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Communication: Vibrationally resolved photoelectron spectroscopy of the tetracyanoquinodimethane (TCNQ) anion and accurate determination of the electron affinity of TCNQ

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Tetracyanoquinodimethane (TCNQ) is widely used as an electron acceptor to form highly conducting organic charge-transfer solids. Surprisingly, the electron affinity (EA) of TCNQ is not well known and has never been directly measured. Here, we report vibrationally resolved photoelectron spectroscopy (PES) of the TCNQ⁻ anion produced using electrospray and cooled in a cryogenic ion trap. Photoelectron spectrum taken at 354.7 nm represents the detachment transition from the ground state of TCNQ⁻ to that of neutral TCNQ with a short vibrational progression. The EA of TCNQ is measured accurately to be 3.383 ± 0.001 eV (27 289 \pm 8 cm⁻¹), compared to the 2.8 ± 0.1 eV value known in the literature and measured previously using collisional ionization technique. In addition, six vibrational peaks are observed in the photoelectron spectrum, yielding vibrational frequencies for three totally symmetric modes of TCNQ. Two-photon PES via a bound electronic excited state of TCNQ⁻ at 3.100 eV yields a broad low kinetic energy peak due to fast internal conversion to vibrationally excited levels of the anion ground electronic state. The high EA measured for TCNQ underlies its ability as a good electron acceptor. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4937761]

Tetracyanoquinodimethane (TCNQ, Fig. 1(a)) is one of the best electron acceptors to form charge-transfer conducting organic solids.¹⁻⁴ The electronic and structural properties of TCNQ and its anion (TCNQ⁻) have been studied quite extensively both experimentally and theoretically.^{5–19} TCNQ possesses a high electron affinity (EA) due to the presence of the highly electron-withdrawing CN groups (Fig. 1(a)). The EA of TCNQ was first measured as 2.8 ± 0.1 eV by Compton and co-workers using collisional ionization between Cs and TCNQ to form Cs⁺ + TCNQ⁻.⁵ A later study by Compton and Cooper refined the EA of TCNQ to be 2.8 + 0.05/-0.3 eV⁶ but the EA value has been usually cited in the literature as 2.8 ± 0.1 eV for TCNQ. Brauman and co-workers measured the photodetachment spectrum of TCNQ⁻ in an ion cyclotron resonance mass spectrometer in the wavelength range of 350–1060 nm.⁷ They observed two resonant bands: a low-energy broad resonance between 600 and 1000 nm (2.1-1.2 eV) and another resonance between 360 and 470 nm (3.4–2.6 eV). These two resonances, corresponding to transitions to two electronic excited states of TCNQ⁻, were found to be very similar to electronic absorption spectrum of TCNQ- in solution.⁸ However, no EA was measured from the photodetachment spectrum. More recently, Verlet and co-workers examined the ultrafast relaxation dynamics of the first excited state of gaseous TCNQ⁻ and also reported the photoelectron spectrum of TCNQ⁻ at a photon energy of 3.1 eV.¹⁰ Two bands were observed in their photoelectron spectrum, a narrower band centered at a photoelectron kinetic energy (KE) of 0.2 eV and a broad band centered at a kinetic energy of 2 eV. The narrower band was interpreted to be due to a one-photon detachment (resonant absorption followed by autodetachment to the ground state of neutral TCNQ), yielding an EA of 2.9 eV, which was considered to be in good agreement with the previous value of 2.8 ± 0.1 eV.

The EA of TCNQ has been calculated in several theoretical studies. Ortiz and co-workers obtained an EA of 2.74 eV using an electron propagator method.¹³ Skurski and Gutowski gave a range of EA between 2.76 and 2.95 eV at the configuration interaction (CI/PM3) level.¹⁵ These computed EAs were considered to be in good agreement with the available experimental EA of 2.8 ± 0.1 eV. More recently, Milian et al. computed the EA of TCNQ using the higherlevel couple-cluster method [CCSD(T)] and obtained an EA of 3.22 eV, which was overestimated by 0.4 eV relative to the 2.8 eV experimental value.¹⁸ However, the authors showed that the same theoretical method tended to underestimate the EAs by 0.1–0.2 eV for similar compounds. This discrepancy made the authors skeptical about the previously measured EA for TCNQ and prompted them to call for additional measurement. Very recently, Nakashima et al. computed an EA of 3.31 eV for TCNQ using the symmetry adapted cluster configuration interaction method.¹⁹

In the current communication, we report vibrationally resolved photoelectron spectroscopy (PES) of TCNQ⁻ using photoelectron imaging at 354.7 nm. The 354.7 nm photoelectron spectrum represented detachment transition from the ground state of TCNQ⁻ to that of neutral TCNQ with a short vibrational progression consisting of seven resolved vibrational peaks. The EA of TCNQ was measured directly and accurately to be 3.383 ± 0.001 eV from the 0-0 vibrational transition. In addition, vibrational frequencies for three totally

