Phosphorus cluster cations formed in doped helium nanodroplets are different

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Abstract

Positively charged cluster ions of phosphorus were formed upon electron ionization of doped helium nanodroplets. The vapors of red phosphorus and a phosphate sample were picked up into neutral and charged helium nanodroplets. Independent on the conditions used, the cluster size distributions exhibit pronounced odd-even oscillations that are opposite to almost all experimental and theoretical patterns published in the literature. The low temperature environment of the superfluid He matrix quenches fragmentation and the charged phosphorus clusters resemble the structure of the neutral precursors.

Introduction

Phosphorus has several allotropes that exhibit strikingly different properties [1]. White phosphorus was the first form of the element to be prepared in 1669 [2], and it is still the best characterized. At room temperature, its crystal structure is a loosely bound aggregation of tetrahedral $P_4$ units. Black phosphorus is the thermodynamically stable allotrope at ambient conditions and forms puckered two-dimensional sheets, similar to graphite. The third and most complex allotrope form of phosphorus is red or violet phosphorus. Vaporizing red phosphorus at low temperatures produces a gas primarily consisting of $P_4$. With increasing temperatures, the relative amount of $P_3$ vapor increases and atomic phosphorus vapor begins to appear at even higher temperatures [3]. Due to its low thermodynamic stability the abundance of $P_3$ in the vapor relative to those of $P_2$ and $P_4$ is negligible. Smets et al. [4] studied photo ionization of $P_4$ vapor and determined $P_4^+$ as the dominant product at all photon energies investigated. At a photon energy of 19 eV the ratios between the ion yields of the fragments $P_3^+$ and $P_2^+$ and the parent cation $P_4^+$ are 0.22 and 0.16, respectively. No atomic fragment $P^+$ was observed. Monnom et al. [5] determined partial electron ionization cross sections of $P_4$ and obtained at an electron energy of 70 eV relative abundances for the fragments $P^+$, $P_3^+$ and $P_2^+$ with respect to the parent cation $P_4^+$ of 0.097, 0.2 and 0.074, respectively.

Phosphorus clusters are likely to display equally rich structural variety. This has motivated many experimental and theoretical studies starting with the pioneering mass spectrometric experiments of Martin in 1986 [6]. They vaporized red phosphorus at 300°C into a reaction chamber filled with 1 mbar helium. The outer mantle of the reaction chamber was cooled with liquid nitrogen and neutral clusters were formed via gas aggregation. Positively charged clusters $P_4^+$ were formed upon electron ionization with 80 eV electrons. The recorded mass spectra showed pronounced odd-even oscillations with odd numbered clusters about twice as intense as even numbered species.

Huang et al. [7-9] formed cationic and anionic phosphorus clusters by laser vaporization of red phosphorus without subsequent ionization. Cluster sizes were reported up to $P_{45}^-$ [10] and $P_{45}^+$ [9]. Particularly intense peaks were observed for $n = 8k + 1$ (k ≥ 5 and k ≥ 3, for anions and cations, respectively). Bulgakov et al. studied phosphorus clusters up to $P_39^+$ utilizing mass spectrometry [11-13]. Electron ionization of neutral phosphorus clusters formed upon laser ablation were preferentially even-numbered with local abundance maxima at n = 8, 10, 14, and 40. In contrast, odd-numbered clusters were more abundant for charged clusters formed during the laser ablation process with local abundance maxima at n = 8k + 1 (k ≥ 5). Kong reported on large phosphorus cluster cations up to n = 300 utilizing a MALDI TOF instrument and anions up to n=500 utilizing a Fourier transform ion cyclotron resonance mass spectrometer system [14]. $P_3^+$ cations with n=8k+1 (k=3-10) exhibit again higher intensities. However, this 8k+1 rule became insignificant for k>11. Similar results can be observed for the anions and the 8k+1 rule was applicable for k<18.

The structure of phosphorus clusters in different charge states has been investigated by various quantum chemical methods [15-26] ranging from a molecular dynamics/density functional MD/DF approach [15] to coupled-cluster theory CCSD(T) [19].
and comprehensive genetic algorithm DFT [26]. Compared to extensive computational studies of neutral phosphorus clusters [16-19, 21, 22, 26], much less is known about charged clusters, which were most frequently investigated experimentally. For neutral phosphorus clusters, odd-membered clusters \( P_{2m+1} \) were calculated to be less stable than the most stable even-membered cluster \( P_n \) [16]. For larger cationic phosphorus clusters with \( n=25+8k \) (\( k=1-8 \)), Chen et al. [20] constructed a series of chain-like configurations by adding cuneane \( P_n \) units to a presumed \( C_4 \) structure of \( P_{25} \). Xue et al. [25] studied the global minimum structures of odd-sized \( P_{2m+1}^+ (m=1-12) \) cations using first-principles simulated annealing.

