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Molecular Vibration Analysis of Ionicity and Phase Transition in TMPD-TCNQ (1:1) Charge Transfer Salt

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The infrared spectra of the (1 : 1) charge transfer salt of *N*, *N*, *N'*, *N'*-tetramethyl-*p*-phenylendiamine (TMPD) with 7, 7, 8, 8-tetracyanoquinodimethane (TCNQ) and with fully deuterated TCNQ are reported. The assignment of the vibrational data is obtained on the basis of the comparison with that of neutral and ionized parent molecules; additional relevant information is extracted from the low temperature (~15 K) infrared and Raman spectra. The vibrational analysis leads one to estimate for TMPD-TCNQ a degree of ionicity of 0.9_2, which corresponds to an almost fully ionic ground state. The interpretation of the vibrational data has been carried out in the light of an appropriate model for the electron-molecular vibration interaction in regular or dimerized mixed stack charge transfer complexes. The study of the temperature dependence of the infrared spectra of TMPD-TCNQ confirms that the already known phase transition at about 220 K is likely associated with a transition from a regular to a dimerized mixed stack.

I. INTRODUCTION

The degree of ionicity (ρ, also referred as the degree of charge transfer) is one of the fundamental parameters characterizing the physical properties of quasi-one-dimensional organic Charge Transfer (CT) crystals.[1] It is worth to underline that ρ assumes a different physical meaning in correspondence with different mutual arrangements of the Donor (D) and Acceptor (A) molecules in the solid. For segregated stack crystals, where all A's and/or D's are arranged in separate face-to-face columns, ρ indicates the (average) charge residing on the D and A stacks, and as such is not directly connected with

the CT interaction along the chain. Thus ρ essentially is the band filling of the A and D chains. On the contrary for mixed stack crystals, that is, those characterized by columns with alternating donor and acceptor molecules, the degree of ionicity corresponds to the charge transferred from D to A. Therefore in this case ρ reflects the mixing between D and A orbitals, i.e. the strength of the CT interaction along the stack.

Several methods have been used to determine the degree of ionicity of segregated stack compounds, obtaining in general very similar values.[2] The situation is not as much clear for the mixed stack systems,[3,4] mainly because they have been comparatively less studied. We have shown[5,6] that vibrational spectroscopy can be conveniently used to estimate the degree of ionicity of mixed stack compounds, provided that the perturbing effect of the electron-molecular vibration (*e-mv*) interaction (see Section III below) is taken into account. It has also been shown[6] that, always as a consequence of the *e-mv* interaction, vibrational studies allow one to distinguish between regular and dimerized[7] mixed stack chains. Thus also phase transitions involving the passage from a regular to a dimerized stack (accompanied or not by a variation of ρ,[5,8]) can be conveniently investigated by vibrational spectroscopy.

In this paper we apply the above interpretative scheme to the vibrational analysis of N,N,N',N'-tetramethyl-*p*-phenylendiamine · 7,7,8,8-tetracyanoquinodimethane (TMPD-TCNQ) mixed stack CT complex. We show that the overall vibrational data clearly indicate an almost fully ionic ($\rho \simeq 0.9_2$) ground state. This conclusion agrees with that suggested by X-ray structural data[9] and removes the apparent contradiction between the values obtained from partial Raman[10] and infrared[4] data. The magnitude of the effect of the *e-mv* interaction on TMPD-TCNQ vibrational spectra corresponds to what has been found for other practically fully ionic mixed stack complexes.[6,8]

We have exploited the temperature dependence of TMPD-TCNQ infrared spectra to investigate the phase transition at about 220 K, which has been already detected by magnetic susceptibility[11] and conductivity[12] data. This phase transition is likely related with a distortion of the room temperature regular stack,[11] but our data suggest that its mechanism is not fully described in this way.

II. EXPERIMENTAL

TCNQ and fully deuterated TCNQ (TCNQd_4) were prepared and purified as previously reported.[13] TMPD was obtained from commer-

cial TMPD-dihydrochloride (recrystallized twice from ethanol) by treatment with NaOH in aqueous solution.[12] The precipitate product was purified by chromatography.

TMPD-TCNQ and TMPD-TCNQd_4 were prepared by mixing equimolar hot acetonitrile solutions of the two neutral components.[12] After cooling at room temperature, the precipitated crystals were filtered under nitrogen and successively stored at low temperature. The elemental analysis gave: calculated for $C_{22}H_{20}N_6$: %C 71.71; %H 5.48; %N 22.81; found: %C 71.27; %H 5.50; %N 22.83.

We have checked spectroscopically that the compound we obtained was the same as that prepared from TMPD · ClO_4 and LiTCNQ.[14] Furthermore, TMPD-$TCNQ_2$ was also obtained by a different experimental procedure.[12] and its infrared spectrum used to rule out its possible presence as an impurity in the 1 : 1 compound.

