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The Microwave Spectrum of Thiirane in Excited Vibrational States

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The microwave spectra in the ground and five low-lying vibrational states of $^{12}C_2H_4{}^{32}S$ and in the ground state of $^{12}C^{13}CH_4{}^{32}S$ and $^{12}C_2H_4{}^{34}S$ have been assigned to high-J transitions. The rotational and centrifugal distortion constants were derived. Four of the five vibrational states were found to be in Coriolis interaction in pairs; one of the pairs was identified as the symmetric and antisymmetric ring deformation modes, $\nu_5(A_1)$ and $\nu_{12}(B_1)$, but another pair was unexplicable from any of the previously reported vibrational assignments. The infrared and Raman spectra in the liquid and gas phases were examined, and the latter pair of vibrations was interpreted as $\nu_{14}(B_2)$ at 945 cm^{-1} and $\nu_8(A_2)$ at about 970 cm^{-1}. This novel assignment of ν_8 around 970 cm^{-1} was based on not only the results of microwave spectroscopy, but also on the observation of an unsymmetric band contour in the infrared spectrum of the gaseous sample.

The vibrational spectrum of thiirane has been studied by several authors;1–7) Thompson and Dupré1), who reported in 1940 their observation of the infrared spectrum in the gas phase and the Raman spectrum of the liquid state, proposed a molecular symmetry of C_{2v}, along with an assignment of the vibrational modes. The study by Thompson and Cave2) revised the assignment on the grounds that the band at 711 cm^{-1} which had been assigned to ν_{12} (ring deformation) in the previous paper was due to the impurity hydrogen cyanide, and that the polarization data from the Raman spectrum also reported in the previous paper were questionable because of the background haze introduced by the formation of a solid polymer during the measurement. Guthrie *et al.*3) reported the observation of the infrared spectra of the liquid thiirane and of the solid polymer which was deposited on the window of the cell, in addition to the calculation of thermodynamic quantities; they proposed an assignment which was different from the previous ones in the ordering of three pairs of modes. Brumant observed the Raman spectrum of liquid thiirane and the infrared spectrum of the solid polymer,4a) the Raman spectrum of the solid at 85 K,4b) and the infrared spectrum of the molecule in an argon matrix at 10 K.4c) The assignment given by Brumant4a) puts ν_7 and ν_8, which are of an infrared-inactive A_2 symmetry, at 1172 cm^{-1} and 900 cm^{-1} respectively. Venkatesuwarlu and Joseph calculated the force constants and mean-square amplitude of vibrations,5) and also the Coriolis coupling constants6) of ethylene oxide and thiirane on the basis of yet another assignment, one differing from those of the previous reports. A recent study by Hirokawa *et al.*7) of the infrared spectrum and the force field of ethylene oxide and thiirane deduced essentially the same assignment as that given by Thompson and Cave, except for the vibrations of A_2 symmetry. The assignments given thus far are compared in Table 1; it can be easily seen that the assignments are not conclusive for the ν_7 and ν_8 modes, as has been pointed out by Hirokawa *et al.* In most of the above studies, the assignment of ethylene oxide is referred to; one of them also refers to the assignment of aziridine.

The observation of the microwave spectrum in excited vibrational states is known to provide complementary information on the vibrational assignment. A recent study of the microwave spectrum of ethylene oxide,8) for instance, cast doubt on the previous assignments which place the ν_8 mode (CH_2 twisting of A_2 symmetry) at about 800 cm^{-1}, because it identified but one vibrational state of symmetric (with respect to C_2 operation) species around 800 cm^{-1} which was assigned to the ν_5 mode (ring deformation of A_1 symmetry) on the basis of the analysis of vibration-rotation interaction. The study concluded that the lowest possible state of A_2 symmetry, ν_8, of ethylene oxide is at about 1000 cm^{-1}.

