The structure of anionic NbH$_n^-$ ($n = 2$–15) clusters and their maximum hydrogen capacity

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Abstract

The geometrical structures of the lowest energy states of anionic niobium-doped hydrogen clusters are determined based on Crystal structure AnaLYsis by the Particle Swarm Optimization (CALYPSO) isomer search method. The geometries and relative stabilities are determined by the B3LYP hybrid density functional theory (DFT) method. The calculated results show that a niobium atom can absorb up to twelve hydrogen atoms in the anionic clusters. In exploring the stability, electronic properties, and photoelectron spectra of NbH$_n^-$ clusters, the NbH$_{12}^-$ cluster is found to possess a relatively high binding energy, high second-order differential energy, and a large HOMO–LUMO gap. The hydrogen storage density of the NbH$_{12}^-$ cluster is calculated as 11.5 wt%. The present findings enrich the database of transition metal doped hydrogen clusters and the insights are important in the pursuit of efficient hydrogen energy storage materials.

1. Introduction

The search for safe, economical and clean energy sources became an active area of research because of the limitations of fossil fuels and the environmental degradation caused by their consumption [1–3]. Hydrogen energy has attracted great attention as an alternative fuel source because of its several useful properties, including having better energy storage abilities and environmental cleanliness [4]. Hydrogen is stored and transported as a component of gasses, liquids, and solids [5–8]. Solid metal hydrides are a good hydrogen storage method because they are safe and have a high hydrogen storage density [9]. Fundamental studies of gas phase species often aids in understanding the properties of real world solid state materials. Much attention has been paid to the adsorption–desorption characteristics of metal hydrides as a necessary step to extract energy from these solid hydrogen storage materials [10]. Basic research on the adsorption of H$_2$ to transition metal surfaces has aided in understanding their potential applications in catalysis, corrosion, and hydrogen storage [11]. In addition, transition metals have shown room-temperature hydrogen storage potential in terms of hydrogen adsorption strength and storage capacity due to their electronic structure. Therefore, research continues on the design of high-density hydrogen storage materials using transition metal based materials.

Several studies on the hydrogen adsorption to different metals have laid a solid foundation for the development of solid hydrogen storage materials. Yildirim et al studied the hydrogen storage behavior of
Ti-doped C_{60} based on density functional theory and found that each titanium atom can adsorb four hydrogen molecules and the hydrogen storage capacity can reach 7.5% \[12\]. Saturation of Co clusters with hydrogen leads to 8.4% content of hydrogen by weight \[13\]. The adsorption of molecular hydrogen on copper-doped transition metal clusters and vanadium clusters indicates that the adsorption strength of hydrogen is related to the adsorption site \[14\]. It is observed that different transition metal elements and charge states can have different hydrogen adsorption capacities. Niobium is an important transition metal as it is often used as a component of hydrogen storage alloys.

Pure niobium is a shiny, off-white, rare, soft, ductile and paramagnetic transition metal \[15\]. Niobium and its alloys have excellent mechanical properties, low neutron capture cross sections, good corrosion resistance, and heat resistance. It can be used as a structural material and has good hydrogen absorption properties \[16\]. It is important to study the relative stabilities of different structural isomers of hydrogen metal complexes and their chemical properties for their use as hydrogen storage materials \[17–19\]. The electron arrangement in the d orbitals of Nb atoms in complexes not only affects its overall electronic structure, but also determines the hydrogen adsorption capacity \[20\].

