Electronic Supporting Information for:

Excited states in electron-transfer reaction products: Ultrafast relaxation dynamics of an isolated acceptor radial anion

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In order to ascertain the molecular orbital contributions and oscillator strengths of the anionic excited states in the 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane radical anion, F_4-TCNQ•$^-$, we have performed time-dependent density functional theory (TD-DFT) calculations, which may be compared to the *ab initio* calculations from the Simons group.[1] In our treatment, the excited states of F_4-TCNQ•$^-$ were calculated at the optimized anion geometry (with D_{2h} symmetry) utilizing the B3LYP functional and a correlation consistent triple-zeta basis-set (TDDFT/B3LYP/cc-pVTZ) using the Gaussian03 software package.[2] The three states identified in reference 1 have been reproduced and their excitation energies and oscillator strengths are indicated in table S1.

State	Excitation Energy [eV]	Oscillator Strength
1^2B_{3u} (D_1)	1.7	0.30
2^2B_{3u} (D_2)	3.5	0.70
^2A_g	4.1	0.00

Table S1. Excited states of F_4-TCNQ•$^-$, calculated at the D_{2h} anion geometry using TD-DFT (B3LYP/cc-pVTZ).

The first state, calculated at 1.7 eV, can be assigned to the experimentally observed D_1 (1^2B_{3u}) state, in agreement with Sobczyk *et al.*. It primarily exhibits core-excited character, but also has an approximate 15% contribution from valence electron excitations. The predominant core-excited character can be used to rationalize the low signal levels

observed for the one-photon photodetachment from the D_1 to the S_0 neutral ground state, as this transition is correlated in Koopmans' picture with a valence excited anion state.

The next calculated excited state is characterised by a large oscillator strength and has a predominant contribution from the $1\pi^* \rightarrow 2\pi^*$ valence transition, leaving the electron in an orbital of b_{3u} symmetry and corresponds to the D_2 state. This transition also contains a significant core-excited $\pi \rightarrow 1\pi^*$ contribution (~10%), which has been used to explain the high energy feature in the photoelectron spectrum at 3.1 eV.[3]

The third bound state identified by Sobczyk *et al*. is of A_g symmetry. We have also identified this state, although the relative state ordering calculated by us differs from that of Sobczyk *et al*.. We stress however, that our calculations have not been performed to yield absolute state or transition energies, but to uncover relative molecular orbital contributions and oscillator strengths, which will be qualitatively correct. The ^2A_g state corresponds to an almost pure excitation of the $1\pi^*$ orbital into a higher unoccupied π^* orbital and, although we calculate this state to be ~1 eV higher in energy, it can clearly be correlated with the ^2A_g state calculated to be marginally bound by Sobczyk *et al*.. [1] The key point of the present discussion is that the ^2A_g state possesses a vanashingly small oscillator strength and will therefore not be directly accessible using photoexcitation in our experiments. We have furthermore calculated a ^2A_u state lying between the 2^2B_{3u} and the ^2A_g states, which corresponds to the $1\pi^* \rightarrow 3\pi^*$ valence transition.

The key point to note from our calculations is that we have reproduced the states and their symmetries calculated by Sobczyk *et al*. and have shown that: (1) some of these are of mixed electronic character, which can be used to explain Koopman's correlations observed in the photoelectron spectra; and (2) only the $D_1(1^2B_{3u})$ and $D_2(2^2B_{3u})$ states have an appreciable oscillator strength.

References

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