

## Reduced oscillator strength in the lithium atom, clusters, and the bulk

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Absolute photoabsorption cross sections have been measured for small lithium cluster ions in the optical range and a significantly smaller oscillator strength than for sodium has been found. This reduction is reproduced in jellium type calculations only if nonlocal effects in the electron-ion interaction are included. It is shown that this reduction is an atomic property which persists throughout the cluster region and into the bulk regime, where it manifests itself as an increased effective electronic mass. The optical spectra of the closed shell clusters are in good agreement with calculations based on the nonlocal jellium model. The smallest cluster,  $\text{Li}_4^+$ , is well described by a quantum chemical calculation. [S0163-1829(99)50812-6]

One of the aims of cluster science is the study of physical or chemical properties as a function of cluster size. In this way a bridge can be built from the domain of atomic/molecular physics to the science of condensed matter. The optical response of alkali metal clusters has been studied extensively, both experimentally and theoretically. The best studied example is sodium where the dependence on cluster size,<sup>1-5</sup> temperature,<sup>6-8</sup> and charge<sup>9</sup> is known. Above a transition region of about 10 to 20 valence electrons per cluster, the optical response is well understood in terms of a collective resonance or surface plasmon. Below this transition size, which depends on the cluster temperature, the molecular picture is applicable.<sup>5,10</sup>

The absolute strength of the optical absorption in clusters has attracted much less interest experimentally, although it carries important information on the interaction between valence and core electrons. In addition, it is a stringent test for theoretical models. In the kindred giant dipole resonance of nuclear physics, the fulfillment of the sum rule always formed a crucial test of experiment and theory.<sup>11</sup>

The purpose of this paper is twofold. First, we show experimentally that the optical oscillator strength in lithium clusters is lower than that expected from the simple jellium model. The oscillator strengths are obtained from measured absolute photo absorption cross sections of  $\text{Li}_n^+$  ( $4 \leq n \leq 21$ ). These span the particularly interesting size region over which the electronic properties change from molecular-like to quasi-free-electron-like behavior.<sup>5</sup> Second, we show that the lower oscillator strength can be understood as an atomic property which persists throughout the cluster region and up into the bulk regime. Thus while many physical parameters show quite a change in going from the atom to the bulk, the physical property reported here does not change although valence electrons are concerned.

The Thomas-Reiche-Kuhn (TRK) sum rule states that the absolute dipole oscillator strength integrated over all photon energies equals the total number of electrons in the entire electron system (i.e., three per Li atom). However, absorption measurements on mass selected clusters are limited presently to the optical photon range. The question arises

whether one can decompose the total sum rule into contributions from different electrons. This can be done, provided two conditions are fulfilled: (1) The electronic excitations of the valence electrons must be well separated from those of the core electrons. This is well fulfilled for Li and Na, with separation energies of 59 and 32 eV, respectively.<sup>12</sup> (2) The interaction of the valence electrons with the ionic cores is well represented by a local pseudopotential.<sup>13,14</sup> This is exactly fulfilled in the jellium model which, by construction, uses a local potential. Therefore, for sodium, which is the best representation of the quasi-free electron model in the bulk as well as in clusters, one expects the valence restricted sum rule to be fulfilled, which could indeed be experimentally verified.<sup>5</sup> However, the second condition is not fulfilled for lithium, which leads to a lower oscillator strength (as observed here).

Lithium was selected for these studies since it is incrementally more complex than sodium. Indeed, bulk lithium can behave quite differently from the other alkalis.<sup>15,16</sup> In addition, since it has only three electrons ( $1s^2 2s$ ), it has very recently become the test bed for comparing different theories.<sup>17,18</sup>

Why is Li so different? Since the lithium atom has a core consisting of  $s$  electrons only, valence electrons with  $l=0$  cannot penetrate deeply into the core region due to the Pauli repulsion, whereas  $p$ -wave electrons do not suffer such a repulsion. Thus the initial and final state wave functions of the  $s$ - $p$  transition experience different potentials. Therefore, a pseudopotential which describes the interaction of the valence electrons with the lithium core should have an  $l=0$  component which differs from the  $l \neq 0$  components. This is called a nonlocal pseudopotential,<sup>13,14,19</sup> nonlocal referring to any dependence different from just position.

It was recently shown that these nonlocal pseudopotentials can explain the large redshift of the dipole resonance in the optical response of Li clusters<sup>20-22</sup> with respect to the jellium model prediction. Moreover, it was predicted<sup>13,14</sup> that this nonlocality results in a lower oscillator strength in the optical region. Thus, a verification of this prediction would support the validity of this extension of the jellium model to

more complex materials. Furthermore, it could explain the difference between the experimentally observed absolute oscillator strengths of lithium and sodium. Note that for sodium, which has a core consisting of both  $s$ - and  $p$ -wave electrons, nonlocal effects are expected to be much weaker.

