Asian Journal of Chemistry Vol. 12, No. 1 (2000), 73–77

An Evaluation of Optical Constants of Organic Compounds in the Solid State

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Using Kramers-Kroing relation optical constants n, K, R and μ (real and imaginary part of refractive index, reflection and absorption coefficients) for organic materials have been evaluated. Our calculated results indicate that real part of the refractive index *n* is always less than 1 for these materials.

INTRODUCTION

Extensive theoretical and experimental work has been done on the excited state of molecular crystals. In the ground state these crystals may be described in a first approach to the problem as an oriented gas. For an appropriate treatment of the excited state, corrections to this picture must be applied which has been developed in the theory of molecular excitations[1]. To a first approximation, one can derive from each excited molecular state a crystal state which is shifted to lower energies. The molecular state splits with a multiplicity equal to the number of nonequivalent molecules in the unit cell. The oscillator strength of all the Davydov components of a transition compound can be shown in the crystal spectrum. The excitation states of the crystal can be observed in the optical properties due to photon excitation spectrum. Their energy levels show up a maxima in the imaginary part of the dielectric constant ε_2 (= Im ε). This also determines the oscillator strength f to the transition of this level. We have a relation

$$\int \varepsilon_2 \, dE = \frac{2\pi^2 e^2 \hbar^2 n}{mE} f, \qquad (1)$$

where n is the number of molecules per unit volume, f is the molecular oscillator strength, *m* and *e* are mass and charge respectively. The integration has to be taken in an appropriate neighbourhood of transition energy. It has been seen that within the framework of molecular excitation theory the ε_2 spectra of the vapour and crystal should be very similar. The theory has been successfully applied to many aromatic crystals in the region of the first π–π^0 excitation[2, 3].

The determination of the optical properties of C_6H_6 (cyclohexene), C_6H_{10} (cyclohexane), C_6H_6 (benzene) C_7H_8 (toluene) and C_6H_5Cl (monochlorobenzene) have been performed by means of electron energy loss experiments. This method

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is certainly less powerful in the visible and near UV than conventional optical techniques but it has a certain importance in the adjacent energy range up to some terms of eV. The basic concept is the following: Fast electrons passing a certain thin film or gas chamber suffer inelastic scattering processes in which they transfer an energy ΔE and a momentum $\hbar q$. The probability of such an event is proportional to q^{-2} Im $[-\varepsilon^{-1}]$ and hence the quantity Im $[-\varepsilon^{-1}]$ can be obtained from the spectra[4]. Then, one compares the spectra of solid to that of vapour by using Kramers-Kroing analysis[5].

In this paper, the authors have obtained the values of ε_1, ε_2 for these organic compounds in their solid phase. Using these two values, they have computed the values of real and imaginary refractive indices n and k, the absorption coefficient μ and reflection coefficient R for these materials using Kramers-Kroing analysis[5] in terms of electron energy ΔE. From our calculation, it has been observed that the value of real part of the refractive index n is always less than unity for all these organic materials whereas there is no specific behaviour observed for the reflection coefficient R (%) and the absorption coefficient μ (10^5/cm) for the electron energy between 5 and 20 eV.

Mathematical Formulae used in the Calculation

To derive the dielectric constant from the energy loss function, a Kramers-Kroning dispersion[5] relation can be used. The real part of the complex function $\frac{1}{\varepsilon} = \left(\frac{1}{\varepsilon_1 + i\varepsilon_2}\right)$ is related to the whole frequency spectrum of its imaginary part

$$\left|\mathrm{Re}\left(\frac{1}{\varepsilon(w)}\right) - 1\right| = \frac{1}{\pi} P \int_{-\infty}^{\infty} \mathrm{Im} \frac{1}{\varepsilon(w')} \frac{dw'}{(w' - w)} \tag{2}$$

where P indicates the Cauchy principal part of the integral. To evaluate the contributions of negative frequencies to the integral eqn. (2), one uses the relation $\varepsilon(-w) = \varepsilon^*(w)$ and obtains

$$\mathrm{Im}\left[\frac{1}{\varepsilon(-w)}\right] = -\,\mathrm{Im}\left[\frac{1}{\varepsilon(w)}\right], \tag{3}$$