Table 1. Comparison of vibrational assignments (cm^{-1})

Mode		Set 1a)	Set 2a)	Set 3a)	Set 4a)	Set 5a)
ν_1:	CH str.	3017	3000	2993	3017	3012
ν_2:	CH_2 sci.	1471	1446	1450	1471	1454
ν_3:	CH_2 wag.	1101	1025	1027	(1040)	1109
ν_4:	ring breath.	—	1112	1115	(1107)	1024
ν_5:	ring def.	626	625	616	626	624
ν_6:	CH str.	3089	3080	3070	3089	3088
ν_7:	CH_2 rock.	—	875	1172	(971)	891
ν_8:	CH_2 twist.	660	1100	900	660	800
ν_9:	CH str.	(3017)	3000	2993	3017	3012
ν_{10}:	CH_2 sci.	1440	1427	1432	1440	1434
ν_{11}:	CH_2 wag.	1050	1051	1050	1050	1050
ν_{12}:	ring def.	685	660	655	685	660
ν_{13}:	CH str.	(3089)	3080	3070	3089	3088
ν_{14}:	CH_2 rock.	945	824	946	945	945
ν_{15}:	CH_2 twist.	825	943	822	825	824

a) 1; Ref. 2, 2; Ref. 3, 3; Ref. 4, 4; Ref. 5, 5; Ref. 7.

This paper will report on the microwave spectrum in the ground and five vibrational states of thiirane. The symmetry properties with respect to the C_2 operation of the respective vibrations were determined from the measurement of the relative intensities, and the effect of Coriolis interaction was observed as a vibrational dependence of the centrifugal distortion. The infrared spectrum of the gas phase and the Raman spectra of the liquid and gas phases were also studied, and the existence of strong interactions among sets of vibrational modes was indicated by the peculiar band shape and/or polarization-depolarization character of the Raman bands. The results of the infrared and Raman spectra will be excerpted to help in the analysis of the microwave spectrum.

Experimental and Results

The sample of thiirane was a distilled fraction of the product of the reaction of ethylene carbonate with potassium thiocyanate;[9] the sample container was wrapped with aluminum foil to inhibit the photochemical decomposition. White particles precipitated slowly during storage, and the presence of ethylene was observed in the infrared spectrum of the gas when sampled without purification. The impurities were removed by evacuating a liquid sample cooled by dry ice and by a subsequent trap-to-trap transfer of the liquid. The NMR spectrum of the distilled liquid showed peaks above 6 ppm with intensities less than 0.1% of the main peak at 3 ppm; the impurities did not show up in the infrared spectrum of a gaseous sample from the outgassed liquid. The infrared spectrum of the gas showed little difference before and after letting the sample container stand for 40 hours and then placing it under sunlight for two hours. No solid deposit was observed on the KBr windows of the cell despite the previous reference to the phenomenon,[3] and all the lines disappeared when the cell was evacuated. It should be mentioned, though, that the intensity of the microwave absorption lines diminished slowly to about half their original height in a couple of hours, without any new line developing; this indicates that the decomposition of the gas is accelerated on a metal (copper and stainless steel in the present case) surfaces, along with a production of a nonpolar gaseous material.

Microwave Spectrum. The microwave spectrum was observed using a conventional Stark modulation spectrometer. The measurement was performed at room temperature of about 293 K. The assignment of the rotational transitions for $^{12}C_2H_4{}^{32}S$, $^{12}C^{13}CH_4{}^{32}S$, and $^{12}C_2H_4{}^{34}S$ from the previous reports[10,11] was extended to transitions with higher J numbers and, for $^{12}C_2H_4{}^{32}S$, to forbidden transitions. The transitions in five excited vibrational states were also assigned on the basis of the Stark effects, the relative intensities, and the spectral pattern. The five states are tentatively designated as ν_a, ν_b, ν_c, ν_d, and ν_e. The results were analyzed by a least-squares method which included centrifugal distortion to the first order. Table 2* lists the observed frequencies of the assigned transitions, along with their differences from the calculated values. The converged values of the parameters are given in Table 3, along with their reliability intervals of 2.5 times the variances. A preliminary analysis indicated that the higher-order effect of centrifugal distortion becomes significant for the transitions with J numbers exceeding 30. Because the transitions with high J numbers are of the Q branch,[12] the inclusion of higher-order effects from centrifugal distortion is not expected to result in any meaningful values to the newly included parameters. Therefore, the higher-order effects in the least-squares fit, which included centrifugal distortion to the first order, were made insignificant by appropriately weighting the larger J transitions; weighting 1 for transitions with the J values less than 20, 0.01 for the J values from 21 to 30, 0.0001 for the J values between 31 and 50, and 0.000001 for the J values of more than 51, with the exception of the forbidden transitions of the ground state of $^{12}C_2H_4{}^{32}S$, for which the intensity of each transition was taken into account.

