

# Rotation-Vibrational Spectrum and Structure of Methanol

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## Abstract

The authors obtain the infrared rotation-vibrational spectrum of gaseous methanol and the Raman spectrum of liquid one. Actually the infrared as well as the Raman spectrum of methanol has been analyzed on the basis of  $C_s$  symmetry.<sup>1, 2)</sup> However, the present observations show that the vibrational bands of methanol obtained can be explained according to  $C_{3v}$  selection rule, that is, it is in agreement with theoretical expectations for  $C_{3v}$  model that four parallel type bands are polarized in Raman and have  $P$ ,  $Q$ , and  $R$  branches in infrared, whose  $P$ - $R$  separations are observed to be  $40\text{ cm}^{-1}$  and estimated to be  $43\text{ cm}^{-1}$  on the basis of the parameters for  $C_{3v}$  model. In addition, the obtained spectra of methanol resemble very closely those of acetonitrile, whose symmetry is  $C_{3v}$ .<sup>1)</sup>

## 1. Introduction

The symmetrical model  $C_{3v}$  for methanol ( $\text{H}_3\text{COH}$ ) has eight fundamentals, four totally symmetric ones ( $A_1$ ) and four degenerate ones ( $E$ ), all of which are both infrared and Raman active, whereas less symmetric model  $C_s$  would give twelve fundamentals ( $8A' + 4A''$ ), all of which are both infrared and Raman active. The vibrational spectrum of  $\text{H}_3\text{COH}$  has been assigned according to  $C_s$  model,<sup>1-6)</sup> but this appears doubtful. Because only eight fundamental bands can be found in the spectrum obtained, some Raman bands as fundamental are missing the corresponding infrared ones and vice versa, and some inconsistencies in the fundamental assignments appear in the preceding literatures.

The authors have therefore found it worthwhile to reinvestigate the structure of methanol by measuring the rotation-vibrational spectrum as well as the vibrational one and by comparing the spectrum of methanol with those of structurally related molecules.

## 2. Experimental

The compounds are purchased from commercial sources and purified by distillation. The Raman spectrum is recorded on *JEOL JRS-S1B* spectrophotometer using argon ion laser and the infrared spectrum is measured with *Shimadzu IR-450* spectrometer, whose gas cell had a path length of 10 cm and *KRS-5* windows.

