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Vibronic Couplings in Vibrational Spectra of Crystalline *p*-Chloroaniline

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The polarized middle (M)IR transmission and ATR spectra, the polarized NIR absorption spectra of the *p*-chloroaniline (*p*-CA) single crystal and the MIR spectra of the *p*-CA and benzene solutions, as well as the Raman spectra of the crystal, solution and molten *p*-CA have been measured. Also the inelastic incoherent neutron scattering (IINS) spectra have been measured for comparison. The dichroic ratios for the crystal plane (111) have been calculated and compared with the observed ones. One previous assumption concerning the applicability of the oriented gas model has been proved within the effective charge-charge flux model. On the basis of the detailed qualitative analysis of the intensities and frequencies of the fundamental vibration bands, many observed features of the spectra have been explained by vibronic couplings.

1. INTRODUCTION

Studies of *p*-CA infrared spectra were undertaken many years ago in order to compare them with the *p*-nitroaniline (*p*-NA) spectra[1]. Later, in the lattice Raman spectra of the *p*-CA crystal, the discrepancies from the tensorial oriented gas model (OGM) were explained by taking into account the coupling between the exciton states resulting from the Davydov splitting of electronic transitions with the non-totally symmetric lattice phonons b_{1g} and b_{3g} [2]. Since the symmetry of the first singlet state in the *p*-CA molecule is that of B_2 [3], the second singlet state was assumed to be B_1 in analogy to the *p*-dichlorobenzene spectra described in [4].

The dipole moment increase of *p*-CA on excitation to the $^1B_2$ state equals 1.26 D[3] and the contribution of the resonance structure with a lone-pair-electron of nitrogen shifted toward the neighbouring carbon atom found in the *p*-CA crystal by Trotter *et al.*[5] indicates that the lowest electronic transition has to some extent a charge transfer (CT) character.

Recently, many similarities to the spectra of CT complexes have been found in the vibrational spectra of nonlinear electrooptic molecule and crystal of meta-nitroaniline (*m*-NA)[6–8], which also has CT electronic transitions. As the *p*-CA crystal is a centrosymmetric one[5] and as far as we know the *p*-CA molecule does not reveal any nonlinearity either, it seems to be a good model system for comparison with *m*-NA in order to find features of its vibrational spectra connected with the nonlinear electrooptic properties.

The goal of this work is to study the vibrational (IR, Raman, IINS) spectra of *p*-CA in the fundamental frequency range in different media, to analyze them in comparison with benzene spectra and by application of the vectorial OGM and of the method proposed in [8] to examine whether vibronic couplings are present and comparable with those in *m*-NA.

The second aim of the paper is a continuation of the previous study [9] on the applicability of vectorial OGM to the group of overlapping bands in the NIR region. Some earlier assumptions could be justified now in terms of the effective charge-charge flux (ECCF) model[10].

The vibrational spectra of *p*-CA were the subject of many studies; Garrigou-Lagrange[11] assigned 21 bands to the fundamental vibrations in the IR spectra of *p*-CA in CCl_4 solution and Singh *et al.*[12] proposed assignments of 26 fundamentals of *p*-CA in KBr pellet. The polarized IR spectra at 20 K of the oriented *p*-CA films were investigated by Tripathi and Katon[13] and the polarized Raman spectra of the crystal by Steger *et al.*[14]. The FIR vapor phase spectra of *p*-CA among other halosubstituted anilines were reported by Kydd and Krueger[15].

2. EXPERIMENTAL

Commercial (BDH) *p*-CA was purified by repeated zone refinement in a nitrogen atmosphere and single crystals were grown by slow evaporation of solvent from the saturated toluene solution in the form of hexagons of dimensions about $6 \times 10 \times 10$ mm^3.

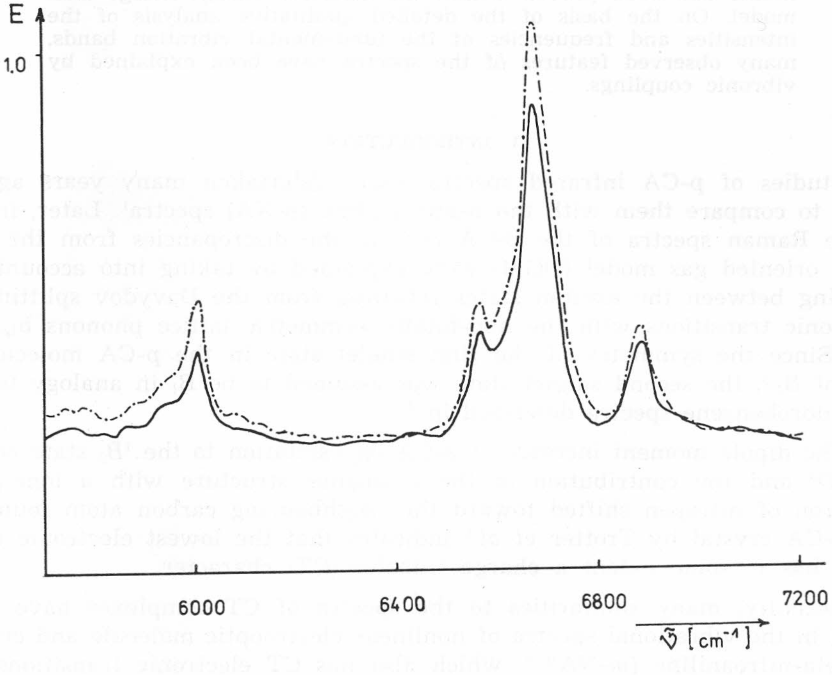

Figure 1. Polarized NIR spectrum of p-CA single crystal (111). ——— $\vec{E} \parallel a'$, —·—·—·— $\vec{E} \parallel b'$.

The plane of the specimens found by the X-ray method was the (111) plane. These plates were used to measure the polarized near infrared (NIR) spectra in the 5800—7200 cm^{-1} region (Figure 1) on the Carl Zeiss spectrometer set-up described in [1] and the polarized attenuated total reflection (ATR) spectra in the middle infrared (MIR) region (Figure 2) on the Perkin-Elmer 621 spectrophotometer. To measure the ATR spectra, the *p*-CA crystals were glued with nujol on the KRS-5 crystal; the angles of incidence used were those of 55 and 60°. In Figure 2 the spectrum taken at 60° is shown.

The MIR spectra of the *p*-CA and benzene (B) solutions in CCl_4, for which the products of the concentration times, the cell thickness, *c. l*, were in relation 1 : 2, respectively ($2.8 \cdot 10^{-4}$ mol dm^{-2} : $5.6 \cdot 10^{-4}$ mol dm^{-2}; $l = 0.07$ mm), measured also on Perkin-Elmer 621 are shown in Figure 3.