Then eqn (2) can be transformed into

$$\mathrm{Re}\left[\frac{1}{\varepsilon(w)}\right] - 1 = \frac{2}{\pi} P \int_{0}^{\infty} \mathrm{Im} \frac{1}{\varepsilon(w')} \frac{w'dw'}{(w'^2 - w^2)} \tag{4}$$

For anistropic crystals, however, the loss function depends on the direction of the wave-vector q. For small scattering angle θ of the order of $\theta\Delta E$ the q-direction is strongly dependent on w. Therefore spectra may be different for q(w) and q(−w). For the integration in the region of negative frequencies one uses the equivalence $q(-w, \theta) = -q(w, -\theta)$. In the case of two measurements in θ and $-\theta$, on opposite sides of the undeflected electron beam, one uses the relation[6, 7]

$$\mathrm{Re}\left[\frac{1}{\varepsilon(w,\theta)}\right] - 1 = \frac{1}{\pi} P \int_{0}^{\infty} \frac{\mathrm{Im}\left[\frac{1}{\varepsilon(w',\theta)}\right]}{w' - w} + \frac{\mathrm{Im}\left[\frac{1}{\varepsilon(w' - \theta)}\right]}{w' + w}\, dw', \tag{5}$$

For limit $w \rightarrow 0$, one obtains

$$\mathrm{Re}\left[\frac{1}{\varepsilon(0)}\right] = 1 - \frac{2}{\pi} \mathrm{P} \int_0^{\infty} \mathrm{Im}\, \frac{1}{\varepsilon(w')} \frac{dw'}{w'}, \qquad (6)$$

and

$$\mathrm{Re}\left|\frac{1}{\varepsilon(0,\theta)}\right| = 1 - \frac{1}{\pi} \mathrm{P}\left[\mathrm{Im}\left(\frac{1}{\varepsilon(w',\theta)}\right) + \mathrm{Im}\left(\frac{1}{\varepsilon(w',-0)}\right)\right]\frac{dw'}{w}, \qquad (7)$$

for the isotropic and anistropic cases respectively. The left hand sides of eqns. (5) and (6) can be estimated theoretically. Now the complex dielectric constant

$$\varepsilon(w) = \varepsilon_1(w) + i\varepsilon_2(w)$$

$$= \frac{\mathrm{Re}\left[\frac{1}{\varepsilon(w)}\right] - i\,\mathrm{Im}\left[\frac{1}{\varepsilon(w)}\right]}{\left[\mathrm{Re}\left(\frac{1}{\varepsilon(w)}\right)\right]^2 + \left[\mathrm{Im}\left(\frac{1}{\varepsilon(w)}\right)\right]^2} \qquad (8)$$

From this one gets the optical constants, the refractive index

$$N = \sqrt{\varepsilon} = n + ik, \qquad (9)$$

with

$$n = \sqrt{\tfrac{1}{2}(\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}, \quad k = \sqrt{\tfrac{1}{2}(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1)} \qquad (10)$$

The absorption coefficient μ can be written as

$$\mu = \frac{2w}{C} k, \qquad (11a)$$

The reflection coefficient R can be written as

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \qquad (11b)$$

RESULTS AND DISCUSSION

In this paper the authors have evaluated the optical constants n (real part of refractive index), k (imaginary part of refractive index), μ (absorption coefficient) and R (reflection coefficient) for organic compounds like C_6H_{12} (cyclohexane) C_6H_{10} (cyclohexene), C_6H_6 (benzene), C_6H_8 (toluene) and C_6H_5Cl (monochlorobenzene). The values of n and k are calculated by taking the experimental values$^{8-10}$ of ε_1 and ε_2 for these materials and using eqn. (10). For calculating the absorption coefficient μ for these materials we have taken the values of $w < w_{pl}$, the observed plasma freuency, *i.e.*, the energy of the peaks in the ε_2 spectra of the polycrystalline films. The results are shown in Tables 1 to 5 as a function of electron energy (eV). In all these organic materials the real part of the refractive index (n) is always less than unity for the electron energy. 5 eV to 20 eV. There is no specific behaviour of reflection coefficient R (%) and absorption coefficient μ (10^5/cm) for these materials.

