

## How the hydrogen bond in NH<sub>4</sub>F is revealed with Compton scattering

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In order to probe electron wave functions involved in the bonding of NH<sub>4</sub>F, we have performed Compton scattering experiments in an oriented single crystal and in a powder. *Ab initio* calculations of the Compton profiles for NH<sub>4</sub>F and NH<sub>4</sub>Cl are used to enlighten the nature of the bonds in the NH<sub>4</sub>F crystal. As a consequence, we are able to show significant charge transfer in the ammonium ion which is not observable using other methods. Our study provides a compelling proof for hydrogen bond formation in NH<sub>4</sub>F.

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The distinction between ionic and hydrogen bondings is not always clear.<sup>1</sup> Ammonium salts in general are similar to the potassium and rubidium salts in crystal form and in other physical properties,<sup>2</sup> and thus are clearly ionic in nature. This similarity is due to the size of the ammonium ion, NH<sub>4</sub><sup>+</sup>, which is almost equal to the size of K<sup>+</sup> and Rb<sup>+</sup> ions. Remarkably, NH<sub>4</sub>F, instead of having a CsCl or NaCl structure like other ammonium salts which are ionic in nature, is isostructural to ice I<sub>h</sub> with NH<sub>4</sub><sup>+</sup> and F<sup>-</sup> ions alternating in the oxygen positions. Besides, ammonium fluoride and ice can form mixed crystals.<sup>3</sup> The fact that ammonium fluoride deviates from the standard isomorphism and prefers to adopt the ice structure is ascribed to the presence of significant hydrogen bonding in this compound.<sup>4,5</sup>

While ice has been the subject of many studies, NH<sub>4</sub>F has not been as widely studied. The crystal structure has been determined by Adrian and Feil,<sup>6</sup> the electrostatic properties have been studied by van Beek *et al.*,<sup>7</sup> and *Ab initio* calculations have been carried out by Alavi *et al.*<sup>8</sup> and by van Reeuwijk *et al.*<sup>9</sup> Given the ionic nature of ammonium salts, it is tempting to consider the force between the NH<sub>4</sub><sup>+</sup> and F<sup>-</sup> ions to be essentially an electrostatic interaction. Nevertheless, charge-density distribution does not provide a good criterion for establishing the existence of hydrogen bonds, as shown, for example, by Alavi *et al.*<sup>8</sup> for this compound. In this work we investigate the nature of chemical bonding in NH<sub>4</sub>F and show that, using the study of electron momentum distributions, we detect the presence of hydrogen bonding in ammonium fluoride.

Recently, Compton scattering, which is inelastic x-ray scattering at large energy and momentum transfers,<sup>10,11</sup> has provided fundamental information on the quantum nature of the hydrogen bond in ice and water.<sup>12-18</sup> The measured Compton profile (CP)  $J(p_z)$  represents the double integral of the ground-state total electron momentum distribution (EMD)  $\rho(\mathbf{p})$ :

$$J(p_z) = \iint \rho(\mathbf{p}) dp_x dp_y, \quad (1)$$

where  $p_z$  lies along the scattering vector of the x rays. Our Compton scattering experiments on NH<sub>4</sub>F will show how

electronic states are modified by the hydrogen bond in contrast to the ionic scenario of NH<sub>4</sub>Cl.

The CPs of the crystalline *a* and *c* directions, and the spherical average of a powder were measured at the European Synchrotron Radiation Facility in Grenoble on high energy beamline (ID15B), using the scanning Compton spectrometer.<sup>19</sup> The energy of incident photons was set to 29.74 keV by use of a Si(111) cylindrically bent crystal and the scattering angle was 173°. The collected Compton spectra were energy analyzed using the Si(400) analyzer and detected by a NaI scintillator counter. The energy-dependent resolution function is deduced from the full width at half maximum (FWHM) at the thermal diffuse scattering peak which was 0.16 (a.u.) which provides at the Compton peak 0.13 a.u. of resolution. After subtracting the background, energy-dependent corrections have been performed: absorption in analyzer and detector, detector efficiency, and analyzer reflectivity.<sup>20</sup> After normalization to the number of electrons, the contribution due to multiple scattering was subtracted from the total measured profile.<sup>21</sup> In order to obtain the valence electrons CPs, a quasi-self-consistent-field calculated core CP is then subtracted from the total corrected measured profile.<sup>22</sup>

