

## Competition between Planar and Nonplanar Structure in Alkali Hexamers: The Example of $\text{Li}_6$

Ph. Dugourd,<sup>(1)</sup> J. Blanc,<sup>(2)</sup> V. Bonacic-Koutecky,<sup>(3)</sup> M. Broyer,<sup>(1)</sup> J. Chevalyre,<sup>(1)</sup> J. Koutecky,<sup>(3)</sup>  
J. Pittner,<sup>(3)</sup> J. P. Wolf,<sup>(2)</sup> and L. Wöste<sup>(2)</sup>

<sup>(1)</sup>Laboratoire de Spectrométrie Ionique et Moléculaire, Bâtiment 205, Université Lyon I,  
43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne CEDEX, France

<sup>(2)</sup>Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-1000 Berlin 33, Germany

<sup>(3)</sup>Institut für Physikalische und Theoretische Chemie, Freie Universität Berlin, D-1000 Berlin 33, Germany

(Received 1 May 1991)

The optical-absorption spectrum of  $\text{Li}_6$  has been observed by depletion spectroscopy in the 400–700-nm range. The experimental results are compared with theoretical spectra calculated for the three  $\text{Li}_6$  structures in competition and we have been able to unambiguously determine the most stable  $\text{Li}_6$  geometry as being the  $C_{2v}$  tripyramidal geometry.

PACS numbers: 36.40.+d, 31.50.+w, 35.20.-i

It is well known from basic solid-state physics that crystalline structure determines electronic and metallic properties of materials [1]. For example, the pentavalent semimetals and carbon, which have various allotropic varieties having very different properties, are striking illustrations of this phenomenon. In clusters physics we expect that the geometric structure plays the role of the crystalline structure. However, the geometry of small metal clusters is quite difficult to determine experimentally. For large size domains, electron diffraction may provide valuable information on the cluster structure [2]. However, for very small clusters  $M_n$  ( $3 \leq n \leq 50$ ), there is no standard method to measure the geometric structure. In dimers or trimers [3–5] the analysis of vibronic and rotational patterns leads to precise determination of internuclear distances and ground-state potential surfaces. For  $n \geq 4$ , the vibronic structure, when it exists [6], is too congested to allow a valuable analysis. In these clusters, only unresolved broadband absorption spectra [7–10] are available.

Theoretical *ab initio* calculations performed on alkali clusters have led to predictions of the ground-state geometric structure in the size range  $2 \leq n \leq 13$  [11]. Sometimes for a given size, two or three isomers have energy values very close together with small energy barriers between them. Moreover, very recently, it has become possible to calculate the optical-absorption spectra of small alkali clusters in the size range  $2 \leq n \leq 8$ , as illustrated by the results obtained for  $\text{Li}_4$  [6,12],  $\text{Na}_4$  [13,14],  $\text{Li}_8$  [15], and  $\text{Na}_8$  [14,16], where the agreement with experimental results is remarkable. It is clear that the optical-absorption spectrum strongly depends on the ground-state geometry and the comparison with experimental results is the key for the determination of the geometric structure. In alkali clusters, the hexamer plays a particular role. For  $n \leq 5$ , alkali clusters are planar, while in the hexamer, competition between planar and nonplanar structures occurs [11,17], namely, three structures have very similar binding energy: the planar  $D_{3h}$  structure, the quasiplanar pentagonal pyramidal  $C_{5v}$  with

only one atom slightly above the pentagon, and the nonplanar tripyramidal  $C_{2v}$  geometry. We present in this Letter experimental results on the  $\text{Li}_6$  optical-absorption spectrum and *ab initio* calculations of the whole absorption spectrum calculated for different geometries. The comparison between them allows us to determine the  $\text{Li}_6$  geometry as being the nonplanar tripyramidal  $C_{2v}$ . This illustrates the ability of spectroscopic techniques combined with *ab initio* calculations to determine the cluster structure and also confirms the attractive character of the hexamer in the alkali cluster as a transition between planar and nonplanar dimensions.

