

# Low-frequency dispersion in hopping electronic systems

G. W. BAK

*Institute of Physics, Technical University of Lodz, Wolczanska 219, 93-005 Lodz, Poland*

A. K. JONSCHER

*Royal Holloway, University of London, Egham, Surrey, TW20 0EX, UK*

*E-mail: jonscher@lynwood.u-net.com*

We present the results of frequency- and time-domain measurements of Low-Frequency Dispersion on organic charge transfer complexes in which charge transport is due to hopping electrons. To our knowledge, this is the first convincing result establishing specifically that LFD can be observed in electronic conductors and this has consequences for the interpretation of these phenomena, which tended to be observed mainly in ionic conductors. © 1999 Kluwer Academic Publishers

## 1. Introduction

The phenomenon of Low-Frequency Dispersion (LFD) is well established in materials in which the dominant contribution to dielectric response is due to hopping ionic charges [1, 2]. This consists in partial storage of carriers during the “charging” period, leading to their recovery in “discharging,” which distinguishes LFD from the familiar direct-current (dc) conduction) which by definition does not involve any charge storage and requires therefore perfectly replenishing contacts.

The characteristic spectral response of LFD consists in the real and imaginary components of the complex dielectric susceptibility following the “universal” fractional power laws in frequency:

$$\tilde{\chi}(\omega) \equiv \tilde{\varepsilon}(\omega) - \varepsilon_{\infty} = \chi'(\omega) - i\chi''(\omega) \propto (i\omega)^{n-1} \quad (1)$$

$0 < n < 1$

with the exponent  $n$  close to zero. Here  $\omega = 2\pi f$  is the radian frequency and  $f$  is the circular frequency in Hz. The significance of this is that  $\chi'(\omega)$  and  $\chi''(\omega)$  both rise steeply at low frequencies following parallel straight lines with slope  $n - 1$  and retaining a frequency independent ratio

$$\chi'(\omega)/\chi''(\omega) = \tan(n\pi/2) \quad (2)$$

The low-frequency highly lossy dispersive branch of LFD response is normally followed at higher frequencies by a less dispersive power law of the type (1) in which the exponent  $n$  is closer to unity, corresponding to lower losses. This corresponds to the normal dielectric response of most materials, whether carrier- or lattice-dominated.

Of the many materials in which LFD has been reported, which are discussed in detail by Jonscher [2], practically all conduct by hopping ionic motions and this leads naturally to the question whether LFD is

intrinsically limited to ionic conductors. The answer to this question is particularly important in view of the fact that some of the theories of LFD refer specifically to electrochemical processes which are by their very nature ionic. The previously presented example of LFD in tetrabenzofulvalene [3] (which is a typical organic electronic conductor) does not exceed two orders of magnitude and cannot be regarded as a decisive example of LFD in electronic conductors. It has been shown that LFD in tetrabenzofulvalene is related to trapping phenomena which may be a hint to understand LFD in electronic conductors. If a convincing example of LFD could be found in which the charge carriers are electrons (or holes), this would validate theories which apply likewise to hopping electrons.

It is evident that only hopping (or trapped) electronic charges like those found in amorphous semiconductors enter into consideration, since “free” electrons cannot give rise to dielectric phenomena at frequencies below the microwave range. Materials entering into discussion in the present context are therefore polycrystalline structures of low-molecular weight (L-MW) organic compounds in which the charge transport is either hopping or controlled by multiple trapping [4–6].

## 2. Molecular solids

Organic molecular crystals represent a special class of solids consisting of molecules bonded to their nearest neighbours with comparatively weak van der Waals forces while the intramolecular forces are strong. Some properties of organic molecular crystals, for instance vibrational frequencies, are those of free molecules, but such properties as charge and energy transfer depend on intermolecular interactions and differ significantly from the corresponding properties of covalent or ionic solids. In general we are dealing with transport of electronic charge (i.e. electrons or holes) either in a narrow

band of conducting states or with hopping of charge carriers among localised states.

The results of investigations of drift mobility of charge in simple aromatic hydrocarbons (which are regarded as typical of the whole class of organic molecular crystals) may be summarised as follows:

1. Charge transport in these materials is definitely electronic, i.e. electrons or holes are the charge carriers. No detectable influence of ionic charge transport has been found [8, 9].

