
Estimation of the Electron Affinities of C_{60} , Corannulene, and Coronene by Using the Kinetic Method

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Novel anions that contain one molecule each of C_{60} and the polycyclic aromatic hydrocarbon coronene are generated in the gas phase by electron attachment desorption chemical ionization. Collision-induced dissociation reveals that these cluster ions are loosely bonded. Fragmentation of the mass-selected cluster anion yields, as the only products, the intact radical anions of the constituent molecules, namely, the C_{60} radical anion and the coronene radical anion, in almost identical relative abundances. This result is interpreted as evidence that the cluster ion can be considered as the anion radical of one molecule solvated by the other molecule. The known very high electron affinity of C_{60} (2.66 eV) and the comparable degree to which C_{60} and the PAH compete for the electron suggests that dissociation may be controlled by the electron affinity of a portion of the C_{60} surface, that is, in this case the kinetic method yields information on the "local" electron affinity of C_{60} . The electron affinity of the bowl-shaped compound corannulene is estimated for the first time to be 0.50 ± 0.10 eV by the kinetic method by using a variety of reference compounds. Unlike coronene, corannulene reacts with $C_{60}^{\bullet-}$ in the gas phase to form a covalently bonded, dehydrogenated cluster ion. Support for the concept of "local" electron affinity of C_{60} comes from a theoretical calculation on the electronic structure of C_{60} anions, which shows evidence for localization of the charge in the C_{60} molecule. The possibility of electron tunneling in the C_{60} -coronene system is discussed as an alternative explanation for the unusual observation of equal abundances of C_{60} anions and coronene anions upon dissociation of the corresponding cluster ion. (*J Am Soc Mass Spectrom* 1996, 7, 619-627)

Since the first observation of C_{60} by Rohlffing et al. [1], its recognition as a unique carbon allotrope by Smalley and Kroto [2], and the discovery by Krätschmer et al. [3] of a method for production of macroscopic amounts of fullerenes, many fullerene derivatives have been reported. Mass spectrometry has played an important role in the identification of these derivatives, which include metallo, alkyl, fluoro, epoxy, and hydrogeno fullerene derivatives [4-6] as well as many derivatives that involve the formation of C-C bonds [7-29]. The production of fullerene derivatives by ion-molecule reactions in the gas phase is also of considerable interest to the mass spectrometry community [30-37].

Although the majority of mass spectrometric investigations on fullerenes have utilized positively charged

ions [38,39], negative-ion mass spectrometry of fullerenes and its derivatives is gaining increasing attention [40-43]. Interest in the electron affinity (EA) of C_{60} and its derivatives is compelled by the importance of electron affinity as a thermochemical property. Ultraviolet photoelectron spectra and threshold photodetachment studies of cold C_{60} anion radicals reveal that vapor phase C_{60} has a large electron affinity (2.65 ± 0.05 eV) [44,45]. Laser photodetachment measurements on $C_{60}^{\bullet-}$ and $C_{70}^{\bullet-}$ ions cooled in a storage ring yield EA values of 2.666 ± 0.001 and 2.676 ± 0.001 eV for cold C_{60} and C_{70} , respectively [46]. The gas-phase EA value is supported by the adiabatic EA of C_{60} in solution, which has been estimated as $(2.10-2.21) \pm 0.1$ eV by measurement of the charge transfer absorption energy and the redox potential [47]. More recently, Boltalina et al. [48,49] utilized an equilibrium method to measure the electron affinities of higher fullerenes and difluorinated derivatives. The electron affinities for C_{70} , C_{76} , C_{78} , and C_{84} were estimated to be $2.72 \pm$

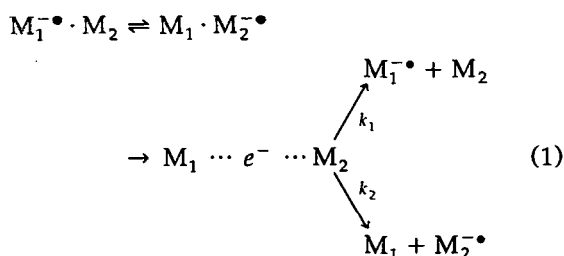
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0.05, 2.88 ± 0.05 , 3.01 ± 0.07 , and 3.05 ± 0.08 eV, respectively [48]. The estimated EA values for $C_{60}F_2$ and $C_{70}F_2$ are 2.74 and 2.80 eV, respectively [49]. A charge exchange "bracketing" method also has been used to estimate the electron affinities of fluorinated fullerenes [50]. These compounds have remarkably high electron affinities; for example, the electron affinity of a mixture comprised principally of $C_{60}F_{44}$ was determined to be 4.06 ± 0.25 eV [50]. In a related study, Märk and co-workers [51] reported the unusual observation of a 0.26-eV barrier to free electron attachment to C_{60} .

Polycyclic aromatic hydrocarbons are of interest for their structural relationship to fullerenes. In particular, the carbon framework of corannulene (Scheme I) has a bowl-like structure that mimics the curvature of C_{60} . Although it can be considered to represent the polar cap of C_{60} , corannulene undergoes rapid bowl-to-bowl inversion in solution [52-54]; it can accept up to four extra electrons into a doubly degenerate, lowest unoccupied molecular orbital in solution [55]. Gas-phase positive-ion-molecule reactions of corannulene with C_{60} have been investigated by mass spectrometry [56, 57]. In addition, a double-electron transfer reaction has been observed between the triply charged C_{60} cation and corannulene [56]. The ionization energy of corannulene was determined to be 7.7 ± 0.1 eV by electron transfer "bracketing" experiments [57]. In spite of this body of work, important electronic properties of corannulene—notably its electron affinity and its negative-ion gas-phase chemistry—remain to be explored.