The gas phase cluster is the intermediate state between small atoms and bulk phase. Investigations of gas phase species being somewhat isolated from neighbors can aid in the design of solid state materials. In order to study the structural evolution and hydrogen storage properties of niobium-doped hydrogen clusters, we have systematically explored the structure of NbH_{n} \((n = 2–15)\) clusters \[21\]. At present, it is difficult to obtain the detailed structure and spectroscopic information of neutral cluster by current measurement. In contrast, the charged state is relatively easy to be achieved, especially for the anionic state. The structural and electronic properties of size-selected anionic cluster can be directly determined by the prominent photoelectron spectroscopy technique, which can also be examined by the DFT theoretical calculations \[22, 23\]. Here, we extend this investigation to include anionic NbH_{n}^{-} clusters, exploring the effect of charge state on the geometric and electronic properties of these niobium-hydrogen clusters. After identifying the global minimum for each cluster size, we analyze the binding energy, second-order differential energy, HOMO–LUMO energy gap, and the average adsorption energy to investigate the cluster stability versus size relationships. The anionic clusters’ photoelectron spectra (PES) are predicted, and the molecular orbitals and Adaptive Natural Density Partitioning (AdNDP) are analyzed to understand the bonding in the most stable cluster structures.

2. Theoretical techniques

We use the CALYPSO structure prediction method to obtain all the structures of NbH_{n}^{-} \((n = 2–15)\) clusters \[24–26\]. It is reliable structure search method for various systems \[27–31\]. We employ the B3LYP density functional theory method to optimize the cluster structures \[32, 33\] with the LANL2DZ pseudopotential and the 6-311++G(d) basis set to represent the electron distribution of the Nb atom and H atoms, respectively \[34, 35\]. Each candidate structure is future reoptimized without symmetry constraints, and vibrational frequencies are calculated to insure true minima structures and obtain the zero point corrected energy. Although initial calculations are performed without constraining symmetry, symmetry is considered and imposed for further optimization and cluster structures are reported with approximate symmetry notations in the results section. Several spin multiplicities are tested for each cluster size. All clusters reported adapt the lowest possible spin multiplicity in the global minima except for the smallest sized NbH_{2}^{-} \((2s + 1 = 5)\), NbH_{3}^{-} \((2s + 1 = 4)\), and NbH_{4}^{-} \((2s + 1 = 3)\). Since the properties of the clusters depends largely on the arrangement of atoms, we conduct a comprehensive study of the geometry and growth patterns of the anionic clusters. The charge of the cluster is calculated by Natural Bond Orbital (NBO), and chemical bonding analyses are performed using the AdNDP method \[36, 37\]. The photoelectron spectroscopy (PES) of the ground-state anion clusters are simulated by time-dependent DFT (TD-DFT) method by Gaussian 09 package and our recently developed CPES code \[38–43\]. It is an effective method to explore the true ground state structures of anionic NbH_{n}^{-} clusters, which can compare with the experiments in the near future.

3. Results and discussion

3.1. Geometrical structures

The lowest energy isomers of NbH_{n}^{-} \((n = 2–15)\) clusters are depicted in figure 1. Isomers are noted as ‘\(nx\)’, where \(n\) is the number of H atoms, and \(x = a^{-}\) denotes the isomer is ground state, while \(x = b^{-}\) and \(c^{-}\) denote the low-lying isomer with higher energy than their corresponding ground state. The picture also lists the energy difference between each isomer and the most stable structure. The spin multiplicity of the
Figure 1. Geometries of the low-energy structure of each anionic NbH\(_n^−\) \((n = 2–15)\) clusters. Relative energies are given in eV.

