

## Electronic and vibronic structure of $\text{Li}_4$ observed by depletion spectroscopy

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We report the observation of electronically excited states of  $\text{Li}_4$ , using depletion spectroscopy. The obtained spectra reveal five electronic bands between 380 and 760 nm. Energetic locations and absorption cross sections (ranging from 0.3 to  $4 \text{ \AA}^2$ ) fully agree with previous molecular configuration-interaction *ab initio* calculations. Vibronic structures are also observed; they look promising for development of accessibility to adiabatic surfaces and equilibrium geometries in metallic tetramers.

Due to simple structure in both atom and bulk, alkali-metal clusters are the easiest systems for studying electronic properties of small metal clusters. *Ab initio* calculations on lithium can be conducted up to sizes where the valence-metallic transition occurs, allowing interesting comparisons between theory and experiment to be considered. Moreover, the lithium light mass makes Li clusters' rovibrational patterns the easiest to resolve among the alkali-metal ones. This advantage has already been used for the lithium trimer, where resolved rotational lines could be assigned,<sup>1</sup> and it is crucial in the present work for studying vibronic patterns of  $\text{Li}_4$ .

Laser spectroscopy of metallic tetramers has been prevented until now by the occurrence of predissociation in the excited states. The usual two-photon-ionization (TPI) spectroscopy, which was successfully applied to dimers and trimers,<sup>2,3</sup> could therefore not be used for tetramers since other spectroscopic techniques had to be developed. Besides photoelectron spectroscopy of anions,<sup>4</sup> which is severely resolution limited, the only suitable mass-selective spectroscopic technique remaining is depletion spectroscopy (DS). Since its first use in  $\text{Cu}_3$  (Ref. 5) and  $\text{Na}_3$  (Ref. 6), DS has been successfully applied to medium-size metallic clusters such as  $\text{Na}_8$ - $\text{Na}_{20}$  (Ref. 7) and  $\text{K}_9^+$ - $\text{K}_{21}^+$ .<sup>8</sup> We report in this paper observation of the excited states of  $\text{Li}_4$ , using DS. Similar work on  $\text{Na}_4$  has been performed almost simultaneously by Wang, Pollack, and Kappes,<sup>9</sup> but vibronic patterns could not be observed at the spectral resolution and particle temperatures that were used.

$\text{Li}_4$  is the first metallic tetramer whose ground and excited states have been calculated *ab initio*. The high-level calculations of Bonacic-Koutecky and co-workers<sup>10</sup> indeed predicted an optimum rhombic ground-state geometry, as well as six optically allowed excited states between 1.7 and 3.2 eV, exhibiting different electronic symmetry. The comparison of these purely molecular atomic-orbital configuration-interaction calculations with recent semiclassical models based on Mie theory,<sup>7</sup> would be very interesting. Moreover, the collective resonances estimated for small lithium clusters by the semiclassical

models<sup>7,11</sup> are expected in the uv range (3.2 eV in  $\text{Li}_8$ ), while intense electric-dipole-allowed transitions in dimers and trimers are found in the visible (2–2.5 eV). In sodium, conversely, the spectral regions corresponding to the same transitions are much closer: 2.6 eV for collective resonances in  $\text{Na}_8$  compared to 2–2.6 eV for internal electric-dipole-allowed transitions in  $\text{Na}_2$  and  $\text{Na}_3$ . Consequently experimental data on  $\text{Li}_4$  excited states should constitute a highly relevant test of the localization properties of the electrons in metallic tetramers.

Lithium tetramers were produced in a highly cooled molecular beam, by coexpansion into the vacuum of 10–100-mbar lithium vapor and 1–5-bar argon through a 100- $\mu\text{m}$  nozzle. Typical vibrational and rotational temperatures of the particles in the beam were, respectively, 70 and 10 K.<sup>1</sup>

DS experiments were performed using two excimer-pumped dye lasers and a time-of-flight mass spectrometer in a cross-beam configuration. The first laser, frequency doubled in a beta barium borate (BBO) crystal (1  $\text{mJ}/\text{cm}^2$  at 225 nm), permanently ionized the lithium tetramers. The second dye laser, pumped by the same excimer, was used for exciting the predissociated excited states of  $\text{Li}_4$ , and scanned for recording the resulting depletion spectra. The accessible spectral region ranged from 380 to 760 nm, using eight different laser dyes. The fluence of the depleting laser was carefully recorded, in order to deconvolute spectra from dye responses, and control that the depletion process remained in the linear region. A 20-ns optical delay was introduced in the ionizing laser path, in order to deplete before ionization and thus avoid interferences with the  $\text{Li}_4^+$  electronic structure.

