Bound-Excited Electronic States of the Anion of 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane†

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The doublet anionic states of TCNQ-F4 (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) have been studied at the Hartree–Fock and the Møller–Plesset (MP) perturbation theory levels (up to fourth order) with aug(sp)-pVDZ basis sets. Our results indicate that TCNQ-F4 forms a stable anion of B2g symmetry whose vertical electron attachment energy is 2.893 eV (at the MP4 level). In addition, we found two valence excited electronic states (2B3u and 1A2g) of the anion that are stable vertically with respect to the neutral parent. The electronic stability of the third excited state (a core-excited 1B3g state) needs to be further investigated. We conclude that the neutral TCNQ-F4 at its equilibrium D2h geometry may attach an extra electron to form any of these four states (i.e., 1B2g, 1B3u, 2B3u, and 1A2g) and the corresponding MP4 vertical attachment energies (VAE) are 2.893, 0.822, 0.244, and 0.072 eV, respectively. However, due to second-order Jahn–Teller distortion, only the ground anionic state (1B2g) possesses a minimum at D2h symmetry. For the two valence excited states (2B3u and 1A2g), negative curvatures cause out-of-plane deformations that lead to (i) an increase of the energy of the latter (1A2g) state and (ii) achieving a minimum-energy structure of C2v symmetry for the former where this state becomes a doublet A state and its vertical electronic stability increases to 2.721 eV.

Figure 1. Atom labeling in TCNQ-F4 used in this work.

1. Introduction

Very few anions possess bound excited electronic states, and the systems characterized to date are primarily atoms or diatomics.1–3 In this contribution we study valence excited anionic states, in which an excess electron occupies a valence orbital of the neutral molecule, rather than dipole-bound anionic states, in which an extra electron is bound primarily due to the electrostatic interactions with the neutral molecule.4–9 In the 90s Simons and Gutowski studied lithium-substituted double-Rydberg anions that possess a few bound valence anionic states.10–12 These states, however, differ in multiplicity. In the present work, we address a molecular system with bound anionic states of the same spin multiplicity.

Brauman and co-workers observed bound valence excited anionic states of TCNQ (7,7,8,8-tetracyanoquinodimethane), TCNE (tetracyanethylene), Me2-DCNQI (2,5-dimethyl-7,7,8,8-tetracyanoquinodimethane), chloranil, and hexacyanobutadiene in electron photodetachment spectroscopy experiments.13,14 The most extensive experimental results are available for TCNQ−, a species that we studied in the past.15 On the basis of CI/PM3 calculations, we suggested that the 1B3u −→ 2B2g and 2B3u −→ 3B2g transitions contributed to the electronic absorption and electron photodetachment spectra of TCNQ−.15 These results supported the experimental claim from the Brauman group that not only the ground anionic state (2B2g) but also certain excited states of TCNQ− (i.e., 1B3u and 2B3u) were electronically stable.13,14 Ab initio calculations on the cationic and anionic states of TCNQ and of TCNE were also performed by Zakrzewski et al.16 The vertical electron binding energy obtained for TCNQ, within the outer valence Green function (OVGF) method,17,18 was found to be 2.74 eV, and the energies of the 1B3u −→ 2B2g transition obtained within the configuration interaction method with single excitations led to the conclusion that the 1B3u anionic state of TCNQ is likely to be electronically stable with respect to the neutral species.16

In this contribution we focus our attention on a well-known electron acceptor molecule TCNQ-F4 (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) shown in Figure 1. This system is of great interest for material chemists because it plays the role of an electron acceptor in the formation of charge-transfer complexes.19 The TCNQ-F4− radical anion forms tight pairs in alkali metal salts such as [Na+/TCNQ-F4−] or [K+/TCNQ-F4−], even at room temperature.20 In 1995 Sugimoto et al. reported the first observation of weak ferromagnetism in purely organic radical solids such as [Li+/TCNQ-F4−].21

Even though the applications of the TCNQ-F4 and its radical anion in various types of salts are widely known, little has been done on determining the properties of TCNQ-F4− itself. In

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particular, to the best of our knowledge, the possibility of forming bound excited anionic states of TCNQ-F4 has not been described thus far. Therefore, we decided to take the first step in this direction by estimating the propensity of this common electron acceptor molecule to form electronically stable excited anionic states.

