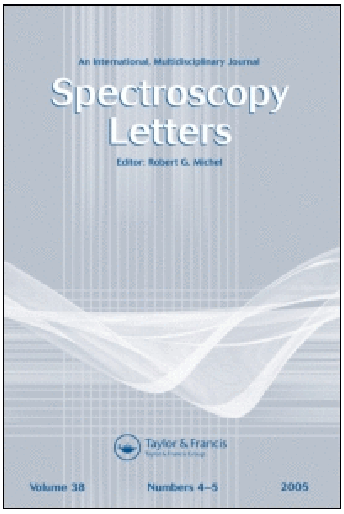

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The Laser Raman Spectrum of Cyclobutanone

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THE LASER RAMAN SPECTRUM OF CYCLOBUTANONE

Keywords CYCLOBUTANONE, RAMAN SPECTRUM

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In a recent paper,[1] we discussed the vibrational spectrum of crystalline Cyclobutanone (CBN) with the main concern over the crystal form stable at 100K. From the dichroism of the infrared bands, the nature of the solid state splittings was ascertained and conclusions were drawn on the symmetry of the unit cell. In doing this, use was made of the crystal Raman spectrum of CBN, to infer the existence of the center of symmetry in the unit cell and to predict the selection rules of the C_{2h}^5 space group.

However, by comparing our diffusion data in the liquid state with those reported by Frei and Gunthard[2] (F. and G.), it was decided that even a Raman study of liquid CBN were justified "per se", since the values of the depolarization factors have been given with large uncertainty,[2] probably owing to the low experimental precision obtainable at that time.

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With the coming of laser exciting sources and photoelectric detection, the Raman spectra now obtainable are doubtless more and more reliable from an assegnative point of view. Therefore we believed it worthwhile to reinvestigate the Raman spectrum of liquid CBN with improved power and resolution; the results obtained are the object of the present note.

Experimental

Cyclobutanone was purchased from Fluka and was used without further purification. The Raman spectrum, between 0 and 3200 wavenumbers, was run with a Cary 81 spectrometer, equipped with Ar^+ ion laser source (4880 Å exciting line and 550 mW output power), using a 16 mm optical glass cell. In Table 1 the Raman frequencies and the depolarization ratios of liquid CBN are collected. Representative spectrum is shown in fig. 1.

Results and discussion

Microwave[3] and far-infrared[4,5] studies of CBN have established a low potential barrier (ca. 5 cm^{-1}) for the ring-puckering motion; therefore the quasi-free rotation of atoms about the single bonds makes the four-membered ring of CBN nearly planar and justifies the assumption of the C_{2v} molecular symmetry for deriving the selection rules of the vibrational levels.

Under the C_{2v} point group symmetry the 27 genuine vibrations of CBN may be cast as $9A_1 + 4A_2 + 7B_1 + 7B_2$.

Whereas the in plane A_1 motions should give rise to polarized Raman lines, depolarized transitions are associated with fundamentals of A_2, B_1 and B_2 species.

It should be noted that the depolarization ratios reported for A_1 motions by F. and G. are large and too close to the uncertainty region in order to get a definite discrimination

