First Observation of an Electronically Excited State of Li_3

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We report the first observation of an excited state of Li_3. With an origin band at 14583 cm^{-1}, this state has been identified as $2^2E'$. Analysis based on the dynamic Jahn-Teller model reveals very weak distortion and localization characteristics ($E_{stab}=57$ cm^{-1}, $E_b=17$ cm^{-1}, $\omega_0=191$ cm^{-1}). The lowest vibronic state is located above the conical intersection, implying a nearly D_{3h} geometry. The frequency of the completely symmetric mode is 326 cm^{-1}. Analyses of rotational states and Franck-Condon factors are also presented.

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Metal trimers have recently emerged as ideal subjects for the study of molecular vibronic interactions.[1,2] However, although ground-state adiabatic surfaces are precisely characterized by *ab initio* calculations,[3,4] few results have been reported for their electronically excited states.[5,6] With only nine electrons Li_3 is unique because it is the smallest and the simplest of the metallic trimers. Therefore it is amenable to *ab initio* calculations, even for excited states, as carried out by Gerber[5] some ten years ago, but never tested experimentally until the present work. More precisely, Gerber succeeded in calculating the adiabatic surfaces of the ground state and the four first excited states using a pseudo-natural-orbitals-configuration-interaction formalism. Theoretical computations have also been performed by Bonacik-Koutecky, Fantucci, and Koutecky[7] for larger clusters for which our spectroscopic results provide a valuable check.

The absence of previous experimental studies has been due to the requirement of a very high source temperature and the corrosive properties of lithium. A special oven has therefore been designed. Trimers are prepared by free jet expansion from a laser-drilled 50-μm orifice, of gas comprising lithium vapor at 25 mbar seeded into argon at 1–10 bars. The source comprised cartridges of titanium-zirconium-molybdenum heated by tungsten filaments and could sustain temperatures up to 1900 K. For source pressures of 10 bars typical terminal rotational and vibrational temperatures for Li_2 were 15 and 100 K, respectively. Cluster ions were formed by resonant two-photon ionization (RTPI) with two excimer-pumped dye lasers and detected with a quadrupole mass filter in a cross-beam configuration. RTPI in conjuction with low jet temperatures made possible the spectroscopic resolution of both cluster size and vibrational state.

Tuning the exciting laser from 430 to 720 nm revealed only one electronically excited state for Li_3 at 690 nm. From symmetry and energy considerations, based on the united-atom picture[6] and calculations of Gerber and Schumacher,[5] we conclude that the observed spectrum is due to the $2^2E'$ state originating from the two degenerate configurations $1s^21d_{xy}$ and $1s^21d_{x^2-y^2}$. Spectra of this observed state, shown in Fig. 1, were recorded at fluences of 2 MW/cm^2 [Fig. 1(a)] and 200 kW/cm^2 [Fig. 1(b)]. The ionization wavelength was 440 nm, in order to exceed the ionization threshold (4.1 eV) of about 3000 cm^{-1}. The saturated spectrum [Fig. 1(a)] exhibits highly structured patterns, which gradually vanish 550 cm^{-1} beyond the origin band (14583 cm^{-1}). Two major series emerge, almost equally spaced, but overlapped. The energy gap between these two series is 227 cm^{-1}. Other weaker features appear at higher energy (beyond 15000 cm^{-1}) and mix with the two stronger series, leading to broad, perturbed bands. This structure can be fully interpreted in terms of the dynamical Jahn-Teller model, derived simultaneously by W. Moffit and A. D. Liehr and by H. C. Longuet-Higgins *et al.* in 1956. It has since been extensively described[8] and was recently applied very successfully to Na_3[2,9] and Cu_3.[10] In the present case of Li_3's $2^2E'$ state, the best fit was obtained for a radial frequency $\omega_0=191$ cm^{-1}, and for linear and quadratic Jahn-Teller parameters $k=0.77$ and $g=0.15$, respectively. Assignment of the lines is given in Table I. At low energies (0–400 cm^{-1}), agreement between observed and calculated transitions is very satisfactory, the relative error always less than 6%. At higher energies the signal-to-noise ratio and density of lines prevent a convincing comparison between model and experiment. The totally symmetric mode (a') of this $2^2E'$ state is also observed, at 326 cm^{-1}.