The stability and fragmentation of phosphorus clusters were also experimentally studied via collision-induced dissociation (CID) mass spectrometry [9, 27]. The primary dissociation pathway of \( P_{2m+1}^+ (6 \leq m \leq 11) \) is the loss of a \( P_6 \) unit. For magic cluster ions of \( P_{6m+1}^+ (3 \leq k \leq 8) \), the dissociation pathways progressively changed from the loss of \( P_6 \) to loss of \( P_8 \).

Here we investigate \( P_n^+ \) cluster ions formed upon pickup into neutral and charged helium nanodroplets (HNDs). The ionization mechanism of dopants in helium nanodroplets depends on their location [28]. Heliopholic dopants, such as alkali atoms [29, 30] or small alkali clusters [31-34] reside in dimples on the surface of the droplets and are most efficiently ionized via Penning ionization by heliophobic metastable helium atoms \( He^+ \). Heliopholic dopants, such as phosphorus and \( P_6 \) clusters submerge into the droplets and are preferentially ionized via charge transfer from an initially formed \( He^+ \) or a small charged \( He_{n}^+ \) cluster ion. This process is highly exothermic as the difference in the ionization energy of He (He+) and \( P_n \) is completely transferred into the dopant cation. The vertical ionization energy of \( P_6 \) is 9.5 eV [5, 35, 36] and its adiabatic ionization energy is 9.2 eV [36]. More than 15 eV excess energy remains in the \( P_n^+ \) ion upon charge transfer from \( He^+ \) as the ionization energy of He is 24.59 eV [37]. If this energy can be transferred to the surrounding helium matrix before fragmentation occurs, the resulting mass spectra match the neutral dopant distribution. The effect of the low temperature matrix on the resulting cluster size distributions is investigated via high-resolution mass spectrometry.

**Experimental**

**XPS measurements**

Resbond® 920 powder was mixed with pure water (14:1). A thin layer of the resulting paste was applied to a stainless steel surface and heated to 150 °C for eight hours in a compartment dryer. This prepared sample was analyzed by XPS using a Thermo MultiLab 2000 spectrometer with an alpha 110 hemispherical analyzer (Thermo Electron) in the constant analyzer energy mode (surveys with pass energy 100 eV, energy resolution 2 eV; detailed spectra with pass energy 25eV, energy resolution 0.8 eV). A twin crystal monochromator provided Al Kα radiation (1486.6 eV) with a focus of 650 µm in diameter.

**Production of helium nanodroplets**

Phosphorus clusters were produced in helium nanodroplets using two different experimental setups, called ClusTOF and Toffy. In both machines, HNDs were produced by supersonic jet expansion of ultrapure helium (99.9999 %) through a 5 µm pinhole nozzle into ultrahigh vacuum. The nozzle was cooled with a closed-cycle cryo cooler (Sumitomo Heavy industries) and counterheated with an ohmic resistor operated with a PID controller (Lakeshore Model 331). Without pressurized helium (2 to 2.4 MPa) in the source the pressure behind the nozzle was below \( 10^{-9} \) Pa and rises during operation with helium to \( 1x10^{-2} \) Pa. According to Gomez et al. [38] the resulting average droplet size is between \( 2.5x10^5 \) and \( 1x10^6 \) He atoms for the present conditions. To prevent destruction of HNDs by collisions with shock fronts, the resulting jet of He was then passing a molecular beam skimmer (Beam Dynamics, Inc), located downstream of the nozzle.

