

Hydrogen bonding in urea

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The hydrogen bond consisting of a hydrogen atom positioned asymmetrically between a nitrogen and an oxygen atom (N—H···O) plays a central role in the structure and functionality of proteins and amino acids. The urea crystal is a simple system in which such a hydrogen bond exists. We have measured Compton profile anisotropies in crystalline urea which reveal subtle modulations linked to this chemical bond. The data presented here have sufficient statistical accuracy to isolate features arising from intermolecular interaction which is weak in urea and consequently difficult to detect experimentally.

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Hydrogen bonds constitute an extremely interesting and unique type of intermolecular interaction. Because they have energies intermediate between strong covalent and very weak van der Waals bonds and because they are directional, they play a central role in determining the behavior of many forms of matter. In particular, wet chemistry and biological complexes are built on a foundation of hydrogen bonds. For example, in water the hydrogen atom is located asymmetrically between the two oxygen atoms on neighboring molecules. In this situation the electron on the hydrogen atom forms a strong covalent bond with the closer oxygen, only 1 Å away, and the charge is effectively transferred to this oxygen. The exposed proton is then attracted electrostatically to the so-called lone pair (nonbonded) electrons on the oxygen of the neighboring molecule, i.e., the hydrogen bond is primarily electrostatic in nature. This attractive force is complemented by quantum-mechanical contributions, including the exchange interaction which is repulsive and polarization and charge-transfer components, which are attractive. These quantum interactions introduce a coherency related to the intermolecular distances in the electronic wave function, especially so for the exchange and charge-transfer components. The interplay between electrostatic and quantum sharing is played out in water, ice, and in all hydrogen-bonded systems to a greater or lesser degree, depending on parameters such as spacing between the neighboring molecules or the electronegativity of the chemical species involved in the associated stronger bond (different for O and N, for example).

Recent experiments on crystalline ice¹ have shown that Compton scattering can be exquisitely sensitive in revealing the detailed quantum interactions involved in the hydrogen bond in this material. The phase relation between the electronic wave functions on different molecules in the crystal leads to characteristic oscillations in the Compton profile which are unambiguous and qualitative indicators of quantum coherency of the electronic wave-function between neighboring sites in a crystal. Urea is an interesting, easily grown single crystal suitable for examining hydrogen-bonding effects very different from those in ice. The hydrogen bond in urea CO(NH₂)₂, connecting neighboring urea molecules, are of the form N—H···O, in contrast to water which consists of O—H···O bonds. The N—H···O=C

bonds found in urea are of paramount interest because of their presence in the proteins and nucleic acids of the living cell and their role in the folding process which transforms a polypeptide chain into an active protein. In particular, structures such as the α -helix and β sheets are stabilized by the formation of hydrogen bonds between an amide hydrogen and a carbonyl oxygen.² These are among the important secondary structures in proteins and as such play a role in their specificity, stability, and function.

It is important to experimentally establish the properties of weak intermolecular interactions, since they often determine the assembly and functionality of complexes of molecules. In particular one would like to study the dependence of these interactions on physically relevant parameters, such as near-neighbor distances, the structure of the stronger covalent bond, and finally the role of the surrounding medium. The charge transfer and exchange terms, for example, are expected to vary exponentially with the O-O distance in the water dimer. An accurate determination of the charge density related to the hydrogen bond could reveal the details of these interactions. However, in practice deviations from a strictly electrostatic picture are very small. In addition, such deviations are present only for the weakly bound outer electron and x-ray diffraction is much more sensitive to the uninteresting core electrons. Finally the relatively mobile proton is often prone to disorder. Though structural information and bond lengths can nevertheless be obtained quite precisely using x-ray and neutron diffraction, these constraints make it impossible to get unambiguous information about the interactions which are responsible for the formation of hydrogen bonds (see Refs. 3 and 4 for recent work on charge densities in urea). Compton scattering⁵ is an inelastic x-ray technique,⁶ which unambiguously measures properties of the ground-state electronic wave function. More precisely, the Doppler-shifted spectrum of large momentum transfer ($\hbar\mathbf{q}$) scattered hard x rays is very accurately proportional to a projection on \mathbf{q} of the ground-state momentum probability,

$$\frac{d\sigma}{d\omega d\Omega} \sim \int n_{\mathbf{p}} \delta(\omega - q^2/2m - \mathbf{q} \cdot \mathbf{p}/m). \quad (1)$$

