Laser Excited Raman Spectra of Some Organic Crystals of the Space Group C_{2h}^5

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Inherent advantages of a gas laser light as an exciting source of Raman scattering are being recognized recently. Especially, its excellent directivity and polarization are ideal for polarization measurements. In the present communication, we will illustrate the advantages of the laser for polarization experiments by reference to several organic single crystals. The crystals reported here are of napthalene, anthracene, *p*-dichlorobenzene and *p*-dibromobenzene. They have the same space group of C_{2h}^5 with two molecules per unit cell and the molecular symmetry is all D_{2h}.

A 4880 Å argon-ion gas laser was used as the light source and operated at the output of 50 mW. The Raman spectra were taken photographically with a three prism Raman spectrograph. Figure 1 shows, as an example, the spectra of lattice vibrational region of naphthalene crystal. Pronounced effects of polarization are seen, which have never being observed in the experiments with mercury lamp.

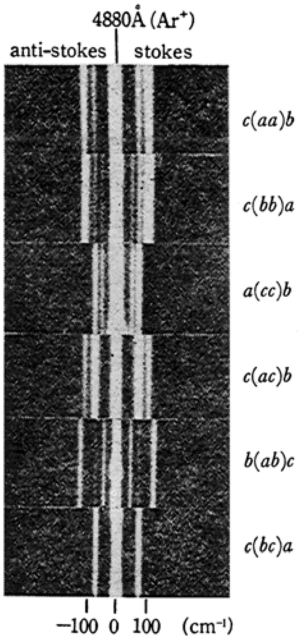

Fig. 1. Polarized Raman spectra of naphthalene single crystal at 30°C in the region of lattice vibrations. The symbols inside the parenthesis indicate, left to right, the polarization of the incident and scattered light while the ones to the left and right outside the parenthesis are the propagation directions of the incident and scattered light respectively.

Group theory predicts six Raman active lattice vibrations. Polarization measurements showed that three lines appear in the (*aa*), (*bb*), (*cc*) and (*ac*) spectra and the other in the (*ab*) and (*bc*) spectra. Thus, the former is readily assigned to A_g, the latter to B_g. As for the region of intramolecular vibrations, relative intensities of a non-totally symmetric molecular vibration among various polarized crystal spectra are predicted only from the crystal structural data on the assumption of the oriented gas model. With these prediction, it is possible to classify the non-totally symmetric Raman lines into specific molecular symmetry species from the observed polarized spectra. The assignments obtained in this way are listed in Table 1. They generally agree well with the assignments based on the normal coordinate calculations of the molecules. Details of the results and further extension of this method to the crystal of more complex molecules are to be reported shortly.

Table 1. Assignments of lattice and intramolecular vibrations (at 77°K)

Assignment*		Naphthalene cm^{-1}	Anthracene cm^{-1}	*p*-Dichlorobenzene cm^{-1}	*p*-Dibromobenzene cm^{-1}
Lattice	A_g	120, 88, 69	131, 80, 49	107, 65	103, 41
	B_g	141, 81, 56	139, 70, 56	114, 58, 32	108, 47, 25
Inter-molecular	b_{1g}	2980, 1636, 1446, 1240, 1168, 953, 514	1631, 1481, 1187, 956, 475, 390	1378, 1293, 629, 350	1360, 1290, 625, 309
	b_{2g}	725, 390	915, 243	691, 310	680, 276
	b_{3g}	980, 786, 878, 467	978, 904, 765, 622, 290	815	811

* Symmetry species of capital and small letters refer to the factor group (C_{2h}) and point group (D_{2h}), respectively.