The infrared and Raman spectra were recorded with the previously reported instruments and methods.[5]

III. ELECTRON-MOLECULAR VIBRATION (*e-mv*) INTERACTION

It is known that the interaction of the molecular vibrations with the electrons involved in the charge transfer may strongly affect the vibrational spectra of quasi one-dimensional CT crystals.[2] A proper understanding of the effects of this interaction is therefore necessary before undertaking the interpretation of the vibrational data. An interpretative model which properly accounts for the effects experimentally observed in the case of mixed stack crystals is outlined in the following.[5,6,15]

The *e-mv* interaction can be conveniently expressed in terms of the linear *e-mv* coupling constants:[15]

$$g_i^{A,D} = \left(\frac{\delta \epsilon^{A,D}}{\delta Q_i^{A,D}} \right)_0 \tag{1}$$

where $\epsilon^{A,D}$ is the energy of the A, D molecular orbital involved in the CT and $Q_i^{A,D}$ are the relevant dimensionless normal coordinates. Only the normal modes that belong to the totally symmetric representation of the A, D molecular point groups can have g's different from zero and thus only these modes can be affected by the *e-mv* interaction. For a ....DADAD.... chain such interaction is expressed by the

Hamiltonian:[15]

$$H_{\text{int}} = \sum_N \left(\sum_i g^{\text{A}}_{N,i} n^{\text{A}}_N Q^{\text{A}}_{N,i} + \sum_j g^{\text{D}}_{N,j} n^{\text{D}}_N Q^{\text{D}}_{N,j} \right) \tag{2}$$

where N counts the unit cells and i, j the (totally symmetric) normal modes of A and D, respectively; $n^{\text{A,D}}$ is the electron occupation number operator. H_{int} is introduced as a perturbation on the electronic-vibrational Hamiltonian which in the Born–Oppenheimer approximation leads to the usual product wavefunctions $\Phi_{e,v} = \Psi_e \chi_v$.

If the stack is strongly dimerized,[7] in a first approximation it can be considered as composed of not interacting DA pairs, for which the electronic part of the unperturbed Hamiltonian can be solved in the framework of the Mulliken's theory.[16] In such a scheme, we obtain two electronic states, Ψ_{GS} and Ψ_E, among which the electronic CT transition takes place. The interaction Hamiltonian (2) mixes the Born–Oppenheimer wavefunctions $\Psi_{GS}\chi_v$ and $\Psi_E\chi_{v'}$, with $v' = v \pm 1$; as a result, the interacting energy levels are pushed apart, so that the frequencies of the totally symmetric vibrational modes of the electronic ground state are lowered. Always as a consequence of the interaction (2), these modes will also borrow infrared intensity from the CT electronic transition, thus displaying in the infrared spectra a strong intensity and a polarization along the stack axis (like the CT transition).

In the other extreme of an entirely regular stack, each D or A molecule has equal probability of exchanging electrons with the left and the right nearby molecule. The left and right exciton states are degenerate, and their combination leads to symmetric (+) and antisymmetric (−) parity excited states.[17] The CT electronic transition takes place between the (symmetric) ground state and the antisymmetric excited state. On the other hand, symmetry considerations easily show that the interaction Hamiltonian (2) can mix only $\Psi_{GS}\chi_v$ and $\Psi_{E^+}\chi_{v'}$ states. Therefore, the totally symmetric vibrational modes of the electronic ground state will be lowered in frequency, as in the case of the dimerized stack. However, they cannot borrow infrared intensity since the electronic CT transition to Ψ_{E^+} is symmetry forbidden.

The above sketched scheme of the effect of the *e-mv* interaction on the vibrational spectra of mixed stack CT crystals has been experimentally substantiated by several examples studied in our laboratory.[5,6,8] We have also found that the magnitude of the two above mentioned effects (frequency shift and, when present, intensity bor-

rowing) is larger the larger is the difference of the degree of ionicity from the extreme values zero or one. This is understandable since in a mixed stack crystal ρ reflects the strength of the CT interaction along the chain.

IV. VIBRATIONAL ASSIGNMENTS

Tables I and II collect the infrared frequencies of TMPD-TCNQ and TMPD-TCNQd_4, respectively, at room temperature ($\sim$300 K) and at $\sim$15 K. Decomposition of the sample under laser irradiation made difficult the collection of the corresponding Raman data; therefore, only the Raman frequencies of TMPD-TCNQ at $\sim$15 K are reported in Table III. The present data agree with the partial[4,10] or preliminary ones[18] previously reported. The infrared spectra of TMPD-TCNQ powders at 300 and 15 K are given in Fig. 1.