Few measurements of the optical properties of free lithium clusters have been reported. Blanc *et al.*<sup>20</sup> measured the response of neutral  $\text{Li}_n$  for  $n \leq 8$  and Bréchnac *et al.*<sup>21</sup> investigated the evolution of the optical properties towards the bulk for very large  $\text{Li}_n^+$  with  $n \geq 139$ .

The experiment (see Refs. 5, 7, and 9 for details) consists of a gas aggregation cluster source with an internal electric discharge (which produces lithium cluster ions at a temperature of approximately 105 K), a tandem time-of-flight (TOF) mass spectrometer, and an excimer pumped dye laser system. With respect to our previous measurements on  $\text{Na}_n^+$  clusters,<sup>5,7,9</sup> most source conditions (He pressure and gas flow rate, gas temperature at the exit) remained unchanged. Only three modifications were made: the Li container had to be manufactured from molybdenum, its temperature was increased to 650 °C (in order to reach a vapor pressure of 0.3 mbar, as in the case of sodium), and a discharge voltage of only 20 V was used.

The clusters entered a first TOF mass spectrometer used for mass selection of the isotopically pure species ( $^7\text{Li}$  only) and were then irradiated by 15 ns visible or UV laser pulses. An electrostatic reflector acted as a second TOF spectrometer to separate the fragments from the parent clusters. The intensity reduction of the initially selected cluster contained the information regarding the photoabsorption cross section. The laser fluence was determined by measuring the pulse energy (using a pyroelectric detector) and converting it to the number of photons per area  $\Phi$ . The ratio of the nonfragmented cluster signal with ( $N$ ) and without ( $N_0$ ) laser irradiation is given by:<sup>9</sup>

$$N/N_0 = 1 - b[1 + \exp(-\sigma\Phi) + f\sigma\Phi\exp(-\sigma\Phi)]. \quad (1)$$

By fitting Eq. (1) to the measured cluster intensity as a function of  $\Phi$ , the absorption cross section  $\sigma = \sigma(\hbar\omega)$ , the overlap  $b$  of cluster and laser beams (typically 90%) and the fraction  $f$  (between 0 and 1) of the clusters, which survive the flight through the second TOF after the absorption of one photon, were determined. While  $f=0$  for small  $\text{Li}_n^+$  (i.e.,  $n \leq 11$ ),  $\text{Li}_{21}^+$  typically needs to absorb two photons at such a low temperature (105 K) to be sufficiently heated such that the cluster evaporates atoms on the time scale of the experiment.<sup>23</sup> Note, that this method allows one to determine absolute absorption cross sections even without knowing the absolute cluster density.

The nonspherical shape of small, open shell clusters ( $n = 4, 7, \text{ and } 11$  in the jellium model) can lead to an anisotropic transition dipole moment which can cause deviations from Eq. (1). Taking this into account by the methods presented in Ref. 24 yielded evidence that for  $\text{Li}_7^+$  two different isomers are present in the cluster beam. While this leads to a 10% larger error bar for  $\text{Li}_4^+$  and  $\text{Li}_7^+$ , no influence of an anisotropic transition moment was found for  $n=11$ .<sup>23</sup> The spherical clusters ( $n=9$  and 21) are not subject to this effect.<sup>24</sup>