2. Methods

2.1. Treatment Employed. The properties of TCNQ-F4 in the lowest singlet state, as well as in the anionic doublet states were investigated at the self-consistent field (SCF) and the second-order Møller–Plesset perturbation (MP2) levels of theory. In addition, the vertical electron attachment energies of TCNQ-F4 were calculated at the fourth-order MP perturbation theory level. For the open-shell anions, we performed geometry optimizations and harmonic vibrational frequency calculations at the unrestricted Hartree–Fock (UHF) level. The values of \( S^2 \) in the UHF calculations were in the 0.773–0.992 range for doublet states; after annihilation they decreased to 0.750–0.805. For each optimized geometry of an anionic state, we undertook single-point MP2 calculations of the energy of the anion and its parent neutral species. In addition, MP4 estimates of the vertical electron binding energies of each anionic state were calculated at the minimum energy structure of the neutral TCNQ-F4.

In our work we use common definitions\(^{22}\) of the vertical electron detachment energy (VDE) and vertical electron attachment energy (VAE) characterizing the electron binding energy of the anion at its equilibrium structure and at the equilibrium geometry of the neutral parent, respectively. In particular, these two quantities are defined as follows:

\[
\text{VDE} = E_N(G_A) - E_A(G_A)
\]

and

\[
\text{VAE} = E_N(G_N) - E_A(G_N)
\]

where \( E_N \) and \( E_A \) indicate the total energy of the neutral and anionic species, respectively, calculated at the equilibrium geometry of the neutral \( (G_N) \) or anion \( (G_A) \).

We employed cc-pVVDZ\(^ {23}\) basis sets with extra s and p sets of diffuse functions on each atom, as implemented in the original aug-cc-pVVDZ basis. However, to make our calculations practical, we had to further limit the number of basis functions, so the \( d \)-symmetry diffuse functions included in the original aug-cc-pVVDZ basis set were omitted in our work. We thus followed the example of Zakrzewski, Dolgounitcheva, and Ortiz who used the same approach to study a similar molecule: 7,7,8,8-tetracyanoquinodimethane (TCNO)\(^ {16}\). We label such basis sets aug(sp)-cc-pVVDZ to indicate the lack of the \( d \)-symmetry basis functions in the diffuse set. The usefulness and relevance of employing that particular basis set is explained in the following section.

All calculations were performed with the GAUSSIAN98 program\(^ {28}\) on Intel Pentium IV, AMD Athlon computers and on a Compaq Sierra numerical server. The three-dimensional plots of molecular orbitals were generated with the MOLDEN program.\(^ {25}\)

2.2. Basis Set Testing. To test the usefulness the aug(sp)-cc-pVVDZ basis set we used to calculate the properties of the TCNQ-F4 anionic states, we compared, for TCNE, results obtained with this basis set to the results when the full aug-(spd)-cc-pVVDZ basis set (i.e., aug-cc-pVVDZ) was used. As described by the Ortiz group, the vertical electron affinity of TCNE (tetracyanoethylene) was found to be 2.03, 2.02, and 2.04 eV with the aug(sp)-cc-pVZD, aug-cc-pVZD, and cc-pVTZ basis sets, respectively.\(^ {16}\) Taking into account that TCNE is similar to TCNQ-F4 (i.e., it is a very strong electron acceptor supporting bound excited anionic states), we conclude that the vertical electron affinity obtained for this species with the aug-cc-pVZD basis set and with the aug(sp)-cc-pVZD basis are likely to be almost the same because the VEAs differ by only 0.01 eV (0.5%) for TCNE. We also tested that, for the TCNQ-F4 anionic states studied in our work, the SCF vertical electron attachment energy (VAE) for the ground doublet \( B_2g \) anionic state decreases by only 0.08 eV when the aug(sp)-cc-pVZD basis is replaced with the aug-cc-pVZD basis set (this corresponds to ca. 2% of the total VAE).

Next we decided to test the ability of the SCF/aug(sp)-cc-pVZD treatment to reproduce the ground-state neutral and anionic equilibrium geometries. We performed SCF/aug(sp)-cc-pVZD geometry optimizations of the neutral TCNQ (tetracyanoquinodimethane) and its anionic daughter (in its ground electronic doublet \( B_2g \) state) because the TCNQ system is a very similar species and its properties are described in the literature. We found that (i) for the neutral singlet \( A_g \) state of TCNQ the SCF/aug(sp)-cc-pVZD bond lengths differ by less than 0.025 Å from those obtained via crystallographic measurements,\(^ {26}\) (ii) for the neutral singlet \( A_g \) state of TCNQ the SCF/aug(sp)-cc-pVZD valence angles differ by less than 0.4° from those obtained experimentally (X-ray),\(^ {26}\) (iii) for the ground doublet \( B_2g \) state of TCNQ the SCF/aug(sp)-cc-pVZD bond lengths differ by less than 0.010 Å from those obtained experimentally (X-ray),\(^ {27}\) and (iv) for the ground doublet \( B_2g \) state of TCNQ the SCF/aug(sp)-cc-pVZD valence angles differ by less than 0.8° from X-ray.\(^ {27}\)

In addition, we compared an X-ray structure\(^ {28}\) of the neutral TCNQ-F4 to our SCF/aug(sp)-cc-pVZD optimized ground-state geometry; see Table 1. We found that the differences in the bond lengths never exceed 0.04 Å and the largest shift is for the C–F bond (the corresponding X-ray estimated bond length is shorter by 0.032 Å than our value). As far as the valence angles are concerned, the differences never exceed 0.7° and the largest change we observe for the C–C–N angle (0.62°).