Here $n_{\mathbf{p}}$ is the probability that an electron has momentum \mathbf{p} . $n_{\mathbf{p}}$ can be described in a fully quantum-mechanical density-

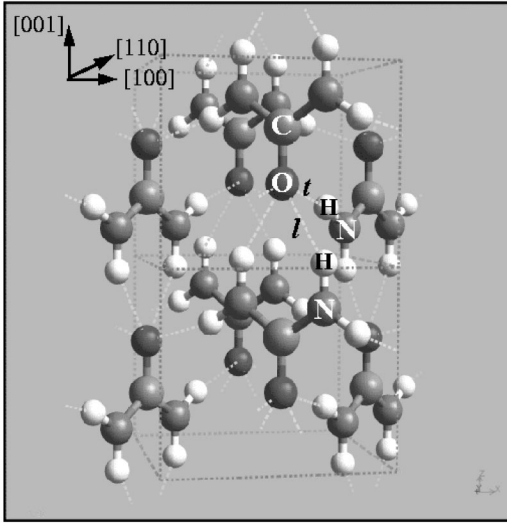


FIG. 1. The structure of crystalline urea. All intermolecular bonds are N—H···O hydrogen bonds. The planar molecules are arranged head to tail in “tapes” running in the vertical ([001]) direction. The hydrogen bonds (dashed lines) either connect molecules in the same tape (linear, marked l) or to the neighboring tapes (transverse, marked t).

functional description using the generalized gradient approximation (GGA) as

$$n_{\mathbf{p}} = \sum_{j=\text{occupied}} \left| \int e^{i\mathbf{p}\cdot\mathbf{r}} \phi_j(\mathbf{r}) d^3r \right|^2, \quad (2)$$

which is the Fourier transform of the one-electron occupied orbitals. Since the outer electrons are the most delocalized in real space they contribute most significantly to the low momentum part of $n_{\mathbf{p}}$. In addition, $n_{\mathbf{p}}$ for the outer electrons depends on the direction of \mathbf{p} relative to \mathbf{q} , in contrast to the core electrons.

The urea molecule is planar and strongly anisotropic with a characteristic “umbrella” shape (Fig. 1). The crystal is composed of “tapes” of molecules aligned head to tail. Adjacent tapes are orthogonal to each other, with the molecules pointing in opposite directions. In the urea crystal every oxygen atom participates in four hydrogen bonds. The fact that the lone-pair electrons of the oxygen are shared among four hydrogen bonds is primarily responsible for these urea bonds being longer and presumably weaker than in water or ice, where each oxygen only participates in two hydrogen bonds. Two of the four bonds are formed within the tape, with the tail of the adjacent molecule, and we shall call them linear bonds. The other two, which we shall call transverse bonds are formed with a molecule in the orthogonal tape on each side of the parent tape. The tapes (and hence the molecules) are contained in the plane defined by the [001] and the [110] or $[\bar{1}\bar{1}0]$ axes. The linear bonds are inclined at 31.7° with respect to the [001] direction and the projected H-bond distance on this direction is 1.77 \AA . The transverse bonds are inclined at an angle of 15.8° with respect to the [110] direction and the projected H-bond distance on the [110] direction is 1.98 \AA . The [100] direction is inclined at 45° with respect