**ClusTOF**

In ClusTOF, the nozzle temperature for HND production was 9.99 K with a stagnant He pressure of 2.4 MPa. The beam is then passing a 0.8 mm skimmer positioned about 5 mm from the nozzle. The He beam was then passing a differentially pumped pickup chamber, containing an oven composed from an alumina ceramics bound with RESBOND® 920 Alumina Ceramic Adhesive (Final Advanced Materials GmbH). The ClusTOF mass spectrum shown in this work was recorded during a test run of a new high-temperature, ceramic based oven without any additional sample. When heated to 720 K, the oven started to emit \( P \) vapor. XPS measurements showed that the adhesive contains phosphorus compounds that are presumably the source of this vapor. Atomic or molecular phosphorus was picked up by the HNDs and agglomeration lead to the formation of neutral phosphorus clusters inside the helium droplets. Subsequently, the doped HND beam passed a 2.5 mm aperture into the next differentially pumped chamber with a pressure of pressure \( 3.8x10^{-6} \) Pa containing a Nier-type electron impact ionization unit. This ion source was operated at an electron energy of 80 eV and an electron current of 50 µA. The probability for an electron to hit the dopant cluster is negligibly small compared to the ionization of a He atom. Ion induced dipole interaction attracts the charge to the dopant and charge transfer from \( He^{+} \) to \( P_6 \) ionizes the phosphorus cluster. Low-mass ions are ejected from the large droplets due to mutual Coulomb repulsion of charge centers in multiply-charged HNDs [39]. These ions are extracted by weak electrostatic fields and guided into the extraction region of a reflectron time of flight mass spectrometer (H-Tof, Tofwerke) via a stack of einzel lenses. For further details of this experimental setup see ref. [40].
In Toffy, HNDs were produced at a nozzle temperature of 9.2 K and a stagnant He pressure of 2.0 MPa. The beam is then passing a 0.5 mm skimmer positioned about 10 mm from the nozzle. In contrast to ClusTOF, the HNDs are ionized by a Nier-type electron impact ionization unit directly after the skimmer. The ion source was operated at an electron energy of 70 eV and an electron current of 200 µA. Charged droplets were then mass per charge filtered for approximately $2.5 \times 10^5$ He/z before pickup of a vapor formed upon heating red phosphorus (99.99 %, Sigma-Aldrich product number 343242) to 690 K in an ohmically heated oven. The polarizability of capured phosphorus vapor is much higher than of He and therefore, ion induced dipole interaction attracts dopants to the charge centers. Charge transfer from He$_n^+$ to the first dopant arriving is highly exothermic and might lead to fragmentation of molecular dopants, unless the surrounding helium matrix is able to quench the excess energy before the fragments are separating. Further dopants will simply attach to an already existing P$_n^+$ cluster and the binding energy will be transferred to the surrounding He and lead to the evaporation of He atoms from the surface of the HND. In a very recent study, we observed that pre-doping of charged HNDs with a small amount of molecular hydrogen leads to the formation of odd-numbered hydrogen cluster ions H$_{2n+1}$ that efficiently transfer a proton to subsequently captured dopants having a higher proton affinity [41]. This is the case for all dopants other than Ne, Ar and O$_2$. Compared to electron transfer, proton transfer is a slow process which enables the surrounding He matrix to quench excess energy, even if it amounts several eV. Thus, proton transfer ionization inside a HND turns out to be a very gentle ionization mechanism that reduces fragmentation completely. After cluster formation, any remaining He atoms were boiled off in an evaporation cell with a He pressure of 47 mPa and the resulting ionic phosphorus clusters were analyzed in a time of flight mass spectrometer (Q-TOF Ultima Waters/Micromass). For further details of this experimental setup see [42].

**Results**

**XPS Analysis of Resbond® 920**

The XPS analysis of Resbond® 920 as showed in Figure 1 displayed several minor peaks resulting from impurities, such as magnesium and silicon. The spectrum was calibrated using the C1s (adventitious carbon) peak at 284.5 eV [43]. Relativ abundance of O:P (58%:16%) and the P2p binding energy indicate that the surface of Resbond® 920 mostly contains P$_2$O$_5$, P$_4$O$_{10}$ or similar. Reference values for P2p shown are taken from in P2p in P$_4$O$_{10}$. 

![Figure 1: XPS analysis of Resbond® 920 paste applied to a stainless steel surface. Characteristic peaks for O, Mg, Si, and P are labelled according to the calibration with C1s (adventitious carbon)](image-url)
Mass Spectra of phosphorus

Figure 2 shows the spectrum of cluster formation upon doping P from Resbond® 920 Alumina Ceramic Adhesive into neutral HNDs with subsequent ionization. The most abundant peaks are phosphorus clusters but also peaks of impurities from residual gas (e.g. N$_2$ and H$_2$O) and complexes of P with O are visible, most likely originating from phosphates and phosphorus pentaoxide of Resbond® 920. The spectrum shows a higher yield of even-numbered clusters compared to odd-numbered clusters. Two exceptions are $P_5^+$ and $P_7^+$ that show comparable of even higher yields than their respective neighbors $P_6^+$ and $P_8^+$. For clusters sizes n ≥ 26, a drop in ion yield after $P_{4k+2}$ steps ($P_{26}^+$, $P_{34}^+$, $P_{42}^+$) is visible. Furthermore, the ion yield of $P_{24}^+$ exceeds that of $P_{22}^+$, suggesting notable stability for that species.

Figure 2: Mass spectrum of cations formed upon electron ionization of HNDs doped with phosphorus vapor emitted from RESBOND® 920 Alumina Ceramic Adhesive. HNDs were produced at a He Pressure of 2.4 MPa and a nozzle temperature of 9.99 K (ionization energy 80 eV). The yield of even-numbered cluster ions is larger than that of neighbouring odd-numbered ones with the exception of $P_5$ and $P_7$. *Peak of residual C$_{60}$. Experimental setup “ClusTOF”. 