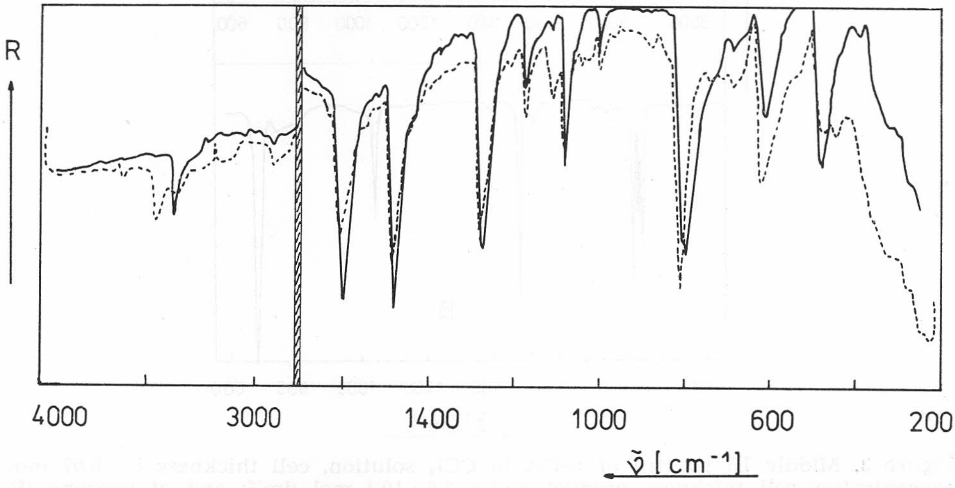

Figure 2. Polarized ATR spectrum of p-CA single crystal (111). ——— $\vec{E} \parallel a'$, – – – – $\vec{E} \parallel b'$, incidence angle 60°.

The polarized transmission MIR and polarized Raman spectra of the crystal are not displayed as they are similar to those reported in ref. 3 and 4, respectively. From the two of the non-crystalline Raman spectra, namely of the solution and melt taken on Coderg PHO with the 488 nm argon exciting line only the polarized spectrum of molten *p*-CA near the melting point (344 K) is shown in Figure 4. Newertheless, the information found in the omitted spectra is included in Table IV.

The inelastic incoherent neutron scattering (IINS) spectra of the powdered *p*-CA at room temperature and at liquid nitrogen temperature were measured in the whole available region (Figure 5) on the spectrometer KDSOG-1 coupled with the reactor IBR-30 in Dubna (USSR). It was described in more detail in ref. 16 where the IINS lattice spectrum of *p*-CA was studied.

In order to find the reference directions for the calculation of dichroic ratios of the infrared bands according to the vectorial OGM, the angles between the extinction directions in the (111) plane labelled *a*' and *b*' and the edges of the hexagon (Figure 6) were measured, as well as the angles between the edges of the hexagon. The latter have the values: 59° ± 2°; 55° ± 1.5° and 66° ± 2.2° and correspond well to the values of angles in the triangle ABC formed by crossing the (111) plane by the crystallographic axes, *e. i.*: $\sphericalangle A = 58.75°$; $\sphericalangle B = 55.15°$ and $\sphericalangle C = 66.13°$. On this basis and by comparison of the experimental and calculated dichroic ratios in the NIR spectra, the angle α (Figure 6) was found to be about 3.5°. One should mention that the dichroic ratio values depend strongly on this value which is impossible to predict theoretically without knowing the values of principal refractive indices.

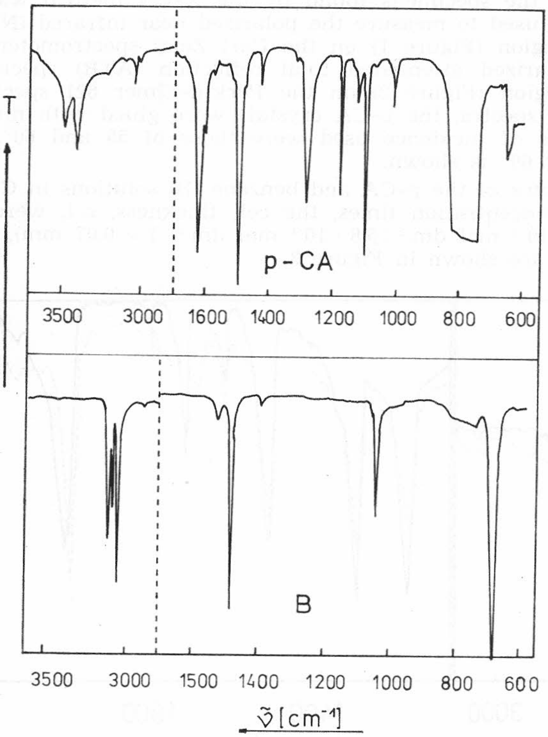

Figure 3. Middle IR spectra of p-CA in CCl_4 solution, cell thickness $l = 0.07$ mm, concentration-cell thickness product $c \cdot l = 2.8 \cdot 10^{-4}$ mol dm^{-2}; and of benzene (B) in CCl_4 solution, $l = 0.07$ mm, $c \cdot l = 5.6 \cdot 10^{-4}$ mol dm^{-2}.

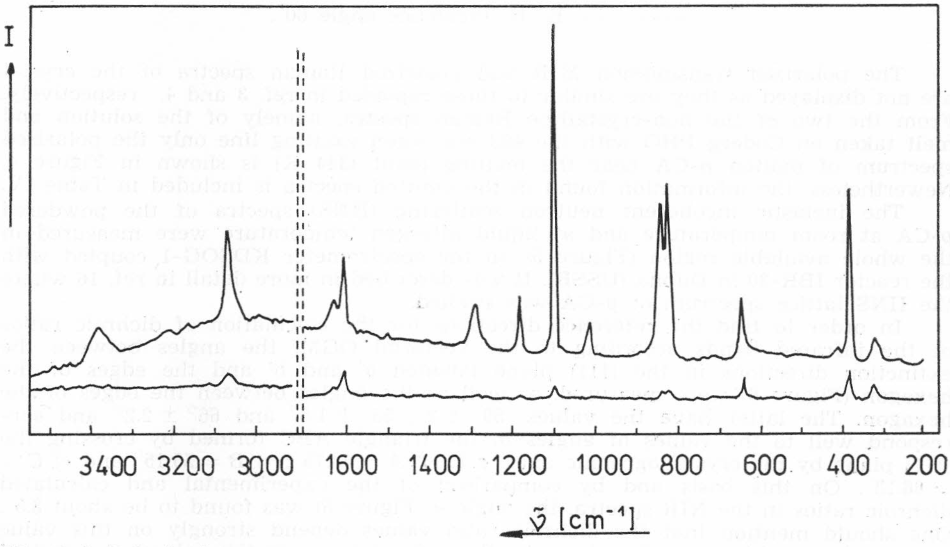

Figure 4. Polarized Raman spectrum of molten p-CA. Upper curve : polarization VV, lower curve : VH.