The measurement of the spectral intensities was only semi-quantitative because of the wide spread of the transition frequencies by vibrational state, and the instrumental instability.** Nonetheless, it was possible to derive the symmetry properties of the vibrations, along with a rough estimate of the vibrational frequencies, from the measured intensities shown in Table 4. A number of lines were left unassigned, but, judging from their intensities, these lines were from vibrational states higher than those for which rotational transitions were identified. The unassigned lines included some of the $J=1\leftarrow0$ and $J=2\leftarrow1$ transitions of ^{33}S species which have been assigned by Shoemaker and Flygare.[13]

The presence of Coriolis interactions between ν_a and ν_b and between ν_c and ν_e is suggested by the large values of the vibration-rotation constants, $\alpha_v{}^{(c)}$'s, which exceed 1% of the rotational constant, C_0, of the ground state. This becomes evident when one compares the vibrational change in the corrections for the centrifugal distortion (Fig. 1). The assignment of the two lowest vibrational states, ν_a and ν_b, to the symmetric and antisymmetric ring deformations, ν_5 and ν_{12}, is rather straightforward. The calculation by Venkatesuwarlu and Joseph gives $\zeta_{5,12}{}^{(c)}=-0.882$, indicating that the Coriolis interaction between the two states should indeed be appreciable about the c-axis. The Coriolis terms in the $\alpha_5{}^{(c)}$ and $\alpha_{12}{}^{(c)}$ constants through $\zeta_{5,12}{}^{(c)}$ are calculated to be $+279$ MHz and -236 MHz respectively by taking the vibrational frequencies of $\nu_5=624\ \mathrm{cm^{-1}}$ and $\nu_{12}=660\ \mathrm{cm^{-1}}$. The above terms are dominant in the harmonic terms in $\alpha_5{}^{(c)}$ and $\alpha_{12}{}^{(c)}$, as the contributions from other Coriolis terms are

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* Table 2 is deposited as Document No. 7612 at the office of the Editor of the Bulletin of the Chemical Society of Japan. Available from the authors on request.

** The transitions used for the measurement of the relative intensities were $1_{0,1}\leftarrow0_{0,0}$, $2_{0,2}\leftarrow1_{0,1}$, $5_{2,3}\leftarrow5_{2,4}$, $7_{2,5}\leftarrow7_{2,6}$, $2_{1,1}\leftarrow1_{1,0}$, $2_{1,2}\leftarrow1_{1,1}$, $3_{1,2}\leftarrow3_{1,3}$, $8_{3,5}\leftarrow8_{3,6}$, and $9_{3,6}\leftarrow9_{3,7}$. The spectral lines of the ^{34}S species, which has the abundance ratio of 4.22% were used as the internal standard instead of those of the normal species in order to avoid the possible saturation of lines and instrumental nonlinearity. A variable attenuator was inserted between the preamplifier and the main amplifier; the depth of attenuation was varied until the spectral line was of the same intensity as the corresponding transition of the ^{34}S species. Although the error in each measurement was from 0.5 to 1 dB, the overall error was estimated to be 2 dB because of the instrumental instability and the possible reflection of microwave power inside the cell. The latter may cause serious error with regard to the transitions of the ν_c, ν_d, and ν_e states since the rotational transitions in these states are widely separated from the corresponding lines of the ^{34}S species (see Table 2). Thus, it is quite possible that ν_d and ν_e are at 824 cm^{-1} and 945 cm^{-1} respectively, as will be estimated in the later part of this paper, despite the result derived from the measurement of the relative intensities of the rotational transitions.

TABLE 3. DERIVED ROTATIONAL, VIBRATION-ROTATION,

Species[b)]	A (α_v^A)[c)]	B (α_v^B)[c)]	C (α_v^C)[c)]	τ_{aaaa}
n, G. S.	21973.86±0.27	10825.11±0.13	8026.29±0.10	−0.182±0.008
^{34}S, G. S.	21972.97±0.67	10551.03±0.34	7874.58±0.22	−0.253±0.26
^{13}C, G. S.	21481.71±0.53	10653.40±0.29	7866.33±0.20	−0.417±0.20
ν_a (A)	+24.69±0.93	+42.95±0.43	+143.81±0.29	−0.509±0.27
ν_b (B)	−70.48±1.1	+79.84±0.57	−54.57±0.38	+0.300±0.33
ν_c (A)	−16.12±1.8	+34.50±0.88	−84.73±0.58	−0.407±0.57
ν_d (B)	−19.73±0.83	+45.87±0.36	+36.57±0.25	−0.123±0.21
ν_e (B)	+67.50±0.82	−0.20±0.39	+99.92±0.27	−0.211±0.23

a) τ_{aacc} was assumed to be zero in the least-squares fit. 2.5 times variances are listed as reliability intervals. state, and ν_a to ν_e: vibrational states of $^{12}C_2H_4{}^{32}S$ with their symmetry properties with respect to C_2 being indi- vibrational states.

