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HYPER RAMAN SPECTRUM OF CYCLOHEXANE

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Hyper Raman spectrum of liquid cyclohexane was observed with frequency doubled YAG laser as an exciting source. In addition to the counterparts of ir absorption bands, a strong band was observed at 1107 cm^{-1} and assigned to an a_{1u} vibration, which was forbidden both in ir and Raman and allowed in hyper Raman.

Hyper Raman spectroscopy still is one of the least investigated fields in spectroscopy. Although it is potentially possible to find modes inactive both in ir and Raman1), experimental difficulties have restricted such observations to only few cases2-6). Cyclohexane gives a nice opportunity for the application of hyper Raman spectroscopy, because it has three a_{1u} modes active only in hyper Raman under D_{3d} (chair form) point group, as well as five a_{2u} and eight e_u modes active also in ir.

Although there have been many studies of vibrational spectra of cyclohexane,7-16) the assignments are not completely established because of the presence of inactive modes. Observation of hyper Raman spectrum will contributes to help in understanding the vibrations of this molecule.

A frequency doubled Nd-YAG laser (532 nm) of 10 pulses per second of about 20 mJ was used as an exciting source. YAG laser has a definite advantage in repetition rate over ruby laser, which is the common excitation source for the hyper Raman spectroscopy. Hyper Raman spectra were obtained by the use of a Nikon P250, F4.5, 25 cm monochromator with 100μ slit width. The signals from the photomultiplier (HTV R562) were preamplified and fed to the input of a gated photon counter. With gate opening time of 100 nsec, dark count rate was less than two for every 1000 shots. After every 400 laser shots the signal count rate was recorded and stored in a microcomputer for storage and further processing, and then the monochromator was step scanned by 0.25 A. It takes about 4 hours to scan 360 data points which correspond to about 1000 cm^{-1}, and the process was repeated and the data were averaged. Cyclohexane was filtered before use through 0.2μ Milipore filter for optical purification.

Hyper Raman signals were looked for between 800 and 1600 cm^{-1} where the existence of a_{1u} vibrations is expected. Six bands were observed in this region and two very strong bands were also found in the CH stretching vibration region. The spectrum is shown in Fig. 1 and the peak positions are listed in Table 1 as well as corresponding infrared absorption bands. It can approximately be said that the hyper Raman spectrum is very similar to the ir spectrum. As is seen from the table 1

