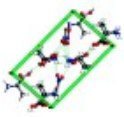

Organic ferroelectrics

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Raman spectroscopy touches on the properties of an organic ionic material, which was the second of its type to be synthesised, that apparently undergoes a phase transition at low temperature endowing it with ferroelectric properties, a property usually preserved for metal-containing materials.

Currently, there are only six published crystal structures of 2:1 salts of the amino acid alanine with an inorganic acid. L-alanine alaninium nitrate (LAAN) was first crystallized in 2001 and was only the second such compound studied in detail. These organic ionic materials are of interest from a technological perspective because a related compound, diglycine nitrate, which is also a 2:1 amino acid-inorganic acid was discovered to be ferroelectric back in the 1950s.

"We have studied the methyl derivative of a material that is a ferroelectric," explains Bruce Hudson of the Department of Chemistry, at Syracuse University, in New York state, "Ferroelectrics develop a macroscopic electric dipole moment when the temperature is lowered below their ferroelectric transition temperature called T_c."

Hudson and colleagues Matthew Hudson, Damian Allis, and Wayne Ouellette, have synthesised and crystallised the LAAN and obtained its vibrational spectrum at 25 Kelvin using incoherent inelastic neutron scattering (INS) spectroscopy. The team determined the INS spectrum of a polycrystalline sample of LAAN using the time-focusing crystal analyser spectrometer TOSCA at the Rutherford Appleton Laboratory, UK.

They also simulated the spectrum using solid-state density functional theory (DFT) based on a crystal structure determination obtained at 90 K. Surprisingly, they revealed features at approximately 450 cm^{-1} in the INS spectrum of L-alanine alaninium nitrate that were not revealed by the DFT calculations, which suggested a physical anomaly not predicted by the theory.

In order to reveal the nature of this anomaly, the team turned to Raman spectroscopy. LAAN's vibrational features are similar to mono-L-alaninium nitrate and L-alanine, which makes the assignments simpler, the team says. One feature an out-of-plane bending of the hydrogen atom in the O-H?O hydrogen bond at 1132 cm^{-1}, is noteworthy as it corroborates that a dimer is formed. A symmetric stretch for the nitrate at 1048 cm^{-1} is the most intense Raman feature.

The experiments showed spectroscopic differences between the spectra at 78 and 293 K with a 454 cm^{-1} feature appearing at low temperature. "The nature of these spectral changes and the disagreement between the INS spectrum and its simulation are [due to] an apparent structural change involving migration of a proton at low (less than 90 K)

Raman sees ferroelectric transition

temperature," the team suggests.

Given that alanine is the next larger homologue of the amino acid glycine and that diglycine nitrate and LAAN are similar in structure and bonding, it is perhaps not surprising that LAAN too might display the elusive property of ferroelectric properties in an organic material. If the proton migrates to the nitrate, rather than the carboxylate, then this would involve the least disturbance of the structure and would not require a reconstruction of the hydrogen bond network. Indeed, this coincides neatly with the team's hypothesis that the Raman feature at 454 cm^{-1} is probably due to a twisting motion of the amino ($-NH_2$) group within the structure.

The team suggests that further studies with a low-temperature single crystal neutron diffraction study of LAAN would confirm this if a a crystal of sufficient size and quality can be produced. Powder neutron diffraction would be the obvious next logical step. They add that reproducing the experiments with a deuterated form of the molecule might prove one way or the other whether the proton migration produces a ferroelectric transition in LAAN or not.

Even if there turns out to be no ferroelectric transition in LAAN, it could still represent an unusual and intriguing structure in which both a neutral and zwitterionic L-alanine amino acid exist in the same crystal cell together with crystalline nitric acid. Such a material might help to improve the computational structural models, improve our understanding of the spectra of related materials and perhaps offer clues to designing a next-generation material that does have the elusive ferroelectric properties.

Related links:

- **Phys. Chem. Chem. Phys., 2009, 11, 9474-948**
- **Bruce Hudson**

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