

# The Rotation-Vibrational Spectra and Structures of Ethane, and Dimethyl Ether, Sulphide, Selenide and Telluride

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(Received October 31, 1974)

## Abstract

There are two possible configurations for  $\text{H}_3\text{C-X-CH}_3$  ( $\text{X}=\text{O}, \text{S}, \text{Se}, \text{Te}$ ), linear or bent C-X-C, the latter having  $C_{2v}$  symmetry. For a linear model the methyl groups may be staggered,  $D_{3d}$  or eclipsed,  $D_{3h}$ . A bent model,  $C_{2v}$  allows 21 fundamentals, all of which are active in Raman and 17 of which are active in infrared. This means that a  $C_{2v}$  symmetry should have 17 coincidences between Raman and infrared spectra among 21 fundamental frequencies.

The obtained spectra indicate the general simplicity of the spectra and the lack of coincidence between Raman and infrared frequencies. In addition, the rotation-vibrational band contours consist of a family of  $Q$  branches having an intensity alternation for degenerate infrared ones, which indicates the existence of  $C_3$  symmetry about the C-X-C axis of rotation. Consequently, the linear models are strongly supported for  $\text{H}_3\text{CXCH}_3$  type molecules and, of the linear configurations, the eclipsed  $D_{3h}$  form is eliminated, because a  $D_{3h}$  symmetry should indicate the coincidence between Raman and infrared frequencies in  $E'$  species. Above all, it seems to the authors sufficient evidence to justify a linear skeleton for  $\text{H}_3\text{CXCH}_3$  that an intensity alternation in  $Q$  branch sequence of perpendicular band( $E_u$ ) is observed.

However the final decision must await the results of the further studies, because structure of  $\text{H}_3\text{CXCH}_3$  type molecule has been determined from electron diffraction and microwave spectroscopy to be approximately  $C_{2v}$  symmetry.

The Raman spectra are recorded on *JEOL JRS-S1B* spectrophotometer using  $\text{Ar}^+$  laser and the infrared spectra are measured with *Shimadzu IR-450* spectrometer, whose gas cell had a path of 10 cm and *KRS-5* windows.

## 1. Introduction

There are two possible structures for C-X-C skelton, linear or bent, the latter

having  $C_{2v}$  symmetry. For a linear model the methyl groups may be staggered,  $D_{3d}$ ; eclipsed,  $D_{3h}$ ; or there may be free rotation,  $D'_{3h}$ .  $D_{3h}$  and  $D'_{3h}$  are governed by the same selection rules.<sup>1)</sup> A bent model,  $C_{2v}$  allows 21 fundamentals, all of which are active in Raman and 17 of which are active in infrared. Accordingly a  $C_{2v}$  symmetry should have 17 coincidences between Raman and infrared spectra among 21 fundamental frequencies. The obtained spectra indicate the lack of coincidence between Raman and infrared frequencies, which means the existence of symmetry center, and the general simplicity of the Raman and infrared spectra. Consequently a  $C_{2v}$  symmetry and of the linear configurations, the eclipsed  $D_{3h}$  symmetry which has coincidence between Raman and infrared in  $E'$  species are eliminated.

On the other hand, the Raman and infrared spectra of  $H_3C-X-CH_3$  ( $X=O,S,Se,Te$ ) type molecules have hitherto been investigated and assigned on the basis of  $C_{2v}$  symmetry. The present authors have therefore found it worthwhile to investigate the structures of  $H_3C-X-CH_3$  type molecules by studying the vibrational spectra and by comparing the spectra with those of structurally related molecule ethane( $D_{3d}$ )<sup>2)</sup>.

## 2. Experimental

Dimethyl ether( $H_3C-O-CH_3$ ) was prepared by dehydration of methanol with concentrated 98 % sulphuric acid, and dimethyl selenide ( $H_3C-Se-CH_3$ ) was synthesized according to the literature<sup>3)</sup>. The other samples, dimethyl sulphide ( $H_3C-S-CH_3$ ) and ethane ( $H_3C-CH_3$ ) were purchased from commercial sources and used after being purified by distillation or low temperature distillation.

Raman spectra are recorded on *JEOL JRS-S1B* spectrometer using argon ion laser (4888 Å), and the infrared spectra are measured with *Shimadzu IR-450* spectrometer, whose gas cell had a path of 10 cm and *KRS-5* windows.

## 3. Results and Discussion

The observed vibrational spectra of  $H_3C-CH_3$ ,  $H_3C-O-CH_3$ ,  $H_3C-S-CH_3$  and  $H_3C-Se-CH_3$  are shown in Fig. 1 and the frequencies of fundamental bands are given in Table 1<sup>\*1,4)</sup> together with the relative intensities, the states of polarization of Raman bands, the band type of infrared ones, and  $D_{3d}$  and  $D_{3h}$  selection rules.

### 3-1 Ethane<sup>2, 5-10)</sup>

There are two plausible configurations for ethane;  $D_{3h}$  model in which there is a plane of symmetry perpendicular to the three fold C-C axis, and  $D_{3d}$  model with a center of symmetry. For the  $D_{3d}$  symmetry whose irreducible representations is  $3A_{1g}(R,p) + 2A_{2u}(IR) + 3E_g(R) + 3E_u(IR)$ , the rule of mutual exclusion holds. For the  $D_{3h}$  model, on the other hand, whose irreducible representations is  $3A'_1(R,p) + 2A''_2(IR) + 3E''(R) + 3E'(R,IR)$ , the doubly degenerate vibrations( $E'$ ) exhibit both Raman and

\*1) The spectra of dimethyl telluride are cited from the literature<sup>4)</sup>.

infrared activity.

