Temperature dependence of fullerene electroabsorption spectra – model calculations

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Abstract

As demonstrated in recent experiments, the electroabsorption spectra of fullerene thin films exhibit rather strong temperature dependence in the energy regions where the signal is attributed to the eigenstates of CT parentage. This is difficult to rationalize in terms of a purely electrostatic model where the CT excitons are viewed as localized charge pairs. In the present paper, a simple dimer model is used to account for the main features of the off-diagonal CT interaction that gives rise to charge delocalization. The results demonstrate that the strong temperature dependence of the EA signal may be explained by disorder-modulated orientational dependence of charge-transfer integrals, and highlight the role of the off-diagonal CT coupling in organic molecular crystals. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Owing to the unusual properties both of the constituent molecules and of the crystals they form, solid fullerenes are recently subject to intensive experimental and theoretical investigations [1–8]. The spectroscopic tools applied for this purpose range from classic measurements of absorption [1–4], emission [4–9] and photocurrent [4] to resonance Raman scattering (RRS) [10], sophisticated time-dependent experiments [10,11], second-harmonic generation (SHG) [12,13] and other non-linear optical techniques [14–16]. Electroabsorption (EA) spectroscopy, which is nowadays a rare but essentially standard technique, has been used for the specific purpose of locating and identifying the charge-transfer (CT) states of the fullerene crystals [1,3,17,18]. The early spectra [1,3] have been recently supplemented by thorough low-temperature measurements [17,18].

The recent comparative study [18] carried out on thin films of the C60 and C70 fullerenes revealed some differences in the temperature dependence of their EA spectra. When the temperature is lowered, practically all the low-energy part of the C60 spectrum exhibits uniform intensity increase, whereas in C70 major changes are observed only for an intense, predominantly second-derivative signal at 2.26 eV. This different behaviour is rationalized in terms of different provenance of the observed excitations: the C70 molecule is endowed with some low-energy spectroscopically active Frenkel states which contribute to the EA spectrum along with CT excitons, while the spectrum of C60 is dominated by these
latter states since the low-energy Frenkel states are spectroscopically mute and only indirectly affect the EA spectrum owing to their coupling with the CT manifold. Theoretical calculations of the exciton structure and EA spectra \[19,20\] of \(C_{60}\) eliminated some uncertainties regarding the role of its optically forbidden states, essentially confirming the above simple picture. On the whole, the available evidence indicates that only the CT signals are substantially affected by temperature changes, and this seems to be a common feature of both investigated fullerenes.

At first glance, this is somewhat unexpected. According to structural data \[21–28\], both in \(C_{60}\) and \(C_{70}\) the temperature changes affect mostly the relative orientation of fullerene molecules (not their spacing), with a gradual transition from the low-temperature orientationally ordered phase to the high-temperature phase with complete rotational disorder. On that view, the weak temperature dependence of the Frenkel part of the spectrum is readily rationalized: owing to the high symmetry of the fullerene molecules, the Frenkel exciton transfer integrals for allowed states, governed by the dipole–dipole interaction, indeed weakly depend on molecular orientation and hence on temperature. Yet, the same argument seemingly applies for the CT states as well: their energies are usually governed primarily by the electrostatic interactions, and the latter are even less orientation-dependent because of the high symmetry of the molecular polarizability tensor. The observed temperature dependence has been qualitatively explained \[18\] by taking into account the fact that the observed states are in reality not localized charge pairs, but the eigenstates of the crystal with contributions from many different charge configurations, and that the different eigenstates deriving from the same set of localized CT configurations are split by the interactions off-diagonal in the localized basis (CT integrals). As the CT integrals critically depend on the relative orientation of the molecules, the temperature dependence of these splittings is likely to be quite strong.

Although the above working hypothesis is qualitatively attractive, it is very difficult to assess a priori whether the experimentally observed extent of temperature changes would actually be compatible with the microscopic energetics of the fullerene crystals. In this paper, this aspect of the hypothesis is probed on a previously proposed simple model of CT excitations \[29\] (presented in Section 4). The structural data and information concerning the temperatures of the relevant phase transitions will be taken for granted and discussed in Sections 2 and 3, with particular emphasis on the orientational disorder in solid fullerenes, which is an important ingredient of the interpretation. Our objective is to derive from these data the shape and temperature dependence of the EA signal. The results will be presented and discussed in Section 5.