2. Drift mobility independent of trapping is close to  $1 \text{ cm}^2/\text{Vs}$  [7–9] at room temperature. The temperature dependence of mobility is well described by  $\mu \propto T^n$  where usually  $0 > n > -2$ . However, such trapping-independent drift mobility may be found only in exceptionally perfect and clean monocrystals [10–13].

3. Even small amount of impurities (of the order of 1 ppm) [9] or structural imperfections [7, 9] strongly influence the charge transport and mobility decreases significantly [8–11]. In this case charge transport is controlled by multiple trapping.

4. In strongly disordered polycrystalline structures charge mobilities are rather low (of the order of  $10^{-5}$ – $10^{-4} \text{ cm}^2/\text{Vs}$ ) and may be interpreted by models of hopping transport [6, 14].

In the case of charge-transfer complexes a partial transfer of an electron takes place from a donor molecule to an acceptor molecule. The new ground state wave function is a mixture of the normal ground state wave function (DA) and the (D + A<sup>-</sup>) function corresponding to the total transfer of an electron:

$$\Psi_G = a\Psi_{DA} + b\Psi_{D+A^-} \quad (3)$$

In general, the lattice energy of organic charge transfer complexes (CTC) is a little larger than that of other organic molecular crystals due to the additional charge transfer interactions. Depending on the degree of charge transfer the physical properties of CTC may change significantly. In particular the electrical conductivity of CTC may vary widely. The first known examples of CTCs were complexes of bromine and iodine with some aromatic hydrocarbons (perylene, violantrene etc.) [15, 16]. It has been found that the electrical conductivity of the complexes is comparatively high, for instance the conductivity equals  $10^2$ – $10^{-1} \Omega^{-1} \text{ cm}^{-1}$  for perylene/bromine complex.

Most investigations of the electrical properties of CTCs have been concentrated on their direct current (dc) conduction, neglecting the dynamic or time-dependent aspects of their behaviour. By contrast, the present paper is concerned entirely with the dynamic response which may be studied by one of two complementary methods: the time-domain response of charging and discharging currents under step-function excitation, and the frequency domain response as function of the frequency  $\omega$  of the applied signal.

### 3. Experimental details

Samples of anthrone/iodine charge-transfer complex were prepared by keeping compressed polycrystalline anthrone pellets in iodine vapour for 2 weeks at room temperature. The thickness of pellets was about 1 mm, their diameter was about 12 mm. Gold electrodes of  $80 \text{ mm}^2$  area were evaporated in vacuum of  $10^{-5}$  Torr. The first dielectric measurements were carried out shortly after iodization. The samples were then annealed for a few hours at 373 K and the second