The current study was designed as an application of the kinetic method to the determination of electron affinities of C_{60} and its subunit corannulene. The kinetic method is an approximate method, based on the rates of competitive dissociation of mass-selected cluster ions [58]. In the case of a dimeric anion $[M_1M_2]^{-\bullet}$, if the cluster ion is loosely bound, it can be thought of as an electron-bound dimer. The fragmentation to give the individual radical anions can be described in terms

of two competitive reaction channels, as shown in eq 1:

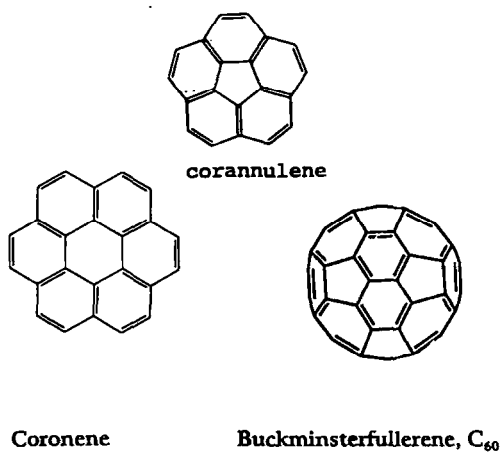


If this rather unusual description of the cluster ion in terms of an electron-bound dimer is valid, the relative rates of competitive dissociation of the electron-bound dimer, namely, the relative abundances of the individual radical anion products, are expected to correlate directly with the electron affinity difference between M_1 and M_2 . The quantitative relationship is given by eq 2,

$$\Delta EA / (RT_{\text{eff}}) = \ln([M_1^{-\bullet}] / [M_2^{-\bullet}]) \quad (2)$$

where T_{eff} is the effective temperature of the activated electron-bound cluster ion and one assumes that the (single) bond between M_1 and M_2 can dissociate to form the complementary sets of products $[M_1^{-\bullet} + M_2]$ and $[M_1 + M_2^{-\bullet}]$. One must recognize that at some point between reactants and completely separated products the Born-Oppenheimer principle breaks down and the electrons can no longer accommodate themselves to the lowest energy state of the system. (This is equivalent to the statement that there is not an electron transfer equilibrium between the two sets of products shown in eq 1.) The non-adiabatic nature of the system allows the description of fragmentation in terms of two competitive reaction channels, as given in eq 1. As will be seen later, this description fits the behavior of some of the systems described here and yields apparently valid results; however, in other cases, notably that of C_{60} , there are additional factors that are discussed in detail in subsequent text.

The kinetic method is best used for chemically similar species, where entropy factors on the rates of the competitive reactions are either negligible or cancel. The method is applicable to polar and nonvolatile samples, even if of low purity [58], and has been used to estimate the proton affinities of various organic molecules as well as their affinities toward other ions [58]. More significantly for this study, the kinetic method has been applied to estimate electron affinities of substituted nitrobenzenes [59] and, more recently, some polycyclic aromatic hydrocarbons (PAHs) [60] and aromatic radicals (Squires, R. R.; Hu, J., unpublished). The present study employs electron attachment-desorption chemical ionization-mass spectrometry (DCI-MS) to make cluster ions of C_{60} and corannulene with PAHs by ion-molecule reactions in the ion source. Collision-induced dissociation of the mass-selected cluster ion is utilized to seek informa-



Scheme I. Structures of C_{60} , coronene, and corannulene (bowl shape).

tion on the relative electron affinities of C_{60} and corannulene. The goals of the study are to investigate the possibility of (1) generation of cluster ions of C_{60} or corannulene in the gas phase and (2) application of the kinetic method to determine the electron affinities of C_{60} , corannulene, and coronene. The results are unexpected and require some consideration of the bonding in the cluster ion and how this changes during dissociation.

Experimental

All experiments were performed with a Finnigan TSQ-700 triple quadrupole mass spectrometer (Finnigan-MAT, San Jose, CA). The corannulene was prepared by using a new three-step synthesis [61]. In pairwise fashion, fullerene-60 (Aldrich Chemical Co., Milwaukee, WI), corannulene, and PAHs (Aldrich Chemical Co., Milwaukee, WI) were dissolved in carbon disulfide solvent. A 1- μ L aliquot of the resulting solution was placed on the rhenium wire filament of a direct evaporation probe and allowed to dry. The probe was then introduced into the chemical ionization source of the mass spectrometer and the sample was thermally desorbed by resistive heating at the relatively slow rate of 800 $^{\circ}$ C/min; the probe was held at 800 $^{\circ}$ C for 2 min, and then stepped to 1200 $^{\circ}$ C to pyrolyze any remaining material. The electron energy and source temperature were set at 70 eV and 150 $^{\circ}$ C. Desorbed species were ionized by electron attachment in an ammonia chemical ionization plasma. The indicated ammonia pressure was 5 torr and the nominal manifold pressure was 1.1×10^{-6} torr. In the experiments that involved C_{60} -coronene, *n*-hexane was added as a relaxation agent (Cleven, C. D.; Hoke, S. H., II; Cooks, R. G.; Hrovat, D. A.; Borden, W. T., unpublished). After addition of *n*-hexane via the gas-chromatograph inlet via a Granville Phillips leak valve (Granville Phillips Co., Boulder, CO), the manifold pressure rose to 1.9×10^{-6} torr. To maximize the residence time of C_{60} in the ion source, the ion repeller voltage was set to zero.

The cluster ion of interest that was generated in the ion source was mass-selected by using the first quadrupole. Collisional activation of the cluster usually was achieved in the second quadrupole under mild conditions, namely, 4-eV collision energy and an argon target at a nominal pressure of 0.4 mtorr ($< 10\%$ beam attenuation). For the experiments that involved C_{60} , a 10-eV collision energy was used to increase the extraction efficiency and, hence, the abundance of the cluster ion. The abundances of the fragment ions then were obtained by recording the product ion mass spectrum obtained by a scan of the third quadrupole, which was operated at approximately unit mass resolution. To minimize molecular weight discrimination on ion transmission in the third quadrupole, 7,7,8,8-tetracyanoquinodimethane (TCNQ, MW = 204 u) and C_{60} were used to tune the third quadrupole under

typical C_{60} -coronene experimental conditions. (TCNQ was chosen because it has a known EA value close to the electron affinity of C_{60} [62].) All peak ratio measurements were taken in triplicate and displayed relative standard deviations of less than 10%. Each set of peak ratios was measured from an average of 15 or more scans. These procedures were necessary because of the low abundances of the product ions in some of the spectra.