2. Orientational disorder and phase transitions

In \(C_{60}\) the phase situation is rather complicated \[21–24\]. At low temperatures, the stable structure is monoclinic. In this phase, the relative orientation of molecular axes is fixed; no rotation is allowed. The phase transition at \(\sim 276\) K changes the crystal towards a distorted hexagonal (hcp) structure where the molecules rotate around their long axes which are set parallel to each other \[21,23\]. Another phase transition, into the ideal hcp structure, occurs at \(\sim 337\) K and sets in motion other rotational degrees of freedom. In effect, at high temperatures free rotation around all molecular axes is allowed, which in alternative description corresponds to complete orientational disorder \[21,23\]. It is reasonable to expect that similar disorder is present in the rhombohedral and finally in the face-centred cubic (fcc) phase, stable at still higher temperatures.

In \(C_{70}\), in the low-temperature simple cubic (sc) phase the molecules are frozen in well-defined relative orientations, with the carbon–carbon bonds that form the edges of one icosahedral molecule directed towards the centres of the five-membered rings of its nearest neighbour. At \(\sim 90\) K, the tunneling of the molecules between different potential minima becomes substantial \[25,26\]. At \(260\) K the phase transition changes the lattice to fcc with rotating (orientationally disordered) molecules. In fact, this phase transition is not a clear-cut borderline between the ordered and disordered structures of the \(C_{60}\) crystal. There is experimental evidence suggesting that the sc and fcc phases coexist over a finite temperature range \[25\]. Microscopically, there is a fair amount of disorder below the phase transition \[27\] and some
residual order in the reorientational motion of the molecules above the transition [28]. Hence, from the point of view of electronic degrees of freedom the change between order and disorder in C\textsubscript{60} is gradual; by analogy, this is probably the case also in C\textsubscript{70}. This feature must be accounted for in the model.

Of the two fullerenes, the structural transitions in C\textsubscript{60} are better understood. Also the fact that for this crystal the charge-transfer integrals can be easily estimated from the existing results of band structure calculations [30,31] makes it more suitable for a model study. Unfortunately, the shape of the CT signals in the EA spectrum of C\textsubscript{60} is complex, with the normal second-derivative features strongly distorted by large first-derivative admixtures [18]. This peculiarity, attributed partly to the interaction with Frenkel excitons and partly to the off-diagonal splitting [18–20], exists for all observed CT manifolds of the C\textsubscript{60} crystal (HOMO-to-LUMO at 2.5–2.75 eV, and HOMO-1-to-LUMO and HOMO-to-LUMO + 1 CT in the 3.5 eV region); in fact, the feature due to the HOMO-to-LUMO CT excitations is even split into two minima (at \( \sim 2.5 \) and \( \sim 2.75 \) eV). This effect is plausibly described as a consequence of interference between the inherent transition moments of many local CT configurations and the transition moments borrowed from high-energy Frenkel states [20]. This interference, due to the off-diagonal CT interactions, would be very difficult to reproduce within a simple model.

As we are seeking a simple description that would emphasize the main conceptual aspects of the problem, the necessity to invoke the coupling between many states would be an obvious disadvantage. For this reason, in the following we will apply our model for C\textsubscript{70}, but will assume that the CT integrals are the same as for C\textsubscript{60}, which seems reasonable in view of the profound similarity between the two crystals. By assumption, we also disregard the complicated interference effects peculiar to C\textsubscript{60}.

3. CT integrals in disordered crystal

Both HOMO and LUMO of the fullerene molecule are degenerate (three- and fivefold, respectively); in principle, the electron and hole transfer integrals should be calculated for each degenerate component separately. As in our previous papers [18–20], also in the present treatment this degeneracy will not be explicitly taken into account, but implicitly included in the parametrization. Accordingly, the effective CT integrals are defined in such a way as to reproduce the overall level splittings, and evaluated as sums of the corresponding integrals calculated for individual degenerate orbital components. The integrals are calculated by means of an adapted version of the semiempirical molecular-orbital approach [32,33]. This is done for a grid of molecular orientations, assumed completely random (complete orientational disorder), as appropriate for the high-temperature limit. The calculated distribution, similar in shape for electrons and holes, is shown (for electrons) in Fig. 1 and will be used in the following sections.

In order to make a bridge to previous treatments [13,18–20,30,31,34] it should be noted in passing that the orientational disorder was not explicitly invoked there: the disordered structure was replaced by an effective hypothetical crystal endowed with translational symmetry, with the appropriate matrix elements averaged over the molecular orientations. However, according to Fig. 1, the mean value of the integral is zero. For this reason, the effective CT integral, as used previously [19,20], has to be related not to the expectation value but to the dispersion of the corresponding distribution, as is often done in similar cases. In the present context, this is justified by the fact that the calculations [19,20] were aimed at level splittings, and those do not average to zero.

