PHYSICAL REVIEW A **75**, 052501 (2007)

Reexamination of the 0_g^- pure long-range state of Cs_2: Prediction of missing levels in the photoassociation spectrum

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(Received 3 April 2007; published 7 May 2007)

A reexamination of the photoassociation spectrum of the external well of the 0_g^- potential of Cs_2 converging to the $(6s_{1/2}+6p_{3/2})$ limit is performed, in order to resolve inconsistencies arising from a previously published paper [Phys. Rev. Lett. **85**, 1408 (2000)]. We use the same analytical description of the potential as in an other previous analysis [Phys. Rev. A **66**, 052506 (2002)], but we make a shift of 2 in the assignment of the observed vibrational lines. The agreement between experimental and calculated energy positions is improved and the intensities calculated using the new potential account well for all available data. The fitting procedure reveals a strong interdependence of the parameters of the model, which limits the accuracy of the determination of the radiative lifetimes of the $6p^2P_{1/2}$ and $6p^2P_{3/2}$ atomic levels. Only a more precise experimental study could allow one to improve the determination of these lifetime values.

DOI: 10.1103/PhysRevA.75.052501 PACS number(s): 33.20.−t, 32.80.Pj, 33.80.Ps, 34.20.−b

I. INTRODUCTION

With the increasing precision of the experiments, laser-cooled atoms and atomic ions have brought significant progress in the domain of precision measurements, for instance, by the design of new atomic frequency standards which can be compared to determine the temporal variation of the fine structure constant [1]. The growing availability of cold molecular samples [2,3] also offers exciting prospects for the measurement of fundamental constants to test the validity of modern theories. As an illustration, huge efforts are put nowadays on the measurement of the electric dipole moment of the electron using cold beams of heavy polar molecules [4,5], as a test of the validity of the standard model.

In addition to these metrology experiments, laser-cooled atoms lead, about fifteen years ago, to the emergence of a new high-resolution molecular spectroscopy, the so-called photoassociation spectroscopy [6]. During the photoassociation (PA) process [7], a pair of colliding laser-cooled atoms absorbs a photon with a frequency detuned to the red of an atomic transition, creating an electronically excited molecule in a rovibrational level which can be very tightly bound. As the kinetic energy distribution of the cold atoms is extremely narrow, the PA process permits high resolution spectroscopy. In addition, one can excite energy levels close to the dissociation limit of the created molecule, i.e., having a large radial elongation. Therefore PA spectroscopy is well adapted to explore the long-range interactions between atoms, and leads to a wealth of spectacular results concerning the "pure long-range" molecules predicted in Ref. [8]. For instance, PA spectroscopy allowed one to improve the determination of ground state molecular dissociation energies [9,10]. It also proved to be an efficient tool for the determination of atomic properties such like the radiative lifetime of the first excited level of alkali atoms, with an accuracy similar to the one of the best atomic physics experiments [11–15].

In this context, the so-called 0_g^- $(6s_{1/2}+6p_{3/2})$ pure long range molecular state of Cs_2 (see Fig. 1) represents a case study, as the radiative decay of this state populated by PA of ultracold cesium atoms led to the first observation of stable ultracold molecules [16]. Furthermore, a reliable description of this state is crucial, as it appears as a suitable intermediate step in the course of the formation of ground state molecules in their lowest $v=0$ vibrational level.

The PA spectroscopy of this state [17] has been interpreted by our group using two inversion methods to extract an accurate potential curve of its outer potential well: a standard spectroscopic procedure based on a Rydberg-Klein-Rees (RKR) analysis [17], and an analytic approach based on the asymptotic representation of long-range atom-atom interactions [14]. The latter study yielded an accurate value for the radiative lifetime of the Cs $6p^2P_{1/2}$ and $6p^2P_{3/2}$ atomic levels. In an other, fully independent work of our group, the experimental spectra of Ref. [16] was used to derive the van der Waals coefficient C_6 characterizing the long-range interaction between two ground state Cs atoms, as well as the triplet scattering length a_T which parametrizes the elastic collision rate of two Cs atoms polarized in the $F=4$, $M_F=4$ state [18].

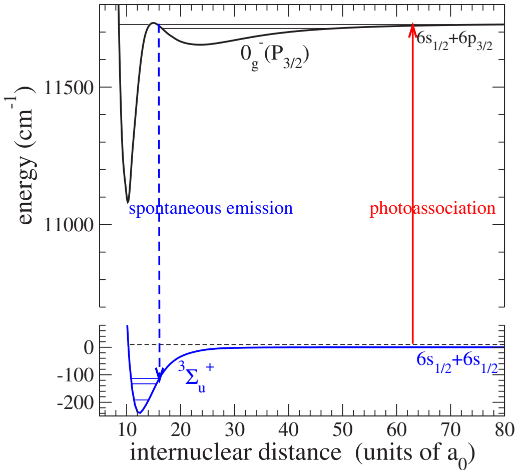

FIG. 1. (Color online) Schematic view of the excitation and decay processes of the 0_g^- state of Cs_2 dissociating towards the $(6s_{1/2}+6p_{3/2})$ limit.

