Ultrafast Changes of Molecular Crystal Structure Induced by Dipole Solvation

M. Braun,[1] C. v. Korff Schmising,[2] M. Kiel,[2] N. Zhavoronkov,[2] J. Dreyer,[2] M. Bargheer,[2] T. Elsaesser,[2] C. Root,[1] T. E. Schrader,[1] P. Gilch,[1] W. Zinth,[1] and M. Woerner[2,*]

[1] *BioMolekulare Optik and MAP, Department für Physik, Ludwig-Maximilians-Universität München, 80538 München, Germany*
[2] *Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, 12489 Berlin, Germany*

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Femtosecond photoexcitation of organic chromophores in a molecular crystal induces strong changes of the electronic dipole moment via intramolecular charge transfer as is evident from transient vibrational spectra. The structural response of the crystal to the dipole change is mapped directly for the first time by ultrafast x-ray diffraction or diffuse scattering. Changes of diffracted and transmitted x-ray intensity demonstrate an angular rearrangement of molecules around excited dipoles following the 10 ps kinetics of charge transfer and leaving lattice plane spacings unchanged. Transient x-ray scattering is governed by solvation, masking changes of the chromophore molecular structure.

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The dislocation of electronic charge upon photoexcitation, i.e., photoinduced charge transfer (CT), plays a fundamental role for the function of many organic and biomolecular systems, among them individual organic chromophores—arrays of chromophores in, e.g., photosynthesis and light emitting and conducting polymers. Both intramolecular couplings and the interaction of the CT system with its environment are relevant for the kinetics and energetics of CT reactions. On a molecular level, CT may be connected with changes in geometry of the charge donating and accepting groups as well as with polar solvation, a stabilization of the CT state by a rearrangement of the surrounding.

Insight into CT induced changes of molecular structure has remained limited as most spectroscopic methods provide only indirect structural information. As a model system, the transient structure of aminobenzonitriles as 4-(diisopropylamino)benzonitrile [DIABN, inset of Fig. 1(a)] [1] has been investigated by ultrafast vibrational spectroscopy in solution [2,3] and by x-ray diffraction [4–6] with a 100 ps time resolution in molecular crystals. However, the molecular structure of the excited intramolecular charge transfer (ICT) state which is characterized by a strong change of the electronic dipole moment compared to the ground state, has remained controversial.

Very few studies treated the transient structure of a molecular ensemble undergoing a (polar) solvation process that is induced by a local photoinduced dislocation of electronic charge [7–9]. In solution, transient vibrational spectra of an excited chromophore in the fingerprint range have revealed changes of local, e.g., hydrogen bond interactions with the first solvent shell [7]. The collective response of the solvent has been addressed by time-resolved Raman studies of intermolecular low-frequency modes during solvation [8]. While such Raman transients clearly demonstrate changes in the frequency spectrum of solvent fluctuations, they leave the transient molecular structure mainly unresolved. This lack of structural information calls for other, in particular, ultrafast structure-resolving x-ray methods [10,11] for following changes in molecular separations and orientations directly.

In this Letter, we demonstrate that the ultrafast rearrangements in a molecular crystal in response to a local dipole change consist of an angular reorientation of molecules leaving the spacing of lattice planes unchanged. A combination of visible-pump midinfrared (IR) probe studies confirming the occurrence of intramolecular CT in DIABN crystals and ultrafast x-ray diffraction or diffuse scattering experiments give direct evidence that the x-ray signals are dominated by solvation-related geometrical changes of the crystal lattice, i.e, a collective response of many molecules, rather than local geometrical changes of excited chromophores. Dipole solvation occurs with a 10 ps rise time which is identical to the CT time. Under the conditions of weak femtosecond excitation applied here, a giant modulation of x-ray extinction around low order reflections is found, an effect which may also be present in many crystals made up of a complex unit cell consisting of light elements ($Z < 10$).

Single crystals of DIABN (colorless plates, 2×2 mm^2, thickness typically 50 μm) [12] with good optical quality were grown by sublimation of crystalline powder in a quartz tube. The crystal structure [Fig. 3(a)] is monoclinic [C12/c1 (no. 15)] with 16 molecules in one unit cell [12]. Basically, the crystal forms 4 layers of molecules per unit cell perpendicular to the c axis, which in turn contains pairwise molecules of parallel or antiparallel orientation.

In the femtosecond experiments, the excitation wavelength was 400 nm in the far red wing of the absorption spectrum of DIABN (peak around 270 nm). This red-wing excitation results in large penetration depths and correspondingly low densities of excited chromophores. Fluorescence experiments give evidence that the ICT-state is formed under these conditions.

