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Direct fit of spectroscopic data of diatomic molecules by using genetic algorithms: II. The ground state of RbCs

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Abstract

We extend our previous methodology based on genetic algorithms (Marques *et al* 2008 *J. Phys. B: At. Mol. Opt. Phys.* **41** 085103) to carry out the challenging fit of the RbCs potential curve to spectroscopic data. Specifically, we have fitted an analytic functional form to line positions of the high-resolution Fourier transform spectrum of RbCs obtained by a laser-induced fluorescence technique. The results for the ground electronic state of RbCs show that the present method provides an efficient way to obtain diatomic potentials with great accuracy.

1. Introduction

The study of diatomic alkali molecules has increased in the last few decades with the appearance of new techniques to produce cold and ultracold molecules; see [1–3] and references therein. The study of these systems has opened doors to scrutinize a new chemical regime. Furthermore, manipulation of these molecules has been treated as a possible device to a new stage of computers industry. Particularly, the heaviest heteronuclear alkali diatomics, RbCs, which has the largest permanent dipole moment among alkali diatomics, is a special candidate in the production of ultracold molecules. An *ab initio* electronic structure computation is a hard task for researchers in this area, since the large number of electrons in the RbCs molecule introduces the need of electronic correlation calculations, including relativistic effects, in order to describe the potential energy curve (PEC) in a better way. This cumbersome problem might be avoided by relying on a direct fitting procedure to spectroscopic information of the molecule.

In the last two decades or so, there has been great interest in the application of direct least-squares fitting procedures to obtain diatomic PECs from large sets of spectroscopic data in order to overcome difficulties arising from *ab initio* methods.

Basically, those procedures consist of fitting the parameters of the radial Hamiltonians associated with the electronic states of interest so that the experimental (rotational–vibrational and pure rotational) spectrum positions of lines are accurately reproduced by the corresponding eigenvalues. In addition, the associated atomic-mass-dependent Born–Oppenheimer breakdown (BOB) radial strength functions may also be obtained through this direct fitting procedure, provided that data are available for various isotopologues. It is worth noting in this context the pioneering work of Coxon and Hajigeorgiou [4–6] and Zimmermann and collaborators [7] who first developed numerical methodologies to perform the direct fits. Since then, many other groups [8–18] have explored and expanded upon the advantage of such methods. In turn, an algebraic approach has been suggested by Ogilvie [19, 20] to deal with the reduction of diatomic spectrum data to a compact set of parameters defining both potential energy and BOB radial functions. Over the years, the numerical and algebraic approaches have led to some apparent discrepancies between each other: Le Roy [13] has recently demonstrated that the source of such disagreement is simply due to the truncation convention adopted by Ogilvie for the Dunham

expansion as it is implemented in the RADIATOM program [19–26].

To obtain PECs to study rovibrational levels or the dynamics of a molecule, a large number of Rydberg–Klein–Rees (RKR) numerical potentials have been built in, through a direct semiclassical inversion method [27–29]. These numerical potentials can be used to describe nuclear dynamics of diatomic molecules. In spite of the great precision of these potentials, the semiclassical approach limits potential accuracy. With the purpose of overcoming these limitations, the inverse perturbation approach (IPA) was developed by Kosman and Hinze [30] and by Vidal and Scheingraber [31]. In opposition to the semiclassical RKR method, IPA has been established as a fully quantum mechanically approach to obtain PECs of diatomics, where corrections are taken as perturbative in a known (usually RKR) potential [32]. However, both RKR and IPA potentials are bounded by regions where vibrational levels are spectroscopically observed. Since these levels to dissociative states are almost never determined, the description of the dissociation region is a cumbersome problem to these methodologies.

