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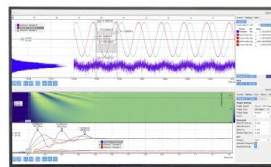
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Doubly charged coronene clusters—Much smaller than previously observed

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The smallest doubly charged coronene cluster ions reported so far, Cor_{15}^{2+} , were produced by charge exchange between bare coronene clusters and He^{2+} [H. A. B. Johansson *et al.*, Phys. Rev. A **84**, 043201 (2011)]. These dications are at least five times larger than the estimated Rayleigh limit, i.e., the size at which the activation barrier for charge separation vanishes. Such a large discrepancy is unheard of for doubly charged atomic or molecular clusters. Here we report the mass spectrometric observation of doubly charged coronene trimers, produced by electron ionization of helium nanodroplets doped with coronene. The observation implies that Cor_3^{2+} features a non-zero fission barrier too large to overcome under the present experimental conditions. The height of the barriers for the dimer and trimer has been estimated by means of density functional theory calculations. A sizeable barrier for the trimer has been revealed in agreement with the experimental findings. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.5028393>

I. INTRODUCTION

Highly charged droplets are unstable with respect to charge separation, i.e., fission (also dubbed Coulomb explosion). Lord Rayleigh developed a continuum model that treats liquid droplets as a fluid with surface tension σ ; it allows us to compute the charge q at which a spherical droplet of radius r becomes unstable with respect to deformation and spontaneously undergoes fission.¹ At this Rayleigh limit, the fissility parameter X , defined as the ratio of Coulomb energy and twice the surface energy, equals 1. Droplets with $X < 1$ are metastable; fission is impeded by a barrier.

Multiply charged atomic or molecular clusters A_n^{z+} undergo fission as well, as evidenced by the absence of z -fold charged ions below a characteristic size, n_{exp} .² Appearance sizes of doubly charged van der Waals and hydrogen-bonded clusters reported so far range from $n_{\text{exp}} = 284$ for neon³ to 13 for pyridine;⁴ even smaller dications have been observed for C_{60} whose appearance size is 5.⁵ In principle n_{exp} might depend on experimental conditions such as the mechanism by which clusters are prepared and ionized or the mass spectral resolution and detection efficiency. In practice, n_{exp} values are stubbornly immune to experimental conditions, at least for van der Waals clusters.^{6–9} For example, photoionization of benzene clusters at 6.41 eV, near a molecular resonance, produces the same appearance size, $n_{\text{exp}} = 23$, as electron ionization at 1000 eV.^{4,7,10}

However, for many systems for which *ab initio* calculations are available, n_{exp} exceeds the Rayleigh limit n_{Ray} by about a factor two, i.e., the fissility of the smallest observed doubly charged clusters is $X = n_{\text{Ray}}/n_{\text{exp}} \approx 0.5$. A major contribution to this discrepancy is the fact that most experiments involve clusters that are vibrationally excited as a result of their formation and/or the ionization process. Consequently, fission may be thermally activated.^{11,12} In a recent experiment, alkali clusters were grown in helium nanodroplets and ionized by electrons, resulting in appearance sizes that were approximately twofold smaller than reported previously and in good agreement with computed Rayleigh limits.^{13,14}

Another approach that tends to produce relatively cold ions is charge exchange in collisions with highly charged, low-velocity atomic ions.¹⁵ Huber and co-workers attained fissilities as large as $X = 0.87$ for tenfold charged sodium clusters.¹⁶ For lower charge states, fissility values were not as large, presumably because the neutral precursor clusters were rather warm. Collisions between clusters of anthracene ($\text{C}_{14}\text{H}_{10}$) and He^+ resulted in doubly charged clusters of anthracene with an appearance size $n_{\text{exp}} = 15$.¹⁷ In later work, the same group produced dications of anthracene and coronene ($\text{C}_{24}\text{H}_{12}$, from here on abbreviated as Cor) clusters in collisions with He^{2+} and observed $n_{\text{exp}} = 15$ for both species.¹⁸

This value is surprisingly large, considering that similar values have been obtained for the much smaller molecule $\text{C}_5\text{H}_5\text{N}$ (pyridine).⁴ In a simplistic but empirically supported liquid drop model, n_{exp} scales as $(T_{\text{boil}}v^{1/3})^{-1}$, where T_{boil} is the atmospheric boiling point (a measure of the cohesive energy) and v is the molecular volume determined from the bulk

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density.¹⁹ Given the appearance size of benzene, $n_{\text{exp}} = 23$,^{4,10} one would expect $n_{\text{exp}} \approx 7$ for coronene.