Figure 3 shows the spectrum obtained from cluster formation upon doping P into positively charged, size selected HNDs. The intensity of the even-numbered clusters exceeds the intensity of odd-numbered clusters even more than in the previous spectrum. However, for both the even-numbered series and the odd-numbered series a pattern with intensity anomalies for the addition of $P_4$ units are visible. For odd-numbered clusters, $P_{4n+2}$ are particularly abundant. The even numbered clusters exhibit particularly intense clusters for $P_{4n+2}$ species up to $P_{18}$ species. However, from $P_{24}$ onwards, ions of the composition $P_{4n}$ are exceedingly abundant.

Figure 3: Mass spectrum of cations formed upon doping the vapor of heated ($690 \text{ K}$) red phosphorus into charged HNDs that were size selected for approximately $2.5 \times 10^5 \text{ He/z}$. HNDs were produced at a He pressure of 2.0 MPa and a nozzle temperature of 9.2 K (ionization energy 80 eV). Even-numbered clusters are predominant, but odd-numbered $P_{4n+1}$ cluster ions remain still clearly visible. Experimental setup “Toffy”.
Figure 4 shows the spectrum obtained from cluster formation upon doping P into positively charged, size selected HNDs that were pre-doped with H$_2$. Clusters of the composition P$_{4n+2}$H$_n^+$ are particularly abundant, especially up to P$_{42}$H$_2^+$. Clusters with an odd number of P atoms are extremely scarce.

Figure 4: Mass spectrum of cations formed upon pickup of vaporized red phosphorus (690 K) into charged HNDs pre-doped with hydrogen. Proton transfer from H$_{2n+1}^+$ to the first phosphorus dopant (most likely P$_4$) forms protonated phosphorus species P$_m$H$_n^+$. HNDs that were size selected for approximately 2.5×10$^5$ He/z. HNDs were produced at a He Pressure of 2.0 MPa and a nozzle temperature of 9.2 K (ionization energy 80 eV). Even-numbered clusters are completely dominant, odd-numbered clusters are hardly visible. Experimental setup "Toffy".
Figure 5 and 6 show a comparison of the data of this work (ClusTOF, Toffy, Toffy H) with data from the literature. For these graphs, the normalized signals (0-100) were plotted logarithmically and shifted by a constant value to each subsequent spectrum. Figure 5 shows the comparison for small cluster (12 ≤ n ≤ 24). All phosphorus cluster ions formed in HNDs show a higher abundance of even-numbered clusters, whereas data from Kong and Martin show a higher abundance of odd-numbered clusters. Bulgakov et al. used two different methods of cluster ion formation. When ions were formed directly upon laser ablation, odd-numbered clusters are more abundant (labelled Bulg.00 in the graph [11]). In contrast, when neutral cluster formed upon laser ablation are subsequently ionized by electron impact ionization, even-numbered clusters were predominant (labelled Bulg.02 in the graph [13]). Figure 6 shows the comparison for larger clusters (25 ≤ n ≤ 67). Also here, cluster ions formed in HNDs show higher abundance of even-numbered clusters in contrast to cluster ions formed by other means. Especially for the data from Bulgakov (Bulg.00) and Huang, cluster ions of the species $P_{33}^+$ are notably prominent.
Discussion

Depending on the means of cluster formation and ionization, P cluster series exhibit vastly different traits. Vaporization of P occurs mainly in even-numbered \( P_2 \) and \( P_4 \) units, resulting in even-numbered aggregates. However, for cationic P odd-numbered closed-shell ions are electronically more stable. It stands to reason that odd-numbered clusters form as more stable products upon the decay of previously formed, even-numbered clusters.

Most results in the literature report a higher abundance for these closed-shell ions after electron ionization of neutral phosphorus clusters formed via gas aggregation [6], ionization upon laser ablation [11], and MALDI TOF analyses [14]. By temporal separation of laser ablation and ionization, Bulgakov et al. reported higher abundance of even-numbered clusters [13]. They hypothesized the formation of particularly stable structures such as even-numbered polyhedra.