Eight or nine Raman bands are observed for the gas, some of which may correspond to overtone or combination bands, and the obtained spectra indicate the lack of coincidence between Raman and infrared frequencies. This seems to be sufficient

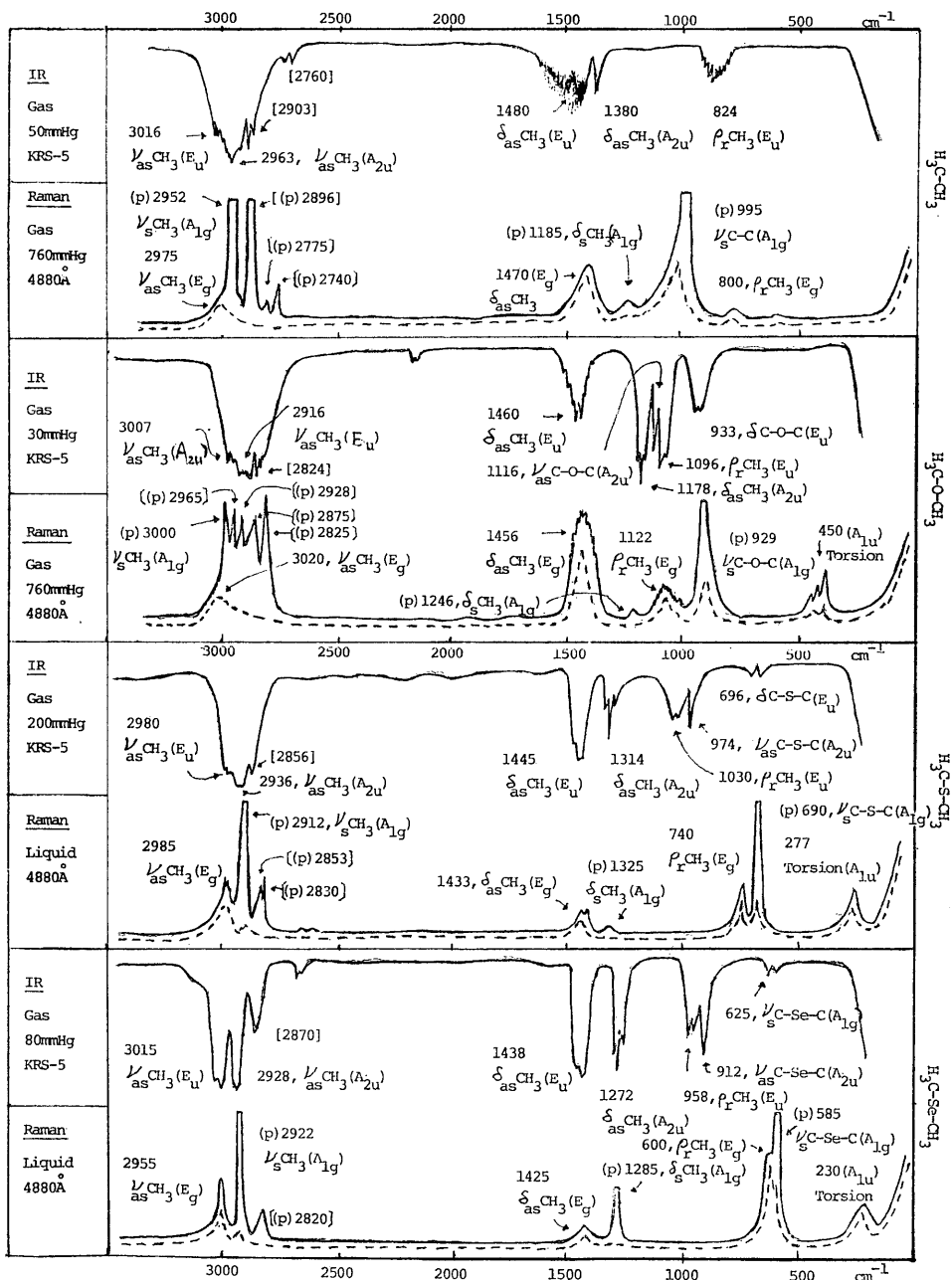


Fig. 1 Rotation-vibrational spectra of  $\text{CH}_3\text{CH}_3$  and  $\text{H}_3\text{CXCH}_3$  ( $\text{X}=\text{O,S,Se,Te}$ )

Table 1 Description, Character, Species, Activity and Bond Type of the Normal Vibrations of  $H_3C-CH_3$  and  $H_3C-X-CH_3$  ( $X=O,S,Se,Te$ )