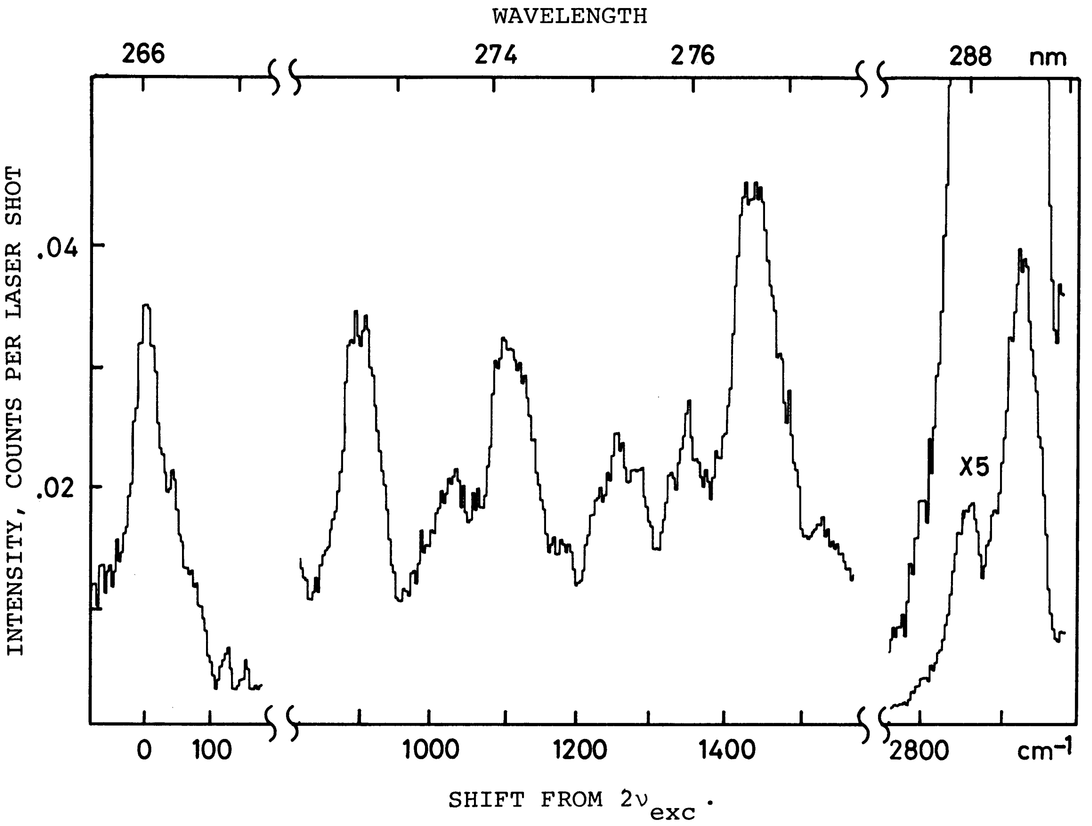

Fig. 1. Hyper Raman spectrum of liquid cyclohexane excited by the frequency doubled YAG laser at 532 nm. The spectral slitwidth is about 40 cm^{-1} and wavelength interval of successive data point is 0.25 A or about 3 cm^{-1}. The presentation is five-point running average of the virgin data, which is the accumulation of four independent measurement.

all bands but one at about 1100 cm^{-1} have strong counterparts in the ir spectra, and leave no doubt in assignment, except for $\nu_{15}(a_{2u})$ to which 910 cm^{-1} 11), 1015 cm^{-1} 14) or 1039 cm^{-1} 15) was proposed in the literature.

A weak band is observed in ir at 1110 cm^{-1} in the liquid cyclohexane and at 1105 cm^{-1} in phase II solid and is attributed to a transition forbidden both in ir and Raman. They coincide in frequency with the band observed at 1107 cm^{-1} in the hyper Raman spectrum. Miller and Golob8) suggested that this is $\nu_{11}(a_{2g})$ (forbidden in ir, Raman and hyper Raman) vibration from the analysis of a combination band, and later Bernard13) gave the same assignment. Wiberg and Shrake15,16) supported this on the basis of normal coordinate calculation. On the other hand, LeRoy and Lecomte10) and Oblemski et al.14) assigned this to an $\nu_9(a_{1u})$ vibration from the proposed structure of phase II crystal. Observation of hyper Raman spectrum unambiguously shows that this belongs to a_{1u} species. Normal coordinate calculation9,16) predicts two a_{1u} frequencies nearby: ν_8 between 1136 and 1192 cm^{-1} and ν_9 between 1049 and 1095 cm^{-1}. Observed band should correspond either of the two.

As for the assignment of ν_{15} the resolution is too poor to give definite conclusion, but the observed peak position of hyper Raman band favours 1039 cm^{-1} to

Table 1. Observed hyper Raman bands of liquid cyclohexane

Hyper Raman* $\Delta\nu$(cm^{-1})		IR** ν (cm^{-1})		Assignment***
		862	s	$\nu_{31}(e_u)$
900	s	904	s	$\nu_{30}(e_u)$
		1015	m	$\nu_{23}(e_g) + \nu_{32}(e_u)$?
1033	w	1039	m	$\nu_{15}(a_{2u})$?
1107	s	1110	w	$\nu_8(a_{1u})$ or $\nu_9(a_{1u})$
1251	w	1258	s	$\nu_{29}(e_u)$
1348	w	1349	m	$\nu_{28}(e_u)$
1447	s	1451	vs	$\nu_{14}(a_{2u})$, $\nu_{27}(e_u)$
2858	vs	2853	vvs	$\nu_{13}(a_{2u})$, $\nu_{26}(e_u)$
2927	vvs	2928	vvs	$\nu_{25}(e_u)$

* $\Delta\nu = 2\nu_{exc} - \nu_{obs}$
** liquid, from Ref. 15)
*** see text.

be a fundamental.

A fact worthwhile to note is the presence of second harmonic seen in Fig. 1, because a centrosymmetric molecule like cyclohexane should show no hyper Rayleigh line. Since existence of boat form cyclohexane is not known this suggests the effect of intermolecular interaction. Similar observation was made by Maker et al. for high pressure ethylene$^{2)}$.

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