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The electronic structure of TEMPO, its cation and anion

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Synopsis The electronic structure of TEMPO (2,2,6,6-tetramethyl-1-piperidiny N-oxide), its cation and anion were studied experimentally using the following electron spectroscopy techniques: electron energy-loss spectroscopy (EELS), measurement of elastic and vibrational excitation (VE) cross sections, HeI photoelectron (PE) spectroscopy and dissociative electron attachment (DEA) spectroscopy.

The motivation for the present study stems from the uses of the TEMPO moiety in many areas of research and applications [1-3], sometimes connected with electron capture or transfer. The knowledge of the electronic structure of TEMPO is useful for understanding its reactivity.

The PE spectrum of TEMPO [4] and Fig. 1 has shown three bands at lower energy and a “mountain” of unresolved bands at higher energy. The first ionization at 7.27 eV is from the singly occupied π^* orbital, leading to the ¹A' cation state. Next ionization is from the *n* orbital, leading to the ³A" and ¹A" pair of states at 8.90 and 9.29 eV respectively.

The EELS-PES comparison reveals a striking similarity of the neutral excited and the cationic states. The PE spectrum has to be shifted by only -2.11 eV to correspond to the Rydberg states.

Electron collisions with TEMPO are found to excite primarily the N-O stretch, the C-H stretch and the N-pyramidalization vibrations. In all these VE cross sections we have seen an extremely broad band extending from about 3 eV to beyond 14 eV. This band is assigned to the resonances with temporary electron capture in σ^* (C-C) and σ^* (C-H) orbitals. The narrow peaks at thresholds are an evidence for dipole-bound anions – the vibrational Feshbach resonances. The dipole moment of TEMPO is 2.9 D, which is above the critical value for dipole binding. A shape π^* resonance, which corresponds to the temporary capture of the incident electron in the π^* orbital, is hardly visible in the 0 – 1 eV range.

To facilitate the assignment of the resonances responsible for the DEA, its spectrum is compared to the EEL spectrum showing the potential parent states and the PE spectrum showing the potential grandparent states, and a representative VE cross section giving an overview

of the shape resonances.

The first DEA band at 5 eV corresponds to the EEL band both in energy and shape, pointing to a core excited resonance – with a doubly occupied Rydberg-like orbital around a positive core. The second DEA band at 6.87 eV corresponds in energy to the pair of the second and third PE bands, indicating that the resonance involved in this DEA band could have them both as grandparents, *i.e.*, this band is also assigned to a core excited resonance.

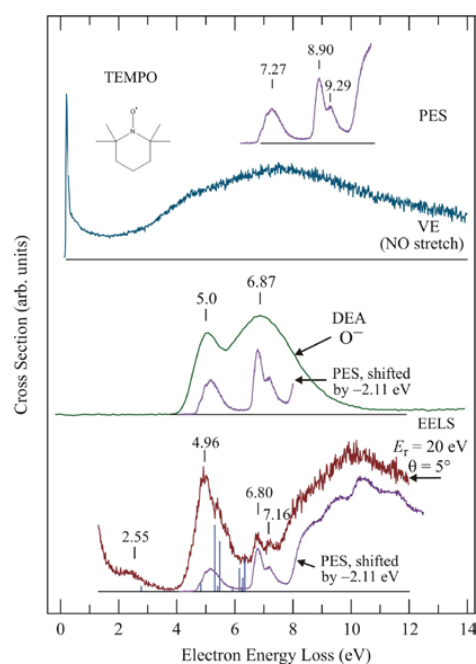


Figure 1. PE, VE, DEA and EEL spectra.

References

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