Results and Discussion

Cluster Ion Formation and Dissociation

Vaporization of C_{60} from a direct evaporation probe into a chemical ionization (CI) source results in electron attachment to generate the intact radical anion when subjected to collisions with thermalized electrons generated by using ammonia as the reagent gas. Cluster ions usually are generated by raising the sample pressure, for example, to achieve reaction between a protonated molecule and the corresponding neutral molecule. This approach was unsuccessful in attempts to form negatively charged clusters that contained C_{60} . However, when *n*-hexane was added to the CI source to cause collisional relaxation of the incipient cluster ions (Cleven, C. D.; Hoke, S. H., II; Cooks, R. G.; Hrovat, D. A.; Borden, W. T., unpublished), the mass spectrum shown in Figure 1 was observed. Most significantly, a peak at -1020 Thomson (= atomic mass units per Charge) [63] was observed, which corresponds to an anion composed of C_{60} and coronene. The spectrum also displayed a second cluster ion at -600 Thomson, which corresponds to $[C_{24}H_{12}]_2^{-\bullet}$.

To explore the structures of these cluster ions, collision-induced dissociation was performed under mild activation conditions. Figure 2 shows a product ion mass spectrum recorded for the mass-selected cluster ion at -600 Thomson. As expected, it dissociates readily and produces only a single fragment ion at -300 Thomson, which indicates that it is the homodimer of coronene. The measured main ion beam at-

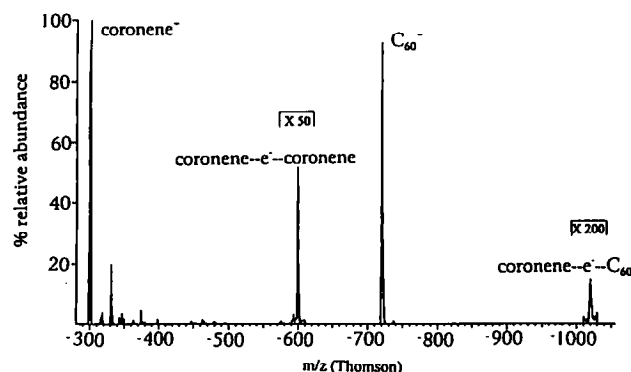


Figure 1. Negative-ion desorption chemical ionization mass spectrum of a mixture of C_{60} and coronene (CI reagent gas NH_3 ; relaxation gas *n*-hexane).

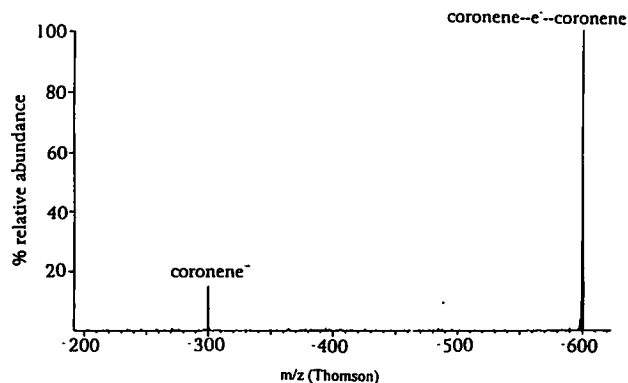


Figure 2. Product ion tandem mass spectrum of the mass-selected coronene dimer anion. Activation was achieved at 10-eV collision energy by using argon target gas at a pressure that gave an ion beam attenuation of 10%.

tenuation (compared to its intensity prior to collision gas introduction) is just 10%, which demonstrates that a single low-energy collision event is responsible for dissociation. In a similar fashion, the product ion mass spectrum of the cluster ion at -1020 Thomson shows two distinct fragment ions that correspond to the coronene radical anion (-300 Thomson) and to the C_{60} radical anion (-720 Thomson), respectively (Figure 3). This behavior is very similar to that seen in previous studies on electron-bound dimers of PAHs [60] and strongly supports the notion that an electron-bound heterodimer of C_{60} and coronene is formed in the gas phase and that such a cluster ion has a loosely bound structure. The weakly bound cluster ion is formally a solvated anion radical, namely, $M_1^- \cdot M_2$ or $M_2^- \cdot M_1$. However, if the barrier to electron transfer is low compared to the barrier to dissociation of the cluster, the electron can be viewed as a bridging entity much like the proton in a proton-bound dimer (eq 1). These anions behave as loosely bound cluster ions; by contrast anion radicals of endohedral complexes of C_{60} , such as $[C_{60} + He]^- \cdot$, represent a completely different

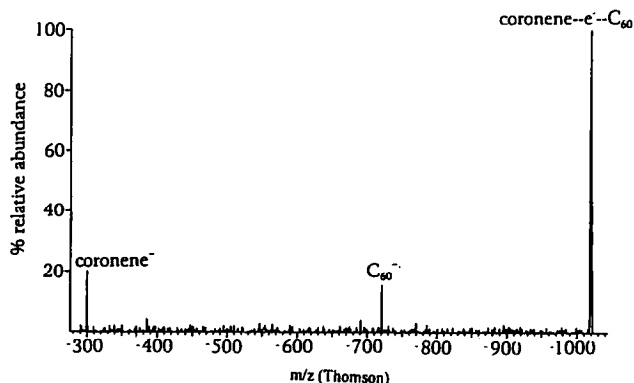


Figure 3. Product ion tandem mass spectrum of the mass-selected cluster anion composed of C_{60} and coronene. Activation was achieved with 10-eV collisions on argon target gas at a pressure such as to cause an ion beam attenuation of 10%.