Several issues remain to be clarified in the interpretation of these experiments. Neither the RKR [17] nor the asymptotic [14] potential curves for the 0_g^- outer well allows one to reproduce the intensity pattern of the experimental spectra of Ref. [16], at least in the large detuning range. In addition, the C_6 and a_T values obtained in Ref. [18] are incompatible with the most precise available values [19,20].

The aim of the present paper is to demonstrate that all these discrepancies can be suppressed if we make a major modification in the assignment of the observed PA lines, corresponding to a shift of two units in the assignment of the vibrational levels of the 0_g^- outer well. We predict now that the lowest observed level is actually $v=2$, and that two deeper levels, namely, $v=0$ and $v=1$, still remain to be discovered. We briefly recall in Sec. II the PA and cold molecule experiment under study, and both previous analysis performed in our group. We then describe, in Sec. III, the asymptotic approach of Ref. [14] that we still use to revisit the interpretation of the PA spectra. We then focus our study on the fitting procedure (Sec. IV) and on the analysis of uncertainty in the parametrization of the potential curve (Sec. V), We finally present and discuss our results concerning radiative lifetimes, ground state van der Waals coefficient and intensity patterns of PA spectra (Sec. VI).

II. EXPERIMENT AND PREVIOUS ANALYSIS

In the experiment [16,17], cold Cs atoms in a vapor cell magneto-optical trap (MOT) are illuminated by a cw laser which produces photoassociation toward excited molecular states. The atoms are prepared in the $F=4$, $M_F=4$ Zeeman hyperfine state. PA lines are observed by detecting the Cs_2^+ ions formed after spontaneous radiative decay and subsequent pulsed laser photoionization of the molecules formed by PA.

In the case of the 0_g^- potential in which we are interested here, the PA reaction illustrated in Fig. 1 reads

$$\mathrm{Cs}(6s^2S_{1/2}F=4)+\mathrm{Cs}(6s^2S_{1/2}F=4)+h\nu \rightarrow \mathrm{Cs}_2(0_g^-,(6s_{1/2}+6p_{3/2}),\nu,J). \qquad (1)$$

The positions of a large number of vibrational levels (133) of this 0_g^- potential have been measured, and the rotational structure (with J values ranging from 0 to 8) was resolved up to $v\sim 75$.

The particular double-well shape of the 0_g^- potential explains the large energy range of observed levels: there is a Condon point on the inner slope of the external well, which lies at an intermediate distance, around $15-20a_0$. As shown in Fig. 1, this allows an efficient stabilization of the cold molecules in the lowest $^3\Sigma_u^+$ state, by spontaneous emission [16]. In Ref. [14], hereafter referred to as paper I, an analytical expression based on an asymptotic development of the potential curve was fitted on the measured positions of 73 PA lines corresponding to the 0_g^- potential [17], providing an accurate description of the external well of this potential. As a result of the fit, values of the cesium $6p^2P_{1/2}$ and $6p^2P_{3/2}$ atomic lifetimes were claimed to be derived with an error one order of magnitude smaller than the one obtained in atomic physics experiments. Using theoretical relationships between the coefficients of the multipole expansion of the asymptotic atom-atom electrostatic interaction [21], a value of the van der Waals C_6 coefficient for the ground state was also derived, in agreement with the available values.

The results of the same experiment of PA spectroscopy of the 0_g^- potential were also used by our group in Ref. [18], hereafter referred to as paper II, in which we interpreted the minimas of the intensity variation of the spectrum of the Cs_2^+ ion yield as a direct manifestation of the nodal structure of the colliding atom wave function. This allowed us to obtain simultaneously a value of the scattering length and of the C_6 coefficient of the lowest triplet molecular state. Unfortunately, both values are definitely incompatible with all other recent values, determined from various experiments. Let us cite the most precise ones, namely, the value obtained in our group using two-color photoassociation spectroscopy [19] and the value obtained at NIST using a large number of magnetically induced Feshbach resonances [20]. Furthermore, the spectrum which is calculated using the 0_g^- potential of paper I together with the best available values of C_6 and triplet scattering length of the ground state [19,20] is qualitatively different from the experimental one in almost half the energy range, the large detuning region.

As a consequence, the 0_g^- potential of paper I might appear as somehow uncertain, and so do all the data one would obtain from this potential. This is, for instance, the case of the atomic radiative lifetime values, which could otherwise be thought as the "best" available ones.

Two main ingredients are involved in the procedure of paper II: the ground state wave function, which relies on the asymptotic method only and the excited state wave functions, which were deduced from the RKR analysis [17]. Concerning the ground state wave function, the asymptotic method is not actually questionable in the range of interatomic distance where it is used, i.e., the range where the external well of 0_g^- does extend. Conversely, the 0_g^- potential curve might have been distorted by being constrained to match a wrong labeling of the observed vibrational levels. The observed line corresponding to the level labeled $v=0$ in paper I is already extremely small and appears as the last line of a series of lines with decreasing intensities. One might thus reasonably assume that lower levels could have escaped to the observation. The analysis of the data, either by the RKR method or by the analytical one, has then to be revisited.

