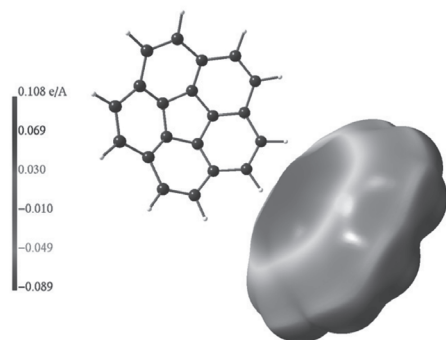


**MS19-01** Synchrotron radiation and extremely low temperatures, best conditions for charge density work. Peter Luger,<sup>a</sup> Manuela Weber,<sup>a</sup> <sup>a</sup>*Institute for Chemistry, Free University Berlin*,  
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It was Peter Debye, who noted already in 1915, hence three years after the discovery of X-ray diffraction, that the electron density (ED) of a chemical structure should be obtainable from this new method<sup>1</sup>. However, it took decades until the powerful experimental, methodical and computational procedures were sufficiently developed for a broad application of experimental ED work and it took 90 years until Philip Coppens stated in 2005 “Charge densities come of age”<sup>2</sup>. This talk will focus on the following aspects: The experimental basis to measure low temperature high resolution X-ray diffraction data sets will be discussed. We have compared data sets measured at different temperatures on the one hand and with synchrotron and conventional radiation on the other hand. It was shown that reducing the temperature from 100 K (which is almost routine nowadays) to extreme values around 10-20 K improves the data quality significantly, especially in the high order regions. Moreover some comments on pros and cons of synchrotron versus in-house diffraction experiments will be made. Although laboratory equipment can lead to proper charge density data sets, we conclude that the combination of synchrotron primary radiation at a wavelength of 0.5 Å (or less!) and a temperature around 10 K provides the optimum conditions for experimental charge density work. These conditions are first choice, especially, if only weakly diffracting crystals are available as holds, for example, in the class of the fullerenes, which will be demonstrated by a few examples. One result of a recent 10 K data collection at a 3<sup>rd</sup> generation synchrotron beamline (15 ID-B at the APS in Argonne/Chicago, USA) is illustrated below, showing the ED of corannulene in form of the experimentally derived electrostatic potential<sup>3,4</sup>.



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**Keywords:** charge density; synchrotron radiation; low temperatures

**MS19-02** Ab-initio lattice dynamics of molecular crystals and related properties with the CRYSTAL code. Bartolomeo Civalleri,<sup>a</sup> Alessandro Erba,<sup>a</sup> Matteo Ferrabone,<sup>a</sup> Elisa Albanese<sup>a</sup> <sup>a</sup>*Department of Chemistry, University of Torino, Italy*  
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In experimental studies of charge densities and vibrations of molecular crystals based on accurate X-ray and neutron diffraction measurements, ab-initio calculation of lattice dynamics offers an alternative tool to interpret results and support conclusions. We review different approaches to compute anisotropic displacement parameters (ADPs) for molecular crystals and present an approach based on periodic ab-initio calculations [1]. Contributions from both intramolecular and intermolecular vibrational motion is analyzed in detail. The dispersion of acoustic phonons is estimated and included through a supercell approach. The results are compared with experimental data from spectroscopy, X-ray and neutron diffraction experiments. Crystalline urea has been used as a case system to test HF and DFT methods and other computational parameters. Results for benzene, urotropine and L-ALA are also reported. Computed ADPs are in good agreement with experiment, in particular with low temperature data and for hydrogen atoms [1].

Investigation of the static charge density requires a proper deconvolution of thermal motion and static density. Complementary information about the thermal motion in molecular crystals is seldom available. In this respect, we show for urea how Debye-Waller factors derived from mean atomic displacements [2] can be used to include thermal motion in X-ray structure factors.

Along with ADPs, we discuss other properties that can be calculated from lattice dynamics such as phonon dispersion, thermodynamic properties, thermal expansion, INS spectra, Grüneisen parameters, elastic constants, ...

All computed data are obtained using the CRYSTAL code [3,4].

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**Keywords:** ab-initio calculations; lattice dynamics; molecular crystals