To test the ability of the SCF/aug(sp)-cc-pVZD treatment to reproduce excited-state anionic equilibrium geometries, we calculated the SCF/aug(sp)-cc-pVZD equilibrium geometry of the lowest excited doublet anionic state of TCNQ (possessing \( B_n \) symmetry) and we compared our results to those reported by Skurski and Gutowski\(^ {15}\) obtained at the CI/PM3 level. We did this because (i) an experimental doublet \( B_n \) excited-state TCNQ- geometry is not available and (ii) the CI/PM3 treatment has proven useful in reproducing the ground and excited-state geometries of the TCNQ/TCNQ-.\(^ {15}\) We found that (i) for the lowest excited doublet \( B_n \) state of TCNQ-, the SCF/aug(sp)-cc-pVZD bond lengths differ by less than 0.036 Å from those calculated at the CI/PM3 level\(^ {15}\) and (ii) for the lowest doublet excited \( B_n \) state of TCNQ- the SCF/aug(sp)-cc-pVZD valence angles differ by less than 0.4° from those calculated at the CI/PM3 level.

To test the ability of the SCF/aug(sp)-cc-pVZD treatment to reproduce ground-state neutral and anionic harmonic frequencies, we compared such calculated vibrational modes to the frequencies obtained experimentally and available in the literature.\(^ {29}\) We conclude that (i) the largest shift for the neutral TCNQ-F4 is 383 cm\(^ {-1} \) for the stiffest \( B_{2g} \) symmetry mode (when unscaled SCF/aug(sp)-cc-pVZD frequencies are used), (ii) the largest shift for the anionic TCNQ-F4 is 220 cm\(^ {-1} \) for the stiffest
Table 1: Geometrical Parameters of Neutral TCNQ-F4 in Its Lowest Singlet State and TCNQ-F4 in Its Ground Doublet $B_{2g}$ State and Excited $A_u$, $A_1$, and $B_2$ States