![Fig. 1. Statistical distribution of values of the charge-transfer integral that results from orientational disorder.](image-url)
because they are in fact governed by the moduli of the CT integrals (as can be readily seen on a two-state model); consequently, the integral evaluated simply as the ensemble expectation value would not reproduce the average splittings in the disordered crystal.

Accordingly, we will identify the effective CT integral with the half-width at half-maximum (HWHM, \( \sim 0.015 \) eV) of the calculated distribution. The electron transfer integral \( V \) evaluated in this way agrees very well with the value obtained by a tight-binding fit to the band structure calculations of Ref. [30]; this provides an independent test of the computational scheme.

It is readily seen that the distribution is neither Lorentzian nor Gaussian – there is no reason for it to be described by a simple two-parameter function. However, it is convenient to use such a description; hence, the distribution of Fig. 1 will be approximated by a Lorentzian curve, which gives a good rendering of the most relevant region corresponding to the maximum incidence. (For a Gaussian shape, inferior in this respect, the final results do not differ much.)

Strictly speaking, the calculated distribution is valid only for the high-temperature disordered phase. Yet, some of its statistical content should persist also in the ordered crystal. In the low-temperature structure, the crystal symmetry axes do not coincide with the molecular symmetry axes, so that the integrals governing charge transfer between a given molecule and its nearest neighbours may in general be different for each neighbour. Thus in \( C_{60} \), for instance, twelve different directions would be sampled; in reality, the existence of different degenerate orbital components would introduce additional spread of the obtained values (its inclusion is irrelevant for the disordered phase, owing to dense orientational sampling). Hence, even in the ordered structure there is some distribution of CT integral values, compounded by the residual disorder, present even at low temperatures [25,26,28]. Although it may actually differ in shape from the calculated one, we will also approximate it as Lorentzian. As previously, its HWHM is identified with the effective value \( V_1 \) of the CT integral, as obtained by a tight-binding fit [19] to the results of band structure calculations [30].

This allows one to simulate the temperature dependence of the CT integrals: their distribution is consistently approximated by the Lorentzian function whose width at very low temperature \( (V_1 = 0.009 \text{ eV}) \) and very high temperature \( (V_2 = 0.015 \text{ eV}) \) is known from the results of other authors [30]. It is only necessary to find a feasible interpolation scheme to estimate the width \( S \) at intermediate temperatures. The interpolating function \( S(T) \) is subject to several constraints:

1. in the high- and low-temperature limit it must asymptotically reproduce the above limiting values;
2. it must account for the collective nature of the phase transition, i.e. most of the change from one limit to the other should occur over a narrow temperature range;
3. it must be smooth, as the change is gradual (vide supra).

It is readily seen that the above requirements are satisfied by the function

\[
S(T) = \frac{V_2 - V_1}{\exp\left(\frac{T_1 - T}{\tau}\right) + 1} + V_1, \tag{1}
\]

where \( T_1 \) is some threshold temperature, \( \tau \) is a parameter characterizing the steepness of the curve, \( V_1 \) and \( V_2 \) are identified with the effective (ensemble-averaged) values of the CT integral in the low- and high-temperature limit, respectively.

The above form of the interpolating function suffers from arbitrariness. However, this drawback is not as serious as it looks. In the terminology of neural network theory, \( S(T) \) is a filter, switching the system from one phase to another. In that context, it is a well-established result that the actual behaviour of a system very weakly depends on the precise functional form of the filter, providing that the requirements (1)–(3) are fulfilled [35]. We believe it to be applicable also in the present context.

On the whole, Eq. (1) can be interpreted as follows. The CT integrals, being limited by intermolecular overlap, are very sensitive to the relative orientation of the molecules participating in the transfer. At low temperatures the molecules tend to adopt the orientations that minimize intermolecular repulsion by minimizing intermolecular overlap. In the high-temperature limit, the molecules freely rotate and on the average the overlap is larger. The CT integrals increase with increasing temperature and their rise should be related to the phase transition.
where large-amplitude librations turn into hindered rotation. Consequently, in order to find the precise value of the threshold temperature $T_1$ in Eq. (1), the details of the librational/rotational motion of the molecules would have to be solved. This would be both very difficult and probably unnecessary, since the present approach is by design only qualitatively valid. Instead, we use the following intuitive argument:

Let us identify the thermal energy $kT^*$ at the phase transition with the height $B$ of the potential barrier for rotation of the molecules. Owing to symmetry of the molecule and of the crystal lattice the potential must be periodic; for simplicity, let us approximate it by a single sine or cosine function. Then in the bottom half of the potential curve, extending on both sides of each minimum to half the barrier height ($\frac{1}{2}B$), the second derivative of the potential is positive and may be identified with some force constant. Accordingly, the motion in that region may be reasonably represented as (anharmonic) librations around the minimum; therefore, for thermal energies $kT < \frac{1}{2}B$ the model represents the ordered phase. On the other hand, for $kT > B$ the molecules freely rotate, which evidently corresponds to the disordered phase. Hence, the temperature range where $\frac{1}{2}B < kT < B$ may be tentatively identified with the transition region between the two phases, so that the switching of the CT integral from the low-temperature value $V_1$ to the high-temperature value $V_2$ takes place at some temperature belonging to the interval $\frac{1}{2}T^* < T_1 < T^*$. ($T^*$ denotes the observed temperature of the relevant phase transition). In the lack of a more precise estimate, it is reasonable to set the threshold temperature in the middle of this interval by taking $T_1 = \frac{1}{2}T^*$.

A similar intuitive argument may be used to estimate the parameter $\tau$, determining the width of the transition region. In order to reproduce the substantial spread of the change from the low- to the high-temperature behaviour, as suggested by structural data, $\tau$ must not be too small. Yet, at the temperature of the phase transition ($T^* = \frac{1}{2}T_1$), the high-temperature value of the CT integrals should be recovered. Consequently, a good guessimate is probably obtained by requiring that $\tau$ be the largest value which at the phase transition reproduces $V_2$ correct to within 1%.

For C$_{70}$, the temperature of the phase transition $T^* = 276$ K yields the threshold temperature $T_1 = 207$ K and the spread parameter $\tau = 20$ K. It should be noted for future reference that the above estimates of $T_1$ and $\tau$, although very crude, in the context of EA spectroscopy introduce no fitting parameters, since they rely solely on the structural data and not at all on the experimental EA spectrum.

### 4. Model and parametrization

In the following, we will use a two-state model proposed in Ref. [29], since it is the simplest model accounting for the splitting of the CT states by the off-diagonal interactions that are the main target of the present paper. It is also the simplest one capable of correct description of the second-derivative EA signals, observed for fullerenes and characteristic of first-order Stark effect. (As shown in Ref. [36], in centrosymmetric crystals, as polyacenes and fullerenes, no eigenstates are endowed with permanent dipole moment and the second-derivative signals have to be attributed to the electric-field-mediated coupling between quasi-degenerate zero-field eigenstates of CT parentage [29,37].)

According to this model, we consider a dimer AB, consisting of two identical molecules, and confine our attention to a pair of degenerate (local) CT states $|A^+B^-\rangle$ and $|A^-B^+\rangle$. These states are coupled by an effective ‘exchange’ integral $V = \langle A^+B^-|H|A^-B^+\rangle$. In an electric field, the energies of the local states (taken as the zero of energy) change by $mF\cos\vartheta$, where $m$ and $F$ denote the dipole moment of the $|A^+B^-\rangle$ state and electric field strength, respectively, and $\vartheta$ stands for the angle between these two vectors. To concentrate on the essentials, we neglect the small polarizability-dependent uniform level shift, quadratic in the electric field. Then the Hamiltonian matrix reads:

$$
\begin{bmatrix}
    mF\cos\vartheta & V \\
    V & -mF\cos\vartheta
\end{bmatrix}
$$

Its eigenvalues and eigenvectors are given as

$$E_{1,2} = \pm \left( (mF\cos\vartheta)^2 + V^2 \right)^{1/2}
$$
\[
\begin{align*}
\Psi_1 &= \cos(\beta/2)\cdot|A^+B^-\rangle + \sin(\beta/2)\cdot|A^-B^+\rangle, \\
\Psi_2 &= -\sin(\beta/2)\cdot|A^+B^-\rangle + \cos(\beta/2)\cdot|A^-B^+\rangle,
\end{align*}
\]
respectively, with
\[
\tan \beta = \frac{V}{mF \cos \vartheta}.
\]

It is readily seen that in the absence of an electric field the two eigenstates are split by the off-diagonal coupling \( V \); in each eigenstate the expectation value of the dipole moment vanishes, but the zero-field eigenstates are coupled by a non-zero dipole moment.