Symmetry Species		Band Type, Activity Polarization State			$H_3C-CH_3$		$H_3C-O-CH_3$		$H_3C-S-CH_3$		$H_3C-Se-CH_3$		$H_3C-Te-CH_3^{4)}$	
$D_{3h}$	$D_{3d}$	Description	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR
$A'_1$	$A_{1g}$	$\nu_s CH_3$	(p)	—	(p) 2952vs	—	(p) 3000vs	—	(p) 2912vs	—	(p) 2922vs	—	(p) 2923	—
		$\delta_s CH_3$	(p)	—	(p) 1185w	—	(p) 1246w	—	(p) 1325w	—	(p) 1285m	—	(p) 1228	—
		$\nu_s C-X-C$	(p)	—	(p) 995vs	—	(p) 929vs	—	(p) 690vs	—	(p) 585vs	—	(?)	—
$A'_1$	$A_{1u}$	Torsion	—	—	—	(450)*	—	(277)*	—	(230)*	—	(198)*	—	
$A'_2$	$A_{2u}$	$\nu_{as} CH_3$	—	(  )	—	2963vs(  )	—	3007vs(  )	—	2936vs(  )	—	2928vs(  )	—	2942
		$\delta_{as} CH_3$	—	(  )	—	1380m(  )	—	1178s(  )	—	1314m(  )	—	1272s(  )	—	1225
		$\nu_{as} C-X-C$	—	(  )	(no)	(no)	—	1116m(  )	—	974m(  )	—	912s(  )	—	880
$E''$	$E_g$	$\nu_{as} CH_3$	(dp)	—	2975m	—	3020m	—	2985m	—	2995m	—	3000	—
		$\delta_{as} CH_3$	(dp)	—	1470m	—	1456s	—	1433m	—	1425w	—	1420	—
		$\rho_r CH_3$	(dp)	—	800w	—	1122m	—	740m	—	600m	—	528	—
$E'$	$E_u$	$\nu_{as} CH_3$	( $D_{3h}$ )	( $\perp$ )	—	3016vs( $\perp$ )	—	2916vs( $\perp$ )	—	2980vs( $\perp$ )	—	3015vs( $\perp$ )	—	3018
		$\delta_{as} CH_3$	( $D_{3h}$ )	( $\perp$ )	—	1480m( $\perp$ )	—	1460m( $\perp$ )	—	1445s( $\perp$ )	—	1438s( $\perp$ )	—	1426
		$\rho_r CH_3$	( $D_{3h}$ )	( $\perp$ )	—	824m( $\perp$ )	—	1096m( $\perp$ )	—	1030m( $\perp$ )	—	958m( $\perp$ )	—	843
		$\delta C-X-C$	( $D_{3h}$ )	( $\perp$ )	(no)	(no)	—	933m( $\perp$ )	—	696w( $\perp$ )	—	625w( $\perp$ )	—	529

— means inactive. ( $D_{3h}$ ) indicates that  $E'$  band of  $D_{3h}$  is Raman active, but  $E_u$  one of  $D_{3d}$  is Raman inactive.

(||) shows parallel type band and ( $\perp$ ), perpendicular type one. (no) means that  $H_3CCH_3$  does not have this vibration and ( ),\* that the band is inactive but appears due to interaction among molecules.

evidence to exclude the  $D_{3h}$  model. Therefore the  $D_{3d}$  model<sup>\*2)</sup> is assumed in subsequent discussion.

### 3-1-1 Raman Bands

3-1-1-1  $A_{1g}$  Bands ..... The three Raman active fundamentals belonging to  $A_{1g}$  species should give rise to polarized bands. The strong polarized Raman band at  $2896\text{ cm}^{-1}$  is not fundamental, but one of Fermi doublet(3-1-1-3). Accordingly there can be no doubt that the strong polarized band at  $2952\text{ cm}^{-1}$  which is the only strong polarized one in  $3000\text{ cm}^{-1}$  region is the symmetric methyl stretching vibration( $\nu_s\text{CH}_3$ ), since only one totally symmetric fundamental is expected in this region. The weak polarized band at  $1185\text{ cm}^{-1}$  is assigned to the symmetric methyl deformation( $\delta_s\text{CH}_3$ ), since the  $\delta_s\text{CH}_3$  bands of  $\text{H}_3\text{C-X-CH}_3$  ( $\text{X}=\text{O,S,Se,Te}$ ) usually appear at  $1200\sim 1300\text{ cm}^{-1}$  as weak polarized band. It is to be noted that in the case of dimethyl acetylene( $\text{H}_3\text{C-C}\equiv\text{C-CH}_3$ )<sup>11)</sup>, like those of  $\text{H}_3\text{C-X-CH}_3$ , the  $1380\text{ cm}^{-1}$  fundamental band which is assigned to  $\delta_s\text{CH}_3$  appears in the Raman effect. There remains the symmetric C-C stretching vibration( $\nu_s\text{C-C}$ ), to which the polarized  $995\text{ cm}^{-1}$  band is easily assigned.

3-1-1-2  $E_g$  Bands ..... The three Raman active fundamentals belonging to  $E_g$  species should give rise to depolarized bands. These can be readily identified with the three depolarized bands at  $2975(\nu_{as}\text{CH}_3)$ ,  $1470(\delta_{as}\text{CH}_3)$  and  $800(\rho_r\text{CH}_3)\text{ cm}^{-1}$ , since only one fundamental which is expected in  $3000\text{ cm}^{-1}$  region is the asymmetric methyl stretching vibration( $\nu_{as}\text{CH}_3$ ), the asymmetric methyl deformation( $\delta_{as}\text{CH}_3$ ) are remarkably constant(ca.  $1450\text{ cm}^{-1}$ ) throughout the molecules having methyl group and there remains the methyl rocking( $\rho_r\text{CH}_3$ ), to which  $800\text{ cm}^{-1}$  band should be assigned.

