Vibrational spectra of CT complexes of acridine orange

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Infrared spectra of acridine orange and its charge transfer complexes with acceptors such as chloranil, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and tetracyano-*p*-ethylene (TCNE) are reported here. Their photo conducting nature is explained with two absorption edges in infrared range associated with non-equivalent sites of chloride ion or formation of bonding, non-bonding and antibonding orbitals. The mid-IR transition is usually direct and the low-energy transition is indirect. Whether the transition is allowed or forbidden depends on average intermolecular distance. This differs from ordinary ternary complexes in which two acceptors give rise to two conduction bands. Also, there is absence of any screening found in two donor based ternary systems. There is some band tailing of phonon bands in absorption function above E_g. Only TCNQ and TCNE complexes show weak Gaussian bands below 800 cm^{-1}. The repetitions of structures associated with the oscillations in the density of states are found which reveal that these CT complexes can work as molecular multi-vibrators.

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Recently, we studied UV-vis and IR spectra of organic photoconductors and their charge transfer complexes[1-3]. These included indigo carmine, green malachite, aniline blue, crystal violet, and biphenyl and their CT complexes with acceptors such as chloranil, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), tetracyano-*p*-ethylene (TCNE) and iodine[1]. Only quinhydrone acted as an acceptor with donors like benzidine, bisquinoline, bipyridyl, N,N,N′,N′-tetramethyl *p*-phenylenediamine (TMPD), N,N′-diphenyl *p*-phenylenediamine (DPPD) and pyrene[2]. All the spectra reveal two types of photoconductors, i.e. those having transmission large and constant above E_g and those developing absorption above E_g. Only crystal violet and its CT complexes show development of absorption above E_g. Recently, we reported pinacyanol chloride showing similar properties. Here, it is one more example of this second type, i.e. acridine orange radical-cation which is stabilized with chloride ion. It is a good photoconductor[4]. The infrared spectra of CT complexes of acridine orange are reported herein. We have earlier reported ternary organic conductors of one donor-two acceptor type based on benzidine as a donor[5]. The present spectral features differ from such ternary systems because of radical-ion salt nature of the parent molecule, where one acceptor (chloride ion) is strongly bound and organic acceptor is weakly bound.

Materials and Methods

Acridine orange [Hemi (Zinc chloride) salt of 3,6-bis (dimethylamino) acridine] was obtained from Sigma Chemical Company, U.S.A. The orange colored dye was mixed with acceptors such as chloranil, DDQ, TCNQ and TCNE in 1:1 molecular weight proportions and grounded using eggate mortar and eggate pastle. The dark (green, blue and black) colored CT complexes were again mixed with dry spectrograde KBr powder. Semitransparent circular discs prepared with a compressing machine were placed in the dark chamber of spectrophotometer model GX-FTIR of Perkin-Elmer Co, U.S.A. The molecular structures of acridine orange and organic acceptors are shown (Scheme 1). The IR spectra in the full IR range from 400 cm^{-1} to 4000 cm^{-1} were recorded.

Results and Discussion

The vibrational spectrum of acridine orange is shown in Fig. 1. There is noise in absorption coefficient above 1700 cm^{-1} corresponding to noise in photocurrent found in photoconductors since the absorption coefficient (α) and optical conductivity (σ) are related by:

DDQ
(2,3-Dichloro-5,6-dicyano-p-benzoquinone

Chloranil

TCNQ
(7,7,8,8, Tetrachyano-p-quinodimethane)

