

Repulsive van der Waals and Dipole-Quadrupole Interaction in the Excited LiCs Molecule

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The authors report strong repulsive van der Waals and dipole-quadrupole interactions in the Σ and Π potentials of the LiCs molecule dissociating into Li $2P$ and Cs $6S$ atoms. Theoretical results derived from second-order perturbation theory are verified by investigating experimentally the wavelength dependence of the quasistatic wings of the Li resonance lines broadened by Cs ground-state atoms.

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When speaking about van der Waals interaction there is the danger of thinking solely of binding interaction. The commonly used term *van der Waals binding* can be regarded as proof of this statement. Of course, having in mind the long-range interaction of two ground-state atoms, attractive forces will act in any case. On the other hand, when looking at the interaction of excited species, the quantum mechanical treatment can result in *repulsive long-range interaction*. In the present paper we will give an example of repulsive van der Waals interaction. More-

over, the investigated system shows exceptionally large contributions from repulsive dipole-quadrupole interaction ($\sim C_8/r^8$) as demonstrated experimentally.

Let us consider a Li atom in the $2P$ state which is interacting with a Cs $6S$ ground-state atom. The C_6 coefficient of the van der Waals interaction energy, $\Delta E = hC_6/r^6$, is given by

$$C_6^M = \sum_{i=1}^2 \rho_i a_i^M, \quad (1)$$

where M is the projection of the total angular momentum, a_i are the angular integrals, and $\rho_{1,2}$ are

$$\rho_1 = e^4 \sum_{Li\ ns} \sum_{Cs\ np} \frac{\langle 2p | r_{Li} | ns \rangle^2 \langle 6s | r_{Cs} | np \rangle^2}{(\Delta E^{Li})_{2p, ns} + (\Delta E^{Cs})_{6s, np}}, \quad \rho_2 = e^4 \sum_{Li\ nd} \sum_{Cs\ np} \frac{\langle 2p | r_{Li} | nd \rangle^2 \langle 6s | r_{Cs} | np \rangle^2}{(\Delta E^{Li})_{2p, nd} + (\Delta E^{Cs})_{6s, np}}.$$

The calculated angular integrals (see, e.g., Fontana¹) and the values for ρ_1 and ρ_2 as found by taking into account the radial matrix elements determined from known oscillator strengths^{2,3} and the atomic energies⁴ are listed in Table I. Applying formula (1) the C_6 constants of the $^4\ ^3\Sigma$ and $^4\ ^3\Pi$ states are $+1.43 \times 10^{-30} \text{ s}^{-1} \text{ cm}^6$ and $+0.13 \times 10^{-30} \text{ s}^{-1} \text{ cm}^6$, respectively. The positive signs are due to the first term in ρ_1 (Li $2p \rightarrow 2s$ and Cs $6s \rightarrow 6p$) where the denominator is *small* ($\approx 3350 \text{ cm}^{-1}$) and *positive*. Moreover, the radial matrix elements are large. It should be noted that all other contributions which have negative

signs are about 4 times smaller.

Because of the closeness of the Cs $5D$ level to the Li $2P$ state it is necessary to include, in addition to the dipole-dipole term, higher-multipole terms (with the proportionality r^{-4} and r^{-5}) in the perturbation expansion. In our case the interaction constant C_8 of the next nonvanishing contribution (dipole-quadrupole interaction, $\Delta E = hC_8/r^8$) can be written as

