A.I.C.F.

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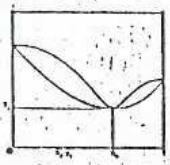

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RAMAN EXCITATION PROFILES OF 9,9'-BIFLUORENYLIDENE AND OF ITS 1:1 COMPLEX WITH TCNQ.

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Recently, resonance Raman spectroscopy has been employed in the study of the electronic properties of complex molecules. This technique is very sensitive to the energy changes of the electronic levels which can be characterized also when the absorption band is broad and unresolved.

We have studied the frequency dependence of the Raman band intensities of 9,9'-bifluorenylidene (Biflu) and of the 1:1 complex with TCNQ in order to get insight on the vibronic structure of their lower energy electronic bands.
Under resonance conditions, bands due to totally symmetric modes are strongly enhanced ; their intensity was found to be dependent from the Franck-Condon factors involving the corresponding vibrational wavefunctions in the ground and in the excited electronic states. In general each Raman band exhibits a different excitation profile with a maximum at a frequency strictly related to the energy of the corresponding vibrational quantum.

From the analysis of the different excitation profiles shown by Biflu in solution, in the solid state and in the complex, it was possible to localize the lowest π-π^* electronic transition. The energy gap between the ground and the first excited states decreases in going from the solution to the solid Biflu ; in the complex it assumes an intermediate value.
Therefore Raman spectra under resonance and pre-resonace conditions could be measured using the Ar^+ laser as exciting source.
The 0-1 vibronic transitions were found to be mainly responsible of the Raman bands enhancements in accordance with the recent achievements of the vibronic theories (1,2).

1) A.Warshel and P.Dauber J.Chem.Phys. 66(1977)5477.
2) P.M.Champion and A.C.Albrecht J.Chem.Phys. 71(1979)1110.