TCNE
(Tetracyanoethylene)
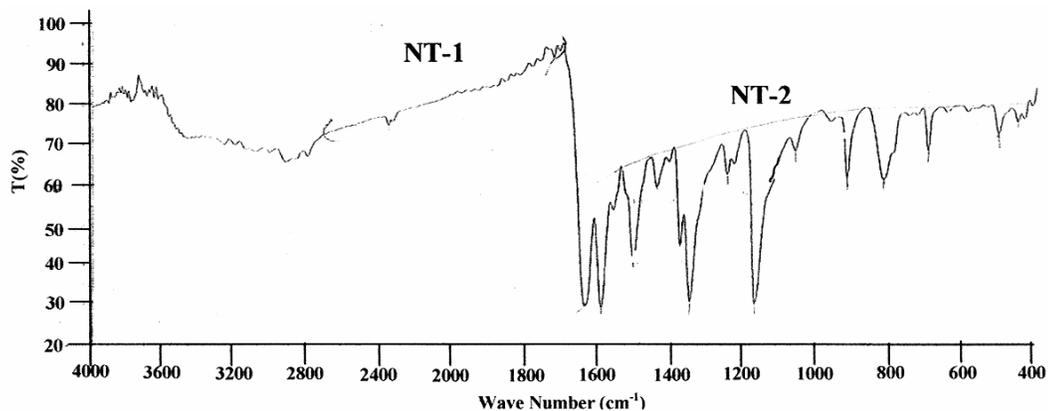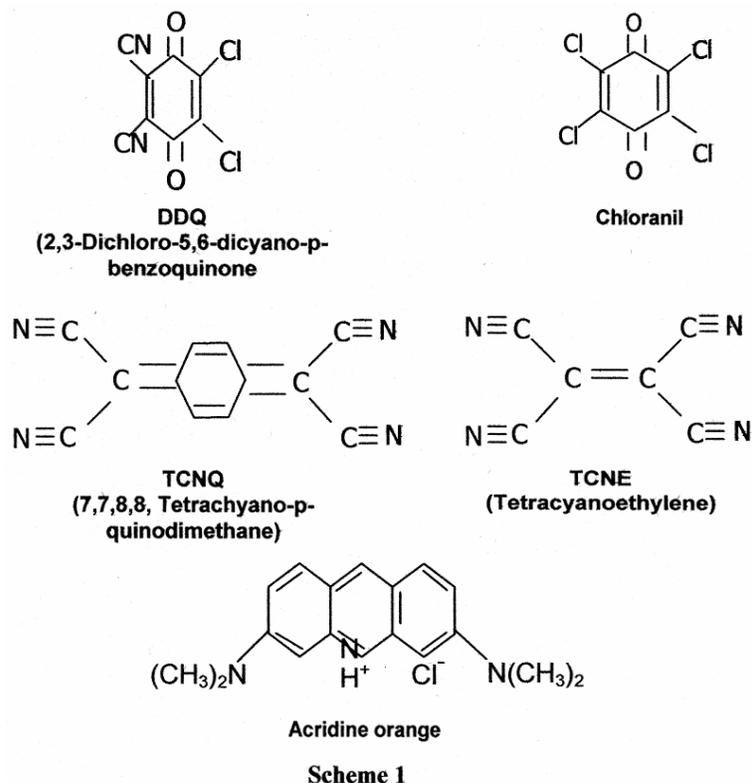
Acridine orange

Scheme 1

Fig. 1 — IR spectrum of acridine orange (AO).

$$\sigma(\omega) = \frac{\alpha(\omega)n_1(\omega)c}{4\pi}$$

The noise exists in two regions: (i) just above 1700 cm^{-1} due to localization near the band edges, and (ii) above 3400 cm^{-1} due to coulomb repulsion among free charge carriers in the conduction band. There are two infrared absorption edges: (i) one with E_g=0.22 eV and (ii) with E_g=0.05 eV.

