Comment on "Measurement of the electron affinity of the lanthanum atom"

Christophe Blondel ●*

Laboratoire de Physique des Plasmas, Centre National de la Recherche Scientifique, Ecole Polytechnique, Université Paris–Sud, Sorbonne Université, Observatoire de Paris, Route de Saclay, F-91128 Palaiseau Cedex, France

The electron affinity of the lanthanum atom was recently measured by slow-electron velocity map imaging in a photodetachment experiment [Y. Lu *et al.*, Phys. Rev. A **99**, 062507 (2019)]. Several detachment threshold energies have been measured, which correspond to different energy levels of the initial ion and/or final atom. Only one measurement, however, has been exploited to determine the electron affinity. Applying the ordinary spectroscopic method to the complete set of data presented by the authors, one obtains a slightly different, more precise and more consistent value of the electron affinity of La: $449\,691(17)$ instead of $449\,697(20)$ m^{-1}, i.e., $0.557\,546(20)$ instead of $0.557\,553(25)$ eV.

I. INTRODUCTION

In a recent article, Lu *et al.* [1] reported on a photodetachment experiment that provided a series of threshold energies for detachment of the La$^-$ ion to a variety of energy levels of neutral La. Even though this is mentioned in one of the tables, the text ignores the alternative measurement of one of these thresholds, starting from the first $^1D_2^o$ level of La$^-$, done by Walter *et al.* [2]. Moreover this measurement, as it appears in the mentioned table, is given a wrong uncertainty. The method used to deduce the electron affinity and optimized threshold values does not actually make optimal use of the existing experimental data. The purpose of this Comment is to show that, applying the standard method of spectroscopic data reduction, one can, with the same set of data, obtain more precise values of the detachment thresholds of La$^-$, including a better value of the electron affinity of lanthanum ^eA(La).

II. THE STANDARD METHOD OF SPECTROSCOPIC DATA REDUCTION

A. General algebra

The standard method to convert spectroscopic data into atomic energy levels relies on the Ritz combination principle [3], which makes the relationship between levels and lines algebraically very simple. Every transition wave number, or frequency, is a difference between two energy levels. Every threshold energy, as measured by Lu *et al.* [1], is the sum of such a difference of energy levels in the La and La$^-$ spectra and the electron affinity of lanthanum ^eA(La). The set of measured thresholds, which can be arranged as a vector $\mathbf{M}_{\mathrm{exp}}$, is thus a linear combination of a finite set of energy levels and ^eA(La). This finite set can be considered as an unknown vector $\mathbf{X}$, to be determined. The former and latter vectors are linked by a linear equation:

$$\mathbf{M}_{\mathrm{exp}} = \mathbf{I}\,\mathbf{X}. \tag{1}$$

The elements of matrix $\mathbf{I}$ are either 0, 1, or -1. Vector $\mathbf{X}$, if unknown, can be determined only if $\mathbf{I}$ has more lines than columns.

Optimization of the $\mathbf{X}$ vector, which contains the targeted spectra and electron affinity, has been described in many detailed articles on the extensive analysis of spectroscopic data [4,5]. The same algebra was precisely used to extract a best-fitting electron affinity from multithreshold measurements in the case of phosphorus [6]. Provided that the dimensions of the involved matrices are not too large, the whole calculation can be easily implemented in a simple spreadsheet.

In short, assuming that the uncertainties attached to the measured energy intervals can be described by a multidimensional normal law, one can define a variance-covariance matrix $\mathbf{\Sigma}$, as associated with vector $\mathbf{M}_{\mathrm{exp}}$. By definition, the best-fitting vector $\mathbf{X}$ is the one that minimizes the quadratic form $(\mathbf{I}\,\mathbf{X} - \mathbf{M}_{\mathrm{exp}})^{\mathrm{T}}\,\mathbf{N}(\mathbf{I}\,\mathbf{X} - \mathbf{M}_{\mathrm{exp}})$, with $\mathbf{N} = \mathbf{\Sigma}^{-1}$. The variance-covariance matrix $\mathbf{S}$ associated with the best-fitting $\mathbf{X}$ vector is just $\mathbf{S} = (\mathbf{I}^{\mathrm{T}}\,\mathbf{N}\,\mathbf{I})^{-1}$. The optimized energies themselves are given by $\mathbf{X} = \mathbf{S}\,\mathbf{I}^{\mathrm{T}}\,\mathbf{N}\,\mathbf{M}_{\mathrm{exp}}$. The optimized values of the initially measured quantities are given by vector $\mathbf{I}\,\mathbf{X}$, with associated variances and covariances given by matrix $\mathbf{I}\,\mathbf{S}\,\mathbf{I}^{\mathrm{T}}$. This can be generalized to any set of energy intervals or thresholds that can be deduced from the energy levels by a linear relation of the form $\mathbf{Y} = \mathbf{J}\,\mathbf{X}$: the variances and covariances attached to those optimized intervals are then given by matrix $\mathbf{J}\,\mathbf{S}\,\mathbf{J}^{\mathrm{T}}$.

