity measurements of microwave absorption in vibrationally-excited states[14] and the analysis of the vibration-rotation interaction[15–18] provide useful information about the energy and symmetry of these vibrational states. In fact, these methods may certainly be advantageous when the vibrational transition is extremely weak or forbidden as in those described above. Thus, the present work was carried to out examine the frequencies and the assignments of the lower fundamental frequencies of ethylene oxide using microwave spectroscopy.

Table 1. Vibrational assignment of ethylene oxide (in cm^{-1})

Symmetry	Type of vibration	Lord and Nolin[a]	Potts[b]	Hirokawa *et al.*[c]	Cant *et al.*[d]
A_1	ν_1(CH stretch)[f]	3005	(3006)[e]	3005	3018
	ν_2(CH_2 deform)	1490	1497.5	1494	1498
	ν_3(ring breath)[f]	1266	1270.5	1270	1270
	ν_4(CH_2 wag)[f]	1120	(1130)[e]	1120	1148
	ν_5(ring deform)	877	877	877	877
A_2	ν_6(CH stretch)	3063	(3065)[e]	3065	3073[g]
	ν_7(CH_2 twist)	(1345)[e]	(1300)[e]	1030	1047[g]
	ν_8(CH_2 rock)	807	(860)[e]	807	825[g]
B_1	ν_9(CH stretch)[f]	3019	3006	3019	3006
	ν_{10}(CH_2 deform)	1470	1471.5	1470	1472
	ν_{11}(CH_2 wag)	1153	1151	1153	1151
	ν_{12}(ring deform)	892	(890)[e]	840	840
B_2	ν_{13}(CH stretch)	3079	3065	3065	3065
	ν_{14}(CH_2 twist)	1143	1142	1143	1142
	ν_{15}(CH_2 rock)	821	821.5	822	821

a) Ref. 5. b) Ref. 6. c) Ref. 12. d) Ref. 13. e) Values in parenthesis were estimated in the original papers. f) ν_1, ν_3, ν_4, and ν_9 respectively, are assigned to the bands at 3018, 1269, 1123, and 3008 cm^{-1} of the Raman spectra of gaseous C_2H_4O obtained by the present authors. g) The values from IR spectra of solids.

Experimental

Ethylene oxide was purchased from the Matheson Co. and was used without further purification. The rotational spectrum was observed with a conventional spectrometer at 300 K mainly in the frequency region from 9 to 42 GHz. Previous results[19–21] were referred to in eliminating the spectral lines of isotopic species. A double resonance experiment was performed on the $2_{11}\leftarrow2_{02}$ and $2_{20}\leftarrow2_{11}$ transitions in order to confirm the assignment of the Q-branch transitions. Spectral line intensities were measured from a chart recorded using a Hewlett-Packard MRR8460A-607 R-band spectrometer.[24] The accuracy of the measurements was checked by measuring the natural abundance ratio of $^{12}C^{13}CH_4O$ to $^{12}C_2H_4O$.

Results and Discussion

The microwave spectra of ethylene oxide and its isotopic species have been investigated in the ground state by a number of authors,[19–23] resulting in the determination of the r_0, r_s, and r_m structures,[19–21] the dipole moment,[19] the centrifugal distortion constants,[21–23] and the ^{17}O quadrupole coupling constants.[23] On the basis of these results, the rotational spectrum of the vibrationally-excited states was identified and frequencies were assigned to the transitions in five low-lying vibrational states, ν_a, ν_b, ν_c, ν_d, and ν_e in increasing order of frequency, as listed in Table 2. Since the molecular dipole moment lies along the b-axis, a rotational transition $J_{K_{-1}K_1}\leftrightarrow J_{K_{-1}'K_1'}$ is allowed only for such $K_{-1}K_1\leftrightarrow K_{-1}'K_1'$ combinations as ee↔oo and eo↔oe, where e and o signify even and odd. The calculated transition frequencies for the three lower vibrational states, ν_a, ν_b, and ν_c, were obtained using the parameters given in Table 3, which were determined by a least-squares fit including the centrifugal distortion effect to the first order.[25] For ν_d and ν_e states no R-branch transitions were identified, so that their calculated transition frequencies were derived from the observed values of $1_{10}\leftarrow1_{01}$ and $2_{20}\leftarrow2_{11}$ *via* Q-branch plots without taking account of the centrifugal distortion.