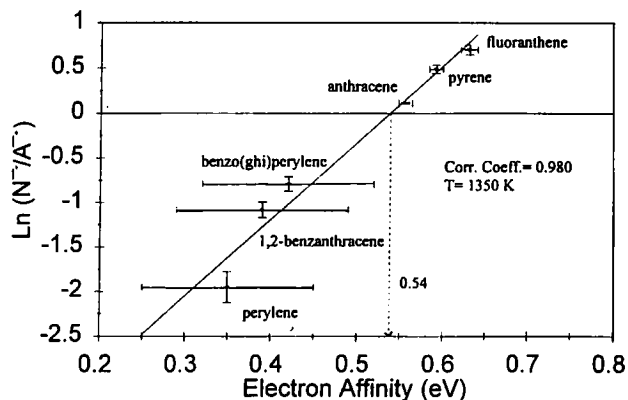


Figure 4. Natural logarithm of relative dissociation rates of electron-bound dimers composed of various reference compounds (PAHs) and coronene versus the electron affinities of the reference compounds (correlation coefficient = 0.980; $T_{\text{eff}} = 1350$ K). The vertical error bars are associated with measured ion abundance ratios; the horizontal error bars are associated with uncertainties in the literature EAs of the reference compounds.

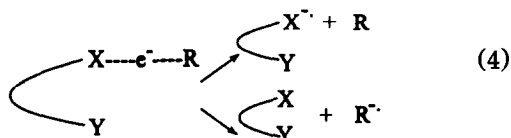
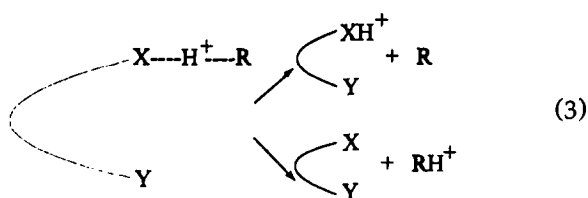
group of gas-phase clusters that are not dissociated readily [64].

If the kinetic method is applicable [58], the relative abundances of the two fragment ions generated from the electron-bound dimer that comprises C_{60} and coronene should reflect the electron affinity values of the two molecules involved in the cluster. However, it is known that in polyfunctional compounds, measured proton affinities may be associated with different binding sites within a molecule ("local" proton affinities) [58]. Even though a cursory examination of Figure 3 suggests that the electron affinity of C_{60} must be almost equal to the electron affinity of coronene due to their almost identical ion abundance ratios, this interpretation must be treated with caution. A literature value for the electron affinity of coronene is not available and the calculated values are uncertain, ranging from 0.18 to 1.88 eV [65]. However, the kinetic method was used to obtain the electron affinity of coronene by the procedure described in a previous study [60]. Figure 4 shows a plot of the natural logarithm of the ion abundance ratios versus the EAs of the reference compounds. The best straight line was determined by a least-squares regression analysis, which yields the EA of coronene as the x intercept and the effective temperature of the electron-bound dimer as the slope. From these data, the EA of coronene is estimated to be 0.54 ± 0.10 eV and the effective temperature of the dimer is found to be 1350 K with a correlation coefficient of 0.980. The uncertainty of 0.1 eV is due largely to the uncertainty in the literature EA values combined with the uncertainty in the measured ion abundance ratios. The EA value obtained falls in the vicinity of electron affinities for PAHs of similar size [65]. This value in turn suggests an electron affinity of C_{60} in the vicinity of 0.54 eV, which is significantly different from previous photodetachment measurements on the electron affinity of C_{60} (2.65 ± 0.05 eV) [44,45]. In fact,

given the EA literature value of 2.65 eV for C_{60} and the value of 0.54 eV for coronene, the expected $C_{60}^{\bullet-}$ to $C_{24}H_{12}^{\bullet-}$ fragment ion abundance ratio is 3.3×10^8 (assuming an effective temperature of 1250 K [60]). Clearly, some other factors must be invoked to explain the experimental data.

Local Affinities

Previous work on proton affinities of polyfunctional compounds by the kinetic method has revealed that cluster ions may be generated in isomeric forms in which binding occurs through different sites in one or both of the monomers. In such a case, binding will not necessarily be through sites that have the highest affinity [58]. In such cases, the relative rates of dissociation measured in a kinetic method experiment reflect the proton affinity of the "local" site involved in the binding. This is illustrated in eq 3 for the case of proton affinities [58], but the extrapolation to electron affinities (eq 4) is straightforward provided that the previously introduced description of these solvated anions as electron-bound dimers is accepted [60]:



Hoke et al. [66] demonstrated the possibility of measuring "local" proton affinities in free radicals derived by H^{\bullet} loss from cresol. They showed that the formation of proton-bound dimers involved either the radical formed by H^{\bullet} loss from the methyl or from the hydroxyl group. The measured "local" proton affinities were shown to be consistent with ab initio calculations [66]. In the case of large biomolecules, where there are a number of binding sites and thermodynamic control cannot be presumed to apply [67], the concept of "local" proton affinities becomes even more important. For example, Kaltashov et al. [68] have shown that the doubly charged proton-bound dimer of bradykinin and leucine enkephalin dissociates upon collisional activation, with preferred retention of the second charge on bradykinin, which suggests that the second proton affinity of bradykinin is higher than the first of leucine enkephalin. Also related to this work are recent studies on the electron affinities of halogenated PAHs. Electron-bound dimers that comprise halogenated PAHs with reference PAHs dissociate in such a fashion as to indicate that "local" binding may

occur, with the result that halogenated PAHs appear to have lower electron affinities than the corresponding unsubstituted PAHs [60].