In the classification of the vibrational normal modes we shall use the molecular rather than the crystal symmetry. In this way we have the advantage of a direct correlation with the vibrational motions of the parent molecules; no relevant information is lost since in the present paper we shall not be concerned with the assignment of the lattice vibrations or with the weak effects due to the crystal field.[2] The only intermolecular interaction we shall consider is the CT one, whose perturbation through the *e-mv* coupling has been described above.

The classification of the vibrational modes of the TCNQ molecule (D_{2h} symmetry) is as follows:[19]

$$\Gamma_{\text{TCNQ}}: \quad 10a_g(\text{R}) + 3b_{1g}(\text{R}) + 5b_{2g}(\text{R}) + 9b_{3g}(\text{R}) + 4a_u + 9b_{1u}(\text{IR}) + 9b_{2u}(\text{IR}) + 5b_{3u}(\text{IR})$$

For TMPD the choice of the molecular symmetry is not so obvious. Also considering the methyl groups as point masses the TMPD molecule is generally not planar, since the N atoms have a pyramidal configuration.[20] The deviation from planarity depends on the crystal packing and on the charge on the molecule; in TMPD-TCNQ this deviation appears to be small.[21] Thus we shall classify the normal modes according to the $C_{2h}(y)$ symmetry[22] of a non planar TMPD molecule:

$$\Gamma_{\text{TMPD}} = 12a_g(\text{R}) + 9b_g(\text{R}) + 10a_u(\text{IR}) + 11b_u(\text{IR})$$

but we shall also keep in mind the correlation with the classification

TABLE I

Infrared spectra of TMPD-TCNQ at room (~300 K) and low (~15 K) temperature[a]

$T \simeq 15$ K		$T \simeq 300$ K		
$\bar{\nu}/\mathrm{cm}^{-1}$	Relative Intensity[b]	$\bar{\nu}/\mathrm{cm}^{-1}$	Relative Intensity[b]	Assignment[c]
326	57	324	w	Q, a_g
346	w			P, a_g
385	42			P, a_g
405	vw			
487	50	488	50	Q, b_{3u}
511	55	508	15	P, a_g ; Q, b_{2u}
517	(18)			P, b_u?
543	26	541	16	Q, b_{1u}
565	w			
587	vw			Q, b_{3u}?
615	19	615	w	Q, a_g
717	92	716	16	P, a_g
726	27			Q, a_g
754	w			
763	72	762	11	P, a_g
817	69	817	53	P, b_u
832	90	832	74	Q, b_{3u}
944	181	941	99	P, b_u ; P, a_g?
971	31			P, a_g?
981	76	981	56	P, b_u ; Q, a_g?
1002	16	1002	15	Q, b_{1u}
1051	sh			
1058	20	1054	w	
1090	sh			
1117	305	1120	31	P, Me
1127	(123)			P, Me?
1147	sh	1148	sh	
1159	sh			
1161	152	1156	19	P, a_g
1186	252	1185	50	Q, a_g
1207	(32)	1205	23	Q, b_{2u}
1228	159	1226	40	P, Me
1336	sh	1330	sh	
1362	(439)	1362	209	P, Me; Q, b_{1u}
1372	(391)	1372	136	Q, a_g?; P, b_u?
1408	sh			P, a_g
1411	20	1410	w	P, Me?
1434	w			
1446	sh			
1457	80	1446	w, br	P, Me
1495	sh			
1505	255	1502	164	$Q, b_1 u$
1515	45			
1532	(82)	1533	sh	

TABLE I (*continued*)

Infrared spectra of TMPD-TCNQ at room (~300 K) and low (~15 K) temperature[a]

$T \simeq 15$ K		$T \simeq 300$ K		
$\bar{\nu}/\text{cm}^{-1}$	Relative Intensity[b]	$\bar{\nu}/\text{cm}^{-1}$	Relative Intensity[b]	Assignment[c]
1542	(177)	1542	86	P, b_u
1587	368	1582	116	Q, a_g
1621	75	1615	15	P, a_g
1634	w	1635	vw	
2124	vw, br	2121	w	
2163	(90)	2158	(73)	Q, b_{2u}
2186	520	2181	325	Q, b_{1u}
2195	s, sh			Q, a_g
2201	w, sh			
2206	w, sh			
2215	w			

[a] KBr pellet. Only the spectral regions 250–1650 and 2100–2250 cm^{-1} are reported.
[b] Intensities expressed as peak absorbance, not corrected for band overlap, relative to a value of 50 assumed for the band at 487 cm^{-1} in the 15 K spectrum. Intensities less than 15 are qualitatively indicated with vw, very weak, and w, weak. Values in parentheses refer to cases in which overlapping is strong; sh, to nearly total overlap.
[c] Symmetry classification in the D_{2h} molecular symmetry for TCNQ (Q) and in the C_{2h} one for TMPD (P). Me refers to methyl modes.