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FIG. 1. (a) The molecular structure of TCNQ; (b) a photoelectron image of TCNQ⁻ at 354.7 nm after inver-Abel transformation. The arrows indicate the laser polarization. (c) the photoelectron spectrum of TCNQ⁻ obtained by summing up several images and integrating the images azimuthally. See Table I for the binding energies of the observed vibrational peaks and their assignments. The 0-0 peak at 27289 cm^{-1} (3.383 eV) defines the electron affinity of TCNQ.

symmetric vibrational modes were obtained for TCNQ, v_1 (114 cm⁻¹), v_2 (331 cm⁻¹), and v_4 (709 cm⁻¹). A photoelectron spectrum was also obtained at 3.100 eV, in resonance with the second excited state of TCNQ⁻, as a result of two-photon detachment, following fast internal conversion.

The experiment was done using our recently developed high-resolution photoelectron imaging apparatus,²⁰ which consists of an electrospray ionization (ESI) source,²¹ a cryogenic ion trap,²² a time-of-flight (TOF) mass spectrometer, and a high-resolution velocity-map imaging (VMI) analyzer.²³ Briefly, the TCNQ⁻ anions were produced by electrospray of a 1 mM solution of TCNQ (Sigma-Aldrich) dissolved in acetonitrile and spiked with a small amount of NaI. Two radio-frequency (RF) quadrupole ion guides and one RF octopole ion guide directed the anions from the ESI source into a cryogenically cooled Paul trap operated at 4.5 K. The stored anions were cooled via collisions with 1 mTorr He/H₂ (4/1 in volume) buffer gas. The cooled anions were pulsed out of the trap at a 10 Hz repetition rate and analyzed by a 2.5 m long TOF mass spectrometer. The TCNQ anions with m/z = 204 were selected by a mass gate before being detached in the interaction zone by either a Nd:YAG laser (354.7 nm or 3.496 eV) or a dye laser operated at 400.0 nm (3.100 eV). Photoelectrons were accelerated out of the interaction zone and projected onto a position-sensitive micro-channel plate detector coupled to a phosphor screen and captured by a charge-coupled device camera. The recorded photoelectron images were inverse-Abel transformed and reconstructed using the pBasex²⁴ and BASEX²⁵ programs. The photoelectron spectra were calibrated with the known spectra of Au⁻ at different photon energies. The KE resolution achieved was 3.8 cm⁻¹ for electrons with 55 cm⁻¹ KE and about 1.5% (Δ KE/KE) for KE above 1 eV.

Fig. 1(b) shows a photoelectron image of TCNQ⁻ at 354.7 nm after the inverse-Abel transformation using pBasex. Integrating the signals azimuthally resulted in the regular photoelectron spectrum shown in Fig. 1(c), which was obtained by adding several images to enhance the signal-tonoise ratios. This spectrum represents detachment transitions from the ground electronic and vibrational state of TCNQ⁻ to the ground electronic state of neutral TCNQ. The binding energies (BEs) of the seven observed peaks are given in Table I, along with their assignments. The peaks correspond to the vibrational levels of neutral TCNQ. The short vibrational progression suggests that there is little geometry change between the anion and neutral TCNQ. The first and most intense peak at 27 289 cm⁻¹ (3.383 eV) corresponds to the 0-0 transition and defines accurately the EA of TCNQ. We note that the most recently computed EAs for TCNQ, 3.22 eV by Milian et al.¹⁸ and 3.31 eV by Nakashima et al.,¹⁹ are in good agreement with the current measurement.

To help assign the vibrational peaks, we computed the vibrational frequencies of TCNQ using density functional theory at the B3LYP/6-31+G(d, p) level, as given in Table S1 of the supplementary material.²⁶ Since both TCNQ and its anion are planar with D_{2h} symmetry, only totally symmetric modes are allowed. Peak *a* represents a vibrational spacing of 114 cm⁻¹ (Table I) which is in good agreement with the calculated frequency of the v₁ mode (118 cm⁻¹). Peak *b* represents the mode with the strongest Franck-Condon factors and the vibrational spacing of 331 cm⁻¹ (Table I) agrees well with the calculated frequency of the v₂ mode (334 cm⁻¹). As shown in Table I, peak *d* represents the first overtone of the v₂ mode, whereas peaks *c* and *f* are combination modes of v₂ and v₁. Peak *e* with a spacing of 709 cm⁻¹ from the vibrational ground state is in good agreement with the

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TABLE I. The measured binding energies (BEs) of the vibrational peaks in the photoelectron spectrum of $TCNQ^-$, their shifts relative to the neutral vibrational ground state (0-0), compared with the computed vibrational frequencies (v_{theo}) for TCNQ and the assignments.

Observed peaks	BE (cm ⁻¹) ^a	Shift (cm ⁻¹)	$\nu_{theo} \left(cm^{-1} \right)^{b}$	Assignment
0-0	27 289(8)	0		
а	27 403(8)	114	118 (v ₁)	ν_1
b	27 620(8)	331	334 (v ₂)	v_2
с	27739(8)	450		$v_2 + v_1$
d	27 952(9)	663		$2v_2$
е	27 998(9)	709	725 (v ₄)	ν_4
f	28 079(10)	790		$2v_2 + v_1$

^aThe number in the parenthesis represents the uncertainty in the last digits.