Over the past 20 years, GAs have revealed to be a powerful tool for searching the global minimum structure of atomic and molecular clusters (see [33] and references therein), as well as for the optimization studies involved in protein folding [34, 35]. Although most of the work has focused on the development of effective GAs for global geometry optimization [36–46], there have also been applications to deal with the fitting process of experimental data (see [47, 48] and references therein). Since the spectral assignment is a very difficult problem, there are advantages in applying GAs to automate this tedious process [49–52], which was traditionally done by the visual identification of patterns. In addition, GAs have been successfully applied to fit other spectroscopic data: nuclear magnetic resonance [53], fluorescence/absorption spectra in polyatomic molecules [54], Mössbauer spectroscopy [55], multi-objective x-ray spectroscopic analysis [56], powder electron paramagnetic resonance (EPR) spectra [57] and near-infrared spectroscopic determination of diesel fuel parameters [58].

Recently, we have developed a real-valued GA that was successfully applied to fit the PECs of NaLi and Ar₂ to both *ab initio* data and experimental vibrational energies [59]. Indeed, the fit of these diatomic systems to an extended Rydberg function led to results with a root-mean-square-deviation (rmsd) of rovibrational levels of 0.008 cm⁻¹ (for Ar₂) and 0.184 cm⁻¹ (for NaLi). More recently, the same GA [59] has been applied to fit a potential function for Ar–C₆H₁₂ [60] and to obtain an analytical model for the interaction of the SiNCS⁺ and (CH₃)₂SiNCS⁺ ions with fluorinated self-assembled monolayers [61].

In this work, we aim to extend the test of the GA fitting methodology to a more challenging RbCs diatomic system. Whilst the direct fits in our previous work [59] used 6 (48) vibrational energy levels for Ar₂ (NaLi), a total number of 2152 experimental spectral line positions are employed here for the ground electronic state of RbCs. Thus, the main goal is to obtain the PEC, with spectroscopic

accuracy, of the RbCs ($X^1\Sigma^+$) molecule from a direct fit procedure of experimental data obtained by Gustavsson *et al* [62, 63] and Fellows *et al* [64]. Specifically, we have employed the experimental wavenumbers of transitions between rovibrational levels of an excited electronic state and the ones of the ground electronic state. For this purpose, we relied on the hybrid real-valued GA previously proposed by us [59] to perform a nonlinear least-squares fit to rovibrational spectra information. The plan of this paper is as follows. In section 2, the genetic algorithm and the fitting procedure, including the functional form of PEC, are briefly described. A discussion about the results for fitting the spectra of RbCs is given in section 3. Conclusions and final remarks are presented in section 4.

2. Methodology

Our direct fit procedure can be seen as the general problem of finding the best set of parameters $\mathbf{z} \equiv (z_1, z_2, \dots, z_n)$ that minimize an objective function:

$$\chi^2(\mathbf{z}) = \sum_{j=1}^N \omega_j [f_j(\mathbf{z}) - y_j]^2, \quad (1)$$

where y_j designates the j th data point of the set of N experimental ones, ω_j is the weight given to y_j and $f_j(\mathbf{z})$ is a model function that represents the experimental y_j from \mathbf{z} parameters obtained by the fitting procedure.

In the present case, the experimental data are wavenumbers determined from v'' -progressions of transitions between a (v', J') rovibrational level of an excited electronic state and (v'', J'') rovibrational ones of the $X^1\Sigma^+$ electronic state of RbCs. These v'' -progressions were obtained by Gustavsson *et al* [62, 63] and Fellows *et al* [64] employing a Fourier transform spectroscopy to analyse spectra of laser-induced fluorescence (LIF); the experimental details can be found in these references. As we are only interested in the ground electronic state, we take the differences between the highest experimentally determined term value and the other lower ones of the same v'' -progression. These differences from various v'' -progressions are what we have called y_j in equation (1). Thus, the model function $f_j(\mathbf{z})$ represents the theoretical estimative of the term values difference (y_j).