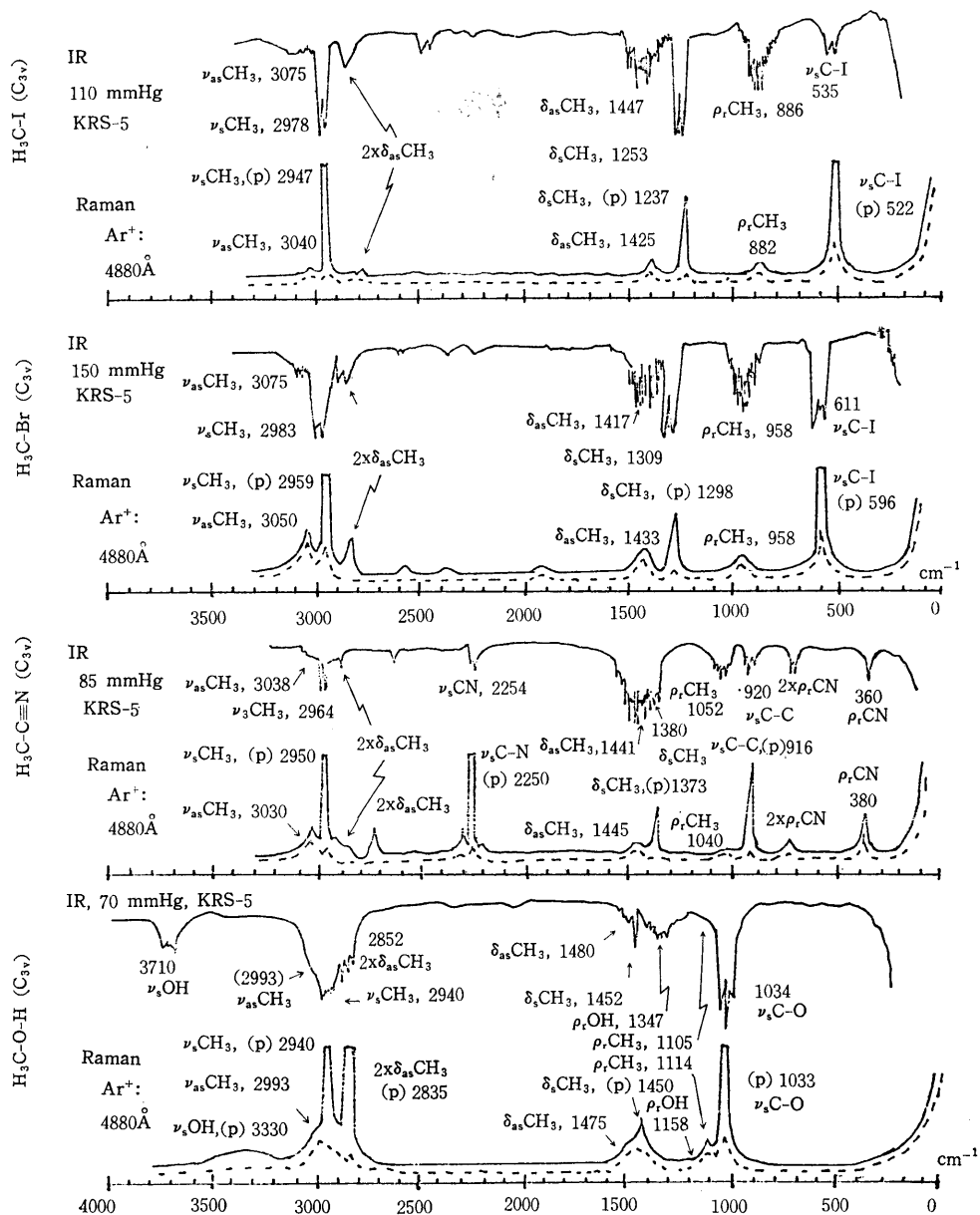


Fig. 1 IR and Raman Spectra of H<sub>3</sub>CI, CH<sub>3</sub>Br H<sub>3</sub>CCN and H<sub>3</sub>COH  
 IR spectra are measured in gas state and Raman spectra, in liquid state using Ar<sup>+</sup> laser(4880 Å).

### 3. Results and Discussion

#### 3-1. Vibrational spectra of acetonitrile( $H_3CCN$ )

From the fact that hydrogen cyanide(HCN) is linear it would appear very likely that in  $H_3CCN$  the C-C-N chain is linear,<sup>1, 7)</sup> that is, that the molecule has a three-fold axis just as methyl iodide( $H_3CI$ ) and methyl bromide( $H_3CBr$ ). Figure 1 shows the Raman and infrared spectra of  $H_3CI$ ,  $H_3CBr$ ,  $H_3CCN$  and  $H_3COH$ . If  $H_3CCN$  and  $H_3COH$  have a three-fold axis of symmetry they would have, according to the irreducible representations shown in Table 1, four totally symmetric ( $A_1$ ) and four doubly

**Table 1** Irreducible Representations of  $C_{3v}$  and  $C_s$  for  $H_3C-X-Y$  and  $C_{3v}$  for  $H_3C-X$

$H_3C-X-Y$	$C_{3v}$	$4A_1[R, p ; IR(\parallel)] + 4E[R, dp ; IR(\perp)]$
	$C_s$	$8A'[R, p ; IR] + 4A''[R, dp ; IR]$
$H_3C-X$	$C_{3v}$	$3A_1[R, p ; IR(\parallel)] + 3E[R, dp ; IR(\perp)]$