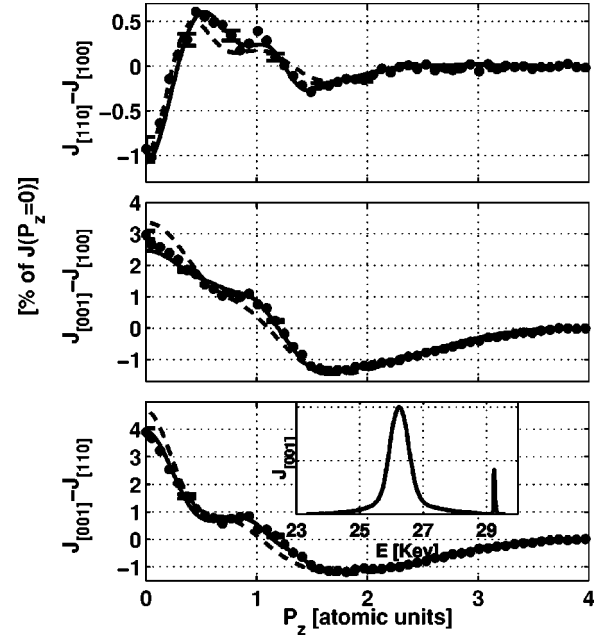


FIG. 2. Compton profile anisotropies. Experiment (dots), compared to the calculation for the crystal (solid line) and the isolated molecule (dashed line). Top panel: $J_{[110]} - J_{[100]}$. Middle panel: $J_{[001]} - J_{[100]}$. Bottom panel: $J_{[001]} - J_{[110]}$; inset: measured Compton profile and elastic line for the [001] direction. The theoretical anisotropies are scaled to the variation in the experiment (see text). The calculation for the crystal clearly matches the data better, reproducing several subtle features.

to the plane of the molecules and so does not represent any favored direction in the crystal. In fact, it was found that the profile measured in this direction is close to the one resulting from the spherical average of the momentum density, measured from a pressed disk of polycrystalline urea.

Compton profiles were measured using the high-resolution scanning spectrometer at ID15B (Ref. 7) at the European Synchrotron Radiation Facility (ESRF). The incident energy was 29.26 keV and the scattering angle was 173.5° , resulting in a Compton profile centered at an energy loss of 3 keV . Compton profiles were measured for the [100], [110], and [001] directions, in symmetric reflection geometry at room temperature with high statistics [5×10^6 counts in a 0.02 a.u. bin at $p_z=0$; $1 \text{ atomic unit (a.u.)}$ of momentum $\cong 1.89 \text{ \AA}^{-1}$]. The effective resolution was 0.1 a.u. (full width at half maximum). The profiles were corrected for absorption, analyzer reflectivity, geometric effects, and a linear background and were normalized and symmetrized.^{1,7} The inset in the lower panel of Fig. 2 shows the Compton profile in the [001] direction (noted $J_{[001]}$), as well as the elastic line resulting from thermally diffused photons.

In order to eliminate contributions of the core electrons to the Compton profiles, we consider differences in the Compton profiles measured in three crystallographic directions ($J_{[110]} - J_{[100]}$, $J_{[001]} - J_{[100]}$, $J_{[110]} - J_{[001]}$). These so-called Compton profile anisotropies also eliminate multiple-scattering effects, as well as residual background. The measured anisotropy is compared to the calculated one for urea, according to two different schemes. The first explicit quan-