Nakamura and Ichimura²⁰ have applied a more refined liquid drop model that does not require scaling;⁶ they predicted $n_{\text{Ray}} = 3$ for Cor_n^{2+} . Furthermore, they estimated the potential energy curve between fission fragments of a doubly charged vertical stack of coronene using computed properties of the coronene dimer.²¹ Again, $n_{\text{Ray}} = 3$ was obtained.

In order to shed light on the huge discrepancy between theory ($n_{\text{Ray}} = 3$) and experiment ($n_{\text{exp}} = 15$), we have recorded electron ionization mass spectra of coronene clusters embedded in cold (0.37 K) nanodroplets of helium. We observe doubly charged coronene clusters as small as Cor_3^{2+} ; they are unmistakably identified by their characteristic pattern of isotopologues. To the best of our knowledge, Cor_3^{2+} is the smallest doubly charged cluster of a van der Waals- or hydrogen-bond compound ever reported;²² the previous record holder was $(\text{C}_{60})_5^{2+}$.⁵

We have applied density functional theory (DFT) to compute the energetics of doubly charged coronene dimers and trimers. The trimer features a sizeable fission barrier of about 0.56 eV, consistent with its appearance in the mass spectra. A smaller barrier of 0.33 eV is obtained for the dimer whose signal, if present, would be overwhelmed by the much more intense singly charged monomer which has the same mass-to-charge ratio.

II. EXPERIMENTAL

Helium nanodroplets were produced by expanding helium (Messer, purity 99.9999%) at a stagnation pressure of 25 bars through a 5 μm nozzle, cooled by a closed-cycle refrigerator to 9.7 K, in a vacuum. At these conditions, the droplets contain an estimated average number of 5×10^5 helium atoms.²³ The expanding beam was skimmed by a 0.8 mm conical skimmer located 8 mm downstream from the nozzle and traversed a differentially pumped pick-up cell filled with coronene vapor produced by heating coronene powder (Sigma-Aldrich, specified purity 97%, used as delivered) to about 102 °C.

The beam of doped helium droplets was collimated and crossed by an electron beam with a nominal energy of 71 eV. Cations were accelerated into the extraction region of a reflectron time-of-flight mass spectrometer (Tofwerk AG, model HTOF) with a mass resolution (for the present experiment) $m/\Delta m = 3500$ ($\Delta m =$ full-width-at-half-maximum). Further experimental details have been provided elsewhere.²⁴

Mass spectra were analyzed by means of a custom-designed software that extracts the abundance of specific ions after deconvoluting possible overlapping contributions to particular mass peaks by different ions and isotopologues.²⁵ The software automatically fits mass peaks, subtracts background signals, and explicitly considers isotopic patterns of all ions that are expected to contribute to a given peak.

III. EXPERIMENTAL RESULTS

A mass spectrum of helium nanodroplets doped with coronene (abbreviated as Cor, $\text{C}_{24}\text{H}_{12}$, mass 300.094 u for the main isotopologue) and ionized at 71 eV is displayed in Fig. 1. The most prominent ion series is due to singly charged Cor_n^+ with n ranging up to 23 (for better visibility of the different ion series, the mass spectrum in Fig. 1 is truncated at 3100 u). Satellite peaks 24 u below Cor_n^+ are due to a benzo[ghi]perylene ($\text{C}_{22}\text{H}_{12}$) impurity in the sample (indicated by blue triangles in Fig. 1).²⁶ Satellites 16–19 u above Cor_n^+ are probably due to water (indicated by green diamonds in Fig. 1); several other satellite peaks indicate additional impurities.