The program used for our *ab initio* calculations was CRYSTAL98,<sup>23</sup> which is especially suitable for molecular crystals. We have used the hexagonal structure of the NH<sub>4</sub>F crystal at room temperature with point-group *P63mc*,  $a = 4.37 \text{ \AA}$ ,  $c = 7.17 \text{ \AA}$ , and the experimental atomic positions.<sup>7</sup> This crystal structure is illustrated in Fig. 1. The occupied orbitals used to determine the EMD and the CPs were calculated using a restricted Hartree-Fock scheme.<sup>16</sup>

In Fig. 2, we show two computed valence CPs for NH<sub>4</sub>F (convoluted with experimental resolution and normalized to unit area) together with the experimental data along the crystallographic direction *a*. In the first calculation, represented by a dashed line, we have built the CP as a superposition of CPs of isolated ions NH<sub>4</sub><sup>+</sup> and F<sup>-</sup> arranged in the same geometry as in the crystal. In comparison with the experiment, the profile of the isolated ions is found to be higher due to the absence of bonding.<sup>17</sup> In the second calculation, represented by a solid line, the two ionic fragments can interact, and an excellent agreement between the crystal calculation and the experiment is obtained.

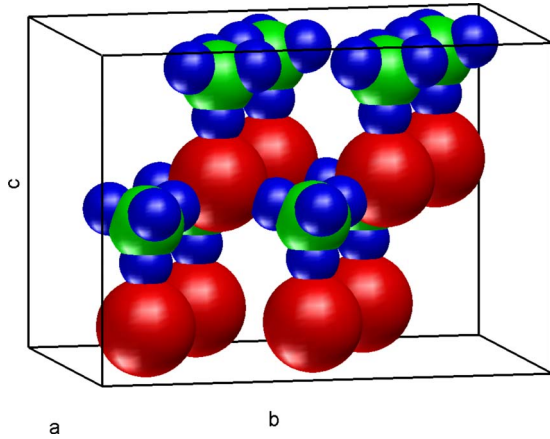


FIG. 1. (Color online) 48 atom cluster extracted from the  $\text{NH}_4\text{F}$  crystal. The (red) largest spheres are F atoms, the small (blue) spheres are H atoms, and the medium (green) spheres are N atoms. The crystallographic directions  $a$ – $c$  are shown along the edges of a box containing the cluster.

Likewise, in Fig. 3, we show that the spherical averaged CP for the  $\text{NH}_4\text{F}$  crystal calculation (solid line) agrees remarkably well with the experimental CP of the powder in contrast to a calculation for two noninteracting neutral molecules  $\text{NH}_3$  and  $\text{HF}$  (dashed line). In this molecular computation, the intramolecular atomic distances are the same as the corresponding distances in the crystal. Interestingly, the spherical averaged CP for two noninteracting neutral molecules  $\text{NH}_3$  and  $\text{HF}$  turns out to be very similar to the spherical averaged CP for the isolated ions  $\text{NH}_4^+$  and  $\text{F}^-$ . In reality, the main difference between the ion and the molecule cases is an exchange in a proton since the  $\text{HF}$  molecule can be formed by the capture of a proton by the  $\text{F}^-$  from the ammonium ion. However, the x-ray Compton scattering has no direct access to the proton wave function.