degenerate( $E$ ) vibrations, all of which are both Raman and infrared active. Eight fundamental bands have indeed been observed for  $H_3CCN$  and  $H_3COH$  in Raman and infrared, respectively, as shown in Fig. 1 and Table 2. If the C-C-N or C-O-H chains were not linear, there would be twelve bands, all of which are both Raman and infrared active. The agreement of the number of observed Raman and infrared fundamentals with that expected on the  $C_{3v}$  model is of course by no means a very strong argument for this model; but the following considerations support it further. As for  $H_3CI$  and  $H_3CBr$ , one would expect for  $H_3CCN$  and  $H_3COH$  a totally symmetric C-H stretching vibration ( $\nu_sCH_3$ ) and a degenerate C-H stretching one ( $\nu_{as}CH_3$ ) and a similar pair of  $CH_3$  symmetric deformation ( $\delta_sCH_3$ ) and  $CH_3$  asymmetric one ( $\delta_{as}CH_3$ ). These are indeed observed, with nearly the same frequencies as for  $H_3CI$  and  $H_3CBr$  as shown in Fig. 1 and Table 2, where  $\nu_sCH_3$  lies around 2950;  $\nu_{as}CH_3$ , around 3000;  $\delta_sCH_3$ , around 1000 and  $\delta_{as}CH_3$ , around 1450  $cm^{-1}$  region as expected. For  $H_3CCN$  one would further expect a C-N vibration ( $\nu_sC-N$ ) and C-C one ( $\nu_sC-C$ ), which are indeed observed at (p)2250  $cm^{-1}$  in Raman and at ( $\parallel$ )2254  $cm^{-1}$  in infrared for  $\nu_sC-N$  and at (p)916  $cm^{-1}$  in Raman and ( $\parallel$ )920  $cm^{-1}$  in infrared for  $\nu_sC-C$ . The two remaining frequencies (dp)1040 and (dp)380  $cm^{-1}$  in Raman which correspond to ( $\perp$ )1052 and ( $\perp$ )360  $cm^{-1}$  in infrared are apparently those of the two remaining degenerate vibrations, a methyl rocking vibration ( $\rho_rCH_3$ ) and CN rocking one ( $\rho_rCN$ ). The totally symmetric vibrations of  $H_3CCN$  give rise to parallel type bands having  $P$ ,  $Q$  and  $R$  branches in infrared, and the degenerate vibrations, perpendicular type bands with succession of  $Q$  branches as shown in Figs. 1 and 2.

These facts are strongly in favor of the  $C_{3v}$  model for  $H_3CCN$  as mentioned in the reference<sup>1)</sup>. The Raman and infrared spectra of  $H_3COH$  seem to be same as those of  $CH_3CN$  except having a symmetric O-H stretching ( $\nu_sOH$ ) and a O-H rocking ( $\rho_rOH$ ) bands instead of  $\nu_sC-N$  and  $\rho_rCN$  bands for  $H_3CCN$ .

Table 2 Symmetry Species, Selection Rules, Band Type, P-R Separation and Frequency Assignments of Skeletal Fundamentals