Table 1 - Raman spectrum of liquid Cyclobutanone

Numbering[a] and Symmetry		Frequencies Ref.[2]		Present work		Approximate description
		$\nu(\mathrm{cm}^{-1})$	ρ_n	$\nu(\mathrm{cm}^{-1})$	ρ_s	
ν_{21}	(B_2)	3005	dp	3007	0.67	$\nu(C-H)_\beta$
ν_1, ν_{14}	(A_1, B_1)	2975	0.63	2974	0.23	$\nu(C-H)_{\beta,\alpha}$
ν_2, ν_{22}	(A_1, B_2)	2930	0.54	2932	0.05	$\nu(C-H)_\alpha$
ν_{10}	(A_2)	2876	?	2892	dp	$\nu(C-H)_\alpha$
ν_3	(A_1)	1782	0.84	1782 ∥ 1775 ⊥	0.45	$\nu(C-O)$
$\nu_{16}+\nu_{26}$	$(B_1 \times B_2)$	1732	?	1735	dp	
$\nu_{13}+\nu_{25}$	$(A_2 \times B_2)$	—	—	1633	?	
ν_4	(A_1)	1464	0.89	1456	0.47	$\delta(CH_2)_\beta$
ν_5, ν_{15}	(A_1, B_1)	1402	0.88	1399	0.63	$\delta(CH_2)_\alpha$
ν_{16}	(B_1)	—	—	1340	?	$\gamma w(CH_2)_\beta$
ν_{17}	(B_1)	—	—	1239	dp	$\gamma w(CH_2)_\alpha$
ν_{11}	(A_2)	1200	0.89	1196	0.64	$\gamma\tau(CH_2)_\alpha$
ν_{12}	(A_2)	—	—	1164	dp	$\gamma\tau(CH_2)_\alpha$
ν_{24}	(B_2)	—	—	1079	dp	$\gamma r(CH_2)_\alpha$
ν_7	(A_1)	958	0.40	957	0.04	ring stretch
ν_{13}	(A_2)	902	0.95	901	0.71	$\gamma r(CH_2)_\alpha$
ν_8	(A_1)	856	?	—	—	ring stretch
ν_{25}	(B_2)	—	—	728	0.60	$\gamma r(CH_2)_\beta$
ν_9	(A_1)	677	0.56	675	0.06	ring def.
ν_{20}	(B_1)	461	0.95	461	0.69	$\delta(C-O)$i.p.
ν_{26}	(B_2)	403	0.93	402	0.64	$\delta(C-O)$o.o.p.
ν_{27}	(B_2)	—	—	63	dp	ring puckering

a) Numbering of vibrations is as reported in refs. [1,2]

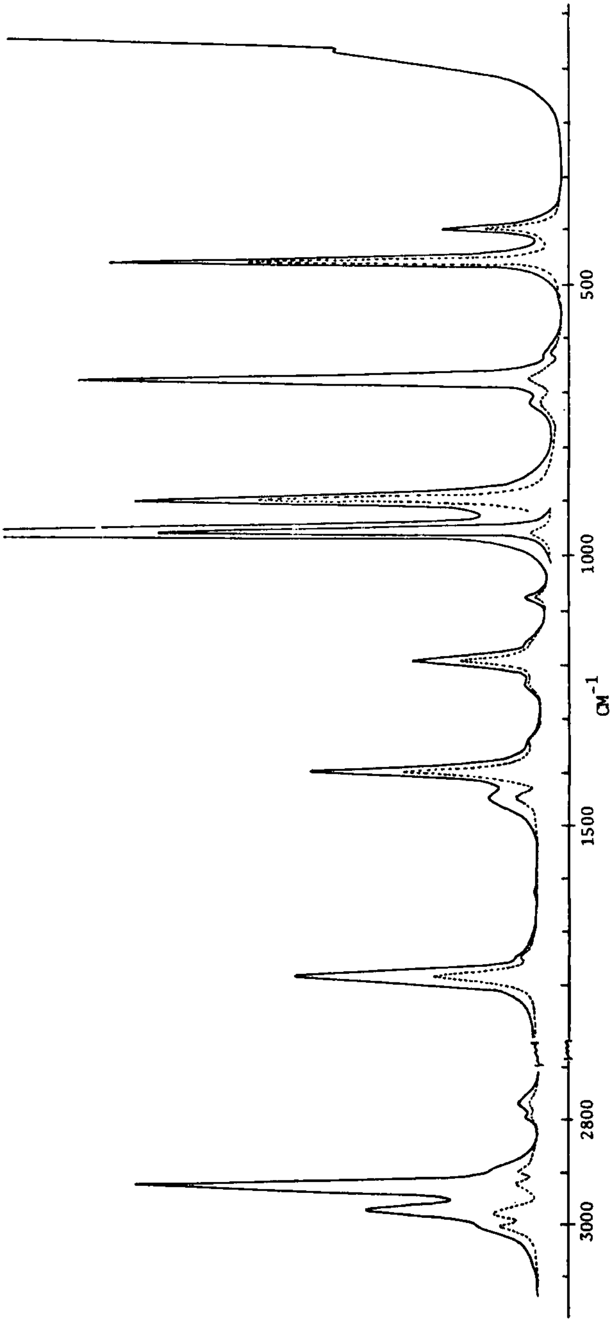

Fig. 1 - Raman spectra of liquid cyclobutanone, (——) axial polarisers, (-----) cross polarisers.

between polarized and depolarized transitions. We have remeasured the depolarization ratios and we found that, in all cases, these are much lower than those previously reported. This fact, enabled us to assigne, without any further experimental information, the motion of A_1 character.