The lithium clusters are produced in a seeded molecular beam by the coexpansion of Li vapor with argon as inert carrier gas. To achieve the high temperatures necessary for reasonable lithium vapor pressure (10–100 Torr), a special oven was built. It is comprised of a cartridge made of titanium, zirconium, and molybdenum heated by tungsten filaments. Nozzle characteristics are typically 100  $\mu\text{m}$  in diameter for a channel length of 300  $\mu\text{m}$ . The argon pressure varies in the range 1–5 bars. The vibrational temperature measured on  $\text{Li}_3$  is typically 25 K [18].

The  $\text{Li}_6$  absorption spectrum was recorded by the depletion technique [6,19] using two dye lasers pumped by two different excimer lasers. The first laser, frequency doubled in a beta barium borate (BBO) crystal (1  $\text{mJ}/\text{cm}^2$  at 225 nm), permanently ionizes  $\text{Li}_6$ . The second dye laser is scanned to the  $\text{Li}_6$  excited states. Relaxation of the excitation occurs by fast dissociation of  $\text{Li}_6$  and induces depletion of the  $\text{Li}_6^+$  ion signal detected by a time-of-flight mass spectrometer. The time delay between the two excimer lasers is electronically adjusted. This arrangement allows the utilization of two separate regions for photodepletion and photoionization which prevents perturbation due to daughter clusters resulting from fragmentation effects following the excitation by the depleting laser. The minimum distance between both laser spots that yields negligible effects from fragments is about 20 mm [15]. During the run of experiments on  $\text{Li}_6$ ,

the distance between both laser spots was only 6 mm due to topological constraints in our apparatus. The fragmentation of  $\text{Li}_7$  on the  $\text{Li}_6$  channel was observed ( $\text{Li}_7^* \rightarrow \text{Li}_6 + \text{Li}$ ). However, by varying the time delay between the two lasers and the power of the depleting laser, it was possible to discriminate between  $\text{Li}_6$  fragments and  $\text{Li}_6$  coming from the beam because they have different velocity distributions.

Eight different dyes were used for recording  $\text{Li}_n$  absorption spectra between 380 and 760 nm. The fluence of the depleting laser was carefully recorded by a calibrated pyroelectric detector in order to deconvolute spectra from dye responses and to ensure that the depletion process remains in the linear region. Absolute cross sections are then deduced from depletion spectra by the usual relation  $\ln(I_{\text{off}}/I_{\text{on}}) = \sigma\phi$ . The absorption cross section obtained is shown in Fig. 1. In the red and yellow regions, the fragmentation effects were negligible and the cross section may directly be deduced from the depletion spectra. In the blue region where a strong depletion occurs in  $\text{Li}_7$  and