The low temperature of HNDs and their high cooling power [44] are able to efficiently quench excess energy from various processes leading to the formation of cluster ions inside. Inelastic collisions of dopant vapor with HNDs and the binding energy of cluster formation introduce energy into the HNDs that leads to vibrational excitation and is released upon evaporation of He atoms. Each eV of internal energy results in the evaporation of about 1600 He atoms, which is determined by the binding energy of a He atom to a HND, i.e., 0.616 meV [45]. Due to the enormous size of HNDs containing millions of He atoms compared to the dopants, the probability for an electron to ionize the dopant directly is negligibly small. The dominant ionization mechanism for heliophilic dopants[28] is charge transfer from an initially formed He\(^+\) or a small He\(_{n}\)\(^+\) cluster. The difference in the ionization energies of \( P_m \) and He\(_n\) (\( n \geq 21 \)) is in the order of 15 eV, which is completely transferred into the dopant cluster ion. All size distributions of charged dopant cluster X\(_n\)\(^+\) formed upon electron ionization of neutral doped HNDs exhibit the same intensity anomalies as X\(_n\)\(^+\) formed by conventional techniques [46]. Therefore, we conclude that some of the excess energy released by the ionization process leads to the evaporation of dopant monomers X. Possible sources for this excess energy are the difference in the ionization energies mentioned above and the enhanced binding energy of X to a charged dopant cluster (solvation energy). In the case of molecular dopants, besides the monomer evaporation also fragmentation of monomers has been reported, although often slightly suppressed compared to electron or photoionization of isolated molecules [47-49]. For molecular decay, reactions that require substantial rearrangement of the molecular constituents can be completely quenched. This includes even highly exothermic reactions, such as the decomposition of trinitrotoluene upon low-energy electron attachment [50]. The vapor of red phosphorus at the presently used temperatures consists predominantly of \( P_4 \) and a small amount of \( P_2 \) units. Odd numberd \( P_2 \) and atomic phosphorus can be neglected. However, electron ionization at 70 eV electron energy of neutral \( P_4 \) leads to roughly 5% \( P_4^+ \) and 7% \( P_4^+ \) formation.

In the experimental setup, where phosphorus vapor is introduced into pristine charged HNDs (Toffy), the collision of the first \( P_2 \) or \( P_4 \) species with a charge center He\(_{n}\)\(^+\) is the only process that can lead to a molecular breakup. Pickup and attachment of further \( P_2 \) or \( P_4 \) units to these dopant ions will not change the ratio of odd to even-numbered \( P_m \)\(^+\) cluster ions. Furthermore, this ratio should be constant for all neighboring peaks in the mass spectra. The experimentally determined odd/even ratio is 0.16 (see Table 1). This indicates that charge transfer from He\(_{n}\)\(^+\) to \( P_2 \) is much more violent than electron ionization which leads to only 12% odd-numbered fragments[5]. A constant odd-even ratio as a function of the cluster size is indicated by a constant displacement of neighboring peak intensities in a plot with a logarithmic y-axis. According to Figs. 4 and 5, the odd/even ratio stays almost constant up to a cluster size of \( n = 50 \) and then drops slightly for larger cluster sizes (red solid circles). In contrast, the protonated phosphorus cluster ions exhibit a constant odd/even ratio of 0.01 throughout the complete mass range (black solid squares, Figs. 4 and 5). Predoping charged HNDs with hydrogen (Toffy H) results in proton transfer from an odd-numbered hydrogen cluster cation to the first phosphorus dopant and any excess energy due to the differences in the proton affinities of the reaction partners will be quenched by the surrounding He matrix, as demonstrated recently for various dopants [41]. Thus, this ionization process will not produce odd-numbered fragments and so aggregation of additional even \( P_2 \) and \( P_4 \) units explains the extreme dominance of even numbered cluster ions.

Finally, ionization of neutral phosphorus clusters formed upon pickup into neutral HNDs upon charge transfer from He\(_n\)\(^+\) (ClusTOF) leads to cationic \( P_m \)\(^+\) clusters with an odd/even ratio of 0.43. In the case of pickup of phosphorus vapor into pristine charged HNDs (Toffy), the same ionization mechanism is operative and so the three times higher odd/even ratio requires an additional explanation. Laimer et al. demonstrated that multiply charged HNDs are stable once they exceed a critical size and that ionization processes lead to a negligible mass loss[39]. In other words, the ions typically observed via mass spectrometry upon electron ionization of HNDs have to be ejected via Coulomb repulsion from neighboring charge centers or some other exothermic process. This reduces the interaction with the cold He matrix and in the case of dopant cluster ions it can lead to the evaporation of monomers or other weakly bound adducts. This agrees well with the presence of magic numbers in dopant cluster size distributions [46] obtained via this ionization method. Separation of fragments due to molecular dissociation can be suppressed in a cluster environment by so-called caging [51, 52]. In the mass spectra, these trapped fragments cannot be distinguished from stoichiometric parent ions. In ClusTOF, where low-mass ions are quickly ejected from the droplet, such loosely bound complexes are likely destroyed. However, in Toffy, stabilized fragments have a good chance to survive. This readily explains the higher abundance of even-numbered phosphorus cluster ions in Toffy.
removal of the surrounding He matrix via collisions with room temperature He gas makes these cluster ions accessible to mass spectrometric analysis [42].