To calculate $f_j(\mathbf{z})$, it is necessary to know the theoretical rovibrational energies, $E_{v'', J''}^{\text{theo}}$, for an adjustable analytical potential function, $V^{\text{fit}}(R; \mathbf{z})$. These eigenenergies are obtained by solving the following radial Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V^{\text{fit}}(R; \mathbf{z}) + \frac{\hbar^2 J''(J'' + 1)}{2\mu R^2} \right] \psi_{v'', J''}(R) = E_{v'', J''}^{\text{theo}}(\mathbf{z}) \psi_{v'', J''}(R), \quad (2)$$

where μ designates the reduced mass of the RbCs system, while $\psi_{v'', J''}(R)$ is the (v'', J'')-state rovibrational wavefunction. Here, we have solved equation (2) by using the discrete variable representation (DVR) method with an equally spaced grid [65–69].

The adjustable analytical function that we have employed to represent the PEC of the $X^1\Sigma^+$ electronic state of RbCs is

Table 1. Range of experimental data for direct fit. The ranges are defined by the J'' and v'' range of each employed v'' -progression.

n	J''	v'' range	n	J''	v'' range	n	J''	v'' range
1	4	2–26	21	83	12–58	41	123	3–78
2	4	5–20	22	83	27–81	42	123	37–99
3	24	14–38	23	97	1–111	43	129	0–39
4	24	94–114	24	97	42–98	44	129	12–68
5	24	5–19	25	97	13–56	45	135	0–53
6	39	12–119	26	101	40–104	46	135	24–85
7	39	2–37	27	101	0–42	47	143	8–58
8	44	0–118	28	104	2–54	48	143	25–75
9	44	1–36	29	104	0–44	49	148	0–48
10	52	37–54	30	104	44–109	50	148	29–85
11	52	1–115	31	107	20–65	51	152	13–71
12	68	0–43	32	107	3–46	52	152	3–47
13	68	37–90	33	107	2–81	53	160	7–78
14	68	36–108	34	107	0–46	54	169	8–61
15	71	2–116	35	113	21–80	55	169	0–36
16	71	12–58	36	113	29–85	56	174	8–61
17	79	1–119	37	113	3–47	57	174	1–37
18	79	25–63	38	113	14–57	58	186	24–73
19	79	5–50	39	118	0–47	59	206	1–47
20	79	13–44	40	118	14–64	60	237	0–44
						61	259	0–42

the following:

$$V^{\text{fit}}(R) = \left(\sum_{i=1}^5 a_i R^{i-2} \right) e^{-(a_6 R + a_7 R^2)} - \sum_{k=3}^5 f_{2k}(a_8 R) \frac{C_{2k}}{R^{2k}}, \quad (3)$$

where

$$f_{2k}(a_8 R) = 1 - e^{-a_8 R} \sum_{i=0}^{2k} (a_8 R)^i / i!$$

are the Tang–Toennies damping functions [70] and the parameters C_n , $n = 6, 8, 10$, are the dispersion coefficients. The $\{a_j\}$, $j = 1, \dots, 8$, parameters and the dispersion ones are the fitting parameters. This potential function was originally proposed by Korona *et al* [71], and its extension has been carried out by Patkowski *et al* [72] to describe the *ab initio* potential for argon dimer. Moreover, new $\{a_j\}$ parameters were included following the strategy employed by Prudente *et al* [73] to fit *ab initio* PECs for LiH and H₂ diatomic molecules.

The determination of the fitting parameters is performed in this work by using a hybrid real-valued GA, where the evolutionary algorithm is complemented by a local search procedure. GAs are unbiased and robust search procedures and therefore are particularly effective in multimodal fitness landscapes with a large number of local minima. Basically, we want to find out the parameter values ($\mathbf{z} = a_1, \dots, a_8, C_6, C_8, C_{10}$) of equation (3) that provide the best least-squares fit of a model function $f_j(\mathbf{z})$ to a data set of N points y_j . According to the standard GA terminology, each parameter z_i is a gene, a specific set of parameters \mathbf{z} (i.e. a solution) is an individual and a group of individuals forms the population. The iterative processing of successive populations is guided by the two fundamental forces of evolutionary systems: a probabilistic selection mechanism gives preference to high-quality individuals from the current population and,

afterwards, variation operators are applied to the selected set to obtain new solutions. These new individuals are then subjected to a local minimum search procedure, to guide each one of them to the nearest local optimum.

