Evolution of the Structural and Electronic Properties of Medium-Sized Sodium Clusters: A Honeycomb-Like Na_{20} Cluster

Wei Guo Sun, Jing Jing Wang, Cheng Lu, Xin Xin Xia, Xiao Yu Kuang, and Andreas Hermann

ABSTRACT: Sodium is one of the best examples of a free-electron-like metal and of a certain technological interest. However, an unambiguous determination of the structural evolution of sodium clusters is challenging. Here, we performed an unbiased structure search among neutral and anionic sodium clusters in the medium size range of 10–25 atoms, using the Crystal structure Analysis by Particle Swarm Optimization (CALYPSO) method. Geometries are determined by CALYPSO structure searches, followed by reoptimization of a large number of candidate structures. For most cluster sizes the simulated photoelectron spectra of the lowest-energy structures are in excellent agreement with the experimental data, indicating that the current ground-state structures are the true minima. The equilibrium geometries show that, for both neutral and anionic species, the structural evolution from bilayer structures to layered structures outides with interior atoms occurs at \( n = 16 \). A novel unprecedented honeycomb-like structure of Na_{20} cluster with \( \mathbf{C}_3 \) symmetry is uncovered, which is more stable than the prior suggested structure based on pentagonal structural motifs.

1. INTRODUCTION

The geometric structure of atomic clusters’ ground state is one of their most interesting properties and is a prerequisite to an accurate calculation of their electronic and other attributes.\(^{1-6}\) A large amount of work has been done, for instance, to determine the ground-state structures of small sodium clusters.\(^{7-12}\) Unfortunately, the lowest-energy structures of clusters are generally not amenable to direct experimental determination. Thus, it is customary to test the obtained structures indirectly, by comparing the experimental vertical detachment energy (VDE) and adiabatic detachment energy (ADE) with theoretical calculations.\(^{13,14}\) To thus confirm ground-state geometries, time-dependent density functional theory (TD-DFT) calculations can be performed to simulate the photoelectron spectrum (PES). The structure of the PES results from the superposition of the spectra of more or less different structures and can provide a detailed electronic fingerprint of those structures, as well as information on the ionization dynamics.\(^{15-17}\) Sodium in the extended state is one of the best representatives of a simple free-electron metal, in part because of the simple valence electron structure of sodium. Small sodium clusters have therefore received considerable attention from both the experimental and theoretical points of view.\(^{18-20}\) In 1984, based on the discovery of “magic numbers” in the abundance spectra of Na\(_n\) with \( n \) up to \( \sim 100 \), Knight et al. established the spherical jellium model,\(^ {21} \), which provides a simplified rule that the valence electrons of a cluster fill the spherical orbitals of a superatom according to the pattern of \([1s^21p^61d^{9\sigma}2s^22p^21g^{1\sigma}2d^{10\sigma}]\). After this seminal discovery in sodium clusters, Bonaic-Koutecký et al. explored computationally the relation between geometric structure and relative stability of small sodium clusters up to \( n = 9 \) and also demonstrated the complete analogy to the electronic properties of Li\(_n\) clusters.\(^ {22}\) The ground-state geometries of anionic sodium clusters \((n = 4-19)\) were investigated by photoelectron spectroscopy and finite-temperature ab initio molecular dynamics calculations.\(^ {14}\) The geometries of neutral and singly charged sodium clusters up to 20 atoms were also calculated systematically, and the influence of electronic correlation on the electronic structure and the dynamic properties of small sodium clusters was examined.\(^ {23}\) Quite recently, Nagare et al. discussed the electronic structure and equilibrium geometries of sodium clusters in the size range from 2 to 20 atoms as a
function of confinement, relying on a real-space implementation of DFT.

