

## Vibrationally resolved B 1s photoionization cross section of BF<sub>3</sub>

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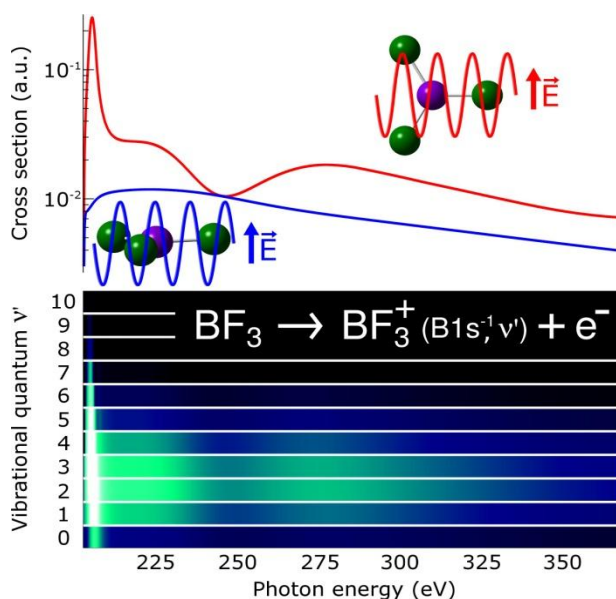
**Synopsis** We present a study of the vibrationally resolved B 1s photoionization cross section of the BF<sub>3</sub> molecule. A combination of high-resolution photoelectron spectroscopy measurements and of state-of-the-art calculations shows the evolution of the photon energy dependence of the cross section from a complete trapping of the photoelectron wave (low energies) to oscillations due to intramolecular scattering [1, 2]. These diffraction patterns allow to access structural information of both the neutral molecule and the core-hole species generated upon photoabsorption [3].

The advent of third-generation synchrotron radiation facilities, in combination with high energy-resolution detection techniques, has opened the way for the investigation of vibrationally-resolved inner-shell photoionization in small molecules, where an electron is emitted from a 1s orbital of a first-row atom. We present a study on B 1s photoionization of BF<sub>3</sub>, comparing experimental results with full first-principle calculations and showing that the most relevant features can be understood by means of simple models.

In order to calculate vibrationally-resolved cross sections, we have evaluated (bound and continuum) electronic wave functions using the static-exchange and the time-dependent DFT methods [4], developed by Decleva and collaborators, for different molecular geometries along the totally symmetric stretching mode. This mode is the most affected by the structural rearrangement accompanying core ionization [1, 2]. Our theoretical results are in good agreement with experimental measurements from SOLEIL synchrotron and, at high energies, qualitatively agree with a first-Born approximation model.

We have found that the relative cross sections show clear oscillations in the high-energy region as a function of photoelectron momentum which are due to an intramolecular scattering mechanism: in its way out of the molecule, the photoelectron is diffracted by the surrounding atomic centers, encoding the geometry of the molecule [1, 2, 3]. Very close to the photoionization threshold a complete trapping of the photoelectron is observed, manifesting itself

as an emission angle dependent shape resonance feature [1, 2].



**Figure 1.** Calculated cross section (upper panel) for different molecular orientations and vibrationally resolved cross section in the totally symmetric stretching mode (lower panel) for the case of randomly oriented molecules.

## References

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