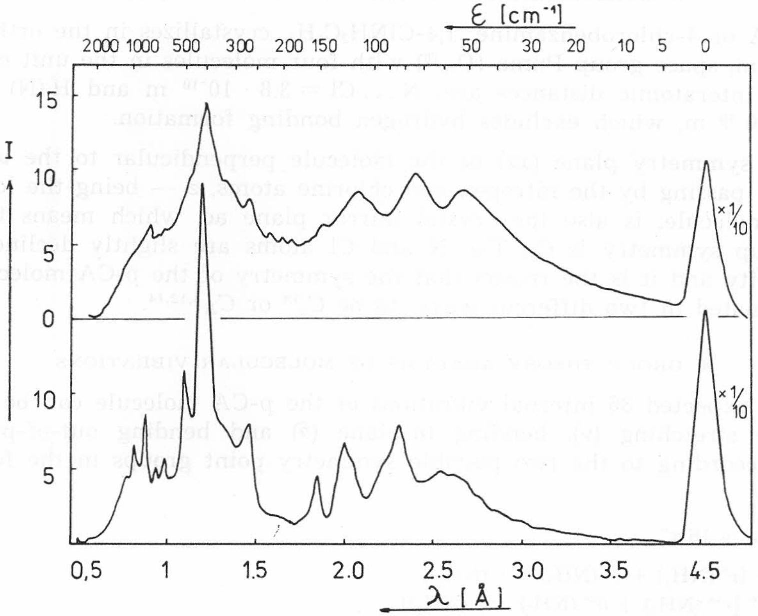

Figure 5. Inelastic incoherent neutron scattering (IINS) spectra of powdered p-CA at room and liquid nitrogen temperatures.

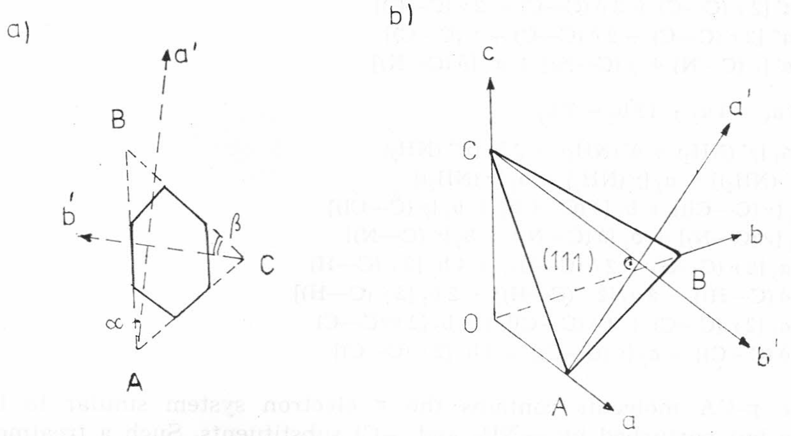

Figure 6. a) Orientation of extinction directions a′ and b′ with respect to the edges of (111) plate. b) Orientation of (111) plane with respect to the crystallographic axes of p-CA crystal.

The refractive indices in the (111) plane corresponding to the a' and b' directions, needed in the OGM calculations, were measured by the immersion Becke method under the polarization microscope MIN-7 and were found to be the following:

$$n(a') = 1.522$$

$$n(b') = 1.533$$

3. MOLECULAR AND CRYSTAL STRUCTURE OF p-CA[5,17]

p-CA or 4-chlorobenzamine, 1,4-$ClNH_2C_6H_4$, crystallizes in the orthorhombic system, space group Pnma (D_{2h}^{16}) with four molecules in the unit cell. The shortest interatomic distances are: $N \ldots Cl = 3.8 \cdot 10^{-10}$ m and $H(N) \ldots Cl = 2.9 \cdot 10^{-10}$ m, which excludes hydrogen bonding formation.

The symmetry plane (xz) of the molecule perpendicular to the aromatic ring and passing by the nitrogen and chlorine atoms, z — being the long axis of the molecule, is also the crystal mirror plane ac, which means that the site group symmetry is C_s. The N and Cl atoms are slightly declined from coplanarity and it is the reason that the symmetry of the p-CA molecule was approximated in two different ways: to be C_s[13] or C_{2v}[3,12,14].

4. GROUP THEORY ANALYSIS OF MOLECULAR VIBRATIONS

The expected 36 internal vibrations of the p-CA molecule can be divided into the stretching (ν), bending in-plane (δ) and bending out-of-plane (γ) modes according to the two possible symmetry point groups in the following way:

$$
\begin{aligned}
C_s &= 20\,a' + 16\,a'' \\
&= 3\,a'\,[\nu^s(\mathrm{NH_2}) + \delta^s(\mathrm{NH_2}) + \gamma(\mathrm{NH_2})] \\
&\quad + 3\,a''\,[\nu^{as}(\mathrm{NH_2}) + \delta^{as}(\mathrm{NH_2}) + \gamma(\mathrm{NH_2})] \\
&\quad + 2\,a'\,[\nu(\mathrm{C{-}Cl}) + \gamma(\mathrm{C{-}Cl})] + a''\,[\delta(\mathrm{C{-}Cl})] \\
&\quad + 6\,\mathrm{a}'\,[2\,\nu(\mathrm{C{-}H}) + 2\,\delta(\mathrm{C{-}H}) + 2\,\gamma(\mathrm{C{-}H})] \\
&\quad + 6\,a''\,[2\,\nu(\mathrm{C{-}H}) + 2\,\delta(\mathrm{C{-}H}) + 2\,\gamma(\mathrm{C{-}H})] \\
&\quad + 7\,a'\,[2\,\nu(\mathrm{C{-}C}) + 3\,\delta(\mathrm{C{-}C}) + 2\,\gamma(\mathrm{C{-}C})] \\
&\quad + 5\,a''\,[2\,\nu(\mathrm{C{-}C}) + 2\,\delta(\mathrm{C{-}C}) + \gamma(\mathrm{C{-}C})] \\
&\quad + 2\,a'\,[\nu(\mathrm{C{-}N}) + \gamma(\mathrm{C{-}N})] + a''\,[\delta(\mathrm{C{-}N})]
\end{aligned}
$$