tum calculation is a GGA-based determination of the electronic wave function for the urea crystal. It includes exchange and correlation among the electrons in an approximate mean-field fashion. However, it gives very good values for the bulk crystalline properties as was the case for ice.⁸ In the second calculation Compton profiles are computed from the electronic wave function of the isolated urea molecule using precisely the same computational methods as for the solid. In this picture any anisotropy in momentum space is due only to the wave function of the isolated molecule and bonds contained within the molecule because of their alignment in the crystal. If the hydrogen bonds in the urea crystal were due only to electrostatic attraction, the anisotropy thus induced would be well described by this picture. Our strategy is to compare data with both calculations and make inferences about the intermolecular hydrogen bonds based on the similarity of the data with one or the other calculation. The amplitude of the anisotropy is larger in the calculation than in experiment by as much as a factor of two. This trend has been observed before in other materials^{1,9} and is only partially understood. In particular, we know that the influence of short-range correlation effects on the electron momentum distribution are not well represented by GGA wave functions and tend to reduce the anisotropy by an overall scale factor,¹⁰ as do thermal vibrations not included in the theory. For easier comparison between experimental and theoretical anisotropies we have scaled the amplitude of the anisotropy calculated for the crystal to the amplitude of the experimental anisotropy. The anisotropy for the molecular model has then been reduced by the same factor. These factors are 2 for $J_{[001]} - J_{[100]}$ and $J_{[001]} - J_{[110]}$, and 1.5 for $J_{[110]} - J_{[100]}$. Figure 2 shows the resulting comparison. The simple scaling of the amplitude of the theoretical anisotropy brings the theory and the data to a good match, especially so in the case for the crystal calculation. Small features in the anisotropy, visible due to the high experimental resolution and statistical quality of the data, are very closely reproduced by the calculated anisotropy for the crystal. These small features are less well reproduced or entirely absent in the anisotropy calculated for the molecule. This clearly shows the sensitivity of Compton profile anisotropies to the subtle effects of intermolecular interactions, as we shall see below. In contrast an earlier measurement at lower experimental resolution¹¹ concluded that experimental Compton profiles agreed with calculations for an isolated urea molecule and that features due to bulk crystalline structure (approximated from calculations for dimers) were too small to be observed.

The $[001]$ - $[110]$ and $[001]$ - $[100]$ anisotropies are large (4% to 5% of the peak of the profile) and are dominated by a modulation with a large period in momentum space. Since all the C=O bonds in the urea molecule are oriented exactly parallel to the $[001]$ direction and perpendicular to the $[100]$ and $[110]$ directions and half the N—H bonds very nearly so, a large anisotropy is in fact expected. This corresponds to electrons being more delocalized along the bonds in real space and thus more localized in momentum space, resulting in a Compton profile which is more “peaked” along $[001]$ than in the directions perpendicular to it. No bonds are directly parallel to either the $[110]$ or the $[100]$ directions, and

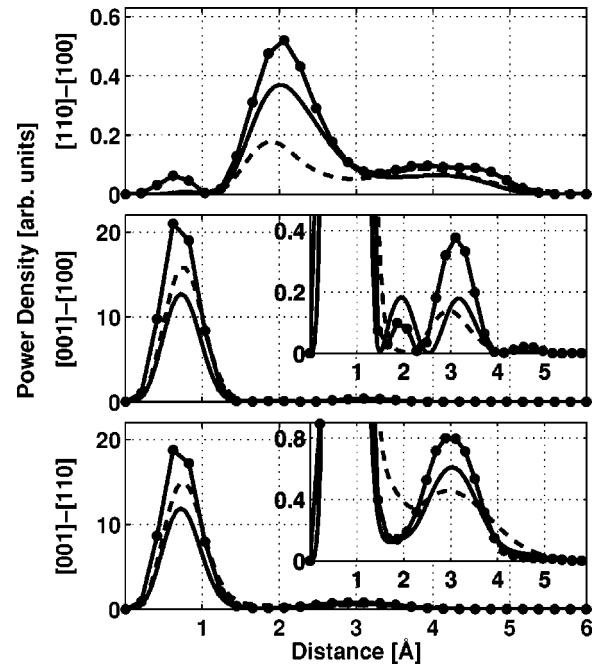


FIG. 3. Power spectral densities of anisotropies. Experiment (solid line with dots), compared to the calculation for the crystal (solid line) and the isolated molecule (dashed line). The insets are enlargements of regions of interest. Top panel: $J_{[110]} - J_{[100]}$. Middle panel: $J_{[001]} - J_{[100]}$. The strong peak at 0.7 Å is due to the structural anisotropy of the molecule. The peak at 1.9 Å in the enlargement can be seen in the experiment and the crystal calculation but not in the calculation for the molecule, and is interpreted as due to hydrogen bonds whose projected length on the $[001]$ direction is 1.8 Å. Bottom panel: $J_{[001]} - J_{[110]}$.