The positions of Cor_n^{2+} dications ($n = 1, 3, 5, 7, 9, 11$) that are identified unambiguously are indicated by red asterisks in Fig. 1. The trimer ($n = 3$), pentamer (5), and heptamer (7) are seen more clearly in Fig. 2, panels (a)–(c), respectively. The position of the isotopically pure isotopologue (containing no ^{13}C) is indicated by a red asterisk. The spacing between background ions (mostly hydrocarbons, plus a few ions marked by purple triangles that contain helium) is $\Delta(m/z) \approx 1.000$. The telltale of Cor_n^{2+} dications is mass peaks that are spaced at $\Delta(m/z) \approx 0.500$; they arise from ions that contain one or more ^{13}C . Cor_n^{2+} ions containing an even number of ^{13}C are positioned at approximately the same position as background ions; those containing an odd number of ^{13}C are positioned midway between.

The amplitudes of the mass peaks attributed to Cor_n^{2+} are consistent with the expected abundance of isotopologues. The natural abundance of ^{13}C is 1.07%. We have simulated the theoretical pattern by assuming a constant contribution from background ions (hatched columns in Fig. 2) plus Cor_n^{2+} isotopologues that contain zero to six ^{13}C (solid red bars). The agreement with the mass spectrum is very good if one takes into account that the simulated spectrum neglects the minor shift between the position of background peaks and Cor_n^{2+} ions that contain an even number of ^{13}C . The agreement implies that the extent of protonation or dehydrogenation

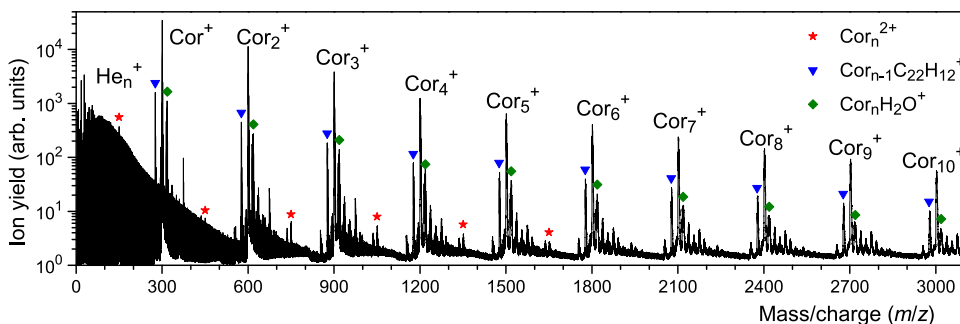


FIG. 1. Mass spectrum of helium nanodroplets doped with coronene ($\text{C}_{24}\text{H}_{12}$, mass 300.09 u for the pure ^{12}C isotopologue). The most prominent ion series is due to Cor_n^+ ; satellite peaks just below and above these peaks are due to ions that contain a benzo[ghi]perylene ($\text{C}_{22}\text{H}_{12}$) or H_2O impurity, respectively. Mass peaks due to Cor_n^{2+} (n odd) are marked by asterisks.

