The Nature of Bonding of Hyperlithiated Molecules Beyond the Octet Rule

Hiroshi Kudo*
Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Received: November 2, 2001

Following an overview on the nature of bonding of such hypervalent molecules as LiX (LiC, LiO, LiO, LiS, LiS, LiP) and MCN (M = Li, Na, K), the present paper deals with the molecular and electronic structures of newly found lithium-rich LiF and LiOH molecules as well as LiF_{m-1} (n = 3, 4) and Li_{10}OH_{n-1} (n = 3–5) clusters which have been detected in supersonic beams effusing from a laser ablation source. The ionization energies (IEs) determined by photoionization were 3.78 ± 0.02 eV for LiF, 4.32 ± 0.2 eV for LiF_{m-1}, and 4.30 ± 0.2 eV for LiF_{n}. Agreements of these IEs with theoretical ones calculated by ab initio MO methods support that LiF is in a hyperlithiated configuration (HLC) in which the excess electron delocalizes over the two lithiums, while LiF_{m-1} and LiF_{m} are in a segregated configuration (SC) comprising ionic and non-ionic lithiums resulting from localization of the excess valence electron. Ionization efficiency curves (IECs) measured for Li_{10}OH_{n-1} (n = 2–5) are well reproduced with a simulation involving Franck-Condon factors, and this enabled us to identify the global-minimum structure of these species predicted by theoretical calculations with the DFT method. The IEs determined were 4.053 ± 0.003 eV for LiOH in HLC, 3.687 ± 0.003 eV for Li_{10}OH_{3} in HLC, 4.133 ± 0.003 eV for Li_{10}OH_{3} in SC, and 3.418 ± 0.009 eV for Li_{10}OH_{3} in SC, and 3.60 ± 0.11 eV for Li_{10}OH_{3} in SC. Also, IE of Li_{3}O was determined as 3.59 ± 0.02 eV from reinvestigation with the photoionization technique. Furthermore, Li_{3}O was found to be a floppy molecule sharing both the D_{3h} and C_{2v} structures from a precise analysis of the observed IEC taking account of the potential energy surface for both neutral and cationic Li_{3}O. This is the first experimental evidence for "electronomers" or electronic isomers of Li_{3}O, which have nearly the same stability but are different in localization of the SOMO. It is eventually stressed that delocalization of the excess valence electron over all of the lithium atoms in a molecule is essential to afford hyperlithiated molecules and that the shape of SOMO or HOMO, which accommodates the excess valence electron or electrons, plays a key role in determining the stability of hyperlithiated molecules.

1. Introduction

Comprehensive understanding of the nature of hypervalent bonding is a subject of current interest since the discovery of Li_{3}O in the equilibrium vapor over Li_{2}O crystals at elevated temperatures in 1978 by Kudo, Wu, and Ihle with Knudsen-effusion mass spectrometry.\(^1\)\(^2\) This molecule possessing nine valence electrons, at least formally, was found to be stable toward dissociation to the corresponding octet molecule Li_{2}O. For a molecular system with covalent bonds of light elements, thermodynamic stability toward dissociation are called "hyperlithiated" or hypervalent molecules. Does the hyperlithiated molecule which accommodates the excess valence electron or electrons, plays a key role in determining the stability of hyperlithiated molecules.

from that of Li_{3}O; i.e., Li_{3}C, Li_{3}O, Li_{3}O, Li_{3}S, Li_{3}S, Li_{3}P and M_{3}CN (M = Li, Na, K), in which the bonding situation was apparently different

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*E-mail: kudoh@mail.cc.tohoku.ac.jp. FAX: +81-22-217-6597.