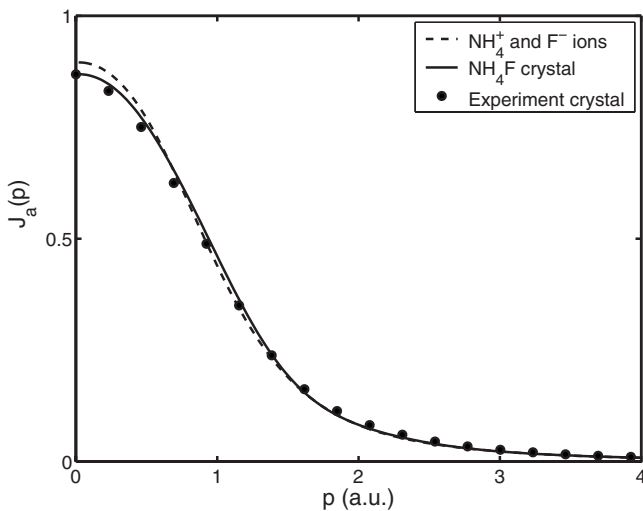


FIG. 2. Comparison of the theoretical and experimental [100] valence CPs. The dots are the experimental points. The dashed line is for the superposition of isolated  $\text{NH}_4^+$  and  $\text{F}^-$  ions. The solid line is for the  $\text{NH}_4\text{F}$  crystal. The curves are normalized to unit area. Symbol size is representative of error bars.

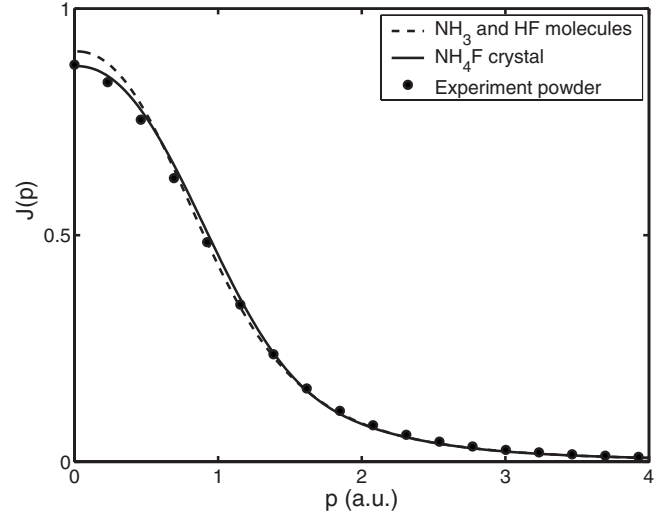


FIG. 3. Comparison of the theoretical spherical averaged valence CPs and the experiment for the powder. The dots are the experimental points. The dashed line is for the superposition of neutral  $\text{NH}_3$  and  $\text{HF}$  molecules. The solid line is for the  $\text{NH}_4\text{F}$  crystal. The curves are normalized to unit area. Symbol size is representative of error bars.

In order to study bonding effects, we now discuss the CP anisotropy,<sup>12</sup> that is, the difference between measured Compton profiles along two crystalline directions. In the present case, we consider

$$A(p_z) = J_c(p_z) - J_a(p_z), \quad (2)$$

where  $J_c(p)$  is the CP along the crystallographic direction  $c$  which is also the direction along which hydrogen bonds are aligned, and  $J_a(p)$  is the CP along the crystallographic direction  $a$ . The anisotropy  $A(p_z)$  has the advantage of highlighting the changes introduced by the bonding. The shape of the anisotropy is very similar to that found in ice  $A(p_z)$  (Ref. 12) as shown in Fig. 4.

The effects produced by the hydrogen bond on the electronic wave functions can be extracted by studying the power density<sup>12,25</sup>

$$P_D(z) = \left| \int dp_z A(p_z) \exp(ip_z z) \right|^2. \quad (3)$$

The peaks in the power-density  $P_D(z)$  indicate characteristic distances over which wave functions are coherent in given crystallographic directions. Figure 5 shows that the experimental data and the theory are in good agreement concerning the locations of the two main peaks. Nevertheless, the long-range peak at about 4 Å in the experimental anisotropy is largely reduced in the calculation. A cause of this discrepancy could be the Hartree-Fock tendency to overestimate wave-function localization. However, the CP in momentum space is not too sensitive to this overestimation.