III. ASYMPTOTIC ANALYTICAL MODEL FOR THE 0_g^- OUTER WELL

For the present revision of the 0_g^- potential, we have preferred to use the analytical asymptotic approach rather than the RKR one. The main reason is that the inner slope of the external well of the potential, resulting from the mixing by spin-orbit interaction of two asymptotic potentials converging toward the $(6s_{1/2}+6p_{1/2})$ and $(6s_{1/2}+6p_{3/2})$ limits, is not as steep as it is supposed to be in the RKR model (see Fig. 1). As a consequence, the weakly bound states are not very well described and there is no hope to derive by this method an accurate value of the C_3 coefficient characterizing the asymptotic behavior of this potential.

Conversely, the whole external well can be described by asymptotic formulas, involving the multipolar expansion of the electrostatic atom-atom interaction and the spin-orbit interaction. However, we showed in paper I that the asymptotic exchange interaction has to be added as a perturbation which becomes important only for interatomic distances corresponding to the repulsive branch of the external well. In the same range, R variation of the spin-orbit terms has been predicted [22]. Corrections related to retardation and to relativistic effects are also included. The main formulas are briefly recalled hereafter, to fix the notation. All details can be found in paper I.

The Hund's case (c) 0_g^- states result from a mixing between the ${}^3\Sigma_g^+(6s+6p)$ and ${}^3\Pi_g(6s+6p)$ Hund's case (a) electronic states. The 2×2 matrix of the Hamiltonian describing this mixing is written as

$$H=\begin{pmatrix} V^{\Pi}(R)-\Delta^{\Pi\Pi}(R) & \dfrac{\sqrt{2}M^2\epsilon}{9R^3}+\Delta^{\Pi\Sigma}(R)\\ \dfrac{\sqrt{2}M^2\epsilon}{9R^3}+\Delta^{\Pi\Sigma}(R) & V^{\Sigma}(R)\end{pmatrix}, \qquad (2)$$

where the $V^{\Sigma}(R)$ $[V^{\Pi}(R)]$ are the ${}^3\Sigma_g^+$ $[{}^3\Pi_g]$ asymptotic potentials, given by

$$V^{\Sigma}=-\frac{C_3^{\Sigma}}{R^3}\left(1+\frac{2\epsilon}{3}\right)-\frac{C_6^{\Sigma}}{R^6}-\frac{C_8^{\Sigma}}{R^8}+V_{\text{exch}}^{\Sigma}, \qquad (3)$$

$$V^{\Pi}=-\frac{C_3^{\Pi}}{R^3}\left(1+\frac{4\epsilon}{3}\right)-\frac{C_6^{\Pi}}{R^6}-\frac{C_8^{\Pi}}{R^8}+V_{\text{exch}}^{\Pi}. \qquad (4)$$

The relativistic effects are introduced in these equations as a small correction to the coefficients of the R^{-3} terms, the parameter ϵ characterizing the ratio of the squared transition moments $M_{1/2}$ and $M_{3/2}$ corresponding to the relativistic $p_{1/2}$ and $p_{3/2}$ states

$$\mathcal{R}=\frac{(M_{3/2})^2}{(M_{1/2})^2}=\frac{2\tau_{1/2}(\lambda_{3/2})^3}{2\tau_{3/2}(\lambda_{1/2})^3}=\frac{2}{(1+\epsilon)^2}. \qquad (5)$$

The M^2 coefficient in Eq. (2) is related to the $C_3^{\Sigma/\Pi}$ coefficients by

$$C_3^{\Pi}=-\frac{C_3^{\Sigma}}{2}=-\frac{M^2}{3} \qquad (6)$$

and it is related to the relativistic atomic transition moment corresponding to $j=3/2$ by

$$M^2=\frac{3}{4}(M_{3/2})^2. \qquad (7)$$

The asymptotic exchange terms $V_{\text{exch}}^{\Pi/\Sigma}$ (see paper I and its appendix), depend on the product of the amplitudes of the atomic asymptotic wave functions a_{6s} and a_{6p}. The spin-orbit terms are modeled by

$$\Delta^{\Pi\Pi}(R)=\frac{\Delta E_{fs}}{3}\tanh(A^{\Pi\Pi}R), \qquad (8)$$

$$\Delta^{\Pi\Sigma}(R)=\frac{\sqrt{2}\Delta E_{fs}}{3}\tanh(A^{\Pi\Sigma}R), \qquad (9)$$

where $\Delta E_{fs}=554.039\ \text{cm}^{-1}$ is the Cs $6p$ fine structure splitting [23].

IV. FITTING PROCEDURE

Diagonalization of the 2×2 matrix of Eq. (2) yields an analytical expression for the potential curve of the 0_g^- external well. Vibrational energies and wave functions are then calculated using a standard Numerov integration. Rotation is accounted for as in paper I. N_p parameters are adjusted to minimize the rms between N calculated and experimental energies

$$\text{rms}=\sqrt{\frac{\sum_{i=1,N}(E_{\text{exp}}-E_{\text{cal}})^2}{N-N_p}}, \qquad (10)$$

by using the so-called generalized simulated annealing (GSA) method [24]. Nine parameters were at first considered, as in paper I: the squared atomic transition moment M^2, the relativistic parameter ϵ, the multipole coefficients C_6^{Σ}, C_6^{Π}, C_8^{Σ}, C_8^{Π}, the values $A^{\Pi\Pi}$ and $A^{\Pi\Sigma}$ of the spin-orbit variation parameters, and the exchange amplitude $a_{6s}a_{6p}$.