TABLE-1
C_6H_{12} (CYCLOHEXANE)
Energy of electron E (ev), ε_1, ε_2, real part of refractive index (n), imaginary part of refractive index (k), reflection coefficient R (percentage) and absorption coefficient (10^5/cm)

E	ε_1	ε_2	n	k	R (%)	μ (10^5/cm)
5	0.95	0.05	0.708	0.160	3.76	1.792
7	0.46	0.54	0.790	0.500	8.31	5.604
9	−1.62	2.62	0.854	1.041	24.4	11.659
11	−1.64	2.64	0.857	1.043	24.4	11.680
13	−1.32	2.32	0.821	0.998	23.8	11.190
15	−0.86	1.86	0.771	0.923	22.6	10.337
20	−0.07	1.07	0.730	0.721	16.8	8.075

TABLE-2
C_6H_{10} (CYCLOHEXENE)
Energy of electron E (ev), ε_1, ε_2, real part of refractive index (n), imaginary part of refractive index (k), reflection coefficient R (percentage) and absorption coefficient μ (10^5/cm)

E (eV)	ε_1	ε_2	n	k	R (%)	μ (10^5/cm)
6	0.160	0.86	0.719	0.650	14.8	8.37
8	−0.625	1.05	0.716	0.729	17.6	9.33
10	−0.796	1.82	0.771	1.913	22.3	11.69
12	−1.475	2.50	0.865	1.026	38.0	13.14
14	−1.275	2.32	0.828	0.995	24.5	12.74
16	−0.755	1.78	0.768	0.906	22.1	11.60
18	−0.515	1.54	0.745	0.855	21.1	10.93
20	0.0745	0.95	0.668	0.684	17.8	8.76

TABLE-3
C_6H_6 (BENZENE)

Energy of electron E (ev), ε_1, ε_2, real part of refractive index (n), imaginary part of refractive index (k), reflection coefficient R (percentage) and absorption coefficient μ (10^5/cm)

E (eV)	ε_1	ε_2	n	k	R (%)	μ (10^5/cm)
5	0.825	0.20	0.919	0.1095	5.21	1.70
10	−0.475	1.50	0.741	1.0120	27.00	15.38
12	−0.674	1.70	0.798	1.1452	30.00	17.41
14	−0.575	1.66	0.750	1.0665	29.00	16.21
16	−0.466	1.65	0.785	1.0402	27.00	15.95
18	−0.425	1.45	0.737	0.9840	26.00	14.96
20	0.375	0.65	0.750	0.4330	8.00	6.58

TABLE-4
C_7H_8 (TOLUENE)
Energy of electron E (ev), ε_1, ε_2, real part of refractive index (n), imaginary part of refractive index (k), reflection coefficient R (percentage) and absorption coefficient (10^5/cm)

E (eV)	ε_1	ε_2	n	k	R (%)	$\mu(10^5/cm)$
5	–2.3	3.5	0.972	1.801	45.5	27.40
10	–0.3	1.5	0.784	0.957	23.5	14.05
12	–0.5	1.7	0.797	1.070	27.3	16.30
14	–0.6	1.8	0.805	1.117	28.5	17.00
16	–0.7	1.9	0.814	1.167	30.0	17.70
20	–0.4	1.6	0.790	1.012	25.2	15.40
25	0.7	0.5	0.883	0.283	2.6	4.30

TABLE-5
C_6H_5Cl (MONOCHLROBENZENE)
Energy of electron E (ev), ε_1, ε_2, real part of refractive index (n), imaginary part of refrac- tive index (k), reflection coefficient R (percentage) and absorption coefficient (10^5/cm)

E (eV)	ε_1	ε_2	n	k	R (%)	μ (10^5/cm)
5	–2.2	3.7	1.026	1.803	44.2	27.4
10	–1.4	2.9	0.954	1.520	27.7	23.1
12	–1.3	2.8	0.945	1.481	36.7	22.5
14	–1.2	2.7	0.937	1.441	35.5	21.9
16	–1.0	2.5	0.920	1.359	33.6	20.6
18	–0.8	2.3	0.904	1.272	31.0	19.1
20	–0.2	1.7	0.869	0.979	22.0	19.9
25	0.7	0.8	0.426	0.426	23.1	6.5

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(*Received*: 28 January 1999; *Accepted*: 5 October 1999) AJC-1853