^bSee Table S1 for the full list of the computed vibrational frequencies and Fig. S1 for the normal modes of the observed frequencies.²⁶

computed frequency of the v_4 mode (725 cm⁻¹). The normal modes of the three observed vibrational frequencies are shown in Fig. S1.²⁶

The highest occupied molecular orbital (HOMO) of TCNQ is a π orbital of b_{3u} symmetry. The lowest unoccupied molecular orbital (LUMO), where the extra electron resides in TCNQ⁻, is an antibonding π^* orbital of b_{2g} symmetry. The LUMO+1 orbital is also of b_{3u} symmetry. The ground state of TCNQ⁻ is ${}^{2}B_{2g}$ with an electron configuration of $3b_{3u}^2 3b_{2g}^1 4b_{3u}^0$. The photoelectron image shown in Fig. 1(b) exhibited an isotropic distribution with a β parameter close to zero, in agreement with detachment of a π electron from the $\pi^* 3b_{2g}$ orbital. The first electronic excited state (1^2B_{3u}) of TCNQ⁻, observed between 600 and 1000 nm (2.1–1.2 eV),⁷ corresponds to excitation of an electron from the HOMO to the LUMO with an electron configuration of $3b_{3u}^{1}3b_{2g}^{2}4b_{3u}^{0}$, whereas the second excited state (2^2B_{3u}) , observed between 360 and 470 nm (3.4-2.6 eV), corresponds to excitation of the electron in the LUMO to LUMO + 1 with an electron configuration of $3b_{3u}^2 3b_{2g}^0 4b_{3u}^1$. Our measured EA of TCNQ indicates that the two excited states of TCNQ- are both bound states, as schematically shown in Fig. 2. Thus, a single photon absorption to the second excited state (2²B_{3u}) of TCNQ⁻ would



FIG. 2. Schematic energy levels for TCNQ⁻ and TCNQ, showing the resonant excitation using a 400.0 nm (3.100 eV) photon to the 2^2B_{3u} excited state of TCNQ⁻, followed by fast internal conversion to the vibrational levels of the TCNQ⁻ ground electronic state, as well as the detachment by a second photon off the vibrationally excited TCNQ⁻ to yield the spectrum in Fig. 3.

be impossible to induce electron detachment, as reported by Verlet and co-workers at a photon energy of 3.1 eV.¹⁰

We have recently observed a bound excited state for AuS⁻ and observed vibrational level-dependent photoelectron spectra via resonant two-photon detachment.²⁷ We tried to carry out a similar experiment using a photon energy of 3.100 eV (400.0 nm), which is in resonance with the $2^{2}B_{3u}$ excited state of TCNQ⁻. Resonant two-photon detachment should yield a photoelectron spectrum similar to Fig. 1, but at a much higher electron kinetic energy ($\sim 2.8 \text{ eV}$). However, we observed a spectrum with a very low electron kinetic energy centered at around 0.2 eV, as shown in Fig. 3. This observation suggests that the $2^{2}B_{3u}$ excited state of TCNQ⁻ must have a very short lifetime and undergoes fast internal conversion to the ground electronic state of TCNQ⁻, producing highly vibrationally excited states. The second photon then detaches an electron from the highly vibrationally excited TCNQ⁻ in its ground electronic state, giving rise to the broad low kinetic energy band shown in Fig. 3. Since our detachment laser pulse had a pulse length of a few nanoseconds, the lifetime of the $2^{2}B_{3u}$ excited state must be much shorter than a few nanoseconds. We note that the spectrum in Fig. 3 is similar to the 0.2 eV KE band observed by Verlet and co-workers.¹⁰ The broad band centered at a KE of 2 eV observed in their spectrum was likely due to resonant two-photon detachment, because of the short laser pulse used in their experiment.

In conclusion, we have obtained the first vibrationally resolved photoelectron spectrum of TCNQ⁻ at 354.7 nm that allowed us to accurately measure the electron affinity of TCNQ to be 3.383 ± 0.001 eV. Additionally, three totally symmetric vibrational modes were observed with frequencies of 114, 331, and 709 cm⁻¹ for the v₁, v₂, and v₄ modes, respectively. The current EA value indicates that the isolated TCNQ⁻ anion possesses two bound electronic excited states



FIG. 3. Two-photon photoelectron spectrum of $TCNQ^-$ at 400.0 nm (3.100 eV). See Fig. 2 for the excitation processes.

(Fig. 2). Resonant excitation to the second excited state suggested a very short lifetime and fast internal conversion to the vibrational levels of the ground electronic state of TCNQ⁻. The current measurement uncovered an extremely high EA for TCNQ, which is comparable to that of the F atom (3.401 eV),²⁸ and underlies its capacity as an excellent electron acceptor.

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