The probabilistic variation operators applied to selected individuals are known as genetic operators. The GA adopted in this work applies both crossover and mutation operators to obtain the new solutions. In our previous work [59], we studied the behaviour of two crossover operators, the one-point crossover and simulated binary crossover (SBX), and two mutation operators, the sigma mutation and random mutation (see the aforementioned reference for details concerning the application of these operators). A detailed analysis led us to conclude that the combination of SBX and sigma mutation helped to enhance the effectiveness of the GA when searching for good quality solutions. In accordance with this previous result, we apply these two operators in the work described in this paper.

The L-BFGS (acronym of Broyden–Fletcher–Goldfarb–Shanno limited memory quasi-Newton) method [74, 75] was adopted as the local optimization method applied to each solution generated by the GA. This is an iterative procedure that only requires the knowledge of $f_i(\mathbf{z})$ and its derivatives, which can be determined by the Hellmann–Feynman theorem [76]. For more details about the GA components and the way they work together, the reader is referred to our previous paper [59].

3. Results and discussion

In this section, we present the results to the direct fit of $X^1\Sigma^+$ PEC of RbCs by using a GA. The experimental data were obtained from 61 v'' -progressions determined by Gustavsson *et al* [62, 63] and Fellows *et al* [64], in a total of $N = 2152$ differences of term values of RbCs spectra. As can be seen in table 1, these selected v'' -progressions span all 120

Table 2. Parameters obtained by the direct fit GA procedure. The a_i parameters are given in atomic units, where distances are given in Bohr and the energy is given in Hartree.

a_1	-1.950 4268
a_2	0.395 934 61
a_3	8.293 3763
a_4	-0.025 994 82
a_5	-0.000 306 92
a_6	0.113 518 98
a_7	0.033 213 60
a_8	0.875 091 16
$C_6(10^6\text{cm}^{-1}\text{\AA}^6)$	29.783 746
$C_8(10^8\text{cm}^{-1}\text{\AA}^8)$	11.085 596
$C_{10}(10^{10}\text{cm}^{-1}\text{\AA}^{10})$	4.850 8464
$\sigma(\text{cm}^{-1})$	0.56

vibrational states and different values of J'' , including high values for it. This guarantees a reasonably good distribution of the rovibrational term values of RbCs spectra. As we are treating spectroscopic information of only one type, i.e. which is formed by positions of spectral lines of RbCs with similar accuracy, we assign all the fitting weights (ω_j) as one in equation (1). Thus, the rmsd between experimental and fitted data is given by $\text{rmsd} = \sqrt{\chi^2/N}$. To compute the energy levels of the ground electronic state, we have utilized 800 DVR basis functions equally distributed on the range from 4.0 a_0 to 40.0 a_0 . This guarantees the convergence of eigenenergies at least of 10^{-3} cm^{-1} .

For the present calculations, the settings of the GA are the following: number of runs, 8; objective-function evaluations, 3×10^3 ; population size, 12; tournament selection with tourney size, 2; crossover operators, SBX; mutation operators, Sigma; σ , 0.1; crossover rate, 1.0; mutation rate, 0.1; maximum number of iterations of the local optimization method, 1000 (see [59] for more details). It is worth noting that we do not set a maximum number of generations. Instead, we specify the maximum number of objective-function evaluations (which also includes the evaluations during the local optimization). The GA iteratively generates new populations and stops when it reaches the above-mentioned 3×10^3 calls to the evaluation function. The numerical values of the best set of parameters are given in table 2. Moreover, we represent in the same table the rmsd value between the fitted and experimental rovibrational term value differences.