The first edge is due to an allowed direct transition very similar to other normal CT complexes and the second edge is the forbidden indirect transition as observed in some degenerate semiconductors[6] like $(TMPD)_{1.5} - KI\text{-}I_2$. The two absorption edges in almost a binary system of acridine orange are not due to two conduction bands involving two types of acceptor levels in ternary materials but due to non-equivalent sites of chloride ion one near to N-H$^\oplus$ group and other type near N$^\oplus$ - $(CH_3)_2$ group. In spite of this, the donor does not behave as two donating molecules, which
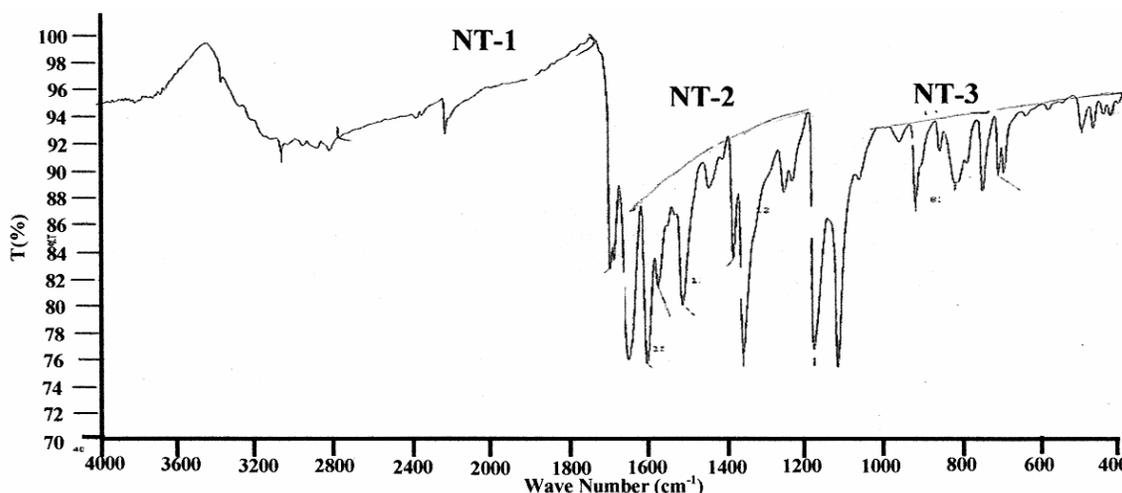
Fig. 2 — IR spectrum of AO-chloranil.

should otherwise lead to screening effects. Zinc plays only a marginal role even if it is present in the sample. Acridine orange works as a donor in spite of partially positive charge getting neutralized by chloride ion. Other possibility is the hybridization of the molecular orbitals upon formation of organic radical-ion salt involving chlorine. This can lead to bonding, non-bonding and anti-bonding orbitals. Non-bonding and anti-bonding orbitals behave as two conduction bands even in a binary salt. This can lead to two absorption edges observed in the IR spectrum of acridine orange.

The second spectrum is the IR spectrum of acridine orange-chloranil (Fig. 2). This spectrum has three clear absorption edges of background absorption. The usual one at 0.225 eV is an allowed direct transition. The analysis is done in the same as in the cases of elemental and compound inorganic semiconductors[7,8]. The second is an edge with E_g=0.15 eV which is not observed in acridine orange. This band gap is related with CT interaction of chloranil with acridine orange, mainly arising from the other $N^{\oplus}$-CH$_3$ group. The second ionization potential is considerably lowered by the internal electric field, i.e. the quaternization of nitrogen occurs at a lower energy. The third absorption edge around 0.05 eV is the same as observed in acridine orange. Thus, an associated band edge is provided by the levels of chloranil molecules which are partially ionized.

Acridine orange-DDQ complex also shows an IR spectrum with two absorption edges (Fig. 3).

Although DDQ molecule is more prone to form semi-quinone ion due to asymmetric in molecular structure, the presence of half-power beta density in the range 1000-1800 cm^{-1} (a flat peak in 100-T) reveals a larger average intermolecular distance required for hopping. Thus, the interaction is weaker than in chloranil complex. The absorption edge at 0.25 eV is a forbidden direct transition and at 0.07 eV is a forbidden indirect transition. There is an exponential band tailing of about 0.03 eV range below the upper edge of 0.25 eV.

Acridine orange-TCNQ also shows a spectrum revealing two transitions both forbidden indirect at 0.25 eV and at 0.10 eV (Fig. 4a). The upper transition shifts to higher energy but with a band tailing between 0. 25 eV and 0.22 eV. The lower transition also shifts to higher energy from 0.05 eV to 0.10 eV as compared to the one in acridine orange. The absorption function shows several humps (partially resolved oscillator models) between 0.10 eV and 0.18 eV due to phonons. A weak Gaussian is found below 800 cm^{-1} (Figs 4a and 4b). The upper edge with E_g=0.25 eV and band tailing down to 0.22 eV is an allowed indirect transition. The lower edge with 0.1 eV threshold is forbidden indirect transition.