Although tremendous progress has been made in the study of sodium clusters, especially regarding the geometric structures of small sodium clusters, the ground-state geometries and corresponding electronic properties of medium-sized clusters have so far resisted interpretation. For example, the fundamental properties of the lowest-energy \( \text{Na}_{20} \) cluster are still a subject of controversy.\(^7,27\) The main reasons may be further optimized using DFT within the hybrid B3LYP functional.\(^{36}\) as implemented in the Gaussian 09 suite of programs.\(^{37}\) The all-electron basis set 6-311+G(d)\(^{38}\) is selected for the determination of the lowest-energy structures of medium-sized sodium clusters. Different spin multiplicities are considered in the geometric optimization process, up to sextet (quintet) for odd (even) electron numbers. Meanwhile, harmonic vibrational frequencies are calculated to ensure that the obtained structures are local minima. The photoelectron spectra of the anionic sodium clusters, which provide information on not only the ground electronic state of the anionic but also the ground and excited electronic states of the neutral species, are simulated using the TD-DFT method\(^39\) and compared with the experimental data.\(^{13,14}\) Each anionic cluster has a unique electronic structure, so the different isomers can be easily distinguished by their photoelectron spectra. Finally, chemical bonding analysis is performed by natural bond orbital (NBO) and adaptive natural density partitioning (AdNDP) methods.\(^40\) To test the reliability of our calculations, we also performed geometric optimization for small neutral and charged sodium dimers (\( \text{Na}_2, \text{Na}_2^+, \text{Na}_2^- \)) through different functionals with 6-311+G(d) basis sets. The calculated results are summarized in Table S1. It can be seen from Table S1 that the calculated bond length, vibrational frequency, dissociation energy, VDE, and ionization potential of the small sodium dimers based on B3LYP methods are in good agreement with the experimental values. In fact, the validity of the hybrid B3LYP functional for small and medium-sized sodium clusters has been confirmed and reported by Solov'ev et al.\(^{25}\) and Chandrakumar et al.\(^{41}\) So, B3LYP/6-311+G(d) is the reasonable method for medium-sized sodium clusters, and it therefore has been selected in our following calculations.

3. RESULTS AND DISCUSSIONS

3.1. Geometric Structure. We used the scheme described in the previous section to obtain the global minimum structures of neutral and anionic sodium clusters in the size range of \( 10 \leq n \leq 25 \). The lowest-energy structures for each size are displayed in Figure 1. The electronic states and point symmetries of these structures are given in the Table 1. Other low-lying isomers with their symmetries and relative energies are shown in Figures S1 and S2 in the Supporting Information.

It can be seen in Figure 1 that, with the exception of \( n = 15, 19, 24 \), the global minimum structures of neutral and anionic clusters are different. The structure of \( \text{Na}_{13} \) is found to be a bicapped antiprism with a bilayer structure, which is in full compliance with Solov'ev et al.\(^{25}\) by using B3LYP/6-311+G(d), while \( \text{Na}_{10}^- \) preserves the bilayer trapezoidal shape. We notice that the energy of \( \text{Na}_{11}^- \) obtained here is only slightly lower than the metastable structure that is shown in Figure S1. \( \text{Na}_{12−13} \) adopt oblate layer structures by fusing hexagonal polyhedral sodium units, while \( \text{Na}_{13}^- \) has a bilayer oblate structure with \( C_{2v} \) symmetry. For \( n = 14−16 \), all of the neutral structures adopt oblate shapes that can be viewed as sodium atoms capping the equatorial waist region of \( \text{Na}_{14} \), while the anionic structures are deformations of the corresponding neutral structures, except for \( n = 15 \). The anions show a structural evolution pattern in agreement with previous findings by Moseler et al.\(^{14}\) For \( n > 16 \), the lowest-energy structures of neutral \( \text{Na}_n \) clusters are also in accordance with theoretical studies,\(^\ast\) with a few exceptions. A distinct structural evolution from bilayer structures to layered arrangements with interior atoms occurs at \( n = 16 \). The lowest-energy structures of the medium-sized anionic clusters are also in excellent agreement
honeycomb-like structure is formed. To further confirm that the honeycomb-like Na$_{20}$ structure is the true global minimum structure, many different functionals have also been examined, and the calculated results are listed in Table S2. However, on the basis of the calculations with both MP2 and CCSD, and 6-311+G(d) basis set, we found that the C$_3$ symmetry Na$_{20}$ structure is always lower in energy than the previous C$_1$ structure.\(^7,27,42,43\) The total energy difference is 0.065 eV (MP2) and 0.150 eV (CCSD), respectively. The optimized atomic coordinates along with the vibration frequency are given in the Tables S3 and S4. As for anionic Na$_{20}$ a structure with C$_1$ symmetry in pyramidal shape emerged as most stable. The C$_{2v}$ structure of the Na$_{21}$ isomer is based on a pentagonal prism with four atoms along the central internal axis, while Na$_{22}$ forms a similar structure that distorts the neutral Na$_{23}$ cluster’s central axis. For $n = 22, 23$, the sodium cluster isomers contain two interior atoms, while for $n = 24, 25$ there are three internal atoms in double icosahedral structures. This structural evolution illustrates that interior atoms in the neutral clusters steadily descend into the icosahedral spherical structures with increased atom numbers. Anionic clusters with 22–25 atoms also prefer spherical and prolate structures derived from the compact double-icosahedron, differing only by slight distortions or minute changes in the positions of capping atoms from the corresponding neutral structures. As stated above, the ground-state structures of the Na$_n^Q (n = 10–25, Q = 0, −1)$ clusters evolve from bilayer structures to layered motifs with interior atoms for $n > 16$, based on icosahedral structures, and CALYPSO emerged as an elegant and effective approach to obtain the novel putative honeycomb-like Na$_{20}$ cluster with C$_3$ symmetry.