TABLE II

Infrared spectra of TMPD-TCNQd_4 at room (~300 K) and low (~15 K) temperature[a]

$T \simeq 15$ K		$T \simeq 300$ K		
$\bar{\nu}/\text{cm}^{-1}$	Relative Intensity[b]	$\bar{\nu}/\text{cm}^{-1}$	Relative Intensity[b]	Assignment[c]
326	65	327	15	Q, a_g
334	sh			P, a_g
384	53	380	w, br	P, a_g
408	w			
428	50	428	28	Q, b_{3u}
511	60	508	w	P, a_g ; Q, b_{2u}
517	(24)			P, b_u ?
527	22	525	w	Q, b_{1u}
558	w			
564	w	562	w	Q, b_{3u}
614	26	614	w	Q, a_g
656	w			
696	50	695	w	Q, a_g
717	59	716	w	P, a_g
730	71	729	49	Q, b_{3u}
741	w			

TABLE II (*continued*)

Infrared spectra of TMPD-TCNQd_4 at room (~300 K) and low (~15 K) temperature[a]

$T \simeq 15$ K		$T \simeq 300$ K		
$\bar{\nu}$/cm^{-1}	Relative Intensity[b]	$\bar{\nu}$/cm^{-1}	Relative Intensity[b]	Assignment[c]
762	97	762	16	P, a_g
803	24			
817	57	817	53	P, b_u ; Q, b_{1u}?
838	44	839	29	Q, b_{2u}
851	104	851	w, sh	
864	101	863	18	Q, a_g?
944	229	941	115	P, b_u ; P, a_g?
974	44	972	(38)	P, a_g?; Q, b_{1u}
980	49	978	(26)	P, b_u ; Qa_g?
990	w	994	w	
1051	w, sh			
1058	24	1054	w	
1090	w			
1118	303	1120	34	P, Me
1127	(124)			P, Me?
1146	sh	1147	sh	
1160	103	1156	21	P, a_g
1176	w			Q, b_{2u}
1220	sh			
1226	221	1220	81	P, Me; Q, b_{1u}
1234	sh	1230	sh	
1364	471	1360	181	P, Me; P, b_u?
1374	sh			Q, a_g?
1408	26	1412	w	P, a_g
1435	sh			
1454	165			P, Me
1472	235	1464	191	Q, b_{1u}
1495	68			
1515	sh			
1531	sh	1530	sh	
1542	(250)	1541	218	P, b_u
1553	(156)			
1564	200			Q, a_g
1605	sh			
1615	276	1610	74	P, a_g
2169	sh	2168	sh	Q, b_{2u}
2177	sh			
2184	(522)			
		2180	476	Q, b_{1u}
2189	(544)			
2194	s, sh			Q, ag

[a,b,c]See corresponding footnotes of Table I.

TABLE III

Raman spectra of TMPD-TCNQ at ~15 K[a]

$\bar{\nu}$/cm^{-1}	Assignment	$\bar{\nu}$/cm^{-1}	Assignment
168 vw		1284 vw	
330 vw	Q, a_g	1409 s	P, a_g
723 m	Q, a_g	1500 m	P, Me?
764 w	P, a_g	1584 w	Q, a_g
975 m	P, a_g?	1622 vs	P, a_g
1162 m	P, a_g	2193 vw	Q, a_g
1192 m	Q, a_g	2212 vw	
1229 s	P, Me		

[a]Exciting line, 488.0 nm. Qualitative relative intensities indicated by: vw, very weak; w, weak; m, medium; s, strong; vs, very strong.

