

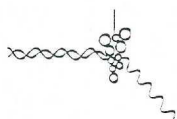
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RAMAN INTENSITIES OF LATTICE VIBRATIONS IN 2,2'-BIPYRIDINE.

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The understanding of the intensity of the external lattice modes of a molecular crystal requires a model for the computation of the scattering tensor. Some models have been devised in the past and recently.

Besides the simple oriented gas approximation (no interactions between molecules, local field effects ignored, additivity of the molecular polarizabilities) [1-3] more elaborated models have been introduced [4,5] which take into account the effect of the molecular interactions on the crystal polarizability.

It has been found that using for the computation of the derivatives of the polarizability tensor with respect to the crystal normal coordinates the eigenvectors from different lattice dynamical models, all correctly reproducing the vibrational lattice energies, completely different Raman intensities can be obtained.

Nevertheless, assuming the eigenvectors of the crystal modes to be correct as they are calculated from some model one can investigate which polarizability can bring about the best agreement between calculated and experimental Raman intensities.

This has been done for the crystal of 2,2'-bipyridine which is well suited for this study as its external modes have all been observed and well reproduced by calculation [6]. Moreover, an important simplification occurs as, being the site symmetry C_1 , only the librational modes show in the Raman spectrum.

RESULTS and DISCUSSION

The space group of 2,2'-bipyridine is $C_{2h}^5-P2_1/c$, with two molecules at C_1 sites. The structure of the reducible representation is then: $\Gamma_{\text{ext}} = 3A_g + 3B_g + 2A_u + 1B_u$. Raman librational modes belong to species A_g : tensor elements xx, yy, zz, xz , and B_g : tensor elements xy, yz , with x, y, z optic indicatrix principal directions [7].

The lattice frequencies have been calculated using different sets of available potential parameters of the exp-6 atom-atom type [8,9]. The calculated frequencies were not much sensitive to the different sets of potential parameters although two sets gave better agreement than others. The same sets brought about crystal structures closest to the experimental one. These sets have been used in the lattice dynamical calculation to obtain the eigenvectors later employed in the evaluation of the Raman intensities. These have been calculated following the model outlined by Schettino and Califano [5].

As the molecular polarizability was unknown the calculated intensities were fitted by least squares to the experiment using diagonal elements as adjustable parameters.

The calculation has been performed without (oriented gas approximation) and with molecular interactions allowed (local field model). The results are reported in the Table.

Both models reproduced rather satisfactorily the spectrum of the pow-

Table 1. Calculated polarizabilities: $\alpha_1, \alpha_2, \alpha_3$, observed and calculated librational mode frequencies (cm^{-1}), normal modes compositions and relative intensities of the Raman spectrum of 2,2'-bipyridine^a.

		intensity																	
		powder ^c						single crystal ^d											
freq.		eigenvectors ^b			calc.		calc.		obs.										
exp.	calc.	R _X	R _Y	R _Z	I	II	obs.	xx	yy	zz	xz	xy	yz	xx	yy	zz	xz	xy	yz
A _g	103	102	.17	.66	.19	32	27	30	21	45	0	0		32	39	1	3		
	78	83	-.47	-.03	.53	38	29	35	51	0	2	12		17	27	2	15		
	56	60	.50	-.25	.43	75	77	74	0	70	44	22		8	28	80	34		
B _g	98	96	.02	.70	.07	8	14	12					2	7				1	23
	82	79	.38	-.06	.59	6	2	7					3	4				2	21
	34	33	-.59	-.02	.38	100	100	100					100	7				100	100
$\alpha_1^I=3.8, \alpha_2^I=36.7, \alpha_3^I=13.7$					$\alpha_1^{II}=2.4, \alpha_2^{II}=46.2, \alpha_3^{II}=20.6 \quad (\times 10^{-24}\text{cm}^3)$														

^a potential parameters: HH, CH, CC from Ref. 8; NH, CN, NN from Ref. 9

^b rotational coordinates: R; molecular inertial axes: X, Y, Z

^c I and II, local field and oriented gas model, respectively

^d calculated from local field model, I

der and fairly the spectrum of the single crystal as a whole, although for few features we were unable to obtain the correct intensities. Principal axis polarizabilities were obtained as result of the fitting.

The similar results obtained with both models suggest that for this crystal and, very likely for a large class of molecular crystals, the long range forces play a minor role in establishing the dynamics of the crystal motions and intensities.

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