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Charge-Transfer Exciton Trapping at Vacancies in Molecular Crystals: Photoconductivity Quenching, Optical Damage and Detonation

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Summary: Calculations are presented that show that vacancies can trap charge-transfer (CT) states in anthracene, acetanilide and hexahydro-1,3,5-trinintro-1,3,5-triazine (RDX). Such trapping provides a mechanism for photoconductivity quenching by geminate recombination, and for optical damage and detonation by concentrating optical or mechanical energy stored in CT states.

Keywords: charge transfer; molecular crystals; theory; trapping; vacancies

1. Introduction

Charge-transfer (CT) states in molecular crystals consist of an anion–cation pair (or an electron–hole pair on different molecules). Such states are well known as obvious precursors to photoconductivity,[1] they may play a role in optical damage, where multiphoton ionization is a possible mechanism,[2] and they have been postulated as initial stages in detonation.[3]

Information on the mechanism of optical damage in molecular crystals is sparse, but it appears not to occur homogeneously and there are questions as to how uniform illumination yields the necessary concentration of energy. The initial mechanism of detonation remains a subject of investigation, but it is known that detonation proceeds at "hot spots" where energy is presumably trapped,[4] and is more facile in less dense and less perfect crystals.[5, 6] These observations suggest a possible role for vacancies, which are necessarily present in some thermodynamic concentration in real crystals. If vacancies trap CT states, they could serve as sites to concentrate the energy that these states store from the optical or mechanical mechanism that generates them. (Recombination would also at once reduce the efficiency of photoconduction.) The energy thereby released could also disrupt the crystal lattice near the vacancy: as Pope and Swenberg remark,[7] "The recombination of a hole and electron releases considerable energy, and

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one of the problems that must be considered is how this energy is disposed of." The larger defective region so produced could presumably trap CT states even more efficiently, and optical damage could thereby ensue. Alternatively, energy concentrated and released in this way could initiate the chemical decomposition involved in detonation, and as Ramaswamy and Field remark,[8]" It is always of prime interest to understand how energy is concentrated in an explosive to form hot spots."

The possibility that vacancies could trap CT states is plausible, given that vacancies can trap single charge carriers, as indicated by theoretical calculations for the aromatic hydrocarbon crystals[9] and some experimental evidence.[10] The energy of an ion in a crystal is lower than that of the isolated ion by the polarization energy P. This is reduced near a vacancy by an amount ΔP because of the loss of the polarizability of the missing molecule by this mechanism, and so by the same mechanism a vacancy scatters charges. However, the loss of the permanent multipole moment of the missing molecule leads to trapping or scattering in different directions, and trapping by this mechanism can readily outweigh the scattering due to ΔP.

Similar arguments can be developed for vacancies and CT states,[11] but need modification because the relevant polarization energy of the CT states is E_{p}, which is the polarization relative to the total polarization energy for the separated charges in the crystal, and there is in addition the stabilizing Coulomb energy E_{C} between the electron and hole. Partial cancellation between the effects of the electron and the hole in the CT state makes E_{p} positive, which serves to reduce the magnitude of the bare Coulomb energy E_{C} to the screened Coulomb energy E_{scr}. Thus polarization is responsible for the screening that weakens the attraction between the separated changes. A vacancy reduces the polarization because of the loss of the polarizability of the missing molecule, and thereby reduces the screening. As a result, the charges attract more strongly and the vacancy acts as a trap for CT states. The loss of the permanent multipole moment at the vacancy should also trap some CT states in some directions, and in this case the trapping can be reinforced by the polarization energy change (rather than offset as for a single carrier).

We have therefore calculated the energetics of charge-transfer states near vacancies in three crystals: anthracene (a benchmark crystal where photoconductivity has been extensively studied), acetanilide (one of the few crystals where optical damage has been studied in any detail), and 1,3,5-trinitrohexahydro-1,3,5-triazin or RDX (a well-known energetic material where detonation has been extensively studied). We first summarize our method, and then report results for each crystal, followed by overall conclusions.

