

# Diffuse Excess Electron States

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Unusual anions result when excess electrons become trapped outside the nuclear frameworks of neutral molecules or clusters by electrostatic fields originating from those frameworks. The excess electrons in such anions are typically loosely-bound and spatially-diffuse. Here, we report on our anion photoelectron spectroscopic studies of two types of electrostatically-bound, diffuse excess electron states.

Anions in which the excess electrons are bound predominantly by dipolar fields are commonly referred to as ‘dipole bound anions’. We have studied many examples, including  $(\text{H}_2\text{O})_2^-$ ,  $\text{CH}_3\text{CN}(\text{H}_2\text{O})^-$ ,  $(\text{HF})_2^-$ ,  $(\text{HF})_3^-$ ,  $\text{Indole}(\text{H}_2\text{O})_n^-$ ,  $\text{HCl}(\text{H}_2\text{O})_n^-$ ,  $\text{HCN}(\text{H}_2\text{O})_n^-$ , molecular nucleic acid base anions, and anions of zwitterionic amino acids. In all of these cases, dipole binding exhibits a distinctive, photoelectron spectral signature. Several selected studies will be highlighted. In the case of  $(\text{HF})_3^-$ , we and our theoretical collaborators found evidence not only for dipole binding between a chain of HF molecules and an excess electron, but also for dipole binding in which both a single HF molecule and a hydrogen fluoride dimer were separately bound to the same excess electron [1]. In the case of uracil, we found that, while its molecular anion is dipole bound, its hydrated anionic form is a conventional, valence anion, illustrating

competition between the two types of electron binding. In the case of amino acids, we relied on the appearance of a dipole bound spectral fingerprint to signal the advent of penta-hydrated glycine's zwitterion. Additional related topics include the close relationship between dipole binding and the formation of solvated electrons and the possibility that quadrupole-bound anions may exist.

Molecular Rydberg radicals are examples of net neutral species in which excess electrons are bound by electrostatic monopolar fields, i.e., by cations. We have found several ammonium-based examples of anions of Rydberg radicals, these being  $\text{NH}_4^-$ ,  $\text{N}_2\text{H}_7^-$ ,  $\text{N}_3\text{H}_{10}^-$ ,  $\text{N}_4\text{H}_{13}^-$ ,  $\text{N}_5\text{H}_{16}^-$  and, in some cases, their solvated complexes [2]. All of these exhibit photoelectron spectral signatures which are suggestive of extremely diffuse excess electron states. In part, because theory [3] finds the excess electron's spatial distribution to be Rydberg-like, these species are commonly referred to as 'double Rydberg anions'.

[1] M. Gutowski, C. S. Hall, L. Adamowicz, J. H. Hendricks, H. L. de Clercq, S. A. Lyapustina, J. M. Nilles, S.-J. Xu, and K. H. Bowen. *Phys. Rev. Lett.* **88**, #143001 (2002).

[2] S.-J. Xu, J. M. Nilles, J. H. Hendricks, S. A. Lyapustina, and K. H. Bowen, *J. Chem. Phys.* **117**, 5742 (2002).

[3] J. V. Ortiz, *J. Chem. Phys.* **117**, 5748 (2002).