<table>
<thead>
<tr>
<th>species state (symmetry)</th>
<th>neutral $A_g$ ($D_{2h}$)</th>
<th>anion $B_{2g}$ ($D_{2h}$)</th>
<th>anion $A_1$ ($B_{2g}$ ($D_{2h}$))</th>
<th>anion $A_1$ ($B_{2g}$ ($C_{2h}$))</th>
<th>anion $A_1$ ($B_{2g}$ ($C_{2h}$))</th>
<th>anion $A_1$ ($B_{2g}$ ($C_{2h}$))</th>
<th>anion $A_1$ ($B_{2g}$ ($C_{2h}$))</th>
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<tbody>
<tr>
<td>bond lengths ($\text{R}_{\text{b}}$) (Å)</td>
<td>$r_{\text{C-C}}$, $r_{\text{C-N}}$</td>
<td>$r_{\text{C-C}}$, $r_{\text{C-N}}$</td>
<td>$r_{\text{C-C}}$, $r_{\text{C-N}}$</td>
<td>$r_{\text{C-C}}$, $r_{\text{C-N}}$</td>
<td>$r_{\text{C-C}}$, $r_{\text{C-N}}$</td>
<td>$r_{\text{C-C}}$, $r_{\text{C-N}}$</td>
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<td>$C_1$-$C_7$</td>
<td>1.351 (1.372)</td>
<td>1.312 (1.334)</td>
<td>1.342 (1.347)</td>
<td>1.342 (1.347)</td>
<td>1.342 (1.347)</td>
<td>1.342 (1.347)</td>
<td>1.342 (1.347)</td>
</tr>
<tr>
<td>$C_2$-$C_3$</td>
<td>1.328 (1.338)</td>
<td>1.334 (1.338)</td>
<td>1.334 (1.338)</td>
<td>1.334 (1.338)</td>
<td>1.334 (1.338)</td>
<td>1.334 (1.338)</td>
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<tr>
<td>$C_9$-$N_{13}$</td>
<td>1.136 (1.142)</td>
<td>1.136 (1.142)</td>
<td>1.136 (1.142)</td>
<td>1.136 (1.142)</td>
<td>1.136 (1.142)</td>
<td>1.136 (1.142)</td>
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<td>$C_1$-$C_2$</td>
<td>1.422 (1.422)</td>
<td>1.422 (1.422)</td>
<td>1.422 (1.422)</td>
<td>1.422 (1.422)</td>
<td>1.422 (1.422)</td>
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<tr>
<td>$C_1$-$C_7$</td>
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<td>1.412 (1.412)</td>
<td>1.412 (1.412)</td>
<td>1.412 (1.412)</td>
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<td>1.430 (1.430)</td>
<td>1.430 (1.430)</td>
<td>1.430 (1.430)</td>
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<tr>
<td>$C_9$-$N_{13}$</td>
<td>1.144 (1.144)</td>
<td>1.144 (1.144)</td>
<td>1.144 (1.144)</td>
<td>1.144 (1.144)</td>
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<tr>
<td>$C_1$-$C_7$-$C_9$</td>
<td>123.12 (123.53)</td>
<td>123.12 (123.53)</td>
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</tr>
<tr>
<td>$C_2$-$F_{17}$-$C_3$</td>
<td>117.98 (117.98)</td>
<td>117.98 (117.98)</td>
<td>117.98 (117.98)</td>
<td>117.98 (117.98)</td>
<td>117.98 (117.98)</td>
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<tr>
<td>$C_3$-$F_{18}$-$C_2$-$C_1$</td>
<td>111.81 (111.81)</td>
<td>111.81 (111.81)</td>
<td>111.81 (111.81)</td>
<td>111.81 (111.81)</td>
<td>111.81 (111.81)</td>
<td>111.81 (111.81)</td>
<td>111.81 (111.81)</td>
</tr>
<tr>
<td>$C_1$-$C_7$-$C_9$-$N_{13}$</td>
<td>149.65 (149.65)</td>
<td>149.65 (149.65)</td>
<td>149.65 (149.65)</td>
<td>149.65 (149.65)</td>
<td>149.65 (149.65)</td>
<td>149.65 (149.65)</td>
<td>149.65 (149.65)</td>
</tr>
</tbody>
</table>

a Experimental parameters are given in parentheses.
when the $1^2B_{2g}$ anion is formed. Indeed, the largest shortening in the bond length upon attachment of an excess electron is for the $C_1$–$C_2$ bond (by 0.041 Å) and the largest elongation is observed for the $C_1$–$C_7$ bond (by 0.061 Å); see Table 1. The changes of the valence angles upon excess electron attachment are relatively small, and we found the largest difference for the $C_2$–$C_3$–$F_{17}$ angle ($+1.56^\circ$) whereas other differences do not exceed $1^\circ$ (see Table 1).

To assist in possible experimental identification of the states of this anion, in Table 2 we give the scaled (by 0.8929) SCF/aug(sp)-pVDZ harmonic vibrational frequencies for the $1^1A_g$ neutral and $1^2B_{2g}$ anion (together with the frequencies calculated for three other excited anionic states that are described in further sections). As shown in Table 2, the frequencies of the stiff modes usually decrease upon electron attachment. In particular, this tendency manifests itself especially for $b_{1u}$, $b_{2u}$, $b_{3g}$, and $a_g$ symmetry modes and the largest shifts we observe for $v_{11}$ ($b_{2g}$) ($-205 \text{ cm}^{-1}$), $v_{40}$ ($b_{2u}$) ($-204 \text{ cm}^{-1}$), $v_{40}$ ($b_{1u}$) ($-168 \text{ cm}^{-1}$), and $v_{10}$ ($a_g$) ($-162 \text{ cm}^{-1}$).

3.2. Excited Anionic States of TCNQ-F4. Because a primary goal was to investigate the stability of excited electronic states of anionic TCNQ-F4, we considered two paths leading to such anions. While studying both, we assumed the ground electronic state of the anion (i.e., the $1^2B_{2g}$ state, possessing $4b_{2g}^1$ configuration) to be the starting point. The states of the “first kind” are the result of promoting an electron from the singly occupied $4b_{2g}$ orbital to low-lying virtual orbitals. In particular, this leads to two valence-excited anionic states: a $1^2A_g$ state ($4b_{2u}^14b_{2g}^17a_d^1$) in which the LUMO+1 of the neutral is singly occupied, and a $2^2B_{3u}$ state ($4b_{2u}^14b_{2g}^15b_{3u}^1$) in which the LUMO+2 of the neutral is singly occupied. These states are called valence-excited because they are derived from the ground anionic state $1^2B_{2g}$ ($4b_{2u}^14b_{2g}^17a_d^15b_{3u}^0$) by exciting an electron from the valence $b_{2g}$ orbital to one of the higher energy virtual orbitals.