2. Method

Our method[11] combines previous treatments for single charges and CT states in perfect crystals and for single charges near vacancies, which use a Fourier-transform method to obtain explicit solutions for polarization energies. These treatments entail the calculation of wave-vector modulated lattice monopole and dipole sums over a mesh of wave-vectors in the first Brillouin zone. Polarization energies are then calculated by summation over wave-vectors, making the mesh finer until convergence is achieved (a process facilitated by using the dependence on mesh size to extrapolate to the continuum limit).

For the calculations on anthracene, these treatments suffice, because they also treat charge–quadrupole energies W_Q. However, acetanilide and RDX are both polar molecules, so that a treatment of charge–dipole energies is also required. This is complicated because it is also necessary to take account of the dipoles induced in the crystal environment by the other molecules, including the effect of the vacancy. Details of the method are given elsewhere.[12] The principal results are that the charge–dipole energy is zero in the perfect crystal if it does not carry a macroscopic dipole moment, and that the change in charge–dipole energy ΔW_D can be obtained by a modification of the method used to calculate the change in polarization energy ΔP, with the permanent dipole field in the perfect crystal $\mathbf{F}^\mathrm{p}$ and the loss of the permanent dipole moment at the vacancy $\boldsymbol{\mu}$ as new source terms. The algebraic expression for ΔP is

$$\Delta P = \tfrac{1}{2}\tilde{\mathbf{F}}^0 \cdot \alpha \cdot \mathbf{Q} \cdot \mathbf{F}^0 / \varepsilon_0 v\,, \tag{1}$$

where $\mathbf{F}^0$ is the field due to the charges, $\boldsymbol{\alpha}$ is the polarizability of the missing molecule at the vacancy, v is the unit-cell volume, and the quantity $\mathbf{Q}$ corrects for the missing polarizability in the dielectric response of the crystal. The expression for ΔW_D is

$$\Delta W_\mathrm{D} = \left(\tilde{\mathbf{F}}^0 \cdot \alpha \cdot \mathbf{Q} \cdot \mathbf{F}^\mathrm{p} - \mu \cdot \mathbf{Q} \cdot \mathbf{F}^0\right) / \varepsilon_0 v\,. \tag{2}$$

All the calculations treat each molecule as a set of point-polarizable submolecules, one at each heavy (non-hydrogen) atom. Effective molecular polarizabilities relevant to the crystal environment are derived by analysing crystal dielectric or optical data with published crystal structure data. The quadrupole moment for anthracene is that used previously.[13] For acetanilide and RDX, the dipole moments are calculated by standard high-level quantum-chemical techniques, using the in-crystal geometry. The change in molecular geometry from the free state to the crystal is the most immediately obvious and tractable environmental effect on the molecules and their properties.[14] In RDX it is particularly significant because the conformation of the nitro groups attached to the ring (which is in the chair conformation) changes from all-axial in the gas phase[15] to two axial and one pseudo-equatorial in the crystal.[16]

3. Results

3.1 Anthracene

Anthracene forms monoclinic crystals with two equivalent molecules in the unit cell,[17] as shown in Figure 1, right. The total energy (polarization energy plus charge–quadrupole energy) for an electron in the perfect crystal is −1.43 eV and for a hole −0.93 eV. The lowest CT states with the hole fixed at the origin have the electron at (½,±½,0) and (0,1,0) with total energies E_P relative to the separate electron and hole of −0.86 eV and −0.73 eV, respectively. There are no other CT states below −0.5 eV. A vacancy at the origin changes the energy of an electron at (½,−½,0) by −0.15 eV and at (½,½,0) by 0.12 eV; for a hole at these sites, the energy changes by 0.26 eV and 0.01 eV. These changes are dominated by those in the charge–quadrupole energy.