$$C_8^M = \sum_{i=1}^5 \delta_i b_i^M, \quad (2)$$

where b_i^M are the angular integrals and δ_i are given by

$$\begin{aligned} \delta_1 &= e^4 \sum_{Li\ ns} \sum_{Cs\ nd} \frac{\langle 2p | r_{Li} | ns \rangle^2 \langle 6s | r_{Cs}^2 | nd \rangle^2}{(\Delta E^{Li})_{2p, ns} + (\Delta E^{Cs})_{6s, nd}}, \\ \delta_2 &= e^4 \sum_{Li\ nd} \sum_{Cs\ nd} \frac{\langle 2p | r_{Li} | nd \rangle^2 \langle 6s | r_{Cs}^2 | nd \rangle^2}{(\Delta E^{Li})_{2p, nd} + (\Delta E^{Cs})_{6s, nd}}, \\ \delta_3 &= e^4 \sum_{Li\ np} \sum_{Cs\ np} \frac{\langle 2p | r_{Li}^2 | np \rangle^2 \langle 6s | r_{Cs} | np \rangle^2}{(\Delta E^{Li})_{2p, np} + (\Delta E^{Cs})_{6s, np}}, \\ \delta_4 &= e^4 \sum_{Li\ nf} \sum_{Cs\ np} \frac{\langle 2p | r_{Li}^2 | nf \rangle^2 \langle 6s | r_{Cs} | np \rangle^2}{(\Delta E^{Li})_{2p, nf} + (\Delta E^{Cs})_{6s, np}}, \\ \delta_5 &= 2e^4 \sum_{Li\ nd} \sum_{Cs\ np} \frac{\langle 2p | r_{Li} | nd \rangle \langle 2p | r_{Li}^3 | nd \rangle \langle 6s | r_{Cs}^2 | np \rangle^2}{(\Delta E^{Li})_{2p, nd} + (\Delta E^{Cs})_{6s, np}}. \end{aligned}$$

TABLE I. The calculated values for ρ_i and the angular integrals a_i^M .

i	ρ_i ($s^{-1} \text{ cm}^6$)	a_i^Σ	a_i^Π
1	$+4.1 \times 10^{-30}$	0.44	0.11
2	-7.6×10^{-31}	0.48	0.42

The most significant contribution comes from the first term in δ_1 (Li $2p \rightarrow 2s$ and Cs $6s \rightarrow 5d$) where the energy difference $E_{2p}^{\text{Li}} - E_{5d}^{\text{Cs}}$ is positive and very small ($\approx 350 \text{ cm}^{-1}$). The radial matrix elements in δ_1 and δ_2 have been derived from Li dipole oscillator strengths² and Cs quadrupole oscillator strengths.⁵ All other matrix elements for Li quadrupole transitions have been calculated in a simple approximation⁶ with use of hydrogenic wave functions and the effective charge for Li. The quality of this kind of approximation was proved by a comparison of the calculated data and experimental values^{5,7} for Cs and Rb quadrupole lines. The accuracy of the approximation was found to be about 30%. But it should be noted that the uncertainties of the approximate values do not affect the theoretical C_8 constant because the contributions of δ_3 , δ_4 , and δ_5 are small compared with the δ_1 term. In Table II the data for b_i^M and δ_i are listed. With these

TABLE II. The calculated values for δ_i and the angular integrals b_i^M .

i	δ_i ($s^{-1} \text{ cm}^8$)	b_i^Σ	b_i^Π
1	$+7.1 \times 10^{-44}$	0.60	0.20
2	-1.3×10^{-45}	0.43	0.38
3	-1×10^{-45}	0.24	0.08
4	-1×10^{-45}	0.77	0.53
5	-3×10^{-45}	0.68	0.34

values the C_8 constants of the $^1,^3\Sigma$ and $^1,^3\Pi$ states are found to be $+4.6 \times 10^{-44} \text{ s}^{-1} \text{ cm}^8$ and $+1.6 \times 10^{-44} \text{ s}^{-1} \text{ cm}^8$, respectively. Because we want to measure the repulsive long-range interaction potentials in a line-broadening experiment, where the quasistatic line wing is related to the difference potentials of the upper and lower states, we have to know the long-range interaction potential of the LiCs $X\Sigma$ ground state. With the use of London's formula⁸ the van der Waals constant of the ground state was found to be $C_6 = -5 \times 10^{-31} \text{ s}^{-1} \text{ cm}^6$, 15% larger than the datum published by Dalgarno and Davison.⁹ In that paper estimates of the core contributions are given which are not taken into account in our calculations. The C_8 constant of the ground state was calculated by the following formula:

$$C_8 = e^4 \sum_{\text{Li } np} \sum_{\text{Cs } nd} \frac{\langle 2s | r_{\text{Li}} | np \rangle^2 \langle 6s | r_{\text{Cs}} | nd \rangle^2}{-E_{np}^{\text{Li}} - E_{nd}^{\text{Cs}}} + e^4 \sum_{\text{Li } na} \sum_{\text{Cs } np} \frac{\langle 2s | r_{\text{Li}} | na \rangle^2 \langle 6s | r_{\text{Cs}} | np \rangle^2}{-E_{na}^{\text{Li}} - E_{np}^{\text{Cs}}}.$$

Including experimental oscillator strengths and the relevant energy levels, the C_8 constant of the $X\Sigma$ ground state was found to be $-2 \times 10^{-45} \text{ s}^{-1} \text{ cm}^8$.