In Table 4, the intensities of the excited state lines

TABLE 2. ROTATIONAL TRANSITIONS OF ETHYLENE OXIDE IN EXCITED VIBRATIONAL STATES (in MHz)

Transition	ν_a state		ν_b state		ν_c state		ν_d state		ν_e state	
	Obsd	Obsd−Calcd[a]	Obsd	Obsd−Calcd[a]	Obsd	Obsd−Calcd[a]	Obsd	Obsd−Calcd[c]	Obsd	Obsd−Calcd[c]
$1_{11}-0_{00}$	39464.11	−0.00	38849.04	−0.00	39939.20	0.00				
$2_{02}-1_{11}$	63135.78	−0.24	62460.26	0.25	64345.03	0.18				
$2_{12}-1_{01}$	67484.20	0.47	66105.41	−0.10	68771.68	−0.36				
$2_{21}-1_{10}$	90368.44	−0.22	89292.51	−0.15	90981.28	0.18				
$1_{10}-1_{01}$	11442.82	0.01	11594.62	−0.11	11104.31	−0.13	11206.23	0.00	10746.71	0.00
$2_{11}-2_{02}$[b]	24875.38	0.04	26462.83	−0.02	23818.16	0.13	24793.06	−0.89	24795.98	8.83
$2_{21}-2_{12}$	34327.74	0.00	34781.85	−0.03	33313.46	−0.04	33618.01	−0.68	32246.05	5.92
$2_{20}-2_{11}$[b]	15790.68	−0.48	15238.77	0.21	15531.11	−0.05	15194.78	−0.02	13978.02	0.00
$3_{21}-3_{12}$	—	—	24869.12	−0.12	22693.94	−0.14	23427.70	−1.70	—	—
$3_{31}-3_{22}$	40008.99	−0.03	39634.30	−0.14	39061.58	−0.07	38864.19	−2.34	—	—
$3_{30}-3_{21}$	23561.09	−0.01	21692.29	0.26	23454.24	−0.07	22304.39	−0.67	19695.59	11.01
$4_{22}-4_{13}$	41406.58	−0.05	—	—	39439.08	0.01	41517.05	−5.06	—	—
$4_{31}-4_{22}$	25002.35	0.31	25211.15	0.31	24361.27	0.10	24395.55	−2.96	23411.99	9.81
$4_{40}-4_{31}$	34884.00	−0.06	31300.39	−0.24	34919.31	0.20	32754.56	−3.69	—	—
$5_{32}-5_{23}$	37613.44	0.15	40960.67	0.16	—	—	—	—	38658.26	31.06
$5_{41}-5_{32}$	30155.73	0.37	28511.53	−0.07	29917.02	0.06	28750.93	−5.80	26126.32	24.97
$6_{42}-6_{33}$	—	—	38061.82	−0.11	34407.62	−0.15	35560.69	−9.55	35836.07	25.12
$6_{51}-6_{42}$	39574.30	0.03	35406.37	0.29	39786.69	−0.18	37052.08	−12.10	32037.08	78.42
$7_{52}-7_{43}$	37680.97	−0.25	37669.26	0.05	36967.51	0.16	36549.65	−14.51	35080.86	33.86
$8_{62}-8_{53}$	—	—	40927.98	−0.15	—	—	41765.74	−29.90	37492.10	91.00

a) Errors in the observed values are generally within ±0.1 MHz. b) The transitions were confirmed by a double-resonance experiment. c) The calculated frequencies of the rotational transitions for the ν_d and ν_e states were derived from the $1_{10}-1_{01}$ and $2_{20}-2_{11}$ transitions using Q-branch plots without taking account of the centrifugal distortion.