3.2. Photoelectron Spectra of Na$_n^−$ Clusters. Photoelectron spectroscopy is one of most significant experimental tools to get insight into, and to extract electronic binding energies from, a wide variety of atomic and molecular clusters as well as condensed-matter systems.\(^14,44\) To confirm the ground-state structures of the sodium clusters, the photoelectron spectra of the Na$_n^− (n = 10–25)$ clusters are simulated using TD-DFT and compared to the available experimental

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The simulated spectra together with the experimental PES data are displayed in Figure 2. The VDE is taken from the first peak position of the spectra, and the ADE for the neutral clusters is obtained by the corresponding intersection between the baseline and the rising edge of the first peak. The VDE and the ADE values are summarized in Table S5 in the Supporting Information, along with the experimental data for comparison. One can see satisfactory overall agreement between theoretical and experimental data, indicating the validity of our theoretical approach.

The simulated spectrum of Na\textsubscript{10} shows three major peaks, and the first peak is located at 1.149 eV, which excellently reproduces the experimental features. In the simulated spectrum of Na\textsubscript{11}, three peaks are also observed as in the experimental PES, although the first peak is moved to higher energy compared to experiment. The first weak peak on the simulated spectrum of Na\textsubscript{12} emerges at 1.184 eV, followed by a broadened area and a distinct peak at 1.653 eV. The major peaks of experimental PES are successfully reproduced by theoretical calculation. In the case of Na\textsubscript{15}, the simulated spectrum shows a broad peak at 1.509 eV, which presents the same characteristic as the experimental one. In the simulated spectrum of Na\textsubscript{16}, it has a weak peak centered at 1.124 eV and an intense peak at 1.751 eV. Such three-peak behavior also occurred in experiment. The simulated spectrum of Na\textsubscript{17} exhibits four major peaks, and the first peak appears at 1.361 eV, which is broadened into two peaks in experimental PES. A similar situation occurs for Na\textsubscript{25}. For the PES of Na\textsubscript{50} both theoretical and experimental PES yield two peaks and have similar VDE value. In the simulated spectrum of Na\textsubscript{79} the first two peaks are separated by a valley, while these peaks merge together in experimental PES. For Na\textsubscript{15}, the simulated spectrum excellently reproduces the experimental PES, and both of them present the same trend and yield three peaks. A similar situation occurs for Na\textsubscript{19} compared with the Na\textsubscript{15}, a weak shoulder emerges in the simulated spectrum of Na\textsubscript{19} because of the appearance of a new 2S shell. In the simulated spectrum of Na\textsubscript{20}, it also has four major peaks as observed in the experimental PES, while the second one is slightly narrow. The simulated spectrum of Na\textsubscript{21} shows a weak peak centered at 1.250 eV and an intense peak at 2.173 eV, which successfully reproduces the experimental characteristics. For Na\textsubscript{22}, the simulated PES shows four major peaks, and the first is located around 1.298 eV. The simulated PES of Na\textsubscript{23} exhibits three obvious peaks, and the first small peak appears at 1.378 eV, which is close to the experimental result. For Na\textsubscript{24}, the simulated spectrum successfully reproduces the experimental spectrum; both of them show the same trend and yield three obvious peaks. The satisfactory agreement between simulated and experimental spectra within measurement error suggest that the lowest-energy structures of the sodium clusters are truly global minima. It should be pointed out that for some odd number of atom (n = 11, 13, 15, ...) clusters, a more pronounced peak splitting is found in the simulated spectrum as compared to the experimental PES. This discrepancy between theory and experiment may be attributed to the following two aspects. In technical aspects, earlier works reported that sodium clusters at room temperature may be considered as liquidlike, and several degenerate isomers are explored, which state of the PES may cannot be well-produced. In theoretical aspects, the odd number of anionic clusters with closed electronic spin shell is more stable than the even clusters with the open spin shell, which is also the major factor for the discrepancy of sodium clusters with odd size. 