Interferences induced by fragmentation of larger sizes in ionization or excitation processes also have to be checked carefully. The mass spectra recorded using only the ionizing laser reflect the clusters' abundances predicted by the shell model demonstrating that the fragmentation is negligible during the ionization. As far as the depleting laser is concerned, no significant effect has been found on the  $\text{Li}_4^+$  channel due to larger neutral clusters ( $\text{Li}_5$ – $\text{Li}_8$ ), even for a strong depletion on their respective

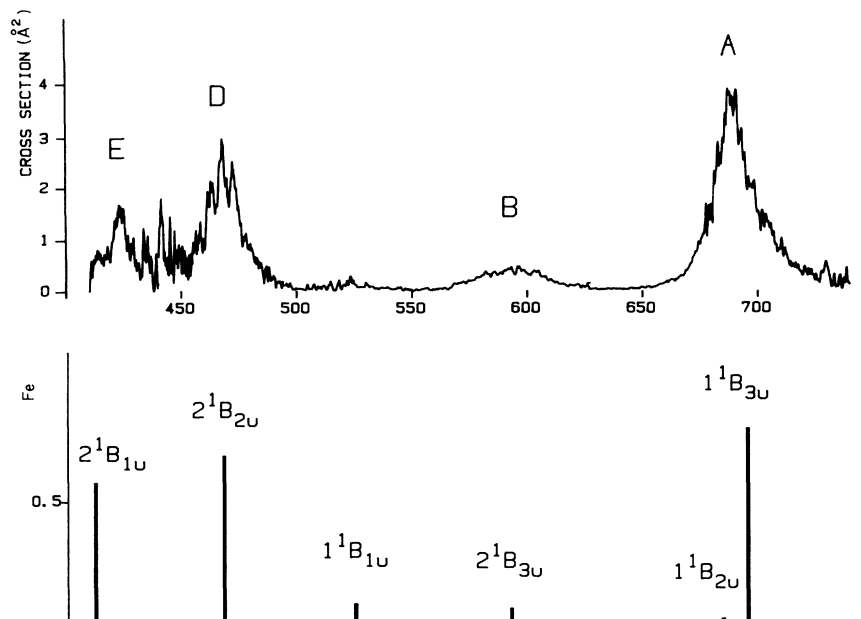


FIG. 1. Absorption spectra of  $\text{Li}_4$ . The experimental cross sections (upper) are compared with the oscillator strengths (lower) of Koutecky and co-workers (Ref. 10).

channels. Moreover, the large amount of neutral  $\text{Li}_4$  in the beam also leads to the relative insensitivity of the experiment of these fragmentation effects.

Figure 1 shows  $\text{Li}_4$  excitation spectrum, between 380 and 760 nm. Four bands (labeled *A*, *B*, *D*, and *E*) are observed, the band heads of which are given in Table I. Their relative intensities are alternated, with a strong band in the near-infrared region (*A*), a weak band in the red-yellow region (*B*), and two strong bands again in the blue and near-uv region (*D* and *E*).

The comparison of the obtained excitation spectrum with the molecular-configuration-interaction *ab initio* calculations of Bonacic-Koutecky and co-workers<sup>10</sup> is shown in Fig. 1. The extremely good agreement between their theoretical predictions and the present experimental data allowed us to assign the observed bands as transitions from the optimized rhombic ground state ( $1^1A_g$ ) to six different electronically excited states (see Table I):  $1^1B_{3u}$  and  $1^1B_{2u}$  overlap forming the *A* band,  $2^1B_{3u}$  corresponds to the weaker *B* band in the red region.  $1^1B_{1u}$  cor-

responds in principle to the weak features observed at about 525 nm, but the experimental intensity is the order of the actual single-to-noise ratio  $2^1B_{2u}$  and  $2^1B_{1u}$  lead to the strong *D* and *E* bands in the blue and near-uv regions.