The contribution of each of the eigenstates to the absorption spectrum is approximated by a Gaussian of width \( \sigma \) (to account for inhomogeneous broadening). The EA signal is obtained by subtracting the absorption spectrum at \( F = 0 \) from that calculated at given \( F \neq 0 \) and then averaged over the angle \( \vartheta \) between the dipole moment \( m \) and the electric field in order to simulate the polycrystallinity of thin films used in the EA experiments.

Leaving the absorption scale arbitrary, the problem is fully parametrized by defining the dipole moment \( m \), the electric field strength \( F \), the spectral width \( \sigma \) of an individual absorption band and the statistical distribution of the values of the CT integral \( V \). The dipole moment is determined from the nearest-neighbour distance in the fullerene lattice (\( \sim 10 \) \( \text{Å} \)); the electric field strength is set at 40 \( \text{kV/cm} \) which is a typical value for EA experiments [18]. Based on the results previously obtained for polyacenes [38], \( \sigma = 0.025 \) eV seems a reasonable estimate of the spectral width for the eigenstates of CT parentage.

The CT integral \( V \) needs some comment. In the actual crystal, there are several molecules in the unit cell and the combined interactions between all of them determine the level splittings; in our present model only two molecules are explicitly included. However, if the crystal EA response is to be correctly reproduced, the order of magnitude of the splittings must be preserved. To achieve this, the CT integral has to be treated as an effective one and judiciously scaled: it must be adjusted in such a way as to fit by 2 V the total energy span of the eigenstates of nearest-neighbour CT parentage in the actual crystal.

The following qualitative arguments may be used to estimate the appropriate scaling factor. The four molecules contained in the unit cell of fullerene can be represented as a set of six different dimers, coupled by off-diagonal interactions. In order to have the splittings correctly reproduced with only one dimer explicitly taken into account, the effective CT integral has to be multiplied by six. Consequently, in our calculations the width of the distribution of Fig. 1 is multiplied by this factor.

Alternatively, the same result may be reached in a different way. As originally suggested for polyacenes [39], for a given localized CT state characterized by the distance \( R \) between the electron and the hole the splitting of the ensuing eigenstates in the crystal is approximately linear in intermolecular overlap integrals, since the propagation of a CT exciton is implemented primarily by the transfer of one charge at a time [39] (occurring without change of the distance \( R \)). In the set of four molecules contained in the unit cell, the electron may be transferred between three equivalent molecules (while the hole remains stationary), and the hole also may be transferred between three molecules (while the electron is stationary). To account for this fact, in the dimer model both the electron and the hole transfer integral has to be multiplied by three. However, the sole effective CT integral \( V \) of the dimer model must imitate the combined effect of electron and hole transfer; as the corresponding two integrals are of the same order of magnitude, another factor of two is introduced into the effective value of \( V \). Ultimately, the total factor of six, obtained in the preceding paragraph, is recovered. It should be emphasized that this factor is not an adjustable parameter, but follows directly from the geometry of the crystal.

5. Results and discussion

Using Eqs. (2)–(5), we have calculated the eigenstates and subsequently the EA signal for 41 representative values of the CT integral, thereby generat-
ing 41 spectra. Each spectrum has been averaged over all possible orientations of the CT dipole moment with respect to the applied electric field vector (to account for the polycrystallinity of the sample) and over the angle between the electric vector of light and the direction of the applied electric field (to simulate unpolarised light used in typical EA experiments). To each spectrum we have attributed the weight defined by the relative incidence of the CT integral, according to the distribution of Fig. 1, and obtained the total EA signal by adding all the spectra. This procedure was repeated for several temperatures, with the width of the distribution of Fig. 1 generated according to the prescription of Eq. (1).

Fig. 2a shows the experimentally observed temperature dependence of the C
0 EA signal. Detailed description of the measurements can be found elsewhere [18] along with the spectra observed at room temperature and at 77 K; the data pertaining to intermediate temperatures have not been published previously.

As it has been mentioned above, the behaviour of the 2.26 eV feature, ascribed to CT states [18], is strikingly different from that of the rest of the spectrum. This is most evident near the EA minimum; the wings of the second-derivative signal partly overlap with other bands, the feature at \( \sim 2.4 \) eV being attributable to an allowed Frenkel transition [18]. The origin of the band on the low-energy side of the CT signal is less obvious; its zeroth-derivative shape might suggest the involvement of a forbidden Frenkel exciton activated by electric-field-mediated coupling to allowed states, although vibronic provenance can hardly be ruled out.