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Alkali halide clusters with one excess alkali atom, \( M_n X_{n-1} \), tend to leave the excess electron localize at a specific site.\(^{35-40} \) The electron localization is one of the important aspects of segregation. The most part of \( M_n X_{n-1} \) clusters is ionically bound (ionic part) in contrast to the metal excessive clusters such as \( Li_n O \) (\( n \geq 8 \)), where the metallic part prevails.\(^{40} \) For instance, Durand et al. revealed the electron-localization in \( Na_n F_{n-1} \) (\( n = 2-29 \)) clusters based on a one-electron pseudopotential calculation, and reported that the measured IEs reflected faithfully the localization character of the excess electron.\(^{49} \)

In the present paper, I will first briefly summarize the nature of bonding of such hypervalent molecules as Li\(_6\)C, Li\(_3\)O, Li\(_4\)O, Li\(_3\)S, Li\(_4\)S, Li\(_4\)P and M\(_2\)CN (M = Li, Na, K), which were detected in equilibrium vapors over solid or liquid samples by Knudsen-effusion mass spectrometry combined with electron impact ionization. This method has an advantage for determining the dissociation energy of the detected species, although it has some disadvantages for obtaining precise values of IE when we use the electron impact ionization. Next, I will discuss on the molecular and electronic structures of hyperlithiated Li\(_3\)F and Li\(_2\)OH molecules as well as lithium-rich clusters Li\(_3\)F\(_{n-1} \) (\( n = 3, 4 \)) and Li\(_i\) (OH)\(_{n-1} \) (\( n = 3-5 \)) detected in supersonic beams effusing from a laser ablation source. The experiments were performed by a time-of-flight mass spectrometer in which species in the supersonic beam were ionized with pulses from a dye laser pumped by an Nd:YAG laser.\(^{50} \) This sophisticated method is advantageous in determining IEs of these species more accurately. A detailed analysis of ionization efficiency curves (IECs) measured by photoionization enables us to identify the global-minimum structure of the clusters existing in the supersonic beam. Furthermore, I will interpret the molecular and electronic structures of the Li\(_i\)O molecule reinvestigated by an IEC analysis combined with simulations.

2. Li\(_A\) (Li\(_i\)C, Li\(_i\)O, Li\(_i\)S, Li\(_i\)S, Li\(_i\)P) and M\(_2\)CN (M = Li, Na, K) Molecules

Despite their unusual stoichiometries, the Li\(_A\) molecules (Li\(_i\)C, Li\(_i\)O, Li\(_i\)S, Li\(_i\)S and Li\(_i\)P) are stable toward dissociation to the corresponding octet molecules.\(^{1, 2, 7-14} \) The dissociation energies are summarized in Table 1. The results of \( ab \) \textit{initio} MO calculations indicate that occupancy of the nine valence electrons in Li\(_3\)S, for instance, is (5a\(_1\))\(^2\)(3e)\(^4\)(6a\(_1\))\(^2\)(7a\(_i\))\(^1\) and that of 10 valence electrons in Li\(_4\)S is (6a\(_1\))\(^2\)(3b\(_1\))\(^2\)(7a\(_1\))\(^2\) (3b\(_2\))\(^2\)(8a\(_1\))\(^2\). The highest orbital (7a\(_i\)) of Li\(_3\)S is singly occupied orbital (SOMO) and the 8a\(_1\) orbital of Li\(_4\)S is HOMO. The excess valence electrons accommodate in SOMO or HOMO. Either one and two excess valence electrons in these molecules delocalize over all of the lithium atoms and contribute to the formation of a Li\(_i\)\(_m\) cage with Li-Li bonds. Figure 1 depicts the features of SOMO in Li\(_3\)S and HOMO in Li\(_4\)S deduced from theoretical calculations at the UHF/STO-3G level.\(^{14} \) The SOMO of Li\(_3\)S seems to build the cage. The widely spreading HOMO of Li\(_4\)S suggests more clearly the lithium cage formation in the molecule. The SOMO of Li\(_3\)S and HOMO of Li\(_4\)S are antibonding between the Li and S atoms, but are bonding between all pairs of lithium atoms in these molecules. In spite of the antibonding character of SOMO and HOMO, the central S atom is bound to lithiums through an electrostatic interaction.