The last is the spectrum of acridine orange-TCNE (Fig. 5). This CT complex shows almost the same behavior as TCNQ complex. There are two absorption edges due to two conduction band model[9] and as found in ternary systems[5]. The lower edge has threshold wavenumber around 900 cm^{-1}, i.e. E_g=0.1125 eV. It is exactly at half-value of the upper
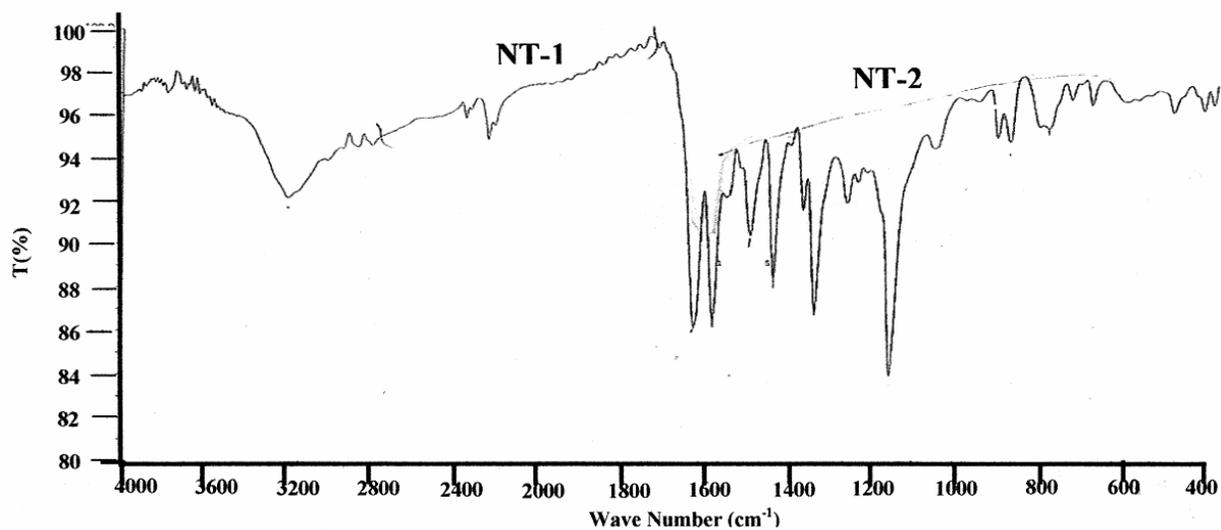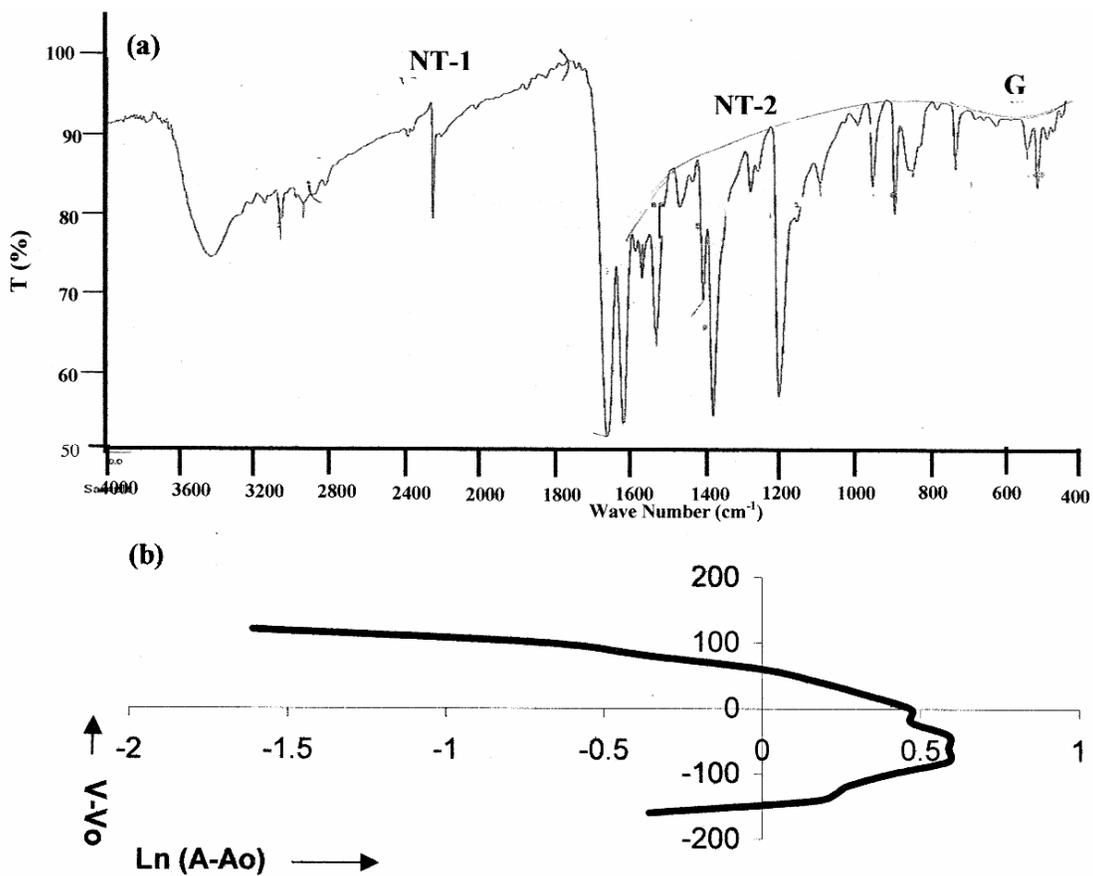
Fig. 3 — IR spectrum of AO-DDQ.