$$
\begin{aligned}
C_{2v} &= 13\,a_1 + 4\,a_2 + 12\,b_2 + 7\,b_1 \\
&= 2\,a_1\,[\gamma^s(\mathrm{NH_2}) + \delta^s(\mathrm{NH_2}] + 2\,b_2\,[\nu^{as}(\mathrm{NH_2}) \\
&\quad + \delta^{as}(\mathrm{NH_2})] + a_2\,[\gamma(\mathrm{NH_2}] + b_1\,[\gamma(\mathrm{NH_2})] \\
&\quad + a_1\,[\nu(\mathrm{C{-}Cl})] + b_2\,[\delta(\mathrm{C{-}Cl})] + b_1\,[\gamma(\mathrm{C{-}Cl})] \\
&\quad + a_1\,[\nu(\mathrm{C{-}N})] + b_2\,[\delta(\mathrm{C{-}N})] + b_1\,[\gamma(\mathrm{C{-}N})] \\
&\quad + 4\,a_1\,[2\,\nu(\mathrm{C{-}H}) + 2\,\delta(\mathrm{C{-}H})] + 4\,b_2\,[2\,\nu(\mathrm{C{-}H}) \\
&\quad + 2\,\delta(\mathrm{C{-}H})] + 2\,a_2\,[2\,\gamma(\mathrm{C{-}H})] + 2\,b_1\,[2\,\gamma(\mathrm{C{-}H})] \\
&\quad + 5\,a_1\,[2\,\nu(\mathrm{C{-}C}) + 3\,\delta(\mathrm{C{-}C})] + 4\,b_2\,[2\,\nu(\mathrm{C{-}C}) \\
&\quad + 2\,\delta(\mathrm{C{-}C})] + a_2\,[\gamma(\mathrm{C{-}C})] + 2\,b_1\,[2\,\gamma(\mathrm{C{-}C})]
\end{aligned}
$$

The p-CA molecule contains the π electron system similar to that in benzene but perturbed by —NH_2 and —Cl substituents. Such a treatment has been the basis for the induced internal electric field model proposed by Oudar and Chemla[18] to explain the nonlinear electrooptic properties of meta- disubstituted benzenes. The distortion of the π electron system, on one hand, creates a permanent dipole moment of a molecule which induces the electric field and, on the other hand, cancels the mutual exlusion rule between the IR and Raman spectra. For this reason, the analyse of the p-CA fundamentals were performed like in[8], *e. i.* by comparison of the intensities of bands in the IR and Raman spectra and by comparison of the p-CA spectra with the parent hydrocarbon-benzene-spectra in order to estimate the degree of the aromatic ring distortion. The comparison should be easier by using the correlation diagram between the corresponding modes in the different (hypothetical or real) symmetry point groups of the p-CA molecule shown in Figure 7.

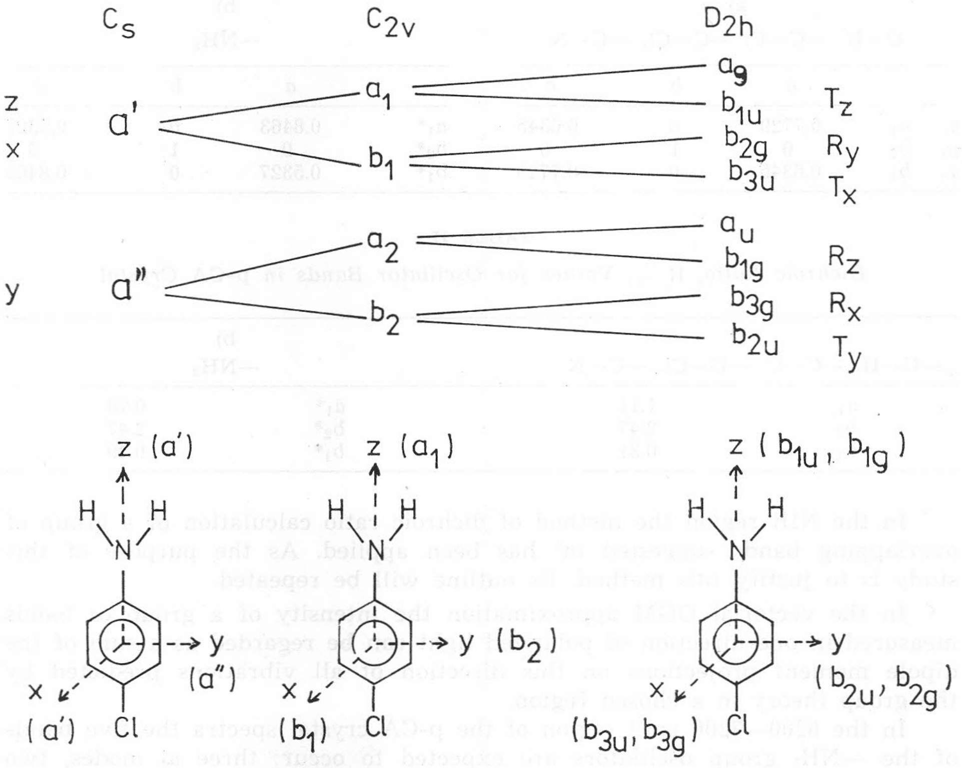

Figure 7. Correlation between the same vibrations in p-CA molecule in different symmetry points groups.

5. DICHROIC RATIO CALCULATIONS ACCORDING TO THE VECTORIAL ORIENTED GAS MODEL

The directional cosines of the C—C and C—H vibration transition moments with respect to the crystallographic axes have been calculated from the equation of the aromatic ring and those of the —NH_2 group oscillators from the atomic coordinates in the p-CA crystal reported in[5]. In the latter case, the direction of the a_1^* vibrations was assumed to be parallel to the direction of the sum of both N—H vectors, whereas that for the antisymmetrical vibration of symmetry b_2^* — to be the direction of their difference, as proposed earlier[9].

These directional cosines are given in Table I. The directional cosines of the x, y, z molecular axes with respect to the reference axes a' and b' have been calculated on the basis of the geometrical consideration described in Experimental, and the resulting values from them dichroic ratios of the p-CA fundamentals are presented in Table II.

TABLE I

Directional Cosines of Oscillators in p-CA *Crystal with Respect to Crystallographic* a, b, c *axes*

		a) —C—H, —C—C, —C—Cl, —C—N			b) —NH$_2$			
		a	*b*	*c*		*a*	*b*	*c*
z,	a_1	0.7729	0	0.6345	a_1*	0.8463	0	0.5327
y,	b_2	0	1	0	b_2*	0	1	0
x,	b_1	0.6345	0	—0.7729	b_1*	0.5327	0	—0.8463

TABLE II

Dichroic Ratio, $R_{a'/b'}$, *Values for Oscillator Bands in* p-CA *Crystal*

a) —C—H, —C—C, —C—Cl, —C—N		b) —NH$_2$	
a_1	1.11	a_1*	0.78
b_2	2.47	b_2*	2.47
b_1	0.31	b_1*	0.49

In the NIR region the method of dichroic ratio calculation of a group of overlapping bands suggested in[9] has been applied. As the purpose of this study is to justify this method, its outline will be repeated.

In the vectorial OGM approximation the intensity of a group of bands measured in one direction of polarized light can be regarded as a sum of the dipole moment projections on this direction of all vibrations predicted by the group theory in a chosen region.