The experimental setup for the investigation of the broadening of the Li resonance line by Cs ground-state atoms is shown in Fig. 1. The expanded light beam of a frequency-stabilized dye ring laser (Spectra Physics 380D; dye, DCM) was shone through a stainless-steel heat pipe cross-loaded with Cs metal and a small amount of Li. The power density of the laser light was always kept smaller than $20 \mu\text{W}/\text{mm}^2$ to avoid power broadening of the line. Neon was used as a buffer gas. The central part of the cross was heated electrically up to temperatures of about 660 K to run the device in the heat-pipe mode. Therefore, in the interaction region of laser field-metal vapor no Ne was present and the Cs vapor pressures were determined by the Ne gas pressures (5, 10, and 15 Torr) which were meas-

ured with a precision manometer. The Li number density was always more than 10^5 times smaller than the density of the Cs atoms. Under these conditions resonance broadening of the Li resonance line could be neglected. The broadening can be studied by scanning the laser across the line and detecting the fluorescence of the total line photoelectrically at the slit of a monochromator (the method of Chatham, Lewis and Gallagher¹⁰) or by locking the laser to one of the fine-structure components of the Li resonance line and scanning the monochromator across the line. We have favored the latter method because for far-wing registration, where the instrumental bandwidth must not be very small, it is more convenient than the method of Chatham, Lewis and Gallagher. At fixed pressure conditions the far wings were measured first with large slit widths of our 1.5-m Jobin-Yvon monochromator (bandwidth about 1 Å). In the region of the line

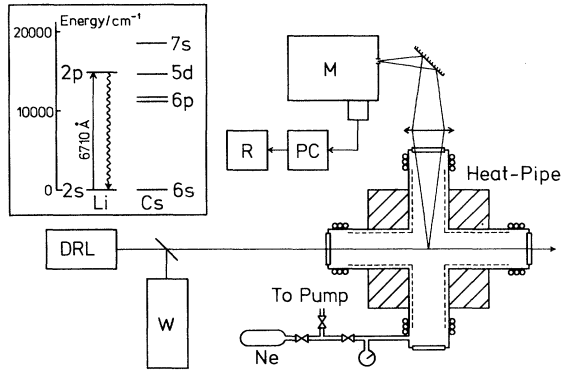


FIG. 1. The experimental setup. (DRL, dye ring laser; W, wavemeter; M, monochromator; PC, photon-counting system; R, strip-chart recorder).

core the laser light was attenuated by a neutral-density filter. Figure 2 displays such a spectrum. Without changing the experimental conditions in the heat pipe for the following scans slit widths were reduced step by step down to 10 μm (bandwidth about 0.05 \AA) to study the near-line wings.

In principle, absolute line wing intensities $I(\lambda)/N_{\text{Cs}} \int I(\lambda) d\lambda$ can be measured if the line center is free of contributions of scattered laser light. This could not be achieved. Moreover, for the most part the line center was optically thick. Therefore we give relative wing intensities.

In Fig. 2 we show the calculated difference potentials $\Sigma - X\Sigma$ ($1,^3\Sigma^{\delta}$) and $\Pi - X\Sigma$ ($1,^3\Pi^{\delta}$) and a directly reproduced scan of the Cs-broadened Li resonance line, both on the same energy scale. The pronounced blue asymmetry of the line, indicating repulsive difference potentials, can clearly be seen. Additional molecular fluorescence on the wings is due to Cs_2 or LiCs molecules which have been excited by the intense light of the cores of the Li resonance lines.

In Fig. 3 we show the reduced absorption coefficient of the quasistatic blue wing which has been calculated with the help of the theoretical difference potentials by applying the simple quasistatic theory¹¹ and taking into account the experimental temperature of about 660 K. The reduced absorption coefficient of the symmetrical Lorentzian wings in the impact region (dashed line) has been determined using the Lindholm approach.¹² The impact width is $\gamma/N_{\text{Cs}} = 3.9 \times 10^{-9} \text{ s}^{-1} \text{ cm}^3$. Because $I(\lambda)$ is proportional to $k(\lambda) \times \exp(-hc \Delta\lambda/\lambda^2 kT)$ we have plotted our measured wing intensities against the wavelength difference $|\Delta\lambda|$ from the center of gravity of the

