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Photoionization of LiₙHₘ clusters

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Abstract - Ionization potentials of LiₙHₘ clusters have been measured from bare Liₙ clusters to hydrogen saturated clusters. The evolution of electronic properties with the number of H is discussed. We found that LiₙHₘ clusters behave like Liₙ₋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 halyde clusters. In the bulk, these systems are salts with a NaCl structure and ionic bounds. For stoechiometric 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 NaₙClₙ₋₁⁺ (or Naₙ₋₁Clₙ⁻) and NaₙFₙ₋₁⁺ (or Naₙ₋₁Fₙ⁻) clusters (see for examples Ref. [1,2]). A stoechiometric 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, LiₙHₘ 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 hydogen atom with a metal and chimisorption of hydrogen on metal surfaces. In recent papers [3,4] we published the first results on LiₙH and LiₙH₂ clusters. By varying nucleation conditions, we managed to produce LiₙHₘ from 0 hydrogen atom to hydrogen saturated clusters. We present in this paper the ionization potentials of LiₙHₘ clusters 3 ≤ n ≤ 11 and 0 ≤ m ≤ 6. These I.P.s are mainly dominated by the number of valence electrons. Evolution of electronic properties from pure metal clusters to stoechiometric 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 ⁷Liₙ₋₁⁶LiH and ⁷Liₙ which have the same mass [3]. This allows us to measure precisely the intensity of LiₙHₘ 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∗Hm clusters. They were recorded with 3 different H2 percentages in the carrier gaz 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 (≈ 1 mJ/cm²). First spectrum has been obtained with no hydrogen in the carrier gaz. Main peaks correspond to the Li∗ clusters. To the right of these peaks, the weak peaks are due to Li∗H clusters (there were traces of hydrogen and water in the experiment). When 2% of H2 is added to the carrier gaz, clusters with 1 and 2 hydrogens are observed to the right of the main peaks. One can notice the particulary high intensity of the Li∗H+ peak. The last spectrum has been recorded with 9% of H2. The most intense peaks correspond to (LiH)3Li+.

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 Li∗Hn-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 Na∗Cln- 1+ (or Na∗-1Cln+) and Na∗Fn- 1+ (or Na∗-1Fn+) 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 stoechiometric clusters. Second, some Na∗Cln- 1+ and Na∗Fn- 1+ clusters present very high intensities for n=2, 4, 6, 8, 12, 15, 18 ..., these clusters have a cuboid structure (little cuboid piece of the bulk). On our spectra, we observe no magic number for any Li∗Hn-1+ clusters, even using a very low photon energy.

We recorded mass spectra (with different H2 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...
Table 1: Ionization potentials of LinHm clusters.

<table>
<thead>
<tr>
<th>n</th>
<th>Lin_H</th>
<th>LinH</th>
<th>LinH2</th>
<th>LinH3</th>
<th>LinH4</th>
<th>LinH5</th>
<th>LinH6</th>
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<tr>
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<td>4.74</td>
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<td>4.31</td>
<td>4.17</td>
<td>5.00</td>
<td>4.38</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.02</td>
<td>4.27</td>
<td>4.04</td>
<td>4.90</td>
<td>4.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4.16</td>
<td>4.02</td>
<td>4.19</td>
<td>4.14</td>
<td>4.50</td>
<td>4.50</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3.95</td>
<td>4.2</td>
<td>4.10</td>
<td>4.20</td>
<td>4.18</td>
<td>4.50</td>
<td></td>
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<tr>
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<td>3.14</td>
<td>3.93</td>
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<td>4.03</td>
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<td>3.88</td>
<td>3.70</td>
<td>4.21</td>
<td>4.19</td>
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In Table 1, Lin, LinH and LinH2 I.P.s have already been discussed in previous papers [7,3,4]. Briefly Lin I.P.s present an odd even alternation due to electronic pairing effect, significant decreases between Li2 and Li3 and Li5 and Li9 correspond to the closing of the 1s and 1p shells of the jellium model. The I.P.s of LinH are very close to Lin-1 I.P.s and LinHn-2 I.P.s to Lin-2 I.P.s (figure 2). This is explained by assuming that one or two valence electrons of the former Lin cluster are localized on the Li-H bound, and that other electrons remain free.

Evolution of the I.P.s for LinH3 and LinH4 with respect to n-m are plotted on figure 2. For these clusters I.P. of LinHm is still very close to Lin-m I.P.. Especially the odd-even alternation is still observable. I.P.s of LinHn-2 clusters are particulary 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 LinHm and Lin-m I.P.s suggests that a bare Lin-m cluster survives inside the LinHm cluster. Are the m H atoms stuck around the Lin cluster, or is the structure of the Lin cluster modified with a separation between a metallic part and an insulator part? The fact that the Lin-m remaining core is little disturbed by the other atoms is in favor of the second hypothesis. This phenomenon is confirmed for LinH2 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 Li4Hn 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$_m$H$_n$ clusters are high (we only observed Li$_5$H$_6$). 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 Cs$_{2n+1}$O$_n$ are particularly low [5]. In the same way, Na$_n$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$_4$F$_n$ clusters [10], globally the potentials decrease whereas they increase for Li$_4$H$_n$. 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 bound 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$_4$F$_3$ where the excess electron is strongly localized in the F vacancy. On the other hand, calculations for Li$_4$H$_3$ [12] give the same structure but the electron is more diffuse and then more bounded to the cluster.

4 Conclusion

We have measured I.P.s of Li$_n$H$_m$ 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$_n$H$_m$ I.P.S and Li$_n$- 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.

References