ground state NbH\(_2^−\), NbH\(_3^−\), and NbH\(_4^−\) isomers are \(2s + 1 = 5, 4, \) and \(3, \) respectively, but larger cluster sizes all adapt the lowest possible spin multiplicities (i.e., singlet state-doublet state for anionic clusters with an even/odd number of hydrogens, respectively). The \(2a^−\) isomer possesses a planar configuration with \(C\text{\textsubscript{2v}}\) symmetry, and the energies of \(2b^−\) and \(2c^−\) isomers are both 0.5 eV higher than \(2a^−\). Trigonal pyramidal isomer \(3a^−\) possesses a \(C\text{\textsubscript{3v}}\) symmetry, while the structure \(4a^−\) contains \(T\text{\textsubscript{d}}\) symmetry. The lowest energy structure of NbH\(_5^−\) is a \(C\text{\textsubscript{2v}}\) structure in which four hydrogen atoms form a cross with the Nb atom. The \(5b^−\) isomer possesses a square pyramidal configuration, in which all H atoms are bound to the Nb atom. Isomer \(6a^−\) with a \(C\text{\textsubscript{3v}}\) symmetry can be seen as adding one extra H atom to \(5b^−\). The three low-lying isomers for NbH\(_7^−\) all have \(C\text{\textsubscript{5v}}\) symmetry. Notably, H\(_2\) units bound to the central Nb atom first appeared in \(7a^−.\) This differs from neutral NbH\(_n\) clusters, where the first H\(_2\) molecule attached to the Nb atom appears in NbH\(_6^\) [21]. Structure \(9b^−\) adapts a \(C\text{\textsubscript{5v}}\) symmetry and can be seen as two more H atoms growing on \(7c^−.\) Likewise, the \(10a^−\) structure is similar to \(9c^−,\) but with an additional H atom. The three NbH\(_{11}^−\) isomers possess \(C\text{\textsubscript{5v}}\) symmetry. The \(12a^−\) cluster contains \(D\text{\textsubscript{2d}}\) symmetry, which possesses a similar configuration to \(11b^−\) but with an additional H atom. From the \(13a^−\) cluster and larger, H\(_2\) units begin to detach from the Nb atom. For neutral NbH\(_n\) clusters, detachment of H\(_2\) occurs for NbH\(_{14}^\) [21]. It is also worth noting a previous matrix isolation experimental study observed an infrared absorption at 1634.0 cm\(^{-1}\) identified as NbH\(_3(H_2)_x\). Given that our previously predicted neutral NbH\(_{13}\) cluster is saturated, shows an enhanced stability compared to other sizes, and is predicted to have its strongest IR absorption around 1640 cm\(^{-1}\), we believe the NbH\(_3(H_2)_x\) cluster we predicted [21] is what was observed experimentally [44]. The change of detachment size with charge state suggests saturation and hydrogen detachment occurs in these clusters for electronic, rather than purely steric, reasons. The symmetry of the ground state structure of NbH\(_{14}^−\) is \(C\text{\textsubscript{1}}\), \(15a^−,\) \(15b^−,\) and \(15c^−\) are also all \(C\text{\textsubscript{1}}\) symmetry, and \(15b^−\) is constructed by adding two molecular hydrogen pairs on isomer \(11b^−.\) Based on the analysis of the above geometric structure, we know that the dehydrogenation of anionic NbH\(_n^−\) clusters occur at \(n = 13,\) and NbH\(_{12}^−\) is saturated and cannot absorb any more hydrogen.
Figure 2. The simulated photoelectron spectra (blue lines) of NbH$_n^-$ $(n = 2–15)$, and the experimental PES of the Nb$_3^-$ cluster (red lines) [45]. (The abscissa of NbH$_n^-$ $(n = 2–15)$ are 0.5–6.5 eV and the abscissa of Nb$_3^-$ is 0.5–3.5 eV.)