TABLE 4. SYMMETRY AND ESTIMATED FREQUENCIES OF VIBRATIONS AS DERIVED FROM THE RELATIVE INTENSITY MEASUREMENT

State	Symmetry[a)]	(cm^{-1})[b)]	Proposed assignment[c)]
ν_a	A_1 or A_2	680 (580—890)	ν_5(624 cm^{-1})
ν_b	B_1 or B_2	710 (640—810)	ν_{12}(660 cm^{-1})
ν_c	A_1 or A_2	920[c)] (850—1050)	ν_7 or ν_8(970 cm^{-1})
ν_d	B_1 or B_2	950 (860—1120)	ν_{15}(824 cm^{-1})
ν_e	B_1 or B_2	800 (700—1020)	ν_{14}(945 cm^{-1})

a) Symmetry properties with respect to the C_{2v} group are indicated. b) Statistical error limits of 2.5 times variances in the relative intensity measurement are transformed and shown in parentheses to indicate the reliability intervals of the derived frequencies. c) Values in parentheses are those reported in Ref. 7 except for that of ν_c which is estimated from the analysis of Coriolis coupling between ν_c and ν_e and the band contour of infrared spectrum of the gas sample in the present study.

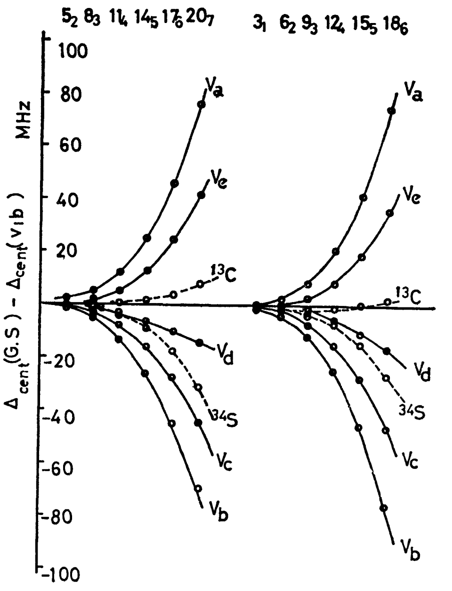

Fig. 1. Vibrational change in the corrections for the centrifugal distortion, $\Delta_{cent}(G.S.)-\Delta_{cent}(v_i)$, and the isotope change are plotted.
Solid and broken lines are drawn to identify the species.

estimated to be within a few megahertz. They are proportional to the inverse of the vibrational difference, $\nu_5-\nu_{12}$, to a good approximation. The observed values are 143.81 MHz and −54.57 MHz for $\alpha_5{}^{(c)}$ and $\alpha_{12}{}^{(c)}$ respectively; the rather large difference between the observed and the calculated values indicates that the ν_{12}-ν_5 separation is larger than 26 cm^{-1}, although the value is derived from the most recent assignment.[7)] At the same time, the anharmonic terms in the α constants are expected to be of the order of 10 MHz, because when one fits the Coriolis terms in $\alpha_5{}^{(c)}$ to 140 MHz by putting $\nu_{12}-\nu_5$ to 52 cm^{-1}, there remains a difference of about 60 MHz between the Coriolis term and the observed value of $\alpha_{12}{}^{(c)}$. A similar situation was encountered in the α constants of ethylene oxide.[8)]

The large departure of the centrifugal distortions of the ν_a and ν_b states, each in opposite directions from the ground state seen in Fig. 1, also distinctly shows the presence of the Coriolis interaction. The large uncertainties that accompany the converged values of the centrifugal distortion constants except for those of the ground vibrational state of normal species unfortunately restricted the analysis of the effect and made it semiquantitative.

