

# Resonance Raman Spectrum of Crystal Violet

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The preresonance Raman spectra, taken under various conditions, of crystal violet have been obtained using the exciting lines of an Ar<sup>+</sup> laser. The analysis of the Raman data and of the IR and UV visible absorption spectra allowed us to determine the structure of the ion (propeller-like in shape with  $D_3$  symmetry), to characterize the unstable single protonated dye cation, and to propose a detailed vibrational assignment in terms of coupled vibrations of the substituted benzenes. In addition, the measurements of the Raman excitation profiles furnished information on the vibronic couplings and provided evidence for a close correlation in the resonance mechanisms between crystal violet and benzene and its monosubstituted derivatives.

## INTRODUCTION

In recent years resonance Raman spectroscopy has received a great deal of attention as a valuable tool for studying the vibrational and the electronic states of complex molecules.<sup>1,2</sup> Further studies of convenient models are, however, still necessary for testing the theoretical approaches.

In order to provide a reliable test, we have undertaken a spectroscopic investigation on crystal violet (tri-*p*-dimethylamino phenylcarbonium ion) (hereafter CV) which is a relatively simple ion with a presumably high symmetry. In the ion three dimethylanilinium groups are linked to a central carbon atom and this offers the possibility of studying the effects of the vibrational and the electronic couplings of such an important model as the benzene chromophore. Moreover, the strong absorption in the visible region of the spectrum shown from CV allows the use of available light sources for resonance Raman experiments. Finally, CV has been shown to give rise to a good quality Raman spectrum.<sup>3</sup>

In the present paper we report on the results obtained from the analysis of the Raman, IR and UV visible spectra, taken under various conditions, of CV.

The analysis allowed us to determine the structure of the ion, to characterize the unstable single protonated dye cation (hereafter HCV) in the acidic solution, and to propose a detailed vibrational assignment in terms of coupled vibrations of the substituted benzenes. Finally, the intensity enhancements of the Raman bands with the variation of the exciting frequency, i.e. the excitation profiles, provided information on the origin of the electronic states and on their normal coordinate dependence. In particular, we have found evidence for the existence of a close correlation in the resonance mechanisms between CV and benzene and its monosubstituted derivatives. The band intensities of CV modes, related to the Raman active modes of benzene, appear in fact to be mainly derived from the electronic transitions involving orbitals localized on the dimethylanilinium groups. On the contrary, the CV breathing mode 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.

## EXPERIMENTAL

CV was purchased from E. Merck and purified by repeated crystallization from water. The Raman spectra were measured with the aid of a double monochromator Jobin-Yvon model HG-2S and a photon counting system equipped with a thermoelectrically cooled type RCA-C31034A photomultiplier. The data were collected by the use of a 'Silena' system BS 27/N multichannel analyser. Six exciting lines (457.9, 476.5, 488.0, 496.5, 501.7 and 514.5 nm) of a Coherent Radiation Laboratory model 52 Ar<sup>+</sup> laser were used as radiation sources.

The spectra of CV were taken with a 90° geometry, even in polarized light, in H<sub>2</sub>O, CHCl<sub>3</sub> and CH<sub>3</sub>OH solutions (10<sup>-4</sup> M). No effects due to photodecomposition were found, as shown by repeated runs of the spectra. In addition, no change was observed in the visible absorption spectra before and after exposure to the laser beam. The reabsorption of scattered light was minimized by keeping the laser beam very close to the edge of the cell. Band intensities were corrected for the change of the sensitivity of the spectrometer with the wavelength, using a calibration curve established with a standard lamp. The intensities of some bands were measured by peak heights and by areas with similar results. Peak height measurements were therefore used throughout, taking the band at 1034 cm<sup>-1</sup> of methanol as internal standard. Corrections were made for the difference in  $\nu^4$  factor between the intensities of the observed Raman bands and of the internal standard.

The Raman spectrum of the powder was also measured in a backscattering geometry. In order to avoid photodecomposition, the laser power was kept very low (<5 mW) for this case.