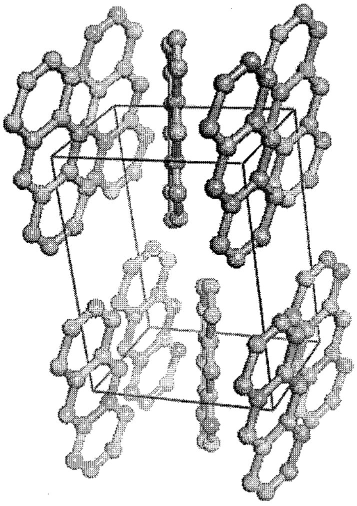

Figure 1. Unit cell of anthracene (hydrogens omitted), looking at the *ac* face.

For the CT state with the hole at the origin and the electron at (½,½,0), a vacancy at a neighbouring site changes the magnitude of the polarization energy change ΔE_P relative to the separate charges by 0.03 – 0.05 eV. The corresponding change in the charge–quadrupole energy reaches −0.16 eV for the vacancy at (1,0,0) and −0.24 eV for the vacancy at (0,1,0). Vacancies at these two sites (both nearest neighbours of the CT electron) therefore yield traps at −0.19 eV and

–0.29 eV, respectively. Hence the postulated existence of trapping of CT states by vacancies is confirmed.

Similar results are found for the CT state with the hole at the origin and the electron at (0,1,0). A vacancy at (½,½,0) yields a trap at –0.29 eV, and a vacancy at (½,1½,0) yields a trap at –0.21 eV; again, both sites are nearest neighbours of the CT electron. Because the lowest CT states are only 0.13 eV apart, it follows that the trap manifolds based on them overlap. However, they remain distinct from those based on higher CT states.

In these cases, ΔE_{P} is negative, consistent with the idea that a vacancy reduces the dielectric screening. However, for some CT states a vacancy on or near the charge-transfer axis can actually increase the screening by up to 0.04 eV. This may be associated with the fact that in an anisotropic dielectric continuum, screening depends not on the component of the dielectric tensor along the CT axis but rather on the components in the plane perpendicular to this axis.[18]

However, overall it is clear that vacancies constitute traps for the lowest CT states, with a depth of several times kT at room temperature. Vacancies could therefore have a significant adverse effect on the yield of photogenerated change by facilitating geminate recombination. A more detailed account of these results is given elsewhere.[11]

We have also investigated the effect of divacancies on CT states. These obviously entail rather complicated calculations, involving two vacant sites and two charged molecules. Overall, we find that the energy changes for divacancies near the lowest two CT states differ very little from the sum of the energy changes for the two separate vacancies. For example, the magnitude of the polarization energy change ΔE_{P} relative to the separate charges lies in the range 0.05 – 0.08 eV for several divacancy arrangements, values that are close to the sum of those for the separate vacancies. The change in charge–quadrupole energy $\Delta W_{\mathrm{Q}}{}^{\mathrm{CT}}$ for the divacancy is already simply the sum of those for the separate vacancies, and dominates the total energy. Then for the CT state with the hole at the origin and the electron at (½,½,0), a divacancy at (1,0,0) and (0,1,0) constitutes a trap of depth 0.48 eV, while for the CT state with the hole at the origin and the electron at (0,1,0), a divacancy at (½,½,0) and (–½,1½,0) constitutes a trap of depth 0.578 eV.

3.2 Acetanilide

Acetanilide forms orthorhombic crystals with eight equivalent molecules in the unit cell,[19] as shown in Figure 2, below. This complicates identification and classification of the CT states. We divide the molecules into two sets, one labelled 1 – 4 and the other labelled 5 – 8, related to 1 – 4 respectively by inversion, and use (k; l_1,l_2,l_3) to denote molecule k in unit cell (l_1,l_2,l_3). Previous work treating the molecule as three submolecules found one surprisingly small local-field component,[20] but the present treatment with all heavy atoms as submolecules removes this anomaly. Details of the analysis that gives the effective molecular polarizability and the local field will be given elsewhere.[21] The dipole moment of an isolated molecule with the crystal structure is calculated using density functional theory as 3.62 D; in the crystal environment the molecules polarize one another through fields of their dipoles[22] and we find the effective moment is 5.41 D.