B. Results

The standard method, for the case of the bound energy levels and photodetachment thresholds of La$^-$, can be applied to a minimum data set including the most precisely measured thresholds a, b, c, d, e, g, and j, plus thresholds h and w, which start from the $^1D_2^o$ level, the binding energy of which w was also measured by Walter *et al.* [2]. The set of data must also include the independent determinations of the $^3F_3$ and $^3F_4$ energy levels of the anion produced by Walter *et al.* [2], and the involved energy levels of La I as given by the NIST table [7].

————
*christophe.blondel@lpp.polytechnique.fr

TABLE I. Energy levels of La$^-$ as deduced from the spectroscopic data that existed prior to the work of Lu *et al.* [2,8–10], as later tabulated by Lu *et al.* [1], and the electron affinity, together with their more precise values obtained in a consistent optimization of the whole set of data, assuming purely statistical uncertainties. Units are cm^{-1}.

Level	After [2,8–10]	Lu *et al.* [1]	Optimized value
$^3F_3$	677.01(18)	677.06(35)	677.03(16)
$^3F_4$	1394.16(26)	1394.45(32)	1394.28(21)
$^1D_2$		2389.34(36)	2389.26(34)
$^3P_0$		3091.7(30)	3091.6(27)
$^1D_2^o$		1797(60)	1789.7(64)
$^3F_2^o$	2772.021(13)	2772.0	2772.021(13)
$^3F_3^o$	3096.15(20)	3096.1	3096.17(20)
$^3F_4^o$	4001.97(26)	4002.0	4002.04(23)
$^3D_1^o$	3221.99(3)	3221.5	3221.99(3)
$^3D_2^o$	3795.18(21)	3795.2	3795.19(21)
$^3D_3^o$	4345.69(20)	4345.7	4345.74(18)
Detachment threshold (^eA)		4496.97(20)	4496.91(17)

However, the energy levels of the anions come from a larger series of 12 measured transitions [2], to which one must add the more precise measurement of the $^3F_2 \rightarrow {}^3F_2^o$ [8] and $^3F_2 \rightarrow {}^3D_1^o$ [9,10] transitions made in 2015. A consistent method thus consists of complementing the data set to encompass the complete set of La$^-$ spectroscopic data [2,8–10]. As the best precisions obtained on detachment thresholds by Lu *et al.* [1] have quite a similar order of magnitude to that of Walter *et al.* [2], about 0.25 cm^{-1}, these main sets of data are expected to have comparable influences on the final variances and covariances of the energies to be determined, in the La$^-$-La system.

Along these lines, the vector of unknown quantities **X** should preferably be composed of all 11 energy levels of La$^-$ studied in one or the other group and the electron affinity ^eA(La). The energy levels of La I can also be formally considered as unknowns, but the much greater precision of the La I spectrum makes them practically invariant. In the present case, whatever the uncertainty attached to the energies given by the NIST table is up to a very conservative value of ± 0.015 cm^{-1}, all variations obtained for the La I energy levels remain smaller than 0.001 cm^{-1}, in absolute value.

The optimized energies are given by Table I, which shows that Lu *et al.* [1] have (i) not taken into account all the information contained in their own data to determine the $^3F_3$, $^3F_4$, $^1D_2$, and $^3P_0$ energy levels; (ii) unjustifiably rounded the $^3F_2^o$, $^3F_3^o$, $^3F_4^o$, $^3D_1^o$, $^3D_2^o$, and $^3D_3^o$ energies with respect to their predecessors' numbers; and (iii) failed to take Walter *et al.*'s measurement of the $^1D_2^o$ [2] into consideration, which has led to an uncertainty of this energy level that is 10 times too large.