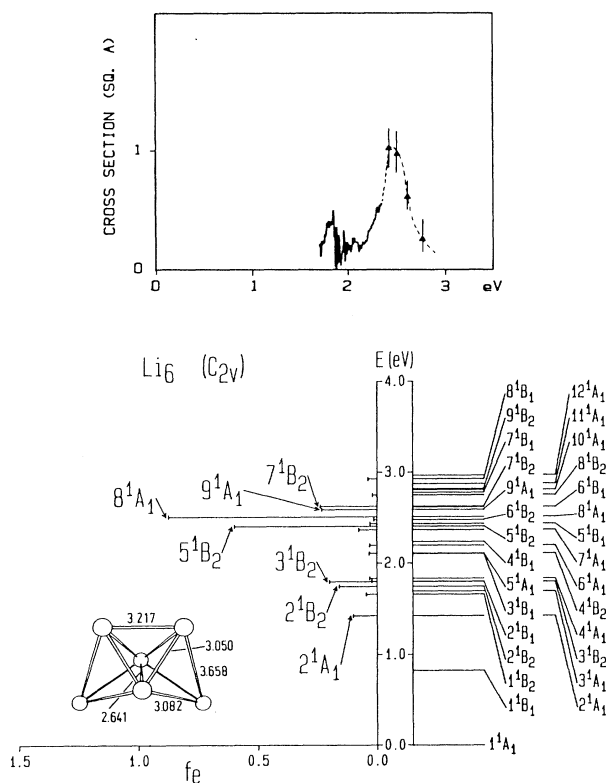


FIG. 1. Experimental optical absorption spectra of  $\text{Li}_6$  (upper) and calculated oscillator strengths of the various transitions (lower) for the tripyramidal  $C_{2v}$  geometry. All electronic states involved in the calculation of line strengths for vertical electronic absorption transitions are shown at the bottom. Only significant line strengths are drawn in the middle part; they exhibit the very good agreement between theory and experiment for this geometry.

$\text{Li}_8$ , fragmentation effects were observed and a detailed study was performed for selected wavelengths by varying the time delay between both lasers and the power of the depleting laser [18], allowing us to correct the  $\text{Li}_6$  absorption cross section from the contribution of daughter fragments ( $\text{Li}_6$  fragments have different velocity distributions). The  $\text{Li}_6$  absorption spectrum exhibits two broadbands: an intense band at about 500 nm (2.5 eV) and a weaker one at 690 nm (1.8 eV). These results may be compared with *ab initio* calculations of optical transition oscillatory strength for various  $\text{Li}_6$  isomers.

The method used for the *ab initio* calculations of the  $\text{Li}_6$  ground state is detailed in Refs. [12] and [17]. The best calculations were obtained with the self-consistent-field, multireference diexcitation, configuration-interaction (SCF-MRD-CI) procedure using a  $(13s, 3p/6s, 3p)$  atomic-orbital basis set. There are three energetically close-lying structures: the planar  $D_{3h}$  structure has a  $1A_1'$  ground state with a total 4.10 eV atomization energy. The pentagonal pyramid of  $C_{5v}$  symmetry has a  $1A_1$  ground state and very similar atomization energy ( $\approx 4.18$  eV). The tripyramidal  $C_{2v}$  geometry ( $1A_1$  ground state) has the lowest atomization energy ( $\approx 4.23$  eV). This energy difference is very small, illustrating the

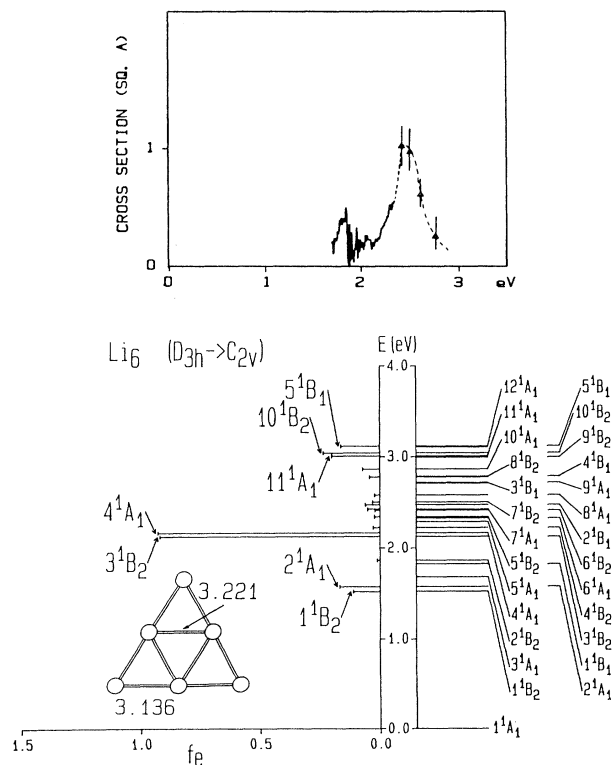


FIG. 2. Comparison between the experimental spectrum (upper) and calculated transitions (lower) for the planar  $D_{3h}$  geometry of  $\text{Li}_6$ . The complete disagreement with the experiment allows us to exclude this geometry.