Species	Form of Vibration	H <sub>3</sub> C-O-H						H <sub>3</sub> C-C≡N						H <sub>3</sub> C-B <sub>r</sub>						H <sub>3</sub> C-I					
		Raman (liq.)	IR (gas)	Δν <sub>PR</sub>			Raman (liq.)	IR (gas)	Δν <sub>PR</sub>			Raman (liq.)	IR (gas)	Δν <sub>PR</sub>			Raman (liq.)	IR (gas)	Δν <sub>PR</sub>						
				Type	obs.	calc.			Type	obs.	calc.			Type	obs.	calc.			Type	obs.	calc.				
A <sub>1</sub>	ν <sub>s</sub> X-Y	(p)3330	3710		40		(p)2250	2254		24		nil	nil		nil		nil	nil		nil					
	ν <sub>s</sub> CH <sub>3</sub>	(p)2940	(2940)	(  )	?	43	(p)2950	2964	(  )	24	26.7	(p)2959	2983	(  )	26	24.7	(p)2947	2978	(  )	21	22.4				
	ν <sub>s</sub> C-X	(p)1033	1034		?		(p) 916	920		24		(p) 596	611		26		(p) 522	535		21					
	δ <sub>s</sub> CH <sub>3</sub>	(p)1450	1452		40		(p)1373	(1380)		?		(p)1298	1309		26		(p)1237	1253		21					
E	ν <sub>as</sub> CH <sub>3</sub>	2993	(2993)				3030	3038				3050	3075				3040	3075							
	δ <sub>as</sub> CH <sub>3</sub>	1475	1480	(⊥)	nil	nil	1445	1441	(⊥)	nil	nil	1433	1417	(⊥)	nil	nil	1425	1447	(⊥)	nil	nil				
	ρ <sub>r</sub> CH <sub>3</sub>	1114	1105				1040	1052				958	958				882	886							
	ρ <sub>r</sub> XY	1158	1347				380	360				nil	nil				nil	nil							
E×E	2×δ <sub>as</sub> CH <sub>3</sub>	(p)2835	2852	(  )	40	43	(p)2876	2876	(  )	?	26.7	(p)2840	2856	(  )	26	24.7	(p)2820	2845	(  )	?	22.4				

( ) shows that the figure comes from that of Raman band, because it is not clear due to overlapping with another band.

	Parallel band (  )				Perpendicular band (⊥)			
	$\nu_s \text{CH}_3$	$\delta_s \text{CH}_3$	$\nu_s \text{C-X}$	$\nu_s \text{X-Y}$	$\nu_{as} \text{CH}_3$	$\delta_{as} \text{CH}_3$	$\rho_r \text{CH}_3$	$\rho_r \text{XY}$
CH <sub>3</sub> -I	$\Delta\nu_{\text{obs.}} = 21 \text{ cm}^{-1}$							nil
				nil				
CH <sub>3</sub> -Br	$\Delta\nu_{\text{obs.}} = 26 \text{ cm}^{-1}$							nil
				nil				
CH <sub>3</sub> -C≡N	$\Delta\nu_{\text{obs.}} = 24 \text{ cm}^{-1}$							
		over-lapped						
H <sub>3</sub> C-O-H	$\Delta\nu_{\text{obs.}} = 40 \text{ cm}^{-1}$						weak	
	over-lapped							

Fig. 2 The Band Shape of Infrared Parallel and Perpendicular Bands of CH<sub>3</sub>I, CH<sub>3</sub>Br, CH<sub>3</sub>CN and CH<sub>3</sub>OH

3-2. *Vibrational spectra of methanol(H<sub>3</sub>COH)*

3-2-1 *Parallel type bands*.....The infrared band at 2845 cm<sup>-1</sup> of H<sub>3</sub>CI might

be considered as fundamental, but the bands at 2845 and 2978  $\text{cm}^{-1}$  form a doublet due to a Fermi resonance<sup>8)</sup>, whose center coincides very nearly with twice the wave number of the band at 1447  $\text{cm}^{-1}$ . Therefore the 2845  $\text{cm}^{-1}$  band of  $\text{H}_3\text{CI}$  is not fundamental one, but the 2978  $\text{cm}^{-1}$  band corresponds to one fundamental only\*<sup>1)</sup>. The band at 2852  $\text{cm}^{-1}$  of  $\text{H}_3\text{COH}$  that corresponds to 2845  $\text{cm}^{-1}$  band of  $\text{H}_3\text{CI}$  has been assigned to  $\nu_s\text{CH}_3$  in one of previous literatures<sup>1-6)</sup>, but it should be assigned to the first overtone of an asymmetric methyl deformation ( $2 \times \delta_{as}\text{CH}_3$ ), which should appear in the region<sup>9)</sup> of 2800  $\text{cm}^{-1}$ . This overtone is usually found to be medium, therefore the strong intensity of the overtone for  $\text{H}_3\text{COH}$  seems due to a strong Fermi resonance of  $2 \times \delta_{as}\text{CH}_3$  band with 2940  $\text{cm}^{-1}$  fundamental one. The 2940  $\text{cm}^{-1}$  band can be assigned to  $\nu_s\text{CH}_3$  which is expected to lie around 2950  $\text{cm}^{-1}$  region, to show *P*, *Q* and *R* envelopes\*<sup>2)</sup> in infrared and to be polarized in Raman. The strong Raman line and strong parallel infrared at 1034  $\text{cm}^{-1}$  obviously is the C-O vibration ( $\nu_s\text{C-O}$ ) corresponding to  $\nu_s\text{C-C}$  of  $\text{H}_3\text{CCN}$ .