In figure 1, we present the difference between the vibrational energy levels determined by solving the Schrödinger radial equation with the potential determined in fit and the energy levels determined from a Dunham-type expansion performed by Fellows *et al* [64]. We are able to see that, to lower vibrational states, the difference between vibrational energies is very small, indicating the quality of our results. Although oscillating, the major difference never reaches 0.5 cm^{-1} , except to higher vibrational states near the dissociation energy, where the difference oscillates stronger than to the lowest states. Table 3 contains both vibrational levels of energy.

The plot of the difference between the IPA potential and the one obtained by the fit is shown in figure 2. The higher difference is noted in the repulsive range where the

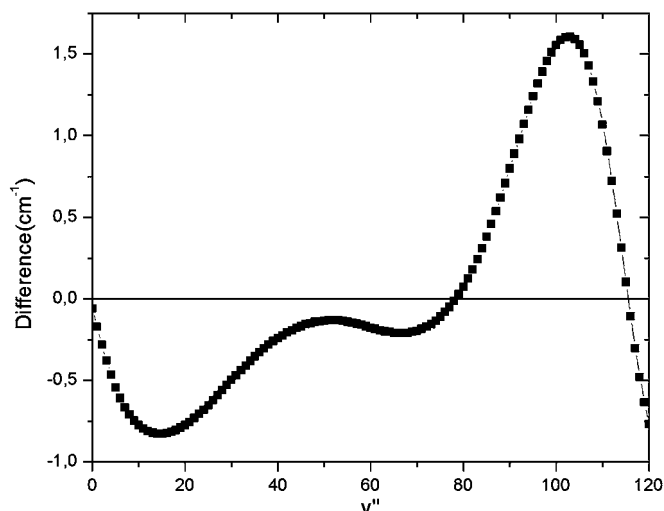


Figure 1. Difference between the vibrational energies obtained by the direct fit GA procedure and the experimental ones determined by Fellows *et al* [64].

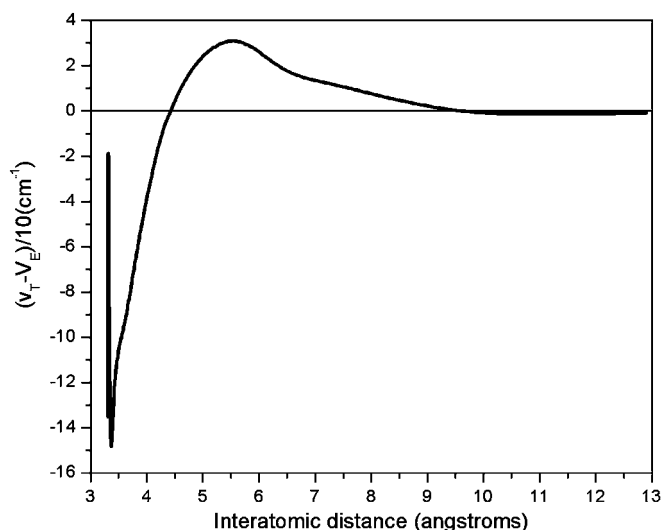


Figure 2. Difference between the PEC of the direct fit GA procedure (V_T) and IPA methodology (V_E) [64].

deviation reaches several tens of cm^{-1} . Note that a part of this discrepancy is due to the ill-posed behaviour of IPA potential to short distances. Furthermore, the behaviour of the fitted potential to the dissociation range is really good, approaching near to zero and allowing us to describe dissociation energy in a very good way. The discrepancy in the repulsive region could be the cause of the greater difference to the highest vibrational states observed in figure 1. In figure 3, we plot both curves just for a simplified comparison.

