NOO peroxy isomer discovered in the velocity-map imaged photoelectron spectrum of NO_2^-

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Synopsis Photoelectron spectra of NO_2^- measured with ANU's state of the art velocity-map imaging spectrometer have revealed unexpected, additional high energy electron structure that cannot arise from detachment of C_{2v} NO_2^-. Our work shows that this additional structure must instead be a signature of a new peroxy NOO isomer, a molecule which has not previously been observed.

NO_2, a toxic gas formed in most combustion processes, is a key component of photochemical smog and an important molecule in the Earth's atmosphere. Photoelectron spectroscopy allows for the structural and photophysical properties of this important molecule, and its parent negative ion, to be studied in detail. By employing the ANU's state of the art spectrometer, this information may be obtained with high resolution.

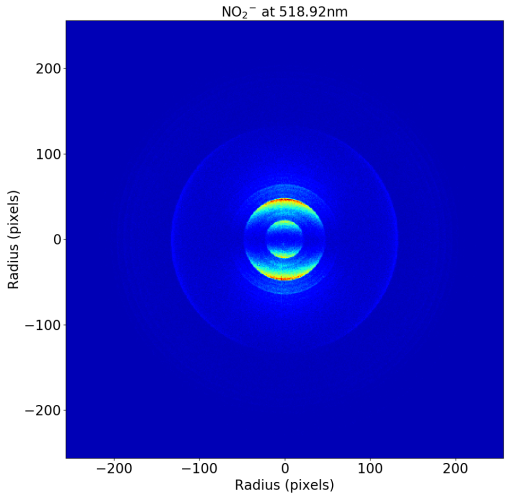
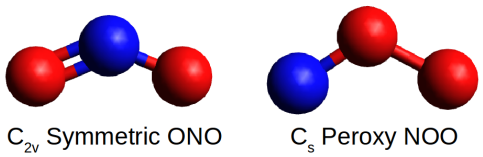


Figure 1. Velocity-map image of NO_2^- at 518.920nm, showing unexpected high eKE structure.

Through the implementation of velocity-map imaging, both the energetic and the angular information from the observed photodestruction events are acquired with 100% electron collection efficiency, allowing for multiple detachment/dissociation channels to be observed simultaneously. This benefit is highlighted in our measurements of NO_2^-, where unexpected additional high eKE photoelectrons are revealed. The surprising high eKE structure persists at detachment energies lower then the EA of ONO^- (2.273eV) [1], confirming that this previously unseen electron structure can not arise from the standard C_{2v} isomer of NO_2^-. Furthermore, the corresponding angular distribution has a negative anisotropy parameter β, opposite in sign to detachment from ONO^-.

Through further experimentation, combined with *ab-initio* calculations, it can be shown that this additional photoelectron structure is the result of another isomer of NO_2^-. The possible existence of a peroxy NOO isomer was first suggested in 1961, however despite numerous theoretical and experimental studies since then, there has been no previous conclusive evidence that a stable NOO isomer exists [2, 3, 4].



This work provides the first direct measurement of the NOO isomer, along with determination of multiple spectroscopic constants. This may have a significant impact on our understanding of this vital NO_2 molecule, a result with many possible implications in atmospheric science.

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References

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