TABLE 3. ROTATIONAL AND CENTRIFUGAL DISTORTION CONSTANTS IN EXCITED VIBRATIONAL STATES (in MHz)[a]

	Ground state[b]	ν_a	ν_b	ν_c
A_s	25483.92	25453.45	25222.09	25521.92
B_s	22120.82	22003.60	22250.62	22041.25
C_s	14097.82	14010.75	13626.91	14417.47
α_s^a		30.47	261.83	−38.00
α_s^b		117.22	−109.80	79.57
α_s^c		87.07	470.91	−319.65
τ_{aaaa}'	−0.2832±0.0084	−0.29±0.27	−0.30±0.20	−0.36±0.17
τ_{bbbb}'	−0.1250±0.0085	−0.01±0.28	−0.29±0.21	−0.21±0.18
τ_{cccc}'	−0.0327±0.0086	−0.06±0.30	0.46±0.23	−0.43±0.19
t_1[c]	−0.2351±0.0110	−0.59±0.37	0.11±0.26	−0.35±0.23
t_2[c]	−0.1021±0.0144	−0.91±0.49	0.65±0.37	−0.29±0.31

	Ground state[b]	ν_d	ν_e
$2B_s-A_s-C_s$	4659.90	4799.59	5404.57
A_s-C_s	11386.10	11206.23	10749.00

a) Error limits for the rotational constants and the vibration-rotation constants (α_s^x) for ν_a, ν_b, and ν_c were estimated from 2.5 times the standard deviations to be less than ±0.5 MHz. For the ν_d and ν_e states the values of $2B_s-A_s-C_s$ and A_s-C_s were derived using Q-branch plots of the observed values of the $1_{10}\leftarrow 1_{01}$ and $2_{20}\leftarrow 2_{11}$ transitions, and the reliability intervals were estimated to be ±0.5 MHz and ±2 MHz or more, respectively, for ν_d and ν_e. The large ambiguity in ν_e is due to the Coriolis interaction. b) The values for the ground state were calculated from the observed transitions reported in Ref. 22. c) $t_1=\tau_{aabb}'+\tau_{ccaa}'(A-B)/(A-C)$, $t_2=\tau_{bbcc}'+\tau_{ccaa}'(B-C)/(A-C)$.

are given by the ratios to those of the corresponding ground state lines. The table is limited within the frequency range covered by the MRR8460A-607 R-band spectrometer, and leaves quite a few lines unlisted because of the uncertainty due to overlapping. It can be noticed, however, that in the ν_a and ν_b states the relative intensity Γ of eo↔oe type transitions is about three times that of ee↔oo type values, while the Γ is approximately equal for both types of transitions in the ν_c, ν_d, and ν_e states.

TABLE 4. VALUES OF $\exp(-h\nu/kT)\cdot g^{\mathrm{v}}(J_{K_{-1}K_1})/g^0(J_{K_{-1}K_1})$,[a] THE BOLTZMANN FACTOR, AND ESTIMATED VIBRATIONAL FREQUENCIES