In a first step, we restricted the experimental data to the $J=2$ lines of the 71 lowest observed vibrational levels up to $v=75$. We recall here that, as we do not include the hyperfine structure in our model, we substract $0.0088\ \text{cm}^{-1}$ from all experimental energies of Ref. [17], to relate them to the barycenter of the $[6s_{1/2}(F=4)+6p_{3/2}]$ manifold. We rapidly eliminated the possibility of labeling by $v=1$ the lowest observed level: with this assumption, we never found a rms smaller than $0.020\ \text{cm}^{-1}$, moreover with unacceptable values of M^2 (15% larger than the one of paper I). In contrast, satisfying adjustment is obtained in the hypothesis of a $v=2$ labeling of this level.

Contrarily to paper I, the values obtained for the parameters $A^{\Pi\Pi}$ and $A^{\Pi\Sigma}$ of Eq. (9) were rather large, so that the spin orbit was hardly varying in the R range of the 0_g^- external well. We therefore suppressed these two parameters by giving them fixed infinite values. We also fixed the value of the parameter ϵ, which rapidly appeared as being better determined from atomic physics experiments [25] than from our fit. The number of remaining parameters, six, seemed still too large since the ultimate convergence was very hard to get and since we obtained rms values of the order of $0.003\ \text{cm}^{-1}$, significantly smaller than the experimental uncertainty $\sigma=0.005\ \text{cm}^{-1}$. Although these six parameters are not strictly correlated, having quite distinct influence on the energy levels, they appear as strongly interdependent, the variation of one parameter being able to roughly compensate the variation of another one. Their number is, however, difficult to reduce. Using theoretical values of the ratios C_n^{Π}/C_n^{Σ} of Ref. [26], as was done to obtain atomic lifetime values of Na [12], gave very unsatisfactory agreement between experimental and calculated values. Theoretical values of the exchange amplitudes were also found not precise enough to be used as fixed values.

TABLE I. Result of our best fit, together with the result of paper I and with some theoretical values. A rough estimation of the error bars associated with our parameter values is given in the text: about 1% for M^2 and a few % for the other parameters. The rms values account for the number of adjusted parameters [see text, Eq. (4)]. The values of the parameters which have been kept fixed are inside brackets.

	this work	paper I	theory
levels	71	73	
number of parameters	6	9	
rsm (cm^{-1})	0.0032	0.0065	
parameters			
M^2 (10^5 cm^{-1} $\mathrm{\AA}^3$)	9.806	9.789 (1)	10.22 [26]
C_6^{Π} (10^7 cm^{-1} $\mathrm{\AA}^6$)	5.869	5.689 (1)	5.701 [26]
C_6^{Σ} (10^7 cm^{-1} $\mathrm{\AA}^6$)	8.788	8.506 (1)	8.381 [26]
C_8^{Π} (10^9 cm^{-1} $\mathrm{\AA}^8$)	3.522	3.180 (3)	3.045 [26]
C_8^{Σ} (10^9 cm^{-1} $\mathrm{\AA}^8$)	17.525	7.715 (3)	6.802 [26]
$a_{6s}a_{6p}$	0.04512	0.03843 (3)	0.054790 [28]
$A^{\Pi\Pi}$ ($\mathrm{\AA}^{-1}$)	[∞]	0.2413 (2)	
$A^{\Pi\Sigma}$ ($\mathrm{\AA}^{-1}$)	[∞]	0.2661 (5)	
ϵ 10^{-3}	[4.81]	4.69 (3)	

The results of our best fit are given in Table I, together with theoretical values of the parameters and with the results of paper I, which were obtained from the same data and in a similar way, but by attributing the energy of the lowest observed level to the $v=0$ vibrational state. One notices that the rms of our fit is notably smaller than in paper I. The new potential shape is shown in Fig. 2, together with the one of paper I: the potential minimum is found at $R_{\mathrm{min}}=12.41(1)$ Å, slightly smaller than the old one ($R_{\mathrm{min}}=12.60$ Å), with a minimum value $E_{\mathrm{min}}=-81.644(5)$ cm^{-1}, which is notably deeper than the old one ($E_{\mathrm{min}}=-78.026$ cm^{-1}), since it has to contain two more levels. Note that in Ref. [27], the depth of the 0_g^- external well was estimated from the absorption spectrum of a cesium vapor at room temperature. The resolution of this experiment is however too low to be compared with the present analysis.