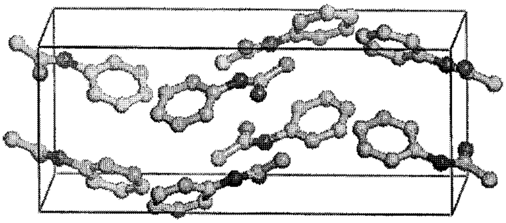

Figure 2. Unit cell of acetanilide (hydrogens omitted), looking at the *ac* face.

The polarization energy of an electron or hole in the perfect crystal is –1.16 eV; the charge–dipole energy is zero assuming that the crystal does not carry a net dipole moment. The lowest CT states with the hole fixed on molecule (1;0,0,0) have the electron on molecule (5;0,–1, –1) with an energy of –1.30 eV, on molecule (7;0,0,0) with an energy of –1.11 eV, and on molecule (3;0,0,0) in the origin cell with an energy of –0.93 eV. All other CT states lie at –0.75 eV or above.

For a charge at molecule (1;0,0,0), a vacancy at these sites changes the polarization energy by 0.09, 0.06 and 0.04 eV respectively. The corresponding changes in the charge–dipole energy for a hole at molecule (1;0,0,0) are –0.10, 0.24 and –0.23 eV (opposite sign for an electron). Thus the total energy changes are –0.01, 0.30 and –0.19 eV for a hole and 0.19, –0.18 and 0.27 eV for an electron. These results show that a vacancy can trap carriers of either sign, but at different sites, through the change in charge–dipole energy. This confirms that vacancies can act as traps in crystals of polar molecules, as well as in crystals of quadrupolar molecules like the linear condensed polyacenes.

Because of the eight molecules in the unit cell, the number of arrangements of a vacancy relative to each CT state is very high. However, the results are rather uniform. For most positions of a vacancy in a cell adjacent to either charge of the CT state, there is a trap with a depth of 0.01 – 0.02 eV. In a few cases the trap depth reaches 0.05 eV, for example for the lowest CT state with the electron at molecule (5;0,–1,–1) and a vacancy at molecule (7;0,0,–1) and for the next lowest CT state with the electron at molecule (7;0,0,0) and a vacancy at molecule (5;0,–1,–1). These values are dominated by the polarization energy change ΔE_{p}. The changes in charge–dipole energy cancel almost exactly, in contrast to the changes in charge–quadrupole energy in anthracene. This difference may reflect the weaker angular dependence of the dipole potential in acetanilide and the larger number of molecules in the unit cell, but further analysis is required.

Calculations have also been performed for a few divacancy arrangements near the lowest CT state. As for anthracene, these confirm that a divacancy constitutes a deeper trap than either vacancy alone, and that to a good approximation the divacancy trap depth is the sum of those for the separate vacancies it comprises. This confirms the feasibility of a mechanism of optical damage whereby a vacancy traps CT states that recombine and release energy to form a larger defective region that acts as a yet deeper trap, so that the process is cumulative and autocatalytic in the sense that the products favour further reaction. This mechanism is also plausible since experimental evidence indicates that the mechanisms of defect formation and crystal destruction are the same.[23]

3.3 RDX

RDX presents a case that is formally very similar to acetanilide. There are again eight equivalent molecules in the unit cell,[16] as shown in Figure 3, right; we label the molecules as before. Detailed dielectric analysis will be reported elsewhere,[24] together with calculations of the dipole

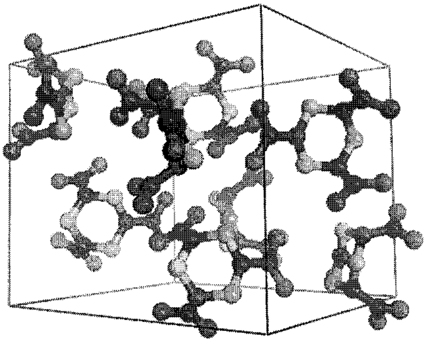

Figure 3. Unit cell of RDX (hydrogens omitted), with the *ac* face on the left.

moment, which is 7.40 D for the isolated molecule and 9.40 D in the crystal.