Another possibility of forming an excited anionic state involves excitation of one of the electrons from a doubly occupied orbital. In our case this led to two states: a $1^2B_{3u}$ state ($3b_{1g}^14b_{2u}^14b_{2g}^2$) and a $1^2B_{1g}$ state ($3b_{1g}^14b_{2u}^14b_{2g}^2$). We consider these as core-excited states because they were formed by promoting an electron in the ground $1^2B_{1g}$ state from a doubly occupied orbital (either $3b_{1g}$ or $4b_{3u}$) to the $4b_{2g}$ orbital (which is the LUMO in the neutral). This leads to a state in which the $4b_{2g}$ orbital is doubly occupied and one of the “core” orbitals (i.e., either $3b_{1g}$ or $4b_{3u}$) becomes singly occupied and thus determines the symmetry.

3.2.1. Excess Electron Binding by the Neutral TCNQ-F4 at Its Minimum-Energy Structure. First we consider the electronic stability of such excited anionic states at the $D_{2h}$ minimum-energy structure of the parent neutral species. The calculated vertical electron binding energies at this geometry correspond to vertical electron attachment energies (VAEs) and describe the propensity of forming anionic states by the neutral TCNQ-F4 in its most stable conformation. Our MP4 results
indicate that four stable anionic states can be created (Table 3), (i) the ground state of the anion 1^2B_2g (4b_u - 4b_d, 4b_g) whose VAE is 2.893 eV; (ii) the core-excited 1^3B_3u state (3b_1g - 4b_u, 4b_d, 4b_g) with vertical electron attachment energy of 0.822 eV; (iii) the valence-excited 2^1B_3u state (4b_u - 4b_d, 4b_g) whose VAE = 0.244 eV; (iv) the valence-excited 1^2A_g state (4b_u - 4b_d, 4b_g) whose VAE is small but positive (0.072 eV). The core-excited 1^2B_1g state (3b_1g - 4b_u, 4b_d, 4b_g) as well as the other (higher) valence-excited anionic states (such as 1^2B_1u) were found to be unstable (at the MP4 level) with respect to electron loss.

It should also be noted that the corresponding MP2 vertical electron attachment energies given in Table 3 are larger than those obtained at the MP4 level for each state but 1^2A_g. In particular, the VAE values calculated at the MP2 level differ by +0.041, +0.328, +0.175, and -0.034 eV, for 1^2B_2g, 1^3B_3u, 2^1B_3u, and 1^2A_g, respectively. Because the VAEs seem somewhat overestimated when calculated at the MP2 level with respect to those obtained at the fourth-order MP perturbation theory, we believe that there should be no other anionic states electronically stable except those that have proven stable at the MP4 level.

### 3.2.2. Valence-Excited Anionic States of TCNQ-F4 and Their Geometric Stability

We search for electronically stable anionic states at the D_2h minimum energy structure of the neutral TCNQ-F4 led to the conclusion that there are four stable doublet states of TCNQ-F4^-.

<table>
<thead>
<tr>
<th>state (configuration)</th>
<th>description</th>
<th>VAE^{MP1}</th>
<th>VAE^{MP2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1^2B_2g (3b_1g - 4b_u, 4b_d, 4b_g)</td>
<td>core-excited</td>
<td>&lt;0</td>
<td>&lt;0</td>
</tr>
<tr>
<td>1^2A_g (4b_u - 4b_d, 4b_g)</td>
<td>externally exc</td>
<td>0.072</td>
<td>0.038</td>
</tr>
<tr>
<td>2^1B_3u (4b_u - 4b_d, 4b_g)</td>
<td>externally exc</td>
<td>0.244</td>
<td>0.419</td>
</tr>
<tr>
<td>1^3B_3u (3b_1g - 4b_u, 4b_d, 4b_g)</td>
<td>core-excited</td>
<td>0.822</td>
<td>1.150</td>
</tr>
<tr>
<td>1^2A_g (4b_u - 4b_d, 4b_g)</td>
<td>ground</td>
<td>2.893</td>
<td>3.294</td>
</tr>
</tbody>
</table>


table 2: Scaled (by 0.8929) Harmonic Vibrational Frequencies (cm^-1) of TCNQ-F4 in the Lowest Singlet State and TCNQ-F4^- in the Low-Lying Doublet Electronic States Calculated at the Hartree–Fock Level with the aug(sp)-cc-pVDZ Basis Sets*  

