Direct Experimental Probe of the On-Site Coulomb Repulsion in the Doubly Charged Fullerene Anion $C_{70}{}^{2-}$

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Vibrationally resolved photoelectron spectra were obtained for cold $C_{70}{}^-$ and $C_{70}{}^{2-}$. Accurate values for the first and second electron affinities (EA's) of C_{70} were measured as 2.765 ± 0.010 and $0.02^{+0.01}_{-0.03}$ eV, respectively, establishing that $C_{70}{}^{2-}$ is an electronically stable dianion in the gas phase. The difference between the first and second EA (2.75 eV) provides a direct experimental measure for the on-site Coulomb and exchange interactions between the two excess electrons in $C_{70}{}^{2-}$. Strong electron correlation effects were also observed between the two excess electrons in $C_{70}{}^{2-}$.

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Electron-electron repulsion and exchange interactions are essential many-body effects in molecular and solid state physics. These effects are particularly important for multiply charged anions since they determine their stability as isolated species [1–3]. The Coulomb and exchange interactions in multiply charged C_{60} anions ($C_{60}{}^{n-}$) have drawn significant attention [4–9] since the discovery of superconductivity in doped fullerides. Theoretical calculations on $C_{60}{}^{2-}$ suggested that it possesses an on-site Coulomb repulsion (U_0) of ~3 eV and an exchange interaction (K) of ~50 meV [6]. However, the on-site Coulomb repulsion of $C_{60}{}^{2-}$ has eluded direct experimental measurement because the isolated $C_{60}{}^{2-}$ dianion is not stable in the gas phase, even though it was observed by mass spectrometry [10,11] and recently produced using charge transfer from Na to $C_{60}{}^-$ [12,13]. Among fullerenes isolated in bulk so far, the next largest after C_{60} is C_{70}. Dianion stability is expected to increase with cage size and, indeed, $C_{70}{}^{2-}$ was also detected along with $C_{60}{}^{2-}$ in the original mass spectrometry observation [10,11]. It has subsequently been produced by electrospray [14] and by electron attachment to $C_{70}{}^-$ in a Penning trap [15], as well as by charge transfer very recently [13]. However, an electrostatic model estimate suggested that $C_{70}{}^{2-}$ is not stable against autodetachment and possesses a negative binding energy for the second electron on the order of ~ -0.28 eV [16,17].

Photoelectron spectroscopy (PES) has been shown to be a powerful experimental technique to probe the stability and electrostatic interactions of multiply charged anions [3,18,19]. In principle, the on-site Coulomb repulsion in $C_{60}{}^{2-}$ and $C_{70}{}^{2-}$ can be directly probed by PES if they have sufficiently long life times. Recently, Ehrler *et al.* [16,17] have reported PES studies of higher fullerene dianions, $C_{76}{}^{2-}$, $C_{78}{}^{2-}$, and $C_{84}{}^{2-}$ (prepared and probed at room temperature), showing that they are all stable with positive binding energies for the second excess electrons. Here we report the first PES study of vibrationally

cold $C_{70}{}^{2-}$ and $C_{70}{}^-$ using a recently developed low-temperature PES apparatus [20,21]. Vibrationally cold anions greatly facilitate the interpretation of PES experiments, yielding vibrationally resolved PES spectra and more accurate electron binding energies due to the elimination of vibrational hot bands. We found that $C_{70}{}^{2-}$ is the smallest stable fullerene dianion with a positive, albeit small, second electron binding energy ($0.02^{+0.01}_{-0.03}$ eV). We were able to directly measure the on-site Coulomb and exchange interactions in $C_{70}{}^{2-}$ to be 2.75 eV from the difference of the first and second electron binding energies. Strong electron correlation effects in $C_{70}{}^{2-}$ were also observed.