The almost identical behavior of the pair of ν_c and ν_e to that of ν_b and ν_a in both the $\alpha^{(c)}$ constants and centrifugal-distortion effects strongly suggests another c-type Coriolis interaction between ν_c and ν_e states, with the vibrational frequency ν_c being slightly more than the ν_e. The study of the infrared and Raman spectra which will be outlined in the next section shows that the second lowest antisymmetric vibration is ν_{15} at 824 cm^{-1}; this band is assigned to the CH_2 twisting mode. Other possible candidates for ν_d and ν_e, which are antisymmetric vibrations, are ν_{14} (CH_2 rocking mode) at 945 cm^{-1} and ν_{11} (CH_2 bending mode) at 1050 cm^{-1}. Our results show that ν_c is the second lowest vibration of A symmetry, that is either $\nu_4(A_1)$ or $\nu_8(A_2)$, and we have already mentioned that no conclusive assignment has been given to the ν_7 and ν_8 modes by the study of the vibrational spectra. The values which determine the Coriolis coupling are listed in Table 5, the coupling constants used in the table being excerpted from the paper by Venkatesuwarlu and Joseph.[6)] Although the values may change when

AND CENTRIFUGAL DISTORTION CONSTANTS (in MHz)[a]

	τ_{bbbb}	τ_{cccc}	τ_{aabb}	τ_{bbcc}
n, G. S.	-0.067 ± 0.003	-0.023 ± 0.002	-0.179 ± 0.01	-0.048 ± 0.003
^{34}S, G. S.	-0.016 ± 0.14	$+0.014\pm0.14$	-0.042 ± 0.25	$+0.018\pm0.17$
^{13}C, G. S.	-0.082 ± 0.12	-0.055 ± 0.12	-0.153 ± 0.22	-0.054 ± 0.15
ν_a (A)	-0.027 ± 0.12	$+0.031\pm0.12$	-0.054 ± 0.22	$+0.023\pm0.15$
ν_b (B)	-0.087 ± 0.18	-0.069 ± 0.18	-0.191 ± 0.33	-0.097 ± 0.21
ν_c (A)	-0.071 ± 0.31	-0.063 ± 0.31	-0.100 ± 0.56	-0.046 ± 0.37
ν_d (B)	-0.085 ± 0.09	-0.049 ± 0.09	-0.172 ± 0.17	-0.076 ± 0.11
ν_e (B)	-0.036 ± 0.11	$+0.016\pm0.11$	-0.105 ± 0.19	-0.006 ± 0.13

b) n, G. S.: $^{12}C_2H_4{}^{32}S$ in ground state, ^{34}S, G. S.: $^{12}C_2H_4{}^{34}S$ in ground state, ^{13}C, G. S.: $^{12}C^{13}CH_4{}^{32}S$ in ground
cated in parentheses. c) Vibration-rotation constants ($\alpha_v^B=X_0-X_v$, $X=A$, B, or C) are listed for excited

TABLE 5. CONSTANTS THAT CAN PARTICIPATE IN CORIOLIS INTERACTION (in MHz)[a)]

$C\zeta^{(c)}_{3,11}$	1585		
$C\zeta^{(c)}_{3,12}$	-51	$C\zeta^{(c)}_{7,14}$	1462
$C\zeta^{(c)}_{4,11}$	1422	$C\zeta^{(c)}_{7,15}$	6175
$C\zeta^{(c)}_{4,12}$	-3186	$C\zeta^{(c)}_{8,14}$	-6154
$C\zeta^{(c)}_{5,11}$	-2015	$C\zeta^{(c)}_{8,15}$	2423
$C\zeta^{(c)}_{5,12}$	-7078		

a) As for the types of vibrations, see set 4 of Table 1. Contributions of Coriolis terms to $\alpha_v^{(x)}$ and the centrifugal distortion constants are expressed as;

$$\Delta\alpha^{(x)}_{v,v'}(\text{Coriolis}) = -8c/\nu_v\cdot\nu^2_{v'}/(\nu^2_v-\nu^2_{v'})\cdot(X\zeta^{(x)}_{v,v'})^2$$

$$\Delta\tau^{v,v'}_{xxxx}(\text{Coriolis}) = c'(\nu_v+\nu_{v'})^4(X\zeta^{(x)}_{v,v'})^4/(\nu_v-\nu_{v'})^3\nu^2_v\nu^2_{v'}$$

where $\Delta\alpha^{(x)}_{v,v'}$ and $\Delta\tau^{v,v'}_{xxxx}$ are the contribution to the vibration-rotation constant $\alpha_v^{(x)}$ and the centrifugal distortion constant τ_{xxxx} in the v-state, respectively, ν_v and $\nu_{v'}$ are the vibrational frequencies of ν_v and $\nu_{v'}$ modes, c and c′ are the constants to give proper units to the quantities, and X is the rotational constant A_0, B_0, or C_0 depending on the principal axis of inertia denoted by x.