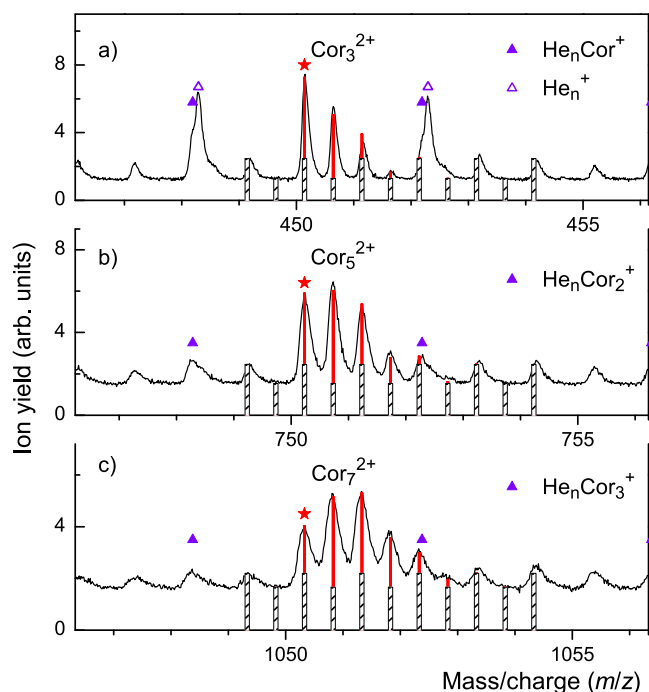


FIG. 2. Three sections of a mass spectrum showing the appearance of Cor_3^{2+} , Cor_5^{2+} , and Cor_7^{2+} . The asterisks indicate the positions of the isotopically pure isotopologue (containing no ^{13}C). The bar histogram simulates the sum of Cor_n^{2+} isotopologues (vertical red lines) and a constant background of singly charged ions (hatched vertical bars). Also marked are ion peaks due to He_x^+ and $\text{He}_x\text{Cor}_n^+$, $n = 1, 2, 3$ (open and closed triangles, respectively).

is small. More specifically, estimated upper limits for the occurrence of protonated, dehydrogenated, and doubly dehydrogenated dications are 6%, 3%, and 15%, respectively. For singly charged ions, we can estimate much tighter upper limits for dehydrogenation and double dehydrogenation, namely, 1% and 0.05%, respectively, for Cor_2^+ , and 0.3% and 0.1% for Cor_3^+ .

Cor_{15}^{2+} is the largest dication that can be identified unambiguously. We have searched for trications, without success. Given an appearance size $n_{\text{exp}} = 3$ for dications one would expect that the appearance size of Cor_n^{3+} is about $2.2 n_{\text{exp}} \approx 7$.^{6,8,27} Inspection of the mass spectrum provides an upper experimental limit for the relative ion yield of $\text{Cor}_n^{3+}/\text{Cor}_n^+$ for $n = 7, 8, 10$, and 11 of about 2×10^{-4} . For comparison, the relative ion yield of $\text{Cor}_5^{2+}/\text{Cor}_5^+$ is 5×10^{-4} ; for $\text{Cor}_7^{2+}/\text{Cor}_7^+$ it is 8×10^{-4} . Hence, the non-observation of coronene trications may be due to limited detection efficiency.

IV. THEORY

We investigated the stability of the doubly charged coronene dimer and trimer by means of DFT. Following the decomposition ansatz proposed previously,²⁸ we optimized the geometry of the neutral coronene monomer, dimer, and trimer at the PBE0/6-31G(d,p) level of theory including Grimme's latest empirical dispersion correction with Becke-Johnson damping;²⁹ these results were corrected for the basis set superposition error according to Boys.³⁰ Vertical ionization energies were calculated at the CAM-B3LYP/6-31G(d,p) level of theory. According to the decomposition ansatz mentioned above,

TABLE I. Computed interplanar distances and binding energies of the neutral coronene dimer for two different structures. The values in parentheses are from the work of Podeszwa.³¹

Structure	R (Å)	E_{bind} (eV)
Graphite	3.46 (3.51)	0.748 (0.753)
Shifted graphite	3.46 (3.50)	0.751 (0.757)

total energy balances for various fragmentation processes were derived by combining the results from the two different density functionals, i.e., taking into account the change in the binding energy of the neutral systems and the change of the ionization energies of the charged systems.

Podeszwa studied the neutral coronene dimer with a symmetry-adapted perturbation theory (SAPT) based on a DFT description of the monomers.³¹ With SAPT, noncovalent interaction energies can be derived without computing the total energy of a system or the total energies of its fragments. He concluded that two stacked, shifted structures were nearly isoenergetic, namely, the one analogous to graphite (*graphite structure*) and another one with a larger shift between the monomers (*shifted graphite structure*). The vertical (sandwich) structures, either twisted or non-twisted, were not competitive.

In Table I, we list the interplanar separations R and binding energies E_{bind} of the graphite and shifted graphite structures obtained with our method. The energies agree closely with those reported by Podeszwa;³¹ the shifted graphite structure is slightly more stable than the graphite structure.