<table>
<thead>
<tr>
<th>1^1A_g</th>
<th>1^2B_2g</th>
<th>1^2A_g(1^2B_3u)</th>
<th>1^2A_g(1^2B_3u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v_1 (a)</td>
<td>136</td>
<td>1418</td>
<td>138</td>
</tr>
<tr>
<td>v_2 (a)</td>
<td>289</td>
<td>1498</td>
<td>290</td>
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<tr>
<td>v_3 (a)</td>
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<td>2219</td>
<td>329</td>
</tr>
<tr>
<td>v_4 (a)</td>
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<td>471</td>
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<tr>
<td>v_5 (a)</td>
<td>620</td>
<td>619</td>
<td>629</td>
</tr>
<tr>
<td>v_6 (a)</td>
<td>620</td>
<td>(618)</td>
<td>620</td>
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<tr>
<td>v_10 (a)</td>
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<td>780</td>
<td>852</td>
</tr>
<tr>
<td>v_11 (a)</td>
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<td>1093</td>
<td>1244</td>
</tr>
<tr>
<td>v_15 (a)</td>
<td>1567</td>
<td>1315</td>
<td>1432</td>
</tr>
<tr>
<td>v_19 (a)</td>
<td>1728</td>
<td>1607</td>
<td>1664</td>
</tr>
<tr>
<td>v_20 (a)</td>
<td>2227</td>
<td>2323</td>
<td>2160</td>
</tr>
<tr>
<td>v_22 (a)</td>
<td>43</td>
<td>102</td>
<td>21</td>
</tr>
<tr>
<td>v_13 (a)</td>
<td>125</td>
<td>251</td>
<td>127</td>
</tr>
<tr>
<td>v_14 (a)</td>
<td>421</td>
<td>322</td>
<td>441</td>
</tr>
<tr>
<td>v_15 (a)</td>
<td>635</td>
<td>465</td>
<td>644</td>
</tr>
<tr>
<td>v_16 (a)</td>
<td>50</td>
<td>465</td>
<td>24</td>
</tr>
<tr>
<td>v_17 (a)</td>
<td>372</td>
<td>330</td>
<td>397</td>
</tr>
<tr>
<td>v_18 (a)</td>
<td>454</td>
<td>945</td>
<td>448</td>
</tr>
<tr>
<td>v_19 (a)</td>
<td>454</td>
<td>945</td>
<td>448</td>
</tr>
<tr>
<td>v_20 (a)</td>
<td>421</td>
<td>92</td>
<td>22</td>
</tr>
<tr>
<td>v_22 (a)</td>
<td>753</td>
<td>159</td>
<td>750</td>
</tr>
<tr>
<td>v_23 (a)</td>
<td>1098</td>
<td>257</td>
<td>1080</td>
</tr>
<tr>
<td>v_29 (a)</td>
<td>1153</td>
<td>587</td>
<td>1143</td>
</tr>
<tr>
<td>v_25 (a)</td>
<td>54 (b)</td>
<td>662</td>
<td></td>
</tr>
<tr>
<td>v_26 (a)</td>
<td>54 (b)</td>
<td>662</td>
<td></td>
</tr>
<tr>
<td>v_27 (a)</td>
<td>54 (b)</td>
<td>662</td>
<td></td>
</tr>
<tr>
<td>v_28 (a)</td>
<td>54 (b)</td>
<td>662</td>
<td></td>
</tr>
<tr>
<td>v_29 (a)</td>
<td>54 (b)</td>
<td>662</td>
<td></td>
</tr>
</tbody>
</table>

* Experimental frequencies are given in parentheses.  

TABLE 3: Vertical (at the Neutral’s Equilibrium Geometry) Electron Attachment Energies (VAE, eV) of TCNQ-F4 Corresponding to the Ground and Various Excited States of the Anion Calculated at the MP2, and MP4 Levels with the aug(sp)-cc-pVDZ Basis Sets  

<table>
<thead>
<tr>
<th>state (configuration)</th>
<th>description</th>
<th>VAE^{MP1}</th>
<th>VAE^{MP2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1^2B_2g (3b_1g - 4b_u, 4b_d, 4b_g)</td>
<td>core-excited</td>
<td>&lt;0</td>
<td>&lt;0</td>
</tr>
<tr>
<td>1^2A_g (4b_u - 4b_d, 4b_g)</td>
<td>externally exc</td>
<td>0.072</td>
<td>0.038</td>
</tr>
<tr>
<td>2^1B_3u (4b_u - 4b_d, 4b_g)</td>
<td>externally exc</td>
<td>0.244</td>
<td>0.419</td>
</tr>
<tr>
<td>1^3B_3u (3b_1g - 4b_u, 4b_d, 4b_g)</td>
<td>core-excited</td>
<td>0.822</td>
<td>1.150</td>
</tr>
<tr>
<td>1^2A_g (4b_u - 4b_d, 4b_g)</td>
<td>ground</td>
<td>2.893</td>
<td>3.294</td>
</tr>
</tbody>
</table>