The IR spectra of CV in Nujol mull and in CHCl<sub>3</sub> solution were measured with the aid of a Perkin-Elmer model 225 spectrometer. The electronic spectra in H<sub>2</sub>O and CH<sub>3</sub>OH solutions were taken on a Cary model 17 spectrophotometer.

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The Raman and UV visible spectra were also registered by changing the acidity of the aqueous solution in an extended range of pH values (0.5–7). Because HCV is rather unstable, the spectra were measured by means of a fast scanning mode.

## RESULTS AND DISCUSSION

### Structure and vibrational assignment of crystal violet

CV, as well as symmetrical triphenylmethyl dyes, is generally considered stabilized by resonance between various canonical forms and the stabilization is expected to be greatest for the all-planar configuration of the ion ( $D_{3h}$  symmetry). However, such a configuration could give rise to steric hindrance between the *ortho*-hydrogen atoms of the three dimethylanilinium groups linked to the central carbon atom. As a consequence, the structure is distorted by a rotation of the groups about the central bonds, assuming a propeller-like shape with a  $D_3$  symmetry in the most symmetrical configuration.

A nearly planar structure, on the other hand, has been proposed on the basis of a preliminary X-ray study.<sup>4</sup> Also, Aleksandrov *et al.*<sup>5</sup> have discussed the vibrational spectra in solution assuming a planar structure.

Lewis *et al.*<sup>6</sup> suggested the existence in solution of two isomers, both showing a non-planar configuration. One isomer is supposed to exhibit a  $D_3$  propeller-like structure, the other being its rotamer, with no symmetry, in which a dimethylanilinium group is rotated about the central bonds in the opposite sense from the other two groups.

Raman spectroscopy provides in principle a powerful tool to deduce the symmetry of the possible configurations. The vibrational selection rules for the various assumed symmetries of CV can be given in terms of correlation diagrams since most vibration frequencies should correspond to coupled vibrations of the three dimethylanilinium groups. The remaining modes are then formally described according to a model consisting of three rigid bodies linked to the central carbon atom.

The correlations between the configurations of higher symmetry ( $D_{3h}$  and  $D_3$ ) of the ion and the local symmetries of the groups are reported in Table 1. The Raman spectra of CV in  $\text{CH}_3\text{OH}$  solution and the spectra in polarized light in  $\text{H}_2\text{O}$  solution are shown in Figs. 1 and 2 respectively. Figure 3 shows the IR spectra in Nujol mull and in  $\text{CHCl}_3$  solution. The peak frequencies together with the vibrational assignment are collected in Table 2.

From a careful inspection of the spectra the following features can be determined:

(i) The Raman spectrum may be considered as formed by multiplets made up of two or three rather spaced ( $\sim 20 \text{ cm}^{-1}$ ) components occurring near the band frequencies of the active and inactive vibrations of benzene.

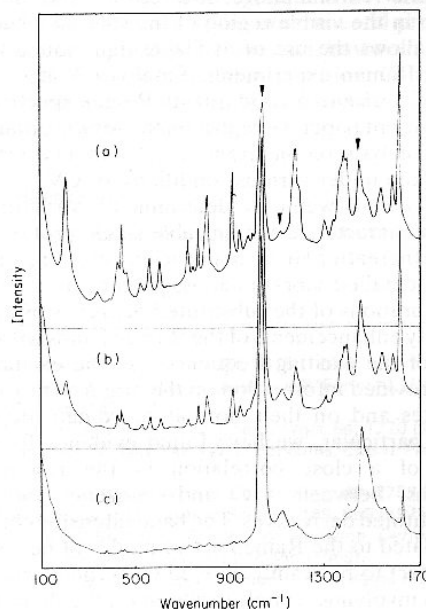
(ii) The overall Raman spectrum is quite similar in both the number and the frequencies of the bands to the Raman spectrum of the triphenylmethyl cation,<sup>7</sup> the most striking difference being the presence in the CV spectrum of a surplus strong doublet at about  $1380 \text{ cm}^{-1}$ .