The CT kinetics in the crystal were studied using a visible-pump IR-probe setup [13] with probe pulses in

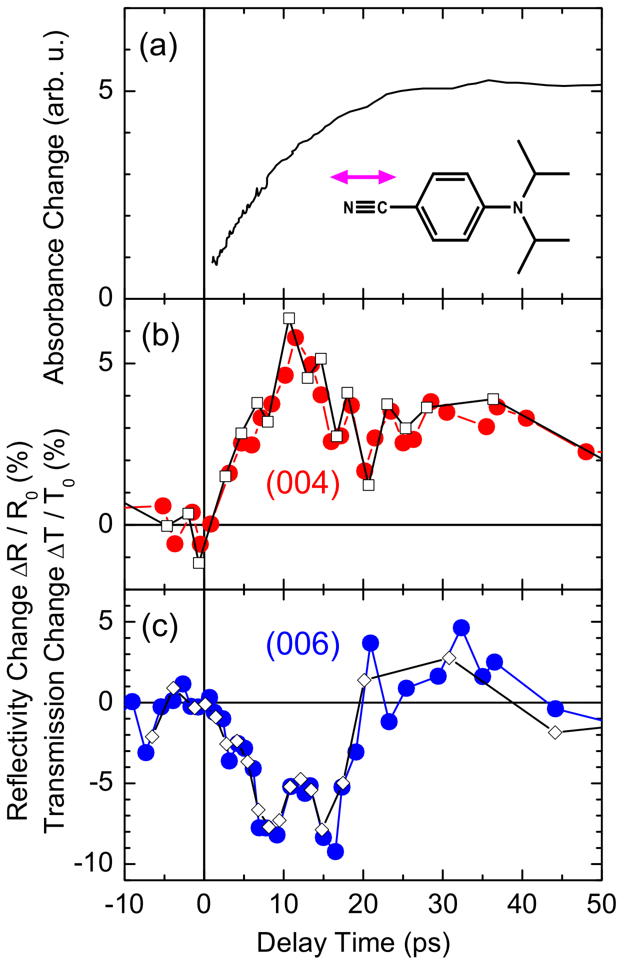

FIG. 1 (color online). Femtosecond pump-probe data measured on single DIABN crystals. In each case the crystal is excited with a 50 fs pulse at $\lambda_{ex} = 400$ nm. (a) Transient rise (time constant: 11 ps) of the CN stretching absorption (inset) of molecules in the ICT state at 2104 cm^{-1} (perturbed free induction decay for $\tau < 1$ ps not shown). (b),(c) Time-resolved change of the x-ray reflectivity $\Delta R/R_0$ measured on the 004 (red circles) and 006 Bragg reflections (blue circles). The respective transmission change $\Delta T/T_0$ (open symbols) is identical to the reflectivity change, i.e., $\Delta T/T_0 = \Delta R/R_0$.

the mid-IR spectral range between 2060 and 2160 cm^{-1}. The polarization of the probe pulses lay in the plane defined by the crystallographic *a* and *b* axis to eliminate artifacts from birefringence. Excitation with 50 fs optical pulses centered at 400 nm populates the so-called locally excited (LE) state from which the ICT state is formed by intramolecular CT. The latter process leads to a shift of the CN stretching mode to lower frequency and a change of its absorption strength [2,3]. In the DIABN crystal, we find the CN stretching absorption in the ICT state at 2104 cm^{-1}, rising with a characteristic time constant of 11 ps, the formation time of the ICT state [Fig. 1(a)].

Under the same excitation conditions the structural response of the DIABN crystal was studied by diffracting (transmitting) femtosecond hard x-ray pulses of 8.05 keV photon energy and 200 fs duration [14] off (through) the excited sample and recording changes of the respective intensity as a function of delay time. The experimental setup is similar to that described in Refs. [15,16]. Here, however, we include a multilayer x-ray mirror for focusing the x-ray beam onto the sample [17]. The direct beam was attenuated with Cu filters after transmission through the sample and recorded together with the Bragg reflected beam on the same x-ray CCD detector. A small fraction of 10^{-4} of the molecules in the crystal was excited by the pump pulses, 2 orders of magnitude less than in earlier studies [6].