...
The equilibrium geometry of this $1^2A$ state is far from planarity. Instead, the structure is strongly bent (see Figure 2 and the right bottom structure in Figure 4). Both $-\text{C(CN)}_2$ groups point in the same direction whereas all four fluorine atoms are directed to the opposite side of the carbon ring (see Table 1 for precise values of geometrical parameters). The vertical electron binding energy of this $1^2A$ state increases when the equilibrium geometry for this anion is achieved, and our best estimate of the VDE at the MP2 level is 2.721 eV; see Table 4. Therefore, we conclude that the $2^2B_{3u}$ anionic state, characterized by VAE_{MP2} = 0.244 eV at the equilibrium $D_{2h}$ geometry of the neutral TCNQ-F4, evolves to a much more electronically stable species at its minimum-energy structure, and the driving force of this geometry deformation is the second-order Jahn–Teller coupling to another excited state of $A_g$ symmetry.

B. Valence-Excited $1^2A_g$ State of TCNQ-F4\(^-\). The other valence-excited anionic doublet state ($1^2A_g$) would be expected to increase in energy while the geometry of this species is deformed along the distortion mode that couples it to the $2^2B_{3u}$ state. This is because the $2^2B_{3u}$ and $1^2A_g$ states avoid each other, and the former’s energy decreases whereas the latter’s energy increase along the distortion in the coupling mode takes place. Unfortunately, unlike for the $2^2B_{3u}$ state, we were not able to follow the $1^2A_g$ state that moves uphill in energy because it evolves into a doublet $A_1$ state (in the $C_{2v}$ symmetry group) as does the $2^2B_{3u}$ state. As a consequence, our attempts to investigate the evolution of that state failed because the SCF procedure we used always converged to the lowest $2^2A_1$ state (corresponding to $2^2B_{3u}$), which is the lowest energy state of that symmetry. We conclude that a multiconfigurational treatment would be necessary if one wants to describe the evolution of the $1^2A_g$ state. However, employing such a treatment for the open-shell system containing twenty heavy atoms (as TCNQ-F4 does) with the aug(sp)-cc-pVDZ basis sets was not practical for us with the computer resources at hand, so we were unable to further explore this particular state.

3.2.3. Core-Excited Anionic States of TCNQ-F4\(^-\). In this section we discuss the core-excited doublet anionic states of $1^2B_{3u}$ and $1^2B_{1g}$ symmetry. As was the case for the two bound valence-excited states described in the previous section, we found these anions to be geometrically unstable at $D_{2h}$ symmetry.

A. Core-Excited $1^2B_{3u}$ State of TCNQ-F4\(^-\). Although the $1^2B_{3u}$ state is characterized by a relatively large value of the vertical electron binding energy calculated for the minimum-energy structure of the neutral (VDE_{MP2} = 0.822 eV), its minimum-energy structure preserving $D_{2h}$ symmetry possesses an imaginary frequency of $b_{2h}$ symmetry. The fact that another valence-excited state ($1^2A_g$) state is close in energy (see Table 3) causes second-order Jahn–Teller instability, which manifests itself as negative curvature along the $b_{2h}$ symmetry mode. We then proceeded in our search for a geometrically stable anionic state by deforming the planar $D_{2h}$ symmetry of the $2^2B_{3u}$ anion along the imaginary mode of $b_{2h}$ symmetry (see Figure 4). This led to lowering of the symmetry (to $C_{2v}$) of the molecule and the singly occupied $b_{2h}$ orbital became an $a_1$ orbital in the final $C_{2v}$ point group. As can be seen in Figure 4, the molecule became nonplanar and especially the $-\text{C(CN)}_2$ groups bent with respect to the carbon ring. Although the geometry optimization procedure led to a stationary point on the potential energy surface, vibrational analysis indicated an imaginary frequency of $a_2$ symmetry. We consequently deformed the geometry along that negative curvature, subsequently achieving a $C_2$ symmetry structure. For this symmetry, the $a_1$ singly occupied orbital became an $a$-symmetry orbital (because it is even with respect to the rotation around the $C_2$ axis). Geometry optimization performed in the $C_2$ group led eventually to a true minimum on the potential energy surface and the corresponding harmonic vibrational frequencies for this final doublet $A$ state (termed $1^2A$) are given in Table 2.

