

Experimental determination of the ionization potentials of the first five members of the nanodiamond series

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The ionization potentials of size- and isomer-selected diamondoids (nanodiamond containing one to five crystal cages) have been measured by means of total-ion-yield spectroscopy. We find a monotonic decrease of the ionization potential with increasing diamondoid size. This experimental result is compared to recent theoretical predictions and comparable investigations on related carbon clusters, the fullerenes, which show isomer effects to be stronger than size dependence. © 2007 American Institute of Physics. [DOI: [10.1063/1.2773725](https://doi.org/10.1063/1.2773725)]

Diamondoids are a class of completely sp^3 -hybridized carbon clusters that perfectly superimpose on the diamond lattice framework. With their size being in the subnanometer to nanometer regime, they bridge the gap from molecular cyclic hydrocarbons to nanodiamonds. There is no surface reconstruction and all dangling bonds are passivated by hydrogen. The smallest diamondoid is adamantane ($C_{10}H_{16}$), and all further members are derived by adding one face fused cage at a time to the preceding diamondoid structure, as shown in Fig. 1. Therefore diamondoids are for practical reasons classified by the number of diamond cages, and the classes are named by adding the corresponding Greek numeral prefix to the ending *-mantane*. With n being the number of cages, up to tetramantane, diamondoids obey the empirical formula $C_{4n+6}H_{4n+12}$. Starting at tetramantane isomers can be constructed and starting at pentamantane different weight classes for the same polymantane order exist. Diamondoids constitute a special subgroup of carbon clusters that, growing only a few atoms at a time while never diverging from the bulk diamond framework, allow unprecedented investigations about the evolution of solid state properties as a function of size and shape.

Even though the diamondoid series has been known for many decades,¹ investigations about this fascinating class of subnanometer to nanometer diamonds were limited due to lack of availability. With the recent isolation of higher diamondoids from crude oil and their size and shape selection,² the interest in diamondoids is greatly growing. The functionalization of diamondoids has been demonstrated recently for a number of polymantane molecules^{3–5} amongst others, allowing the self-assembly of diamondoid monolayers on noble metal surfaces via thiol groups.⁶ With more applications

yet to come, diamondoids and their derivatives yield high scientific as well as technological potential.⁷ A first breakthrough for their technological use has been the observation of monochromatic electron emission from diamondoid monolayers, making them a promising candidate for negative electron affinity materials.⁸

Data on the physical properties of diamondoids are still scarce. First investigations about their electronic structure showed that the lowest unoccupied states are dominated by their hydrogen surface and no size-dependent effects could be observed.⁹ Investigations on highest occupied states showed size-dependent valence band shifts as expected within the simple quantum confinement model.¹⁰ However, the observed size-dependent changes are significantly smaller than in other group IV semiconductor nanocrystals,¹¹ underlining the special role of diamond within this group of elemental semiconductors.

In this paper we report the experimental determination of the ionization potentials (IPs) for the diamondoid series from adamantane to pentamantane shown in Fig. 1. The IPs, or work function for macroscopic structures, are one of the fundamental values for all materials. They are of central importance for all potential technological applications as well as for benchmarking theoretical predictions.

The IPs are determined from photoion yield measurements of diamondoids in the gas phase. With this technique the photoions are collected with a $\Omega=4\pi$ efficiency, improving the signal-to-noise ratio.¹² Performing the experiments in the gas phase avoids changes in the cluster electronic structure due to particle-particle and particle-substrate interactions.¹³ For taking the photoion yield spectra, a monochromatized light beam is crossed with the diamondoid sample beam under the aperture of a time-of-flight spectrometer and the total ion yield as a function of excitation energy is measured. As excitation light source the vacuum-

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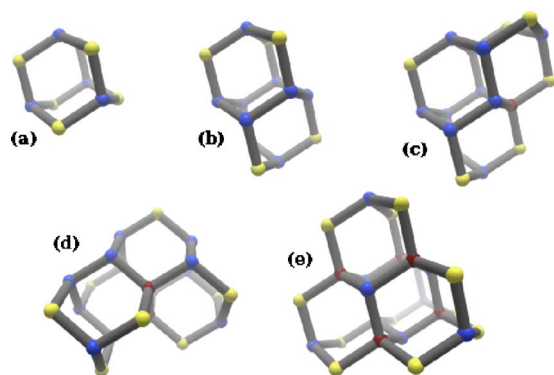


FIG. 1. (Color online) Investigated diamondoid structures: (a) adamantane, (b) diamantane, (c) triamantane, (d) [123]-tetramantane, and (e) [1(2,3)4]-pentamantane. The hydrogen surface atoms are not shown for clarity. The different colors of the C atoms indicate the respective coordination of the carbon atoms (C_2H_2 : yellow, C_3H : blue, C_4 : red).

