APPENDIX

RAMAN SPECTRUM OF COUMARIN.
Changes in the Raman Spectrum of Coumarin due to change of state were first noted by Venkateswaran. In this note the relative intensities of Raman lines in the solid and molten states of Coumarin are reported. The spectra were obtained using a Zeiss three prism spectrograph and the intensity estimates made with a Lépho microphotometer. Identical conditions have been maintained while recording the spectra of the substance in the two states.

In the case of the solid the peak intensities of the lines are compared with that of the 1174 cm\(^{-1}\) which is taken to have an intensity of 10. The line at 1180 cm\(^{-1}\) is taken as standard in the case of molten solid. The intensities and frequencies are given in Table I. The contours of the lines are different in the two phases of the substance. In the solid phase the lines are slightly broad and diffuse. From Table I, it can be noted that the relative intensities as well as the frequencies undergo marked changes due to the change of state. C-H frequencies are not reported here.

Most of the lines have slightly lower frequency and intensity in the solid. But the lines at 764 and 1454 cm\(^{-1}\) show the reverse trend. The C=C frequency of Coumarin in CCl\(_4\) (1570, 1610, 1625)\(^2\) compares favourably with those for the molten solid (1568, 1611, 1626). The C=O frequency (1732) is not only reduced in intensity but also has become diffuse and split into two in the solid.

Murthy and Seshadri have proposed a mechanism based on hydrogen bonding for the lowering and splitting of the carbonyl band.\(^2\) Another reason may be the existence of correlation field splitting of non-degenerate vibrational bands of molecular crystals as predicted by Hexter.\(^3\)

Seven low frequency lattice lines are observed and are given in Table II (visual intensities are given in brackets). Venkateswaran has observed five lattice lines.\(^1\) Two more lines (29 and 146 cm\(^{-1}\)) are reported here for the first time.

When the substance is molten there is a continuous wing extending up to 90 cm\(^{-1}\) in the place of the lattice lines. Further work in this direction is in progress.

One of the authors (C.P.G.) is thankful to Government of India for the award of a Junior Research Fellowship.

Kerala University, C. P. GIRIJAVALLABHAN.
Dept. of Physics, K. VENKATESWARLU.
Alwaye-4, December 7, 1967.