PHOTOELECTRON SPECTROSCOPY OF RARE-GAS SOLVATED NUCLEOBASE ANIONS

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Gas-phase polar molecular anions [uracil (U^-), thymine (T^-), 1-3 dimethyluracil (DMU^-)] solvated by rare gas atoms were studied by means of negative ion photoelectron spectroscopy[a]. The photoelectron spectrum (PES) of U^-, T^-, and DMU^- each exhibit a distinctive dipole-bound (DB) spectral signature. The spectra of U^-, U^- $(Ar)_1, 2$ and U^- $(Kr)_1$ also only displayed the DB anion feature. Upon the solvation of more rare gas atoms, the spectra of U^- $(Ar)_3$, U^- $(Kr)_2$, and U^- $(Xe)_{1-3}$ not only retained the DB signature but also exhibited the valence anion features. Moreover, the DB and the valence features shifted together to higher electron binding energies (EBEs) with increasing numbers of rare gas solvent atoms. Therefore, the co-existing DB and the valence anions appeared to be strongly coupled with each other, i.e. they effectively form a single state that is a superposition of both DB and valence anion states. For both U^- and T^- series, the "onset size" of the Xe, Kr, and Ar solvents for the co-existing of the two anionic states was 1, 2, and 3 respectively. In addition, a minimum of 2 methane (CH_4) molecules or 1 ethane (C_2H_6) molecule were required to induce the coupling between the two states in the T^- series. Thus, the nucleobase anion interaction with non-polar solvent atoms tracks as the sum of the solvent polarizabilities. However for the DMU- series, the DB and the valence anions of $DMU^-(Xe)_1$, $DMU^-(Kr)_2$, and $DMU^-(Ar)_3$ were completely absent in both the mass spectra and the PES. Beyond these "holes", their PES displayed the similar behaviors to the U^- and T^- series. Extrapolated EA values for these missing species were at or very close to zero, which may explain why they were not seen. However, why this was the case is not clear. With better Franck-Condon overlap between the origins of the NB^- $(Rg)_n$ valence anion and the neutral NB(Rg)n than between those of the NB^- (H2O)n valence anion and the neutral NB(H2O)n, extrapolation of the valence electron affinities, measured from the $NB(Rg)_n^-$ valence anions, should lead to significantly improved estimations of the valence electron affinity values of canonical, molecular nucleobases. EA_v(U) = 36 $\pm$3 meV, EA_v(T) = 32 $\pm$ 7 meV, EA_v(1,3-DMU) = -34 $\pm$ 8 meV, and EA_v(A) = -80 meV, are our best recommended extrapolated EA_v values from our experiments.

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