In the 6200—7200 cm^{-1} region of the p-CA crystal spectra the five bands of the —NH$_2$ group oscillators are expected to occur: three a_1 modes, two overtones $\nu^{as}\,(0 \rightarrow 2)$, $\nu^{s}\,(0 \rightarrow 2)$ and combination $\delta^{s}\,(0 \rightarrow 2) + \nu^{s}$, and two b_2 modes: $\nu^{as} + \nu^{s}$ and $\delta^{s}\,(0 \rightarrow 2) + \nu^{as}$. The integrated intensity in the a' direction, $I\,(a')$, may be expressed as follows[9]:

$$I\,(a') = 3\,A_1 \cos^2 (a_1, a') + 2\,B_2 \cos^2 (b_2, a') \tag{1}$$

where:

(a_1, a') — angle between transition moment a_1 and electric vector $\vec{E}$ of the electromagnetic wave polarized along direction a' in the crystal

A_1, B_2 — coefficients of intensity of the normal vibrations a_1 and b_2 respectively: $A_1 \sim (\partial\mu/\partial q)^2\,(a_1)$, $B_2 \sim (\partial\mu/\partial q)^2\,(b_2)$

By assuming that for vibrations of different symmetry species of the same oscillator: $A_1 = B_2$, one obtains:

$$I\,(a') \sim [3 \cos^2 (a_1, a') + 2 \cos^2 (b_2, a')]\,A_1 \tag{2}$$

and the dichroic ratio of the —NH$_2$ band group in the p-CA crystal is:

$$R_{a'/b'} = \frac{I\,(a')}{I\,(b')}\;\frac{n\,(b')}{n\,(a')} = \frac{[3 \cos^2 (a_1, a') + 2 \cos^2 (b_2, a')]\,n\,(b')}{[3 \cos^2 (a_1, b') + 2 \cos^2 (b_2, b')]\,n\,(a')} \tag{3}$$

The same procedure has been applied to the 5700—6200 cm^{-1} region where ten bands of the overtones and combination tones of the —CH oscillators are expected: 6 a_1 and 4 b_2. Also in this case the equality of intensity coefficients for the a_1 and b_2 species have been presumed. The validity of these assumptions will be considered in Section 7. In Table III the results of the calculations and experiments are given.

TABLE III

Comparison of the Calculated and Observed Dichroic Ratios of Bands in MIR Region and of Group of Overlapping Bands in NIR Region in p-CA *Crystal*

Oscillator(s)	$R_{a'/b'}$ (calc.)	$R_{a'/b'}$ (obs.)
a_1* —NH$_2$	0.78	0.55
b_2* —NH$_2$	2.47	2.8
3 a_1* + 2 b_2*, —NH$_2$	1.11	1.19 ± 0.07
6 a_1 + 4 b_2, —C—H	1.51	1.5

6. ASSIGNMENTS OF p-CA FUNDAMENTALS

The assignments have been collected on the basis of those reported earlier directly for vibrational spectra[11–15], especially the Garrigou-Lagrange interpretations[11] and the dichroic ratios reported by Tripathi and Katon[13], as well as on the information taken from the electronic emission or absorption spectra[3,19,20]. A few new assignments have been proposed taking into account the spectra obtained in this work and the substituent effects characterized by Varsányi[21].

All assignments are given in Table IV together with benzene frequencies[11] for comparison.

In spite of many studies devoted to the interpretation of the aniline derivatives spectra[6,11-15,22-26], there are still controversies concerning assignments of the out-of-plane bending (γ) vibrations of the —NH$_2$ group. It has been decided to assign the band about 850 cm^{-1} to γ wagging (b_1), as proposed alternatively in[13]. In the crystalline aniline spectra γ wagging was found at about 660 cm^{-1} [22], in 2,4,6-tribromoaniline at 704 cm^{-1} [23], in dichloroanilines at about 660 cm^{-1} [26]. In the vapor phase spectra of p-CA the wagging vibration was found at 311.3 cm^{-1} [15].

Torsional vibration γ (a_2) is forbidden in the IR spectra of the »free« p-CA molecule but becomes allowed by the D_{2h} unit cell group. In all papers devoted to the p-CA vibrational spectra in condensed phase[11–14] it was not attributed *at all*. In the vapor phase it was found at 311.3 cm^{-1} [15]. In the crystalline 2,6-dichloroaniline it was assigned tentatively to the band at 450 cm^{-1} [26]. In the electronic absorption spectrum of the p-CA crystal Marchetti found a fundamental band of a_2 symmetry at 260 cm^{-1} [3]; Schweiss *et al.*[27], who investigated the IINS spectra of anilinium bromide and its deuterated derivative assigned the band at 33 meV (~ 260 cm^{-1}) to the torsion of the — NH$_3^+$ group. Also in the IINS spectra in Figure 5 the band at about 260 cm^{-1} is rather strong and assignment to the —NH$_2$ torsion has been proposed.

TABLE IV

Assignments of Fundamentals in p-CA Molecule and Crystal

No.	Mode of vibration	C_s	C_{2v}	D_{2h}	ν_{IR}/cm^{-1}		Dichroic ratio $R_{a'/b'}$	ν Raman/cm^{-1}			Labeling of vibr.	Corresponding benzene frequency[11]	Remarks
					solution (CCl_4)	crystal		solution (CCl_4)	melt	crystal			
1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	$\nu^s_{NH_2}$	a'	a_1	—	3402	3381—82	< 1	3397	3377	3387	—	—	
2	$\nu^{as}_{NH_2}$	a''	b_2	—	3488	3470	$\gg 1$	3470 vw	3462 dp	3480 vw	—	—	
3	$\delta^s_{NH_2}$	a'	a_1	—	1620	1618—20	< 1	1619	1622 w	1616	—	—	
4	$\delta^{as}_{NH_2}$	a''	b_2	—	1070	1052—55	> 1	—	—	—	—	—	
5	γ_{NH_2}	a'	b_1	—	840	865?	—	—	—	—	—	—	
6	γ_{NH_2}	a''	a_2	—	—	250?	—	—	—	—	—	—	IINS 260 s
7	ν_{C-Cl}	a'	a_1	—	642	675?	< 1	—	—	—	—	—	
8	δ_{C-Cl}	a''	b_2	—	—	—	—	—	377	380	—	—	
9	γ_{C-Cl}	a'	b_1	—	—	—	—	—	—	145	—	—	
10	ν_{CN}	a'	a_1	—	1290	1290—94	< 1	1277 w	1282	1290	ν_{13}		
11	δ_{CN}	a''	b_2	—	—	—	—	—	317	326			
12	γ_{CN}	a'	b_1	b_{2g}	—	—	—	—	—	365	ν_{10b}?	850	
13	ν_{CH}	a'	a_1	a_g	3039	3040	< 1	3035 sh	—	3054	ν_{7a}	3047	
14	ν_{CH}	a''	b_2	b_{3g}	3058	3060	> 1	3065	3058 dp	3064	ν_{7b}		
15	ν_{CH}	a'	a_1	b_{1u}	3088?	—	—	—	—	—	ν_{20a}	3080	
16	ν_{CH}	a''	b_2	b_{2u}	3100?	—	—	—	—	—	ν_{20b}		
17	δ_{CH}	a'	a_1	a_g	1170	1182—85	< 1	1172 w	1172	1184	ν_{9a}	1176	
18	δ_{CH}	a''	b_2	b_{2u}	1120	1125	> 1	—	—	—	ν_{18b}	1037	
19	δ_{CH}	a'	a_1	b_{1u}	1094	1090—93	< 1	1093	1090	1092?	ν_{18a}		
20	δ_{CH}	a''	b_2	b_{3g}	1315	1330	> 1	—	—	—	ν_3	1326	

Table IV continued.