The odd-even ratio obtained for ClusTOF (electron ionization of neutral HNDs doped with phosphorus) is still lower than for electron ionization of neutral pristine phosphorus clusters formed upon laser ablation (0.71) [13] and much lower than for electron ionization of neutral P₅ clusters formed upon gas aggregation of vapor sublimated upon heating of red phosphorus (2.39) [6]. This indicates reduced fragmentation, either by stabilizing P₅⁺ or caging of odd numbered fragments into a weakly bound P₅⁺-P₃ complex. Mass spectra of cations formed directly upon laser ablation of red phosphorus exhibit the largest odd/even ratios up to 3.87 [14].

Table 1: Ratio of intensity of odd-numbered P cluster ions to even-numbered cluster ions from different measurements.

| Measurement       | Odd/Even Ratio |
|-------------------|----------------|
| Toffy H           | 0.01           |
| Toffy             | 0.16           |
| ClusTOF           | 0.43           |
| Bulgakov02 [13]   | 0.71           |
| Huang [7]         | 0.97           |
| Martin [6]        | 2.39           |
| Bulgakov00 [11]   | 2.76           |
| Kong [14]         | 3.87           |

**Conclusions**

We demonstrated that the size distribution of cationic phosphorus clusters strongly depend on the method of production. Whereas most literature data show odd-even oscillation with a high prevalence of closed shell, odd-numbered cations P₅₊₁⁺, our data show distinct dominance of even-numbered cations P₅⁺. Decreasing the input of energy into the formed cluster ions by softer methods of ionization leads to a further reduction of the abundance of odd-numbered clusters. This leads us to the conclusion that cluster formation in HNDs with soft ionization via proton transfer emulates the distribution of neutral phosphorus clusters formed by adding even-numbered P₂n units. Harsher cluster formation and ionization conditions on the other hand lead to a size distribution determined by the greater thermodynamic stability of closed-shell, odd-numbered cationic phosphorus clusters.