ultraviolet beamline I with the cluster physics endstation CLULU (Ref. 14) of the Hamburg synchrotron facility Hasylab at DESY is used. The photon energy is scanned from 6.5–11.3 eV which well covers the ionization energies of the investigated samples. The photon energy resolution was determined to be better than 20 meV for the present measurements. Second and higher order harmonics are suppressed using a LiF filter with an energy cutoff of 11.8 eV. All data are normalized to the photon flux. The diamondoid samples are extracted from crude oil and isolated with purities >99%, as described in Ref. 2. The diamondoids are brought into the gas phase by sublimation at room temperature (adamantane) or by gentle heating up to 175 °C (diamantane through pentamantane, compare Table I) with a temperature-stabilized in-vacuum furnace. The base pressure in the chamber is on the order of low 10^{-6} mbar. Typical background pressures during evaporation are up to the mid- 10^{-5} mbar. It should be pointed out that the diamondoid partial pressure in the cluster beam crossing the interaction region is considerably higher. Photoion yield scans without any sample yield no appreciable signal in the investigated photon energy regime.

The photoion yield spectra for adamantane through pentamantane are shown in Fig. 2. Additionally, cyclohexane as the closest related cyclic hydrocarbon molecule has been measured as a reference. The spectra are the average of multiple individual scans. Diamondoids larger than adamantane are evaporated with a temperature-stabilized oven and guided by a heated nozzle to within 15 mm of the interaction region. The cyclohexane reference and adamantane sample are evaporated from a reservoir at room temperature, and

TABLE I. Experimentally determined ionization potentials and evaporation temperatures for the investigated diamondoids.

Diamondoid		t_{evap} (°C)	IP (eV)
Adamantane	$C_{10}H_{16}$	24	9.23 ± 0.12
Diamantane	$C_{14}H_{20}$	62	8.80 ± 0.06
Triamantane	$C_{18}H_{24}$	85	8.57 ± 0.08
[123]-tetramantane	$C_{22}H_{28}$	175	8.18 ± 0.13
[1(2,3)4]-pentamantane	$C_{26}H_{32}$	153	8.07 ± 0.12

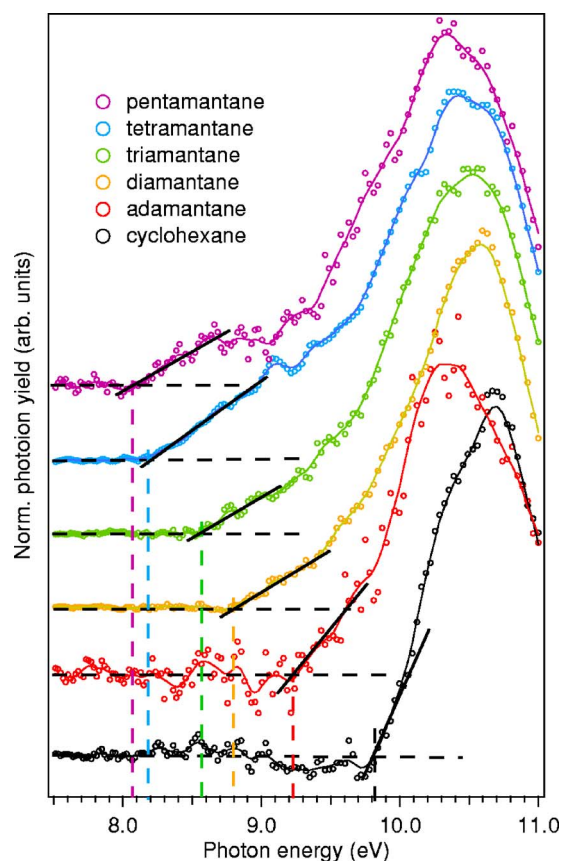


FIG. 2. (Color online) Ion yield data for diamondoids from adamantane to pentamantane with a cyclohexane reference. The extrapolation of the ionization potential is indicated with solid and dashed lines as explained in the text.

their flow is controlled with a leak valve. Due to geometrical constraints, these two samples could only be guided to within 45 mm of the interaction region. This leads to a systematically lower sample density in the interaction region at the maximum tolerable chamber pressures for the detector of about a factor of 10. Hence, for these two samples a lower signal-to-noise ratio is obtained, resulting in significantly lower data quality.