Even for non totally-symmetric modes our ρ_s values are quite different from those reported in ref. 2. However, in such cases, the attribution to vibrations of A_2, B_1 and B_2 species is done without doubt, because the corresponding lines are clearly depolarized and this is outside of any experimental uncertainty.

In the region where the C-H stretchings produce Raman scattering, we must assigne six motions; of these, four are concerned to the methylene groups in α position and two to the methylene group in β . We observe two strong lines at 2974 and 2932 cm^{-1}, both having side-peaks at 3007 and 2892 cm^{-1}, respectively. If these lines are all assigned with C-H fundamentals, it is clear that at least two vibrational levels, among the C-H stretchings, must be accidentally degenerate. We assigne the shoulder at 2892 cm^{-1} to the A_2 mode of α-methylenes, essentially because this is depolarized and is lacking in the IR spectrum of liquid CBN, whereas it appears in the solid state infrared spectrum with appreciable intensity.[1] Since the second shoulder, at 3007 cm^{-1}, has the depolarization factor equal to 0.67, we believe that it should be associated with the B_2 mode of β-methylene. The lines at 2974 and 2932 wavenumbers are strongly polarized and therefore must be assigned to the two A_1 motions of α- and β-methylene groups. However, in view of their strong intensity, pseudo-degenerate vibrational levels, if any, should be searched below these. Thus, we have performed the assignment reported in table 1 by considering these factors and using also the information obtained from the solid state infrared and Raman spectra.[1]

The carbonyl stretching mode produces a medium strong scattering at 1775 cm^{-1}. There is, on the higher frequencies side, an evident shoulder which becomes a strong line in the diffusion spectrum parallel polarized, when the carbonyl peak almost disappears: Since this line coincides with the position of the infrared absorption, we believe that it could derive from a possible failure of the "single molecule" vibrational selection rules; a dipolar interaction between two ordered molecules should give rise to a species for which the mutual exclusion rule must be applicable. Similar details have been commonly observed in the Raman effect of certain carbonyl compounds[6,7] and have been interpreted under the assuption of short range dipole-dipole type interactions.

The line at 1399 cm^{-1} has two corresponding absorptions in the infrared.[1] It may be interpreted as resulting from two components quasi-degenerate of opposite polarization character; this view is supported by its hybrid depolarization factor ($\rho_s = 0.63$) and by the appearance of two peaks in the solid state IR and Raman spectra. The attribution is therefore, as reported in ref. 1, in favour of the A_1 and B_1 in plane deformations of the α-methylenes.

The wagging mode of A_1 species due to the α-methylenes was assigned at 1402 cm^{-1} by F. and G.. We questione such an assignment essentially because the corresponding line (1399 cm^{-1}) has the depolarization factor too high for deriving from a single, totalsymmetric mode. Further, the frequency value is too high to be attributable to a wagging mode because these vibrations are commonly regarded as characteristic group frequencies and are assigned in a restrict zone of hundred wavenumbers between 1330 and 1230 cm^{-1}.[8,9] In this range we found two weak lines at 1340 and 1239 cm^{-1}; the latter being depolarized, is straightforward attributed to a B_1 wagging mode. The former, having uncertain depolarization factor, could be, in principle, correlated with both the remaining A_1 and B_1 methylene wagging motions. However, we prefer assigne the A_1 mode with the peak at 1291 cm^{-1} found in the infrared crystal spectrum.[1]

The Raman shift at 1079 cm^{-1} results clearly depolarized. This fact, even if desagrees with the gas-phase profile which is definitely of A-type in infrared, leads to the assignment of this line as B_2 rocking mode of the α-methylenes.

Similar conflicting features are shown from the line at 957 cm^{-1}. In particular, whether as measured by us,[1] and as detectable from the profile of the drafts in the paper of F. and G.,[2] the separation between R and P branchs of the corresponding infrared band in the gas-phase is 19 cm^{-1}, which makes the band of C-type and then attributable to a B_2 mode. However, since in the liquid Raman spectrum the line at 957 cm^{-1} is the strongest polarized one, we believe that it should be assigned as ring mode of A_1 species.

The remaining Raman lines of liquid CBN have numerical values of depolarization factors which give no problems from an assegnative point of view. Although these factors are always quite different from those reported by F. and G., we found an almost complete consistence between the two assignments. Thus, we do not give any other detail for the discussion of these lines.

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