The two infrared bands at ( $\parallel$ )1452 and ( $\perp$ )1480  $\text{cm}^{-1}$  which are corresponding to the Raman bands at (p)1450 and (dp)1475  $\text{cm}^{-1}$ , are not well resolved, but are readily explained as corresponding to  $\delta_s\text{CH}_3$  and  $\delta_{as}\text{CH}_3$  of  $\text{H}_3\text{CCN}$ , respectively. The O-H stretching vibration corresponds obviously to the infrared band ( $\parallel$ )3710  $\text{cm}^{-1}$ , which has a frequency very similar to that of the symmetrical O-H stretching vibration of  $\text{H}_2\text{O}$ . The very considerable difference between the frequency (p)3330  $\text{cm}^{-1}$  measured in the Raman spectrum and that (3710  $\text{cm}^{-1}$ ) measured in the infrared spectrum is due to the fact that the Raman frequency refers to the liquid. The infrared spectrum of the liquid<sup>10, 11)</sup> has shown the  $\nu_s\text{OH}$  band, just as does the Raman spectrum.

The frequencies of  $\nu\text{CX}$  ( $X=\text{O,C,Br,I}$ ) and  $\nu_s\text{XY}$  ( $\text{XY}=\text{OH,CN}$ ) should deeply decrease in which the frequency change in going from the lighter to the heavier atom.

*3-2-2 Perpendicular type band*.....It is well known that the frequencies of  $\nu_{as}\text{CH}_3$  and  $\delta_{as}\text{CH}_3$  are remarkably constant throughout the series of molecule  $\text{H}_3\text{CY}$  ( $Y=\text{F,Cl,Br,I}$ )<sup>12, 13)</sup>. This is, also, the case for  $\text{H}_3\text{CXY}$  ( $\text{XY}=\text{OH,CN}$ ), Therefore the depolarized Raman band at 2993  $\text{cm}^{-1}$  of  $\text{H}_3\text{COH}$  can be assigned to  $\nu_{as}\text{CH}_3$ , which shows the perpendicular type band in infrared. The 1475  $\text{cm}^{-1}$  Raman band which corresponds to the 1480  $\text{cm}^{-1}$  band in infrared can easily be assigned to  $\delta_{as}\text{CH}_3$  in a similar manner as above.

The rocking vibration of a O-H group ( $\rho_s\text{OH}$ ) should give a frequency of the same order as the bending vibration in  $\text{H}_2\text{O}$  (of course modified by the different distribution of masses). It may be identified both with the depolarized Raman band at 1158  $\text{cm}^{-1}$

\*1) It is seen that the envelope of 2978  $\text{cm}^{-1}$  band has *P*, *Q* and *R* branches in high resolution spectrum.

\*2) The 2940  $\text{cm}^{-1}$  infrared band does not show *P*, *Q* and *R* branches. This is due to overlapping of this band with the *Q* sequence of  $\nu_{as}\text{CH}_3$ .

and the infrared band at  $1347\text{ cm}^{-1}$  of perpendicular type. The large difference of frequencies in  $\rho_r\text{OH}$  bands between gaseous infrared and liquid Raman spectrum is due to strong hydrogen bonding in liquid state, as does  $\nu_s\text{OH}$ . There remains the rocking vibration of  $\text{CH}_3$  group ( $\rho_r\text{CH}_3$ ), accordingly the infrared band at  $1105\text{ cm}^{-1}$  must be assigned to the  $\rho_r\text{CH}_3$ , whose corresponding Raman band is weak one at  $1114\text{ cm}^{-1}$ .

