

EUCMOS

ABSTRACTS
OF CONTRIBUTED PAPERS

XIV. EUROPEAN CONGRESS ON
MOLECULAR SPECTROSCOPY
MODERN TRENDS IN SPECTROSCOPY

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Editors

Frankfurt (M) 3. - 7. September 1979

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RESONANCE RAMAN SPECTRA OF CONJUGATED CHROMOPHORES. EVIDENCE FOR
ELECTRONIC AND VIBRATIONAL COUPLINGS IN CRYSTAL VIOLET.

The resonance Raman spectra of crystal violet, which is a relatively simple and symmetric ion, have been measured to provide an experimental support to the recent theoretical approaches¹.

The analysis of the data allowed us, first of all, to determine the structure (D_3 symmetry) and to propose a detailed vibrational assignment in terms of coupled vibrations of the substituted benzenes. The structure consists in fact of three dimethylanilinium groups linked to a central carbon atom and is particularly suitable for studying the effects of the vibrational and electronic couplings of such an important model as the benzene chromophore. We have therefore measured the intensity enhancements of the Raman bands with the variation of the exciting frequency. The comparison with the calculated excitation profiles provided information on the origin of the electronic states and their normal coordinate dependence. In particular evidence was found for the existence of a close correlation in the resonance mechanisms of some modes between crystal violet and benzene and its monosubstituted derivatives. The band intensities of those modes of crystal violet which are related to the Raman active modes of benzene, are mainly derived from the electronic transitions involving orbitals localized on the dimethylanilinium groups. On the contrary the breathing mode of the ion and other vibrations implying remarkable changes of the bonds to the central carbon atom, gain their intensities from the transitions which directly affect the conjugation between the three dimethylanilinium groups.

1) B.B. Johnson and W.L. Peticolas; Ann. Rev. Phys. Chem. 27(1976)465