The Jahn-Teller calculations allowed us to characterize in detail the vibronic structure and the geometry of the $2^2E'$ state (Fig. 2). The shape of the adiabatic surface is very flat at the bottom, with a stabilization energy of only 57 cm^{-1}, and almost no pseudorotation barrier (17 cm^{-1}), reflecting very low distortion and localization characteristics. Its curvature is significantly lower than that of the ground state, corresponding to 191 cm^{-1} in the harmonic approximation (against 278 ± 60 cm^{-1} for the ground state[4]). Even the lowest-energy level (zero-

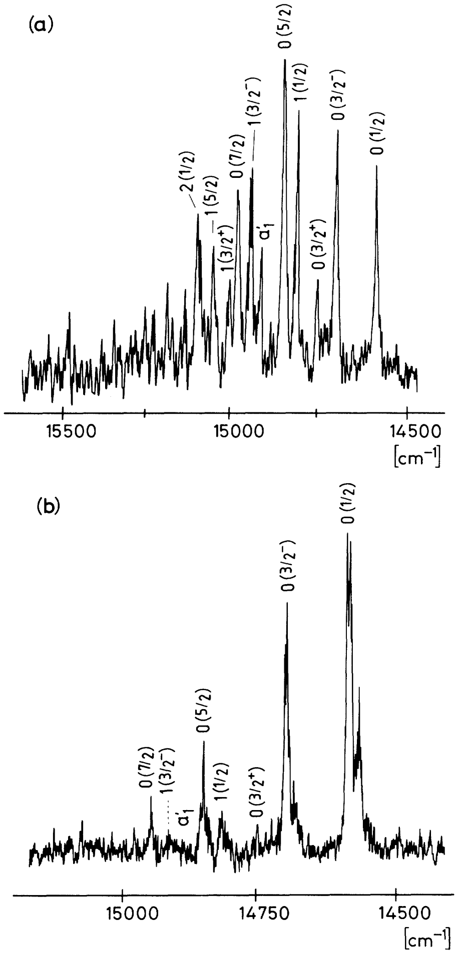

FIG. 1. Resonant two-photon ionization spectra of the Li_3 $2^2E'$ state, obtained at (a) high and (b) low laser fluences, exhibiting the vibronic assignment $n(j)$ of the levels.

point energy $=151$ cm^{-1}) is located well above the conical intersection (Fig. 2), implying a nearly equilateral geometry.

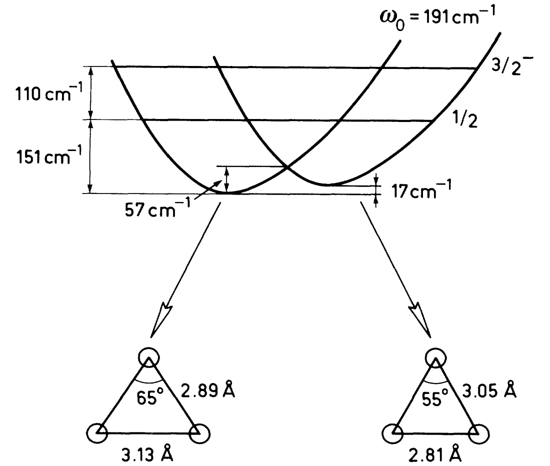

FIG. 2. Vibronic and geometric characteristics of the $2^2E'$ excited state.

The lower-surface absolute minimum corresponds, in terms of geometry, to an obtuse-isosceles equilibrium configuration, very close to an equilateral triangle, the Jahn-Teller distortion amplitude ρ_0 being as small as 0.16 Å, and the apex angle about 65° ($R_0=2.97$ Å, taken from *ab initio* calculations[5]). In comparison, the ground state is predicted to be more distorted ($\rho_0=0.25$ Å, $E_{\mathrm{stab}}=450$ cm^{-1}), but also weakly localized ($E_b\sim35$ cm^{-1}).[5]

The $2^2E'$-state spectrum recorded at low fluence [Fig. 1(b)] allows one to determine the real line intensities. Compared to the saturated spectrum, only one series remains ($n=0$), which seems to be highly favored by the transition probabilities. In order to confirm this observation, Franck-Condon computations were performed. Because of the significant difference in radial frequency between the ground and $2^2E'$ states, we used a basis set from a virtual potential with an intermediate ω_0 (235 cm^{-1}) to decompose the vibronic wave functions in both electronic states.