3-1-1-3 Overtone and Combination Bands ..... The polarized Raman band at  $2896\text{ cm}^{-1}$  might be considered as fundamental, but the bands at  $2896$  and  $2952\text{ cm}^{-1}$  form a doublet due to a Fermi resonance<sup>12)</sup>, whose center coincides very nearly with twice the wave number of the  $\delta_{as}\text{CH}_3$  band at  $1470\text{ cm}^{-1}$ . Therefore the  $2896\text{ cm}^{-1}$  band is not fundamental, but the (p)  $2952\text{ cm}^{-1}$  band corresponds to one fundamental only (3-1-1-1). The overtone is usually found to be medium, therefore the strong intensity of the overtone at  $2896\text{ cm}^{-1}$  seems due to a strong Fermi resonance of  $2\times\delta_{as}\text{CH}_3$  band with  $2952\text{ cm}^{-1}$  fundamental one. The polarized bands at  $2775$  and at  $2740\text{ cm}^{-1}$  seem due to overtone or combination, since only the symmetric methyl stretching mode is expected to lie in this region and the mode has already been assigned.

### 3-1-2 Infrared Bands

3-1-2-1  $A_{2u}$  Bands ..... This species contains two vibrations giving rise to parallel infrared bands having  $P$ ,  $Q$ , and  $R$  branches. The asymmetric methyl stretching band occurs, as expected, at  $2963\text{ cm}^{-1}$ , whose  $P$ - $R$  separation is observed to be  $38\text{ cm}^{-1}$  as shown in Fig. 2. The methyl deformation vibration band occurs at  $1380\text{ cm}^{-1}$  as expected. The  $P$  and  $R$  branches of this band are not observed, but the sharp  $Q$  branch shows clearly that the vibration is a parallel one.

\*2) The literature 2) strongly supports the  $D_{3d}$  model for ethane.

*3-1-2-2 E<sub>u</sub> Bands* ..... The three infrared active fundamentals should give rise to perpendicular type bands, which consists of a family of Q branches having an intensity alternation which indicates the existence of C<sub>3</sub> symmetry<sup>1,3)</sup> about the C-C axis of rotation. The infrared bands at 3016, 1480 and 824 cm<sup>-1</sup> can be readily assigned to

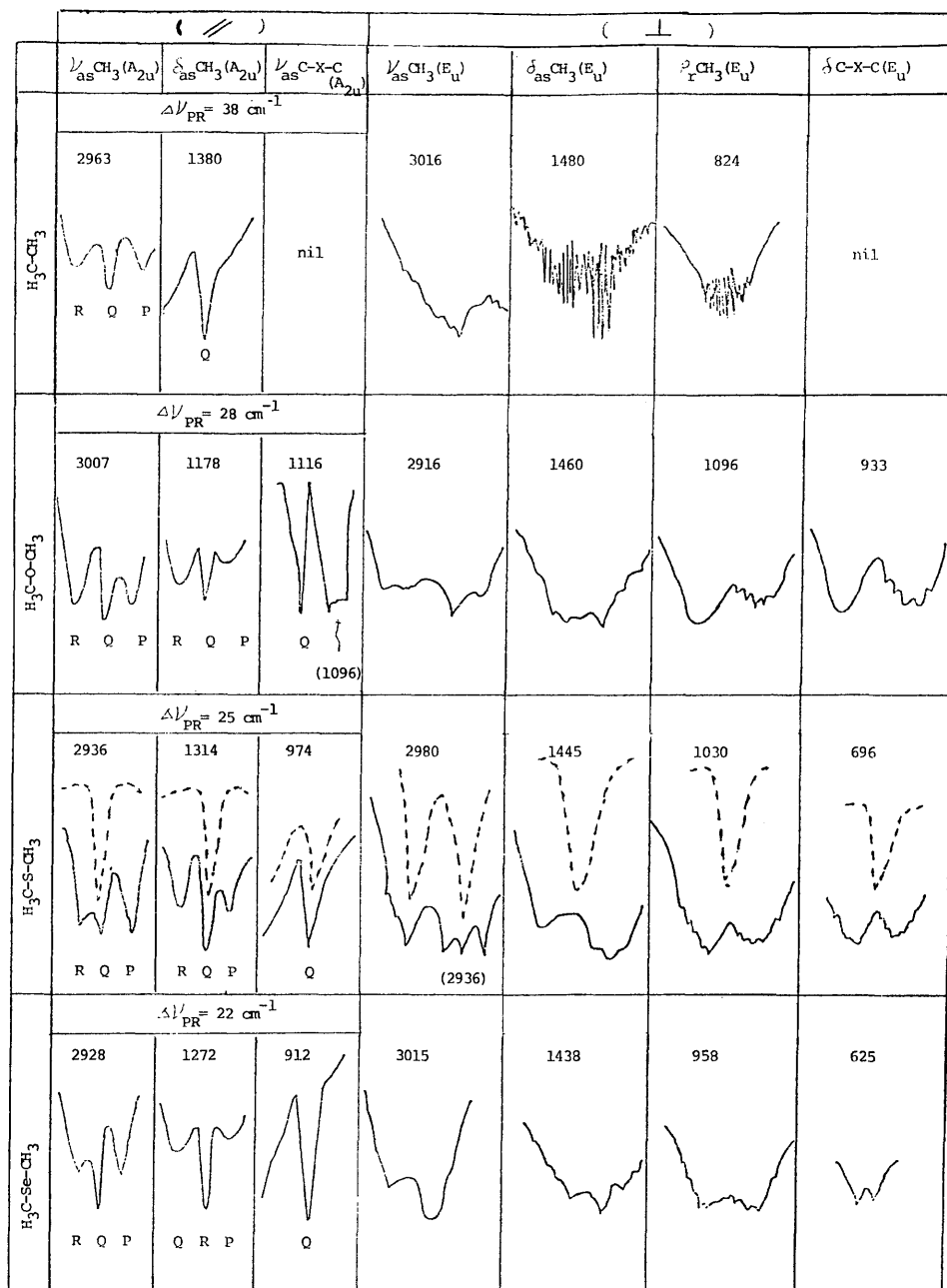


Fig. 2 The Band Shape of Infrared Parallel(//) and Perpendicular( $\perp$ ) Bands of  $H_3C-CH_3$ ,  $H_3C-O-CH_3$ ,  $H_3C-S-CH_3$  and  $H_3C-Se-CH_3$   
 —————, gas state; ..... , soln./CCl<sub>4</sub>