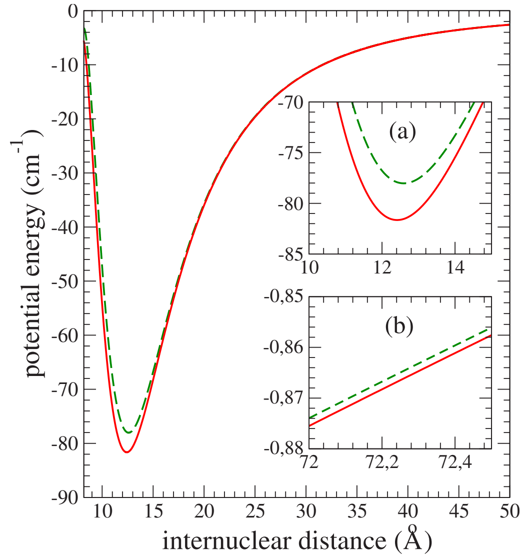

FIG. 2. (Color online) Potential curve of the 0_g^- external well, obtained in the present work (red full lines) and in paper I (green dashed lines). Insets (a) and (b) emphasize the differences between the two curves in the region of the minimum and at large distance, respectively.

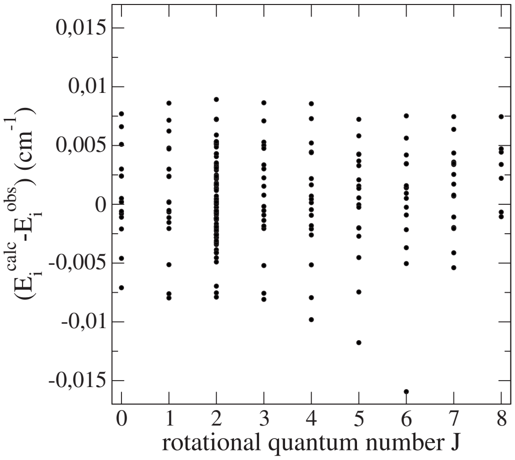

FIG. 3. Residues $E_i^{\mathrm{calc}}-E_i^{\mathrm{exp}}$ for all the 202 levels measured in the PA experiment of Ref. [17], as a function of the rotational quantum number J. The parameter values used here are those of the fit of Table I, which was performed using a subset of $J=2$ components, corresponding to the 71 best resolved and most intense lines of the PA spectrum.

The adjusted values of the C_3 and C_6 parameters are not very different from the ones of paper I, but incompatible with the error bar given there. There are much bigger differences in the values of the C_8 parameters. The new value of C_8^{Σ} is more than twice as large as the old one and as the theoretical value of Ref. [26]. The value obtained for the asymptotic exchange amplitude $a_{6s}a_{6p}$ is also different than the one of paper I, closer to the values of Refs. [28,29].

Using the results of our fit, we have calculated all the 202 measured energy positions up to $v=75$, with J values ranging from 0 to 8 [17]. As shown in Fig. 3, there is still a very good agreement with the experimental values (the new rms is 0.004 cm^{-1}). As the value of the rotational energy is very sensitive to the position of the well minimum, this gives us an additional indication of the reliability of our potential.

V. PARAMETER UNCERTAINTIES

We have used several different methods to estimate the standard deviation of the parameters. According to a most restrictive definition, this deviation is obtained by calculating the maximum variation of a given parameter which induces an energy variation of each level smaller than twice the experimental uncertainty. One obtains in this way uncertainties of the order of the ones given in paper I. It is, however, clear that such an estimation does not take into account the interdependences of the parameters. We did not use the method adopted, for instance, by Allard *et al.* [30,31] which consists of fitting a large number sets of "artificial" experimental energies, obtained by adding to the measured values a Gaussian random distribution with parameter 0.005 cm^{-1}. In our situation, this method could introduce an unnecessary bias, by assuming that the experimental values are the center of a stochastic distribution. We have tried to estimate our uncertainties by linearizing the dependence of the energy positions E_i on the different parameters θ_α in the vicinity of the minimum of the rms. One calculates then the Jacobian matrix J defined by

$$J_{i,\alpha} = \frac{\partial E_i}{\partial \theta_\alpha} \tag{11}$$

and the covariance matrix V_c, which allows one to define the confidence ellipsoid, is given by

$$V_c = (\sigma_{\mathrm{exp}})^2 (J^T J)^{-1}. \tag{12}$$

In the linear approximation, the one-parameter standard errors are the diagonal elements of the covariance matrix V_c. The values obtained in this way were very large (about a few percent for M^2 and tens of percent for the other parameters), so that the linear approximation is certainly no more valid in such parameter ranges. We finally estimated the error on the M^2 parameter by doing a series of fits at various fixed values of this parameter, the other five remaining free. However, the result of the GSA procedure was found to depend in an unpredictable way on the initial values and on the allowed variation range given to the free parameters. This peculiar behavior is related to the fact that the rms value that we obtain is smaller than the experimental uncertainty σ. Very different parameter sets can yield a rms value equal to σ. To illustrate this point, we show in Fig. 4 several examples of parameter sets giving a rms approximately equal to σ. What is remarkable is that all these parameter sets lead to almost undistinguishable potential shapes. In other words, the fit provides a lot of different parameter sets, but a single potential. We have checked that any of these parameter sets can be used for calculating the intensities of PA spectra without changing the result. Concerning the confidence intervals for the parameter values, standard theory (see, for instance Ref. [32]) is not applicable, due to the strong interdependence of the parameters. From our exploration of the variations of the rms when changing the M^2 parameter around its central value, we finally estimate, very roughly, that its uncertainty is of the order of 1%. The uncertainty on the other parameters is even larger, of the order of a few percents.