Charge populations calculated by the natural bond orbital (NBO) analysis\(^{51} \) on the central atoms in Li\(_i\)A were -0.93 for C in Li\(_i\)C, -0.87 for O in Li\(_i\)O, -1.89 for S in Li\(_i\)S, and -1.92 for S in Li\(_i\)P. The calculated charges on C, O, and S do not increase appreciably as more Li atoms are added; e.g., Li\(_4\)C (C, -0.81), Li\(_2\)O (O, -0.81), and Li\(_3\)S (S, -1.84). The fact indicates that the excess valence electron is not associated with the central atom and that the central atom remains content with its normal octet.\(^{5, 15} \) For hyperlithiated Li\(_i\)A molecules, therefore, it is concluded that the electronegative central atom (A\(_m\)) is embedded in the Li\(_i\)\(_m\) cage. Although the Li-A bond is antibonding in character, the electrostatic attraction between Li\(_m\) and A\(_m\) would play a role in enhancing the overall stability of neutral Li\(_i\)A molecules. As listed in Table 1, M\(_2\)CN (M = Li, Na, K) molecules with one excess valence electron are all stable toward the dissociation to give M and MCN.\(^{28-32} \) Of these hypervalent molecules, the

<table>
<thead>
<tr>
<th>Number of excess valence electrons</th>
<th>Molecule (Point group)</th>
<th>( D_s^0 ) (kJ mol(^{-1}))</th>
<th>IEs (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li(<em>i)O (D(</em>{3h}))</td>
<td>198.3(^a)</td>
<td>3.48(^b)</td>
</tr>
<tr>
<td>1</td>
<td>Li(<em>i)S (C(</em>{3v}))</td>
<td>148.5</td>
<td>3.40(^b)</td>
</tr>
<tr>
<td>1</td>
<td>Li(_i)P (T(_d))</td>
<td>141.8</td>
<td>4.08(^b)</td>
</tr>
<tr>
<td>2</td>
<td>Li(_i)C (O(_h))</td>
<td>273(^f)</td>
<td>4.71(^b)</td>
</tr>
<tr>
<td>2</td>
<td>Li(_i)O (T(_d))</td>
<td>120.9(^p)</td>
<td>4.09(^b)</td>
</tr>
<tr>
<td>2</td>
<td>Li(<em>i)S (C(</em>{1v}))</td>
<td>123.2(^p)</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Li(<em>i)CN (C(</em>{3v}))</td>
<td>103.8</td>
<td>5.13</td>
</tr>
<tr>
<td>3</td>
<td>Na(<em>i)CN (C(</em>{3v}))</td>
<td>72.8</td>
<td>4.66</td>
</tr>
<tr>
<td>3</td>
<td>K(<em>i)CN (C(</em>{3v}))</td>
<td>74.5</td>
<td>3.70</td>
</tr>
</tbody>
</table>

\(^a\) Vertical ionization energy (vIE).
\(^b\) Schleyer et al.\(^{5, 6, 15} \)
\(^c\) Cl\(_i\)(g) → Cl\(_{i+1}\)(g) + Li\(_i\)(g) process.
Li₂CN (D₀₀ = 137 kJ/mol) is the most stable. Each of M₂CN molecules has several structural isomers with a global minimum. Figure 2 illustrates molecular structures of all isomers of Li₂CN calculated at the MP2(FC)/6-31-G* level, together with the SOMOs of the planar 1 and linear 4 isomers. The optimized geometries calculated for Na₂CN and K₂CN at the MP2(FC)/6-31-G* level also gave four structural isomers to each molecule, similar to the case of Li₂CN. For M₂CN, the most stable isomer in the planar structure is Li₂CN, a hypervalent molecule in which the extra valence electron delocalizes over the two alkali-metal atoms forming a M⁺⁺ cation. The IE observed for these molecules, 5.4 ± 0.4 eV for Li₂CN, 4.9 ± 0.2 eV for Na₂CN, 4.5 ± 0.5 eV for K₂CN, are close to those for Li → Li⁺⁺ (4.9 eV), Na → Na⁺⁺ (4.9 eV), and K → K⁺⁺ (4.1 eV). The fact suggests that the ionization occurs from the SOMO. M₂CN molecules possessing the M⁺⁺ unit in it can be described as M⁺⁺CN⁻. On the other hand, the linear isomers of M₂CN, that are less stable than the planar isomers, would be complexes described as M⁺CN⁻•·M and M•·CN⁺•·M⁺; these are "electroomers" or electronic isomers in which the localization of the excess valence electron is different each other.