	ν_a	ν_b	ν_c	ν_d	ν_e	$^{12}C^{13}CH_4O$
$e^{-h\nu/kT}\cdot g^{\mathrm{v}}(J_{ee})/g^0(J_{ee})$ and/or $e^{-h\nu/kT}\cdot g^{\mathrm{v}}(J_{oo})/g^0(J_{oo})$						
$1_{11}-0_{00}$	—	0.012_0	0.014_1	—	—	0.016_4
$3_{31}-3_{22}$	—	—	0.017_0	0.007_9	—	—
$4_{41}-4_{31}$	0.012_6	—	0.014_3	0.007_6	—	—
$6_{42}-6_{33}$	—	0.011_3	0.015_0	0.007_5	0.004_4	0.016_7
$6_{51}-6_{42}$	(0.014_4)[b]	0.012_7	0.015_4	0.007_6	0.005_0	—
Average	0.012_6	0.012_0	0.015_2	0.007_7	0.004_7	0.016_6
$e^{-h\nu/kT}\cdot g^{\mathrm{v}}(J_{eo})/g^0(J_{eo})$ and/or $e^{-h\nu/kT}\cdot g^{\mathrm{v}}(J_{oe})/g^0(J_{oe})$						
$2_{21}-2_{12}$	0.035_1	0.034_8	0.015_3	0.006_6	—	0.028_5
$5_{41}-5_{32}$	0.034_8	0.034_2	0.015_9	—	—	0.027_7
$5_{32}-5_{23}$	0.037_5	—	—	—	0.005_2	—
$7_{52}-7_{43}$	0.034_7	0.033_6	0.015_1	0.007_6	0.005_0	0.029_3
Average	0.035_5	0.034_2	0.015_3	0.007_1	0.005_1	0.028_5
$e^{-h\nu/kT}$	0.021_3	0.020_2	0.015_3	0.007_5	0.004_9	0.021_1
2.5σ[c]	0.001_8	0.002_1	0.002_3	0.001_1	0.000_9	0.001_5
ν(cm^{-1})	803 ±18[c]	814 ±23[c]	872 ±34[c]	1020 ±33[c]	1109 ±42[c]	

a) $g^0(J_{K_{-1}K_1})$ and $g^{\mathrm{v}}(J_{K_{-1}K_1})$ denote the spin weights of the $J_{K_{-1}K_1}$ rotational level for the ground and excited vibrational states, respectively. b) Since Stark components were not fully resolved, the value was not used in the subsequent analysis. c) 2.5 times the standard deviations introduced by $\exp(-h\nu/kT)\cdot g^{\mathrm{v}}/g^0$ are indicated.

Now, this fact can be understood as arising from the degeneracy of the hydrogen nuclear spin states. Namely, the symmetry requirement for the composite wave functions formed by the vibrational, rotational, and nuclear spin parts leads to the following statement for the present C_{2v} case:[26] in the vibrational states of the A_1 and A_2 species, ee and oo type rotational levels are associated with a 10-fold nuclear spin weight, while eo and oe levels are associated with a 6-fold weight, with the situation in the B_1 and B_2 vibrational states, however, being inverted, *i.e.*, ee and oo are 6-fold while eo and oe are 10-fold. Then, since the ground state is necessarily an A_1 species, the Γ of the A_1 and A_2 states should be equal to the vibrational Boltzmann factor irrespective of the type of rotational transition. In B_1 and B_2 states, however, the Γ of ee↔oo type and eo↔oe type transitions prove to be equal to 6/10 and 10/6 times the Boltzmann factor, respectively. Thus, it is evident from Table 4 that ν_a and ν_b are of the B-type species and the rest are of the A-type. The energy of each vibrational state is calculated from the Boltzmann factor obtained as is given in Table 4. Slight changes in the dipole moment, rotational energies, and line widths in different vibrational states were ignored in the above discussion, as they are not expected to influence the conclusion significantly.