The PES experiment was carried out using a new low-temperature electrospray PES apparatus [20,21]. The $C_{70}{}^{n-}$ anions were formed in solution via bulk chemical reduction of neutral C_{70} by a reducing agent according to Ref. [22] and transported to vacuum by electrospray. Anions from the electrospray source were guided into an ion trap, where they were stored for 0.1 s and collisionally cooled by a 0.1 m Torr N_2 background gas. The ion trap was connected to a closed cycle helium refrigerator operated at 70 K for the current experiment. The cooled anions were then pulsed out at a 10 Hz repetition rate into a time-of-flight mass spectrometer for mass and charge analyses. We observed that the $C_{70}{}^{2-}$ ion intensity was relatively weak and unstable in comparison to that of $C_{70}{}^-$. The $C_{70}{}^{n-}$ anions were each selected and decelerated before photodetachment by a laser beam (355, 266, and 193 nm for $C_{70}{}^-$; and 532, 355, and 266 nm for $C_{70}{}^{2-}$). The apparatus has an electron kinetic energy resolution of $\Delta E_k/E_k \sim 2\%$, i.e., about 20 meV for 1 eV electrons.

Figure 1 displays the spectra of $C_{70}{}^-$ at the three photon energies. The 193 nm spectrum [Fig. 1(c)] agrees with a previous report [23] except for a slightly better resolution. The 1.55 eV HOMO-LUMO energy gap (see Fig. 3) obtained from the current data is also consistent with the
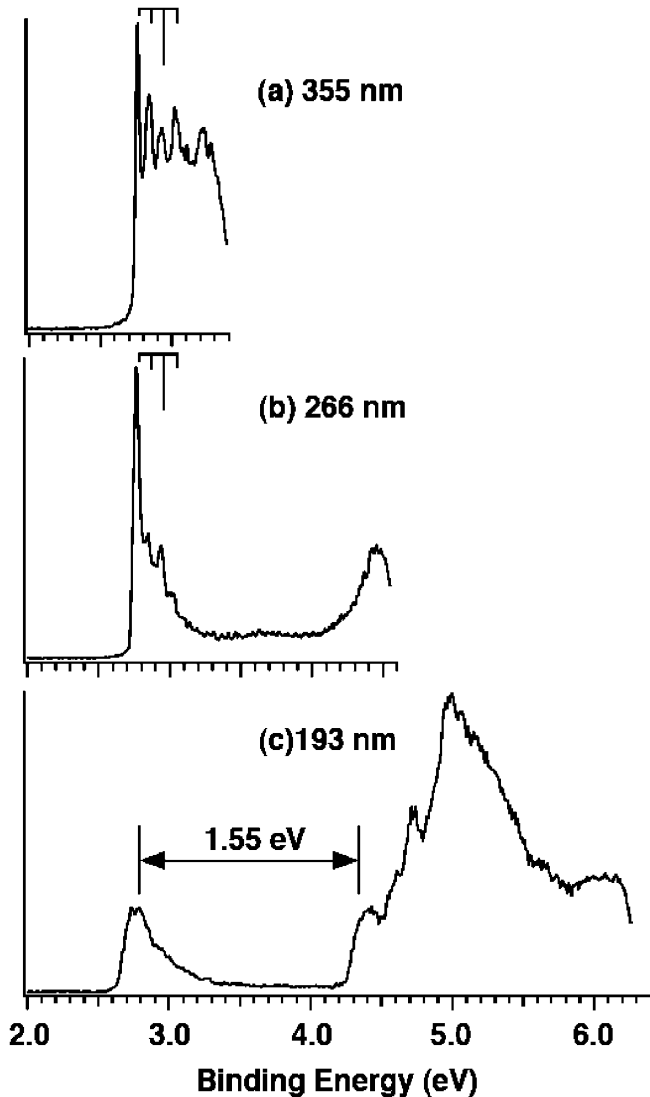
FIG. 1.   Photoelectron spectra of cold C_{70}^- at (a) 355 nm (3.496 eV); (b) 266 nm (4.661 eV); (c) 193 nm (6.424 eV). The vertical lines in (a) and (b) represent vibrational structures.