In table 4, our results are compared with the theoretical [77, 78] and experimental [62, 64] results previously presented in the literature. The theoretical results were calculated using *ab initio* CI methodology with different treatment of core-valence effects. Spectroscopic constants are of great interest in the interpretation of spectra of diatomics. One of these constants is the interatomic equilibrium distance, which is in better agreement with the experimental one of Gustavsson

Table 3. The vibrational energy levels obtained by the direct fit GA procedure and the experimental ones [64]. The last six experimental levels were extrapolated by Fellows *et al* [64].

v	$G_v(\text{fit})$	$G_v(\text{exp})$	v	$G_v(\text{fit})$	$G_v(\text{exp})$	v	$G_v(\text{fit})$	$G_v(\text{exp})$
0	24.910	24.970	42	1913.533	1913.741	84	3284.598	3284.288
1	74.587	74.761	43	1952.994	1953.187	85	3308.849	3308.468
2	124.056	124.337	44	1992.167	1992.346	86	3332.631	3332.175
3	173.315	173.695	45	2031.048	2031.215	87	3355.939	3355.402
4	222.363	222.830	46	2069.634	2069.792	88	3378.765	3378.144
5	271.199	271.742	47	2107.925	2108.074	89	3401.101	3400.393
6	319.820	320.429	48	2145.915	2146.057	90	3422.941	3422.144
7	368.226	368.890	49	2183.603	2183.740	91	3444.277	3443.389
8	416.416	417.125	50	2220.985	2221.118	92	3465.101	3464.122
9	464.387	465.132	51	2258.059	2258.191	93	3485.404	3484.335
10	512.137	512.912	52	2294.821	2294.953	94	3505.180	3504.024
11	559.667	560.462	53	2331.269	2331.402	95	3524.420	3523.180
12	606.973	607.784	54	2367.399	2367.535	96	3543.116	3541.796
13	654.055	654.876	55	2403.208	2403.349	97	3561.258	3559.867
14	700.910	701.736	56	2438.692	2438.839	98	3578.840	3577.384
15	747.537	748.364	57	2473.849	2474.003	99	3595.852	3594.341
16	793.935	794.758	58	2508.675	2508.836	100	3612.285	3610.731
17	840.101	840.917	59	2543.166	2543.335	101	3628.133	3626.546
18	886.034	886.840	60	2577.319	2577.496	102	3643.385	3641.781
19	931.732	932.524	61	2611.130	2611.315	103	3658.035	3656.429
20	977.194	977.968	62	2644.595	2644.788	104	3672.074	3670.484
21	1022.417	1023.172	63	2677.711	2677.911	105	3685.496	3683.940
22	1067.400	1068.132	64	2710.474	2710.679	106	3698.295	3696.792
23	1112.141	1112.848	65	2742.879	2743.088	107	3710.464	3709.036
24	1156.638	1157.318	66	2774.923	2775.134	108	3721.999	3720.668
25	1200.889	1201.541	67	2806.601	2806.812	109	3732.897	3731.687
26	1244.893	1245.515	68	2837.909	2838.118	110	3743.158	3742.090
27	1288.646	1289.238	69	2868.843	2869.047	111	3752.780	3751.877
28	1332.148	1332.708	70	2899.398	2899.595	112	3761.768	3761.049
29	1375.396	1375.925	71	2929.570	2929.756	113	3770.128	3769.606
30	1418.388	1418.886	72	2959.354	2959.526	114	3777.867	3777.554
31	1461.122	1461.589	73	2988.744	2988.900	115	3784.997	3784.896
32	1503.596	1504.033	74	3017.737	3017.872	116	3791.533	3791.640
33	1545.808	1546.216	75	3046.327	3046.438	117	3797.494	3797.796
34	1587.755	1588.135	76	3074.508	3074.591	118	3802.901	3803.381
35	1629.435	1629.789	77	3102.277	3102.327	119	3807.776	3808.412
36	1670.847	1671.175	78	3129.626	3129.639	120	3812.147	3812.914
37	1711.987	1712.291	79	3156.550	3156.522	121	3816.040	3816.907
38	1752.853	1753.135	80	3183.045	3182.970	122	3819.482	3820.413
39	1793.443	1793.705	81	3209.103	3208.977	123	3822.503	3823.468
40	1833.755	1833.997	82	3234.718	3234.536	124	3825.131	3826.132
41	1873.786	1874.010	83	3259.885	3259.642	125	3827.393	3828.667

Table 4. Spectroscopic constants for the ground state of the RbCs molecule.