### Table 1. The VDE from simulated photoelectron spectra of NbH$_n^-$ $(n = 2–15)$ clusters.

| Clusters | Peak position (eV) |
|----------|-------------------|
| NbH$_2^-$ | 1.07, 1.79, 3.44, 4.23, 5.08, 5.92 |
| NbH$_3^-$ | 1.47, 1.61, 2.49, 2.74, 4.23, 5.06, 5.99, 6.27 |
| NbH$_4^-$ | 2.04, 4.68, 5.49 |
| NbH$_5^-$ | 2.10, 4.20, 4.54, 4.85, 5.15, 5.47 |
| NbH$_6^-$ | 4.57, 5.11 |
| NbH$_7^-$ | 2.11, 4.17, 4.54, 4.98, 5.22, 5.39, 6.39 |
| NbH$_8^-$ | 4.55, 4.69, 4.91, 5.21 |
| NbH$_9^-$ | 2.38, 4.33, 4.67, 5.06, 5.41, 6.41 |
| NbH$_{10}^-$ | 4.23, 4.45, 5.33, 6.35 |
| NbH$_{11}^-$ | 2.36, 4.14, 4.46, 4.86, 5.06, 5.31, 6.00 |
| NbH$_{12}^-$ | 2.86, 4.46, 5.23 |
| NbH$_{13}^-$ | 2.30, 4.79, 5.09, 5.46, 5.71, 6.01, 6.25 |
| NbH$_{14}^-$ | 4.31, 5.08, 5.30, 6.11 |
| NbH$_{15}^-$ | 2.26, 4.30, 4.70, 3.15, 5.35, 5.74, 6.35 |

### 3.2. Photoelectron spectra of NbH$_n^-$ clusters

Photoelectron spectroscopy (PES) is an experimental technique to determine the electronic structure of atoms and molecules. Thus, it can be viewed as an electronic fingerprint for cluster, as well as facilitate structural and chemical bond analysis of clusters by comparison with theoretical calculations. The successful application of PES combined with advanced quantum chemical calculations makes it an effective avenue to probe the geometric and electronic properties of clusters. Thus, we calculate the PES of anionic NbH$_n^-$ clusters by using TD-DFT method and CPES code, which offer crucial information for future PES spectroscopic measurements. In order to confirm the accuracy of our level of theory in simulating photoelectron spectrum, we first compared the simulated the photoelectron spectra of Nb$_3^-$ with previously reported experimental results [45]. The photoelectron spectra are shown in figure 2, where the red curve is the experimental photoelectron spectrum of Nb$_3^-$ [45]. It is clear that the simulated
Figure 3. Electronic properties of NbH$_n^-$ ($n = 2$–15) clusters, which are indicative of the stability. (a) Binding energies, (b) second-order difference energy, (c) HOMO–LUMO energy gaps, (d) average adsorption energy.

The photoelectron spectrum of NbH$_3^-$ agrees well with the experimental photoelectron spectrum. The theoretically predicted first VDE value for the lowest energy structure is 1.10 eV, which is consistent with the previously reported experimental VDE value of 1.09 eV [45]. Therefore, our theoretical approach appears accurate in describing the photoelectron dissociation energy of niobium based clusters.

To analyze the electronic structure of anionic NbH$_n^-$ ($n = 2$–15) clusters in more detail, we used TD-DFT method to simulate PES of our ground state clusters. The peak positions of theoretical PES are presented in table 1. In the spectra depicted in figure 2, the first peak represents the photo-dissociation of an electron from the HOMO of the ground state anionic isomer, while the following peaks are corresponding to the transitions from lower energy orbitals. In the photoelectric spectrum of NbH$_2^-$, the first peak appears at a binding energy of 1.07 eV. The VDE of NbH$_3^-$ is 1.47 eV and the second peak is close at 1.61 eV. The photoelectron spectrum of NbH$_4^-$ displays only three intense peaks, and its first VDE value is 2.04 eV. For NbH$_5^-$, the first VDE value is 2.10 eV, and the subsequent five peaks are relatively close together at 4.20 eV, 4.54 eV, 4.85 eV, 5.15 eV, and 5.47 eV, respectively. Only two peaks are apparent for anionic NbH$_6^-$ at 4.57 eV and 5.11 eV. From the photoelectron spectrum of NbH$_7^-$, the first peak appears at the binding energy of 2.11 eV. The first VDE value of NbH$_8^-$ is at 4.55 eV, whereas the first VDE value of NbH$_9^-$ is at 2.38 eV. The remaining five peaks of NbH$_9^-$ appear at 4.33 eV, 4.67 eV, 5.06 eV, 5.41 eV, and 6.41 eV. The first VDE values of NbH$_{10}^-$ and NbH$_{11}^-$ are at 4.23 eV and 2.36 eV, respectively. NbH$_{12}^-$ has only three sharp peaks in the spectrum with a first VDE value of 2.86 eV. NbH$_{13}^-$ has a first VDE value of 2.30 eV, whereas NbH$_{14}^-$ has four sharp peaks with a first VDE value of 4.31 eV. The latter three peaks appear at 5.08 eV, 5.30 eV and 6.11 eV. The first VDE value of NbH$_{15}^-$ is 2.26 eV. The highest energy first VDE value of 4.57 eV appears in the anionic cluster NbH$_6^-$, the second largest first VDE value of 4.55 eV appears in the anionic cluster NbH$_8^-$, and the lowest energy first VDE value appears in the small-sized anionic cluster NbH$_2^-$ at 1.07 eV.
3.3. Relative stabilities and band gaps