**Table 1. Correlation tables and vibrational activity for  $D_{3h}$  and  $D_3$  groups**

$D_{3h}$	$C_{2v}$	$D_{6h}$	$C_2$	$D_3$
$A_1'$ R(p) $A_2'$ $E'$ R(dp) $A_1''$ $A_2''$ IR $E''$ R(dp)	$A_1$ $B_1$ $E$ $A_2$ $B_2$ $E$	$A_{1g}$ $A_{2g}$ $B_{1g}$ $B_{2g}$ $E_{1g}$ $E_{2g}$ $A_{1u}$ $A_{2u}$ $B_{1u}$ $B_{2u}$ $E_{1u}$ $E_{2u}$	$A$ $B$ $E$	$A_1$ R(p) $A_2$ IR $E$ R(dp) IR

clearly assigned to the  $\nu(\varphi-\text{N})$  stretching mode. Bands due to the vibrations of the  $-\text{N}(\text{CH}_3)_2$  groups are therefore missed.

(iii) The polarization character of the Raman bands is well defined, being  $\rho = \frac{1}{8}$  for the polarized bands and  $\rho = \frac{3}{4}$  for the depolarized ones. The value  $\rho = \frac{1}{3}$  for the band at  $830 \text{ cm}^{-1}$  can be interpreted as due to overlapping of two components with different polarization. Only one component of each multiplet is polarized and in general missed in the IR spectrum. The Raman-IR near coincidence of the bands at  $1170$  and  $940 \text{ cm}^{-1}$  should be accidental.



**Figure 1.** Raman spectra of CV in  $\text{CH}_3\text{OH}$  solution ( $10^{-4} \text{ M}$ ) taken with the 514.5 nm (a), 488.0 nm (b) and 457.9 nm (c) exciting lines. Bands due to the solvent are indicated.

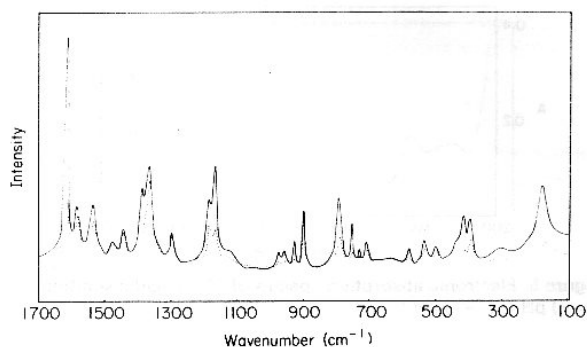


Figure 2. Polarized Raman spectra (488.0 nm exciting line) of CV in H<sub>2</sub>O solution: (—) parallel and (---) perpendicular polarization.

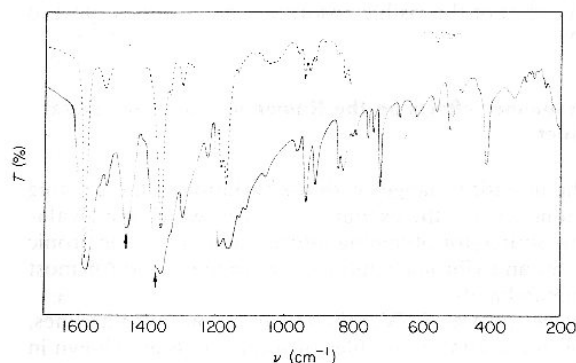


Figure 3. IR spectra of CV in Nujol mull (—) and CHCl<sub>3</sub> solution (---).

From the analysis of the spectra, taking into account the selection rules, the correlation tables and the band polarization character, we can now show that CV assumes a  $D_3$  point group symmetry. In fact at most three components, only one polarized, are observed for each degenerate benzene vibration as expected for  $D_{3h}$ ,  $D_3$ ,  $C_{3v}$  and  $C_3$  ion symmetries. One more component would occur for groups of lower symmetry. In addition, the value of the depolarization ratio ( $\rho = \frac{1}{8}$ ) proves that the ion actually has a 3-fold symmetry axis. On the other hand,  $C_{3v}$  and  $C_3$  groups are ruled out since in these cases the polarized Raman bands would coincide with IR active counterparts. Finally, the occurrence of triplets, each showing a polarized component, due to the out-of-plane 'benzene' modes strongly favours the  $D_3$  structure. In fact, whereas for a  $D_{3h}$  group each out-of-plane mode would give rise to two components, both depolarized, for a  $D_3$  structure three components, one polarized and two depolarized, are expected.