other vibrational assignments are used, the changes are expected to be small, as is the case in ethylene oxide. Table 5 indicates that the two pairs, ν_7 and ν_{15}, and ν_8 and ν_{14}, are capable of similar interaction, and thus likely candidates for the ν_c and ν_e pair. The infrared spectrum of the gaseous sample shows a band contour at 945 cm^{-1} (ν_{14}) unsymmetric about the sharp Q-branch peak. The perturbation through Coriolis interaction between ν_{14} and ν_8 modes is a plausible explanation for the peculiar band shape; the assignment of ν_c and ν_e to ν_8 and ν_{14} respectively is then more likely than the other sets. The remaining state, ν_d, can then be assigned to ν_{15} at 825 cm^{-1}. Thus the present study of the microwave spectrum suggests the assignment of ν_8 at 970±5 cm^{-1}.

Infrared and Raman Spectra. The vibrational spectrum of thiirane was reexamined; the infrared spectrum in the gas phase was observed from 400 cm^{-1} to 10000 cm^{-1} using a Perkin-Elmer 125 spectrograph, while the Raman spectrum was recorded on a JEOL model JRS-Sl spectrometer in both gas and liquid phases by using a 488-nm line of the Ar$^+$ laser (Coherent Radiation CR-52G) as the exciting source. The sample was outgassed prior to each measurement to get rid of the ethylene impurity produced by decomposition. The cell used for the infrared spectrum was a 10-cm-long Pyrex tube with KBr windows. The liquid sample for the Raman spectrum was distilled and sealed in a conventional cell made of a Pyrex tube of about 8 mm i. d., while the Raman spectrum of the gas was recorded at a pressure of 148 Torr using a multipass configuration of about 30 beams.

A summary of the Raman spectrum is given in Table 6, with the previous observation by Brumant in the liquid phase being given for reference. The infrared spectrum of gaseous thiirane from 800 to 1180 cm^{-1} is shown in Fig. 2. Corresponding to a weak Q-branch peak observed in the infrared spectrum, the Raman spectrum of the liquid sample showed a depolarized band at 825 cm^{-1}, leading us to the assignment of this band to the lowest mode of B$_2$ symmetry, ν_{15}. The polarized Raman band at 1607 cm^{-1} can then be readily assigned to the overtone, $2\nu_{15}$. A very weak band was observed in the Raman spectrum of the liquid sample; it was also reported by Brumant[4b)] at 895 cm^{-1}. The observation of this band in the infrared spectrum too was reported by Hirokawa *et*

TABLE 6. SUMMARY OF RAMAN BANDS OF THIIRANE (in cm^{-1})

liquid[a)]		gas[b)]	liquid[a)]		gas[b)]
612*	s,P	632	1430	m	1434$^+$
650	m	662$^+$	1448	m,P	1454$^+$
825	w,dP		1607	m,P	
895	vw,P?		2230*	w,P	
947	w,dP		2845	m,P	2860
1023	m,P	1028	2885	m,P	2900
1113	s,P	1115	(2904)		
(1172)			2995	vs,P	3011
1235	w,P		3076	m	3060$^+$
1377*	w,P				

a) Bands that are not reported in Ref. 4b is indicated by * while the bands which were not observed in the present study despite the reported observation (Ref. 4b) as very weak bands are indicated in parentheses. Intensities are indicated by; vs: very strong, m: moderately strong, w: weak, and vw: very weak. Polarized bands are indicated by the letter P. b) Bands with broad contour are indicated by $^+$.