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References

[1] M.E. Schlesinger, The thermodynamic properties of phosphorus and solid binary phosphides, Chem. Rev., 102 (2002) 4267-4301.
[2] E. Wiberg, N. Wiberg, Lehrbuch der anorganischen Chemie, Walter de Gruyter & Co., Berlin, New York, 2007.
[3] K.A. Gingerich, Gaseous Phosphorus Compounds. III. Mass Spectrometric Study of the Reaction between Diatomic Nitrogen and Phosphorus Vapor and Dissociation Energy of Phosphorus Mononitride and Diatomic Phosphorus, J. Phys. Chem., 73 (1969) 2734-2741.
[4] J. Smets, P. Coppens, J. Drowart, Photo-ionization with mass spectrometric analysis of the tetraphosphorus molecule, Chem. Phys., 20 (1977) 243-251.
[5] G. Monnom, P. Gaucherel, C. Paparoditis, Electron impact ionization cross sections of phosphorus and arsenic molecules, Journal De Physique, 45 (1984) 77-84.
[6] T.P. Martin, Compound Clusters, Zeitschrift für Physik D Atoms, Molecules and Clusters, 3 (1986) 211-217.
[7] R.B. Huang, P. Zhang, W.Y. Li, J.R. Sun, L.S. Zheng, Mass Spectrometry of Laser Generated Positive and Negative Phosphorus Cluster Ions Acta Phys.-Chim. Sin., 7 (1991) 646-647.
[8] R.B. Huang, H.D. Li, Z.Y. Lin, S.H. Yang, Experimental and Theoretical Studies of Small Homoatomic Phosphorus Clusters, J. Phys. Chem., 99 (1995) 1418-1423.
[9] R.B. Huang, Z.Y. Liu, H.F. Liu, L.H. Chen, Q. Zhang, C.R. Wang, L.S. Zheng, F.Y. Liu, S.Q. Yu, X.X. Ma, Collision-induced dissociation of mass-selected phosphorus cluster cations, Int. J. Mass Spectom. Ion Process., 151 (1995) 55-62.
[10] R.B. Huang, Z.Y. Liu, L.S. Zheng, Lognormal size distributions of elemental clusters, Chem. Phys. Lett., 227 (1994) 103-108.
[11] A.V. Bulgakov, O.F. Bobrenok, V.I. Kosyakov, Laser ablation synthesis of phosphorus clusters, Chemical Physics Letters, 320 (2000) 19-25.
[12] A.V. Bulgakov, O.F. Bobrenok, I. Ozerov, W. Marine, S. Giorgio, A. Lassesson, E.E.B. Campbell, Phosphorus cluster production by laser ablation, Appl. Phys. A-Mater. Sci. Process., 79 (2004) 1369-1372.
[13] A.V. Bulgakov, O.F. Bobrenok, V.I. Kosyakov, I. Ozerov, W. Marine, M. Hedén, F. Rohmund, E.E.B. Campbell, Phosphorus clusters: Synthesis in the gas-phase and possible cage-like and chain structures, Physics of the Solid State, 44 (2002) 617-622.
[14] X.L. Kong, Size Effect on the Signal Intensity Difference between Odd- and Even-Numbered Phosphorus Cluster Ions Acta Physico-Chimica Sinica, 29 (2013) 486-490.
[15] R.O. Jones, D. Hohl, Structure of phosphorus clusters using simulated annealing — P_2 to P_6, J. Chem. Phys., 92 (1990) 6710-6721.
[16] R.O. Jones, G. Seifert, Structure of phosphorus clusters using simulated annealing. II. P_9, P_10, P_11, anions P_2^-, P_{10}^-, P_{11}^-, and cations P_n^+ to n = 11, J. Chem. Phys., 96 (1992) 7564-7572.
[17] M. Häser, U. Schneider, R. Ahlrichs, Clusters of Phosphorus: A Theoretical Investigation, J. Am. Chem. Soc., 114 (1992) 9551-9559.
[18] P. Ballone, R.O. Jones, Density functional study of phosphorus and arsenic clusters using local and nonlocal energy functionals J. Chem. Phys., 100 (1994) 4941-4946.
[19] M. Häser, O. Treutler, Calculated properties of P_2, P_6, and of closed-shell clusters up to P_{18}, J. Chem. Phys., 102 (1995) 3703-3711.
[20] M.D. Chen, J.T. Li, R.B. Huang, L.S. Zheng, C.T. Au, Structure prediction of large cationic phosphorus clusters, Chem. Phys. Lett., 305 (1999) 439-445.
[21] B. Song, P.L. Coa, W. Zhao, B.X. Li, The structures of P_8 and P_9 clusters, Phys. Status Solidi B-Application Solid State Phys., 226 (2001) 305-314.
[22] B. Song, P.L. Cao, Structures of P_20 cluster using FP-LMTO MD method, Phys. Lett. A, 291 (2001) 343-348.
[23] D. Wang, C.L. Xiao, W.G. Xu, The phosphorus clusters P_n (n=1-6) and their anions: Structures and electron affinities, Theochem-J. Mol. Struct., 759 (2006) 225-238.
[24] M.D. Chen, Q.B. Chen, J. Liu, L.S. Zheng, Q.E. Zhang, C.T. Au, Parity alternation of ground-state \( P_n \) and \( P_n^+ \) (n=3-15) phosphorus clusters, J. Phys. Chem. A, 111 (2007) 216-222.
[25] T. Xue, J. Luo, S. Shen, F.Y. Li, J.J. Zhao, Lowest-energy structures of cationic \( P_{2m+1}^+ \) (m=1-12) clusters from first-principles simulated annealing, Chem. Phys. Lett., 485 (2010) 26-30.
[26] L.W. Sai, X.M. Huang, X.Q. Liang, X. Wu, R.L. Shi, D. Wu, Structural Evolution of Medium-Sized Phosphorus Clusters (\( P_{20-P_{24}} \)) from Ab Initio Global Search, J. Clust. Sci., 31 (2020) 567-574.
[27] S.M. Yang, L. Mu, X.L. Kong, Collision-induced dissociation mass spectrometry of phosphorus cluster anions \( P_{2m+1}^- \) (3 \( \leq m \) \( \leq 20 \)), Int. J. Mass Spectrom., 399 (2016) 27-32.
[28] F. Ancilotto, P.B. Lerner, M.W. Cole, Physics of solvation, J. Low Temp. Phys., 101 (1995) 1123-1146.
[29] A. Leal, D. Mateo, A. Hernando, M. Pi, M. Barranco, Capture of heliophobic atoms by \(^4\)He nanodroplets: the case of cesium, Phys. Chem. Chem. Phys., 16 (2014) 23206-23213.
[30] L. An der Lan, P. Bartl, C. Leidlmair, R. Jochum, S. Denifl, O. Echt, P. Scheier, Solvation of \( Na^+ \), \( K^+ \), and Their Dimers in Helium, Chem.-Eur. J., 18 (2012) 4411-4418.
[31] L. An der Lan, P. Bartl, C. Leidlmair, H. Schöbel, S. Denifl, T.D. Märk, A.M. Ellis, P. Scheier, Submersion of potassium clusters in helium nanodroplets, Phys. Rev. B, 85 (2012) S5.
[32] L. An der Lan, P. Bartl, C. Leidlmair, H. Schöbel, R. Jochum, S. Denifl, T.D. Märk, A.M. Ellis, P. Scheier, The submersion of sodium clusters in helium nanodroplets: Identification of the surface \( \rightarrow \) interior transition, J. Chem. Phys., 135 (2011) 6.
[33] M. Renzler, M. Daxner, L. Kranabetter, A. Kaiser, A.W. Hauser, W.E. Ernst, A. Lindinger, R. Zillich, P. Scheier, A.M. Ellis, Communication: Dopant-induced solvation of alkalis in liquid helium nanodroplets, J. Chem. Phys., 145 (2016) 4.
[34] A.W. Hauser, M.P. de Lara-Castells, Spatial quenching of a molecular charge-transfer process in a quantum fluid: the \( Cs_6C_{60} \) reaction in superfluid helium nanodroplets, Phys. Chem. Chem. Phys., 19 (2017) 1342-1351.
[35] J.S. Kane, J.H. Reynolds, Mass Spectrometer Study of the Vapors from Red Phosphorus and Arsenic, J. Chem. Phys., 25 (1956) 342-349.
[36] S. Evans, P.J. Joachim, A.F. Orchard, W.D. Turner, A study of the orbital electronic structure of the \( P_4 \) molecule by photoelectron spectroscopy, Int. J. Mass Spectrom. Ion Phys., 9 (1972) 41-49.
[37] W.C. Martin, Energy Levels and Spectrum of Neutral Helium \((^4\)He\)), Journal of Research of the National Bureau of Standards Section a-Physics and Chemistry, 64 (1960) 19-28.
[38] L.F. Gomez, E. Loginov, R. Sliter, A.F. Vilesov, Sizes of large He droplets, J. Chem. Phys., 135 (2011) 9.
[39] F. Laimer, L. Kranabetter, L. Tiefenthaler, S. Albertini, F. Zappa, A.M. Ellis, M. Gatchell, P. Scheier, Highly Charged Droplets of Superfluid Helium, Phys. Rev. Lett., 123 (2019) 5.
[40] H. Schöbel, P. Bartl, C. Leidlmair, S. Denifl, O. Echt, T.D. Märk, P. Scheier, High-resolution mass spectrometric study of pure helium droplets, and droplets doped with krypton, Eur. Phys. J. D, 63 (2011) 209-214.
[41] L. Tiefenthaler, S. Kollotzek, A.M. Ellis, P. Scheier, O. Echt, Proton transfer at subkelvin temperatures, (submitted) (2020).
[42] L. Tiefenthaler, J. Ameixa, P. Martini, S. Albertini, L. Ballauf, M. Zankl, M. Goulart, F. Laimer, K. von Haefen, F. Zappa, P. Scheier, An intense source for cold cluster ions of a specific composition, Review of Scientific Instruments, 91 (2020).
[43] K.L. Smith, K.M. Black, Characterization of the treated surfaces of silicon alloyed pyrolytic carbon and SiC, Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 2 (1984) 744-747.
[44] J.P. Toennies, A.F. Vilesov, Superfluid Helium Droplets: A Uniquely Cold Nanomatrix for Molecules and Molecular Complexes, Angewandte Chemie International Edition, 43 (2004) 2622-2648.
[45] M. Rosenblit, J. Jortner, Electron bubbles in helium clusters. I. Structure and energetics, The Journal of Chemical Physics, 124 (2006).
[46] A. Mauracher, O. Echt, A.M. Ellis, S. Yang, D.K. Bohme, J. Postler, A. Kaiser, S. Denifl, P. Scheier, Cold physics and chemistry: Collisions, ionization and reactions inside helium nanodroplets close to zero K, Physics Reports, 751 (2018) 1-90.
[47] A.M. Ellis, S.-f. Yang, Role of Helium Droplets in Mass Spectra of Diatomics: Suppression of Dissociative Reactions, Chinese Journal of Chemical Physics, 28 (2015) 489-492.