In a true ionic crystal the main differences from the isotropic picture occur in the region where the ionic spheres are in contact as in the hard-sphere model. Thus, in the picture developed by Pattison *et al.*<sup>26</sup> one expects peaks at distance corresponding to the ionic diameters. The first main peak of

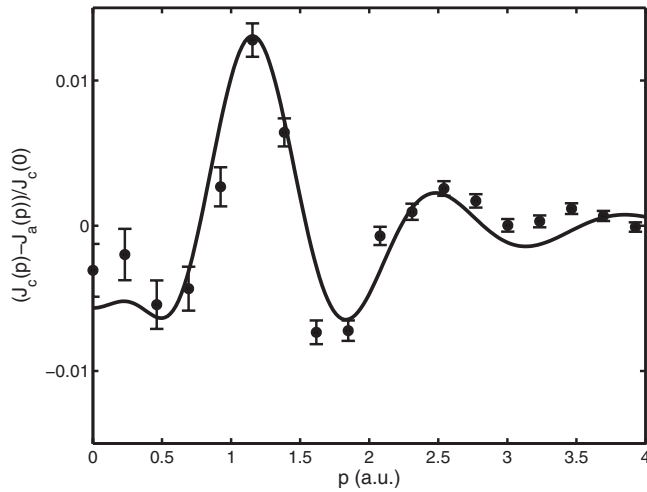


FIG. 4. Comparison of the theoretical and experimental Compton anisotropy [001]–[100]. The circles are the experimental points while the solid line is for the *ab initio* simulation of the NH<sub>4</sub>F crystal. The amplitude of the experimental anisotropy has been rescaled as in Ref. 12.

$P_D(z)$  should correspond to the cation diameter while the second main peak should give the anion diameter. Figure 5 also compares NH<sub>4</sub>F to the more ionic salt NH<sub>4</sub>Cl.<sup>27</sup> One can see that the second main peaks for NH<sub>4</sub>F and NH<sub>4</sub>Cl (Ref. 27) are close to accepted values for F<sup>−</sup> and Cl<sup>−</sup> diameters (2.7 and 3.6 Å, respectively<sup>28</sup>). The first peak is however at a distance systematically smaller than that of the hard-sphere ionic diameter of ammonium (2.8 Å) even in NH<sub>4</sub>Cl signifying that the purely ionic hard-sphere model is not adequate. Moreover, the distance corresponding to this peak is smaller for both the theoretical calculation and the experiment in NH<sub>4</sub>F than the calculation for NH<sub>4</sub>Cl although the ion is identical. As for NH<sub>4</sub>F, the interpretation becomes straightforward when the connection is made with results obtained for the hydrogen bonded ice I<sub>h</sub> since the measured and calculated anisotropies bear a striking resemblance. In

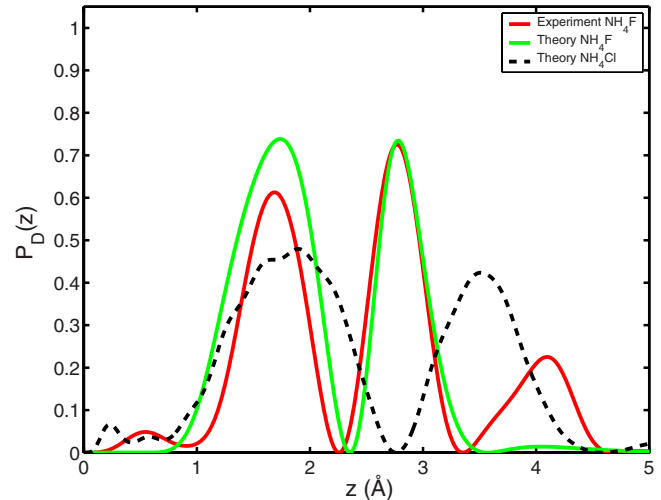


FIG. 5. (Color online)  $P_D(z)$  or the power spectrum of the Compton anisotropy for NH<sub>4</sub>F (experiment and theory) and NH<sub>4</sub>Cl (theory). The curves are normalized to unit area.

the more appropriate hydrogen bond picture the two predominant peaks of  $P_D(z)$  located at about 1.7 and 2.75 Å can be assigned to the hydrogen bond-length F–H (1.67 Å) and the nearest-neighbor F–N distance (2.77 Å), respectively, implying the existence of coherent charge transfer as in the case of ice I<sub>h</sub>.<sup>16</sup>

In conclusion, our study shows that high-resolution directional CPs of ammonium fluoride provide clear signatures of the hydrogen bond. The ionic picture is just a starting point since highly charged states such as the NH<sub>4</sub><sup>+</sup> and F<sup>−</sup> are mitigated by the hydrogen bond: bonding electrons are shared in states that cannot be assigned solely to ammonium or F.

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