In the x-ray diffraction experiments we study the 004 and 006 Bragg peaks in the extended face geometry [18] using copper K_α radiation ($\lambda = 0.154$ nm). We measure the reflected intensity integrated over the Bragg peak. For a typical crystal thickness of $d = 50\ \mu$m, the steady-state peak reflectivity has values of $R(004) \approx 0.005$ (width 0.15°) and $R(006) \approx 0.001$, in good agreement with the kinematic diffraction theory for ideally imperfect crystals [18]. In Fig. 2 the measured x-ray transmission (solid line) is plotted as a function of the angle θ. The transmission curve indicates a strong anisotropic beam extinction which is much stronger than the losses caused by Bragg reflection, isotropic x-ray absorption of mainly core electrons (calculated, dashed line) or inelastic Compton scattering. The high extinction thus originates from elastic diffuse x-ray scattering [19].

In femtosecond time-resolved x-ray diffraction, we observe strong transient changes of x-ray reflectivity of the

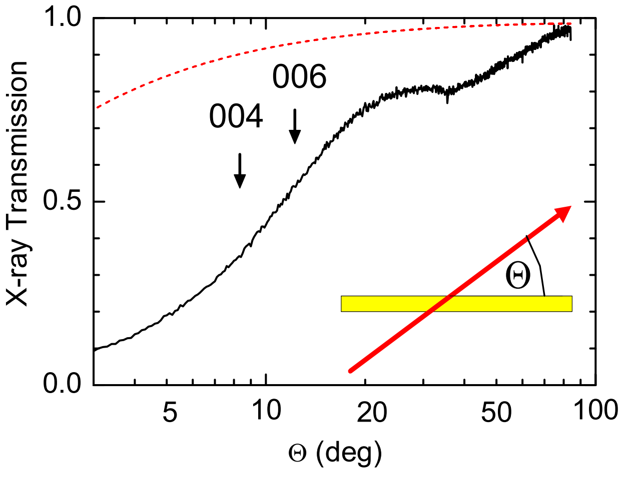

FIG. 2 (color online). Measured x-ray transmission (solid line, $\lambda = 0.154$ nm) of a single (50 μm thick) DIABN crystal as a function of the angle θ explained in the inset. Since the extinction is not an intrinsic property (i.e., it depends also on the degree of disorder, purity, etc.) the measured curve varies slightly from crystal to crystal. The positions of the Bragg angles of the 004 and 006 reflections are shown for comparison. The calculated x-ray absorption contribution (dashed line) to the entire beam extinction plays a minor role. The latter is dominated by diffuse x-ray scattering.

004 and 006 Bragg peaks which are of the order of $\Delta R/R_0 \approx 0.1$. In Figs. 1(b) and 1(c) the time-resolved change of the x-ray reflectivity $\Delta R/R_0$ measured at the angles of the 004 (red circles) and 006 Bragg reflections (blue circles) is plotted as a function of the time delay between the 400 nm pump and the x-ray probe pulse. Both transients display a rise with a time constant of approximately 10 ps, close to the CT time found in the IR studies [Fig. 1(a)]. After this rise, the reflectivity transients are strongly modulated and exhibit oscillatory features. The reflectivity changes are accompanied by simultaneous changes of x-ray transmission $\Delta T/T_0$ [open symbols in Fig. 1(b) and 1(c)] which have the same sign and amplitude, i.e., $\Delta T/T_0 = \Delta R/R_0$ in both cases.

We now discuss the origin of the transient x-ray signals which rise in parallel with the ICT formation within 10 ps, a fact that points to an intramolecular origin. Yet, the magnitude of the measured $(\Delta R/R_0)$ is orders of magnitude higher than a potential reflectivity change originating from *local* changes in geometry of the small fraction (10^{-4}) of excited molecules. Instead, both reflection and transmission changes are caused by a major fraction of molecules, i.e., a collective response of the crystal to the local photoinduced dipole changes.

The time-dependent x-ray transmission and reflection of an extended face mosaic crystal of the length L are given by $T(t) = \exp(-\mu(t)L)$ and $R(t) = \delta R(t)[1 - \exp(-2\mu(t)L)]/2\mu(t)$, with the reflectivity per unit crystal thickness δR [18]. The experimental finding that $\Delta T/T_0 = \Delta R/R_0$ for $\tau < 100$ ps demonstrates that both transmission and reflectivity changes are dominated by the transient x-ray extinction coefficient $\mu(t)$, whereas the transient change of the angle-integrated Bragg reflectivity $\delta R(t)$ of the small mosaic blocks plays a minor role. A strong modulation of the latter would result in $\Delta T/T_0 \neq \Delta R/R_0$. By far the dominant term in $\mu(t)$ is diffuse scattering (Fig. 2). The differences in signal sign and temporal evolution of the 004 and 006 curves point to a pronounced anisotropy of diffuse x-ray scattering [20].