3. Li₂F Molecule and Li₂Fn⁻¹ (n = 3, 4) Clusters

Although theoretically predicted hyperlithiated Li₂F was hardly observed with Knudsen-effusion mass spectrometry, it was eventually detected in a supersonic beam of vapors generated by laser ablation of a solid mixture of LiF and Li₅N. The observed IE of Li₂F (3.78 ± 0.3 eV) agrees well with the theoretical adiabatic IE (alIE = 3.9 eV). This fact verifies a result of theoretical calculations that the Li₂F molecule (1a) is one of the hyperlithiated molecules and the excess valence electron delocalizes on the two Li atoms. Also, the fact that the IE of Li₂F is significantly lower than that of the Li atom (5.39 eV) is ascribed to the antibonding character of the SOMO between the Li and F atoms, as described by Gutsev and Boldyrev for "superalkali" species. Although the presence of the isomer 1b is suggested theoretically, only the isomer 1a existed in the supersonic beam because 1a (D₀₀ = 147.4 kJ/mol) is more stable than 1b (D₀₀ = 129.8 kJ/mol). In addition, new clusters Li₃F₁₋₁ (n = 3, 4) with an excess electron were detected in the same supersonic beam. Table 2 lists the IEs of Li₃F₁₋₁ (n = 2–4) species determined by photoionization, together with the dissociation energy (D₀₀) of the isomers calculated at the MP2(FULL)/6-311+G(d)//B3LYP/6-311+G(d) level of theory. Figure 3 illustrates the theoretically deduced structures of Li₃F₁₋₁ (n = 2–4) isomers.

![Figure 2](image)

Figure 2. Structural isomers of Li₂CN and features of SOMO of the planar isomers 1 [Li₂⁺⁺(CN⁻•·)] and the linear isomer 4 [Li⁺⁺(CN⁻•·Li⁺⁺)] derived from calculations at MP2(FC)/6-31-G*; roman letters are the bond length in Å and italic letters the natural charge.

![Figure 3](image)

Figure 3. Structural isomers of Li₂Fn⁻¹ (n = 2–4) obtained by calculations at B3LYP/6-311+G(d); roman letters are the bond length in Å and italic letters the natural charge.

<table>
<thead>
<tr>
<th>TABLE 2: Ionization Energies and Dissociation Energies of Li₃F₁₋₁ (n = 2–4)</th>
</tr>
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<tbody>
<tr>
<td><strong>Experimental IE/eV</strong></td>
</tr>
<tr>
<td>Li₃F</td>
</tr>
<tr>
<td>Li₃F₂</td>
</tr>
<tr>
<td>Li₃F₃</td>
</tr>
<tr>
<td>Li₃F₄</td>
</tr>
<tr>
<td>Li₃F₅</td>
</tr>
<tr>
<td>Li₃F₆</td>
</tr>
<tr>
<td>Li₃F₇</td>
</tr>
<tr>
<td>Li₃F₈</td>
</tr>
<tr>
<td>Li₃F₉</td>
</tr>
</tbody>
</table>

* Vertical and adiabatic ionization energies (vIE and alIE) at MP2(FULL)/6-311+G(d) // B3LYP/6-311+G(d).
* At B3LYP/6-311+G(d).
* HLC, the hyperlithiated configuration; SC, the segregated configuration.
stable than 1b ($D_{e}^{a} = 26.7 \text{ kJ/mol}$). The isomer 1b is in a segregated configuration (SC).