Referring to Table 3, it is noted that the rotational constant C and the centrifugal distortion constant τ'_{cccc} of the ν_b and ν_c states show unusually large deviations from those of the ground state in opposite directions. This observation indicates the presence of a c-type Coriolis interaction between the ν_b and ν_c states. It can be shown that the Coriolis terms in α^c and τ'_{cccc} are approximately given by $\mp 4C^2(\zeta_{b,c}^{(c)})^2/(E_b-E_c)$ and $\mp 64C^4(\zeta_{b,c}^{(c)})^4/(E_b-E_c)^3$, where the upper and lower signs refer to the ν_b and ν_c states at the vibrational energies E_b and E_c respectively.[16,18,27] Taking the conclusion of the preceding paragraph into consideration, the Coriolis coupling constant $\zeta_{b,c}^{(c)}$ proves to vanish except when the ν_b and ν_c states belong to either B_1 and A_1 or B_2 and A_2 species. Accordingly, after comparing the ν_b and ν_c energies in Table 4 with those in Table 1, their possible assignments are reduced to the following two cases: (i) ν_b to ν_{12} (B_1, ring deform) and ν_c to ν_5 (A_1, ring deform), or (ii) ν_b to ν_{15} (B_2, CH_2 rock) and ν_c to ν_8 (A_2, CH_2 rock). A tentative calculation using the force field fitted to the assignment of Lord and Nolin gives $\zeta_{12,5}^{(c)}=0.9965$ and $\zeta_{15,8}^{(c)}=0.3689$.[28] Then, the Coriolis parts of α^c and τ'_{cccc} are calculated to be ±454 MHz and ±0.473 MHz in case (i), and ±62 MHz and ±0.009 MHz in case (ii), respectively. Comparing these results with Table 3, the assignment of case (i) appears to be more probable, though not definite because of the uncertainty in E_b-E_c value used above. Assuming case (i) above to be correct, ν_a, ν_d, and ν_e may be reasonably assigned to ν_{15} (B_2, CH_2 rock), ν_7 (A_2, CH_2 twist) and ν_4 (A_1, CH_2 wag), respectively, in view of their frequencies and symmetries (see Table 1). Then the situation arises that the present microwave results lack an assignment for the vibrational state ν_8 (A_2, CH_2 rock). As it is very unlikely that the present study should have missed a vibrational state as low as about 800 cm^{-1},[29] this means that the frequency of ν_8 should be higher than those proposed by other authors, as listed in Table 1. In fact, we observed several spectral lines in addition to those listed in Table 4 in the same frequency region, but their intensities gave little indication of the sixth vibrational state below 1000 cm^{-1}.

This conclusion is in fair agreement with the assignments of Hirokawa *et al.*[12] and the very recent one by Cant *et al.*[13] except for the location of ν_8 (A_2). The frequency of the last mode has, so far, always been based on solid spectra obtained at low temperature,[7,10,13] for which the infrared prohibition of A_2 modes may perhaps be lifted. In solid spectra, however, the appearance of crystal field splittings has always to be taken into account in dealing with such closely lying lines as 825 and 818 cm^{-1}, which have been assigned to ν_8 and ν_{12} by Cant *et al.* The present result suggests that they are not separate fundamental frequencies but are the split components of ν_{12}, contrary to the conclusions in Ref. 13. Incidentally, Cant *et al.* assigned the corresponding C_2D_4O frequencies at 587 and 779 cm^{-1}, but the former was also very close to the 595 cm^{-1} line which they assigned to ν_{15}. In view of their observation on a dilute C_2D_4O/C_2H_4O mixture, which gave only a single evident line near 590 cm^{-1}, it seems that the lines at 587 and 595 cm^{-1} are more likely to be the crystal field doublet of ν_{15}.

Finally, the possibility for case (ii) is mentioned, though it was previously discarded on the basis of Coriolis interaction behavior. Assuming the choice of case (ii), we can conclude that the ν_5 (A_1) state is missing in the present result, instead of ν_8. Such a case is very improbable, however, because the ν_5 frequency given in Table 1 has been established quite convincingly.

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29) There are two possible causes of missing the rotational lines of a vibrational state as low as about 800 cm^{-1}: (1) overlapping of the lines with those of the ground state, or (2) extremely strong Coriolis interaction which shifts all the transitions outside of the frequency region of the present observation. For the former case, all the three rotational constants of the vibrational state have to be equal to those of the ground state to within a few megahertz, thus, case (1) is unlikely though not impossible. Although, for the latter case, such a strong Coriolis interaction requires a fifth vibrational state located very close to the fourth state, none of the ν_a, ν_b, and ν_c states is perturbed as strongly and no rotational spectra that can be assigned to the fourth and fifth vibrational states were observed in this region. Furthermore, infrared and Raman spectra do not indicate the existence of the fifth state around 800 cm^{-1}. Therefore, this case can be ruled out.