In Fig. 2 the individual data points are plotted as open circles, and a smoothed solid line is added to guide the eye. To determine the ionization energy of the diamondoids, the commonly used linearization procedure is applied. It is indicated in Fig. 2 as linear extrapolation of the lowest photon energy features (black solid lines) to the base line (black dashed lines). This is a standard method for determining the adiabatic ionization potentials and has been successfully applied to such diverse systems as fullerenes,¹⁵ metal oxide,¹⁶ and metal¹⁷ clusters. However, there exists no sound theoretical justification for this method as two important assumptions are made. First, the Franck-Condon factors are said to be nonzero between the neutral and ionic ground states. If this is not the case, the measured IP is higher than the adiabatic IP. Second, the thermal occupation of excited states of the neutral clusters is neglected. Here, the IP determined with the linearization method is potentially too low. For completeness it shall be mentioned that the spectral fingerprint of the vertical IP, corresponding to the energy difference between

the ground state of the neutral cluster and the ionized cluster in the same geometry, can be considered the maximum increase in the ion signal.^{16,17} The main experimental error sources are thermal occupation of excited states and the graphical data analysis. The thermal effect can be estimated to be no bigger than 0.04 eV from thermodynamical considerations, causing lowering of the ionization potential. The error from the graphical data analysis is determined by varying the extrapolation as well as the background fit to a reasonable extreme on either side. This error ranges from 0.05 to 0.12 eV. The resulting ionization potentials are summarized in Table I. Comparison of our results for cyclohexane (9.82 ± 0.06 eV) and adamantane (9.23 ± 0.12 eV) to average values in the NIST data bank¹⁸ (9.88 ± 0.03 and 9.25 ± 0.04 eV, respectively) shows very good agreement.

Comparing the overall shape of the spectra in Fig. 2, they all exhibit a broad resonance above 10 eV. This resonance slightly shifts, with exception of adamantane, toward lower photon energies with increasing cluster size. Further, additional spectral intensity arises at the lower photon energy side of the large resonance. For adamantane, the additional feature appears only as a shoulder of the large resonance. Within the diamondoid series it grows in intensity and in the pentamantane spectrum it is already a clearly distinguishable peak centered at about 8.7 eV. It is interesting to note that the observed decrease in the IP with increasing size is predominantly due to the appearance of this additional spectral intensity and not an overall shift of the spectra. The large resonance shifts only by a few hundred meV in contrast to a shift of 1.8 eV for the IP going from cyclohexane to pentamantane.

The IP of diamondoids has previously been subject to theoretical investigations,^{3,19,20} in particular, in the context of their potential application for negative electron affinity materials.²⁰ In Fig. 3 the experimental IPs are compared to the theoretical predictions for adiabatic IPs. Here, filled markers are used for the structures corresponding to the experimental data, and open markers are used for additionally calculated isomers. Density functional calculations at the B3LYP/6-31G(*d*) level of theory were performed by Fokin *et al.*³ using the GAUSSIAN03 and Lu *et al.*¹⁹ using the GAUSSIAN98 quantum chemistry package. Fokin *et al.* additionally calculated the vertical IPs. Drummond *et al.*²⁰ applied quantum Monte Carlo (QMC) methods. With QMC only adamantane has been calculated out of the measured diamondoids. Moreover, a bigger diamond cluster with the empirical formula $C_{29}H_{36}$ is taken for comparison at the large cluster end of Fig. 3. This cluster has been constructed to be approximately spherical exhibiting T_d symmetry.²⁰ Its size lies between penta- and hexamantane, but it is not a true diamondoid due to its different round shape and the lack of the cage-only structure. Therefore, comparability is limited and it is displayed as open triangle.

In general, the theoretical predictions agree with the overall trend of the experimental data, i.e., decreasing IPs with increasing size. However, a closer look reveals important differences. The QMC calculations for adamantane differ from the experimental results by more than 1 eV, while for the bigger diamond cluster $C_{29}H_{36}$, the calculated IP lies