The magnitude of x-ray extinction determined experimentally for the DIABN crystal ($\mu \approx 30\ \mathrm{cm}^{-1}$ for $\Theta \approx 8°$) is now compared with a theoretical estimate based on coherent elastic x-ray scattering. The extinction coefficient as a function of the direction of the incoming beam is given by [21]

$$\mu(\vec{k}_0) = N_e \int d\Omega_S \frac{d\sigma_e(\vec{k}_0)}{d\Omega_S} \quad \text{with}$$
$$\frac{d\sigma_e(\vec{k}_0)}{d\Omega_S} = \frac{r_e^2}{Z} \left\langle \left| \sum_{i=1}^{Z} \exp(i(\vec{k}_0 - \vec{k}_S)\vec{x}_i) \right|^2 \right\rangle |\vec{\epsilon}_0 \vec{\epsilon}_S|^2, \qquad (1)$$

$\vec{k}_0 = (2\pi/\lambda, \theta_0, \phi_0)$, and $\vec{k}_S = (2\pi/\lambda, \theta_S, \phi_S) = (2\pi/\lambda, \Omega_S)$ are the wave vectors of the incoming and scattered x-ray photons. N_e is the average electron density of the crystal and $d\sigma_e(\vec{k}_0)/d\Omega_S$ is the differential cross-section per electron which depends on the positions $\vec{x}_i$ of all electrons. r_e is the classical electron radius and $|\vec{\epsilon}_0 \vec{\epsilon}_S|^2$ accounts for polarization averaging. The angle brackets $\langle\rangle$ stand for ensemble averaging of the electron positions within the atoms and molecules as well as the spatial and rotational disorder of the molecules themselves. Z is the number of electrons scattering coherently, which can belong to the same atom, the same molecule or even a well-ordered fraction of the crystal [22]. To illustrate the consequences of Eq. (1) we consider a situation where Z electrons belonging to a heavy atom scatter coherently. Here, $\mu = (N_e/Z)(\sigma_{\mathrm{Thomson}} Z^2)$ with the Thomson cross section $\sigma_{\mathrm{Thomson}}$. Assuming $Z \geq 100$, one calculates an extinction in agreement with the experimental value. The coherent enhancement of $d\sigma_e(\vec{k}_0)/d\Omega_S$ is weaker for an ensemble of electrons more separated in space like in molecules or in a small cluster of the latter. Here, correlations in the spatial positions and angular orientations of the molecules (rigid bodies) determine the anisotropic extinction coefficient $\mu(\vec{k}_0)$. This estimate indicates that at least all 110 electrons of one DIABN molecule contribute coherently to the x-ray extinction.

We calculated the anisotropic extinction due to elastic x-ray scattering in DIABN crystals for copper K_α radiation ($\lambda = 0.154$ nm) with the help of Eq. (1) for different sizes of molecular clusters within the crystal structure [12]. It turns out that spatial positions of the core electrons of carbon and nitrogen essentially determine the anisotropy of $\mu(2\pi/\lambda, \theta_0, \phi_0)$. The black mesh in Fig. 3(b) shows the result for a cluster of 100 DIABN molecules (the polar coordinate system θ_0, ϕ_0 is aligned to the crystal axes $\vec{a}$, $\vec{b}$, $\vec{c}$). The extinction is larger for the incident wave vector $\vec{k}_0$ parallel to $\vec{a}$ or $\vec{b}$ than for the wave vector parallel to $\vec{c}$. This pronounced anisotropy is due to alignment of the molecules in the lattice planes of the crystal shown in Fig. 3(a). The anisotropy is already present for a single molecule and increases slowly ($\approx N^{4/3}$) with the size of the cluster (N: number of molecules). The circles in Fig. 3(b) show a cut through the anisotropic distribution for $\phi_0 = 150°$ around small values of $\Theta_{\mathrm{Bragg}} = 90° - \theta_0$ (the dependence on ϕ_0 is less pronounced in this area).

