Reanalysis of the photoassociation spectrum of $^{133}Cs_2$ $(6P_{3/2})$ 1_g state*

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Reanalysis of the photoassociation spectrum of the weakly binding $(6S_{1/2}+6P_{3/2})$ 1_g $^{133}Cs_2$ levels, reported in the previous study [*J. Mol. Spectro.* **255** (2009) 106], is performed by using a Lu–Fano graph coupled to the improved LeRoy–Bernstein formula including two additional modified terms. A more accurate coefficient (c_3) is obtained for the leading long-range potential $(-c_3/R^3)$ of a diatomic molecule.

Keywords: photoassociation spectroscopy, Lu–Fano graph, improved LeRoy–Bernstein formula, long-range molecular coefficient

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1. Introduction

The topic of long-range atomic interaction is an interesting one for both physicists and chemists as it plays an important role in understanding weakly binding state molecules, ultracold atom–atom collision, atom–molecule collisions, and storage of quantum information. Photoassociation spectroscopy (PAS) as a new high-resolution molecular spectroscopy,[1–3] used in the laser-cooling of neutral atoms, has been demonstrated to be a very accurate technique for extracting more information about the long-range interactions of diatomic molecules,[4,5] including energy levels and the long-range potential coefficient c_3. The binding energy of molecular vibrational levels obtained from PAS is essential data for determining the molecular parameters and potential curves, thereby exploring long-range dipole–dipole interaction and scattering properties.[6–8] For cesium molecules, the reported experimental and theoretical studies have mainly focused on the long-range molecular state 0_g^- with a special double potential well structure, which is helpful for effectively forming the ground state molecules during the photoassociation of ultracold atoms.[6,9–11] So far, only few studies have been made of the 1_g state.[3,12,13] With the aim of further extending the study to obtain the richer energy levels with larger red detuning, we have reported on high-sensitivity Cs_2 PAS with red detuning as much as 70 cm^{-1} below the $(6S_{1/2}+6P_{3/2})$ dissociation limit by using a fluorescent spectrum modulation technique,[13] and obtained the molecular potential coefficient c_3 using the semi-classical LeRoy–Bernstein equation (LRB) proposed in Ref. [14].

LeRoy and Bernstein[14] established the analytical semi-classical LRB formula based on the WKB method and Bohr–Sommerfeld quantization in 1970 to assign the long-range part of the molecular vibrational levels located in a potential varying as $-c_n/R^n$ by fitting PAS, and derived an experimental c_n coefficient. The basic LRB formula used to analyze PAS data was modified by Comparat first in 2004, and an improved LRB formula was obtained by considering the multipole expansion as in Ref. [15]. Later Jelassi *et al.*[16] analyzed the PAS of $^{87}Rb_2$ $(5S_{1/2}+5P_{1/2})$ long-range molecular 0_g^- state by using the improved LRB formula with only one additional term varying linearly with binding energy, and obtained very good agreement between experimental data and theoretical curve. Jelassi *et al.*[17] reexamined the basic LRB formula in 2008, and corrected the basic LRB formula by adding three additional terms. It is also demonstrated that the improved LRB formula including only one linear term is very important for deducing a more accurate coefficient c_3 from experimental data in Ref. [18].

In the present paper, we introduce quantum defect into the molecular vibrational progression, and then reexamine the PAS data of 1_g state of Cs_2 in an energy range of $\sim$ 70 cm^{-1} below the $(6S_{1/2}+6P_{3/2})$ dissociation limit and show the molecular Lu–Fano graph.[19] The Lu–Fano graph is explained by considering the improved LRB formula including

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two additional modified terms, and the more accurate value of c_3, which is compared with the value from the theoretical calculation[20] and previous fitting results[5,12,13] from experimental data, is obtained by fitting the improved LRB formula to the experimental data in Ref. [13].

