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Raman Spectra in Molecular Solids
I. A Study of Low Frequency Modes as a Function of Temperature

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Abstract—The study of the low frequency modes in some molecular solids as a function of temperature shows a drastic decrease of these frequencies as the melting temperature is approached. These results provide a demonstration of the validity of the theory, illustrated by calculations of Cochran and Rosenstock, according which the occurrence of certain phase changes should be accompanied by a decrease or a vanishing of some intermolecular force constants. Furthermore our results allow a tentative discrimination between external and internal modes.

This study was undertaken in order to continue a series of researches carried out in our laboratory on molecular solids.(1,2,3,4) The purpose of this work was to use the molecules of the solid as a probe in their own environment in order to find some relationship between the variation of the frequencies of external modes and the binding forces in a molecular crystal. So, we chose to follow some of the low frequency Raman modes by increasing the temperature, hoping that the variation of frequency near the melting point could give us some insight on the phenomena that occur in the range of stability of the crystalline phase.

1. Experimental

Raman spectra were obtained with a PH1 " Coderg " doublemonochromator spectrometer. The samples were excited with a " Spectra-Physics " 141 Argon laser at 4880 Å or 5145 Å. We used a narrow band interferential filter in order to get rid of the argon lines. Low temperatures were obtained with a modified " Coderg Cryocirc " cell; in our modified system, the thermocouple is embedded within the solid sample very near the laser exciting beam.

In our experimental conditions, the actual resolution was always better than 2 cm^{-1}.

2. Results

We have studied the frequency shifts of the most intense low frequency modes in benzene, fluorobenzene, biphenyl, cyclobutanone† and CS_2.

Absolute error in the determination of the frequencies is of the order of 2 cm^{-1} because of the finite width of the lines and the signal to noise ratio (2 : 1 in the worse cases), but the relative error on the frequency of one particular mode from one spectrum to another is certainly less than 0.5 cm^{-1} for a narrow line and 1 cm^{-1} for a large one.

Spectra were recorded from the lowest possible temperature for each compound to its melting point, with the smallest obtainable temperature increment (5 to 10 °C) in order to determine accurate temperature shift curves. All the curves, except one (Fig. 1), show the same features: a near linear decrease at low temperatures followed by an increasingly rapid decrease as the melting temperature is approached (Figs. 2–6).

These results are in contradiction with those of Ito *et al.*(5) and with the calculations of Harada and Shimanouchi.(6) In our case, we can see on the plot of frequency vs. temperature that frequency is going rapidly down, in a non linear way, near the melting points and should reach a very low value if melting did not interfere.

We can notice here that in benzene the lowest frequency mode near the melting point occurs around 35 cm^{-1} as pointed out by Fruhling.(7) The temperature shift of that line (Fig. 3–C) as calculated by Harada and Shimanouchi(6) on the basis of a De Boer potential is in good agreement with our experimental results far below the melting point but cannot give an account of the variation near that temperature: this discrepancy probably arises from a rapid decrease of density in a pre-melting process(8) and a correlated

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† We would like to thank Prof. J. M. Conia and Prof. M. Fetizon for supplying the cyclobutanone.

increase of the anharmonicity of external modes, as revealed by the important width of the lines in this range.

Our results give an experimental support to the view according which the limit of stability of a crystalline phase is approached as the frequency of a particular mode of intermolecular vibration approaches zero.(9) On this basis, Cochran(10) and Rosenstock(11) think that the occurrence of certain phase changes should also be accompanied by such a decrease and vanishing of some force constants.

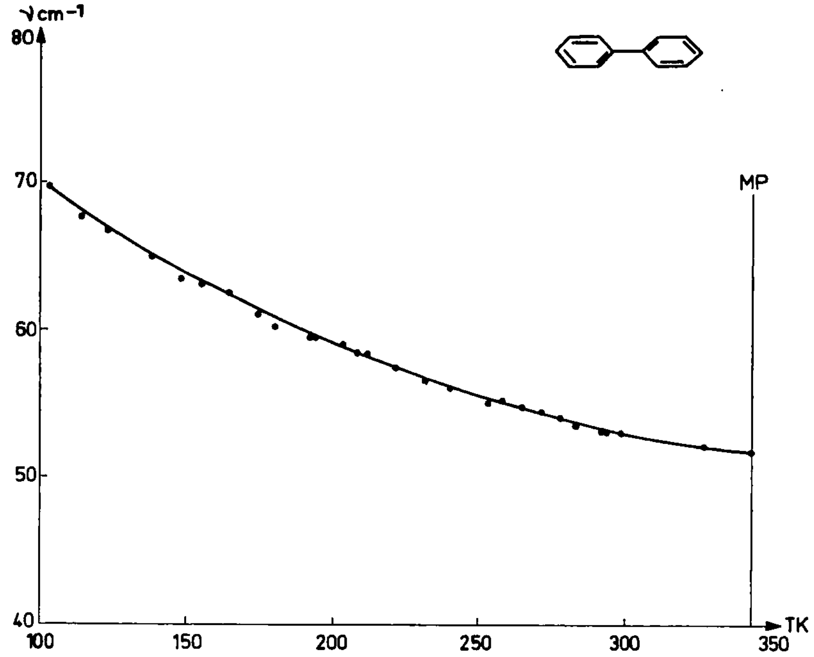

Figure 1. Unusual behavior of the temperature shift of one low frequency mode of biophenyl.