Steric Effects

An alternative reason for fragmentation behavior that does not follow thermodynamics is the existence of large steric interactions within the cluster ion. This can alter the strength of binding and also lead to affinities that are lower than expected. If thermodynamic values are known, steric effects can be measured in this way and the steric bulk of various ortho substituents in pyridines has been determined for Cl^+ , CN^+ , and $OCNCO^+$ binding cations [69-71]. However, the magnitudes of these steric effects, even in cases where molecules are deliberately chosen for steric hindrance, are not nearly as large as the effects encountered here. For this reason, and based on studies of models, we conclude that steric effects are unlikely to explain the C_{60} -coronene behavior.

Local Electron Affinities

Because the ratio of the molecular weights for C_{60} and coronene is 2.4:1, additional experiments were performed to assess the magnitude of mass discrimination effects on ion transmission. Coronene (MW = 300) and anthracene (MW = 178) were chosen as a pair of compounds with a similar molecular weight ratio. The heterodimer of coronene and anthracene was formed under similar ionization conditions to those used for the C_{60} studies and collision-induced dissociation of this dimer was found to yield the two individual radical anions as the only fragments. Their ion abundance ratio, 1.12, accurately reflects the difference in electron affinities ($\Delta EA = 0.016$ eV) [72]. Additional experiments also were performed on C_{60} -coronene at a lower resolution. No effect is observed on the appearance of tandem mass spectrometry product ion spectrum of the heterodimer comprised of C_{60} and coronene. It appears from these and other data that the difference in molecular weight does not cause significant errors in ion transmission under the conditions used here. The enormous discrepancy between the experimental product ion abundance ratio and the value expected may instead be understood by applying the concept of "local" electron affinity.

Previous studies on autodetachment of negative ions by Brauman, Lineberger, and co-workers [73-78] reveal that local sites with high electron affinity do not necessarily participate in autodetachment processes. In the case of CH_2CN^- , where the dipole bound electron is in a diffuse orbital at the CH_2 end of the CCN axis, the end-over-end rotating states detach much faster than the CH_2 propeller-like rotations. A breakdown of the Born-Oppenheimer principle allows such a detachment process to occur [76].

In the present study, the two constituents in the electron-bound dimer of C_{60} and coronene have very similar structural features. C_{60} is formed of 20 hexagonal and 12 pentagonal rings and has a cage diameter of 7.1 Å [79]. The structure of C_{60} reaches an energy minimum when all pentagonal rings are completely surrounded with hexagons [80,81]. Coronene is a planar polycyclic aromatic compound, composed of seven hexagonal rings. Scheme I shows a two-dimensional structure of C_{60} for comparison with the molecular structure of coronene. In the electron-bound dimer comprised of the spherical C_{60} and the planar coronene, it is speculated that the "extra" electron may be localized most likely in the region between coronene and C_{60} . In the absence of such localization, bonding in the cluster must be considerably weakened. Only part of C_{60} is affected by the interactions with the shared electron, namely, $C_{60}^{\bullet-}$ must be polarized to accommodate a "solvent" coronene molecule. As the electron-bound dimer begins to undergo dissociation after mild activation, the interaction of only a part of the C_{60} surface with the shared electron may remain responsible for the (weakened) binding. The behavior of the dissociating cluster in the transition state is proposed not to be affected significantly by the fact that the final product $C_{60}^{\bullet-}$ is much more stable than the alternative product $C_{24}H_{12}^{\bullet-}$. (In terms used in molecular dynamics, the transition state occurs early on the reaction surface.) Thus, the measured electron affinity for C_{60} does not represent the electron affinity of the whole C_{60} molecule; rather it better represents the "local" electron affinity of a portion of the C_{60} surface. The interaction region of C_{60} is probably of comparable size to that of coronene. This may explain the observation that the measured "local" electron affinity of C_{60} is almost equal to the electron affinity of coronene. Additional support for the concept of "localized electron affinity" comes from studies of geometrical and electronic structures of C_{60} anions [82]. These theoretical studies indicate the existence of "self-localized" defects in C_{60} anions. In the case of $C_{60}^{\bullet-}$, the geometrical distortion and the negative charge are found to be localized in the equatorial region of the spherical molecule, that is, a clear case of localization of charge in $C_{60}^{\bullet-}$ is observed [82].

An alternative explanation is based on the possibility of electron tunneling in the C_{60} -coronene dimer. This possibility is presented here to encourage more work in this area, even though the localized bonding explanation is considered to be adequate to explain the present results. Electron tunneling is well known in field ionization where electrons can tunnel a few angstroms from a molecule, through the potential barrier, to a suitably charged surface. Electric field strengths on the order of volts per angstrom are required for tunneling [83]. Similar phenomena also are observed in scanning tunneling microscopy [84]. In the C_{60} -coronene system, if the system is treated classi-

cally, where movement of a single negative charge represents the current flow between the two molecules, a potential drop across the molecules will be generated due to the unsymmetrical charge. This phenomenon can be expressed as $U = Q/C$, where U is the generated potential drop, Q is the charge, and C is the capacitance. If we use the classical equation $C = \epsilon A/d$, where ϵ is the dielectric constant, A is the area of the capacitor, and d is the distance between the two molecules, the calculated potential drop is in the tens of volts range on the assumption that the interaction region is comparable to the size of the coronene and the interaction distance is several angstroms. Then, the generated field strength is calculated to be on the order of 10^{10} V/m, which is sufficiently high to permit electron tunneling between the two molecules. Consequently, rapid and reversible tunneling may lead to the observed almost equal abundances of two constituent anions upon dissociation of the cluster ion.