On the basis of a  $D_3$  symmetry for the ion and of a  $C_2$  local symmetry for the dimethylanilinium groups, the detailed assignment of the observed Raman bands is reported in Table 2. Apart from the  $\nu(\varphi-N)$  stretching mode at  $\sim 1380$  cm<sup>-1</sup> and the two bands at low frequencies (335 and 202 cm<sup>-1</sup>), all the bands are assigned to

Table 2. Vibrational frequencies and assignments of CV and HCV

IR <sup>a</sup> CV	Raman <sup>b</sup>			Symmetry species			Assignment <sup>c</sup>
	CV	Pol	HCV	Ion $D_3$	Group $C_2$	Chrom $D_{6h}$	
—	1620	p	1620	A	A		8a
1584	1589	dp	1605	E	B	$E_{2g}$	8b
s	1540	dp		E	B		19a
s	1483	dp	1517	E	A	$E_{1u}$	19b
1442	1449	dp		E	B		
—	1396	p	1432	A	A		$\nu(\varphi-N)$
1362	1370	dp	1228	E	B	$B_{2u}$	14
	1311	dp		E	B		
1300	1301	dp		E	B		
1188	1191	dp	1200	E	A		9a
	1172	p	1177	A	B	$E_{2g}$	9b
1171				E	B		
—	990	p		A	A	$A_{1g}$	1
—	975	p		A	A	$E_{1u}$	18a
960				E	B		18b
943	941	p	932	A	A	$B_{1u}$	12
914	914	dp	910	E	B		10b
830				E	B	$E_{1g}$	10a
s	804	p	790	A	A		17a
s	768	p		A	A		
	743	dp	727	E	B	$E_{2u}$	17b
s	724	dp		E	B		6a
—	608	p		A	A		
560	565	dp	545	E	B	$E_{2g}$	6b
522	528	dp		E	B		16b
	463	dp		E	B	$E_{2u}$	
	441	p	437	A	A		16a
	421	dp	417	E	A		
	335	dp		E			$\delta(\varphi-C-\varphi)$
	202	p		A			Breathing

<sup>a</sup> Frequencies in cm<sup>-1</sup>. Spectrum measured in CHCl<sub>3</sub> solution. s = solvent absorption.

<sup>b</sup> Frequencies in cm<sup>-1</sup>. Spectra measured in H<sub>2</sub>O solution.

<sup>c</sup> Classified according to the normal modes of benzene.

'benzene' vibrations. We assign the strong polarized band at 202 cm<sup>-1</sup>, which also appears in other triphenylmethyl dyes,<sup>5,7</sup> to the breathing vibration of the central bonds. The lower the frequency of this band, the

larger are the masses of the substituted groups as expected for such a mode. Finally, the depolarized band at  $335\text{ cm}^{-1}$  could be due to the degenerate bending of the bonds to the central carbon atom.

From the above discussion it seems clear that we have found no evidence for the existence of two isomers in solution as proposed in Ref. 6 on the basis of the occurrence of two bands in the visible absorption spectrum (Fig. 4). The close resemblance between the solid and the solution spectra is a further proof that only one species exists in the neutral solution.

In conclusion, we propose for CV a propeller-like  $D_3$  structure similar to that found for triphenylmethyl cation in the solid state.<sup>8</sup>

### Singly protonated crystal violet cation

CV gradually changes its colour by increasing the acidity of the aqueous solution, being blue-green at pH 2–5 and yellow at pH 1.

In order to ascertain the number and the nature of the species in solution we have measured the Raman and the electronic spectra at various pH values. We found that only two species are in equilibrium, CV and its singly protonated dye cation (HCV), the different colours being simply given by different concentration ratios between CV and HCV. This is clearly shown from the absorption spectra (Fig. 5), the spectrum at pH 4 being actually a summation of the spectra at pH 1 and pH 7. Correspondingly, in the Raman spectrum, bands due either to CV or to HCV are observed.