3.3. Relative Stabilities of Na\textsubscript{n}\textsuperscript{Q} (n = 10–25, Q = 0, –1). The average binding energy (E\textsubscript{b}) is representative of the intrinsic stability of sodium clusters, and it is calculated as

\[ E_b(Na_n^Q) = \left[ (n - 1)E(Na) + E(Na^2) - E(Na_n^Q) \right] /n \]

where E is the total energy corresponding to the respective neutral or anionic sodium clusters. E\textsubscript{b} indicates the energy gain of adding a neutral or anionic Na atom to an existing cluster. As shown in Figure 3a, all of the neutral Na\textsubscript{n} clusters have lower E\textsubscript{b} values than their anionic states, suggesting it is always favorable to delocalize anionic charge in the clusters as opposed to a single atom. The curve of E\textsubscript{b} shows opposite odd—even oscillating behaviors from n = 10 to 17 for neutral and anionic clusters: for the neutral Na\textsubscript{n} clusters, the binding energy curves increase nonmonotonically with even maxima in the range of n = 10–20 and reach a global maximum at n = 20, followed by a flat energy trend for n > 20. As for anionic Na\textsubscript{n}\textsuperscript{−} clusters, odd-size maxima are followed by a global maximum of 0.707 eV at n = 19. Thus, Na\textsubscript{20} and Na\textsubscript{21} are more stable than their adjacent clusters. This is in line with the explanation by closed-shell effects, which predict the stability of clusters with 20 valence electrons (1s\textsuperscript{2}2s\textsuperscript{2}2p\textsuperscript{6}3s\textsuperscript{2}3p\textsuperscript{6}4s\textsuperscript{2}4p\textsuperscript{6}5s\textsuperscript{2}) by the spherical jellium model.

As is well-known, the second-order energy difference (\Delta\textsuperscript{2}E) is another parameter that can reflect the relative stability of clusters. Figure 3b shows the size dependence of \Delta\textsuperscript{2}E for sodium clusters, where \Delta\textsuperscript{2}E is defined as

\[ \Delta^2E(Na_n^Q) = E(Na_{n-1}^Q) + E(Na_{n+1}^Q) - 2E(Na_n^Q) \]

The apparent peaks for the neutral sodium are formed at n = 12, 14, 16, 18, 20, 22, and 24, suggesting that even-sized clusters Na\textsubscript{n} are of greater stability than neighboring odd-sized clusters. Moreover, the overall highest \Delta\textsuperscript{2}E value of Na\textsubscript{20} again demonstrates its strong relative stability. The trend of the \Delta\textsuperscript{2}E curves is in accordance with the average binding energy. Except
for Na_{13}^-, the anionic Na^- clusters show opposite odd—even oscillating trends compared to the neutral counterparts. Several distinct peaks of the Δ^2E curve for anionic clusters indicate that Na_{13,15,17,21,23} are more stable than the even-sized clusters. The same phenomenon has been reported by Aguado et al.\(^7\) and Huber et al.\(^13\) based on the DFT level with exchange-correlation effects treated within the local density approximation.

