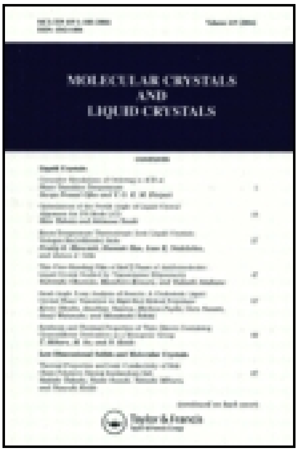

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Effect of Deuteration on the Infrared Characteristics of TCNQ-based Solid-Solid Charge-Transfer Systems

E. Ghezzal [a] , A. Brau [a] , J. P. Farges [a] & P. Dupuis [b]

[a] Université de NICE-SOPHIA ANTIPOLIS, Laboratoire de Biophysique, U. F. R., Faculté des Sciences, Pare VALROSE, 06034, NICE, Cedex, FRANCE

[b] Laboratoire de Chimie Physique Macromoléculaire, E. N. S. I. C., B. P. 451, 54001, NANCY, FRANCE

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EFFECT OF DEUTERATION ON THE INFRARED CHARACTERISTICS OF TCNQ-BASED SOLID-SOLID CHARGE-TRANSFER SYSTEMS

E. GHEZZAL, A. BRAU, J.P. FARGES and P. DUPUIS*
Université de NICE-SOPHIA ANTIPOLIS, Laboratoire de Biophysique, U.F.R., Faculté des Sciences, Parc VALROSE, 06034 NICE Cedex, FRANCE.
*Laboratoire de Chimie Physique Macromoléculaire, E.N.S.I.C., B.P. 451, 54001 NANCY, FRANCE.

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Abstract Significant modifications of the powder infrared spectra of TCNQ-based crystalline salts and composites, simply induced by deuteration of TCNQ, are presented and discussed.

Keywords: solid-solid charge transfer, TCNQ, deuteration, infrared spectra, composites

We reconsider, here, solid-solid charge-transfer (C-T) reaction between the insulating 1:1 salt: TEA-TCNQ and pure TCNQ (TEA = triethylammonium, TCNQ = tetracyanoquinodimethane), by which the conducting 1:2 salt: TEA-$TCNQ_2$ is directly formed:

$$\text{TEA-TCNQ} + \text{TCNQ} \rightarrow \text{TEA-TCNQ}_2 \quad [1]$$

For this purpose, we present a comparative infrared (IR) absorption study, in KBr, of equimolar mixtures of the following series of closely related binary systems:

/a/ TEA-TCNQ / TCNQ
/b/ TEA-TCNQ(d) / TCNQ
/c/ TEA-TCNQ / TCNQ(d)
/d/ TEA-TCNQ(d) / TCNQ(d)

In all these systems, TCNQ and TCNQ(d), whether neutral (^{0}) or ionized ($^-$), stand for the un-deuterated ($C_{12}N_4H_4$) and deuterated ($C_{12}N_4D_4$) forms of the molecule, respectively, those infrared characteristics are significantly different [1-2-3].

It is appropriate, for subsequent discussion, to report, first, the powder IR spectra of 1:1 salts TEA-TCNQ and TEA-TCNQ(d).

These two spectra are presented in Table 1.

Incidentally, a special mention may be made here of the two out-of-plane (o.o.p.) modes ($b_{3u}\nu_{50}$ and $b_{3u}\nu_{52}$) [3-4], observed at 863±1 and 476±1 cm^{-1} in $TCNQ^0$, at 755±1 and 419±1 cm^{-1} in $TCNQ(d)^0$, thus corresponding to a common frequency ratio: 1,81±0,02. These two modes are observed at 825±1 and 481±1 cm^{-1} in $TCNQ^-$ (i.e. in TEA-TCNQ), and at 727±1 and 422±1 cm^{-1} in $TCNQ(d)^-$ (i.e. in TEA-TCNQ(d)) (see table 1). This corresponds also to a common ratio for these charged species, but its value now is only: 1.72±0.01, that is, significantly lower than the value for the neutral ones.

TABLE I Powder infrared spectra of TEA-TCNQ and TEA-TCNQ(d) (frequencies in cm^{-1}; w = weak, m = medium, s = strong, vs = very strong, br = broad; the a_g modes of the salts [6-7] and the structure proper to cation TEA$^+$ are also indicated)

TEA-TCNQ			TEA-TCNQ(d)		
331	m,br	a_g9	330	m,br	a_g9
481	m	o.o.p.	422	m	o.o.p.
518	w		440	vw	
550	w		456	vw	
618	w	a_g8	470	vw	
721	m	a_g7	516	w	
760	w		536	w	
805	w	cation	564	w	
825	s	o.o.p.	616	w	a_g8
850	w	cation	699	m	a_g7
876	vw		727	m	o.o.p.
942	vw		804	m	cation
957	vw		830	vw	
982	w	a_g6	849	m	cation
989	m		858	vw	
1037	m	cation	869	s	a_g5
1173	w		975	w	a_g6
1184	vs	a_g5	1037	m	cation
1217	vw		1069	vw	
1223	m		1172	w	
1337	vs		1188	w	
1346	vs	a_g4	1233	vw	
1367	s		1298	vw	
1384	w		1333	vs, br	a_g4
1399	m	cation	1365	vw	
1434	m		1385	vw	
1477	m		1399	m	cation
1509	vs		1434	w	
1580	vs	a_g3	1460	vs	
1625	vw		1477	w	
1914	vw		1538	vs	a_g3
			1557	w	
			1574	w	
2130	vw		2128	vw	
2170	s		2156	vw	
2184	vs		2181	vs	
2200	vs	a_g2	2198	vs	a_g2
2230	w		2492	m	cation
2493	m	cation	2679	m	cation
2680	m	cation	2740	m	cation
2742	m	cation	2764	w	
2766	w		2804	vw	
2805	vw		2938	m	cation
2936	m	cation	2976	w	cation
2974	w	cation			

