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Photoionization of Li_nH_m clusters

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Abstract - Ionization potentials of Li_nH_m clusters have been measured from bare Li_n clusters to hydrogen saturated clusters. The evolution of electronic properties with the number of H is discussed. We found that Li_nH_m clusters behave like Li_{n-m} clusters. This similarity may be due to a segregation between a metallic part and an insulator part inside the cluster.

1 Introduction

Alkali metal are among the most studied clusters, from both experimental and theoretical point of view. They are the prototypes of small metallic particles and they are well described by the jellium model. For a few years, scientists are interested in alkali halide clusters. In the bulk, these systems are salts with a NaCl structure and ionic bounds. For stoichiometric clusters, the cohesion is dominated by electrostatic forces and they have the bulk structure which make calculations easier. Numerous experimental results have been obtained on $\text{Na}_n\text{Cl}_{n-1}^+$ (or $\text{Na}_{n-1}\text{Cl}_n^-$) and $\text{Na}_n\text{F}_{n-1}^+$ (or $\text{Na}_{n-1}\text{F}_n^-$) clusters (see for examples Ref. [1,2]). A stoichiometric cluster is an insulator whereas, in a bare metal clusters valence electrons are delocalized. A significant transition of electronic properties and of the structure is expected when the proportion of metal atoms increases in the cluster. However little is known about clusters with intermediate composing. Does a gradual attenuation of the metallic character occur in all the cluster volume, or does a segregation between a metallic part and an insulator appear inside the cluster ?

Due to their little number of electrons, Li_nH_m clusters appear to be the ideal system to study this evolution : it is the mixed system the

most accessible to calculations. Moreover, it allows to investigate the bounding of an hydrogen atom with a metal and chemisorption of hydrogen on metal surfaces. In recent papers [3,4] we published the first results on Li_nH and Li_nH_2 clusters. By varying nucleation conditions, we managed to produce Li_nH_m from 0 hydrogen atom to hydrogen saturated clusters. We present in this paper the ionization potentials of Li_nH_m clusters $3 \leq n \leq 11$ and $0 \leq m \leq 6$. These I.P.s are mainly dominated by the number of valence electrons. Evolution of electronic properties from pure metal clusters to stoichiometric cluster is discussed and compared with results on NaCl and NaF clusters.

2 Experiment

Hydrogenated clusters were produced in a seeded molecular beam by coexpansion of 10-100 mbars of lithium vapor and 1-5 bars of a mixture of Argon and Hydrogen. For this experiment we used pure isotopic ^7Li lithium (purity > 99.88%). It avoids superposition of peaks such as $^7\text{Li}_{n-1}^6\text{LiH}$ and $^7\text{Li}_n$ which have the same mass [3]. This allows us to measure precisely the intensity of Li_nH_m clusters with more than 2 hydrogen atoms. Moreover, we are able to vary the proportion of hydrogen in the carrier gaz from 0% to 15% and so to favorize clusters with few

hydrogen atoms or, in the other hand, hydrogen saturated clusters. The clusters were ionized by mean of an XeCl excimer pumped tunable dye laser and the required UV range was obtained by frequency doubling using either a BBO crystal (from 220 nm to 270 nm) or a KDP crystal (from 270 to 330 nm). Ions were collected and mass analyzed through a time of flight mass spectrometer.

Figure 1 : mass spectra of photoionized Li_nH_m clusters. They were recorded with 3 different H_2 percentages in the carrier gas a) 0% b) 2% c) 9%.

3 Results and discussion

Figure 1 shows 3 mass spectra recorded with a photon energy of 5.4 eV, with a low power ($\approx 1 \text{ mJ/cm}^2$). First spectrum has been obtained with no hydrogen in the carrier gas. Main peaks

correspond to the Li_n clusters. To the right of these peaks, the weak peaks are due to Li_nH clusters (there were traces of hydrogen and water in the experiment). When 2% of H_2 is added to the carrier gas, clusters with 1 and 2 hydrogens are observed to the right of the main peaks. One can notice the particular high intensity of the Li_9H^+ peak. The last spectrum has been recorded with 9% of H_2 . The most intense peaks correspond to $(\text{LiH})_n\text{Li}^+$. These ionic species are saturated in hydrogen, no valence electron remains free. For clusters with less hydrogen, intensities alternation in respect of valence electrons number ($n-m$) is striking. Ionic clusters with an even number of valence electrons are the more intense. This is due to electronic pairing effects. High intensity of $\text{Li}_n\text{H}_{n-1}^+$ species is similar to what have been observed for other mixed clusters. CsO [5] and LiO [6] clusters are saturated in oxygen for a number of oxygen equal to half the number of metal atoms (due to the valence 2 of oxygen). Concerning the alkali halide, only $\text{Na}_n\text{Cl}_{n-1}^+$ (or $\text{Na}_{n-1}\text{Cl}_n^-$) and $\text{Na}_n\text{F}_{n-1}^+$ (or $\text{Na}_{n-1}\text{F}_n^-$) clusters ions are observed [1,2], in most experimental conditions.