#### 4. Band Contours

4-1. *P-R separation*.....The parallel bands are those for which the electric moment oscillates along the symmetry axis, and the envelope of those bands possesses *P*, *Q*, and *R* branches, whose *P-R* separation,  $\Delta\nu_{\text{PR}}$  is expressed by Gerhard and Denisson<sup>14)</sup> as follows;

$$\Delta\nu_{\text{PR}} = S(\beta) / \pi \sqrt{kT / I_A}$$

where the separation function  $S(\beta)$  is given by the following empirical formula,

$$\log_{10} S(\beta) = 0.721 / (\beta + 4)^{1.13}$$

whose parameter  $\beta$  is equal to  $(I_B/I_A) - 1$ .

On the assumption that the structure of  $\text{H}_3\text{COH}$  is  $C_{3v}$  having the following parameters,  $\text{O-H} = 0.96\text{ \AA}$ ,  $\text{O-C} = 1.427\text{ \AA}$ ,  $\text{C-H} = 1.10\text{ \AA}$ , tetrahedral  $\text{HCH}$  angle and  $\text{COH}$  angle of  $180^\circ$ , the authors estimated the moment of inertia about top axis to be  $I_A = 5.09 \times 10^{-40}\text{ g}\cdot\text{cm}^2$ , and that about the axis perpendicular to the top axis to be  $I_B = 32.13 \times 10^{-40}\text{ g}\cdot\text{cm}^2$ . Thus the *P-R* separation of the parallel bands of  $\text{H}_3\text{COH}$  at  $25^\circ\text{C}$  is estimated to be  $43\text{ cm}^{-1}$ . The *P-R* separation for the bands,  $\nu_s\text{O-H}$ ,  $\nu_s\text{C-O}$  and  $2 \times \delta_{\text{as}}\text{CH}_3$  are observed to be  $40\text{ cm}^{-1}$  in Fig. 2. Therefore, the agreement is good and may be regarded as fairly satisfactory. The separation for  $\nu_s\text{CH}_3$  can not be observed due to overlapping\*<sup>2)</sup>, and that for  $\delta_s\text{CH}_3$  can not be observed due to be too weak. The observed and calculated *P-R* separations for the parallel bands of  $\text{H}_3\text{CCN}$ ,  $\text{H}_3\text{CBr}$  and  $\text{H}_3\text{CI}$  are shown in Table 2. The agreements seem to be fairly good.

4-2. *Rotational fine structure*.....The rotational constant  $B$  is calculated to be  $0.87\text{ cm}^{-1}$  from the equation<sup>15)</sup>,  $B = h/8\pi^2cI_B$  and  $I_B = 32.13 \times 10^{-40}\text{ g}\cdot\text{cm}^2$  calculated previously. The constant  $B$  can, too, be obtained from the frequency separation between lines in *P* or/and *R* branches which is equal to  $2B$ <sup>15)</sup>. Fig. 3 shows that the frequency separation in *P* branch of  $\nu_s\text{CO}$  band is  $1.88\text{ cm}^{-1}$ . The agreement of the observed value with that calculated on the basis of  $C_{3v}$  symmetry is regarded as satisfactory.

4-3. *Family of Q branches*.....The perpendicular type bands are those bands for which the electric moment oscillates perpendicular to the figure axis, and which consists of a family of *Q* branches in infrared and are depolarized in Raman. It is seen in Figs. 1 and 2 that the *Q* branches of the perpendicular bands exhibit an intensity alternation of the type strong, weak, weak etc. Observation of such an intensity alternation in a *Q* branch consequence is sufficient to establish that the rotating species





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