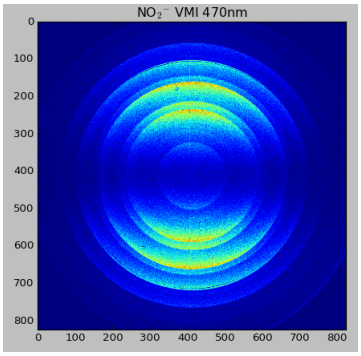
VARIABLE MIXED ORBITAL CHARACTER IN THE PHOTOELECTRON ANGULAR DISTRIBUTION OF NO_2

BENJAMIN A LAWS, STEVEN J CAVANAGH, BRENTON R LEWIS, STEPHEN T GIBSON, *Research School of Physics and Engineering, Australian National University, Canberra, ACT, Australia.*

NO_2 a key component of photochemical smog and an important species in the Earth's atmosphere, is an example of a molecule which exhibits significant mixed orbital character in the HOMO. In photoelectron experiments the geometric properties of the parent anion orbital are reflected in the photoelectron angular distribution (PAD), an area of research that has benefited largely from the ability of velocity-map imaging (VMI) to simultaneously record both the energetic and angular information, with 100% collection efficiency.



Photoelectron spectra of NO_2^-, taken over a range of wavelengths (355nm-520nm) with the ANU's VMI spectrometer, reveal an anomalous jump in the anisotropy parameter near threshold. Consequently, the orbital behavior of NO_2^- appears to be quite different near threshold compared to detachment at higher photon energies. This surprising effect is due to the Wigner Threshold law, which causes p orbital character to dominate the photodetachment cross-section near threshold, before the mixed s/d orbital character becomes significant at higher electron kinetic energies.[a]

By extending recent work on binary character models[b] to form a more general expression, the variable mixed orbital character of NO_2^- is able to be described. This study provides the first multi-wavelength NO_2 anisotropy data, which is shown to be in decent agreement with much earlier zero-core model predictions[c] of the anisotropy parameter.

[a] K. J. Reed, A. H. Zimmerman, H. C. Andersen, and J. I. Brauman, *J. Chem. Phys.* **64**, 1368, (1976). doi:10.1063/1.432404

[b] D. Khuseynov, C. C. Blackstone, L. M. Culberson, and A. Sanov, *J. Chem. Phys.* **141**, 124312, (2014). doi:10.1063/1.4896241

[c] W. B. Clodius, R. M. Stehman, and S. B. Woo, *Phys. Rev. A.* **28**, 760, (1983). doi:10.1103/PhysRevA.28.760

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