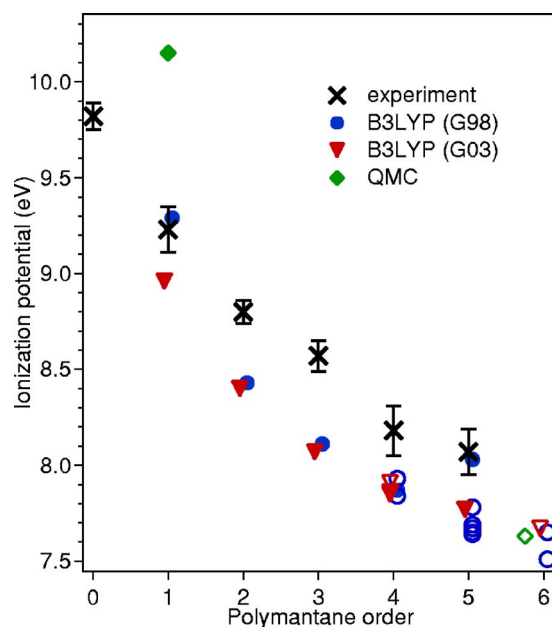


FIG. 3. (Color online) Comparison of the experimental data and DFT [B3LYP/6-31G(*d*)] calculations with GAUSSIAN03 (Ref. 3) and GAUSSIAN98 (Ref. 19) as well as QMC (Ref. 20) predictions for the ionization potentials of diamondoids. Calculated values corresponding to the experimental data are shown with solid markers. Additional calculated isomers are shown with open symbols.

well within the trend of comparable size diamondoids. The two DFT calculations^{3,19} agree with each other except for adamantane and [1(2,3)4]-pentamantane. Comparing them to the data, the calculations of Fokin *et al.* systematically underestimate the experimental IP by about 0.3–0.4 eV. For completeness it should be mentioned that the vertical IPs calculated by Fokin *et al.* are close to the experimental data. However, the experimental method yields the adiabatic IP, as discussed above. For the calculated IPs of Lu *et al.*,¹⁹ the same deviation is observed except for adamantane and [1(2,3)4]-pentamantane. For these two diamondoids the theoretical values almost precisely coincide with the experimental data. For further discussion of this aspect, the IPs calculated by Lu *et al.* for all other tetramantane and pentamantane structures as well as hexamantane are also added to Fig. 3 (open circles). It can be seen that in the calculations of Lu *et al.*, a general monotonic trend exists and that [1(2,3)4]-pentamantane is a clear outlier. The calculated IP for [1(2,3)4]-pentamantane is about 200 meV higher than that of any other pentamantane structure and still at least 100 meV higher than the IP for any of the three tetramantanes.

To shed further light on this discussion, the present data shall be compared to earlier findings on another carbon cluster system, the fullerenes. Fullerenes are sp^2 -hybridized carbon clusters that can also be size selected and investigated in their neutral form in the gas phase. Therefore, similar detailed comparisons between theoretical predictions and experimental data have been made for fullerenes as in the present investigation of diamondoids. In a recent study Sánchez *et al.*²¹ applied the same theoretical methods, using the same program package as Lu *et al.*¹⁹ for diamondoids, to calculate

the adiabatic IPs of different size fullerenes. Again, the results yield good overall agreement with experimental IPs. The absolute theoretical values, however, systematically underestimate the experimental results by about 0.5 eV. In contrast to diamondoids, the IPs of fullerenes exhibit no monotonous trend regarding size dependence.²¹ The highly stable “magic number” fullerenes C₅₀, C₆₀, and C₇₀ exhibit considerably higher ionization energies.

Taking a closer look at the calculations for diamondoids from Lu *et al.*,¹⁹ it can be seen that here a similar effect is predicted for diamondoids. The IPs of the highly symmetric [1231241(2)3]-decamantane (*T* group) and [1(2,3)4]-pentamantane (*T_d* group) are calculated to stand out and to be several hundred meV higher than their lower symmetry neighbors. For diamondoids, however, such strong isomeric effects predicted by Lu *et al.* are not confirmed by the experiments (see, e.g., [1(2,3)4]-pentamantane in Fig. 3). The data show no deviation from the monotonic trend with decreasing size for the IPs of diamondoids and no evidence for magic numbers in the IP is found, similar to the calculations of Fokin *et al.*³ More generally, it can be seen from the calculations of Sánchez *et al.*²¹ for fullerenes and from the comparison of this work (Fig. 3) with the calculations from Fokin *et al.*³ and Lu *et al.*¹⁹ for diamondoids that the employed theoretical techniques tend to systematically underestimate the ionization energies of carbon clusters by several hundred meV. The data are reproduced only by the calculations of Lu *et al.* for high symmetry diamondoids, which are standing out from the otherwise too low values. In this context it should be mentioned that adamantane is also highly symmetric belonging to the *T_d* group. The isomeric effects predicted by the DFT calculations may still be expected to exist as only a single isomer of each diamondoid class has been investigated. Nonetheless, in case of diamondoids the monotonic decrease of the IP shows that the size is the dominating factor, whereas for fullerenes it is their structure.

In summary the ionization potentials for diamondoids from adamantane through pentamantane have been measured. A strictly monotonic trend as function of size has been found. From the present results for diamondoids and earlier investigations on fullerenes, it can be seen that DFT calcula-

tions systematically underestimate the IPs of carbon clusters by several hundred meV.

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