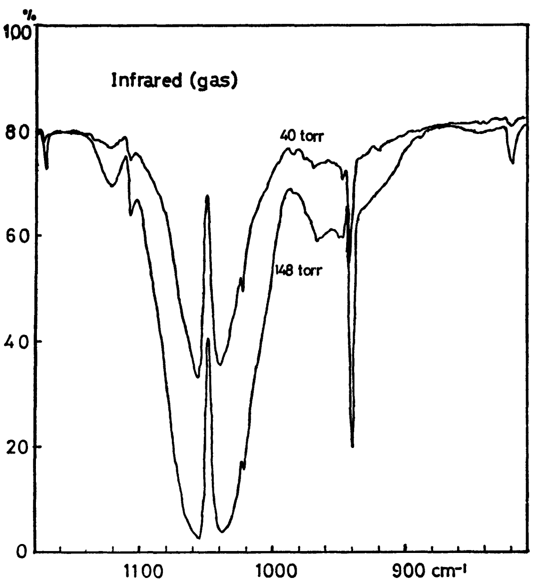

Fig. 2. Infrared spectrum of thiirane at gas phase between 810 to 1180 cm^{-1}.

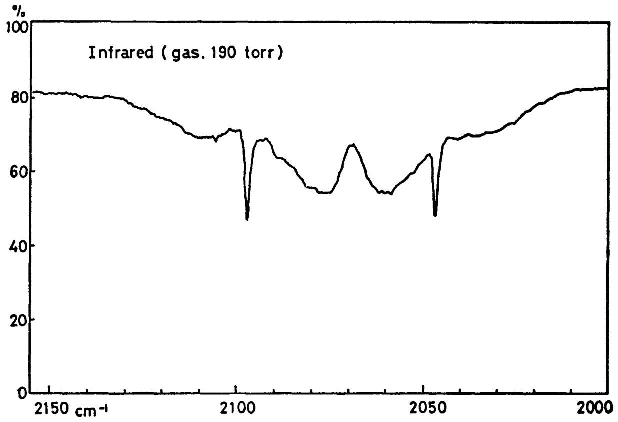

Fig. 3. Infrared spectrum of thiirane in the overtone region of 2000—2150 cm^{-1}.
A B-type band center is situated between the A-type Q-branches of overtones.

al.,[7] who assigned it to the infrared-inactive ν_7 mode, but the present study failed to detect it (see Fig. 2). Since all of the infrared-active fundamentals are found at other frequencies, the band at 895 cm^{-1} has to be interpreted either as an infrared-inactive ν_7 or ν_8 or as due to some impurity. There is no infrared band near 895 cm^{-1} which can give some intensity to an infrared-inactive mode through Coriolis interaction; thus, the assignment of ν_7 or ν_8 at 895 cm^{-1} can be ruled out if the observation by Hirokawa *et al.* is to be retained.

Four vibrational modes have been assigned in the region from 900 to 1200 cm^{-1}; two CH$_2$ bending modes, $\nu_3(A_1)$ at 1109 cm^{-1} and $\nu_{11}(B_1)$ at 1050 cm^{-1}, a ring breathing, $\nu_4(A_1)$ at 1024 cm^{-1}, and a CH$_2$ rocking mode, $\nu_{14}(B_2)$ at 945 cm^{-1}.[7] The Raman spectrum of the liquid gave one depolarized band at 947 cm^{-1} and two polarized bands at 1023 and 1113 cm^{-1}. The two polarized bands were also observed in the Raman spectrum of the gas phase. A polarized band was observed at the overtone region of 2230 cm^{-1} in the liquid phase. Although the infrared spectrum of this region is quite complicated, as may be seen from Fig. 2, the assignment of the bands is rather straightforward: $\nu_{14}(B_2)=945$ cm^{-1}, $\nu_4(A_1)=1024$ cm^{-1}, $\nu_{10}(B_1)=1050$ cm^{-1}, and $\nu_3(A_1)=1109$ cm^{-1}, when one takes the Raman results into account. The assignment cf lines at 1024 and 1050 cm^{-1} is further confirmed by the appearance of two A-type bands and a B-type band center in between them in the overtone region of the infrared spectrum, as is shown in Fig. 3.