Test of Local Electron Affinity Hypothesis

In an attempt to test the hypothesis that this experiment measures the "local" electron affinity of C_{60} , the bowl-shaped molecule corannulene ($C_{20}H_{10}$) was used to form a heterodimer with C_{60} . The negative-ion DCI mass spectrum (Figure 5) shows two cluster ions: one at -500 Thomson and the other at -968 Thomson. Under mild activation conditions, collision-induced dissociation of the cluster ion at -500 Thomson produces only a single fragment ion at -250 Thomson, which indicates that it is a homodimer of corannulene. The peak at -968 Thomson, however, does not correspond to an intact cluster ion composed of C_{60} and corannulene, but to the dehydrogenation product [$C_{60} + C_{20}H_8$]. Collision-induced dissociation of this ion shows no detectable fragment ions, even under more vigorous conditions. The binding between C_{60} and $C_{20}H_8$ is clearly covalent. The cluster ion may well adopt the "stacked umbrella" configuration shown previously in the case of $C_{60}^{\bullet+}$ -corannulene cluster ions, although the binding in these positively

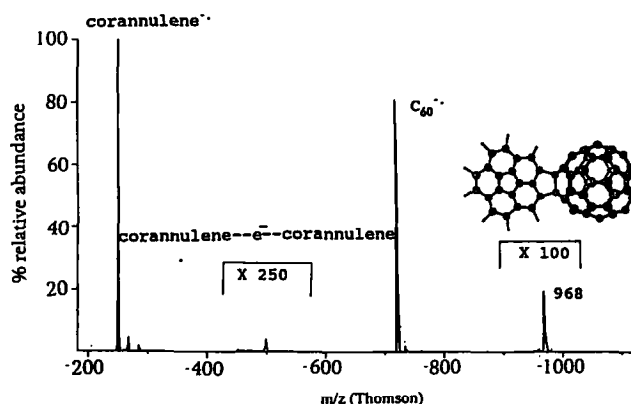
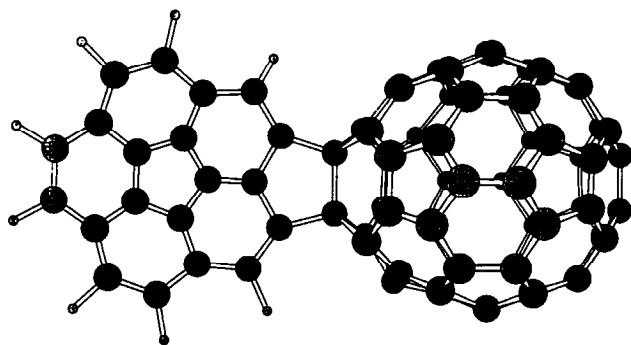


Figure 5. Negative-ion desorption chemical ionization mass spectrum of a mixture of C_{60} and corannulene.

Scheme II. Proposed structure of C_{60} and corannulene adducts.

charged cluster ions is probably due to electrostatic interactions [57]. Scheme II illustrates a possible structure of the covalent anion product (mass 968 u), which is analogous to the benzyne adduct of C_{60} , the structure of which is established [24]. The reaction is rationalized by the well-known tendency of C_{60} to react with free radicals, which form stable adducts with the odd electron highly delocalized on the C_{60} [7-11, 85]. Correspondingly, corannulene is known to be susceptible to addition by carbanions, that is, the attachment of a carbanion to the rim of corannulene through a single bond gives very stable adducts with the negative charge highly stabilized by the five-membered ring core [61]. Such a dehydrogenation reaction is not unprecedented; previous studies on gas-phase additions of aromatic compounds to C_{60} have shown that multiple additions are accompanied by loss of molecular hydrogen [30].

Electron Affinity of Corannulene

Additional experiments were performed to assess the electron affinity of corannulene and its reactivity with other PAHs by the same procedures as described in a previous study [60]. Figure 6 is a plot of ion abundance ratios versus the EAs of the reference compounds. From this data the EA of corannulene is estimated to be 0.50 ± 0.10 eV. No previous determination of the EA of corannulene is available in the literature. Note that the EA of corannulene (0.50 ± 0.10 eV) is very close to the EA of coronene (0.54 ± 0.10 eV). This closeness allows the possibility that partial localized bonding exists in the electron-bound dimer of corannulene and coronene, as is the case for C_{60} -coronene. However, the quality of the correlation shown in Figure 6 is more consistent with behavior that expresses a single, normal EA value.

Conclusion

A novel loosely bound dimeric anion of C_{60} has been generated in the gas phase by electron attachment DCI-MS and the same method has been used to form

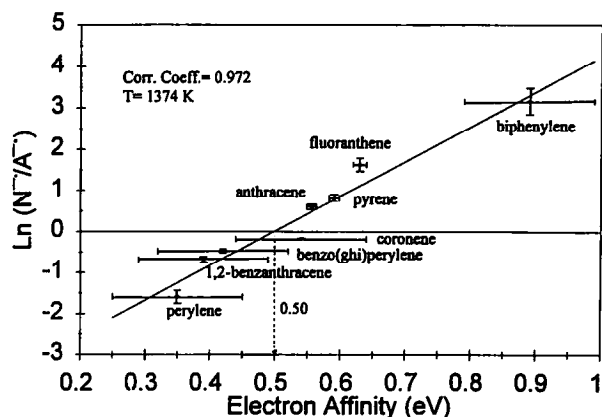


Figure 6. Natural logarithm of relative dissociation rates of electron-bound dimers composed of various reference compounds (PAHs) and corannulene versus the electron affinities of the reference compounds (correlation coefficient = 0.972; $T_{eff} = 1374$ K). The vertical error bars are associated with the measured ion abundances ratios; the horizontal error bars are associated with uncertainties in the literature values of the EAs of the reference compounds.

an electron-bound dimer composed of C_{60} and coronene. This latter cluster ion dissociates under mild activation conditions to give two radical anions, namely, the C_{60} anion and the coronene anion. The ratio of the product ion abundances is approximately unity, which suggests that the participating groups have very similar strengths of attachment to the extra electron in the cluster. Application of the kinetic method of determining electron affinities yields an estimated electron affinity of coronene of 0.54 ± 0.10 eV, which indicates the electron affinity of the participating C_{60} moiety as 0.54 ± 0.10 eV. This result may be interpreted as the "local" electron affinity of the (unspecified) portion of the C_{60} sphere that is involved in binding with coronene. This result is analogous to previous determinations of "local" proton affinities of biological compounds also made by the kinetic method. An alternative explanation based on "electron tunneling" is introduced and deserves further exploration.