2. Improved LeRoy–Bernstein (LRB) formula

In the process of deriving the LRB formula, the density of states is calculated and given by an analytical expression that is a power law formula versus the binding energy in a long range near the dissociation limit. And the binding energy is deduced from the density of the states via integrating with respect to energy variable. The basic LRB formula is shown below as indicated in Ref. [14].

$$v_{\mathrm{D}} - v = \left(\frac{\varepsilon}{E_n}\right)^{(n-2)/2n}, \tag{1}$$

$$E_n = \left(\frac{\sqrt{\pi}}{\sqrt{2u}}\right)\frac{\hbar(n-2)}{c_n^{1/n}}\frac{\Gamma(1+1/n)}{\Gamma(1/2+1/n)}\Bigg)^{2n/(n-2)}. \tag{2}$$

In Eqs. (1) and (2), v_{D} is a constant related to the dissociation limit, v the excited molecular vibrational quantum number, ε the binding energy, and E_n a function of reduced mass u, long-range molecular coefficient c_n, and gamma function Γ.

For an alkali-metal dimer, the long-range potential of the excited molecule is known as the asymptotic form $\sim -c_3/R^3$ or $-c_6/R^6$, because both the atoms that constitute the excited molecular dimer undergo the atomic dipole–dipole interaction. Here we focus on the cesium molecule. The 1_{g} state potential curve concentrating on the $(6S_{1/2}+6P_{3/2})$ dissociation limit is asymptotically described by $V(R) = -D - c_3/R^3$ where D is a constant and R is the internuclear distance. The theoretical coefficient c_3 is given as 17.46 in Ref. [17]. The values of fitted coefficient c_3[3,12,13] by applying basic LRB formula to spectral data are presented in Table 1.

Table 1. Values of c_3 (in atomic units) obtained from present studies and the previous work.

	Year	c_3 for 1_{g}	LRB formula
This work	2012	16.600(2)	S-LRB
This work	2012	16.568(8)	F-LRB
Experiment[13]	2009	16.382(10)	usual LRB
Experiment[15]	2004	15.898(14)	usual LRB
Experiment[12]	1999	15.72(5)	usual LRB
Theory[20]	1995	17.46	–

We define the effective molecular vibrational quantum number based on the basic LRB formula as indicated in Ref. [16] as follows:

$$v^* = \left(\frac{\varepsilon}{E_3}\right)^{1/6}. \tag{3}$$

Then the molecular vibrational quantum defect is defined as the non-integer part of as shown in Ref. [17]

$$\delta = v^* - \mathrm{int}[v^*]. \tag{4}$$

According to the definition of the effective molecular vibrational quantum number, if a set of experimental data satisfies the basic LRB law, the quantum defect should be a constant in a big energy range and equals $\delta_{\mathrm{D}} = v_{\mathrm{D}} - \mathrm{int}[v_{\mathrm{D}}]$.

Here, we employ the molecular vibrational quantum defect in our experimental data, and the Lu–Fano graph is presented in Fig. 1(a). There is no sharp change in a large red detuning with 70 cm^{-1} below the $(6S_{1/2}+6P_{3/2})$ dissociation limit, but a linear variation of the quantum defect versus binding energy is just like the result shown in Ref. [16],

$$\delta = \delta_{\mathrm{D}} + \gamma\varepsilon. \tag{5}$$

This behavior can be related to the following improved LRB formula:

$$v_{\mathrm{D}} - v = \left(\frac{\varepsilon}{E_3}\right)^{1/6} + \gamma\varepsilon. \tag{6}$$

This equation includes only one additional linear term $\gamma\varepsilon$, but the difference is that our Lu–Fano graph is separated into four parts, and each part shows a linear variation.