the $J_{[110]} - J_{[100]}$ anisotropy is correspondingly smaller (1.5% of the peak of the profile). This variation between different crystalline directions can also be gauged by noting that while the $[001]$ direction is contained in the plane for all molecules in the crystal, the $[110]$ direction is in-plane for only half the molecules and perpendicular for the other half and the $[100]$ direction is always inclined at 45° to the molecular planes.

The effects discussed above are due to the strong structural anisotropy of the molecule and intramolecular bonding and are the strongest effects observed. However, more subtle effects can be observed as the comparison with theory in Fig. 2 has shown and to investigate these further we have computed the power spectral density of the anisotropy defined as $|\int_{-\infty}^{\infty} [J_a(p) - J_b(p)] \exp\{-ipr\} dp|^2$. As argued in Refs. 12–14, a coherent electronic interaction over a certain distance scale in real-space modulates the Compton profile in momentum space. The anisotropy carries these modulations, too, and peaks in the power spectrum indicate the real-space distances involved.^{1,9} Only the positions and relative intensities of the peaks in the spectra are significant since the theoretical anisotropies have been scaled. It must be remembered, however, that the differences between Compton profiles also contain structure due to anisotropy of the atomic wave functions themselves as well as the localization and/or delocalization effects mentioned above. Figure 3 shows the power spectra. The middle and bottom panels ($J_{[001]}$

$-J_{[100]}, J_{[001]} - J_{[110]}$, respectively) are dominated by a strong peak which is a manifestation of the localization in momentum space parallel to the $[001]$ axis, already discussed above. Due to the large period in momentum space, the corresponding distance (about 0.7 \AA) is small. The insets in these panels show an enlargement of the small structure at higher distances. In the $J_{[001]} - J_{[100]}$ spectrum, interestingly enough, a peak at 1.9 \AA is seen both in the experiment and in the crystal calculation but is absent in the calculation for the isolated molecule. This peak is clearly due to the intermolecular interaction arising from the linear hydrogen bonds that have a projected length of 1.8 \AA on the $[001]$ direction and connect molecules within a given tape. The amount of charge involved in this bond is estimated to be small (about $0.04e$ as estimated for the bond population by Dovesi *et al.*³) and it is remarkable that an interaction of this kind in a molecular crystal with a nontrivial structure is visible in Compton profile anisotropies. The other peaks at $\sim 3 \text{ \AA}$ in these two spectra are visible in the experiment as well as both calculations, and could be due to the projected transverse dimension of the molecule along $[110]$. In the top panel ($J_{[110]} - J_{[100]}$), the strong peak at 0.7 \AA has all but disappeared, for reasons given above. The remaining features are seen in the data as well as the two calculations, making it

difficult to isolate effects due to the transverse hydrogen bonds. We remark also that the intensities for this spectrum are comparable to those of the small structure in the other two spectra. The level of statistical noise in the data is almost two orders of magnitude below the level of this smaller structure.

In conclusion, we have shown in this work that a state of the art synchrotron-based Compton spectrometer can be used to study chemical bonding in relatively complex molecular crystals. This will allow the study of hydrogen bonds in different chemical environments and eventually in samples of biological relevance. Measurements of Compton profiles and corresponding momentum density calculations have led us to clearly observe the effects of intermolecular hydrogen bonds of urea. Further work will focus on other hydrogen-bonded substances as well as the dependence of this interaction on external parameters like temperature and pressure. Since hydrogen bonding between molecules is a local effect, we believe that such studies will ultimately enable us to “parametrize” the quantum character of the hydrogen bond by such things as bond lengths and average properties of the chemical environments of a dimer.

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