previous estimate of 1.6 eV [23]. At 266 nm [Fig. 1(b)], the ground state transition was considerably better resolved due to the cold C_{70}^- anions. Two vibrational modes were observed with spacings of 690 and 1410 cm^{-1} for the low and high frequency modes, respectively. These vibrational spacings agree with previous Raman spectra of C_{70} [24]. Weak continuous electron signals were discernible in the 266 nm spectrum in the band gap region. These weak signals were likely due to autodetachment, similar to that observed in the PES of C_{60}^- [21]. At 355 nm [Fig. 1(a)], the vibrational structures were better resolved. The relative intensity change of the vibrational peaks between the 355 and 266 nm spectra was caused by stronger autodetachment transitions and possible multiphoton processes at 355 nm. The first vibrational feature represents the transition from the ground vibrational state of C_{70}^- to that of C_{70} and defines the electron affinity (EA) of C_{70}. The peak

position of the 0-0 transition yields a relatively accurate EA for C_{70} as 2.765 ± 0.010 eV. This EA value is higher than that reported previously (2.676 ± 0.001 eV) using laser detachment of C_{70}^- in a storage ring [25], but agrees with that (2.73 ± 0.05 eV) obtained from charge transfer reactions [26]. We suspect that the discrepancy is most likely due to insufficient cooling of the C_{70}^- anions in the previous experiment, similar to that in the case of C_{60}^- [21]. Despite the tighter error bar for the previously reported EA, we consider the current measurement to be more reliable due to the complete elimination of vibrational hot bands.

Because of the weak ion intensity of C_{70}^{2-}, we were only able to measure its photoelectron spectra at the three lower photon energies (Fig. 2). Several important observations can be immediately made. First, all spectra displayed a cutoff at the higher binding energy side, due to the repulsive Coulomb barrier (RCB) universally present in multiply charged anions [3]. All three spectra gave the
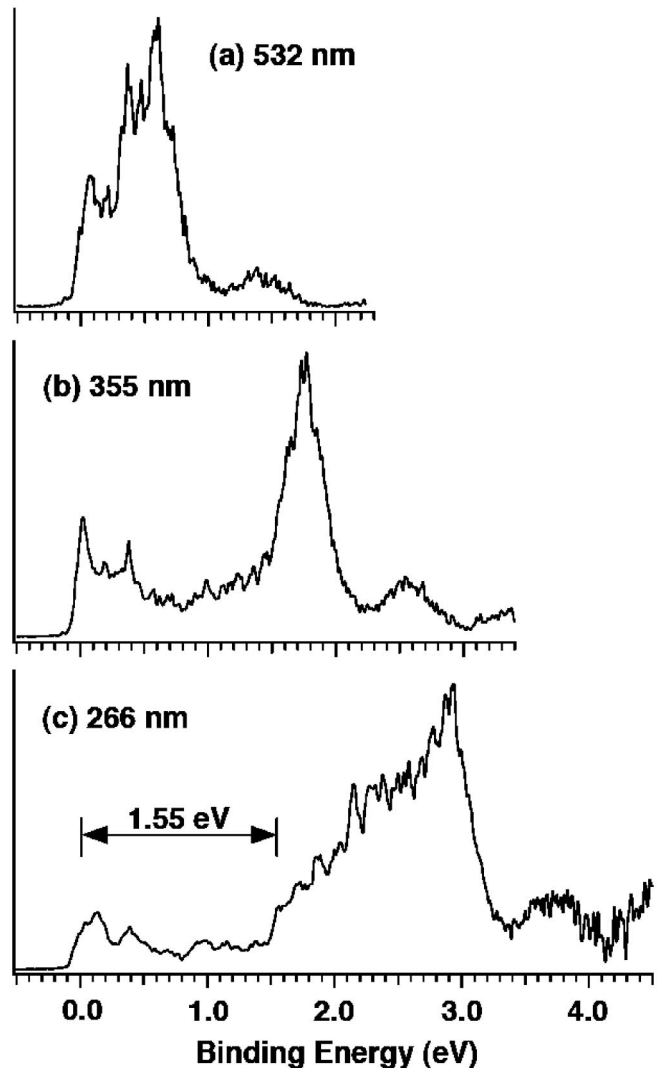