The observed IE of Li$_{3}$F$_{2}$ (4.32 eV) indicates the predominance of SC in this cluster. This IE value is close to $aIE$ calculated for the isomer 2b, which is in SC with $D_{e}^{a} = 94.9 \text{ kJ/mol}$. Here, one can consider that the isomer 2a in another SC with a similar stability ($D_{e}^{a} = 94.9 \text{ kJ/mol}$) would be present because the observed IE is in between the theoretical $aIE$ and vertical ionization energy (vIE) of 2a. However, the presence of 2a in the supersonic beam is denied from a comparison of IECs between the experiment and the simulation shown in Figure 4; the theoretical IEC was obtained by taking account of the Franck-Condon factor for the ionization process, the detail of which will be described elsewhere. The isomer 2c with a hyperlithiated configuration (HLC) is obviously minor, because the observed IE (4.32 eV) is significantly higher in energy than vIE calculated for 2c (3.7 eV). Furthermore, the dissociation energy of 2c is calculated to be quite small ($D_{e}^{a} = 33.0 \text{ kJ/mol}$) in comparison with the other isomers of Li$_{3}$F$_{2}$ as listed in Table 2. The Li$_{3}$F$_{2}$ cluster would prefer SC. The IE observed for Li$_{4}$F$_{3}$ (4.3 eV) is close to vIEs calculated for 3a and 3b, both of which are in SC. No big difference is seen in dissociation energies between 87.4 kJ/mol for 3a and 74.8 kJ/mol for 3b, but the shape of IEC shown in Figure 4 indicates that the isomer detected in the supersonic beam is 3b.

In the Li$_{n}$F$_{n-1}$ system, Li$_{n}$F is a hypervalent molecule, but Li$_{n}$F$_{n}$ prefers to be in SC despite a possibility to be in HLC. Every isomer of Li$_{n}$F$_{n}$ is in SC. Thus, at $n \geq 3$ the Li$_{n}$F$_{n-1}$ clusters tend to take SC in which the excess valence electron is localized at any of the Li atom.

4. Li$_{n}$OH Molecule and Li$_{n}$(OH)$_{n+1}$ ($n=3-5$) Clusters

To detect Li$_{n}$(OH)$_{n+1}$ ($n=2-5$) species, we injected small amounts of water vapor diluted with air into an laser ablation source in which lithium metal pressed on a sample disk was irradiated by 532 nm laser pulses. Figure 5 shows ionization efficiency curves (IECs) of the Li$_{3}$(OH) molecule as well as Li$_{n}$(OH)$_{n+1}$ ($n=3-5$) clusters. The experimental values of IE determined here for each isomer of these species are summarized in Table 3, together with both the theoretical vertical ionization energy (vIE) and adiabatic ionization energy (aIE) calculated at the MP2(FULL)/6-311+G(d)//B3LYP/6-311+G(d) level as well as the dissociation energies calculated at the B3LYP/6-311+G(d,p) level. The structural isomers and features of SOMO of Li$_{3}$(OH) and Li$_{5}$(OH)$_{5}$ deduced by theoretical calculations at the B3LYP/6-311+G(d,p) level are illustrated in Figure 6. The theoretically obtained molecular structures and isosurfaces of SOMO of Li$_{3}$(OH)$_{3}$ and Li$_{5}$(OH)$_{4}$ are shown in Figures 7 and 8, respectively.

The results of our theoretical investigation reveal that IEs of Li$_{n}$(OH)$_{n+1}$ ($n=2-5$) species with an excess lithium atom depend largely on their structure. Every cluster has several stable structural isomers, the structure of which is closely related to the charge population associated with the location of the excess valence electron of the Li atom. In some isomers, the excess electron delocalizes over all of the lithium atoms in the cluster, forming a metallic network (Li$_{n}^{+}$) similar to hyperlithiated molecules like Li$_{3}$O and Li$_{6}$C. In other isomers, the excess valence electron localizes at a specific site, making the metallic and ionic parts segregated. In the Li$_{n}$(OH)$_{n+1}$ ($n=2-5$) system, the isomers 1a and 2a seem to have HLC with respect to the charge population. All of the lithium atoms possess almost the same atomic charge in these isomers as
shown in Figures 6 and 7. To confirm whether or not these isomers are in HLC, we examined their electronic structure and stability in terms of a character of SOMO which accommodates the excess electron. As described in the previous section, hyperlithiated molecules Li₃O, Li₆C, and Li₃S are stabilized by an electrostatic attraction between the anionic center and the cationic lithium network which is maintained by sharing the excess electron. The SOMO spatially covers all lithium atoms, making their structures highly symmetric; e.g., D₃h for Li₃O, O₆ for Li₆C, and C₃v for Li₃S. The SOMO should have an antibonding character between, at least, one of the lithium atoms and the central atom. However, the equal positive charge on all lithiums produces an equal electrostatic attraction between each Li atom and the central atom. The SOMO spreading over the whole lithium network plays a key role in the formation of molecules with HLC.