### Table 4: Vertical Electron Detachment Energies (VDE, eV) of TCNQ-F4\(^-\) Corresponding to the Ground and Various Excited States of the Anion Calculated at the MP2 Level with the aug(sp)-cc-pVDZ Basis Sets

<table>
<thead>
<tr>
<th>Final state (original state)</th>
<th>description</th>
<th>VDE_{MP2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^2B_1$ ($1^2B_{1u}$)</td>
<td>core-excited</td>
<td>&lt;0</td>
</tr>
<tr>
<td>$1^2A$ ($2^2B_{3u}$)</td>
<td>externally exc.</td>
<td>2.721</td>
</tr>
<tr>
<td>$1^2A_g$ ($1^2B_{3u}$)</td>
<td>core-excited</td>
<td>&lt;0</td>
</tr>
<tr>
<td>$1^2B_{2g}$ ($1^2B_{2g}$)</td>
<td>ground</td>
<td>3.665</td>
</tr>
</tbody>
</table>

Figure 4. “Evolution” of the singly occupied molecular orbital in the $2^2B_{3u}$ anionic state caused by second-order Jahn–Teller effects leading to the $1^2A$ anionic state.
Electronic States of the Anion of TCNQ-F4

The equilibrium geometry achieved for the anion in its $1^2A_u$ state is depicted in Figure 2, and the geometrical parameters are collected in Table 1. It can be seen that the $1^2A_u$ anionic structure differs from the structures obtained for other anionic states primarily because the two C(CN)$_2$ groups remain in one plane although they are twisted with respect to the carbon ring.

Although the SCF vertical electron binding energy of the $1^2B_{3u}$ state increases when the equilibrium geometry for this anion is achieved, we verified that the inclusion of electron correlation renders this anion electronically unstable (i.e., the calculated value of the VDE at the MP2 level is negative). Therefore, we conclude that the core-excited $1^2B_{3u}$ anionic state, although electronically unstable with respect to the neutral molecule at its $D_{2h}$ minimum energy structure, even though we spent considerable effort searching for a geometry at which the $1^2B_{3u}$ state would be electronically stable, we were not able to find any. In particular, we verified that the $1^2B_{3u}$ state lowers its energy if deformed along the $a_u$ imaginary mode (achieving $D_2h$ symmetry) but the energy decrease is not large enough to render this anion electronically stable. Moreover, our attempts to form other bound core-excited states of the anion failed; thus we are reasonably confident the $1^2B_{3u}$ (becoming eventually $1^2A_u$) core-excited state is the only such state that is stable with respect to the neutral parent molecule, although its electronic stability should be confirmed by higher-level calculations (see section 3.2.3.A).

4. Summary

The ground and bound excited anionic states of the common electron acceptor TCNQ-F4 were studied at the SCF, MP2, and MP4 levels of theory with the one-electron aug(sp)-cc-pVDZ basis sets. On the basis of our calculations we conclude that the ground electronic state of TCNQ-F$^-$ is the $1^2B_{3g}$ state (4b$_{3u}$ 4b$_{2g}$ 1) whose MP4 vertical electron attachment energy is 2.893 eV. This state possesses its minimum for $D_{2h}$ symmetry.

There are three excited anionic states of TCNQ-F4 that are vertically electronically stable at the $D_{2h}$ minimum energy structure of the neutral system. These are the core-excited $1^2B_{3u}$ state (3b$_{1g}$ 4b$_{3u}$ 4b$_{2g}$ 2), the valence-excited $2^2B_{3u}$ state (4b$_{3u}$ 4b$_{2g}$ 5b$_{3u}$ 0), and the valence-excited $1^2A_g$ state (4b$_{3u}$ 4b$_{2g}$ 0 17a$_g$ 1), whose MP4 vertical electron attachment energies are 0.822, 0.244, and 0.072 eV, respectively (see also Figure 6 where the SCF electron affinities of these anions are depicted).

Although the ground anionic $1^2B_{3g}$ state is geometrically stable at the $D_{2h}$ symmetry, the other excited states are second-order Jahn–Teller unstable, which leads to the symmetry lowering for these species. As a consequence, the geometries of two $2^2B_{3u}$ and $1^2A_g$ valence-excited states deform and the former achieves a bent $C_2$ symmetry. However, the SCF vertical electron detachment energy of the resulting $1^2A_g$ state estimated to be 2.721 eV at the MP2 level. The energy of the $1^2A_g$ state could not be followed to its minimum-energy structure because of variational collapse. The structure of the core-excited $1^2B_{3u}$ anion deforms to $C_{2v}$ symmetry, but this state was found to be electronically unstable when electron correlation is taken into account at the MP2 level. We believe that more sophisticated calculations are necessary to test the electronic stability of this particular state.

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References and Notes