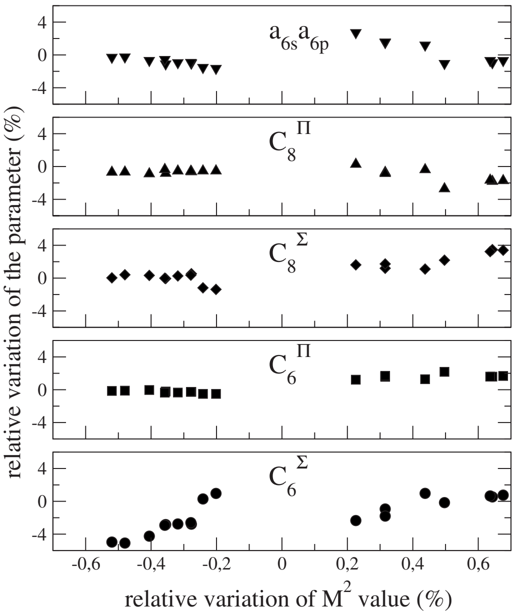

FIG. 4. Examples of parameter sets giving a rms of the order of the experimental uncertainty 0.005 cm^{-1}. We present here the parameter difference (in %) from the central values of Table I. Abscissa corresponds to M^2, ordinate to the other parameters. All these sets correspond to individual fits with fixed M^2 values, with various initial values and allowed variation ranges for the other parameters. For the central values of M^2, the rms was always smaller than 0.005 cm^{-1}.

VI. ATOMIC LIFETIMES, C_6 VALUE AND INTENSITY PATTERNS

The atomic lifetimes values can be deduced from the adjusted parameter M^2 by

$$\tau_{3/2} = \frac{9\hbar}{4M^2}\left(\frac{\lambda_{3/2}}{2\pi}\right)^3, \tag{13}$$

$$\tau_{1/2} = \tau_{3/2}\left(\frac{\lambda_{1/2}}{\lambda_{3/2}}\right)^3 \frac{1}{(1+\epsilon)^2}. \tag{14}$$

The values corresponding to the fit of Table I, $\tau_{3/2} = 30.41 \pm 0.30$ ns and $\tau_{1/2} = 34.82 \pm 0.36$ ns, are shown in Table II together with the determinations of paper I and the available experimental values. The relative uncertainty on these values is the same as the one on M^2, of the order of 1%, i.e., larger than the one obtained from atomic physics experiments [33,34]. The explanation of the small error bar given in paper I is probably twofold. First, the bias introduced in the model by the absence of the two deepest levels makes it probably more difficult to obtain the least mean square solution. As a consequence, it was necessary to use a larger number of parameters, with more restrained values, leading to a larger rms value. Secondly, only binary correlations between parameters were considered in the error estimation.

As in paper I, we can deduce from the M^2 parameter a value of the van der Waals C_6 coefficient, by using the method of Ref. [21]. The value that we obtain here is

TABLE II. Radiative lifetimes of the Cs atomic $6p\,^2P_{3/2}$ and $6p\,^2P_{1/2}$ states, together with the values of the relativistic parameter ϵ which fixes the ratio between them.

	$\tau_{3/2}$ (ns)	$\tau_{1/2}$ (ns)	ϵ (10^{-3})
this work	30.41(0.30)	34.82(0.36)	[4.81]
paper I	30.462(0.003)	34.89(0.02)	4.69(0.03)
[25]			4.81(0.23)
[33]	30.57(0.07)	35.07(0.10)	3.92(2.60)
[34]	30.41(0.10)	34.75(0.07)	5.88(2.60)
[39]	30.39(0.06)	34.80(0.07)	4.81(2.10)