The polarization energy of an electron or hole in the perfect crystal is −1.14 eV, with zero charge–dipole energy. The lowest CT state with the hole fixed on molecule (1;0,0,0) has the electron on molecule (5;–1,0,0) with an energy of −1.27 eV. After that, there are three states with the electron on molecule (7;0,0,0), on molecule (3;–1,0 0) and on molecule (6;0,0,0) with energies of –0.88, –0.83 and –0.81 eV. Thus the lowest CT state is well separated from the manifold of higher CT states.

For a charge at molecule (1;0,0,0), a vacancy at molecule (5;–1,0,0) changes the polarization energy by 0.10 eV, with the corresponding change in the charge–dipole energy for an electron as –0.52 eV. Thus the total energy change is –0.42 eV, and this vacancy can trap electrons. Other electron traps are found for vacancies at molecule (3;–1,–1,0), depth 0.28 eV, and at molecule (6;0,0,0), depth 0.19 eV. Hole traps are found for vacancies at molecule (8;0,0,0), depth 0.28 eV, and for molecules (3;–1,0,0) and (6;–1,0,0), depth 0.22 eV. Vacancies in RDX thus form rather deeper traps for single carriers than in acetanilide, because the dipole moment is larger.

As for acetanilide, the effect of vacancies is dominated by the polarization energy changes ΔE_p. The deepest traps lie at –0.04 eV, for vacancies at molecule (3;–1,0,0) and molecule (7;0,0,0), which are symmetrically related to the CT state. Thus vacancies can act as rather shallow traps for CT states in RDX.

4. Conclusions

We have presented calculations of the energies of charge-transfer states near vacancies in anthracene, acetanilide and RDX. The results confirm qualitative arguments that vacancies can trap CT states. The polarization energy change due to the vacancy is almost always negative, i.e. trapping. The charge–multipole energy change due to the vacancy is positive or negative, depending on the direction, and dominates the polarization energy change for anthracene in most directions but tends to cancel for acetanilide and RDX. Trap depths for a single vacancy are as large as 0.3 eV for anthracene, but for acetanilide and RDX are shallower at no more than 0.05 eV, or only twice kT at room temperature. For acetanilide, defects that are microscopic precursors to macroscopic optical damage are found to accumulate at low temperatures but not at room temperature,[2] which is consistent with calculated trap depths comparable to *kT* at room temperature.

These results show that vacancies can have a significant influence in processes where CT states are important participants. This could be explored experimentally given crystals with differing vacancy concentrations. In anthracene, the efficiency of photogeneration of charge carriers via CT states will be reduced by geminate recombination of CT states trapped at vacancies. In acetanilide, the energy released by this process would be available to cause further disruption of the lattice. Our calculations show that divacancies produce traps for CT states of depths roughly equal to the sum of the depths for the two separate vacancies, and this provides a mechanism for optical damage to accumulate. Similarly, in RDX vacancies can trap CT states produced by mechanical excitation and thereby concentrate the energy so that it can initiate the chemical process of detonation. This mechanism is consistent with the identification of "hot spots" for detonation as vacancies (or similar lattice imperfections).[4, 25, 26, 27] We find that the trapping is dominated by the polarization energy change at the vacancy, and hence is rather isotropic, which is consistent with the weakness of directional effects on detonation RDX but not in other crystals.[28] Our suggestion that the mechanisms for optical damage and initiating detonation may have features in common (specifically the trapping of CT states by vacancies) is consistent with the observation of laser-induced detonation,[8] often used to explore the mechanism of detonation.

We have concentrated here on our overall results, which show how different processes typical of three different crystals can share an underlying mechanism, namely trapping of CT states by vacancies. Detailed results for the individual crystals are given elsewhere,[11, 21, 24] as is the derivation of the change in the charge–dipole energy.[12] All our results use exact algebraic solutions, including the change in the dielectric response of a crystal with a defect.[29] Such rigorous treatments of electrical interactions in perfect and imperfect crystals can yield quantitative insights into a wide range of problems, as the present work illustrates.

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