Imaging Molecular Vibrations in Rydberg Excited N-Methylmorpholine by Ultrafast Gas-Phase X-ray Scattering

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For many years, scattering measurements have been the gold standard for experimental determination of molecular structures. However, measurements of gas-phase samples that have inherently low molecular concentrations require either a high scattering cross-section (such as in electron scattering) or a high photon flux. The recent development of XFELs such as LCLS has provided exceptionally high x-ray photon flux, opening the door for new experimental methods such as ultrafast gas-phase x-ray scattering. In a pioneering study, we combined experimental ultrafast gas-phase scattering data with calculated trajectories to image the ring-opening of 1,3-cyclohexadiene. By incorporating many new experimental developments, we have improved significantly the signal-to-noise level of these experiments, and are now able to image a wider range of more subtle molecular changes.

In the present study, we investigate coherent vibrational motions in N-methylmorpholine (NMM). Previous ultrafast photoelectron spectroscopic results show that, upon excitation to the 3p Rydberg state, a coherent vibrational wavepacket is launched along the amine umbrella coordinate, which survives following ultrafast internal conversion to 3s. In this work, we are able to image this coherent vibration using ultrafast gas-phase x-ray scattering in real time. We find an oscillation period of 648 ± 30 fs, with an exponential dephasing time of 730 ± 246 fs, both of which are in good agreement with previous photoelectron results. This result demonstrates the extraordinary sensitivity of this technique, given that the vibrational motion yields a change in the time-dependent scattering amplitude of only ~0.1%. In addition, preliminary ab-initio calculations indicate that the effect of electronic excitation on the observed scattering signal is well above our experimental noise level, and may also be observed in these measurements.

Since the scattering signal derives from the total molecular wave function, the time-dependent scattering patterns carry the signatures of rotations, nuclear positions and even electron density distributions. We demonstrate that the anisotropy of the scattering signal, before rotational dephasing destroys the alignment, can be used to identify the orientation of the optical transition dipole moment with respect to the molecular frame.

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