So we are left with one mode in biphenyl (Fig. 1) the behavior of which is different. Its frequency decreases from 70 cm^{-1} at 104 K to 52 cm^{-1} at the melting point (343 K), the slope of the curve approaching zero at this temperature.

We are led to conclude that, contrary to the assignment proposed by others,(12) this particular frequency corresponds to an internal mode, probably to the torsion of the phenyl-phenyl bond.

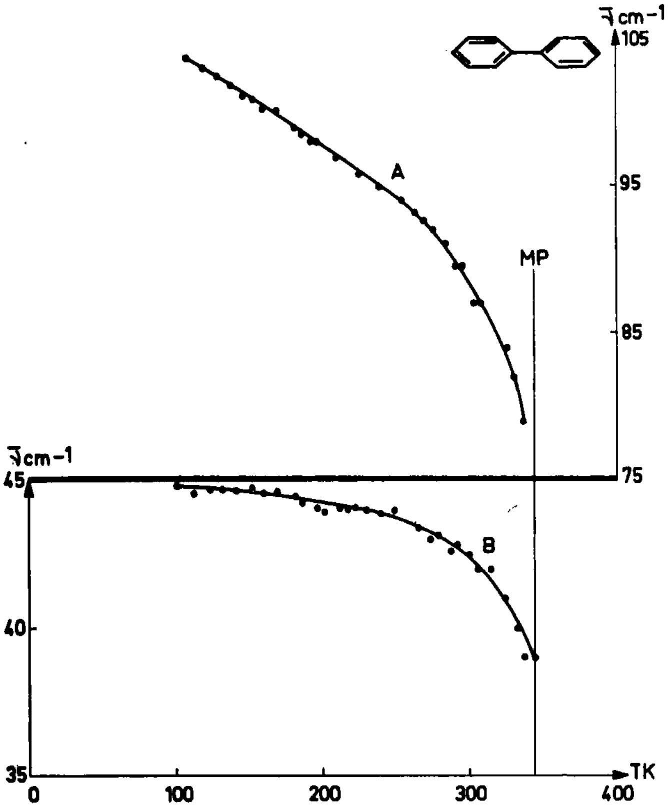

Figure 2. Temperature shift of some low frequency modes in biphenyl.

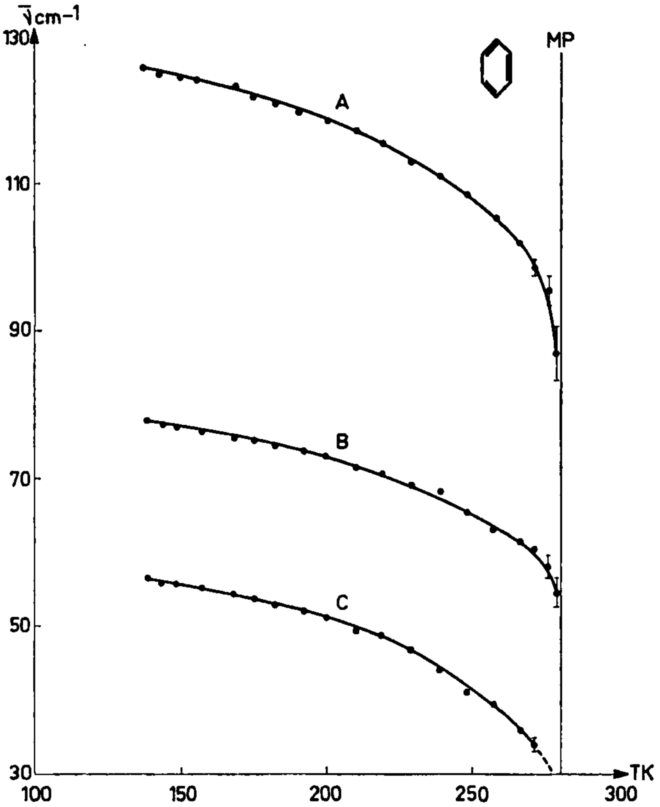

Figure 3. Temperature shift of some low frequency modes in benzene.