This comparison between calculated excited states and observed bands has to be performed using the band maxima and not the band heads, because only vertical transitions are calculated by Bonacic-Koutecky and co-workers (geometrical relaxation of the excited states is not accounted for in the *ab initio* calculations). The agreement remains in any case within 1 or 2%, except for the  $2^1B_{1u}$  state.

Our experimental data also provide very useful information for testing semiclassical models based on modified Mie theory and an ellipsoidal shell model, which were recently developed by de Heer and co-workers.<sup>7</sup> Assuming similar electronic characteristics for lithium and sodium, one can estimate the collective oscillation frequencies expected from the modified Mie theory. For the lithium tetramer, the ellipsoidal shell model predicts a prolate

TABLE I. Band heads of the five observed bands.

	Maximum of band ( $\text{cm}^{-1}$ )	$\sigma^a$ ( $\text{cm}^{-2}$ )	<i>ab initio</i> calculations ( $\text{cm}^{-1}$ )	Oscillator strength	Symmetry
<i>A</i>	14 526	4	14 360	0.7926	$1^1B_{3u}$
	14 750	...	14 600	0.0189	$1^1B_{2u}$
<i>B</i>	16 807	0.3	16 860	0.0619	$2^1B_{3u}$
<i>C</i>	...	...	19 040	0.0812	$1^1B_{1u}$
<i>D</i>	21 386	2.5	21 370	0.6814	$2^1B_{2u}$
<i>E</i>	23 618	1	24 280	0.5699	$2^1B_{1u}$

<sup>a</sup>The absorption cross section  $\sigma = \ln(I_{\text{off}}/I_{\text{on}})/\phi$ , where  $I_{\text{on}}$  and  $I_{\text{off}}$  are, respectively, the depleted and undepleted ion signal and  $\phi$  the laser number of photons per surface unit.

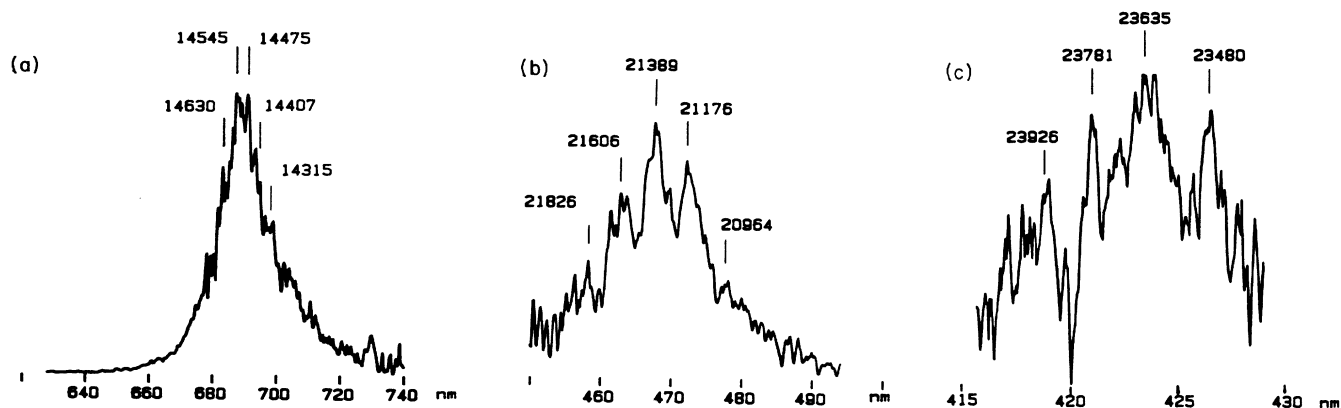


FIG. 2. Vibronic structure of the most intense  $\text{Li}_4$  bands: (a)  $A$  band, (b)  $D$  band, (c)  $E$  band.