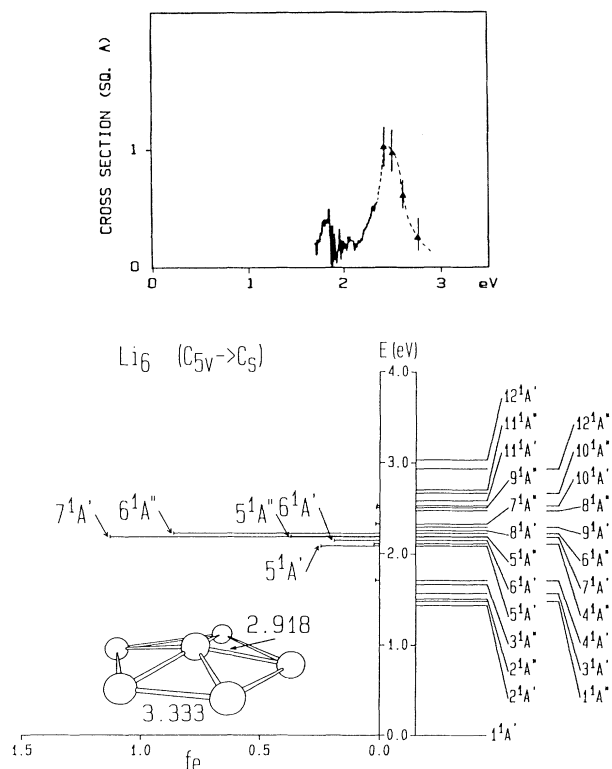


FIG. 3. Comparison between the experimental spectrum (upper) and calculated transitions (lower) for the pentagonal pyramid  $C_{5v}$  geometry of  $Li_6$ . The complete disagreement with the experiment allows us to exclude this geometry.

competition between these various structures. Particularly, it is interesting to remark that for  $Na_6$  the planar  $D_{3h}$  structure has the lowest energy. A comparison of the calculated and experimental absorption spectrum is therefore crucial.

The excited states of  $Li_6$  have been calculated using similar methods as for  $Li_4$ ,  $Li_7$ , and  $Li_8$  [12,15]. The oscillator strengths of the vertical transitions are obtained for the three  $Li_6$  geometries from their ground state. The results are compared to the experimental spectra (Figs. 1–3). The nonplanar tripyramidal  $C_{2v}$  geometry gives an absorption spectrum in fair agreement with the experiment (Fig. 1). For the two other structures (Figs. 2 and 3), the absorption spectrum is dominated by an intense peak around 600 nm (2.07 eV) in complete disagreement with the experimental results. These features unambiguously demonstrate that the  $Li_6$  clusters produced in our seeded molecular beam have a nonplanar tripyramidal geometry.

It is also interesting to notice that the  $Na_6$  absorption spectrum [20,21] exhibits an intense peak at 600 nm (2.5 eV) in agreement with the spectrum calculated for a planar structure  $D_{3h}$  and for a pentagonal pyramid  $C_{5v}$  [22].

Since in other lithium and sodium clusters ( $Li_4$ ,  $Na_4$ ,  $Li_7$ ,  $Na_7$ ,  $Li_8$ ,  $Na_8$ ) geometric structures and absorption spectra are rather similar, this difference of behavior in  $Li_6$  and  $Na_6$  illustrates the competition between planar and nonplanar structures in small alkali hexamers.

In conclusion, we have recorded the optical-absorption spectrum of the  $Li_6$  cluster. By comparison with the theoretical spectra obtained by *ab initio* calculations for the various  $Li_6$  isomers, we have proved that  $Li_6$  produced in our seeded molecular beam has the nonplanar tripyramidal  $C_{2v}$  geometry. Since the clusters in our beam are very cold, this indicates that this isomer is probably the most stable, in agreement with the best *ab initio* SCF-CI calculations. This example illustrates clearly the importance of the position of nuclei for interpretation of absorption spectra in very small clusters. In the future, it would be very interesting to study the  $Li_6$  absorption spectrum as a function of the temperature, for example, by heating  $Li_6$  through the absorption of infrared photons. We could then expect the appearance of spectra related to the different isomers, where the thermal energy allows passage through the energy barriers between these isomers.