A change of the molecular alignment by a dipole-induced angular reorientation changes the ensemble average of the anisotropic total cross section [circles in Fig. 3(b)] towards an isotropic one (dashed line), thereby modulating the x-ray extinction. For the Bragg angle of the (004) reflection [Fig. 1(b)], the extinction of the incoming beam due to diffuse scattering is decreased and therefore both the Bragg reflection and the transmission increase, whereas a decrease occurs for the (006) reflection [Fig. 1(c)]. In the molecular crystal DIABN molecules are coupled through their (static) dipole moment which has a value of 8.5 D in the electronic ground state. Femtosecond excitation and the subsequent population of the CT state increase the dipole moment of the excited molecules by $\approx$8.5 D [1]. The increased dipole moment is the source of additional electric fields of 10^6–10^{10} V/m

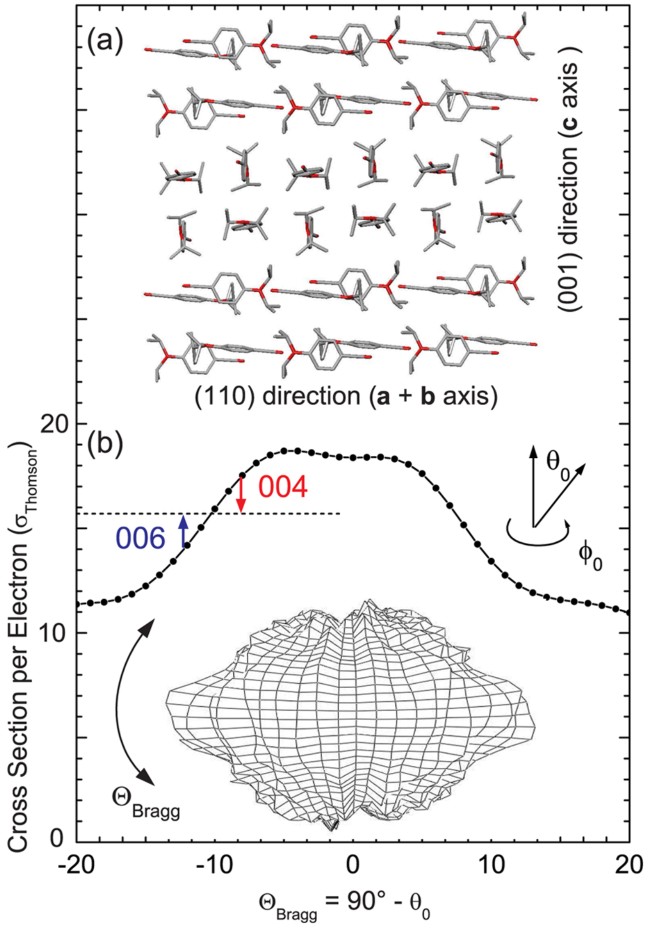

FIG. 3 (color online). (a) Cluster of 72 molecules in the crystal structure of DIABN. (b) The calculated total elastic x-ray scattering cross section per electron of a nanocrystal containing 100 DIABN molecules as a function of the direction of the incident x-ray beam ($\lambda = 0.154$ nm.). The black mesh [orientation as molecules in (a)] shows the strongly anisotropic result along the axis of the aligned molecules. Circles: detailed anisotropy for directions of the incident beam around the 004 and 006 Bragg reflections.

depending on the distance to the CT dipoles. These inhomogeneous electric fields generate the torque on the unexcited molecules which drives their angular reorientation. The dipolar forces and torques can also excite phonons, which might be the origin of oscillatory features observed after ~10 ps.

Finally, we estimate the expected rotational disorder from the solvation point of view. A solvation energy of $\Delta E_{\text{solv}} \approx 2000\ \text{cm}^{-1}$ (derived from the fluorescence Stokes shift [1]) together with the measured refractive index of $n = 1.8$ allows for an estimate of the contribution of molecular reorientation to the static dielectric function of the crystal $\epsilon(\omega \rightarrow 0)$. The corresponding elastic torque constant of $D_{\text{rot}} \approx 10\,000\ \text{cm}^{-1}$ gives—for electric fields between 10^6 and 10^{10} V/m—molecular rotation angles from 0.01° up to ≈10° (upper limit due to steric hindering), i.e., a sufficient rotational disorder to break the calculated anisotropy.

In conclusion, structural changes underlying a polar solvation process were directly observed by ultrafast x-ray diffuse scattering. The photoinduced CT of a small fraction of chromophores in a molecular crystal causes angular reorientation of the unexcited polar environment and determines the transient x-ray response of the system whereas local changes of the chromophore geometry play a negligible role. Monitoring local changes of molecular structure by x-ray diffraction requires a suppression of such solvation processes, e.g., by dissolving the system of interest in a nonpolar crystalline environment.

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*woerner@mbi-berlin.de

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