	R_e (Å)	D_e (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (10 ² cm ⁻¹)
Present	4.410	3836.1	50.33	0.1241	1.673 0
Fellows <i>et al</i> [64]	4.4272	3836.1	50.0137	0.109 529	1.660 059
Gustavsson <i>et al</i> [62, 63]	4.418	3845	50.013 58	0.109 83	1.660 092
Pavolini <i>et al</i> [77]	4.385	4183	45.60		
Allouchet <i>et al</i> [78]	4.379	3873	51.35		1.690

and co-workers [62, 63] than other theoretical ones, e.g. Pavolini *et al* [77] and Allouchet *et al* [78]. The discrepancies between our result and experimental ones are about 0.008 Å for Gustavsson *et al* [62] and 0.017 Å for Fellows *et al* [64]. Comparing it with that obtained by Pavolini *et al* and Allouchet *et al*, the discrepancies between them and the experimental ones are, respectively, 0.033 and 0.039 Å. Both theoretical works have underestimated the equilibrium distance value. R_e

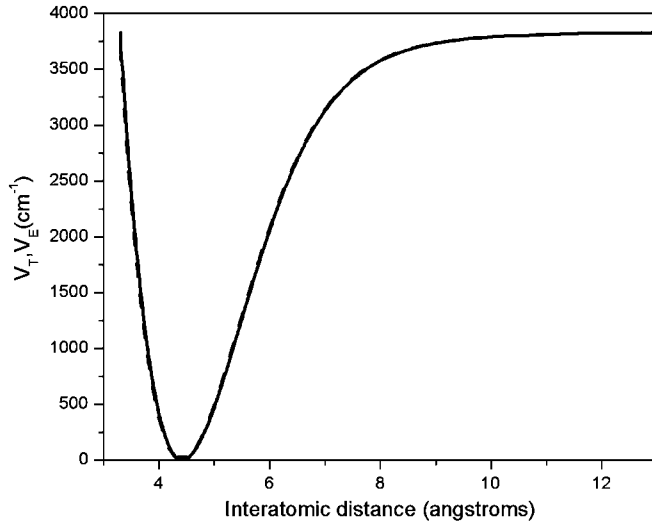
was obtained by a direct observation of the curve and the error in this determination is around the discrepancy magnitude.

The same can be stated to dissociation energy D_e . We have estimated a dissociation energy of around 3836.1 cm⁻¹ by using the following expression of the asymptotic approach:

$$V(r) = D_e - \frac{C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}}. \quad (4)$$

Table 5. Multipolar electrostatic coefficients (C_6 , C_8 and C_{10}) for the ground state of the RbCs molecule.

	$C_6(10^6\text{cm}^{-1}\text{\AA}^6)$	$C_8(10^8\text{cm}^{-1}\text{\AA}^8)$	$C_{10}(10^{10}\text{cm}^{-1}\text{\AA}^{10})$	$\chi_4 = C_6C_{10}/C_8^2$
Present	29.783 746	11.085 596	4.850 8464	1.18
Marinescu <i>et al</i> [80]	25.466	9.859	4.0932	1.07
Patil <i>et al</i> [81]	26.42	9.597	3.629	1.04
Bussery <i>et al</i> [82]	35.44	11.97		
Dalgarno <i>et al</i> [83]	25.88			
Fellows <i>et al</i> [64]	26.403	11.57	4.3	0.85
Fellows <i>et al</i> [64]	26.377	11.62	4.3	0.84
Fellows <i>et al</i> [64]	26.241	11.66	4.4	0.85

**Figure 3.** PEC of the $1^1\Sigma^+$ state of RbCs: the dashed line represents the potential of the direct fit GA procedure and the solid line represents the IPA methodology curve [64].