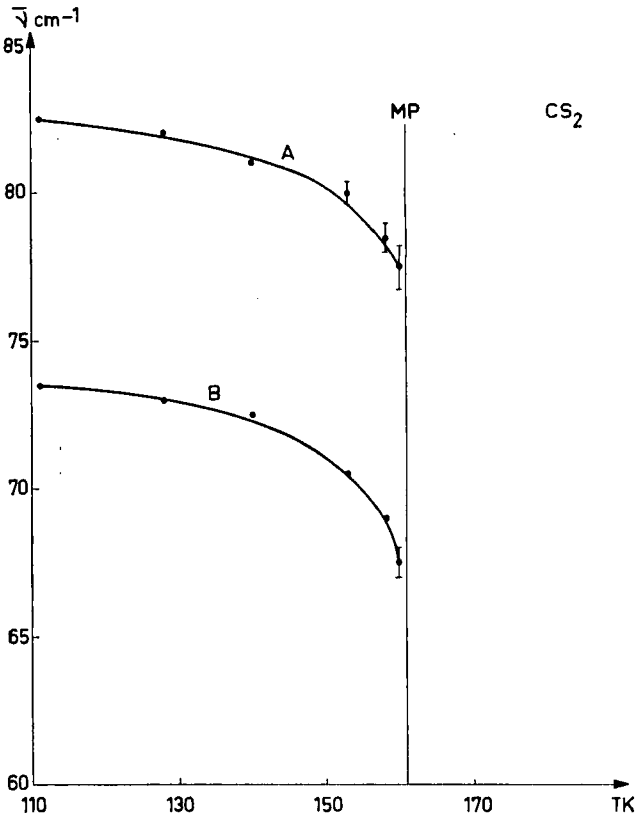

Figure 4. Temperature shift of low frequency modes in CS$_2$.

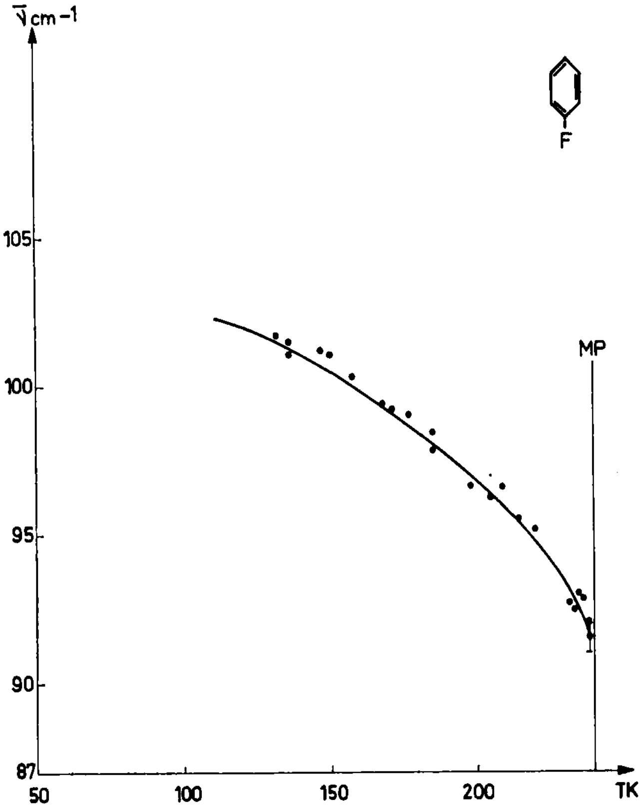

Figure 5. Temperature shift of a low frequency mode in fluorobenzene.

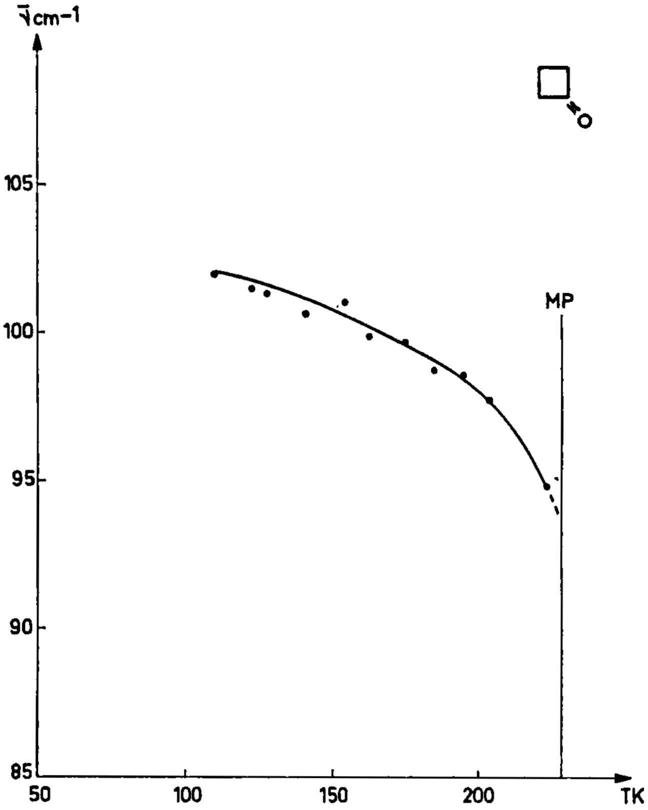

Figure 6. Temperature shift of a low frequency mode in cyclobutanone.

If this conclusion should be proved correct, this method could be helpful in discriminating between external and internal low frequency modes in ambiguous cases.

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