Figure 6. Structures and features of SOMO of Li₃(OH) and Li₅(OH)₄ obtained by calculations at B3LYP/6-311+G(d,p); roman letters are the bond length in Å and italic letters the natural charge.

Figure 7. Structural isomers of Li₄(OH)₃ and Li₅(OH)₄ obtained by calculations at B3LYP/6-311+G(d,p); roman letters are the bond length in Å and italic letters the natural charge.

| Isomer | Experimental IE/eV | Isomer | Theoretical aIE/eV | aIE/eV | Classification
<table>
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<tr>
<td>Li₃OH</td>
<td>4.35 ± 0.12</td>
<td>1a (C₃v)</td>
<td>4.45</td>
<td>4.03</td>
<td>146.7</td>
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<td></td>
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<td>1b (C₃v)</td>
<td>6.58</td>
<td>5.55</td>
<td>19.4</td>
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<td>Li₅(OH)₃</td>
<td>3.66 ± 0.02</td>
<td>2a (D₃h)</td>
<td>3.57</td>
<td>3.57</td>
<td>92.5</td>
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<td></td>
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<td>2b (C₁)</td>
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<td>Li₆(OH)₃</td>
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<td>3.60 ± 0.11</td>
<td>4a (C₁)</td>
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<td>4f (C₁)</td>
<td>5.62</td>
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<td>12.5</td>
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</table>

a Vertical and adiabatic ionization energies (vIE and aIE) at MP2/6-311+G(d,p).

b At B3LYP/6-311+G(d,p).

HLC, the hyperlithiated configuration; SC, the segregated configuration.
The result of theoretical calculations indicates further that IEs of the isomers of Li$_n$(OH)$_{n-1}$ depend on the number of terminal lithium atoms as shown in Figure 9, irrespective of the stability toward dissociation (Table 3). For example, the difference in IEs between the isomer 2a and 2c of Li$_3$(OH)$_2$ is as large as 1.43 eV, although the difference in the dissociation energies is only 0.1 eV (9.9 kJ/mol). The IEs of planar isomers (1a, 2c, 3e, 4f) with two terminal lithiums ($n_{\text{TL}} = 2$) tend to increase from 4.5 to 5.6 eV with an increase of $n$. The IE of Li-tail isomers (2b, 3c, 4d) with $n_{\text{TL}} = 1$ is around 4.2 eV independent of $n$. The isomers without terminal Li atoms have IE lower than 3.7 eV. The vIE of the linear isomer 1b (6.58 eV) is quite higher than that of the Li atom (5.39 eV).

Based on the Koopmans theorem that the vertical ionization energy directly corresponds to the orbital energy of SOMO, the present result is explained by considering the stability of SOMO, from which the extra electron is removed in the ionization process. In the Li$_n$(OH)$_{n-1}$ clusters, the OH$^-$ groups with negative charge would deform the SOMO as a consequence of the electronic repulsion as suggested from the spatial distribution of SOMO. When repulsion by OH$^-$ groups becomes larger, the SOMO becomes less stable and then the ionization energy becomes lower. This leads to the importance of spatial arrangement of the OH$^-$ groups against the SOMO within the cluster. We focus the discussion on the spatial distribution of the SOMO to explain the correlation between the ionization energy and the number of terminal lithium atoms in the Li$_n$(OH)$_{n-1}$ clusters. The SOMO tends to localize around the terminal lithium atom. In the planar isomers with the highest IE, the SOMO distributes in a space between the two terminal lithium atoms, independent of the cluster size. The deformation of SOMO from a spherical symmetry is rather small in these planar isomers, because the neighboring OH$^-$ is fairly distant from the SOMO. In the Li-tail isomers with the second highest ionization energy in each size of the cluster, the SOMO localizes around the terminal Li atom and is deformed by the nearest OH$^-$ group as seen in 2b (Figure 6). It is to be noted that the Li-tail isomers in which the SOMO localizes around only one Li atom have lower ionization energy than the planar isomers in which the SOMO delocalizes between two Li atoms. In the isomers without terminal lithium, the SOMO delocalizes over the lithium network. In particular, the SOMO is largely deformed and widely distributed over the whole lithium network in the hyperlithiated isomers 2a (Figure 6). The ionization energies of these isomers are significantly low as seen in Table 3.