HCV is unstable and its colour fades since its concentration, as measured from the absorption spectrum, is reduced to about half in 1 h. However, we were able to measure the Raman spectrum of HCV (Fig. 6), including the polarization data, by a fast scanning procedure. It is seen that several bands are missed with respect to the spectrum of CV. However, the vibrational assignment is straightforward since the observed bands are clearly related to those occurring in the CV spectrum. The assignment, assuming a  $C_2$  symmetry and taking into account that all bands are polarized ( $\rho = \frac{1}{3}$ ), is reported in Table 2. It is seen that whereas bands due to 'benzene'

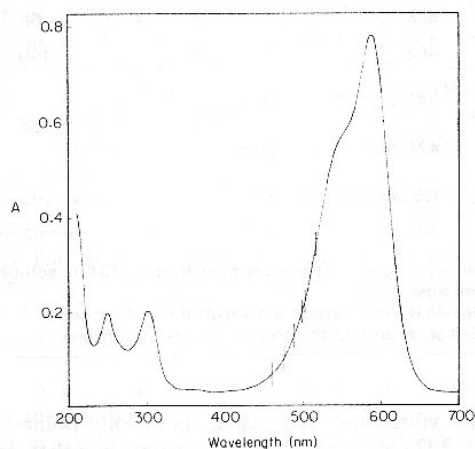


Figure 4. Electronic absorption spectrum of CV in  $\text{CH}_3\text{OH}$  ( $10^{-5}\text{ M}$ ). Exciting wavelengths used for Raman data are marked.

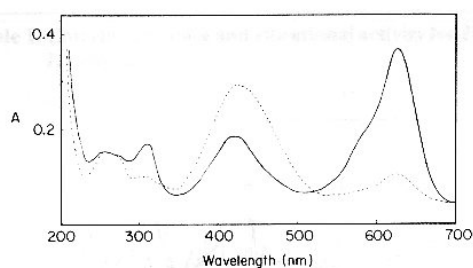


Figure 5. Electronic absorption spectra of CV in acidic solution: (—) pH 4, (---) pH 1.

modes occur at about the same frequencies with respect to the CV spectrum, the two bands belonging to the  $\nu(\varphi-N)$  stretching vibrations occur far apart from each other. This is not unexpected since it is consistent with the electron withdrawing effect of a protonated dimethylamino group and with the strong distortion of the chromophoric framework as proved from the large blue shift of the visible absorption band with respect to CV.

### Resonance effects on the Raman spectrum of crystal violet

The intensity changes with the variation of the exciting frequency, i.e. the excitation profiles, which are a valuable source for obtaining information on the electronic states and vibronic couplings, were measured for most Raman bands.

The spectra of CV, taken with various exciting lines, and the excitation profiles of some bands are shown in Figs. 1 and 7 respectively. It is seen that the relative intensities of several bands, due to modes belonging to both the  $A_1$  and  $E$  Raman active species, are greatly enhanced with the shift of the exciting wavelength.

Two theories, due to Albrecht<sup>9</sup> and Peticolas *et al.*,<sup>10</sup> have been preferentially used to explain the experimental results. The two treatments have been shown to be equivalent in preresonance or far from resonance conditions<sup>10</sup> and also, under proper conditions, at rigorous resonance.<sup>11,12</sup>

In preresonance cases, assuming a vibronic coupling between only two electronic excited states  $e$  and  $s$ , the