FIG. 2.   Photoelectron spectra of cold C_{70}^{2-} at (a) 532 nm (2.331 eV); (b) 355 nm (3.496 eV); (c) 266 nm (4.661 eV).

same cutoff, about 1.6 eV below the photon energies in each case, at about 3.0, 1.9, and 0.7 eV binding energies in the 266, 355, and 532 nm spectra, respectively, (Fig. 2) [27]. The 1.6 eV cutoff defines the RCB height for electron emission from C_{70}^{2-}. Second, the detachment threshold of C_{70}^{2-} was indeed observed to be very low. The 355 nm spectrum [Fig. 2(b)] was vibrationally resolved with a spacing of $\sim$1370 cm^{-1}, consistent with the high frequency mode observed in the C_{70}^{-} spectra. The 0-0 transition at 0.02 eV defines the second electron binding energy of C_{70}^{2-}, which is barely stable and should be the smallest stable fullerene dianions. Our best estimate of the second EA of C_{70} was $0.02^{+0.01}_{-0.03}$ eV. The larger magnitude of the lower bound was to take into account the instrumental resolution and possible excitation of unresolved low frequency modes in the ground state transition in the spectra of C_{70}^{2-}. Third, the spectra of C_{70}^{2-} were observed to resemble those of C_{70}^{-}. The energy gap observed in the spectra of C_{70}^{2-} [Fig. 2(c)] is identical to that observed for C_{70}^{-} [Fig. 1(c)], suggesting that the extra electrons in C_{70}^{n-} enter the LUMO of C_{70} with very little perturbation to the overall electronic structure of C_{70} (see Fig. 3). This observation is consistent with the fact that the fullerene cages are very stable and rigid. Fourth, the main surprise in the C_{70}^{2-} spectra was the presence of relatively strong features in the band gap region in comparison to the spectra of C_{70}^{-}. In particular, a well-defined peak at 0.38 eV binding energy was observed, which could not be a vibrational feature for the ground state transition because it would yield too high a vibrational frequency. This feature gained intensity with decreasing photon energies and became a dominating peak at 532 nm [Fig. 2(a)], where more intense features were also present on the high binding energy side. These features could not be due to autodetachment, which was expected to exhibit photon energy dependence. As will be discussed later, these features are most likely due to two-electron transitions, as a result of strong electron correlation effects between the two excess electrons in C_{70}^{2-}.

To help interpret the PES results, we optimized the D_{5h} structure of C_{70} and computed its molecular orbitals using density functional theory and the B3LYP hybrid functional [28–30] with a standard double-ζ quality 6–31G^* basis set, as shown in Fig. 3 [31]. The LUMO (e_1'') is a doubly degenerate orbital with a close-lying LUMO + 1 (a_1''). The LUMO's are all π-type orbitals delocalized over the surface of the C_{70} cage (Fig. 3). In C_{70}^{-}, the extra electron enters the e_1'' LUMO, giving rise to a doublet ground state ($^2A_2$) of C_{2v} symmetry due to the Jahn-Teller effect. However, the distortions of C_{70}^{-} from the D_{5h} structure are relatively small due to the rigidity of the fullerene cage, as evidenced by the short vibrational progression in the ground state transition of the photoelectron spectra of C_{70}^{-} (Fig. 1). In C_{70}^{2-}, the two extra electrons enter the LUMO. The most likely candidate for the ground state of C_{70}^{2-} is a triplet state with the e_1'' orbital half occupied, consistent
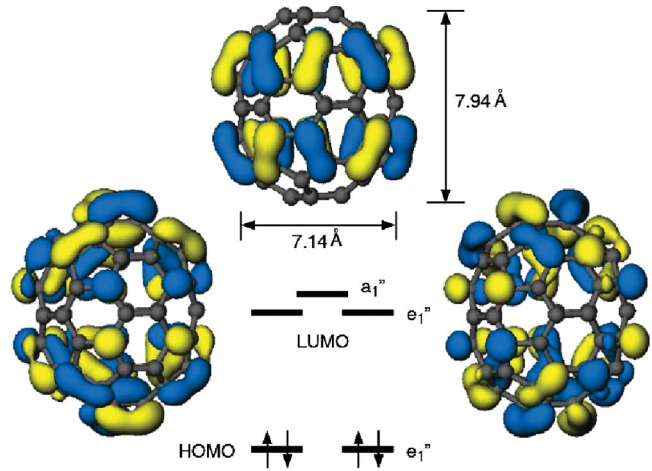