A study devoted to the DC electrical conductivity σ of composites /a/ was already presented previously [5] : it was found that σ in such systems is larger than in TEA-TCNQ by five orders of magnitude and, then, becomes comparable to σ in TEA-TCNQ₂.

A first result of the present work is that equimolar mixtures of composite systems /a/ and /d/ are found to reproduce quite closely the very distinctive spectral features of the 1:2 salts: TEA-$TCNQ_2$ and TEA-$TCNQ(d)_2$, respectively. The powder IR absorption spectra of these two salts have already been presented and discussed elsewhere [6-7] and, so, they do not require further comments.

In the following, we rather pay attention to "cross-systems" /b/ and /c/, the interest of which being that they involve two distinguishable TCNQ molecules: TCNQ and TCNQ(d). In composites /b/, all TCNQ molecules are initially neutral and all TCNQ(d) molecules are ionized, whereas this situation is inverted in composites /c/.

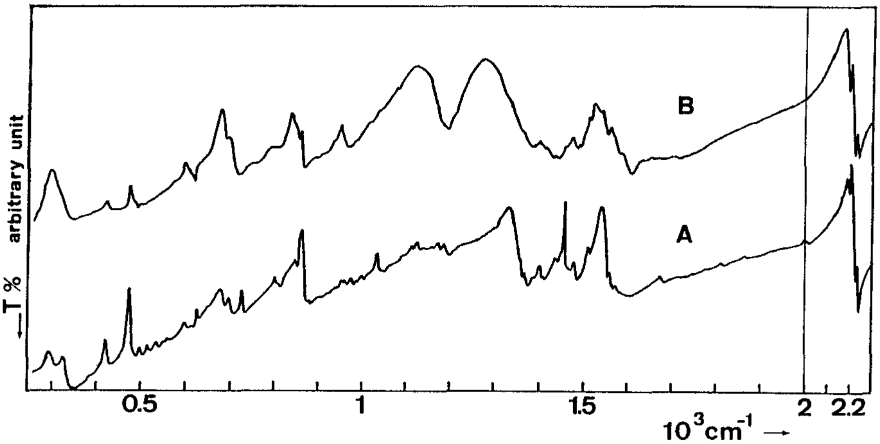

FIGURE 1 Powder infrared spectra of TEA-TCNQ(d) / TCNQ composites. Spectrum A is after a mechanical treatment of 0.5 hour, and spectrum B after a mechanical treatment of 4 hours (see text).

In any case, the solid-solid C-T reaction requires, to be optimized, a mechanical grinding of the two components for some appropriate time τ_M. For instance, Figure 1 shows the IR spectrum of composite system /b/ obtained, with the same procedure, for τ = 0.5 hour, figure 1A, and for τ_M = 4 hours, figure 1B.

Another result of the present work is that equimolar mixtures of composites /b/ and /c/, once optimized the charge-transfer reaction (i.e. $\tau = \tau_M$), develop two IR spectra which are essentially similar. These spectra are highly different from those of the starting components, in particular of TEA-TCNQ or TEA-TCNQ(d), and they appear roughly as a superposition of the IR spectra of the two 1:2 salts: TEA-$TCNQ_2$ and TEA-$TCNQ(d)_2$ already considered in the preceding section. This seems to indicate that, in the process of solid-solid CT reaction [1], the two involved TCNQ molecules are chemically equivalent, in spite of the fact that one of them is already ionized and attached to a TEA^+ cation, as if there were some local fusion with complete dissociation.

Such an hypothesis is greatly reinforced by the following observation. It is known that intensive grinding (i.e. $\tau >> \tau_M$) of a KBr pellet containing a 1:2 salt such as TEA-$TCNQ_2$ introduces new strong modifications of the IR spectrum of the material, by which the spectrum of the corresponding 1:1 salt TEA-TCNQ plus the spectrum of neutral TCNQ are reformed [7].

When this procedure is applied for instance to composite system /b/ above: TEA-TCNQ(d) / TCNQ, one gets in this way not only the spectra of the starting components: TEA-TCNQ(d) and TCNQ, but also, and in comparable proportions, the spectra of the two new cross-components: TEA-TCNQ and TCNQ(d). Thus, the original system is recovered but, now, with a statistical redistribution of TCNQ and TCNQ(d) molecules into the neutral and ionized forms.

More precisely, one obtains, on regrinding equimolar samples of composite /b/, the following new structures (in cm^{-1}): 750w and 1512s for TCNQ(d); 825s, 989m, 1184vs, 1337vs, 1367s, 1509vs and 1580vs for TEA-TCNQ (see table I) (one also gets, with both systems /b/ and /c/, a rather strong unidentified peak at 1387 cm^{-1} which has no equivalent in any of the starting components).

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