From comparison of IEs between the experiment and the theory listed in Table 3 it is concluded that the isomers exited in the supersonic beam of the present experiment were Li$_2$(OH)$_1$, Li$_3$(OH)$_2$, Li$_4$(OH)$_3$, Li$_5$(OH)$_4$, and Li$_6$(OH)$_5$. The global-minimum structure is in HLC at $n = 2$ and 3 and in SC at $n = 4$, indicating the occurrence of the transition from HLC to SC between $n = 3$ and 4. The second stable isomer 2b in SC was also observed for Li$_3$(OH)$_2$. This might be attributed to nearly the same stability of the two isomers; $D_0 = 92.5$ kJ/mol for 1a and $D_0 = 92.0$ kJ/mol for 2b. The conclusion was also confirmed by comparing the shape of measured IECs with that obtained by simulations involving the Franck-Condon factor (FCF), the detail of which is reported elsewhere.\footnote{5}

5. Reinvestigation of Molecular Structure and Ionization of Li$_3$O: Evidence for Electronomers

When we reported the first evidence for the existence of hyperlithiated Li$_3$O,\footnote{1, 2} the ionization energy (IE) determined by electron impact ionization was $4.5 \pm 0.2$ eV. The dissociation energy of Li$_3$O to give Li$_2$O was determined as $212 \pm 42$ kJ/mol. Although the dissociation energy agreed considerably well with the theoretical value (198.3 kJ/mol) calculated by Schleyer et al.,\footnote{7} a rather large difference was seen in the IE between the experiment and theory (3.48 eV). The question remained to be solved for a long time. Recently, Lievens et al. have reported an experimental value (3.54 $\pm$ 0.3 eV) for IE of Li$_3$O by photoionization measurements.\footnote{40} This stimulated us to reinvestigate the ionization process of Li$_3$O present in the same supersonic beam used for detecting the Li$_n$(OH)$_{n-1}$
species described in the previous section. Figure 10(a) shows the ionization efficiency curve (IEC) for \( \text{Li}_3\text{O} \) obtained by time-of-flight mass spectrometry combined with photoionization. There are two prominent features in the profile of IEC, i.e., two-stage rise and gradual linear rise between the threshold (3.59 ± 0.02 eV) and the second onset (4.4 ± 0.1 eV). The two-stage rise has already been reported by Lievens et al. and attributed to some ionization processes other than the first ionization of \( \text{Li}_3\text{O} \) to give the ground state \( \text{Li}_3\text{O}^- \) of current interest. The threshold determined here is in excellent agreement with the theoretical IE. Both the theoretical vIE and aIE are calculated as 3.59 eV at a sophisticated level of CCSD(T)/6-311+G(d) assuming the \( D_{3h} \) structure for the neutral geometry.

Schleyer et al. reported in 1982 that the most stable structure of \( \text{Li}_3\text{O} \) was in \( C_\infty \) symmetry from the calculation at the HF/3-21G level, and then reported in 1992 that their higher level of calculation at MP2(FULL)/6-31G* revealed the \( D_{3h} \) symmetry. Figure 11 illustrates the result of our calculation on molecular structures of neutral and ionic \( \text{Li}_3\text{O} \) at the MP2/6-311+G(d) level of ab initio MO theory. For the neutral, both the \( D_{3h} \) and \( C_\infty \) structures are local minima on the potential energy surface. Single-point energy calculations at the CCSD(T)/6-311+(d) level indicate that the \( D_{3h} \) structure is slightly favorable in energy (0.8 kJ/mol), but the energy difference between those structures is much smaller than the accuracy of the calculation. The true minimal energy structure is still unpredictable. However, a simulation of the profile of IEC for \( \text{Li}_3\text{O} \) shown in Figure 10(b) provided a new clue to the molecular structure.