TABLE I. Observed bands and assignment.

ν (cm^{-1})	$\nu-\nu_{00}$ (cm^{-1})	$(\nu-\nu_{00})/\omega_0$[a] Expt.	$(\nu-\nu_{00})/\omega_0$[a] Calc.	$n(j)$	Error $\lvert\Delta E\rvert/E$	FC[b] Expt.	FC[b] Calc.
14583	0	0.0	0.0	$0(\frac{1}{2})$	0	12.5	15
14693	110	0.57	0.57	$0(\frac{3}{2}^-)$	0	40	50
14747	164	0.85	0.85	$0(\frac{3}{2}^+)$	0	3.2	0.1
14810	227	1.18	1.18	$1(\frac{1}{2})$	0	5.3	0.1
14845	262	1.39	1.48	$0(\frac{5}{2})$	0.06	21.1	23
14909	326	1.71	···	a'	···	···	···
14945	362	1.9	1.97	$1(\frac{3}{2}^-)$	0.03	4.2	1.1
15003	420	2.19	2.13	$0(\frac{7}{2})$	0.03	11.5	8
···	···	···	2.30	$1(\frac{3}{2}^+)$	···	0	0.1
15057	474	2.48	2.32	$1(\frac{5}{2})$	0.06	0.1	0.1
15099	516	2.72	2.87	$2(\frac{1}{2})$	0.05	2.1	1.1

[a] $\omega_0=191$ cm^{-1}.

[b] Franck-Condon factors $\times 10^2$.

Comparison between line intensities (deconvoluted from the dye output power curve) and the results of these calculations (for $J=0$) is shown in Table I. As in the spectrum, the $n=1$ series is dominant. Furthermore, the intensity envelope follows the calculated Franck-Condon factors very closely. This envelope reflects the similar values of equilibrium position for both states ($\rho_0'=0.16$ Å; $\rho_0''=0.25$ Å), and the large difference in the adiabatic potential curvatures ($\omega_0'=191$ cm^{-1}; $\omega_0''=278\pm60$ cm^{-1}). The range of the observed line intensities, however, still seems a little compressed compared to the transition probabilities, suggesting that a slight saturation remains at the laser fluence used.

Franck-Condon calculations are also important for confirming the same E' electronic symmetry for the state which is known to apply to the vibronic ground state of Li$_3$. The pseudorotation selection rules depend on the excited-state symmetry in the following way: If the excited state's electronic term is E'', only one of the two $|j|=\frac{3}{2}$ bands is observable in each series, because the E'-A_1'' transition is rigorously dipole forbidden. On the contrary, if the excited state is of E' electronic symmetry, both components $j=\frac{3}{2}^-$ and $j=\frac{3}{2}^+$ are visible (E'-A_1' allowed). Now, in the saturated spectrum [Fig. 1(a)], both $\frac{3}{2}$ levels are observed, but one is much stronger than the other. This is even clearer in the real-intensity spectrum [Fig. 1(b)], where the $\frac{3}{2}^+$ is very weak. The Franck-Condon calculations confirm that the weakness of this latter band is due to overlap of the wave functions, not to symmetry. Both transitions are allowed by symmetry and the electronic term of the observed excited state is thus well determined to be E'.

