Probing neutral atmospheric collision complexes with anion photoelectron imaging.¹

CAROLINE JARROLD, None

Photodetachment of anionic precursors of neutral collision complexes offers a way to probe the effects of symmetry-breaking collision events on the electronic structure of normally transparent molecules. We have measured the anion photoelectron imaging (PEI) spectra of a series of O₂ · X complexes, where X is a volatile organic molecule with atmospheric relevance, to determine how the electronic properties of various X molecules affect the low-lying electronic structure of neutral O₂ undergoing O₂ − X collisions. The study was motivated by the catalog of vibrational and electronic absorption lines induced by O₂ − O₂, O₂ − N₂, and other collisions. The energies of electronic features observed in the anion PEI spectra of O₂⁻ · X (X = hexane, hexene, isoprene and benzene) relative to O₂⁻ PEI spectroscopic features indicate that photodetachment of the anion does indeed access a repulsive part of the O₂ − X potential. In addition, the spectra of the various complexes show an interesting variation in the intensities of transitions to the excited O₂(¹Δg) · X and O₂(¹Σ⁺g) · X states relative to the ground O₂(³Σ⁻g) · X state. With X = non-polar species such as hexane, the relative intensities of transitions to the triplet and singlet states of O₂ · X are very similar to those of isolated O₂, while the relative intensity of the singlet band decreases lower in energy relative to the triplet band for X = polar molecules. A significant enhancement in the intensities of the singlet bands is observed for complexes with X = isoprene and benzene, both of which have low-lying triplet states. The role of the triplet states in isoprene and benzene, and the implications for induced electronic absorption in O₂ undergoing collisions with these molecules, are explored.

¹National Science Foundation NSF CHE 1265991