No.	Mode of vibration	C_s	C_{2v}	D_{2h}	ν_{IR}/cm^{-1}		Dichroic ratio $R_{a'/b'}$	ν Raman/cm^{-1}			Labeling of vibr.	Corres-ponding benzene frequency[11]	Remarks
					solution (CCl_4)	crystal		solution (CCl_4)	melt	crystal			
1	2	3	4	5	6	7	8	9	10	11	12	13	14
21	γ_{CH}	a''	a_2	b_{1g}	840	832	—	832	834	840	ν_{10a}	850	
22	γ_{CH}	a'	b_1	b_{2g}	—	970	—	—	—	—	ν_5	985	
23	γ_{CH}	a''	a_2	a_u	—	940	—	932?	—	—	ν_{17a}	970	IINS
24	γ_{CH}	a'	b_1	b_{3u}	824	823	<1	815	815	820	ν_{11}	671	
25	ν_{C-C}	a'	a_1	a_g	1580	1579—89	≈ 1	—	—	—	ν_{8a}	1585	
26	ν_{C-C}	a''	b_2	b_{3g}	1600	1605	≈ 1	1599	1597 dp	1600	ν_{8b}		
27	ν_{C-C}	a'	a_1	b_{1u}	1426	1442—45	<1	—	—	—	ν_{19a}	1480	
28	ν_{C-C}	a''	b_2	b_{2u}	1496	1498—1502	≈ 1	—	—	1493	ν_{19b}		
29	δ_{C-C}	a'	a_1	a_g	1007	1005—07	<1	1005	1003	—	ν_1	992	
30	δ_{C-C}	a''	b_2	b_{3g}	630	623	>1	635	634	637	ν_{6b}	v 606	
31	δ_{C-C}	a'	a_1	a_g	—	723?	—	—	—	—	ν_{6a}		
32	δ_{C-C}	a''	b_2	b_{2u}	1260 sh	1270? sh	—	—	—	—	ν_{14}	1319	
33	δ_{C-C}	a'	a_1	b_{1u}	—	—	—	—	—	—	ν_{12}	1010	
34	γ_{C-C}	a''	a_2	a_u	—	405 KBr	—	—	400	403	ν_{16a}	405	IINS vs
35	γ_{C-C}	a'	b_1	b_{3u}	516	518 KBr	≈ 1	—	—	—	ν_{16b}		IINS s
36	γ_{C-C}	a'	b_1	b_{2g}	—	690	>1	—	—	702	ν_4	703	

sh — shoulder, w — weak, s — strong, vw — very weak, vs — very strong, dp — depolarized, KBr — frequency observed in KBr pellet.

Detailed examination of the obtained spectra and assignments collected in Table IV enabled us to formulate some interesting findings:

1. The bands of the ν_{CH}, ν_{CC} and δ_{CC} vibrations which can be derived from the a_g, b_{1g}, b_{2g} and b_{3g} species of D_{2h} symmetry (»*g*« modes) are the most intense bands in the Raman spectra of both solution and crystal *p*-CA. The bands of C—C and C—H vibrations »originating« from the b_{1u}, b_{2u} and b_{3u} species (»*u*« modes) are the most intense bands in the IR spectra.
2. The IR intensities of the —CH stretching vibration bands, ν_{CH}, increase in the order: *p*-CA (crystal) $<$ *p*-CA (solution) $<$ benzene (B), (cf. Figures 2 and 3).
3. The IR intensities of ring vibrations are enhanced in *p*-CA in comparison with benzene, as seen in Figure 3. The c · l value in case B is twice as large as in the *p*-CA solution but the intensities of some bands (ν_{CC} at ~ 1500 cm^{-1} and ν_{CH} at ~ 1090 cm^{-1}) are comparable.
4. The bands of the two out-of-plane bending vibrations: γ_{CH} (no. 23) and γ_{CC} (no. 34) of symmetry a_2 are very weak in the Raman spectrum of the crystal but become clearly stronger in the Raman spectra of *p*-CA in solution and in melt (Figure 4).
5. The band of ν^s(—NH_2) vibration is a little stronger than that of the ν^{as}(—NH_2) one in the IR solution spectrum but the opposite is true in the crystal spectrum, as it can be seen in Figure 8.

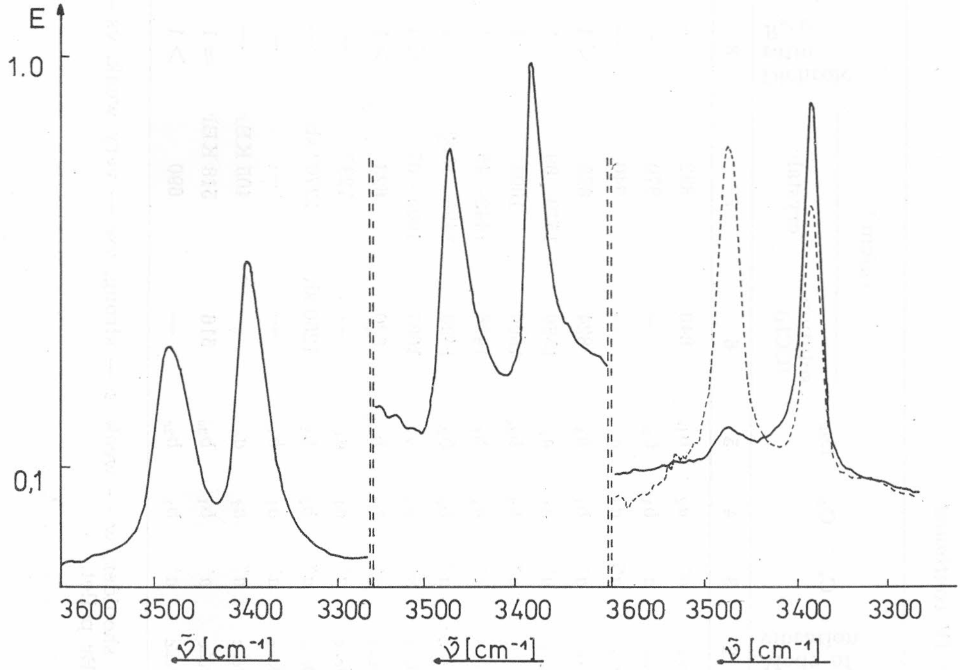

Figure 8. Stretching vibration bands of —NH_2 group in IR spectra of *p*-CA in different media: 1) in CCl_4 solution, 2) in KBr pellet, 3) in the crystal.