The $E_b$, $\Delta^2 E$, HOMO–LUMO gaps, and $E_{ads}$ of anionic NbH$_n^-$ ($n = 2–15$) clusters are shown in figure 3. The details are given in table S1 (https://stacks.iop.org/NJP/24/043038/mmedia). The binding energy $E_b$ is calculated as

$$E_b (\text{NbH}_n^-) = \frac{[E (\text{Nb}^-) + nE (\text{H}) - E (\text{NbH}_n^-)]}{(n + 1)}. \quad (1)$$

By this definition, a positive value of $E_b$ corresponds to exothermic cluster formation. From figure 3(a), the binding energy increases monotonically up to NbH$_4^-$, and then remains relatively constant as the cluster size increases. The maximum $E_b$ value of NbH$_n^-$ ($n = 2–15$) clusters occurs at $n = 4$ with an $E_b = 2.38$ eV, with the second largest value of 2.36 eV when $n = 6$. The second-order difference energy $\Delta^2 E$ shows the relative stability of each cluster relative to adjacent sized clusters. It is calculated as

$$\Delta^2 E (\text{NbH}_n^-) = E (\text{NbH}_{n-1}^-) + E (\text{NbH}_{n+1}^-) - 2E (\text{NbH}_n^-). \quad (2)$$

Compared with clusters of adjacent sizes, the larger the second-order energy difference, the more stable it is. From figure 3(b), one can see that the $\Delta^2 E$ values of the anionic clusters show an expected oscillatory behavior, with maxima for even values of hydrogen atoms in NbH$_n^-$. This is opposite of the neutral NbH$_n$ counterparts where odd $n$ values of hydrogens were found to be more stable [21], again illustrating the effect on an additional electron on cluster structure and stability. The maximum value of the second order difference energy (0.95 eV) of the anionic clusters appears at $n = 12$ showing a strong stability of this NbH$_{12}^-$ anionic cluster.

The $E_{gap}$ reflects how easily an electron can transition from an occupied orbital to an unoccupied orbital. These frontier orbitals are also the most important in regards to bonding and ionizing processes of the cluster. A larger $E_{gap}$ value indicates that the energy required to perturb the electronic structure is
higher, and hence the species is more inert. The calculated $E_{\text{gap}}$ values are shown in the figure 3(c). The maximum value of the anionic cluster appears at even $n$ numbers, and these even-numbered NbH$_n^-$ clusters are more chemically inert than clusters of other sizes. As shown in figure 3(d), the $E_{\text{ads}}$ of NbH$_n^-$ clusters are positive, indicating that the process of the clusters adsorbing hydrogen atoms is favorable and exothermic. As the cluster size increases, the interaction between hydrogen atoms may cause a decrease in adsorption energy. As shown in the figure, all $E_{\text{ads}}$ exceed 2.40 eV, which is considered strong chemisorption for the average hydrogen atom in a given cluster. The observed oscillatory behavior in $E_b$, $\Delta E$, and $E_{\text{gap}}$, shows a larger stability for clusters with an even number of hydrogen atoms. This appears to arise from the number of hydrogen atoms, rather than H$_2$ molecules, adsorbed by niobium atom. Bonding interactions between H atom can occur when the number of adsorbed hydrogen atoms is even, so that the cluster as a whole tends to show a greater stability. It is also worthwhile to note that the spin multiplicity fluctuates with the addition of H atom switching between closed shell and open shell structures. Considering the $E_b$, $\Delta E$ and $E_{\text{gap}}$ of the ground state clusters discussed above, one can conclude that NbH$_{12}^-$ is the most stable of the NbH$_n^-$ ($n = 2–15$) clusters studied here. A slight increase in $E_{\text{ads}}$ for NbH$_{12}^-$ compared to its neighboring sizes provides further support for the stability of this sized cluster. The hydrogen storage capacity of NbH$_{12}^-$ is 11.5 wt%, which is a dense hydrogen storage material.