The energy gap (\(E_{\text{gap}}\)) is another physical quantity that can reflect clusters' chemical stability, via the energy cost of an electronic excitation from the highest occupied molecular orbitals (HOMO) to the lowest unoccupied molecular orbitals (LUMO); higher values imply chemical inertness (or at least less reactivity). On this basis, the calculated \(E_{\text{gap}}\) values are listed in Table 1 and are also plotted in Figure 3c as a function of cluster size. We can clearly see that, for neutral clusters, the \(E_{\text{gap}}\) values of even-sized clusters are higher than for odd-sized clusters. This suggests that even clusters possess stronger chemical stability than their neighbors. As the neutral curve shows, the largest \(E_{\text{gap}}\) for neutral Na clusters occurs at \(n = 20\), which is in accordance with the results from both \(E_b\) and \(\Delta^2E\). The number of valence electrons of Na_{20} is 20 (1s^21p^61d^102s^2), which exhibits the magic properties according to the jellium model. The variation of the \(E_{\text{gap}}\) values matches \(\Delta^2E\) as the cluster sizes increases. This suggests that cluster stability is driven by electronic, instead of structural, effects. Accordingly, for anionic clusters, the odd—even alteration behaviors of \(E_{\text{gap}}\) curve present the opposite trend compared to the corresponding neutral clusters: the values of \(E_{\text{gap}}\) show odd—even alterations with odd-sized maxima, where overall maxima occur at \(n = 11, 13, 17,\) and 19, which suggests that these clusters have stronger chemical stability than their adjacent clusters. On the basis of the above analysis, we can conclude that honeycomb-like Na_{20} is a unique magic cluster and should be highly stable and chemically inert. There is a less-distinct magic number effect for the anionic clusters, where Na_{15} and Na_{17} also exhibit significantly higher stability than others.

3.4. Chemical Bonding Analysis. To further elucidate the stability of the neutral magic Na_{20} cluster with C\(_3\) symmetry, which features the highest electronic \(E_{\text{gap}}\) across all our neutral clusters structures, we analyze its bonding nature by displaying HOMO–LUMO molecular orbitals in Figure 4. Since sodium clusters can be viewed as typical model systems rationalized by the spherical jellium model, this can also be demonstrated by the occupied molecular orbitals. The nondegenerate HOMO is primarily a 2s-type atomic orbital, corresponding to the spherical shell structure within the peripheral and internal Na–Na bonds. Meanwhile, the LUMO resembles a f-type atomic orbital. The molecular orbitals of HOMO\(^q\) (\(q = 1–5\)) are d-type atomic orbitals: the HOMO–3 orbital exhibits the distinctive d\(_z^2\) direction, while the other directions of d-atomic orbitals (such as d\(_{x^2−y^2}\), d\(_{yz}\), d\(_{xy}\), and d\(_{x^2−y^2}\)) feature in HOMO–1, HOMO–2, HOMO–4, and HOMO–5, respectively. The HOMO–6 to HOMO–8 orbitals are of p-type atomic orbital character (HOMO–8, for instance, can be assigned the p\(_z\) orbital). Lastly, the orbital of the HOMO–9 is a classical s-type atomic orbital within the spherical shell structure, and it is formed by σ NaNa bonds. We can deduce that the neutral Na_{20} cluster's electronic structure is best described as 1s^21p^61d^102s^2, which is consistent with the HOMO, LUMO, and lower occupied molecular orbitals. The level degeneracies are broken by the nonspherical cluster geometry; however, some remain: the molecular orbitals of HOMO–1, HOMO–2, as well as HOMO–4, HOMO–5, HOMO–6, and HOMO–7 are degenerate. The large gap between the superatom 2s and 1f states is, to the best of our knowledge, the reason why the neutral Na_{20} exhibits the sizable energy gap of 1.43 eV between the HOMO–LUMO.

To gain alternate insight into the chemical bonding of neutral honeycomb-like C\(_3\)–Na_{20}, we performed chemical bonding analysis for Na_{20} by using the AdNDP method,\(^35,46\) which represents the bonding of a molecule in terms of localized and
delocalized \( n \)-center two-electron (\( nc-2e \)) bonds, with \( n \) potentially ranging from one to the total number of atoms in the systems. The detailed AdNDP analysis of the \( \text{Na}_{20} \) cluster is depicted in Figure 5, ordered by occupation number (ON).

\[ \alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3n} \]