$\nu_{\text{as}}\text{CH}_3$ ,  $\delta_{\text{as}}\text{CH}_3$  and methyl rocking ( $\rho_{\text{r}}\text{CH}_3$ ), since they are the perpendicular type bands and there are no other such fundamentals.

*3-1-2-3 Overtone and Combination Bands* ..... The parallel type bands at 2903 and  $2963\text{ cm}^{-1}$  form a doublet due to a Fermi resonance<sup>12)</sup> of  $2 \times 1480$  with  $2963\text{ cm}^{-1}$  band. The *P-R* separation of the  $2903\text{ cm}^{-1}$  band is observed to be  $38\text{ cm}^{-1}$ , too. The  $2760\text{ cm}^{-1}$  band which is a parallel type band seems to be assigned to  $2 \times \delta_{\text{as}}\text{CH}_3$  ( $A_{2u}$ ).

### 3-1-3 Summary

As mentioned above, the obtained spectra of ethane can be explained according to  $D_{3d}$  selection rules and the assignments for ethane are given in Table 1.

### 3-2 Dimethyl Ether<sup>14-20)</sup>

Dimethyl ether ( $\text{H}_3\text{C-O-CH}_3$ ) is considered as a derivative in which  $\text{CH}_3$  group is connected to  $\text{CH}_3$  in opposite direction along the  $z$  axis and an oxygen atom is inserted between the two  $\text{CH}_3$  groups. Consequently for a linear C-O-C model, the vibrational spectra of  $\text{H}_3\text{COCH}_3$  should be similar to those of  $\text{H}_3\text{C-CH}_3$ , except being added an asymmetric C-O-C stretching and a C-O-C bending band. However there are two possible configurations for dimethyl ether ( $\text{H}_3\text{C-O-CH}_3$ ), linear or bent C-O-C. The symmetry of  $\text{H}_3\text{C-O-CH}_3$  would be  $C_{2v}$  if C-O-C is bent, and would be  $D_{3d}$  or  $D_{3h}$  if C-O-C is linear. For a  $C_{2v}$  symmetry whose irreducible representations is  $7A_1(R,p;IR) + 4A_2(R) + 6B_1(R;IR) + 4B_2(R;IR)$ , all 21 fundamentals are allowed in the Raman effect (7 of them as polarized lines) and 17 fundamentals are allowed in infrared absorption. The irreducible representations of a  $D_{3d}$  symmetry is  $3A_{1g}(R,p) + 3A_{2u}(IR) + 3E_g(R) + 4E_u(IR)$ , indicating the general simplicity of the Raman and infrared bands which are mutually exclusive. The irreducible representations of a  $D_{3h}$  is  $3A_1'(R,p) + 3A_2''(IR) + 3E''(R) + 4E'(R;IR)$ , which is different from that of the  $D_{3d}$  in  $E'$  ( $E_u$  for  $D_{3d}$ ) species which are both Raman and infrared active.

The observed spectra of  $\text{H}_3\text{C-O-CH}_3$  shown in Fig. 1 are too simple to be explained on the basis of  $C_{2v}$  symmetry and are very similar to those of  $\text{H}_3\text{C-CH}_3$  in every point of views, except the few additional bands which are due to C-O-C stretching and bending vibrations. Especially the obtained bands seem to be mutually exclusive in Raman and infrared. Therefore the consequent discussions shall be given on the basis of  $D_{3d}$  symmetry, though the all previous references<sup>14-20)</sup> support  $C_{2v}$  symmetry for  $\text{H}_3\text{C-O-CH}_3$ .

### 3-2-1 Raman Bands

*3-2-1-1  $A_{1g}$  Bands* ..... The three Raman active fundamentals belonging to  $A_{1g}$  species should give rise to polarized bands. Dimethyl ether has more Raman bands at  $3000\text{ cm}^{-1}$  region than  $\text{H}_3\text{C-CH}_3$ ,  $\text{H}_3\text{C-S-CH}_3$  and  $\text{H}_3\text{C-Se-CH}_3$ . This reason shall be mentioned in section 3-2-1-3. Anyway it can be seen that the assignment of  $\nu_{\text{s}}\text{CH}_3$  which should lie at  $3000\text{ cm}^{-1}$  region is difficult due to appearance of many polarized bands at  $3000\text{ cm}^{-1}$  region. Therefore the polarized  $3000\text{ cm}^{-1}$  band tentatively assigned to  $\nu_{\text{s}}\text{CH}_3$ . The weak polarized band at  $1246\text{ cm}^{-1}$  seems to be due to the symmetr-

ic methyl deformation ( $\delta_s\text{CH}_3$ ), as compared with that of  $\text{H}_3\text{C}-\text{CH}_3$  which is the weak polarized band at  $1185\text{ cm}^{-1}$  (3-1-1-1). The polarized band at  $929\text{ cm}^{-1}$  can be assigned to the symmetric C-O-C stretching, compared with  $\nu_s\text{C}-\text{C}$  of  $\text{H}_3\text{C}-\text{CH}_3$ ,  $\nu_s\text{C}-\text{S}-\text{C}$  of  $\text{H}_3\text{C}-\text{S}-\text{CH}_3$  and  $\nu_s\text{C}-\text{Se}-\text{C}$  of  $\text{H}_3\text{C}-\text{Se}-\text{CH}_3$ .