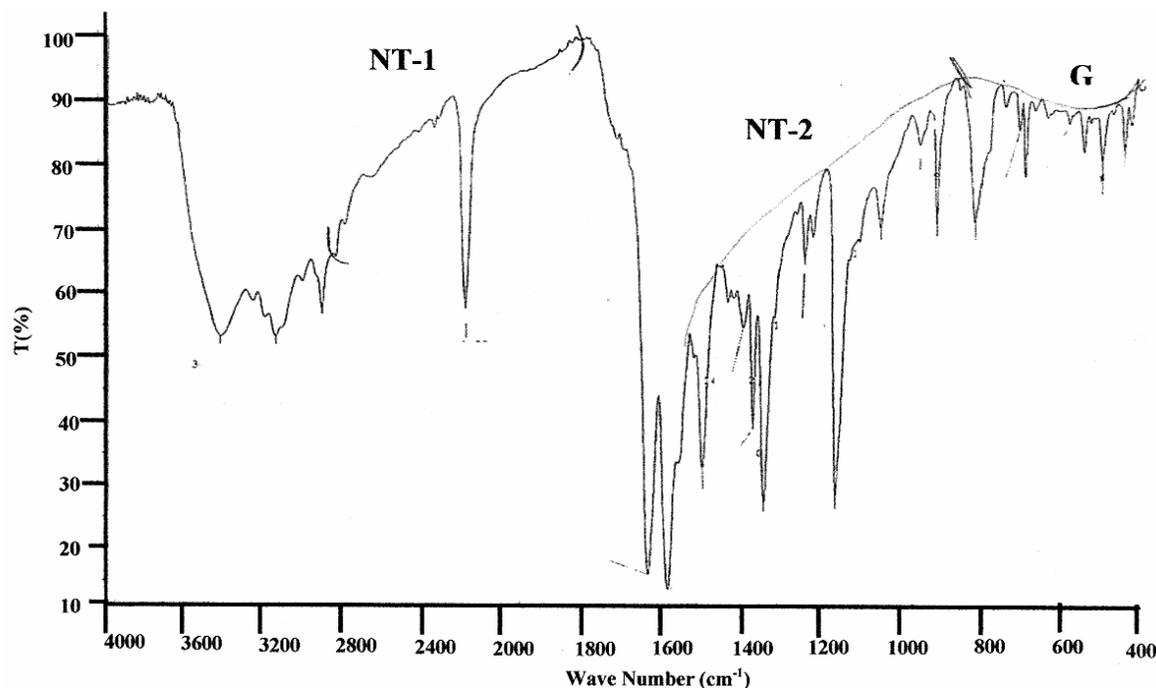Fig. 4 —(a) IR spectrum of AO-TCNQ; (b) ln A versus (K-K_O) (Gaussian below 800 cm^{-1}).

Fig. 5 — IR spectrum of AO-TCNE.

edge at 0.225 eV. A low frequency Gaussian around 560 cm^{-1} is also observed and is verified.