Here we present and analyze the results on the size dependence of the polarizabilities of \( \text{Na}_{n}^Q \) \( (n = 10-25, Q = 0, -1) \) clusters as determined from the respective lowest-energy structures. As illustrated in Figure 6, the overall polarizability per atom is decreasing nonmonotonically with increasing cluster size \( n \). Obviously, the values of anionic sodium clusters are higher than the neutral, and also demonstrate their sensitivity to the details of the cluster structure. The anisotropy of the anionic cluster structures is particularly sensitive to the details of the cluster structure. The anisotropy of the anionic cluster structures is particularly sensitive to the details of the cluster structure. The anisotropy of the anionic cluster structures is particularly sensitive to the details of the cluster structure. The anisotropy of the anionic cluster structures is particularly sensitive to the details of the cluster structure. The anisotropy of the anionic cluster structures is particularly sensitive to the details of the cluster structure. The anisotropy of the anionic cluster structures is particularly sensitive to the details of the cluster structure. The anisotropy of the anionic cluster structures is particularly sensitive to the details of the cluster structure.

![Figure 5](image_url)

**Figure 5.** Chemical bonding analysis of the \( \text{Na}_{20} \) cluster using the AdNDP method. ON stands for occupation number.

![Figure 6](image_url)

**Figure 6.** Polarizabilities per atom for \( \text{Na}_{n}^Q \) \( (n = 10-25, Q = 0, -1) \) clusters. The experimental data (in red) stem from Ma.27

In summary, a family of geometric structures and electronic properties of medium-sized sodium clusters \( \text{Na}_{n}^Q \) \( (n = 10-25, Q = 0, -1) \) has been acquired by CALYPSO searching method and subsequent DFT optimizations; the global minima of the neutral \( \text{Na}_{20} \) with \( C_3 \) symmetry has been proposed as a novel honeycomb-like isomer. Meanwhile, according to the considerable influence of the jellium model and electron shell structures, the structures evolve from bilayer structures to layered motifs with interior atoms relatively gradually for \( n > 16 \), with the latter based on icosahedral structures. The simulated photoelectron spectra show satisfying agreement with the experimental spectra for most sizes across the range of cluster sizes up to 25 atoms, which demonstrates that the structures we obtained are truly global minima. In particular, the \( \text{Na}_{20} \) cluster is found to be the most stable structure in the size range of \( n = 10-25 \) through an analysis of the relative stabilities.

**4. CONCLUSIONS**

The first bond depicts a lone pair on the internal Na with ON = 1.998 \( \text{e} \), compared to 2.00 \( \text{e} \) \( \text{in} \) the ideal case, meaning that 0.002 \( \text{e} \) participates in \( \pi \) bonding with the surrounding sodium atoms. Moreover, the AdNDP reveals a \( 4c-2e \) bond describing stronger Na−Na bonds including delocalized bonding in the structure and form three \( 8c-2e \) σ-bonds with ON = 1.945 \( \text{e} \), ON = 1.940 \( \text{e} \) and ON = 1.934 \( \text{e} \), respectively. Additional delocalized bonding is provided in the shape of five \( 12c-2e \) σ-bonds with ON ranging from 1.815 \( \text{e} \) to 1.950 \( \text{e} \). For each of these bonds, the internal sodium atom together with two peripheral sodium atoms contributes to the σ-bonds. The \( 16c-2e \) bond, finally, describes a σ-bond with the lowest occupation number ON = 1.815 \( \text{e} \), where the internal atom forms a strong σ-bond and contributes to the high-energy gap in the \( \text{Na}_{20} \) clusters. Conceivably, most of the σ-bonds contribute to the substantial stabilization of the neutral \( \text{Cs}_{6}-\text{Na}_{20} \) cluster.

**3.5. Polarizability.** The static electric dipole polarizability can determine the dynamical response of a bound system to external fields, and the analysis of atomic polarizabilities suggests a strong dependence on the structure of the clusters.27,28 For the curves shown in Figure 6, the polarizability per atom is defined in terms of the diagonal polarizability tensor components, and it is expressed as follows:

\[ \alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3n} \]
estimated and that a significant polarizability minimum related to electronic shell closings at \( n = 18 \).

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02340.

The details of the low-lying isomers, the calculated VDE, ADE for the ground-state \( \text{Na}_n \) \((n \geq 10-25, \text{Q} = -1)\) together with the available experimental data and the Cartesian coordinates of \( \text{Na}_{20} \) cluster (PDF)

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Notes

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