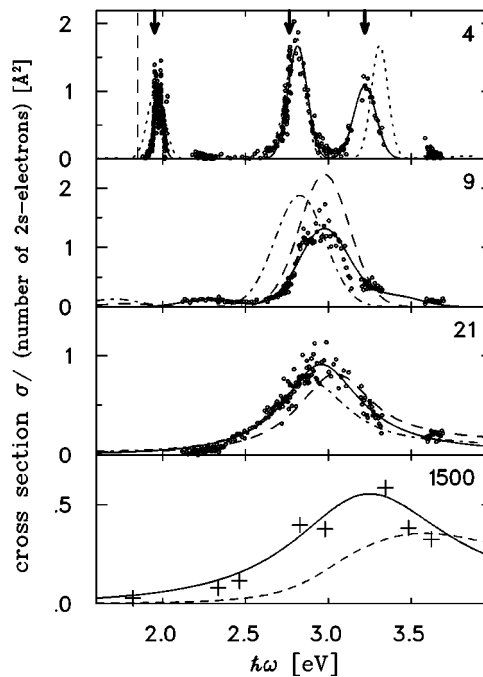


FIG. 1. Experimental absorption spectra of  $\text{Li}_n^+$  ( $n=4, 9, 21$ , this work;  $n=1500$  from Ref. 21). The data were fitted with Gaussians for  $n=4$  and 9, and with Lorentzians for the larger clusters (solid lines). The absorption curve for a large lithium sphere, derived from the measured dielectric constant of the bulk, is plotted in the lowermost graph as a dashed line. The absolute absorption cross section is normalized to the number of  $2s$  electrons. The quantum chemical calculation (convoluted with Gaussians) for  $\text{Li}_4^+$  (Ref. 26) is plotted as a dotted line. Note the striking similarity of the resonance positions compared to  $\text{Na}_4^+$  as marked by the three arrows. The  $2s$ - $2p$  transition of the Li atom is indicated by a vertical dashed line. The calculated resonances for  $\text{Li}_9^+$  and  $\text{Li}_{21}^+$ , based on the modified jellium model in RPAE (Ref. 14) (dash-dotted line) and in RPA in the local density approximation (Ref. 13) (dashed line), were convoluted with a Gaussian line shape of experimental width for  $n=9$  (Lorentzian for  $n=21$ ).

The absolute absorption cross sections were obtained as a function of the photon energy for  $\text{Li}_n^+$  ( $n=4, 7, 9, 11, \text{ and } 21$ ).<sup>25</sup> In Fig. 1, only those spectra are shown for which theoretical data are available ( $n=4, 9, \text{ and } 21$ ). The spectrum of  $\text{Li}_4^+$  shows three clearly distinct resonances, whose line positions and widths are almost identical to those obtained for  $\text{Na}_4^+$  previously<sup>5</sup> (arrows in Fig. 1). There are two more similarities between  $\text{Li}_4^+$  and  $\text{Na}_4^+$ : they have the same rhombic geometry and the ratios of bond lengths agree within 1%.<sup>10,17</sup> The spectrum of  $\text{Li}_4^+$  has recently been calculated by quantum chemical methods<sup>26</sup> (dashed line in Fig. 1), and is for the two lower peaks in very good agreement with the experiment. The closed electronic shell clusters containing 8 and 20 valence electrons show one single resonance. The lowermost plot in Fig. 1 shows the absorption profile for  $n=1500$  from Ref. 21 (Lorentzian fit as solid line). The dipole response of a large jellium sphere, which is still smaller than the wavelength of the excitation laser, is given by the dashed line, which was calculated from the measured dielectric constant of bulk lithium<sup>27</sup> based on the optical theorem.<sup>23</sup> For small species, the resonances are clearly distinct whereas they merge into a broad resonance

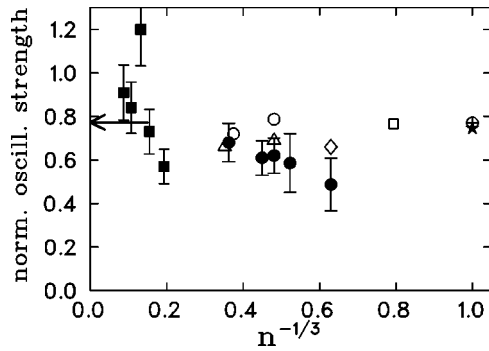


FIG. 2. Experimental and theoretical values of the total oscillator strength normalized to the number of  $2s$  valence electrons: ●, this work; ■, experimental values of Ref. 21. Modified jellium calculations for  $\text{Li}_9^+$  and  $\text{Li}_{21}^+$ :  $\triangle$  in RPAE, (Ref. 14) and  $\circ$  in RPA in the local density approximation (Ref. 29);  $\square$ , model potential calculation for  $\text{Li}_2^+$  (Ref. 30);  $\diamond$ , all electron quantum chemical calculation (full CI) for  $\text{Li}_4^+$  (Ref. 26); the atomic value ( $\oplus$ ) for Li, calculated in RPAE, is in very good agreement with the experimental value ( $\star$ ) (Ref. 12). The arrow indicates the oscillator strength for a large lithium sphere based on the experimental bulk dielectric constant. The simple jellium model predicts an oscillator strength equal to one per valence electron.

for  $n=9, \dots, 21$  and greater.<sup>21</sup> Thus the electronic resonances of small lithium and sodium clusters exhibit a qualitatively similar behavior.