Efforts have been made to determine the electron affinity of corannulene, a subunit of C_{60} , with a comparable size to that of coronene. The EA of corannulene is estimated for the first time to be 0.50 ± 0.10 eV, which is close to the value of the EA of coronene. One cannot rule out the possibility that only a portion of the corannulene molecule is involved in bonding with the various reference molecules employed and the EA value must, therefore, be accepted as a lower limit. The similar EAs of corannulene and coronene as well as their comparable sizes suggest that the concept of "local" electron affinity involved in the C_{60} -coronene system possibly operates in the corannulene system. However, it was not possible to test this hypothesis because corannulene and C_{60} form a covalently bound dehydrogenated product instead of the expected loosely bound cluster ion.

Acknowledgments

This work was supported at Purdue University by the National Science Foundation (CHE 92-23791) and at Boston College by a grant from the Department of Energy. We thank Weston T. Borden, Tilmann D. Märk, Kermit K. Murray, and Steve H. Hoke II for helpful discussions.

References

- Rohlfing, E. A.; Cox, D. M.; Kaldor, A. *J. Chem. Phys.* **1984**, *81*, 3322.
- Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
- Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.
- Hirsch, A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1138.
- Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685.
- Schwarz, H. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 293.
- Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Holler, E. R., Jr.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *J. Am. Chem. Soc.* **1991**, *113*, 6274.
- Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183.
- Morton, J. R.; Preston, K. F.; Krusic, P. J.; Wasserman, E. *J. Chem. Soc., Perkin Trans.* **1992**, *2*, 1425.
- Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Phys. Chem.* **1992**, *96*, 3576.
- Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Am. Chem. Soc.* **1992**, *114*, 5454.
- Hoke, S. H., II; Molstad, J.; Payne, G. L.; Kahr, B.; Ben-Amotz, D.; Cooks, R. G. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 472.
- Bausch, J. W.; Prakash, G. K. S.; Olah, G. A.; Tse, D. S.; Lorents, D. C.; Bae, Y. K.; Malhotra, R. *J. Am. Chem. Soc.* **1991**, *113*, 3205.
- Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1991**, *113*, 9385.
- Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 766.
- Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697.
- Taylor, R.; Langley, G. J.; Meidine, M. F.; Parsons, J. P.; Abdul-Sada, A. K.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1992**, 667.
- Wood, J. M.; Kahr, B.; Hoke, S. H., II; Dejarme, L.; Cooks, R. G.; Ben-Amotz, D. *J. Am. Chem. Soc.* **1991**, *113*, 5907.
- Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829.
- Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* **1991**, *254*, 1186.
- Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *J. Am. Chem. Soc.* **1992**, *114*, 7300.
- Vasella, A.; Uhlmann, P.; Waldraff, C. A. A.; Diederich, F.; Thilgen, C. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1388.
- Shi, S.; Khemani, K. C.; Li, Q. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656.
- Hoke, S. H., II; Molstad, J.; Dilettato, D.; Jay, M. J.; Carlson, D.; Kahr, B.; Cooks, R. G. *J. Org. Chem.* **1992**, *57*, 5069.
- Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *Chem. Lett.* **1992**, 2333.
- Rubin, Y.; Kahn, S.; Freedberg, D. I.; Yerezian, C. *J. Am. Chem. Soc.* **1993**, *115*, 344.
- Kahn, S. I.; Oliver, A. M.; Paddon-Row, M. N.; Rubin, Y. *J. Am. Chem. Soc.* **1993**, *115*, 4919.
- Wilson, S. R.; Kaprinidis, N.; Wu, Y.; Schuster, D. I. *J. Am. Chem. Soc.* **1993**, *115*, 8495.
- Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khamani, K.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T.; Rickborn, B.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 1594.
- Hoke, S. H., II; Molstad, J.; Kahr, B.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1994**, *138*, 209.
- Ross, M. M.; Callahan, J. H. *J. Phys. Chem.* **1991**, *95*, 5720.
- Sunderlin, L. S.; Paulino, J. A.; Chow, J.; Kahr, B.; Ben-Amotz, D.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 5489.
- Petrie, S.; Javahery, G.; Wang, J.; Bohme, D. K. *J. Am. Chem. Soc.* **1992**, *114*, 9177.
- Javahery, G.; Petrie, S.; Wincel, H.; Wang, J.; Bohme, D. K. *J. Am. Chem. Soc.* **1993**, *115*, 5716, 6295.
- Martin, T. P.; Náher, U.; Schaber, H.; Zimmermann, U. *Phys. Rev. Lett.* **1993**, *70*, 3079.
- Yerezian, C.; Hansen, K.; Diederich, F.; Whetten, R. L. *Nature* **1992**, *359*, 44.
- Pradeep, T.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1994**, *135*, 243.
- McElvany, S. W.; Ross, M. M.; Callahan, J. H. *Acc. Chem. Res.* **1992**, *25*, 162.
- McElvany, S. W.; Ross, M. M. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 268.
- Moriwaki, T.; Matsuura, H.; Aihara, K.; Shiromaru, H.; Achiba, Y. *J. Phys. Chem.* **1992**, *96*, 9092.
- Moriwaki, T.; Shiromaru, H.; Achiba, Y. *Z. Phys. D* **1993**, *26*, S320.
- Gunnarsson, O.; Handschuh, H.; Bechthold, P. S.; Kessler, B.; Ganteför, G.; Eberhardt, W. *Phys. Rev. Lett.* **1995**, *74*, 1875.
- Matejčík, Š.; Märk, T. D.; Španěl, P.; Smith, D. *J. Chem. Phys.* **1995**, *102*, 2516.
- Yang, S. H.; Pettiette, C. L.; Conceicao, J.; Cheshnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1987**, *139*, 233.
- Wang, L.; Pettiette, C. L.; Conceicao, J.; Cheshnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1991**, *182*, 5.
- Brink, C.; Andersen, L. H.; Hvelplund, P.; Mathur, D.; Voldstad, J. D. *Chem. Phys. Lett.* **1995**, *233*, 52.
- Saito, G.; Teramoto, T.; Otsuka, A.; Sugita, Y.; Ban, T.; Kusunoki, M.; Sakaguchi, K. *Synthetic Metals* **1994**, *64*, 359.
- Boltalina, O. V.; Sidorov, L. N.; Borschhevsky, A. Ya.; Sukhanova, E. V.; Skokan, E. V. *Rapid Commun. Mass Spectrom.* **1993**, *7*, 1009.
- Boltalina, O. V.; Sidorov, L. N.; Sukhanova, E. V.; Sorokin, I. D. *Chem. Phys. Lett.* **1994**, *230*, 567.
- Hettich, R.; Jin, C.; Compton, R. *Int. J. Mass Spectrom. Ion Processes* **1994**, *138*, 263.
- Smith, D.; Španěl, P.; Märk, T. D. *Chem. Phys. Lett.* **1993**, *213*, 202.
- Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920.
- Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1994**, *116*, 1533.
- Rabideau, P. W.; Sygula, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1497.
- Ayalon, A.; Rabinovitz, M.; Cheng, P. C.; Scott, L. T. *Angew. Chem.* **1992**, *104*, 1691.
- Javahery, G.; Becker, H.; Petrie, S.; Cheng, P. C.; Schwarz, H.; Scott, L. T.; Bohme, D. K. *Org. Mass Spectrom.* **1993**, *28*, 1005.
- Becker, H.; Javahery, G.; Petrie, S.; Cheng, P. C.; Schwarz, H.; Scott, L. T.; Bohme, D. K. *J. Am. Chem. Soc.* **1993**, *115*, 11636.
- Cooks, R. G.; Patrick, J. S.; Kotiaho, T.; McLuckey, S. A. *Mass Spectrom. Rev.* **1994**, *13*, 287.
- Burinsky, D. J.; Fukuda, E. K.; Campana, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 2770.
- Chen, G.; Cooks, R. G. *J. Mass Spectrom.* **1995**, *30*, 1167.

61. Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082; Scott, L. T.; Cheng, P. C.; Bratcher, M. S. *Seventh International Symposium on Novel Aromatic Compounds*; Victoria, BC, Canada, July 19-24, 1992; Abstract 64.
62. Christodoulides, A. A.; McCorkle, D. L.; Christophorou, L. G. In *Electron Molecule Interactions and Their Applications*; Christophorou, L. G., Ed.; Academic: New York, 1984; Vol. 2, p 601.
63. Cooks, R. G.; Rockwood, A. L. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 93.
64. Sprang, H.; Mahlkow, A.; Campbell, E. E. B. *Chem. Phys. Lett.* **1994**, *227*, 91.
65. Christodoulides, A. A.; McCorkle, D. L.; Christophorou, L. G. In *Electron Molecule Interactions and Their Applications*; Christophorou, L. G., Ed.; Academic: New York, 1984; Vol. 2, p 423.
66. Hoke, S. H., II; Yang, S. S.; Cooks, R. G.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 4888.
67. Campbell, S.; Beauchamp, J. L. *Proc. SPIE-Int. Soc. Opt. Eng.* **1992**, *1636*, 201.
68. Kaltashov, I. A.; Fabris, D.; Fenselau, C. Presented at the *42nd ASMS Conference on Mass Spectrometry and Allied Topics*, Chicago, IL, June, 1994.
69. Eberlin, M. N.; Kotiaho, T.; Shay, B. J.; Yang, S. S.; Cooks, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 2457.
70. Yang, S. S.; Bortolini, O.; Steinmetz, A.; Cooks, R. G. *J. Mass Spectrom.* **1995**, *30*, 184.
71. Yang, S. S.; Chen, G.; Ma, S.; Cooks, R. G.; Gozzo, F. C.; Eberlin, M. N. *J. Mass Spectrom.* **1995**, *30*, 807.
72. Wentworth, W. E.; Chen, E.; Lovelock, J. E. *J. Phys. Chem.* **1966**, *70*, 445.
73. Mullin, A. S.; Murray, K. K.; Schulz, C. P.; Lineberger, W. C. *J. Phys. Chem.* **1993**, *97*, 10281.
74. Mead, R. D.; Lykke, K. R.; Lineberger, W. C.; Marks, J.; Brauman, J. I. *J. Chem. Phys.* **1984**, *81*, 4883.
75. Marks, J.; Brauman, J. I.; Mead, R. D.; Lykke, K. R.; Lineberger, W. C. *J. Chem. Phys.* **1988**, *88*, 6785.
76. Lykke, K. R.; Neumark, D. M.; Andersen, T.; Trapa, V. J.; Lineberger, W. C. *J. Chem. Phys.* **1987**, *87*, 6842.
77. Marks, J.; Wetzel, D. M.; Comita, P. B.; Brauman, J. E. *J. Chem. Phys.* **1986**, *84*, 5284.
78. Andersen, T.; Lykke, K. R.; Neumark, D. M.; Lineberger, W. C. *J. Chem. Phys.* **1987**, *86*, 1858.
79. Huffman, D. R. *Physics Today* **1991**, Nov. 22.
80. Curl, R. F. *Philos. Trans. R. Soc. London, Ser. A* **1993**, *343*, 19.
81. Boo, W. O. *J. Chem. Educ.* **1992**, *69*, 605.
82. Stafström, S. *Int. J. Modern Phys. B* **1992**, *6*, 3853.
83. Brown, P.; Bruschweiler, F. R.; Pettit, G. R.; Richstein, T. *J. Am. Chem. Soc.* **1970**, *92*, 4470.
84. Binnig, G.; Rohrer, H.; Gerber, Ch.; Weibel, E. *Phys. Rev. Lett.* **1982**, *49*, 57.
85. McEwen, C. N.; McKay, R. G.; Larsen, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 4412.