Laboratoire de Spectrométrie Ionique et Moléculaire is associated with CNRS (No. 171).

- [1] N. W. Ashcroft and N. D. Mermin, in *Solid State Physics* (Saunders College, Philadelphia, PA, 1976).
- [2] J. Farges, M. F. de Feraudy, B. Raoult, and G. Torchet, *J. Chem. Phys.* **84**, 3491 (1986).
- [3] M. Broyer, G. Delacrétaz, P. Labastie, R. L. Whetten, J. P. Wolf, and L. Whetten, *Z. Phys. D* **3**, 131 (1986).
- [4] J. P. Wolf, G. Delacrétaz, and L. Wöste, *Phys. Rev. Lett.* **63**, 1946 (1989); Ph. Dugourd, J. Chevalyere, M. Broyer, J. P. Wolf, and L. Wöste, *Chem. Phys. Lett.* **175**, 555 (1990).
- [5] M. D. Morse, J. B. Hopkins, P. R. R. Langridge-Smith, and R. E. Smalley, *J. Chem. Phys.* **79**, 5316 (1983).
- [6] M. Broyer, J. Chevalyere, Ph. Dugourd, J. P. Wolf, and L. Wöste, *Phys. Rev. A* **42**, 6954 (1990).
- [7] K. Selby, M. Vollmer, J. Masui, V. Kresin, W. A. de Heer, and W. D. Knight, *Phys. Rev. B* **40**, 5417 (1989).
- [8] J. Blanc, M. Broyer, J. Chevalyere, Ph. Dugourd, H. Kuhling, P. Labastie, M. Ulbrich, J. P. Wolf, and L. Wöste, *Z. Phys. D* (to be published).
- [9] C. R. Wang, S. Pollack, and M. M. Kappes, *Chem. Phys. Lett.* **166**, 26 (1990).
- [10] C. R. C. Wang, S. Pollack, D. Cameron, and M. M. Kappes, *J. Chem. Phys.* **93**, 3787 (1990).
- [11] I. Boustani, W. Pewestorf, P. Fantucci, V. Bonacic-Koutecky, and J. Koutecky, *Phys. Rev. B* **35**, 9437 (1987).
- [12] V. Bonacic-Koutecky, P. Fantucci, and J. Koutecky, *Chem. Phys. Lett.* **146**, 518 (1988).
- [13] V. Bonacic-Koutecky, P. Fantucci, and J. Koutecky,

- Chem. Phys. Lett. **166**, 32 (1990).
- [14] V. Bonacic-Koutecky, P. Fantucci, and J. Koutecky, J. Chem. Phys. **93**, 3802 (1990).
- [15] J. Blanc, V. Bonacic-Koutecky, M. Broyer, J. Chevalere, Ph. Dugourd, J. Koutecky, C. Scheuch, J. P. Wolf, and L. Wöste, J. Chem. Phys. (to be published).
- [16] V. Bonacic-Koutecky, M. M. Kappes, P. Fantucci, and J. Koutecky, Chem. Phys. Lett. **170**, 26 (1990).
- [17] J. Koutecky, I. Boustani, and V. Bonacic-Koutecky, Int. J. Quantum Chem. **38**, 149 (1990).
- [18] Ph. Dugourd, thesis, Université Lyon I (1991); Ph. Dugourd, J. Blanc, M. Broyer, L. Wöste, J. Chevalere, and J. P. Wolf (to be published).
- [19] M. Broyer, G. Delacrétaz, P. Labastie, J. P. Wolf, and L. Wöste, Phys. Rev. Lett. **57**, 1851 (1986).
- [20] K. Selby, V. Kresin, J. Masui, M. Vollmer, W. A. de Heer, A. Scheidemann, and W. D. Knight, Phys. Rev. B **43**, 4565 (1991).
- [21] M. M. Kappes (private communication).
- [22] V. Bonacic-Koutecky *et al.* (to be published).