spheroidal configuration, with plasma resonances<sup>7</sup>

$$\omega_{0i}^2 = \frac{Ne^2}{m_e a_i}, \quad (1)$$

where  $a_i$  is the polarizability of the metal ellipsoid, along each of the three principal axis. In the classical limit, the average polarizability  $\bar{\alpha} = \frac{1}{3} \sum_i a_i$  is

$$\bar{\alpha} = (R_s N^{1/3} + \delta)^3, \quad (2)$$

where  $R_s$  is the radius of the Wigner-Seitz cell and  $\delta$  is the electronic spillout.<sup>12,13</sup> In lithium,  $R_{s\text{Li}} = 3.25$  a.u. and  $\delta_{\text{Li}} = 1.41$  a.u.<sup>11</sup> Assuming the same ellipsoidal deformation in  $\text{Li}_4$  as in  $\text{Na}_4$  (Ref. 7), the plasmlike resonances should occur in  $\text{Li}_4$  at  $\lambda_x = \lambda_y = 317$  nm and  $\lambda_z = 490$  nm ( $x$ ,  $y$ , and  $z$  are the ellipsoidal axes). The agreement with the observed spectrum is thus relatively poor. On the other hand, scaling the model onto the experiment ( $\lambda_x \approx \lambda_y \approx 440$  nm and  $\lambda_z = 680$  nm) would lead to an anomalously high value of the electron spillout, 3 a.u., inconsistent with the static polarizability  $\alpha$  calculated in the jellium model frame.<sup>11</sup> The description of  $\text{Li}_4$  in a simple jellium model appears, therefore, relatively unsatisfactory. We could also calculate the  $\text{Li}_4$  collective resonances using formula (2) and static polarizability  $\alpha$  deduced from molecular configuration-interaction *ab initio* calculations. The calculated polarizability of  $\text{Li}_4$  (Ref. 10) ( $\alpha_x = 354$  a.u.,  $\alpha_y = 394$  a.u., and  $\alpha_z = 419$  a.u.) leads to collective resonances at 428, 452, and 466 nm in disagreement with our experimental results. This unsatisfactory situation can be attributed to the low number of atoms in  $\text{Li}_4$ , the well-defined geometric structure, and local ionic effects in the density of charge.

This strong electron-ion coupling is emphasized by the occurrence of vibronic structure in every excited state. Figure 2 compares the different vibronic characteristics obtained in the three strongest bands of the DS spectrum.

The clearest vibronic pattern is observed in the  $D$  band, corresponding to the ( $2^1B_{2u}$  state). The spectrum indeed exhibits a pronounced progression of five peaks, almost equally spaced by  $210 \text{ cm}^{-1}$ . The harmonicity and mode frequency, close to  $\text{Li}_2$  in the same energetic region ( $\omega_e = 269.7 \text{ cm}^{-1}$  in the  $\text{Li}_2 B$  state<sup>14</sup>), would suggest in this case a possible predominance of the breathing mode. Conversely, the sequence observed in the  $E$  band ( $2^1B_{1u}$ ) appears shorter and more perturbed, with a typical frequency of  $145 \text{ cm}^{-1}$ . In both cases, however, interpretation of vibronic bands needs more experimental data, performed on colder particles, and a careful Jahn-Teller analysis. The  $A$  band [Fig. 2(c)] will be more difficult to interpret, since two different electronic states ( $1^1B_{3u}$  and  $1^1B_{2u}$ ) are involved, leading to perturbed levels and a high density of states.

The only theoretical calculations of vibronic frequencies performed so far in  $\text{Li}_4$  concern the ground state.<sup>15</sup> Six frequencies were calculated in the same frequency range as the experimental ones found in the excited states.

In conclusion, the excitation spectra of  $\text{Li}_4$  presented in this paper demonstrate the accessibility to both precise electronic characteristics through high-level molecular calculations, and vibronic interpretation. Adiabatic surfaces and equilibrium geometry of  $\text{Li}_4$  will be deduced in the future from more resolved spectra. They require colder particles. Work is in progress in our laboratory on this problem.

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