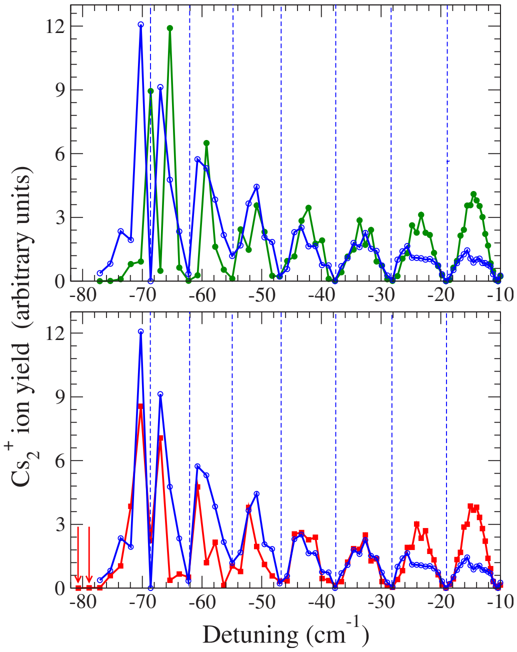

FIG. 5. (Color online) Simulations of the PA spectrum, compared to the corresponding experimental spectrum. The latter shows measured Cs_2^+ ion yield vs laser detuning (in cm^{-1}) of the PA laser with respect to the $(6s_{1/2}+6p_{3/2})$ limit; it was here obtained with atoms polarized in the $F=4$, $M_F=4$ state (paper II). In both graphs, the experimental spectrum is displayed as blue open circles. In the upper graph we show the simulation obtained with the 0_g^- potential of paper I (green full circles); in the lower graph, we show similar calculations but with the 0_g^- potential of the present paper (red full squares). Exactly the same ground state wave function, corresponding to a collision energy of 140 μK (see text) is used in both cases. Arbitrary units are used for both types of spectra. The vertical dashed lines correspond to the positions of the intensity minimas. Both additional levels are indicated by red arrows.

6850±140 a.u., in agreement with the most precise recent values 6846±16 a.u. [19] and 6860±25 a.u. [20], but with an uncertainty of the order of 2%.

A fit of positions of the intensity minimas of the experimental spectrum of Fig. 5, following the same procedure as in paper II, but now including seven minimas (from second to eighth) gives a value of the van der Waals coefficient $C_6 \sim 6960$ a.u. and a triplet scattering length value $a_T \sim 1150 a_0$. By simply changing the labeling of the 0_g^- levels, we obtain values very different from those of paper II, which were 6510 a.u. and $-530 a_0$. Taking into account the limited precision of the PA intensity measurements, the new values are, contrarily to those of paper II, in reasonably good agreement with the values of Refs. [19,20] (see above).

We have simulated the experimental spectrum of paper II by calculating the overlap between the 0_g^- radial wave functions corresponding to our best fit and a single radial wave function of two colliding atoms at the trap temperature. We assumed at first a transition dipole moment constant at all distances. The ground state wave function was obtained using a triplet potential consisting in an inner part from Ref. [35] and an asymptotic part identical to the one of Ref. [19]. The repulsive wall was adjusted to fit the triplet scattering length $2440 a_0$ of Ref. [20]. We recall that the experimental spectrum of paper II corresponds to an excitation towards $J=2$ rotational states of the 0_g^- potential, with atoms initially prepared in the $F=4$, $M_F=4$ state. The temperature of the atoms was about 140 μK so that only the $l=0$ partial wave has to be considered and the laser light was linearly polarized perpendicularly to the small magnetic field allowing to polarize the atoms. In Fig. 5, we show the comparison between the experimental spectrum and two different simulations. Both calculations are performed for a collision energy of $E=140$ μK. For the upper theoretical curve of Fig. 5, we used, for the 0_g^- states, the vibrational wave functions of paper I; for the lower one, we used the results of the present work. The ground state wave function is exactly the same in both cases. A smoothly varying correcting term was added, to roughly account for subsequent spontaneous deexcitation of the 0_g^- states formed by PA (see Ref. [36]). One can see in Fig. 5 that, whereas in the upper graph the part of the calculated spectrum corresponding roughly to $E<-50$ cm^{-1} is qualitatively different from the experimental one, the agreement is quite satisfying in the lower one. This is in fact the key argument in favor of the v labeling chosen here.

We have performed a similar comparison with another experimental 0_g^- spectrum, obtained with atoms prepared in the $F=3$, $M_F=3$ atomic state, in a magnetic field of 0.7 mT [37]. Whereas a single triplet channel is sufficient in the case of $F=4$, $M_F=4$ atoms to describe the initial state of two colliding atoms, it is here necessary to take into account hyperfine structure and five coupled channels have to be considered. We have used the asymptotic description of the Cs_2 ground state given in Ref. [19], which is based on the concept of nodal lines. In this method, which is very similar to the accumulated phase method [38], we impose on the radial wave functions to vanish at some nodal lines located near the frontier of the asymptotic region and these lines themselves are adjustable parameters which are fitted to the experimental results. Relationships between the nodal lines corresponding to the different values of the angular momentum f (the sum of the momenta of the two colliding atoms) allow one to obtain, by extrapolation from the results of Ref. [19], the nodal lines corresponding to any f value. This permits the calculation of the initial ground state wave function corresponding to any specific preparation of the atoms, with or without magnetic field. Concerning the final 0_g^- state, the present potential provides the required radial wave functions. Complete wave functions of initial and final states, including nuclear spins and rotation, are finally constructed and the dipole matrix element corresponding to the experimental polarization of the laser light is calculated. It is possible to account for the asymptotic R variation of the dipole moment since the diagonalization of the matrix gives for each R value the components on the two Hund's case (a) states. We present in Fig. 6 the comparison of the experimental 0_g^- spectrum of Ref. [37] with corresponding theoretical curves obtained using either paper I or the present work. The agreement is again better when using the present potential rather than the one of paper I. The remaining discrepancies in the relative intensities of the maxima may be due to calibration issues in the experimental recording. It is worth mentioning that, concerning the spectrum of paper II, the results we ob-