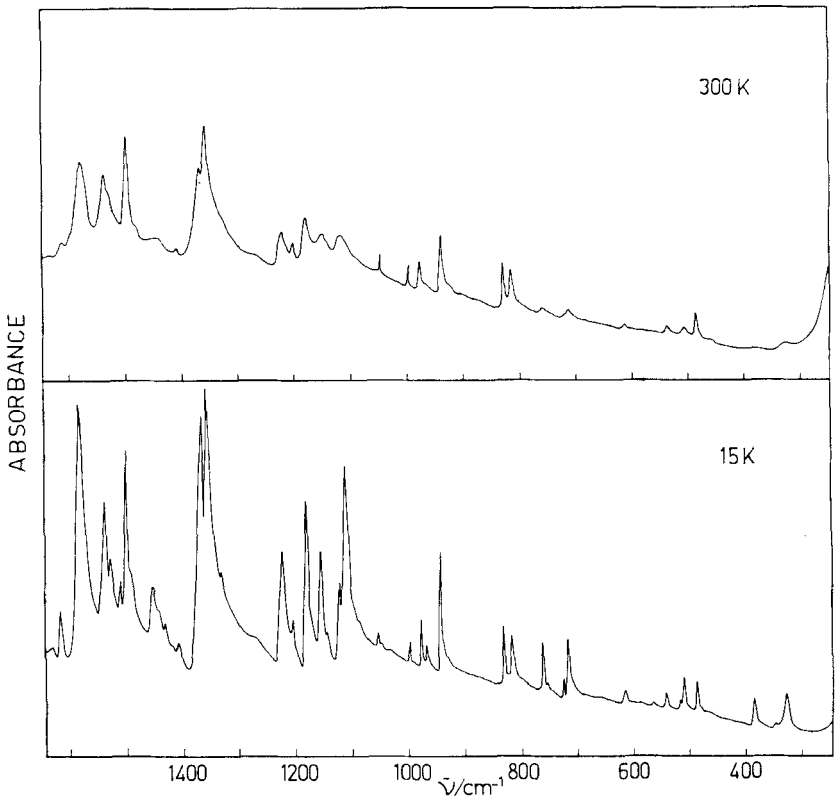

FIGURE 1 Infrared spectra of TMPD-TCNQ powders (KBr pellet).

of the TMPD normal modes in terms of a D_{2h} symmetry. $C_{2h}: 12a_g \rightarrow D_{2h}: 8a_g + 4b_{2g}$; $9b_g \rightarrow 7b_{3g} + 2b_{1g}$; $10a_u \rightarrow 7b_{2u} + 3a_u$; $11b_u \rightarrow 7b_{1u} + 4b_{3u}$.

The internal vibrations of the methyl groups above considered as point masses are classified only in terms of their approximate description, that is: 12 CH stretching modes, 20 deformations and 4 torsions, for a total of 36 normal modes.

The vibrational assignment of the TMPD-TCNQ spectra (Table I–III) is based mainly on the correlation with the assignments of the parent molecules and of their radical ions. The vibrational spectra of TCNQ and $TCNQ^-$ are well known and interpreted[19] whereas the corresponding ones of TMPD have been comparatively less studied. For this molecule we adopt an assignment which agrees with that of Kubinyi *et al.*,[23] as supported by additional measurements obtained in our laboratory.[24] The only variation is that of the $a_g\nu_3$ mode of $TMPD^0$ (Table IV below) that we attribute to the 521 cm^{-1} Raman line (polarized in the melt) in place of the unpolarized one at 505 cm^{-1}. In the assignment of the methyl group vibrations the $N(CH_3)_2$ characteristics frequencies sorted out by Gates *et al.*[25] have also offered a convenient reference scheme.

The comparison of the infrared spectra of TMPD-TCNQ (Table I) with those of TMPD-TCNQd_4 (Table II) helps to disentangle the modes of the TMPD from those of the TCNQ unit. Additional information is given by the comparison of the 300 K and 15 K infrared spectra. From Tables I and II and Fig. 1 it is in fact evident that the intensity of several infrared bands increases dramatically in the low temperature spectra. Their frequency practically coincides with that of the few observed Raman lines (Table III), which are certainly attributable to totally symmetric a_g modes. The intensity increase is the clear manifestation of the *e-mv* interaction, as discussed in Section III, since it follows a phase transition involving the dimerization[7,11] of the TMPD-TCNQ room temperature regular stack.[21] Apart from the details of the phase transition, which will be discussed in Section VI, we can safely assume that the infrared bands showing dramatic intensity increase in the low temperature spectra have to be associated with the a_g modes of the TMPD and TCNQ molecular units.

The proposed vibrational assignments of the TMPD and TCNQ moieties in the TMPD-TCNQ are reported in the last column of Tables I–III, and are compared with the corresponding ones of the neutral and fully ionized molecules in Tables IV and V. We have not considered the CH stretching spectral region, since the assignment of

TABLE IV

Assignment of the fundamental modes of TMPD moiety in TMPD-TCNQ[a]

Symm. species[b]	TMPD^0	TMPD-TCNQ	TMPD$^+$	Symm. species[b]	TMPD^0	TMPD-TCNQ	TMPD$^+$
$a_g\nu_2$	1620	1621	1628	$b_u\nu_{33}$	1520	1542	1542
ν_3	1340	1408	1419	ν_{34}	1323	1362?	1380
ν_4	1155	1161	1177	ν_{35}	1019c	981	978$^+$
ν_5^*	951c	971?	949c	ν_{36}	953	944	943
ν_6	945	944?	932	ν_{37}^*	816	817	829
ν_7	777	763	771	ν_{38}	660	—	668
ν_8^*	717	717	715c	ν_{39}^*	542	517?	520
ν_9	521$^+$	511	512$^+$	ν_{40}	450	—	466
ν_{10}^*	418	384	401c	ν_{41}^*	203c	—	205c
ν_{11}	324	334	336	ν_{42}^*	63c	—	63c
ν_{12}^*	106c	—	106c				