7. DICHROIC RATIOS AND EFFECTIVE CHARGE-CHARGE FLUX MODEL

In order to interpret the NIR spectra of the crystalline *p*-NA[1] and *p*-CA[28], the —NH$_2$ groups in these compounds were treated as pseudo-triatomic molecules and then the local mode model could be used to calculate the anharmonicity coefficients for the three —NH$_2$ vibrations: ν^{s}, ν^{as} and δ^{s}.

The same triatomic molecule approximation enables the ECCF model to be applied to the —NH$_2$ group in the form given by Decius and Mast.[10] Namely, for a triatomic molecule with C_{2v} symmetry, lying on the *zy* plane, the atomic polar tensors are as follows:

For H atoms [on a local site C_s with species 2 a' (y, z) and a'' (x)]:

$$\begin{matrix} H_x & 0 & 0 \\ 0 & H_y & H_{yz} \\ 0 & H_{yz} & H_z \end{matrix} \qquad (4)$$

where:

$$H_x = [\partial\mu_x/\partial x\,(H)]$$

$$H_{yz} = [\partial\mu_z/\partial y\,(H)]$$

μ_x, μ_y, μ_z — Cartesian components of total molecular dipole moment

For *N* atom [on C_{2v} site, with species 2 $a_1\,(z)$ and $b_2\,(y)$]:

$$\begin{matrix} N_x & 0 & 0 \\ 0 & N_y & 0 \\ 0 & 0 & N_z \end{matrix} \qquad (4)$$

where:

$$N_x = [\partial\mu_x/\partial x\,(N)]$$

Vibrations ν^{s} (—NH$_2$) and δ^{s} (—NH$_2$) are the a_1 modes with the transition dipole moment parallel to the twofold axis *z*, and the vibration ν^{as} is the b_2 mode parallel to the *y* axis. It implies that the atomic tensor elements $N_z + 2\,H_z$ contribute to the derivative $|(\partial\mu/\partial q)\,(a_1)| = \sqrt{A_1}$ and $N_y + 2\,H_y$ to the $|(\partial\mu/\partial q)\,(b_2)| = \sqrt{B_2}$.

According to Decius and Mast, the above contributions correspond to translational conditions[10]:

$$N_z + 2\,H_z = \xi$$

$$N_y + 2\,H_y = \xi \qquad (5)$$

where ξ — phenomenological effective charge of the molecule (group).

If

$$|\sqrt{A_1}| = |(\partial\mu/\partial q)|\,a_1 = N_z + 2\,H_z = \xi$$

and

$$|\sqrt{B_2}| = |(\partial\mu/\partial q)|\,b_2 = N_y + 2\,H_y = \xi$$

it means that:

$$A_1 = B_2$$

which had to be proved.

It also results from this equality that the effective charge on the —NH$_2$ group must not be zero because in that case the expression (3) would lose all sense.

8. DISCUSSION AND CONCLUSIONS

The observed »memory« of the mutual exclusion rule by the C—C and C—H ring vibrations (point 1 in Section 6) confirms the fact that the aromatic ring in *p*-CA is only slightly distorted by the substituents and only a little more in the crystal than in the »free« molecule.

On the other hand, the substitution deenhances intensities of the ν_{CH} bands (p. 2) and enhances those of some other vibrations (p. 3). These observations are cosistent with the changes in the IR spectra of aromatic hydrocarbons caused by the formation of weak CT complexes with tetracyanoethylene (TCNE) where the hydrocarbons are electron-donors[29]. The changes were explained by electron-vibration couplings.

These changes can be also accounted for by the vibronic coupling mechanism. According to the vibronic theory of infrared intensities[30,31], the lower lying is the lowest electronic transition in a molecule, the stronger is the enhancement or deenhancement of a relevant vibration band intensity. The larger is the shift, $\Delta\nu_{el}$, of the 00 band of the forbidden benzene transition ($B_{2u} \leftarrow A_{1g}$, $\nu_{00} = 38089$ cm^{-1} in the gas phase[32]) allowed in a given benzene derivative, the stronger are the vibronic couplings[18,31,8].

The lowest singlet transition in the *p*-CA solution in hexane lies at 307 nm (32210 cm^{-1}) [33] and in the crystal at 320.1 nm (31265 cm^{-1}) [3]; thus, the corresponding $\Delta\nu_{el}$ values are: ~ 6000 cm^{-1} in the solution and ~ 7000 cm^{-1} in the crystal. It seems that the observed distortion of the aromatic ring and the intensity changes with respect to benzene parallel the magnitudes of the $\Delta\nu_{el}$ values.

The occurrence of strong a_2 vibration bands in the Raman spectrum of molten *p*-CA (p. 4) confirms the previous[2] assumption about the symmetry of the second singlet state. In accord with the pre-resonance theory of Raman intensities[34], the intensity of a non-totally symmetric vibration arises from the vibronic coupling between two dipole-allowed electronic states. If the symmetry of the second singlet is that of B_1, then the simple product of its symmetry times the first singlet state symmetry B_2 multiplied by a_2 gives indeed the totally symmetric representation of the C_{2v} symmetry group, i. e. A_1: $B_2 \otimes B_1 \otimes a_2 = A_1$.

As far as the relative intensities of ν^{s} and ν^{as} of the —NH$_2$ group bands are concerned, their near equality can be explained by the influence the first singlet electronic transition of symmetry B_2 exerts on the ν^{as} vibration also of symmetry b_2. In the CT complexes, both the already mentioned weak[29] and the strong salts like tetracyanoquinodimethane (TCNQ)[35], the CT direction forces the same direction of the intramolecular transition dipole moments coupled with the CT.

In the »free« —NH$_2$ group the dipole moment of the free electron pair of the nitrogen atom contributes more to the intensity of ν^{s} than ν^{as}. [36]

The markedly stronger intensity of ν^{as} band than of the ν^{s} band can be seen in Figure 1. of[37] where the spectra of *p*-CA strongly adsorbed on aluminum bromide are shown. In that case, the lone pair was consumed by forming a covalent bond with the aluminum atom and this interaction was followed by the shift of the lowest lying electronic band toward higher frequencies[37,38]. When *p*-CA was weakly adsorbed on aluminum chloride, the C—N bond gained partly an ionic character and the frequency of the C—N stretching mode decreased from 1289 cm^{-1} in the *p*-CA evaporated film to 1188 cm^{-1} [37,38]. In the crystalline *m*-NA, where the $\Delta\nu_{el}$ is nearly 13000 cm^{-1}, the ν_{CN} appears at 1335 cm^{-1} [8,6]. All the facts may be understood bearing in mind that the partial charge on the nitrogen atom in the crystal is positive[5] and in the complex formed by adsorption — negative[37].