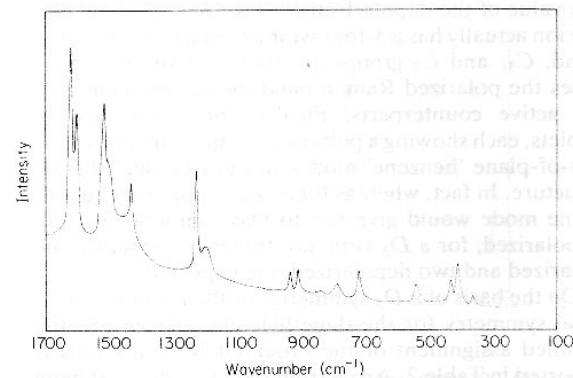
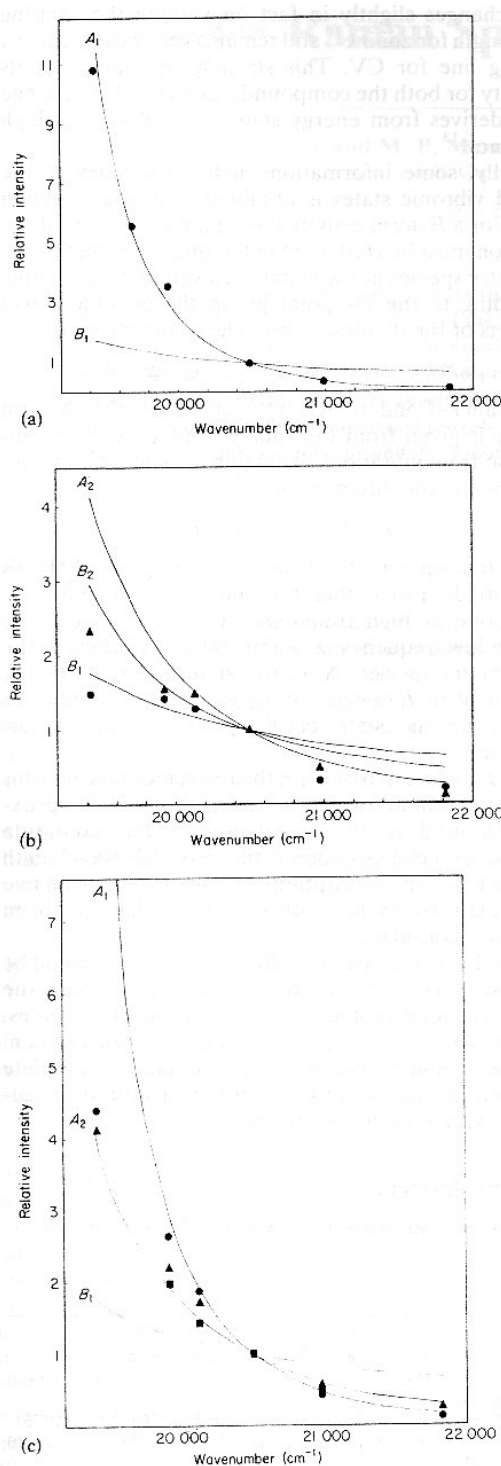


Figure 6. Raman spectrum of HCV in  $\text{H}_2\text{O}$  solution taken with the 488.0 nm exciting line.

# RESONANCE RAMAN SPECTRUM OF CRYSTAL VIOLET



**Figure 7.** (a) Relative intensity (●) of the 202 cm<sup>-1</sup> band as a function of the exciting frequency. Solid lines indicate the calculated profiles according to  $F_A^2$  with  $\lambda_e = 550$  nm ( $A_1$ ) and to  $F_B^2$  with  $\lambda_e = 589$  nm,  $\lambda_s = 300$  nm ( $B_1$ ). (b) Relative intensity of the 1620 cm<sup>-1</sup> (●) and 1589 cm<sup>-1</sup> (▲) bands as a function of the exciting frequency. Solid lines indicate the calculated profiles according to  $F_A^2$  with  $\lambda_e = 589$  nm ( $A_2$ ), to  $F_B^2$  with  $\lambda_e = 550$  nm,  $\lambda_s = 300$  nm ( $B_2$ ) and as in (a) ( $B_1$ ). (c) Relative intensity of the 914 cm<sup>-1</sup> (●), 941 cm<sup>-1</sup> (▲) and 1396–1370 cm<sup>-1</sup> (■) bands as a function of the exciting frequency. Solid lines indicate the calculated profiles as in (a) ( $A_1$ ,  $B_1$ ) and (b) ( $A_2$ ).