We can make simulations of IEC for small molecules by a "direct counting of vibrational states" method, using the same procedure as applied to the \( \text{Li}_3\text{OH}_{n-1} \) system. An essential idea of simulation is to calculate Franck-Condon factors (FCF) within harmonic approximation. The calculation includes the displacement of molecular geometry, the frequency change, and the normal mode rotation between the neutral and cationic states. All of these parameters can be computed by density functional theory (DFT) or \textit{ab initio} MO theory calculations. The simulated IECs for \( \text{Li}_3\text{O} \) are superimposed on the experimentally observed IEC in Figure 10(b). The ionization of the \( D_{3h} \) structure of neutral \( \text{Li}_3\text{O} \) does not reproduce well the observed gradual linear rise. Even with parameters for the \( C_\infty \) structure, the simulation is far from the observed linear rise of IEC. The well-fitted curve in Figure 10(b) was obtained when two in-plane bending frequencies were adjusted to 10 cm$^{-1}$ and the molecule is restricted to populate only on the zero-point level in these modes; i.e., no vibrational excitation in these two bending modes. We assumed a flat potential energy surface for the neutral \( \text{Li}_3\text{O} \) to reproduce the observed curve. In fact, the \textit{ab initio} MP2 calculation gives a very flat potential well in the two Li-O-Li bending modes.
minima and the $D_{3h}$ minima. With this large amplitude of vibrational motion, a wide range of cationic potential energy surface is accessible by the vertical ionization from the $v = 0$ level as shown in Figure 12(c). Thus the Li$_3$O molecule is described as a floppy molecule sharing both the $D_{3h}$ and $C_{2v}$ structures which have nearly the same stability but are different in the localization of the SOMO.

The most significant difference between the $D_{3h}$ and $C_{2v}$ structures is the shape or spatial distribution of their SOMO. The shape of SOMO is important characteristics in hyperlithiated molecules. The $D_{3h}$ structure shows fully delocalized SOMO, while it is localized and forms a salt consisting of Li$^+$ and LiO$^-$ in the $C_{2v}$ structure.

In hyperlithiated or hypervalent molecules such as Li$_n$A (Li$_n$C, Li$_n$O, Li$_n$O, Li$_n$S, Li$_n$P, M-CN (M = Li, Na, K), Li$_n$F$_{n-1}$ (n = 2–4), and Li$_n$(OH)$_{n-1}$ (n = 2–5), the excess valence electron is not associated with the electronegative C, O, F, S, P atoms as well as CN and OH groups, and the electronegative constituent remains content with its normal octet. The excess valence electron delocalizes over lithium atoms contributing to the formation of a lithium network or cage (Li$^{n+}$) with the Li-Li bond, and the hyperlithiated molecules are stabilized by the electrostatic attraction between the cationic Li$^{n+}$ and the anionic species (e.g., C$^{0-}$, O$^{0-}$, F$^{1-}$, S$^{1-}$, CN$^{0-}$, OH$^{1-}$), despite the antibonding character between each of the lithium atom and the electronegative constituent.

Delocalization of the excess valence electron is essential to afford hyperlithiated molecules, and the spatial distribution or shape of SOMO and HOMO, which accommodates the excess valence electron, plays a crucial role in determining the stability of hyperlithiated molecules. In the Li$_n$F$_{n-1}$ (n = 2–4) and Li$_n$(OH)$_{n-1}$ (n = 2–5) systems, SOMO widely spreads over the whole molecule giving a hypelithiated configuration (HLC) at small $n$, but tends to localize around a specific site affording a segregated configuration (SC) with an increase of $n$. Of these Li-rich clusters, IE is relatively high in planar isomers with two terminal lithium atoms ($n_{TL} = 2$) reflecting the stability of SOMO.

From the reinvestigation of ionization processes of Li$_3$O, this hypelithiated molecule was found to be a floppy molecule sharing both $D_{3h}$ (HLC) and $C_{2v}$ (SC) structures which have nearly the same stability but are different in the localization of SOMO. This is the first experimental evidence for electronomers or electronic isomers.

5. Conclusion

The most significant difference between the $D_{3h}$ and $C_{2v}$ structures is the shape or spatial distribution of their SOMO. This is the first experimental evidence for electronomers or electronic isomers.

References

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