Several groups have calculated the optical response of lithium clusters, i.e., the resonance energies and their absolute strengths. On the one hand, Alasia *et al.*,<sup>13</sup> as well as Blundell and Guet<sup>14</sup> used realistic pseudopotentials to describe the interaction of the valence electrons with the ionic background, but neglected the discrete geometry of the clusters. The electronic excitations of  $\text{Li}_9^+$  and  $\text{Li}_{21}^+$  were calculated in Ref. 14 in the random phase approximation with exchange (RPAE); solid line in Fig. 1.<sup>28</sup> The pseudopotentials were folded over the jellium sphere, which is referred to as nonlocal jellium model. In Refs. 13 and 29 the detailed atomic core positions are also neglected and the RPA in the local density approximation is employed. The calculated resonance energies for  $n=9$  (for  $n=21$ ) are convoluted with Gaussians (Lorentzians) each having a linewidth of 350 meV (570 meV) (dashed lines in Fig. 1). Both calculations yielded a resonance energy within 3 to 6% to the experimental position of the absorption maximum. Using simplified pseudopotentials but treating the ionic structure more precisely, Yabana and Bertsch<sup>22</sup> calculated the optical response for Li clusters of 138 atoms and greater, in good agreement with the experimental results of Ref. 21.

The oscillator strength (Fig. 2) is obtained by integrating the absorption spectra

$$f_{\text{tot}} = \frac{2\epsilon_0 mc}{\pi \hbar e^2} \int \sigma(E) dE \quad (2)$$

with the electron mass  $m$ , the speed of light  $c$ , and the dielectric constant of vacuum  $\epsilon_0$  (SI units). The error bars of 13% result mainly from the calibration of the pyroelectric

detector which was used for the absolute measurement of the laser pulse intensity, i.e., the photon flux density. Whereas the oscillator strength in the optical region for sodium clusters with  $n \leq 21$  is very close ( $>90\%$ ) to the number of valence electrons,<sup>5</sup> it is 20–40% lower for lithium clusters.

It is gratifying to see that an all electron calculation for  $\text{Li}_4^+$  also yields a lower optical oscillator strength,<sup>26</sup> thereby underpinning the pseudopotential approach of Refs. 13 and 14. The calculated oscillator strength in the visible and UV amounts to 0.66 per  $2s$  electron, in reasonable agreement with the experimental value of  $0.5 \pm 0.13$ .

How do the cluster data compare to the results for the atom, the diatomic molecule and the bulk? Our RPAE calculations for the lithium and sodium *atoms* yield oscillator strengths of the valence electrons of 0.98 (for Na) and 0.77 (for Li). This is in good agreement with experiment, which gives  $1.05 \pm 0.03$  and  $0.750 \pm 0.008$ , respectively.<sup>12</sup> For  $\text{Li}_2^+$  a model potential calculation including Hartree-Fock-type exchange between the valence and core electrons gives an oscillator strength value of 0.766.<sup>30</sup> The bulk limit is taken to be the dipole response of a large Li sphere, but still smaller than the laser wavelength, calculated from the measured dielectric function of the bulk.<sup>27</sup> Integrating the optical response up to 10 eV in order to account for the broad line, one obtains an oscillator strength of 0.76 per  $2s$  electron, which is indicated by the horizontal arrow in Fig. 2. Band structure calculations for lithium give an effective electronic mass of  $m^* = 1.3$  (Refs. 14 and 22) due to the nonlocal contribution in the electron-ion potential. This corresponds to an absorption strength for the bulk of 77% in good agreement with the empirical value for the large sphere.

Thus one has a consistent picture: over the whole size range one has a similar reduction of the oscillator strength. We therefore conclude that this lower oscillator strength is an atomic property, which persists in the transition from the atom to the bulk. With the benefit of hindsight, this can be understood as follows: the reduction in the atom results from a different coupling, due to the Pauli principle, of the  $2s$  and  $2p$  valence electrons to the  $1s^2$  core electrons. This effect persists for all cluster sizes and up to the bulk metal because the size of the  $1s$  orbital does change only marginally along this transition.

Since the TRK sum rule for the entire electron system has to be fulfilled, the “missing” oscillator strength is not lost, but shifted to higher photon energies, and will reappear if the absorption spectrum is extended to higher photon energies;  $\approx 100$  eV should be sufficient to cover most of the absorption strength of the  $1s$  electrons.

In conclusion, we have measured the absolute photoabsorption cross section of  $\text{Li}_n^+$ , with  $n=4, \dots, 21$ , at a temperature of approximately 105 K. The closed shell clusters ( $n=9$  and 21) exhibit one single giant resonance, the position of which agrees within 6% with jellium calculations modified by nonlocal pseudopotentials, which account for the Pauli repulsion between  $1s$  and  $2s$  electrons. The  $\text{Li}_4^+$  resonances can be described by quantum chemical methods which take into account the  $1s^2$  core electrons explicitly. The oscillator strengths calculated from the measured spectra are only 0.6 to 0.8 per electron. This reduction can be explained by the effects of the nonlocal contributions to the

pseudopotentials and can be interpreted as an atomic property, which appears relevant for all cluster sizes and even in the bulk limit. If the interaction between core and valence electrons via a nonlocal pseudopotential is included, the jellium model can well describe metal clusters with a more complicated valence core interaction than sodium.

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