The corresponding simulated spectra, calculated for different temperatures, are displayed in Fig. 2b. It is readily seen that the general shape of the experimental spectrum is reasonably well reproduced, and so is the energy scale defined, for example, by the width of the EA minimum. Also the temperature dependence is well accounted for, notably the gradual disappearance with increasing temperature of the low-energy positive lobe of the EA signal, which in the experimental spectrum is somewhat less pronounced owing to the overlap with the neighbouring band on the low-energy side.

In order to gain more quantitative insight into the temperature dependence, Fig. 3 shows the calculated depth of the EA minimum plotted against temperature. The experimental points (squares) are located very close to the predicted curve, confirming again the qualitative validity of the model.
Fig. 3. Calculated (solid line) and experimental (squares) temperature dependence of the depth of the EA minimum. The depth of the minimum at 77 K is taken as unit.

In order to assess to what extent this agreement is significant, it is worthwhile to analyze the provenance of different ingredients of the applied theoretical description. The dimer model is simplistic, but qualitatively describes the off-diagonal CT splitting. The validity of its conclusions may be upgraded to semiquantitative by scaling the CT integrals; the scaling is based on structural considerations alone and in the context of EA spectroscopy may be regarded as non-empirical. The distribution of CT integral values (Fig. 1) is also non-empirical, being a computational result, and so are the limiting values of the integral, used in Eq. (1). The equation itself results from an admittedly arbitrary guess; however, its implied latitude is highly reduced by intuitively appealing constraints. There are reasons to suppose [35] that the residual uncertainty should not affect the conclusions very much, and the extensive averaging of the spectra should further reduce this influence.

The final results do depend on the actual estimates of the threshold temperature $T_1$ and threshold width $\tau$, which are based on qualitative and fairly arbitrary arguments. In fact, these same arguments cannot rule out for $T_1$ any value from the interval $\frac{1}{2}T^* < T_1 < T^*$ (i.e., between 144 and 287 K). Accordingly, the choice to locate $T_1$ in the middle of this interval ($T_1 = \frac{1}{2}T^* = 207$ K) is rational; it also turns out to be serendipitous, although is by no means the only one acceptable in the circumstances. If $T_1$ were regarded as a fitting parameter, the experimental temperature dependence of the EA signal could be reproduced practically perfectly; we refrain from this in order to maintain the essentially non-empirical (although crude) character of the approach. In the present situation, apart from the depth in absolute scale of the EA minimum at one temperature, there are no adjustable parameters invoked specifically to fit the EA spectrum, and there is no fitting.

The agreement with experiment is very good, although one should not be overly impressed by its being seemingly quantitative. As analyzed above, the applied model is admittedly and deliberately simplified, and the parametrization, although entirely non-empirical in the sense that there are no parameters adjusted specifically to fit the experimental data being interpreted, is generally rather sketchy. Hence, considerable caution should be exercised in attributing quantitative significance to the results; nevertheless, as long as its inherent limitations are duly recognized, the model allows one to rationalize within a coherent conceptual framework a set of rather puzzling experimental data. The results confirm the working hypothesis presented in Section 1: if attributed to off-diagonal CT interactions, the observed temperature dependence of the EA spectra is entirely consistent with the microscopic energetics of the fullerene crystals.

The physical picture emerging from this conclusion is noteworthy in a broader context. The original concept of CT states, as invoked to interpret the EA spectra of linear polyacenes [39,40], implied complete localization of the charges and a non-zero dipole moment of the pair. The consequences of charge delocalization, i.e. the absence of the diagonal dipole moment in the actual eigenstates of the system [36,37] and their off-diagonal splitting [41] were recognized later. At that stage, the size of the splitting between the minima in the low-energy signals of CT provenance was essentially the only experimental basis for the new interpretation [37]. Subsequently, complete theoretical calculation of the EA spectra of polyacene crystals, based on a micro-
scopic model [38], brought further confirmation. As noted recently [19,20], the double minimum ob-
erved in the low-energy EA signal of C_{60} [18] is also a manifestation of the off-diagonal CT splitting
[19,20]. Our present results show that the unusually strong temperature dependence of the EA signals
attributed to fullerene CT excitons provides a new demonstration of this splitting. Although indirect, it
is a spectacular one: the observed effect would be very difficult to rationalize within a completely lo-
calized model of charge-transfer states.

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