dependence of the band intensity upon the exciting frequency is given<sup>13</sup> by

$$I(\nu) \propto (\nu_0 - \nu_i)^4 F^2(e, s)$$

where

$$F(e, s) = \frac{\nu_e \nu_s + \nu_0^2}{(\nu_e^2 - \nu_0^2)(\nu_s^2 - \nu_0^2)} = F_B$$

$\nu_e$  and  $\nu_s$  being the transition frequencies for the electronic states  $e$  and  $s$ ,  $\nu_0$  the frequency of the incident radiation and  $\nu_i$  the Raman shift.

This expression holds for a vibronically allowed Raman transition, whereas for a Franck-Condon overlap allowed transition, where  $e = s$ , the frequency factor is given by

$$F_e = \frac{\nu_e^2 + \nu_0^2}{(\nu_e^2 - \nu_0^2)^2} = F_A$$

The above simplified expressions are no more valid for rigorous resonance, where we have to deal with the damping factor and with the sum over the vibrational levels of the resonant state.

Although our exciting lines are not very far from the maximum of the absorption curve (Fig. 4), it seems possible, however, to reach some conclusions on the electronic and the vibrational states involved in the resonance mechanisms from a comparison between the frequency factors  $F_A$  and  $F_B$  and the experimental profiles.

The most remarkable intensity enhancement in the spectrum is shown from the band at 202 cm<sup>-1</sup> assigned to the breathing of the bonds to the central carbon atom. It is the maximum possible enhancement predicted by the frequency factors. The  $F_A$  term with  $\lambda_e = 550$  nm in fact fits the experimental excitation profile very well (Fig. 7a). This indicates that the intensity of the band is due to a purely Franck-Condon allowed transition. In accordance with the rule of Hirakawa and Tsuboi<sup>14</sup> that the equilibrium conformation of the molecule is distorted along the normal coordinate in the vibronic transition, the phenyl-central carbon bonds of CV should be remarkably longer in the state originating at the 550 nm band than in the ground state. As a consequence, the conjugation between the dimethylanilinium groups is broken in this excited state.

The strong band found in the low frequency region of the preresonance Raman spectra of some symmetric triphenylmethyl cations,<sup>5,7</sup> which seems a peculiar feature of such compounds, should take the same origin as in CV. The band is missed in the spectrum of HCV, which exhibits a chromophoric framework strongly distorted from the  $D_3$  propeller-like structure.

As far as the other bands in the Raman spectrum of CV are concerned, some distinctive features can be characterized. In general, rather small differences are found between the excitation profiles of the components of  $A$  and  $E$  species originated by coupling of each vibration of the dimethylanilinium groups (Figs. 7b and 7c). On the contrary, the excitation profiles of the multiplets, taken as a whole, are very different.

We now restrict our discussion to some vibrations, namely the  $\nu_8$ ,  $\nu_9$ , and  $\nu_{12}$  'benzene' planar modes and the  $\nu(\varphi-N)$  stretching mode, which are surely localized and show well-defined excitation profiles. The Raman

active 'benzene' modes  $\nu_8$  and  $\nu_9$ , also giving rise to strong bands, show moderate intensity enhancements (Fig. 7b). Therefore their intensities should be caused by a vibronic coupling ( $B$  term) between the higher ( $\lambda_e = 240\text{--}300\text{ nm}$ ) and the lower ( $\lambda_e = 550\text{--}589\text{ nm}$ ) energy states. On the other hand, the  $\nu_{12}$  and the  $\nu(\varphi\text{--}N)$  modes show steep rising profiles as expected for an  $A$  term ( $\lambda_e = 589\text{ nm}$ ) activity (Fig. 7c).