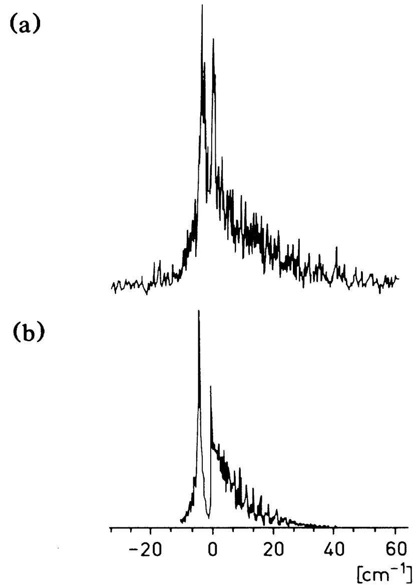

FIG. 3. (a) Rotational structure of the $0(\frac{1}{2})$ band, and comparison with (b) the results of the simulations.

A high-resolution scan of the $0(\frac{1}{2})$ band has also been performed, in order to observe the rotational structure [Fig. 3(a)]. The experimental conditions (100-μm-diam nozzle, 1 bar of carrier gas), however, were less favorable than for the spectra of Figs. 1(a) and 1(b), in the sense that the rotational temperature was higher. The observed spectrum exhibits two clear peaks, emerging from an unresolved rotational pattern (laser bandwidth 0.2 cm^{-1}). The very high density of lines is the result of the numerous subbands occurring in perpendicular transitions (E'-E'). The spectroscopic constants[11] B, A, ξ (Coriolis coupling), and q_v have been determined by numerical fits to the observed spectrum [Fig. 3(b)]. The analysis is based on the usual rotation-energy calculation and selection rules ($\Delta J=0,\pm1$; $\Delta K=\pm1$),[11] assuming a rigid symmetric top. The ground-state constants[11] are furnished by the *ab initio* calculations of Gerber and Schumacher ($B=0.57$, $A=0.2752$, $\xi=-0.4279$, and $q_v=0.0559$).[5]

The best fit was obtained for a temperature of 50 K, and the following constants: $B=0.50$, $A=0.26$, $\xi=-0.37$, and $q_v=0.045$. The results of the simulations are in reasonable agreement with the observed structure, although some discrepancies remain, probably due to rotation-pseudorotation coupling. However, for a more precise analysis of the rotational motion, a very high-resolution experiment must be performed.

The agreement of the calculations of Gerber with the present results is very satisfying. The *ab initio* computations indeed predicted the presence of the $2^2E'$ state at 13670 cm^{-1} (origin band), which is only about 900 cm^{-1} lower than the experimental observation. However, most of the theoretical analysis has been devoted to the ground and the $^2E''$ excited state (expected at 17700 cm^{-1}). Therefore we performed our own fit of the calculated $2^2E'$ adiabatic surfaces (Table II), and obtained a stabilization energy of 65 ± 15 cm^{-1}, a pseudorotation barrier of 15 ± 5 cm^{-1}, and a symmetric stretch frequency of 310 ± 15 cm^{-1}, respectively. A direct comparison with the experimental data ($E_{\text{stab}}=57$ cm^{-1}, $E_b=17$ cm^{-1}, $\omega_{a'}=326$ cm^{-1}) demonstrates the precision of these high-level calculations.

Compared to Na$_3$, which represents the best known alkali-metal trimer, the $2^2E'$ state of Li$_3$ presents surprising similarities with the Na$_3$ C state[9] (except for

TABLE II. $2E'$-excited-state parameters.

	Bandhead (cm^{-1})	Jahn-Teller stabilization energy (cm^{-1})	Barrier of pseudorotation (cm^{-1})	Symmetric stretch (cm^{-1})
Observed[a]	14583	57	17	326
Ab initio[b] calc.	13670	65 ± 15	15 ± 5	310 ± 15

[a] Jahn-Teller analysis. [b] Ref. 5.

electronic symmetry), close vibronic characteristics, and both are the highest state observable by RTPI. In Na_3, indeed, the excited states at higher energies were all predissociated, presumably by level crossing with repulsive potential surfaces. The Na_3 C state itself is partially predissociated, leading to a short RTPI progression. A similar observation can be applied to the Li_3 $2^2E'$ state, which could also suggest a possible predissociation. However, the Franck-Condon calculations do not predict strong lines at higher energies, and no definitive conclusion can be reached with the presently available data. A depletion experiment[9] would therefore be extremely interesting to perform in the future.

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