In order to investigate the stability of the dimer and trimer dications with respect to Coulomb explosion, we carried out one-dimensional scans of parts of their potential energy hypersurfaces. For the dimer, we scanned the interplanar distance between the two coronene molecules; for the trimer, we scanned the interplanar distance between a pair of coronene molecules, kept at a fixed interplanar distance, and the third coronene molecule. The energies are calculated according to the decomposition ansatz described elsewhere.²⁸ The results

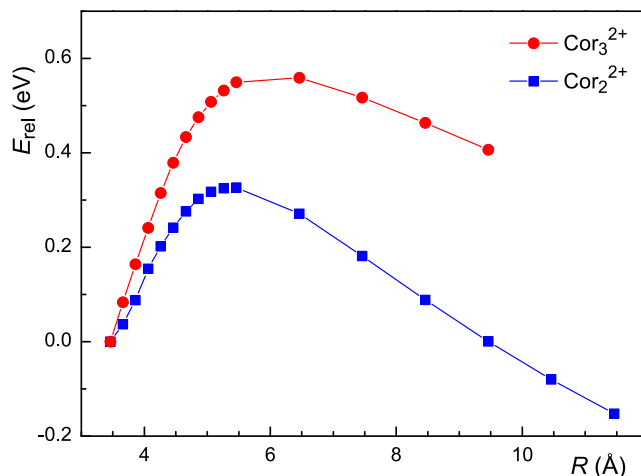


FIG. 3. Potential energy surface scans for the doubly charged coronene dimer and trimer. The fission barrier for the coronene dimer is approximately 0.33 eV, whereas that for the coronene trimer it is approximately 0.56 eV.

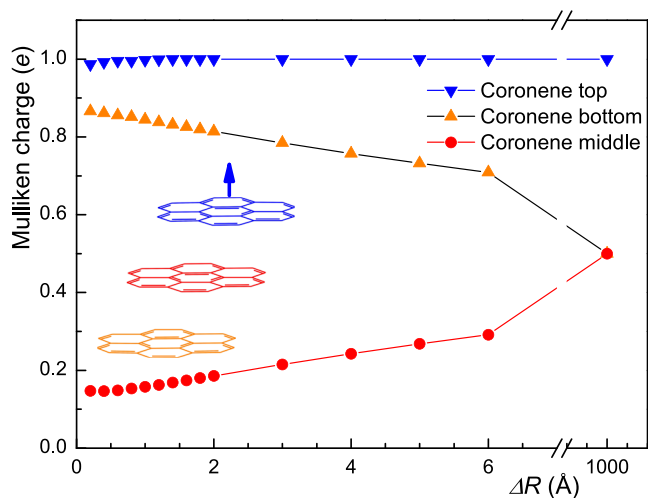


FIG. 4. Mulliken charges of the doubly charged coronene trimer summed up on each individual coronene. The two lower coronene molecules shown in the inset are kept fixed, while the third one is moved away along the arrow.

are depicted in Fig. 3. We find that the fission barrier for the doubly charged dimer (~ 0.33 eV) is significantly smaller than for the trimer (~ 0.56 eV). In the decomposition ansatz,²⁸ only vertical processes are considered. Thus the detection of Cor_3^{2+} indicates that the relaxation energy, which is not included in these calculations, is not high enough to overcome the fission barrier of the trimer.

In Fig. 4, we depict the Mulliken charges of the coronene molecules in the trimer for the potential energy surface scan. The abscissa specifies ΔR , the difference to the interplanar spacing in the optimized neutral trimer. Already after small displacement from the neutral minimum structure, the charge located at the top coronene molecule (which is moved away from the other two) is very close to one elementary charge, whereas the remaining elementary charge of the dicationic system is located mainly on the bottom coronene. For increasing distance between the top coronene and the remaining pair of coronene molecules, the charge distribution of the latter slowly converges to one in which the two coronene molecules in the pair equally share one charge (indicated for $\Delta R = 1000$ Å in Fig. 4). This result is in agreement with the finding that the barrier for the trimer is higher than in the case of the dimer because the two elementary charges are partially shielded from each other by the coronene molecule between them.