*3-2-1-2  $E_g$  Bands* ..... The three Raman active fundamentals belonging to  $E_g$  species should give rise to depolarized bands. The asymmetric  $\text{CH}_3$  stretching mode ( $\nu_{as}\text{CH}_3$ ) of the species should lie at  $3000\text{ cm}^{-1}$  region, therefore the band at  $3020\text{ cm}^{-1}$  which is depolarized can be assigned to  $\nu_{as}\text{CH}_3$ . The asymmetric  $\text{CH}_3$  deformation ( $\delta_{as}\text{CH}_3$ ) of this species presumably lies near  $1450\text{ cm}^{-1}$ , therefore the depolarized  $1456\text{ cm}^{-1}$  band can be assigned to  $\delta_{as}\text{CH}_3$ . This was also the case in  $\text{H}_3\text{C}-\text{CH}_3$ , as was mentioned in section 3-1-1-2. There remains the  $\text{CH}_3$  rocking ( $\rho_r\text{CH}_3$ ), to which the depolarized  $1112\text{ cm}^{-1}$  band is assigned.

*3-2-1-3 Violation of Selection Rules and Fermi Resonance* ..... There are five polarized bands in  $3000\text{ cm}^{-1}$  region. Two of them form a doublet due to a Fermi resonance<sup>1,2)</sup>, the one of which is due to  $\nu_s\text{CH}_3$  and the another of which, due to overtone of  $\delta_{as}\text{CH}_3$  ( $E_g$ ) as mentioned in section 3-1-1-3. The remains may be due to the overtone of  $\delta_{as}\text{CH}_3$  ( $E_u$ ) or due to a violation of the selection rules for  $D_{3d}$  by intermolecular forces.

The Raman band at  $450\text{ cm}^{-1}$  is considered as a torsion ( $A_{1u}$ ). This mode should be forbidden in both Raman and infrared, but it may be that the appearance is due to a violation of the selection rules for  $D_{3d}$  by intermolecular forces. This intermolecular forces may be stronger in  $\text{H}_3\text{C}-\text{O}-\text{CH}_3$  than in  $\text{H}_3\text{C}-\text{CH}_3$ ,  $\text{H}_3\text{C}-\text{S}-\text{CH}_3$  and  $\text{H}_3\text{C}-\text{Se}-\text{CH}_3$ , because of hydrogen-bond like forces in  $\text{H}_3\text{C}-\text{O}-\text{CH}_3$ . This is the reason why the violation of the selection rules occurs even in gas state of  $\text{H}_3\text{COCH}_3$  and more bands at  $3000\text{ cm}^{-1}$  and  $450\text{ cm}^{-1}$  regions appear in  $\text{H}_3\text{COCH}_3$  than in  $\text{H}_3\text{CCH}_3$  and  $\text{H}_3\text{CXCH}_3$  ( $X=\text{S, Se}$ ).

### 3-2-2 Infrared Bands

*3-2-2-1  $A_{2u}$  Bands* ..... This species contains three vibrations giving rise to parallel infrared bands having  $P$ ,  $Q$ , and  $R$  branches. The  $\text{CH}_3$  stretching band occurs, as expected, at  $3007\text{ cm}^{-1}$ , which is near frequencies of the  $\nu_s\text{CH}_3$  ( $A_{1g}$ ) vibration. The  $P$ - $R$  separation of this band is observed to be  $28\text{ cm}^{-1}$  as shown in Fig. 2. The parallel type band at  $1178\text{ cm}^{-1}$  ( $Q$ -branch) whose  $P$ - $R$  separation is observed to be  $28\text{ cm}^{-1}$  can be assigned to  $\delta_{as}\text{CH}_3$ , compared with those of  $\text{H}_3\text{C}-\text{CH}_3$  and of  $\text{H}_3\text{C}-\text{X}-\text{CH}_3$  ( $X=\text{S, Sc, Te}$ ). The band at  $1116\text{ cm}^{-1}$  shows only the sharp  $Q$ -branch, because the  $P$  and  $R$  branches may be overlapped with neighbor bands. This band can be assigned to the asymmetric C-O-C stretching ( $\nu_{as}\text{C}-\text{O}-\text{C}$ ). This assignment is in agreement with those of some authors<sup>5, 15, \*3)</sup>, but in disagreement with that of the other author<sup>\*3, 20)</sup>, in which the  $1116\text{ cm}^{-1}$  band is considered as  $R$  branch of  $1096\text{ cm}^{-1}$  band assigned to  $\nu_{as}\text{C}-\text{O}-\text{C}$ . However the latter assignment<sup>20)</sup> is questionable for the

\*3) However they say that the molecule of dimethyl ether has  $C_{2v}$  symmetry.