It is known that in semiconductors, the absorption coefficient near the band gap is given by $\alpha h\nu=A(h\nu-E_g)^r$ where $r=1/2$ or $3/2$ for direct allowed or forbidden transition and $r=2$ or 3 for indirect allowed or forbidden transitions for the interband transitions. For analyzing these transitions, $(\alpha h\nu)^2$ or $(\alpha h\nu)^{2/3}$ are plotted for direct transitions. The best fits are straight lines revealing nature of transitions. These transitions are summarized in Table 1.

The Gaussian distributions found in TCNQ and TCNE complexes in the low frequency region of IR spectra, marked with G in the original spectra of these CT complexes are given by:

$$A=A_o+A_1e^{[-(K-Ko)^2/2M_2]}$$

where A is absorbance, A_o is the background absorbance, A_1 is the absorbance at the peak of the Gaussian band, K_o is the central wavenumber and M_2 is the second moment of the distribution. Therefore,

$$\ln[(A-A_o)/A_1]= -(K-K_o)^2/2M_2$$

We plot $\ln[(A-A_o)/A_1]$ versus $(K-K_o]$ where $K=K_o$, $A-A_o=A_1$ and $\ln(A-A_o)/A_1=0$. If $A=A_o$, logarithm n goes to negative infinity. The curve is parabolic between $[\ln(A-A_o)/A_1]$ versus $K-K_o$. The parabola extends to negative infinity for large values of $K-K_o$ on both positive and negative sides.

Apart from all of the above spectral features, there are repeated structures due to oscillations in the density of states observed in acridine orange spectrum and in the spectra of CT complexes. The absorption coefficients and the density of states are directly proportional. As there are oscillations in the density of states, this will lead to periodic variations in the absorption or reflection. These features are different from resonance-anti-resonance spikes in highly ionic radical-ion salts[10], second-harmonic generation in non-linear optical materials[11] and normal band assignments[12]. Such periodic variations are also found in the CT complexes of organometallic chelates[13,14]. This is a special characteristic in solid state spectroscopy. The optical constants are determined through solid state effects. These all CT complexes behave like a multivibrator in electronic circuits. There is a damped-repetition of the same line-shape arising from electron-phonon coupling. There is a damping in low-frequency collective vibration as frequency increases. The overall damping coefficient or relaxation time of these collective modes is different from these parameters for independent vibrational modes. The repeated structures are identified from the persistence of the line-shape, i.e. the line-shape remains intact or is preserved although the amplitude decreases upon damping.

Table 1 — Nature of transitions in acridine orange and its CT complexes

Name of complex	Upper edge absorption function and E_g (eV)		Lower edge absorption function and E_g (eV)	
Acridine Orange (AO)	$\alpha h\upsilon = A(h\upsilon - E_g)^{1/2}$ $E_g = 0.22$ eV	Allowed direct	$\alpha h\upsilon = A(h\upsilon - E_g)^3$ $Eg = 0.05$ eV	Forbidden indirect
AO-Chloranil	$\alpha h\upsilon = A(h\upsilon - E_g)^{1/2}$ $E_g = 0.225$ eV	Allowed direct	$\alpha h\upsilon = A(h\upsilon - E_g)^3$ $E_g = 0.15$ eV	Forbidden indirect
			$\alpha h\upsilon = A(h\upsilon - E_g)^3$ $E_g = 0.05$ eV	Forbidden indirect
AO-DDQ	$\alpha h\upsilon = A(h\upsilon - E_g)^{3/2}$ $E_g = 0.24$ eV	Forbidden direct	$\alpha h\upsilon = A(h\upsilon - E_g)^3$ $E_g = 0.07$ eV	Forbidden indirect
AO-TCNQ	$\alpha h\upsilon = A(h\upsilon - E_g)^3$ $E_g = 0.25$ eV	Forbidden indirect	$\alpha h\upsilon = A(h\upsilon - E_g)^3$ $E_g = 0.1$ eV	Forbidden indirect
AO-TCNE	$\alpha h\upsilon = A(h\upsilon - E_g)^2$ $E_g = 0.25$ eV	Allowed indirect	$\alpha h\upsilon = A(h\upsilon - E_g)^3$ $E_g = 0.10$ eV	Forbidden indirect