This is an approximation to describe the potential for long internuclear separations. The multipolar approach is possible since, in that range of internuclear separations, the overlap of the electronic cloud can be neglected and the atoms can be treated as compounded by multipolar electrostatic terms [79]. Our D_e estimative is essentially the same as the more recent experimental results of Fellows *et al* [64], and it differs from the Gustavsson *et al* experimental one by 9.1 cm^{-1} . The result that we have found also agrees in a better way than the theoretical ones, which differ by several tens of cm^{-1} . In Pavolini *et al*'s [77] work, this difference is even bigger than 300 cm^{-1} .

Moreover, we have also computed the B_e value with the estimated value of R_e to the analytical potential, since it is given in a first approximation by $\hbar^2/2\mu R_e^2$. This value is in excellent agreement with the experimental one, as can be seen in table 4. Our result essentially matches, within our precision limited by the R_e determination, with the experimentally determined ones by Fellows *et al* [64] and Gustavsson *et al* [62]. The theoretical value that we have found in the literature is the one obtained by Allouchet [78], which has a small discrepancy with respect to the experimental result. Note that, as expected, our results show better agreement with experimental results than theoretical ones because here we performed a direct fit from spectroscopic data, while the theoretical results were

based on *ab initio* methodologies without any experimental information.

In table 5, we present the coefficients of multipolar electrostatic expansion of the interaction between the two atoms of the diatomic molecules. The coefficients determined in this work are compared with other values found in the literature [80–83]. Our results differ by 10–15% from the other ones, but compared to experimental results, the relative difference is not larger than 10%. One feature of the determination of dispersion coefficients in this work is that they are obtained by a direct fit of experimental results. Moreover, it should be emphasized that the results of Fellows *et al* [64] were obtained by the fit of expression (4) and other similar ones, where the exchange energy and damping functions are considered, to the IPA numerical potential, which is just an approximation of experimental information [84].

Furthermore, our results present the best agreement to multipolar electrostatic coefficients considering an experimental estimation of $\chi_4 = C_6C_{10}/C_8^2$, as suggested by Le Roy [85], to the coefficients that describe long-range potentials related to electronic states of Σ symmetry. In particular, Le Roy suggests that χ_4 is close to $4/3$ based on the observation of this dimensionless ratio to the ground state of diatomic inert gases and ground and excited states of the H_2 molecule. Our χ_4 result presents the best estimation also considering the results present by Takkar [86] and Mulder *et al* [87], which suggest from *ab initio* analysis that χ_4 should be higher than 1.2. As before, our χ_4 result is very close to the *ab initio* speculation, indicating a good estimative for the C_6 , C_8 and C_{10} dispersion coefficients.

4. Conclusions and final remarks

We proposed a hybrid GA fitting procedure to obtain diatomic potential curves with spectroscopic accuracy. The method was applied to RbCs, a complex system to be handled by *ab initio* methodologies since the huge number of electrons in its configuration introduces a great problem in computation of correlation electronic energy. Specifically, we have fitted a simple functional form of PEC to spectroscopic data. The method has proved to be accurate for searching the best parameters that fit the spectrum information.

This methodology may be extended to other analytic diatomic potentials, e.g. the extended Rydberg function which has been employed in our previous work about NaLi and Ar_2 [59]. Moreover, the application of the GA method to fit diatomic PECs directly to the experimental line positions

resulting from transitions between the rovibrational levels of the electronic excited state and the corresponding ones of the electronic ground state is straightforward, allowing us to perform a real direct fit of the spectrum information without auxiliary quantities retrieved from the spectrum, as RKR potentials or rovibrational levels of energy obtained by the Dunham fit.

The prospect of fitting both electronic states of the analysed system of bands here is a challenging task and the results of this work encourage us to pursue it. The only new requested information to comprise a double fit is the knowledge of the rovibrational excited state associated with analysed progression.

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