V. DISCUSSION

Coronene ($\text{C}_{24}\text{H}_{12}$, point group D_{6h}) is a prototypical polycyclic aromatic hydrocarbon (PAH). Studies of doubly charged PAHs have been motivated, last but not least, by the proposal that the ambient physical conditions in the interstellar medium permit their formation by sequential photon absorption;³² another proposed formation mechanism is charge exchange with He^+ .³³ Although not yet unambiguously identified, PAH dications have been hypothesized to contribute to emission and absorption spectra in the infrared and ultraviolet region.³⁴

Experimental studies of PAH^{2+} include measurements of the double-ionization energy of PAHs,³⁵ gas-phase reactions with rare gases,³⁶ and characterization of dissociation channels.³⁷ The single and double ionization energies of coronene have been measured by electron ionization,³⁸ photoionization, charge stripping, and reactivity studies in a selected-ion flow tube.³⁹ Reitsma *et al.* have investigated ionization of Cor^+ and dissociation of the di- and trication using soft X-ray photoabsorption.⁴⁰ Johansson *et al.* have applied DFT with the M06-2X functional to compute the first and second ionization energies of coronene clusters.¹⁸ A DFT study of coronene by Paris *et al.*⁴¹ provides, in addition to ionization energies, dissociation energies and fragmentation barriers for various reaction channels, for charge states as large as $z = 9$.

The main finding of the present study is the existence of long-lived coronene cations Cor_n^{2+} as small as the trimer. They have been produced by electron ionization of helium nanodroplets doped with coronene and identified unambiguously via the characteristic pattern of their isotopologues. This is the smallest doubly charged molecular cluster reported so far.²² Note that our data cannot prove the presence or absence of Cor_2^{2+} . Although the mass-to-charge ratio of ions containing an odd number of ^{13}C atoms would not coincide with that of any singly charged coronene isotopologues, the large yield of the latter precludes the identification of Cor_2^{2+} .

The smallest doubly charged coronene cluster previously observed is Cor_{15}^{2+} , five times larger than our present value; those ions were formed by charge exchange between He^{2+} and coronene clusters produced by gas aggregation in cold (77 K) helium gas.^{18,42} Such a huge discrepancy between experimental values is extraordinary. Given the current observation of Cor_3^{2+} , we can conclude that the fissility of Cor_{15}^{2+} is less than $3/15 = 0.2$. In general, charge exchange is a proven method to produce atomic clusters with high fissilities. For example, the fissility of Na_n^{10+} , produced in collisions between bare Na_n and Xe^{28+} , reached $X = 0.85 \pm 0.07$.¹⁶ Other methods, e.g., electron ionization or photoionization, do not produce such highly fissile clusters because they involve vertical ionization; subsequent structural relaxation leads to vibrationally hot clusters which undergo thermally activated fission if X exceeds approximately 0.5.¹⁵

Why did charge exchange fail to produce highly fissile Cor_n^{2+} ? Actually, charge exchange of coronene clusters with highly charged Xe ions did not show any cluster dications,¹⁸ but only a weak series of singly charged cluster ions and a strong Cor^+ signal. The authors concluded that clusters were produced in charge states much larger than $z = 2$, resulting in Coulomb explosion and hot singly charged clusters. High charge states could be avoided in collisions with He^{2+} but here charge exchange requires small impact parameters, hence large electronic stopping and concomitant heating of the nascent doubly charged coronene clusters. Hence, charge exchange neither with highly charged Xe ions nor with He^{2+} produced cold doubly charged clusters, hence the fissilities were low.

Nakamura and Ichimura have already pointed out that Cor_{15}^{2+} has low fissility. They applied a liquid drop model which derives the Rayleigh limit of van der Waals clusters from Lennard-Jones parameters and the dielectric constant⁶

and predicted $n_{\text{Ray}} = 3$.²⁰ Furthermore they proposed an atomistic model based on an empirical intermolecular potential to describe the interaction between singly charged fragment ions of Cor_n^{2+} . They assumed a vertically stacked coronene cluster geometry^{20,21} and, again, obtained $n_{\text{Ray}} \approx 3$.