Table 2 — Special characteristics of the infrared absorption function

Name of complex	Break in the slope of straight line for nature of transition	Humps in absorption due to exciton-phonon coupling (Ref. 8)	Band tailing with $\alpha = \alpha_0 Exp \dfrac{h\upsilon - E_1}{E_O}$
AO	Observed in upper edge at $E_b = 0.29$ eV	Two, one at 0.26 eV and the other at 0.3 eV	Not observed
AO-Chloranil	Observed at $E_b = 0.3$ eV	Two below 0.25 eV	Not observed
AO-DDQ	Not observed in upper edge	One at 0.3 eV in upper edge	Linear Ln α vs hυ between 0.22 and 0.25 eV
	Two breaks One at 0.17 eV and the other at 0.105 eV	One at 0.08 eV	Not observed
AO-TCNQ	One break at 0.31 eV	Not observed	Linear Ln α vs hυ between 0.23 and 0.25 eV
	Two breaks at 0.175 eV and 0.13 eV	Two at 0.145 eV and 0.13 eV	Not observed
AO-TCNE	One break at 0.34 eV	Three at 0.275 eV, 0.25 eV and 0.24 eV	Linear Ln α vs hυ between 0.23 and 0.25 eV

These kinds of oscillations in the density of states are found in the case of applied magnetic field[15]. Here, a transverse effect like magnetic force arises from transverse phonons. The monoatomic lattice with only nearest neighbour interaction lead to the density of states[16] given by:

$$D(\omega) = \frac{2L(\omega_m^2 - \omega^2)^{-\frac{1}{2}}}{\pi a} = \frac{L}{\pi v_g}$$

and the conductivity is connected as,

$$\sigma = \frac{ne^2 \lambda \upsilon}{m^* v_g}$$

where the group velocity v_g is given by,

$$\alpha(\omega) = \left(\frac{4\pi}{n_1 c}\right)\left(\frac{ne^2 \lambda \upsilon}{m^*}\right)\frac{2}{a}\sum_n (\omega_{m_n}^2 - \omega^2)^{-\frac{1}{2}}$$

Thus,

$$\alpha = \left(\frac{4\pi}{n_1 c}\right)\sigma = \left(\frac{4\pi}{n_1 c}\right)\left(\frac{ne^2 \lambda \upsilon}{m^*}\right)\frac{\pi D(\omega)}{L}$$

leading to,

$$\alpha(\omega) = \left(\frac{4\pi}{n_1 c}\right)\left(\frac{ne^2 \lambda \upsilon}{m^*}\right)\frac{2}{a}\sum_n (\omega_{m_n}^2 - \omega^2)^{-\frac{1}{2}}$$

Thus, as frequency increases, α increases. This is found in all the spectra between 600-1600 cm^{-1}. The repetition is because of different

$$\omega_{m_n} = \left(\frac{4c_n}{m_n} \right)^{\frac{1}{2}}$$

due to the vibrations of different masses.

There is frequency dependent polarization for $E>E_g$, and the spectra are governed by the electric vector parallel to donor-acceptor pair contacts due to charge transfer. For $E<E_g$, the electric vector is perpendicular to these contacts, i.e. in the direction of stacking of donor and acceptor molecules. Thus, the 5 or 6 repeated structures are due to the vibrations involving 5 or 6 atoms or ions in the stacking direction. Such a vibration is also known as Friedel oscillations with $q=2K_F$ arising from screening effects with electron-ion and ion-ion interactions[17]. The square-root singularity in the density of states for lattice vibrations in one-dimension leads to such singularity in the absorption coefficient.

The nature of transitions for acridine orange and its CT complexes are listed (Table 1). Also the deviations of the absorption functions arising from band tailing or lattice absorption (phonons) or splitting and their causes are tabulated (Table 2).

Conclusions

The acridine orange and its four CT complexes with acceptors like chloranil, DDQ, TCNQ and TCNE reveal two or more absorption edges due to non-equivalent sites of chloride ions or non-bonding and anti-bonding orbitals and not due to two conduction bands as found in usual ternary systems, arising from two types of acceptor levels. There is slight increase in the band gaps in the CT complexes

associated with an increase in inter-molecular distance providing an exponential band tailing in these complexes.

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