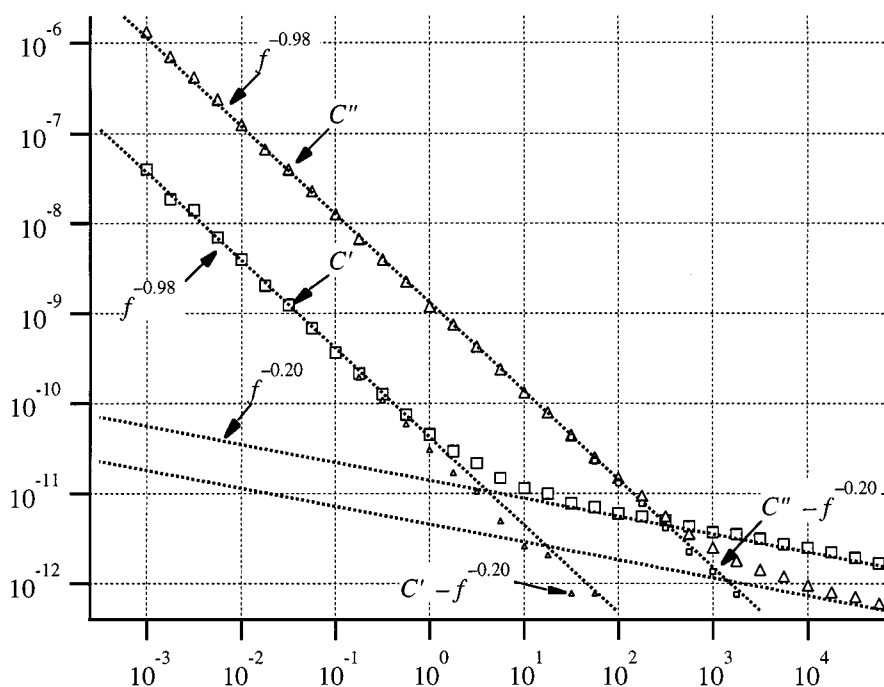


Figure 1 The dielectric spectrum of iodised Anthrone at room temperature showing clear evidence of LFD with a logarithmic slope of  $-0.98$  indicated by two slopes drawn in K-K compatible ratio of 31. The high-frequency trend is consistent with a logarithmic slope of  $-0.20$  indicated by the two lines drawn in the K-K compatible ratio of 3.08. Subtracting the  $-0.20$  slopes from  $C'$  and  $C''$  we obtain the points indicated which provide a good fit to the  $-0.98$  slopes, confirming the splitting of the spectrum into the two power laws.

measurement was then carried out. Because the dielectric response after annealing proved to be very similar to that of pure anthrone, the sample was re-iodized and the third measurement was carried out immediately afterwards. The preparation of Fluorene samples was similar.

Measurements were made using the Solartron Frequency Response Analyser (FRA) with Chelsea Dielectric Interface in the frequency range  $10^{-3}$ – $10^4$  Hz with a signal amplitude of 0.1 V. In our presentation we use the components  $C'(\omega)$  and  $C''(\omega)$  of the complex capacitance instead of permittivity  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  which differ only by a geometrical factor but which have the same frequency dependence.

The time-domain measurements were carried out with a Chelsea TD equipment [2].

#### 4. Results

Fig. 1 shows the results for a sample of iodised Anthrone in which  $C'(\omega)$  varies by five decades and  $C''(\omega)$

by six. A few significant points should be mentioned. Firstly, the ratio  $C''(\omega)/C'(\omega) = 31$  is rather high, indicating a charge storage of some 3% of the transported charge. Secondly, the range of LFD is very large and there is no evident need to subtract a dc contribution  $G_0/\omega$  from  $C''(\omega)$  and neither is it necessary to subtract a value of  $C_\infty$  from  $C'(\omega)$ . The latter means that at least several decades of the  $-0.20$  power law are necessary before the onset of  $C_\infty$ .

Time-domain measurements confirm that there exists in anthrone/iodine CT complexes long-time charge storage, Fig. 2. The shape of time-domain depolarisation current may be well described with the power law

$$i_d \propto t^{-n} \quad (4)$$

with the exponent  $n$  equal to  $-0.04$  which is in a reasonable agreement with the value of  $n$  describing the low frequency  $C''(\omega)$  curve in Fig. 1, confirming definitely that we are dealing with LFD processes.

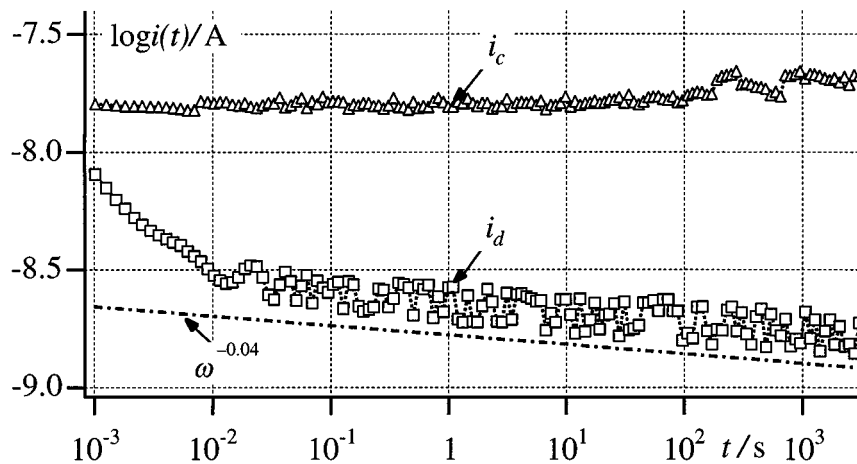


Figure 2 The charging and discharging currents of the same sample of which the FD response is shown in Fig. 1. The discharge current shows a power-law dependence  $t^{-0.04}$  which should be related to the LFD slope in Fig. 1 which is  $1 - 0.020$ .