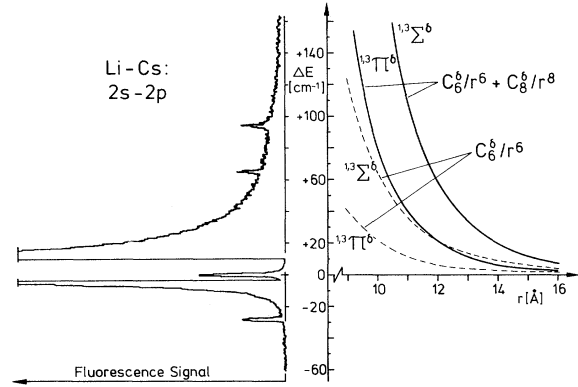


FIG. 2. A directly reproduced scan of the Cs-broadened Li resonance line (left side) and the long-range difference potentials $1,^3\Sigma^{\delta}$ ($1,^3\Sigma - X\Sigma$) and $1,^3\Pi^{\delta}$ ($1,^3\Pi - X\Sigma$) on the same energy scale. Dashed potentials: van der Waals interaction only; solid potentials: van der Waals and dipole-quadrupole interaction.

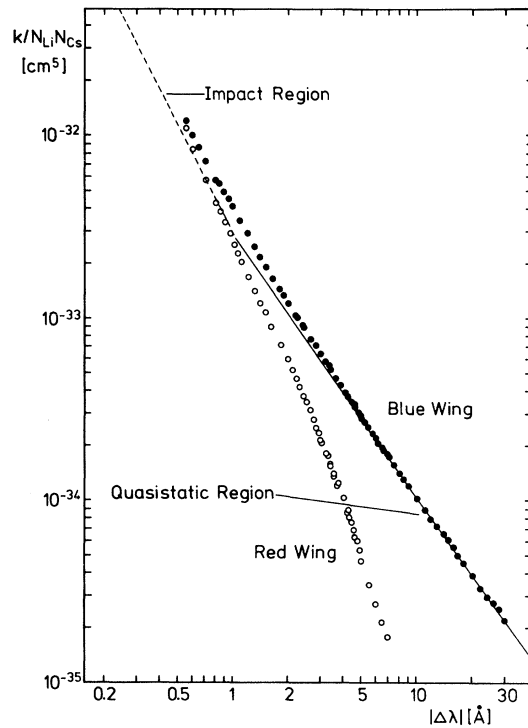


FIG. 3. Double-logarithmic graph of the reduced absorption coefficient $k/N_{\text{Li}} N_{\text{Cs}}$ of the Li resonance line against the wavelength difference $|\Delta\lambda|$ from the line center. The dashed line and the solid curve (small curvature) are the theoretical impact and quasistatic blue wings, respectively. The experimental wing intensities have been normalized to the theoretical far-blue wing.

fine-structure components (fine-structure interval: 153 mÅ) normalizing the intensity data to the theoretical absorption coefficient in the far-blue wing (see Fig. 3). The wavelength dependence of the experimental wing was found to be proportional to $(\Delta\lambda)^{-1.41(6)}$ in the region between -10 and -30 Å. This value is in agreement with the theoretical slope of -1.41 in this region. Note that pure van der Waals interaction would produce a slope of -1.5 (see, e.g., Ref. 11), which is outside the error bar of the experimental datum. It should also be concluded that overlap and exchange forces are not significant in the investigated region.

The red wing arises from nonstatic effects caused by the relative motion of the colliding atoms. This effect varies approximately as $(\Delta\lambda)^{-3}$, which is in line with theoretical prediction.¹³

The transition from the quasistatic and nonstatic wings to the Lorentzian region¹⁴ is expected at about $|\Delta\lambda| = 1$ Å. This is in agreement with observation. As a consistency check it can be observed that the experimental data in the impact region are only slightly larger than the theoretical values. The slightly larger experimental data are not due to the influence of the fine structure of the line. This correction would be less than 2% for $|\Delta\lambda| \geq 0.6$ Å. But it is likely that it is due to experimental influences (laser light scattering and apparatus function). Uncertainties due to the Lindholm approach could also be a reason for the small difference.

We conclude that the long-range interaction potentials of the excited LiCs molecule dissociat-

ing into Li 2P and Cs 6S atoms are repulsive. The observed wavelength dependence in the quasi-static blue wing confirms, in addition to the repulsive van der Waals interaction, a very strong dipole-quadrupole interaction.

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