following reasons; The  $P$ - $Q$  separation should be equal to the  $Q$ - $R$  one in a parallel type band having  $P, Q$  and  $R$  branches. However that is not the case. Therefore the  $1116\text{ cm}^{-1}$  band can not be assigned as a  $R$  branch. And it is evident that the  $1116$  and  $1096\text{ cm}^{-1}$  bands of  $\text{H}_3\text{C-O-CH}_3$  correspond to the  $974$  and  $1030\text{ cm}^{-1}$  ones of  $\text{H}_3\text{C-S-CH}_3$  and to the  $912$  and  $958\text{ cm}^{-1}$  ones of  $\text{H}_3\text{C-Se-CH}_3$ , when the spectrum of  $\text{H}_3\text{C-O-CH}_3$  is compared with those of  $\text{H}_3\text{C-S-CH}_3$  and  $\text{H}_3\text{C-Se-CH}_3$ . Accordingly the  $1116$ ,  $974$  and  $912\text{ cm}^{-1}$  bands can be assigned to  $\nu_{\text{as}}\text{C-X-C}$  ( $\text{X}=\text{O,S,Se}$ ), and the  $1096$ ,  $1030$  and  $958\text{ cm}^{-1}$ , to  $\rho_r\text{CH}_3$

*3-2-2-2  $E_u$  Bands* ..... These are infrared active and Raman inactive. These should give rise to perpendicular type bands, which consists of a family of  $Q$  branches as  $\delta_{\text{as}}\text{CH}_3(E_u)$  ( $1480\text{ cm}^{-1}$ ) of  $\text{H}_3\text{C-CH}_3$  shows. Therefore the bands at  $2916$ ,  $1460$ ,  $1096$  and  $933\text{ cm}^{-1}$  whose band contours show a perpendicular type band as shown in Fig.2, are assigned to  $\nu_{\text{as}}\text{CH}_3$ ,  $\delta_{\text{as}}\text{CH}_3$ ,  $\rho_r\text{CH}_3$  and  $\delta\text{C-O-C}$ , respectively.

*3-2-2-3 Overtone and Fermi Resonance* ..... The parallel type bands at  $2824$  and  $3007\text{ cm}^{-1}$  form a doublet due to a Fermi resonance. The  $P$ - $R$  separation of the band at  $2824\text{ cm}^{-1}$  ( $2 \times \delta_{\text{as}}\text{CH}_3$ ) is observed to be  $28\text{ cm}^{-1}$  which is equal to that of  $\delta_{\text{as}}\text{CH}_3$  ( $A_{2u}$ ) bands of  $\text{H}_3\text{C-O-CH}_3$ .

### 3-2-3 Summary

The spectra of  $\text{CH}_3\text{OCH}_3$  are too simple to permit satisfactory assignments according to the selection rules of  $C_{2v}$  symmetry which allow 21 fundamentals to be active in the Raman effect and 17 of them to appear in the infrared spectrum, since the observed Raman spectrum shows only seven lines that can plausibly be assigned to fundamental vibrations. Above all, it strongly supports  $D_{3d}$  model for  $\text{H}_3\text{C-O-CH}_3$  that there is no coincidence between Raman and infrared frequencies.

### 3-3 Dimethyl Sulfide, Selenide and Telluride<sup>4, 21-25)</sup>

The spectra of  $\text{H}_3\text{C-S-CH}_3$  and  $\text{H}_3\text{C-Se-CH}_3$  are measured by the present authors, but the band frequencies of  $\text{H}_3\text{C-Te-CH}_3$  are cited from the literature<sup>4)</sup>.

#### 3-3-1 Vibrational Spectra

The vibrational spectra of  $\text{H}_3\text{C-S-CH}_3$ ,  $\text{H}_3\text{C-Se-CH}_3$  and  $\text{H}_3\text{C-Te-CH}_3$  can be assigned according to  $D_{3d}$  selection rules as shown in Table 1, compared with those of  $\text{H}_3\text{C-CH}_3$  and  $\text{H}_3\text{C-O-CH}_3$ , and taken consideration of the polarization states, the band contours and the fact that the  $\nu_{\text{as}}\text{CH}_3$  and  $\nu_s\text{CH}_3$  in  $3000\text{ cm}^{-1}$  region, and the  $\delta_{\text{as}}\text{CH}_3$  in  $1450\text{ cm}^{-1}$  region should remarkably be constant throughout the molecules,  $\text{H}_3\text{C-CH}_3$ ,  $\text{H}_3\text{C-O-CH}_3$ ,  $\text{H}_3\text{C-S-CH}_3$  and  $\text{H}_3\text{C-Te-CH}_3$  having methyl groups, and the doublets of such molecules which are due to a Fermi resonance between  $\nu_{\text{as}}\text{CH}_3(A_{2u})$  and  $2 \times \delta_{\text{as}}\text{CH}_3(E_u)$ , should appear in  $2900\text{ cm}^{-1}$  region, respectively.

The frequencies of  $\nu_s\text{C-X-C}$ ,  $\nu_{\text{as}}\text{C-X-C}$ ,  $\delta\text{C-X-C}$ , and  $\rho_r\text{CH}_3$  ( $\text{X}=\text{O,S,Se,Te}$ ) decrease, as expected, in which the frequencies change in going from the lighter to the heavier atom. In addition, the band contours, the band types, the simplicity of the spectra and the mutual exclusion in Raman and IR are in excellent agreement with the theoretical expectations for  $D_{3d}$  model of  $\text{H}_3\text{C-X-CH}_3$  ( $\text{X}=\text{O,S,Se,Te}$ ).