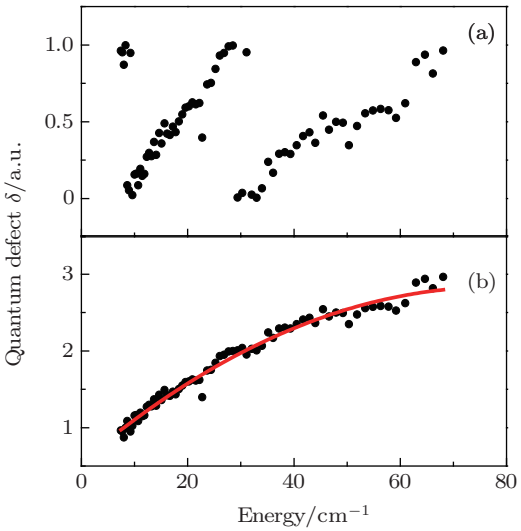


Fig. 1. (color online) (a) The Lu–Fano graph for the variation of quantum defect with binding energy, obtained with modulo 1; (b) Lu–Fano graph and the quadratic fitting to the data, obtained with modulo 4.

In order to analyze the variations of quantum defect with energy for all energy levels in a graph, we redefine the quantum defect using the modulo 4 in Fig. 1(b) by referring to the method of employing modulo 3 in Ref. [21] but not modulo 1 in Fig. 1(a). Such a definition is helpful to exhibit the variation of δ with energy variable, as a quadratic function shown as follows:

$$\delta = \delta_{\mathrm{D}} + \gamma\varepsilon + \beta\varepsilon^2, \tag{7}$$

which hints that the basic LRB formula can be extended to include two additional modified terms,

$$v_{\mathrm{D}} - v = \left(\frac{\varepsilon}{E_3}\right)^{1/6} + \gamma\varepsilon + \beta\varepsilon^2. \tag{8}$$

where γ and β are parameters of the improved LRB formula.

3. Reexamination of experimental data and deducing the c_3 coefficient by using the improved LeRoy–Bernstein formula

In the PA process, two colliding cold ground state atoms resonantly absorb a photon and so form an electronically excited molecule in a certain ro-vibrational level as shown in Fig. 2. The electrostatic dipole–dipole long-range interaction results in molecular potential curve converging to the $(6S_{1/2}+6P_{3/2})$ dissociation limit that presents an asymptotic behavior (R^{-3}). The analysis that we present in this paper focuses on experimental spectral data for $(6S_{1/2}+6P_{3/2})$ 1_g state of Cs_2 where 72 energy levels with the large red detuning (~ 70 cm^{-1}) below the $(6S_{1/2}+6P_{3/2})$ dissociation limit were obtained by our group.[13] The weakly binding energy levels are detected by a trap-loss spectrum that is understood as the trapped cold atomic loss when partially optically associated with the excited molecules, and we can know whether the excited molecule is produced by monitoring the fluorescence of the trapped cold atoms.

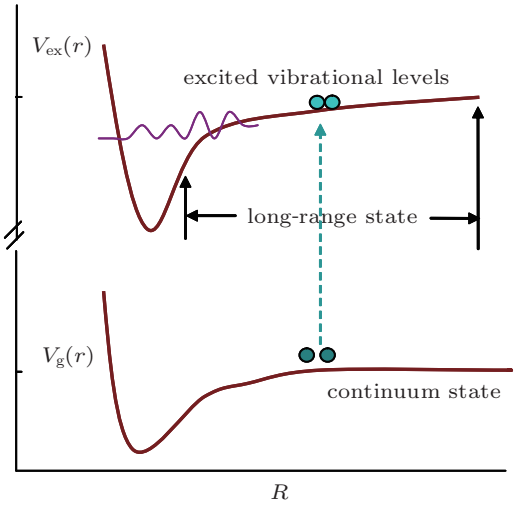


Fig. 2. (color online) Long-range molecular potential curves of the cesium dimer correlated to the $(6S_{1/2}+6P_{3/2})$ disassociation limit and the process of photoassociation.

