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Probing neutral atmospheric collision complexes with anion photoelectron imaging.¹

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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 $O_2^- \cdot X$ 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 O_2 undergoing $O_2 - X$ collisions. The study was motivated by the catalog of vibrational and electronic absorption lines induced by O_2-O_2 , O_2-N_2 , and other collisions. The energies of electronic features observed in the anion PEI spectra of $O_2^- \cdot X$ (X = hexane, hexene, isoprene and benzene) relative to O_2^- PEI spectroscopic features indicate that photodetachment of the anion does indeed access a repulsive part of the $O_2 - X$ potential. In addition, the spectra of the various complexes show an interesting variation in the intensities of transitions to the excited $O_2(^1\Delta_g) \cdot X$ and $O_2(^1\Sigma_g^+) \cdot X$ states relative to the ground $O_2(^3\Sigma_g^-) \cdot X$ state. With X = non-polar species such as hexane, the relative intensities of transitions to the triplet and singlet states of $O_2 \cdot X$ are very similar to those of isolated O_2 , while the relative intensity of the singlet band decreases and becomes 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 O_2 undergoing collisions with these molecules, are explored.

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