FIG. 3 (color). The highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of C_{70} calculated using density functional theory [28–31]. Pictures for the degenerate LUMO (e_1'') and the close-lying LUMO + 1 (a_1''), as well as the molecular dimensions of C_{70}, are also shown.

with a previous experimental measurement suggesting a triplet ground state for C_{70}^{2-} [32].

The current result clearly showed that C_{70}^{2-} is stable with a slightly positive second electron binding energy. Ehrler *et al.* [16,17] estimated a negative second electron binding energy of -0.28 eV for C_{70}^{2-} using a scaled classical electrostatic model, which seemed to have underestimated the stability of C_{70}^{2-}. Thus the previous observation of "metastable" decay of C_{70}^{2-} in a Penning trap [14] was most likely due to vibrationally hot C_{70}^{2-}, as suggested in the recent lifetime measurement in a storage ring [13]. With a binding energy only slightly above zero, it can be expected that at room temperature a large fraction of C_{70}^{2-} would exist in vibrationally excited states, which would be above the 0.02 eV detachment threshold and could decay via vibrationally induced tunneling through the 1.6 eV RCB [33]. This also explains the relatively weak C_{70}^{2-} ion intensity from our electrospray source because a large number of the dianions would be expected to undergo autodetachment during the ion transport into the ion trap and before they were vibrationally cooled.

The difference between the first and second EA of C_{70} (2.765 eV $-$ 0.02 eV $\approx$ 2.75 eV) yields a direct experimental measure of the on-site Coulomb (U_0) and exchange (K) interactions between the two excess electrons in C_{70}^{2-}. The exchange interaction is expected to be relatively small on the basis of the theoretical estimate of that in C_{60}^{2-} [6]. If we use the 50 meV exchange interaction estimated for C_{60}^{2-} to approximate that in C_{70}^{2-}, we obtain an on-site Coulomb repulsion (U_0) of $\sim$2.80 eV for C_{70}^{2-}, which is smaller than the 3 eV value calculated for C_{60}^{2-} as expected. The 2.80 eV Coulomb repulsion in C_{70}^{2-} is considerably higher than what one would get from the classical electrostatic interaction of two electrons localized on the opposite sites of the C_{70} cage (1.8 to 2.0 eV). This discrep-

ancy is due to quantum effects (the wave nature of the two electrons) or the delocalized nature of the LUMO (Fig. 3), where the two electrons reside. The strong Coulomb interaction can lead to strong electron correlation effects between the two excess electrons in C_{70}^{2-}, as revealed by the strong features observed in the band gap region in the spectra of C_{70}^{2-} (Fig. 2). These features were most likely due to two-electron processes, a manifestation of strong electron correlation effects. For example, the 0.38 eV peak observed in the C_{70}^{2-} spectra could be due to the ejection of one electron and the simultaneous excitation of the other electron from the LUMO to higher-lying orbitals (Fig. 3). Alternatively, the features in the band gap region could result from resonant tunneling from excited C_{70}^{2-}, as observed previously for multiply charged anions [34]. The excited C_{70}^{2-}, which is above the detachment threshold, could be produced via absorption of a detachment photon followed by an internal conversion. In any case, the multiply charged fullerenes are interesting molecular and quantum systems and merit further experimental and theoretical interrogations.

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