For the cesium dimer, the molecular spin–orbit coupling was observed first from PAS perturbations between two electronic states of the same symmetry belonging to different asymptotic potentials below the $(6S_{1/2}+6P_{1/2})$ and the $(6S_{1/2}+6P_{3/2})$ dissociation limits respectively by Pichler *et al.*,[4] and they indicated that the perturbations can be manifested through irregular vibrational level spacing, which is particularly applicable for the 0_u^+ symmetry series. Jelassi *et al.*[19] analyzed the energy spacing between two consecutive energy levels from Stwalley's group for $(6S_{1/2}+6P_{3/2})$ 0_u^+ state, and the vibrational energy spacings showed obvious regular deviation due to molecular spin–orbit coupling. They noticed that there are four experimental data that are marked as wrong assignments but belong to other molecular states. This mistake can easily occur in the process of assigning vibrational progressions. Besides, other perturbations also exist, for example, the different electronic states $(0_g^-, 1_g)$ mixing[21–25] and the dissociation energy level assignment.[26] Here we use the same analysis method as in Ref. [19] to reexamine our spectral data reported in Ref. [13] for $(6S_{1/2}+6P_{3/2})1_g$ state. The perturbations resulting from the molecular spin–orbit coupling are observed through a regular deviation of the energy spacing just as shown in Fig. 3 for the $(6S_{1/2}+6P_{3/2})$ 0_u^+ state, but the amplitudes of the perturbations are smaller than those shown in Ref. [19].

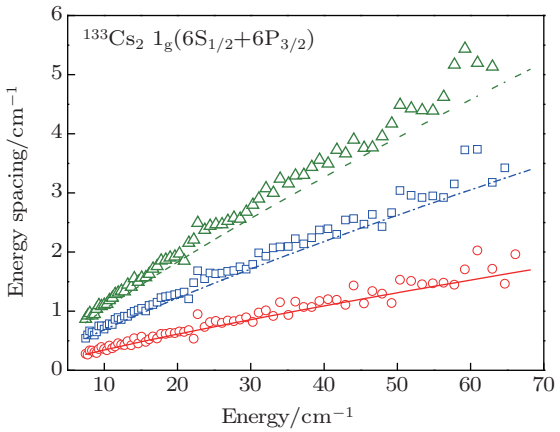


Fig. 3. (color online) Circles represent energy spacing between two consecutive data points versus energy; squares denote energy spacings to the second neighbors; triangles refer to energy spacings to the third neighbor. Solid line represents the theoretical energy spacing $\Delta\varepsilon = 6E_3(\varepsilon/E_3)^{5/6}$; dash–dot line denotes $2\Delta\varepsilon$, and dash line refers to $3\Delta\varepsilon$.

The data shown in Table 2 of Ref. [13] are reexamined to analyze the perturbation from the molecular spin–orbit coupling. We analyze the different energy spacings between consecutive energy levels and compare theoretical energy spacings with experimental ones. As shown in Fig. 3, the data set is consistent with the derivative energy law given by the LRB formula (1), namely an energy spacing $\Delta\varepsilon$ given by $\Delta\varepsilon = 6E_3(\varepsilon/E_3)^{5/6}$ for $n = 3$. The observed regular deviations (at ~ 22.76 cm^{-1}, ~ 32.08 cm^{-1}, ~ 44.05 cm^{-1}, ~ 50.38 cm^{-1}, ~ 57.81 cm^{-1}) indicate the perturbations from other energy levels corresponding to the $(6S_{1/2}+6P_{1/2})$ dissociation limit. Thus our PAS reflects the physical result of the molecular spin–orbit coupling between two electronic states having the same symmetry and belonging to different asymptotic potentials below the $(6S_{1/2}+6P_{1/2})$ and the $(6S_{1/2}+6P_{3/2})$ dissociation limits, respectively.

Besides, the improved LRB formula is used to reanalyze the reexamined spectral data to obtain a more accurate coefficient c_3 for the $(6S_{1/2}+6P_{3/2})1_g$ state of Cs_2 by a nonlinear fitting. We use Eqs. (6) and (8) to fit our spectral data presented respectively and compare the fitting results. Hereafter we regard Eqs. (6) and (8) as the first improved LRB (F-LRB) formula as shown in Ref. [16], including only one linear term of energy, and the second improved LRB (S-LRB) formula as given in Ref. [17], including two additional modified terms, respectively.