The relation between the infrared intensities and the charges on atoms : : effective or equilibrium ones have already been recognized quite well in several simple hydrocarbons by Gussoni and Zerbi, *e. g.* in[39]. In the light of[39], the decrease of the ν_{CH} intensity in the *p*-CA crystal in comparison with benzene could be explained as being caused by larger $q_H{}^0$ — equilibrium charge on H atoms — due to the CT from —NH_2 group to the aromatic ring.

A more detailed comparison of the *p*-CA spectra with those of the *m*- and *p*-nitroanilines will be given elsewhere[40].

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REFERENCES

1. M. M. Szostak and J. W. Rohleder, *Acta Phys. Polon.* **A40** (1971) 517.
2. M. M. Szostak, M. Sanquer, and A. Girard, *J. Raman Spectrosc.* **11** (1981) 449.
3. A. P. Marchetti, *J. Chem. Phys.* **56** (1972) 5101.
4. T. Urabe and M. Ito, *J. Raman Spectrosc.* **2** (1974) 301.
5. J. Trotter, S. H. Whitlow, and T. Zobel, *J. Chem. Soc.* A (1966) 353.
6. M. M. Szostak, *J. Raman Spectrosc.* **8** (1979) 43.
7. M. M. Szostak, *J. Raman Spectrosc.* **12** (1982) 228.
8. M. M. Szostak, submitted to publication.
9. T. Luty, M. M. Szostak, and E. Karwowska, *Mol. Cryst. Liq. Cryst.* **29** (1974) 175.
10. J. C. Decius and G. B. Mast, *J. Mol. Spectrosc.* **70** (1978) 294.
11. C. Garrigou-Lagrange, *Thèses,* Bordeaux 1962.
12. V. B. Singh, R. N. Singh, and J. S. Singh, *Spectrochim. Acta* **22** (1966) 927.
13. G. N. R. Tripathi and J. E. Katon, *J. Chem. Phys.* **70** (1979) 1383.
14. E. Steger, S. Garbe, and J. Klosowski, *J. Raman Spectrosc.* **14** (1983) 194.
15. R. A. Kydd and P. J. Krueger, *J. Chem. Phys.* **69** (1978) 827.
16. M. M. Szostak, A. V. Belushkin, and I. Natkaniec, *phys. stat. sol.* (*b*) **127** (1985) K1.
17. J. H. Palm, *Acta Cryst.* **21** (1966) 473.
18. J. L. Oudar and D. S. Chemla, *Opt. Commun.* **13** (1975) 164.
19. E. Kanezaki, N. Nishi, M. Kinoshita, and K. Niimori, *Chem. Phys. Letters* **29** (1974) 529.
20. N. Nishi and M. Kinoshita, *Bull. Chem. Soc. Japan* **49** (1976) 1221.
21. G. Varsányi, *Vibrational Spectra of Benzene Derivatives,* Academic Press, New York, 1969.
22. G. N. R. Tripathi, *J. Chem. Phys.* **73** (1980) 5521.
23. R. M. P. Jaiswal, J. E. Katon, and G. N. R. Tripathi, *J. Chem. Phys.* **79** (1983) 1.
24. M. Harrand, *J. Raman Spectrosc.* **4** (1975) 53.
25. L. Smetankine and J. Etchepare, *J. Mol. Struct.* **14** (1972) 61.
26. M. V. Fraile Dotes, C. Sigüenza, and P. F. Gonzalez-Diaz, *Spectrochim. Acta* **43A** (1986) 1029.

27. B. P. Schweiss, H. Fuess, G. Fecher, and A. Weiss, *Z. Naturforsch.* **38a** (1983) 350.
28. M. M. Szostak, unpublished results (*Proc. IX Bulgarian Conf. Mol. Spectrosc.*, Albena, 1980 p. 217).
29. B. Moszyńska-Mierzecka, *Acta Phys. Polon.* **A52** (1977) 355.
30. W. L. Peticolas, L. Nafie, P. Stein, and B. Fanconi, *J. Chem. Phys.* **52** (1970) 1576.
31. M. Mizuno, *Spectrochim. Acta* **34A** (1978) 979.
32. E. M. Averianov and V. F. Shabanov, *Zh. Prikl. Spektrosk.* **29** (1978) 479.
33. I. Iweibo, R. A. Oderinde, and J. A. Faniran, *Spectrochimica Acta* **38A** (1982) 1.
34. J. Tang and A. C. Albrecht, *J. Chem. Phys.* **49** (1968) 1144.
35. A. Graja, A. Szyszkowski, J. Petzelt, N. Rysava, and K. Král, *Acta Phys. Polon.* **A61** (1982) 123.
36. W. J. Orville-Thomas, A. E. Parsons, and C. P. Ogden, *J. Chem. Soc.* **195** (1958) 1047.
37. H. Sato, Y. Kusumoto, S. Arase, M. Syenaga, and S. Kammura, *J. Phys. Chem.* **82** (1978) 66.
38. H. Sato, Y. Kusumoto, S. Arase, M. Suenaga, and S. Kammura, *Sci. Rep. Kagoshima Univ.* **27** (1978) 151.
39. M. Gussoni, P. Jona, and G. Zerbi, *J. Chem. Phys.* **78** (1893) 6802.
40. M. M. Szostak, to be published.

SAŽETAK

Vibronske sprege u vibracijskim spektrima kristaliničnog *p*-kloranilina

Maria Magdalena Szostak

Snimljeni su polarizirani srednji infracrveni transmisijski i ATR spektri, polarizirani infracrveni apsorpcijski spektri monokristala *p*-kloranilina (*p*-CA), te srednji infracrveni spektri otopina *p*-CA i benzena, kao i Ramanovi spektri kristala, otopine i taline *p*-CA. Za usporedbu su snimljeni i spektri neelastičnog nekoherentnog neutronskog raspršenja (IINS). Izračunani su dikroični omjeri za kristalnu ravninu (111), te uspoređeni s eksperimentalnima. Ranije pretpostavka koja se tiče primjenljivosti modela orijentiranoga plina provjerena u okviru modela efektivni tok naboj-naboj. Na temelju detaljne kvalitativne analize intenziteta i frekvencija fundamentalnih vibracijskih vrpci, mnoga zapažena obilježja spektara mogu se objasniti vibronskim spregama.