[a] Frequencies in wavenumbers. The frequencies of TMPD and TMPD$^+$ are taken from Ref. 23 (solid state spectra); those marked with $^+$ are the assignments different from those of Ref. 23, chosen on the basis of Ref. 24 data. The calculated frequency (c) is given when the experimental assignment is not available. The frequencies of TMPD-TCNQ are those of the 15 K infrared spectra. The CH stretching fundamentals are not included.

[b] Based on C_{2h} symmetry for the TMPD molecule with the methyl groups considered as point masses. The modes marked with * would correspond to out-of-plane vibrations (b_{2g} and b_{3u} for the two symmetry groups considered in the Table) in the D_{2h} symmetry of a planar TMPD molecule (see text).

TABLE V

Assignment of the fundamental modes of TCNQ and TCNQd_4 moieties in TMPD-TCNQ[a]

Symm. Species	TCNQ^0	TMPD-TCNQ	TCNQ$^-$	TCNQd_4^0	TMPD-TCNQd_4	TCNQd_4^-
$a_g\nu_2$	2229	2195	2206	2232	2194	2206
ν_3	1602	1587	1615	1564	1564	1581
ν_4	1454	1372?	1391	1449	1374?	1389
ν_5	1207	1186	1196	954	980?	970
ν_6	948	981?	978	864	864?	871
ν_7	711	726	725	690	696	701
ν_8	602	615	613	599	614	612
ν_9	334	326	337	333	326	337
ν_{10}	144	—	148	143	—	145
$b_{1u}\nu_{19}$	2228	2186	2181	2229	2184	2179
ν_{20}	1545	1505	1504	1533	1472	1461
ν_{21}	1405	(1362)	1361	1246	(1226)	1222
ν_{22}	998	1002	1008	966	974	974
ν_{23}	962	(981)?	987	801	(817)?	826
ν_{24}	600	—	607c	602	—	607c

ν_{25}	549	543	541	536	527	528
ν_{26}	146	—	160c	142	—	159c
$b_{2u}\nu_{33}$	2228	2163	2153	2229	2174	2162
ν_{34}	1540	—	1518	1510	—	1514c
ν_{35}	1354	—	1388	1316	—	1320
ν_{36}	1209c	1207	1210	1156	1176	1181
ν_{37}	1125	—	1133c	855	838	840
ν_{38}	498	(511)	512	496	(511)	512
ν_{39}	301c	—	297c	299c	—	292c
ν_{40}	60c	—	60c	60c	—	60c
$b_{3u}\nu_{50}$	859	832	836	756	730	732
ν_{51}	—	587?	585	—	564?	565
ν_{52}	475	487	483	418	428	423
ν_{53}	220	—	225	220	—	220
ν_{54}	103	—	—	105	—	—

[a] Frequencies in wavenumbers. The frequencies of $TCNQ^0$ and $TCNQ^-$ are taken from Ref. 19. The calculated frequency (c) is given when the experimental assignment is not available. The frequencies of TMPD-TCNQ are those of the 15 K infrared spectra. The CH stretching fundamental modes are not included. Values in parentheses refer to cases of assumed overlap.

these modes is rather obvious and is not important to the aim of the present paper.

Due to the large number of vibrational modes of both TMPD and TCNQ, the vibrational spectra are very complicated and several overlaps are likely to occur. In particular, the spectral regions 1350–1400 cm^{-1} and 900–1000 cm^{-1} are difficult to interpret unambiguously. In the former, the very strong infrared band typical of methyl deformations at about 1360 cm^{-1} obscures the presence of other TMPD and TCNQ modes. In the 900–1000 cm^{-1} region additional problems arise from the uncertainty in the proper location of the TMPD $a_g\nu_5$ and ν_6 fundamentals. Consequently, the proposed assignments for these two spectral regions remain tentative.

The assignments of TMPD moiety reported in Table IV do not include the vibrations of the methyl groups. Twenty CH_3 angle deformation motions need to be considered in the spectral regions studied in the present paper. We expect these angle deformation motions to be grouped in five rather narrow frequency intervals. It is in fact reasonable to assume that the vibrations of the four different CH_3 groups are weakly coupled, so that their frequencies are almost degenerate. The calculation and the correlation with the vibrational spectra of other molecules containing $N(CH_3)_2$ groups[23,25] justify the above assumption and indicate the following five spectral regions for the methyl angle deformations: 1460–1450, 1450–1400, 1380–1340, 1230–1190 and 1130–1100 cm^{-1}.