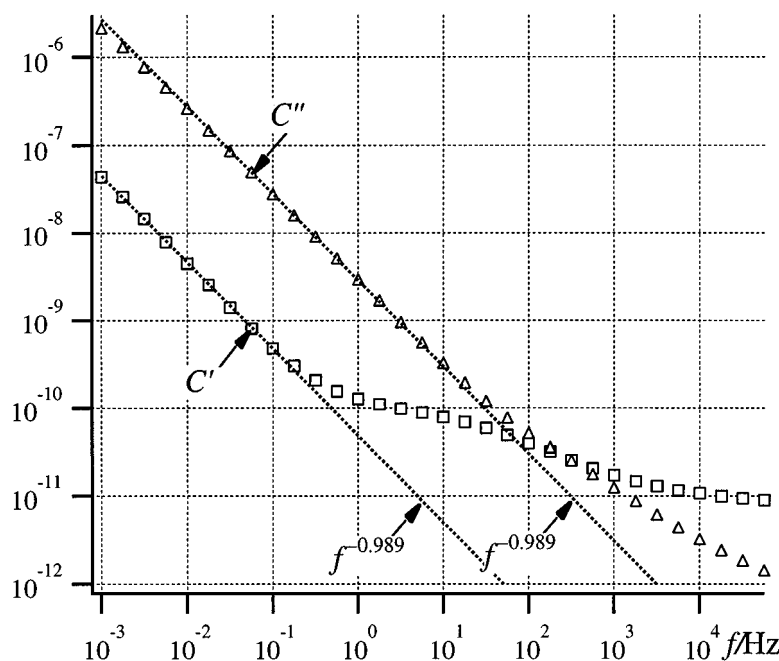


Figure 3 The dielectric spectrum of iodised Fluorene at room temperature with clear evidence of LFD. A dipolar process is apparent with a loss peak at around 10 Hz partially buried under the LFD.

Fig. 3 shows similar data for iodised Fluorene where the LFD is partially overshadowed by a loss peak at some 50 Hz. Here there is a clearer case for the presence of  $C_{\infty}$  but once again no evidence for dc conduction.

## 5. Conclusions

The experimental evidence presented in this paper shows clearly that LFD can be present in materials in which the dominant polarisation process is due to hopping electrons, as distinct from ions. This would appear to rule out for these materials mechanisms relying on electrochemical interactions which may well be applicable in some situations, for example in humid mica [17]. An alternative process might be that proposed by Jonscher [18] in which a fraction of transported carriers fails to pass the end electrodes and is returned on reversal of the cycle.

The detailed mechanism may have to be determined later, the important conclusion is that it must be also compatible with electronic transport processes.

## References

1. A. K. JONSCHER, *J. Mater. Sci.* **26** (1991) 1618.
2. A. K. JONSCHER, "Universal Relaxation Law" (Chelsea Dielectrics Press Ltd, London, 1996).

3. G. W. BAK, *J. Mater. Sci.* **23** (1988) 2365.
4. E. STARYGA and J. SWIATEK, *Thin Solid Films* **311** (1979) 311.
5. G. W. BAK, *J. Phys. C:Solid State Phys.* **21** (1988) 3447.
6. W. MYCIELSKI, *J. Non-Cryst. Solids* **37** (1980) 267.
7. E. A. SILINSH, "Organic Molecular Crystals, Their Electronic States" (Springer-Verlag, Berlin, 1980).
8. M. POPE and C. E. SWENBERG, "Electronic Processes in Organic Crystals" (Clarendon Press, Oxford, 1982).
9. E. A. SILINSH and V. CAPEK, *Organic Molecular Crystals, Interaction, Localization, and Transport Phenomena* (American Institute of Physics, New York, 1994).
10. N. KARL, *J. Crystal Growth* **99** (1990) 1009.
11. KARL, J. MARKTANNER, R. STEHLE and W. WARTA, *Synthetic Metals* **41-43** (1991) 2473.
12. W. WARTA and N. KARL, *Phys. Rev. B* **32** (1985) 1172.
13. W. WARTA, R. STEHLE and N. KARL, *Appl. Phys.* **A36** (1985) 163.
14. S. KANIA, J. KONDRASIUK and G. W. BAK, *Proc. SPIE* **3179** (1997) 190.
15. H. AKAMATU, H. INOKUCHI and Y. MATSUNAGA, *Nature* **173** (1954) 168.
16. *Idem.*, *Bull. Chem. Soc. Japan* **29** (1956) 213.
17. A. K. JONSCHER and T. RAMDEEN, *IEEE Transactions* **EI-22** (1987) 35.
18. A. K. JONSCHER, *Materials Science Letters* **17** (1998) 1975.

*Received 3 December 1998  
and accepted 21 April 1999*