In order to give an interpretation of the above results, we have to consider the approximate nuclear displacements involved in these modes.<sup>15</sup> In  $p$ -disubstituted benzene derivatives the 1 and 4 carbon atoms undertake noticeable displacements along the 1–4 direction during the  $\nu_{12}$  and the  $\nu(C\text{--}X)$  vibrations, whereas for  $\nu_8$  and  $\nu_9$  modes, they are unshifted or vibrating perpendicularly to that direction. It therefore seems reasonable to assume that in CV the  $\nu_{12}$  and the  $\nu(\varphi\text{--}N)$  modes give rise to large changes of the phenyl–central carbon distances, whereas the  $\nu_8$  and  $\nu_9$  modes hardly affect them.

The  $A$ -term activity of the  $\nu_{12}$  and  $\nu(\varphi\text{--}N)$  modes clearly indicates that the equilibrium conformation of CV is distorted along these normal coordinates and that the phenyl–central carbon bonds change their character from 'bonding' to 'antibonding' with the low frequency ( $\lambda_e = 589\text{ nm}$ ) transition.

Also, the  $B$ -term activity displayed from the  $\nu_8$  and  $\nu_9$  modes is clearly consistent with the predicted nuclear displacements. These modes can in fact couple the higher ( $\lambda_s = 240\text{--}300\text{ nm}$ ) with the lower ( $\lambda_e = 550\text{--}589\text{ nm}$ ) excited energy states without affecting the equilibrium conformation of the ion on going from the ground state to the lower excited states. This means that the higher frequency transitions involve molecular orbitals localized on the dimethylanilinium groups.

According to this interpretation, it is interesting to note that in the Raman spectrum of aniline the bands due to  $\nu_8$  and  $\nu_9$  modes are greatly enhanced on changing the exciting wavelength from 514.5 to 363.8 nm.<sup>16</sup> This has been interpreted in terms of a distortion of the equilibrium conformation of the aniline molecule just along the normal coordinates of  $\nu_8$  and  $\nu_9$  in the transition from the ground state to the lowest excited states ( $\lambda = 234, 290\text{ nm}$ ).

The close correlation between the Raman and UV visible spectra of aniline and CV is confirmed from the behaviour of the ring breathing band  $\nu_1$  at  $998\text{ cm}^{-1}$  for aniline and at  $990\text{ cm}^{-1}$  for CV. The intensity of this

band changes slightly in fact on varying the exciting wavelength for aniline<sup>16</sup> and remains very weak with any exciting line for CV. This strongly indicates that its intensity for both the compounds, as well as for benzene itself, derives from energy states located at very high frequency.<sup>13</sup>

Finally, some information on the symmetry of the excited vibronic states is obtained from the selection rules. For a  $B$ -term activity the symmetry species of the vibration must be contained in the direct product of the symmetry species of the states involved in the coupling. According to the  $D_3$  point group the possible direct products of the dipole-allowed electronic states are

$$E \times E = A_1 + A_2 + E; \quad A_2 \times E = E$$

For Franck–Condon overlap transitions, the  $A$ -term activity is given from the totally symmetric vibrations and also from vibrations belonging to symmetry species contained in the direct product:<sup>13</sup>

$$E \times E = A_1 + A_2 + E$$

The  $B$ -term activity of the  $A_1$  component of the  $\nu_8$  and  $\nu_9$  modes proves therefore that at least two vibronic states, one at high frequency ( $\lambda = 240\text{--}300\text{ nm}$ ), the other at low frequency ( $\lambda = 550\text{--}589\text{ nm}$ ), belong to the  $E$  symmetry species. Also, the  $A$ -term activity of the component of  $E$  species of  $\nu_{12}$  and  $\nu(\varphi\text{--}N)$  indicates that a vibronic state of  $E$  species occurs at low frequency.

In the above discussion on the resonance mechanisms and on the symmetries of the states, due to the approximations used in the calculation of the excitation profiles, we have considered the two high wavelength (550 and 589 nm) absorptions as a whole. Also, the two wavelength absorptions (240 and 300 nm) have not been separately considered.

Even if in some cases the effects of each state could be resolved in view of the good agreement between the frequency factor profiles and the experimental profiles, from the data at our disposal it does not, however, seem possible to obtain more detailed information. Complete excitation profiles have to be either measured or calculated with a proper approach.

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