Accordingly, we assign to CH deformations the infrared bands at 1457, 1362, 1228 and 1117 cm^{-1}. The mode occurring around 1450–1400 cm^{-1} is very weak in infrared[25] and is left unassigned.

The achieved TMPD-TCNQ vibrational assignment is incomplete, as the attribution of many fundamental modes (the non-totally symmetric *gerade* modes on both TMPD and TCNQ and the TMPD a_u ones) is lacking. On the other hand, all the observed main infrared and Raman bands have found a proper interpretation. Attempts to extend further the assignment are almost hopeless, but its present status is more than adequate to give a sound basis to the following discussion.

V. DETERMINATION OF THE DEGREE OF IONICITY

The estimate of the degree of ionicity from the vibrational frequencies[2] is based on the assumption (that should be tested whenever possible) of linearity of the frequency variation upon ρ. On the other

hand we have seen in Section III that in a mixed stack crystal the frequencies of the totally symmetric modes may be perturbed by the *e-mv* interaction. Therefore the estimate of the degree of ionicity of TMPD-TCNQ must rely on the frequencies of the *ungerade*, infrared active modes.

In the choice of the diagnostic frequencies we exclude those which display small ionization shifts (less than 25 cm^{-1}) and of course those which are not based on safe assignments. It turns out that according to these criteria no reliable diagnostic mode can be found in the case of TMPD (Table IV). In fact the only one with sufficiently large ionization shift ($b_u\nu_{34}$) is difficult to assign due to the concurrence of several fundamentals in the same spectral region (See section IV). Thus one is left with the following TCNQ and TCNQ-d_4 fundamental modes: $b_{1u}\nu_{19}$ and ν_{20}, $b_{2u}\nu_{33}$ (Table V). The ρ value obtained from them by making the average weighted for the magnitude of the ionization shift is 0.88 and 0.97 for the 15 K and 300 K TMPD-TCNQ, respectively. The error of the above determination is about 10% so that we cannot consider significant the variation of ρ with temperature and give the best estimate as $\rho = 0.9_2$. This value agrees with the estimate made from X-ray structural data,[9] and confirms the results previously obtained from the highest frequency CN stretching mode alone. We notice that the latter method may be misleading if applied without distinguishing the proper symmetry species of the used CN stretching frequency.[4,6]

The Raman frequency at 1409 cm^{-1} has been previously used to estimate $\rho \simeq 0.7$ for TMPD-TCNQ.[10] Such a value was obtained by assigning the above frequency to the TCNQ $a_g\nu_4$ mode and without being aware of the recently evidenced[6] possible perturbing effect of the *e-mv* interaction (Section III). This perturbation prevents the use of totally symmetric modes for the estimate of ρ since, as shown experimentally, it is present in the case of both regular and dimerized mixed stack compounds with ρ appreciably different from 0 or 1. For a $\rho \simeq 0.7$ the perturbation on the frequencies should be large,[5,26] contrarily to what is observed for the other TMPD and TCNQ a_g modes (Tables IV and V). Furthermore, the assignment of the 1409 cm^{-1} band to the TCNQ $a_g\nu_4$ mode is made uncertain by the fact that in this frequency region one cannot disregard the presence of a fundamental mode of TMPD radical cation (Table VI, $a_g\nu_3$), as clearly shown by the comparison with the Raman spectra of other systems containing this species (TMPD · ClO_4[23] and TMPD-Chloranil[26]). In the light of the above considerations and taking into account the overall assignment obtained in this paper (Tables V and

VI) the almost complete ionic nature of the TMPD-TCNQ complex ($\rho \simeq 0.9$) is clearly recognized.

VI. PHASE TRANSITION

TMPD-TCNQ crystal is known to undergo a phase transition in the 210-180 K temperature range.[11,12] Whereas the room temperature X-ray crystal structure indicates that the TMPD-TCNQ stack is regular,[21] the low temperature magnetic susceptibility data have been interpreted in terms of a chain of almost isolated (interdimer exchange coupling $J' \simeq 0$) dimers.[11] Our infrared data (Fig. 1 and Tables I and II) lead to a similar conclusion: the strong intensity of the totally symmetric modes in the low temperature spectra can be in fact only attributed to the effect of the *e-mv* interaction in a dimerized chain (see Section III).