The exact agreement between the value of n_{Ray} predicted by Nakamura and Ichimura²⁰ and our experimental n_{exp} value may be somewhat fortuitous. Liquid drop models do not take into account molecular anisotropy which is unusually large for coronene. In the atomic model, the interaction between the fission fragments was described by a sum of the Morse and the Coulomb potential; the ground state structure of the neutral dimer was adapted from work by Rapacioli *et al.*²¹ who had concluded that the vertical, twisted stack is lowest in energy. However, later studies of the coronene dimer concluded that shifted-stack structures are significantly lower in energy.^{31,43}

The results of our DFT study of Cor_2^{2+} and Cor_3^{2+} are described in Sec. IV. The ions feature fission barriers of 0.33 and 0.56 eV, respectively. Thus, even the doubly charged dimer (whose presence or absence we cannot establish) has a fissility below 1. Even so, the observation of Cor_3^{2+} in the present study is not entirely trivial. The smallest cluster dications that are commonly observed have fissilities around $X \approx 0.5$ because nascent cluster ions are usually hot and prone to thermally activated fission. Several observations and theoretical arguments suggest that the appearance size n_{exp} corresponds to the size at which the rate constant of fission equals that of monomer evaporation.^{12,44} In other words, n_{exp} marks the size at which the fission barrier equals the evaporation energy.^{14,48} The former rapidly increases with size, whereas the latter is approximately constant, explaining while the ion yield of cluster dications abruptly increases above n_{exp} .

The computed binding energy of the neutral dimer, i.e., its evaporation energy, is 0.757 eV (Table I). The evaporation energy of the trimer is hardly smaller; therefore, it would exceed the fission barrier of Cor_3^{2+} (0.56 eV) and, by the criterion discussed in the previous paragraph, make Cor_3^{2+} unobservable, unless dications are either formed cold or their fission is quenched by the helium droplet. In general, helium droplets have a mixed record as far as their ability to quench ionization-induced dissociation is concerned,⁴⁵ but they have been shown to quench fission of multiply charged alkali clusters.¹³ Thus it is likely that the helium droplet plays a role in lowering the appearance size of Cor_n^{2+} from 15 in previous work¹⁸ to 3 in our current experiments.

Indeed, our current mass spectra provide evidence for reduced intramolecular fragmentation. Duley has postulated that dehydrogenated singly charged coronene ions are the source of many diffuse interstellar bands;⁴⁶ thus hydrogen loss has been subject of numerous experiments and computational studies. Direct loss of H_2 features the lowest dissociation barrier for Cor^+ as well as Cor^{2+} (see Refs. 40 and 41 and references therein). The most intense fragment ion peak above $m/z = 150$ in the NIST mass spectrum of coronene recorded at 70 eV corresponds to H_2 loss; it amounts to 17%. Charge exchange between coronene and He^{2+} causes H_2 loss from Cor^+ with a probability of about 5%;⁴⁷ in our data that mass

peak accounts for less than 2% (we can only quote upper limits because of the background signal). For Cor_2^+ and Cor_3^+ , H_2 loss is suppressed even further, to <0.05%. Unfortunately we cannot provide a meaningful upper limit for H_2 loss from cluster dications because the signal-to-background ratio of the parent ions is only 10:1.

VI. CONCLUSION

The smallest doubly charged coronene cluster ion observed in previous experiments, employing charge exchange between neat coronene clusters and He^{2+} , was $(\text{Cor})_{15}^{2+}$.¹⁸ We have shown that the appearance size drops to $n_{\text{exp}} = 3$ if coronene clusters are embedded in helium nanodroplets and ionized by electrons. Such a large reduction in appearance size is extraordinary. Furthermore, to the best of our knowledge, Cor_3^{2+} is the smallest doubly charged cluster of a van der Waals- or hydrogen-bound compound ever reported;^{22,49} the previous record holder was $(\text{C}_{60})_5^{2+}$.⁵

DFT calculations indicate that Cor_3^{2+} features a significant fission barrier of about 0.56 eV, considerably larger than that of the dimer (~ 0.33 eV). Still, if nascent cluster ions were hot, one would not expect the observation of Cor_3^{2+} because their fission barrier is less than the evaporation energy. Thus it is likely that the helium matrix promotes the formation of long-lived dications because it cools and/or quenches dissociative reactions.

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