The infrared spectrum shows an anomalous shoulder on the R-branch side of ν_{14} at 945 cm^{-1}. The pressure dependence of the shoulder indicates that it originates from the sample itself. As vibrational modes of A$_1$, B$_1$, and B$_2$ symmetry species are identified at other frequencies, as has been mentioned before, the shoulder can be explained as resulting from the intensity borrowing of an A$_2$ mode through the Coriolis interaction with ν_{14}. Judging from the values of the Coriolis coupling terms listed in Table 5, the assignment of the symmetric CH$_2$ twisting at about 970 cm^{-1} is probably the most reasonable. Finally, the weak band observed at 1172 cm^{-1} in the infrared spectrum was explained by Hirokawa *et al.* as due to a polymer,[7] but the pressure dependence of the band (see Fig. 2) seems to indicate that the band is from the sample itself. The explanation is open to speculation at the moment, but it should be remembered that weak and polarized Raman bands were observed at 1230 and 1377 cm^{-1} which can best be explained as the $2\nu_5$ and $2\nu_{12}$ overtones respectively.

Conclusion

Of the five vibrational states for which the rotational spectrum has been identified, the lowest two states, ν_a and ν_b, are in resonance through a Coriolis term; they were assigned to ν_5 and ν_{12} (symmetric and antisymmetric ring deformation modes). Another coupling between the ν_c and ν_e, as observed in the microwave spectrum, indicates the assignment of ν_c to ν_8 (CH$_2$ twisting) of A$_2$ symmetry and ν_e to ν_{14} (CH$_2$ rocking) at about 970 cm^{-1} and 945 cm^{-1} respectively. The fact that ν_c is slightly more than ν_e and that the ν_4 and ν_{11} states are free from Coriolis interactions, as seen by the infrared spectrum in the overtone region (Fig. 3), excludes the assignment of ν_c and ν_e to ν_8 at 970 cm^{-1} and ν_{15} at 824 cm^{-1} or to ν_4 at 1024 cm^{-1} and ν_{11} at 1050 cm^{-1}, respectively. The complicated-looking band contour observed in the infrared spectrum around 950 cm^{-1} supports the present assignment. The remaining state, ν_d, which is antisymmetric to the C$_2$ operation, is assigned to ν_{15} (CH$_2$ twising) at 824 cm^{-1}, the lowest vibration of B$_2$ symmetry and the second lowest of the antisymmetric modes. The very weak Raman band at 895 cm^{-1}, which Hirokawa *et al.* claim to have observed also in the infrared spectrum of the gas phase, may be the remaining mode of A$_2$ symmetry, although its appearance in the infrared spectrum would present a serious contradiction to this assignment since there is no neighboring band which can couple with and give away a part of its infrared intensity to the infrared-inactive ν_8 mode. Thus, the band at 895 cm^{-1} may well be due to an impurity. In any event, there is little chance for the ν_8 mode to be around the previously estimated 800 cm^{-1}. This conclusion is in accord with that obtained for ethylene oxide.$^{8)}$

The present study revealed the existence of couplings among several sets of vibrations and suggests the need of further investigations to establish the vibrational assignment of thiirane.

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References

1) H. W. Thompson and D. J. Dupré, *Trans. Faraday Soc.*, **36**, 805 (1940).

2) H. W. Thompson and W. T. Cave, *ibid.* **47**, 951 (1951).

3) G. B. Guthrie, Jr., D. W. Scott, and G. Waddington, *J. Am. Chem. Soc.*, **74**, 2795 (1952).

4) a) L. LeBrumant, *C. R. Acad. Sci. Paris*, *Ser. B*, **266**, 283 (1968) b) J. LeBrumant, *ibid*, **268**, 486 (1969), c) J. LeBrumant, *ibid*, **270**, 801 (1970).

5) K. Venkatesuwarlu and P. A. Joseph, *J. Mol. Struct.*, **6**, 145 (1970).

6) K. Venkatesuwarlu and P. A. Joseph, *Ind. J. Pure Appl. Phys.*, **10**, 754 (1972).

7) T. Hirokawa, M. Hayashi, and H. Murata, *J. Sci. Hiroshima Univ.*, **37A**, 2831 (1973).

8) N. Yoshimizu, C. Hirose, and S. Maeda, *Bull. Chem. Soc. Jpn.*, **48**, 2529 (1975).

9) *Org. Synth.*, **42**, 59 (1962).

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

11) K. Okiye, C. Hirose, D. G. Lister, and J. Sheridan, *Chem. Phys. Lett.*, **24**, 111 (1974).

12) Q-branch transitions were classified into several sets as indicated in Table 2; successive transitions in a set have J values changing by 3 and K_{-1} by 1. This classification was of help in predicting the transitions to be measured.

13) R. L. Shoemaker and W. H. Flygare, *J. Am. Chem. Soc.*, **90**, 6263 (1968).