[48] A.A. Scheidemann, V.V. Kresin, H. Hess, Capture of lithium by 4He clusters: Surface adsorption, Penning ionization, and formation of HeLi+, The Journal of Chemical Physics, 107 (1997) 2839-2844.

[49] S. Yang, S.M. Brereton, A.M. Ellis, Electron impact ionization mass spectrometry of aliphatic alcohol clusters in helium nanodroplets, International Journal of Mass Spectrometry, 253 (2006) 79-86.

[50] A. Mauracher, H. Schöbel, F. Ferreira da Silva, A. Edtbauer, C. Mitterdorfer, S. Denifl, T.D. Märk, E. Illenberger, P. Scheier, Electron attachment to trinitrotoluene (TNT) embedded in He droplets: complete freezing of dissociation intermediates in an extended range of electron energies, Physical Chemistry Chemical Physics, 11 (2009).

[51] S. Yang, S.M. Brereton, M.D. Wheeler, A.M. Ellis, Soft or hard ionization of molecules in helium nanodroplets? An electron impact investigation of alcohols and ethers, Physical Chemistry Chemical Physics, 7 (2005).

[52] S. Yang, S.M. Brereton, M.D. Wheeler, A.M. Ellis, Electron Impact Ionization of Haloalkanes in Helium Nanodroplets, The Journal of Physical Chemistry A, 110 (2006) 1791-1797.