We compare the results obtained by using Eqs. (6) and (8) and demonstrate the importance of the S-LRB formula in Eq. (8). Figure 4(a) shows nonlinear fittings by using the F-LRB formula in Eq. (6) to the reexamined spectral data and figure 4(b) shows nonlinear fitting by using the S-LRB formula in Eq. (8) to the same reexamined spectral data. The value of the effective coefficient c_3 could be deduced from the fitting parameter E_3. The values of c_3 for the $(6S_{1/2}+6P_{3/2})1_g$ state of Cs_2 have been found to be 16.568(8) and 16.600(2) respectively by using the F-LRB and the S-LRB formulae.

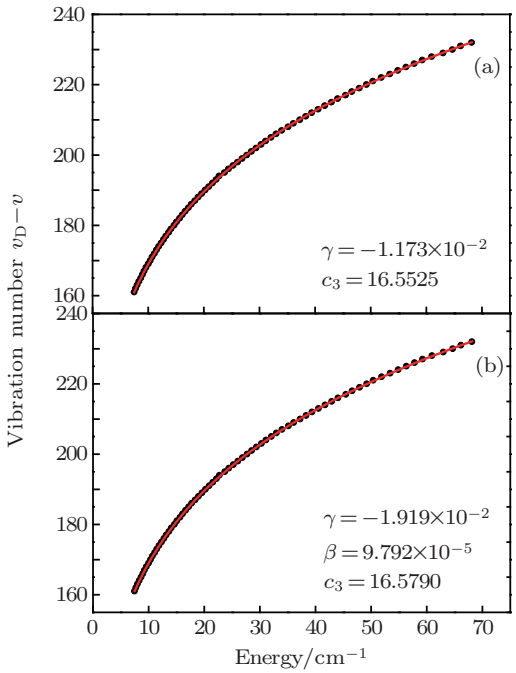


Fig. 4. (color online) Nonlinear fittings of the vibrational levels for the $(6S_{1/2}+6P_{3/2})1_g$ state of Cs_2 using the improved LRB formula containing only one additional term (a) and two additional terms (b).

For comparison, we list other theoretical and experimental fitting values of c_3 for the long-range 1_g state of Cs_2 in Table 1. Considering the previous experimental value of c_3, deduced from experimental data by using the basic LRB formula in Eq. (1), there is the least difference between the experimental value of coefficient c_3 and the theoretical value in Ref. [13], and their discrepancy is 6.17%. The discrepancy for the experimental values from Ref. [12] even reaches ~10%. However, our result, deduced by using the S-LRB formula (8) to fit the reexamined spectral data, improves 1.27% compared with the value given in Ref. [13], at the same time the result obtained by using the S-LRB formula (8) to fit improves 0.2% compared with the value by using the F-LRB formula (6). According to Table 1, the value of c_3, obtained using the S-LRB formula, presents the least difference from the theoretical value in Ref. [20] and the discrepancy decreases to 4.9%. This highly accurate value for the coefficient c_3 is expected to be very significant in determining experimental molecular potential curve and exploring pure long-range dipole–dipole interaction of the exited molecular dimer.

4. Conclusion

In this paper, we reexamine spectral data by using the same method as that shown in Ref. [15], and our data present a good agreement with theoretical energy spacings. At the same time, the regular deviations of some energy levels are attributed to the molecular spin–orbit coupling. Then the vibrational quantum defect is employed and the corresponding Lu–Fano plot is presented. The vibrational quantum defect shows quadratic variation with energy, which can be coupled to the improved LRB formula including two additional modified terms with the first varying linearly with energy and the second varying squarely with energy. The more accurate coefficient c_3 with the least discrepancy ~ 4.9% compared with theoretical value that is obtained by fitting the reexamined spectral data to the S-LRB formula. Compared with our results early reported in Ref. [13] that has 6.17% error, the new result obtained by using the S-LRB formula improves 1.27%. This improvement is significant for determining the long-range molecular potential curve and other molecular parameters, and also for accurately exploring long-range dipole–dipole interactions.

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