To gain more insight into the nature of the phase transition, we have studied the temperature evolution of the infrared intensity of several totally symmetric modes. The intensity of most of the observed bands displays the same trend with varying temperature (Fig. 2, shaded area), evidencing the presence of a rather broad phase

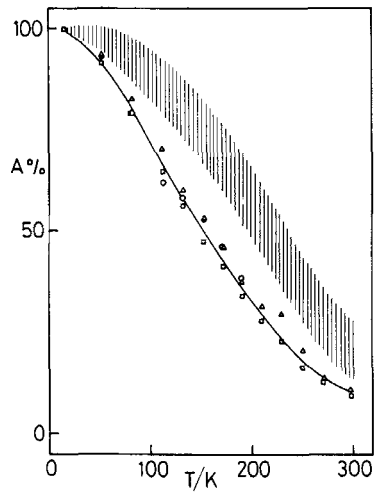

FIGURE 2 Normalized integrated intensities of TMPD-TCNQ infrared absorptions (Nujol mull spectra) vs temperature. The shaded area refers to the following modes: TCNQ, $a_g\nu_3$, ν_5, ν_8 and ν_9; TMPD, $a_g\nu_4$, ν_7, ν_8 and the methyl CH deformation at 1227 cm^{-1}. The circles, triangles and squares refer to the TMPD $a_g\nu_5$, ν_{10} and to the methyl CH deformation at 1117 cm^{-1}.

transition around 220 K. The measurements have been always made starting from low temperature so that hysterisis effects have not been investigated.

Fig. 2 also shows that three TMPD bands, namely the $a_g\nu_5$ and ν_{10} and the methyl deformation mode at 1117 cm^{-1}, exhibit a temperature intensity variation significantly different from that of the other bands. A possible explanation of this anomalous behavior can be given in terms of a TMPD molecular distortion consequent to the stack dimerization. An increase of the pyramidal angle at the N atoms has been indeed observed in correspondence with the dimerization of the TMPD stack in TMPD · ClO_4.[27] Such a deformation implies a change of the delocalization of the N lone pair over the benzenic ring. Thus one would expect that the *e-mv* coupling of the vibrations involving the out-of-plane motion of the N atoms (like to $a_g\nu_5$ and ν_{10}) is the most affected by the change in N pyramidal angle. The intensity variation of the corresponding infrared bands would then be a consequence of both the stack distortion and of the molecular deformation. The latter, which is not necessarily due to the *e-mv* interaction, induces the "retard" of the observed intensity increase. This kind of explanation is of course only tentative, and for instance does not explain why the methyl deformation at 1117 cm^{-1} has a behavior different in respect to the other methyl modes like the 1228 cm^{-1} one. In any case the present data evidence the complex nature of the phase transition, that cannot be directly ascribed to a simple Peierls instability as it has been done for the other mixed[8] or segregated stack[28] systems.

One last thing to comment on is the room temperature residual infrared intensity (about 20% of the low temperature value) of the totally symmetric modes (Fig. 2). We have verified that the intensity decreases further by increasing the temperature up to ~350 K (above this temperature the sample decomposes). It is therefore clear that the broad TMPD-TCNQ phase transition has not completely ended at room temperature, that is, some degree of stack distortion still exists at ~300 K. This finding appears to be in contradiction with the X-ray measurements,[21] that indicate a regular stack structure. This contradiction is however removed if we interpret the large thermal motion detected by X-ray[21] as actually due to disorder in the stack structure.[20] Static (defects) or dynamic (fluctuations) stack distortions randomly distributed along the chain could not be detected by X-ray but still would give rise to detectable infrared absorptions of the totally symmetric modes. This interpretation appears plausible and strongly suggests that the presence of disorder should be taken into

account in interpreting the rather anomalous behavior of the TMPD-TCNQ magnetic susceptibility.[11] This behavior has been previously explained[3,10] in terms of an intermediate degree of ionicity ($\rho \simeq 0.7$), but this hypothesis is not tenable in the light of our present results which are clearly in favour of an almost complete charge transfer.

VII. CONCLUSIONS

This paper gives the first rather detailed interpretation of the complex vibrational spectra of TMPD-TCNQ. The result shows that even unsophisticated experimental data—the infrared spectra of the powders—can lead to useful information. The most important one is the value of the degree of ionicity, that removes early contradictions[4,9,10] and stimulates a reinterpretation of the magnetic data.[11] The procedure followed in this paper underlines that, although it is often a cumbersome task, an interpretation as complete as possible of the vibrational data has to precede their exploitation for the determination of ρ. Even if only a few vibrational modes will be eventually used to such aim, the focusing of the attention over only one vibrational feature can lead to erroneous results.[6]

The significant informations gained on the TMPD-TCNQ phase transition demonstrate that the effects of the *e-mv* interaction on the vibrational spectra are a very sensitive probe of the physical properties of CT crystals. The interpretative scheme we have proposed to account for the *e-mv* interaction effects in mixed stack systems[15] appears to work out well also for the present example.

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