The method used by Lu *et al.* [1] to determine the electron affinity of La, which consisted in subtracting the NIST-tabulated energy of the $^2F_{5/2}$ of La I, 7011.909 cm^{-1}, from the single threshold value a, 11508.88 cm^{-1}, appears inexpert. The attached uncertainty of ± 0.20 cm^{-1} does not allow for the uncertainty of the NIST-tabulated level, nor for the rounding error put in a final difference that makes 7011.909 equal to 7011.91 cm^{-1}, and should have been raised to ± 0.22 cm^{-1}. In contradistinction, the 4496.91(17) cm^{-1} figure drawn from the whole set of data in the present study does accommodate both the error and the uncertainty, and provides us with a much

more reliable, slightly smaller, value of the electron affinity of lanthanum.

In addition, an anomaly appears, in Table I of Lu *et al.* [1], as concerns thresholds h and w, starting from the $^1D_2^o$ level of La$^-$. Thresholds h and w have been measured by Lu *et al.* [1] with a precision of ± 60 and ± 40 cm^{-1}, respectively. Threshold w was measured by Walter *et al.* [2], who actually obtained a more precise figure of 0.3356(8) eV, or 2706.8(65) cm^{-1}. In the absence of any other known information on the $^1D_2^o$ level of La$^-$, this is definitely not enough to assign as precise an energy to thresholds h and w as ± 0.24 cm^{-1} [1]. This assigned uncertainty thus probably results from a confusion, by the authors, of the precision of the w threshold measurement by Walter *et al.* [2], actually ± 6.5 cm^{-1}, with the much better precision they got on discrete-to-discrete resonances only, actually ± 0.24 cm^{-1}.

III. CONCLUSION

The standard method of atomic spectroscopy has been applied to the detachment threshold measurements carried out by Lu *et al.* [1]. This has led to corrections of the published data, both for the involved atomic energy levels and the electron affinity of lanthanum, the latter found to be 449 691(17) m^{-1}, or 0.557 546(20) eV.

An error has been corrected concerning the precision of the only other measurement of a detachment threshold of lanthanum carried out by an independent team [2]. The good news from this revision is that all revised levels or transitions are still found inside their initial uncertainty bars, which confirms the consistency of the data and initial uncertainty estimates. This is one more reason not to deprive oneself of the efficiency of an optimal analysis of spectroscopic data.

ACKNOWLEDGMENTS

[1] Y. Lu, R. Tang, X. Fu, and C. Ning, Measurement of the electron affinity of the lanthanum atom, Phys. Rev. A **99**, 062507 (2019).

[2] C. W. Walter, N. D. Gibson, D. J. Matyas, C. Crocker, K. A. Dungan, B. R. Matola, and J. Rohlén, Candidate for Laser Cooling of a Negative Ion: Observations of Bound-Bound Transitions in La⁻, Phys. Rev. Lett. **113**, 063001 (2014).

[3] W. Ritz, On a new law of series spectra, Astrophys. J. **28**, 237 (1908).

[4] L. J. Radziemski, Jr., K. J. Fisher, D. W. Steinhaus, and A. S. Goldman, Calculation of atomic energy level values, Comput. Phys. Commun. **3**, 9 (1972).

[5] A. Kramida, The program LOPT for least-squares optimization of energy levels, Comput. Phys. Commun. **182**, 419 (2011).

[6] R. J. Peláez, C. Blondel, M. Vandevraye, C. Drag, and C. Delsart, Photodetachment microscopy to an excited spectral term and the electron affinity of phosphorus, J. Phys. B **44**, 195009 (2011).

[7] A. Kramida, Y. Ralchenko, J. Reader, and NIST ASD Team, *NIST Atomic Spectra Database (ver. 5.6.1)* (National Institute of Standards and Technology, Gaithersburg, MD, 2018), available at https://physics.nist.gov/asd [2019, September 25] .

[8] A. Kellerbauer, G. Cerchiari, E. Jordan, and C. W. Walter, High-resolution laser spectroscopy on bound-bound transitions in La⁻, Phys. Scr. **90**, 054014 (2015).

[9] E. Jordan, G. Cerchiari, S. Fritzsche, and A. Kellerbauer, High-Resolution Spectroscopy on the Laser-Cooling Candidate La⁻, Phys. Rev. Lett. **115**, 113001 (2015).

[10] G. Cerchiari, A. Kellerbauer, M. S. Safronova, U. I. Safronova, and P. Yzombard, Ultracold Anions for High-Precision Antihydrogen Experiments, Phys. Rev. Lett. **120**, 133205 (2018).