The Raman bands at 450 of  $\text{H}_3\text{C-O-CH}_3$ , 277 of  $\text{H}_3\text{C-S-CH}_3$ , 230 of  $\text{H}_3\text{C-Se-CH}_3$  and  $198\text{ cm}^{-1}$  of  $\text{H}_3\text{C-Te-CH}_3$  were assigned to  $\delta\text{C-X-C}$ . If the symmetries of  $\text{H}_3\text{C-X-CH}_3$  were considered to be  $C_{2v}$  as indicated in the previous literature<sup>4)</sup>. The  $\delta\text{C-X-C}$  band for  $C_{2v}$  should be polarized and be infrared active. However those bands of  $\text{H}_3\text{C-X-CH}_3$  are observed to be depolarized<sup>\*4)</sup> and do not appear in infrared, therefore the above assignment<sup>4)</sup> seems to be doubtful. These can be assigned to the torsion ( $A_{1u}$ ), appearing in the Raman effect through a breakdown of the selection rules due to hydrogen-bond like force active even in the gas or due to intermolecular force active in the liquid. That is to say, this frequency would actually be permitted in the Raman effect even if the selection rules appropriate to  $D_{3d}$  configuration apply to  $\text{H}_3\text{C-X-CH}_3$ <sup>6)</sup>.

### 3-3-2 Rotation-Vibrational Spectra

Ethane has  $D_{3d}$  symmetry, therefore parallel type bands ( $A_{2u}$  species) show a  $PQR$  structure with  $P-R$  separations of  $38\text{ cm}^{-1}$ , whereas perpendicular type bands ( $E_u$  species) exhibit a fine structure made up of closely spaced  $Q$  branches as shown in Fig. 2. If  $\text{H}_3\text{C-X-CH}_3$  type molecules would have  $D_{3d}$  symmetry (linear model), the parallel type bands are expected to show a  $PQR$  structure, and perpendicular type bands, to exhibit a fine structure with a family of  $Q$  branches. Such rotation-vibrational details are observed in every ethers as follows; the parallel type bands ( $A_{2u}$  species) possess  $P, Q$  and  $R$  branches with  $P-R$  separations of  $28\text{ cm}^{-1}$  for  $\text{H}_3\text{C-O-CH}_3$ , of  $25\text{ cm}^{-1}$  for  $\text{H}_3\text{C-S-CH}_3$  and of  $22\text{ cm}^{-1}$  for  $\text{H}_3\text{C-Se-CH}_3$ , and the perpendicular type bands ( $E_u$  species) consist of a family of  $Q$  branches. The perpendicular bands of  $\text{H}_3\text{C-CH}_3$  exhibit rotation-vibrational details with strong, weak, weak alternations which is sufficient to establish that the rotating species has  $C_3$  symmetry about the axis of rotation<sup>13)</sup>. On the other hand, such details of perpendicular bands are not so clearly observed in these ethers as in ethane, due to that the moments of inertia of the ethers are larger than those of ethane, however the band contours for perpendicular bands can be explained on the basis of  $D_{3d}$  selection rules.

## 4. Conclusion

The experimental results are in excellent agreement with the theoretical expectations for  $D_{3d}$  model of  $\text{H}_3\text{C-X-CH}_3$  ( $X=\text{O, S, Se, Te}$ ), as mentioned above. However the only argument against  $D_{3d}$  model of these ethers is that the  $\text{C-X-C}$  chain should be bent, because the fact that the  $\text{H}_2\text{O}$  molecule is bent suggests strongly that the  $-\text{O}-$  chain is bent as well<sup>5)</sup>. However it is possible to consider the  $2s$  and  $2p_z$  orbitals in oxygen atom as being hybridized<sup>\*5)</sup> to be linear  $-\text{O}-$ . In addition, some literatures support

\*4) The  $450\text{ cm}^{-1}$  band of  $\text{H}_3\text{C-O-CH}_3$  seems to be polarized. This might be due to strong hydrogen-like force, too.

\*5) The ground state of the oxygen atom is  $1s^2 2s^2 2p^4$ . In order to display a linear valence of two, the oxygen atom must have two electrons with uncoupled spins. The way to obtain this condition is to excite one of the  $2s$  electrons into the  $2p$  state, and to have the resulting  $2p_z$  electron with uncoupled spin, and  $2p_x$  and  $2p_y$  electrons with coupled spins. Then the  $180^\circ$  bond angle in  $\text{C-O-C}$  could be produced by mixing 50 per cent  $2s^1$  and 50 per cent  $2p_z^1$ <sup>39)</sup>.

experimentally a linear -O- for gaseous  $\text{Z-O-H}$  ( $\text{Z}=\text{K,Rb,Cs}$ )<sup>27-30</sup>,  $\text{Cl}_3\text{Si-O-SiCl}_3$ <sup>31</sup> and  $\text{F}_3\text{Si-O-SiCl}_3$ <sup>32</sup>). The literatures<sup>33-35</sup> support the compounds having linear -Se- and -Te-. Accordingly it seems to be sure that these ethers have  $D_{3d}$  symmetry (linear C-X-C), but the final decision must await the results of the further study, because some literatures support  $C_{2v}$  model for  $\text{H}_3\text{C-X-CH}_3$  on the basis of microwave spectroscopy<sup>36-38</sup> and of vibrational spectroscopy<sup>14-20</sup>, even if the assignments would be questionable as above mentioned.

Grateful appreciation is expressed for financial support of this work by the Science Research Fund of the Ministry of Education.

Correction : The assignment for  $625\text{ cm}^{-1}$  infrared band of  $\text{H}_3\text{C-Se-CH}_3$  in Fig. 1 should be corrected to be  $\delta_s\text{C-Se-C}(E_u)$  instead of  $\nu_s\text{C-Se-C}(A_{1g})$ .

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