Natural population analysis is used to explore the charge transfer in anionic NbH$_n^-$ ($n = 2–15$) clusters, and the results are shown in the figure 4. The amount of negative charge on the Nb atom increases with the number of H atoms when $4 \leq n \leq 12$. Part of this negative charge can be accounted for by the additional electron in the anionic cluster, while additional negative charge indicates an increasing tendency for hydrogen to act as an electron donor and Nb atom as an electron acceptor. The amount of charge reaches a minimum of $-0.96\text{e}$ when $n = 12$. When $n = 13$ in the anionic clusters, an oscillatory behavior begins as the cluster is saturated and the Nb atom no longer adsorbs more hydrogen atoms.

3.4. Chemical bonding analysis

Having shown that NbH$_{12}^-$ has an enhanced chemical stability relative to other sizes, we analyzed a molecular orbital structure on this cluster. From figure 5, the NbH$_{12}^-$ cluster has $D_{\text{4d}}$ symmetry, and the 4d orbitals of the Nb atom are the major contributor to the core orbitals. The orbital component of the LUMO is mainly composed of two bonding H$_2$ units (88.51%), with minimal niobium character. The HOMO is mainly contributed from the Nb-4d$_{xy}$ orbital, which contributes up to 88.12%. The HOMO-2 and HOMO-2' are made mostly of the Nb-4d$_{xy}$ orbital, contributing 51.58% of these MOs. HOMO-n ($n = 1$, 3–6) are made up mainly by different combinations of hydrogen AOs. In the HOMO-9, there is a 96.73% contribution from the niobium 4pz orbital. The results of the AdNDP analysis are shown in figure 6. The occupation values for each are 1.97[$\text{e}$] or higher. The hydrogen atoms have only s orbitals, and only $\sigma$ bonds are formed between them and the niobium atom. Chemical bonding in the cluster includes four 2c–2e $\sigma$ Nb-H bonds formed by the central niobium atom and its adjacent four hydrogen atoms. Four additional
3c–2e σ bonds exists between the central Nb atom and the H₂ molecules attached to it, and one delocalized 13c–2e σ bonds extends over the entire cluster.

4. Conclusions

A systematic theoretical investigation on the ground state structures and relative stabilities of anionic NbHₙ⁻ (n = 2–15) clusters are performed. The results showed that the NbHₙ⁻ (n = 2–15) cluster reached saturation after adsorbing 12 hydrogen atoms. Relative stability analyses indicate the NbH₁₂⁻ can be identified as the most stable cluster with respect to its neighbors. The natural population analysis displays that the Nb atom accepts electron density from hydrogen atoms up to the cluster size n = 12. Notably, the anionic NbH₁₂⁻ cluster shows a high hydrogen storage capacity of 11.5 wt%. The present results offer insights into the geometric and electronic structures of anionic NbHₙ⁻ clusters, which provide detailed information for the synthesis of novel hydrogen storage nanomaterials.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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