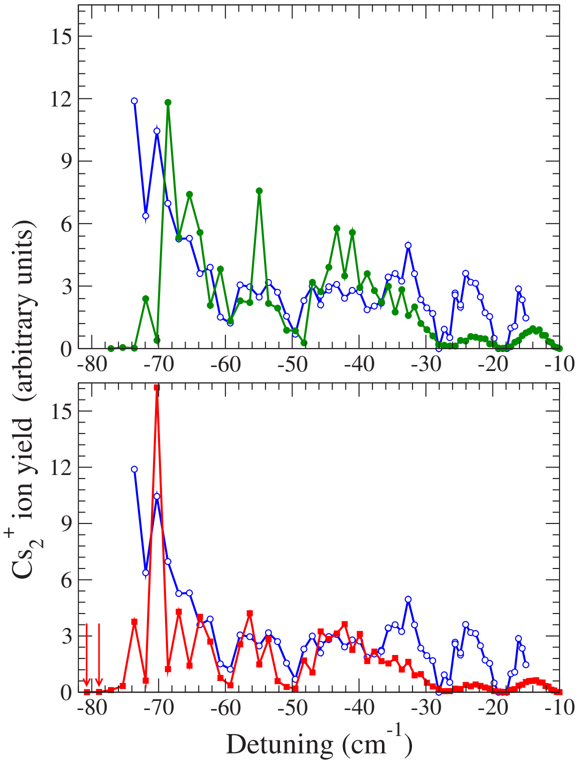

FIG. 6. (Color online) Same as Fig. 5, but for an experimental spectrum obtained with atoms polarized in the $F=3$, $M_F=3$ state and placed in a magnetic field of 0.7 mT [37]. Note that the experimental spectrum stops at a detuning roughly equal to 73.63 cm^{-1} ($v=4$ in paper I, $v=6$ in the present one).

tain with the complete formalism described above are almost identical (apart from a general angular factor) to the results of fig 5.

It will probably be very difficult to observe the two deepest vibrational states, indicated by arrows in Figs. 5 and 6. As shown in Fig. 7, the overlap between the $v=0$ state and the triplet ground state wave function is expected to be very small because the local periode of vibration of the ground state is small compared to the spatial extension of the excited state. The situation is less critical for $v=1$. The ratio of the intensities of the lines corresponding to $v=0$ ($v=1$) and $v=2$, which is the lowest observed level, is predicted to be equal to 10^{-3} (0.8) in the case of PA from atoms polarized in the $F=4$, $M_F=4$ state. For the $v=0$ state, similar ratios are obtained for any excitation scheme, with or without magnetic field, since the local periode of vibration of the triplet ground state radial component is always the same.

VII. CONCLUSION

We have shown here that a shift of two in the assignment of the observed vibrational lines allows one to fully clarify the interpretation of the PA spectroscopy of the 0_g^- state of Cs_2. The "natural" choice made in papers I and II, assigning $v=0$ to the lowest observed level, provided wrong values of the ground state triplet scattering length and C_6 coefficient (paper II). Although this choice provided a convincing analytical expression for the external well of the 0_g^- potential curve and convincing atomic lifetimes (paper I), it finally appears that only a new v labeling, with a shift to two of all v values, makes the ensemble of observations coherent. The new potential shape is accurately defined and is significantly different from the one of paper I. It now allows one to account for all available experimental data. However, at the present stage of experimental precision, the accuracy of the parameter values remains limited, due to their interdependence. It is worth mentioning that we have already tried, in vain, to observe the two missing levels. Such hidden levels, especially the $v=0$ one, are indeed expected to give rise to PA lines with a very low intensity.

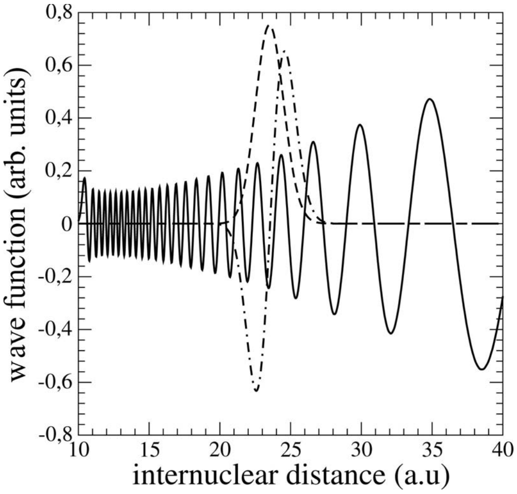

FIG. 7. Excited $v=0$ (dashed line), $v=1$ (dotted-dshed line), and triplet ground state (full line) wave functions, in arbitrary units.

Values of the van der Waals coefficient C_6 of the ground state and of the $6p^2P_{1/2}$ and $6p^2P_{3/2}$ atomic lifetimes are obtained, in agreement with all available values but with a rather poor precision. As a consequence, the present results do not allow one to choose among the different atomic measurements [34,33]. In any case, the good agreement that we obtain with the intensity patterns of all available experimental spectra is a decisive argument in favor of the present analysis.

ACKNOWLEDGMENTS

The authors thank Claude Amiot, Cyril Drag, Nicolas Vanhaecke, and the other members of the group of cold molecules in Orsay for fruitful discussions.

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