There are two major differences between our results and NaCl or NaF spectra. First, we are able to produce non stoichiometric clusters. Second, some $\text{Na}_n\text{Cl}_{n-1}^+$ and $\text{Na}_n\text{F}_{n-1}^+$ clusters present very high intensities for $n=2, 4, 6, 8, 12, 15, 18 \dots$, these clusters have a cuboid structure (little cuboid piece of the bulk). On our spectra, we observe no magic number for any $\text{Li}_n\text{H}_{n-1}^+$ clusters, even using a very low photon energy.

We recorded mass spectra (with different H_2 percentages) varying the wavelength of the ionizing laser from 220 nm to 400 nm. For each wavelength, we checked that no multiphotonic processes took place. Then we obtained

n	Li _n	Li _n H	Li _n H ₂	Li _n H ₃	Li _n H ₄	Li _n H ₅	Li _n H ₆
3	4.06	4.74	4.45				
4	4.31	4.17	5.00	4.38			
5	4.02	4.27	4.04	4.90	4.33		
6	4.16	4.02	4.19	4.14		4.50	4.50
7	3.95	4.2	4.10	4.20	4.18		4.50
8	4.14	3.93	4.17	4.05	4.35	4.31	
9	3.53	4.18	4.01	4.03	4.16		4.15
10	3.96	3.75	4.00	4.03	4.20	4.20	
11	3.83	3.88	3.70	4.21	4.19		

Table 1 : Ionization potentials of Li_nH_m clusters. Figure 2 : Ionization potentials of Li_nH_m clusters plotted with respect to the number n-m of valence electrons.

photoionization curves of Li_nH_m clusters $3 \leq n \leq 11$ $0 \leq m \leq 6$ [3], I.P.s were determined by linear extrapolation. Ionization potentials are listed

in table 1. Li_n, Li_nH and Li_nH₂ I.P.s have already been discussed in previous papers [7,3,4]. Briefly Li_n I.P.s present an odd even alternation due to electronic pairing effect, significant decreases between Li₂ and Li₃ and Li₈ and Li₉ correspond to the closing of the 1s and 1p shells of the jellium model. The I.P.s of Li_nH are very closed to Li_{n-1} I.P.s and Li_nH_{n-2} I.P.s to Li_{n-2} I.P.s (figure 2). This is explained by assuming that one -or two- valence electrons of the former Li_n cluster are localized on the Li-H bond, and that other electrons remain free.

Evolution of the I.P.s for Li_nH₃ and Li_nH₄ with respect to n-m are plotted on figure 2. For these clusters I.P. of Li_nH_m is still very closed to Li_{n-m} I.P.. Especially the odd-even alternation is still observable. I.P.s of Li_nH_{n-2} clusters are particularly high and closed to Li₂ I.P., in the same way the closing of the 1p shell was observed after Li₉H and Li₁₀H₂. In the very hydrogenated clusters, one electron is still localized by every H atom and n-m electrons remain delocalized. The perfect similarity between Li_nH_m and Li_{n-m} I.P.s suggests that a bare Li_{n-m} cluster survives inside the Li_nH_m cluster. Are the m H atoms stuck around the Li_n cluster, or is the structure of the Li_n cluster modified with a separation between a metallic part and a insulator part ? The fact that the Li_{n-m} remaining core is little disturbed by the other atoms is in favor of the second hypothesis. This phenomenon is confirmed for Li_nH₂ by geometric structures determined by ab initio calculations [8].

To compare these I.P. with other mixed clusters, it is pertinent to study their evolution for a given n as a function of the number of hydrogen (evolution for Li₄H_n is displayed on figure 3). As previously noticed, an odd-even alternation occurs.

Up to $n-m=2$, these potentials are roughly equal, then an increase is observed. The I.P.s of Li_nH_n clusters are high (we only observed Li_6H_6) This global trend is different from what occurs in NaCl, NaF or CsO clusters. On CsO, the I.P.s decrease when the number of oxygen increases, the I.P.s of $\text{Cs}_{2n+1}\text{O}_n$ are particularly low [5]. In the same way, $\text{Na}_n\text{F}_{n-1}$ I.P.s [9] are lower than those of bare Na_n clusters. Figure 3 displayed the evolution of calculated adiabatic I.P.s of Na_4F_n clusters [10], globally the potentials decrease whereas they increase for Li_4H_n . In NaCl and NaF cuboid clusters, the low I.P. is explained by the fact that the place occupied by the only valence electron is well determined (F center) and the bond between this electron and the remaining cluster is weak. This is particularly clear in ab initio calculations of Landman [10] and Koutecky [11] for Na_4F_3 where the excess electron is strongly localized in the F vacancy. On the other hand, calculations for Li_4H_3 [12] give the same structure but the electron is more diffuse and then more bounded to the cluster.

Figure 3 : evolution of measured Li_4H_m I.P.s and of calculated Na_4F_m I.P.s [10].

4 Conclusion

We have measured I.P.s of Li_nH_m clusters from bare metal to hydrogenated saturated clusters. Electronic properties are dominated by the number of valence electrons $n-m$. The very strong similarity between Li_nH_m I.P.s and Li_{n-m} I.P.s may be due to a segregation between a metallic part and an insulating part. Determination of absorption cross section and their comparison with ab initio calculations will be useful to conclude. Finally concerning the comparison with alkali halide, the "F center" appears to behave differently.

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