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A Na_2 $X^1\Sigma_g^+$ and $(1)^1\Pi_g$ electronic states long range analysis

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Abstract. In this paper the Na_2 $X^1\Sigma_g^+$ and $(1)^1\Pi_g$ electronic states long range tail functional behavior is analysed in the light of multipolar expansion theory combined with damping functions. The experimental data used here is the one reported by Barrow et al. [1]. In the present paper this experimental data is used in a nonlinear reduction to van der Waals C_n constants using the multipolar expansion $\sum_n C_n/r^n$. Since the internuclear distance reached by the biggest part of the data is still out of the Le Roy's region (where the internuclear distance must be grater than r_{lim}:

$$r_{lim} = 2(\langle r_A^2 \rangle^{1/2} + \langle r_B^2 \rangle^{1/2}),$$

being the outermost electron orbital radii for the $\langle r_A \rangle$ and $\langle r_B \rangle$ two atoms), the exchange energy must be taken into account. Due to the fact that the $1/r^n$ expansion diverges when $r \to 0$, the damping functions has been included in order to prevent this. The obtained values for the C_n coefficients, as well as the exchange energy constants, show a good agreement with the theoretical available data, for both electronic states.

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1. Introduction

The Na_2 molecule is one of the most studied diatomic molecules. The sodium dimer is one of the few diatomic molecules whose spectra were observed during the last century [2], long before the first theoretical models were established for the interpretation of the spectral lines. Ever since, the sodium dimer has been very studied by classical and laser spectroscopy by several groups. From the theoretical point of view this molecule is of great interest since its quite simple structure can serve as a good test for new calculation models. An extensive review involving all this studies can be found in the article by Verma et al. [3] and in the references therein.

In spite of the enormous amount of work done since 1874, there still remains a lot to be done in the Na_2 molecule spectroscopy alone. To prove this assertion, this paper presents a long range study in one of the most studied electronic states of diatomic molecules, the $X^1\Sigma_g^+$ ground electronic state, and the $(1)^1\Pi_g$ excited electronic state. This study has been done using the experimental data from Barrow et al. [1]. This data, for both electronic states, has been observed by Laser Induced Fluorescence combined with Fourier Transform Spectroscopy. The reported potenial energy curves cover a range from $v = 45$ to $v = 62$ for the $X^1\Sigma_g^+$ electronic state and $v = 39$ to $v = 52$ for the $(1)^1\Pi_g$ electronic state.

2. Analysis

Long range developments

The long range behavior of the potential energy curves, $V(r)$, for both electronic states, $X^1\Sigma_g^+$ and $(1)^1\Pi_g$, has been treated in the article of Barrow et al., using a multipolar expansion:

$$V(r) = D_e - \sum_n \frac{C_n}{r^n} \tag{1}$$

where D_e is the dissociation energy of the considered electronic state, r is the external turning point and the C_n coefficients are the second order perturbation van der Waals constants. Combined with this multipolar expansion, the exchange energy E_{exc} was introduced, in the way that the long range part of the potential energy curve could be described by the following development:

$$V(r) = D_e - \sum_n \frac{C_n}{r^n} - E_{exc}. \tag{2}$$

The reason to introduce the exchange term was that the greatest part of the experimental data was still below the Le Roy's limit. In his article LeRoy [4] suggests

a lower limit for the internuclear distance r_{lim} where the multipolar expansion (1) can be used without considering exchange terms, and r_{lim} is calculated by:

$$r_{lim} = 2(\langle r_A^2 \rangle^{1/2} + \langle r_B^2 \rangle^{1/2}), \qquad (3)$$

where $\langle r_A \rangle$, $\langle r_B \rangle$ denote the outermost electron orbital radii for the two different atoms. Considering that the expectation values $\langle r^2 \rangle$ for the Na $3s$ and $3p$ atomic states, calculated by Hartree-Fock method, are $17.738\ \text{Å}^2$ [5] and $41.857\ \text{Å}^2$ [6], respectively, a r_{lim} values of 16.847 Å for the $X\ ^1\Sigma_g^+$ ground electronic state and 21.363 Å for the (1) $^1\Pi_g$ excited electronic state can be obtained by LeRoy's limit (3).

Another point that should be considered is the dispersion terms C_n used in the multipolar expansion (2). In the $X\ ^1\Sigma_g^+$ ground state, considering this electronic state as a product of two S-state atoms, the van der Waals coefficients with $n = 6, 8$ and 10 will contribute to the potential. On the other side, in the (1) $^1\Pi_g$ electronic excited state the leading term in (2) is $n = 3$. This first order perturbation term arises as a "*resonance*" interaction between a pair of atoms of the same species which are in electronic states between which electric dipole transitions are allowed [7]. For the (1)$^1\Pi_g$ electronic state the term $n = 6$, that *always* contribute to te potential [4], has been added to the truncated development.

The choice of the experimental data points to be used in the calculations for the $X\ ^1\Sigma_g^+$ electronic ground state, has been done following the criterium that the term $m + 2$ of the inverse-power expansion (2) is no longer valid for internuclear distance values $r \lesssim (2C_{m+2}/C_m)^{1/2}$ [8–11]. Using the theoretical C_8 and C_{10} values reported by Tang et al. [12], the calculated limit for the r value to be used is 7.3 Å. Considering that this value is not a strict one, that a maximum number of experimental data is needed and in order to compare with the previous work by Barrow et al. [1], the data points used start with $r = 7.1963$ Å. The data points used for the $X\ ^1\Sigma_g^+$ electronic ground state are shown in Table 1, being those reported in Barrow's et al. article.

For the (1) $^1\Pi_g$ electronic excited state, since no criterium linking the C_n coefficients and the external turning points has been ever established, we used in our calculations the same data set used in Barrow's article [1]. The data points used in the calculations for this state are shown in Table 2.

Table 1. Vibrational term-values $G(v'')$ and outer turning points $r(\mathring{A})$ for the $X\ ^1\Sigma_g^+$ electronic ground state used in the calculations

v''	$G(v'')$ (cm^{-1})	$r(\mathring{A})$
55	5913.599	7.1963
56	5940.206	7.4575
57	5962.606	7.7689
58	5980.870	8.1493
59	5995-155	8.6279
60	6005.748	9.2517
61	6013.094	10.0922
62	6017.856	11.2310

Table 2. Vibrational term-values $G(v'')$ and outer turning points $r(\mathring{A})$ for the (1) $^1\Pi_g$ electroic ground state used in the calculations

v''	$G(v'')$ (cm^{-1})	$r(\mathring{A})$
39	22839.900	11.2310
40	22850.601	11.4992
41	22860.691	11.7787
42	22870.194	12.0700
43	22879.135	12.3735
44	22887.538	12.6899
45	22895.427	13.0197
46	22902.825	13.3638
47	22909.755	13.7231
48	22916.238	14.0988
49	22922.290	14.4928
50	22927.926	14.9077
51	22933.155	15.3475
52	22937.980	15.8180

Direct fitting of the external turning points

A simple question should be placed here. "Why to perform new calculations in this long range part of both potential energy curves if they have been already performed by Barrow et al. [1]?" The answer is quite simple and there are two reasons to do these new calculations.

The first one is that in Barrow's article [1], the van der Waals coefficients, as well as exchange energy constants A and a, used in the multipolar expansion were theoretical ones and they have been held fixed in all calculations. Actually in their article a simple inversion of (2) is performed in order to calculate the dissociation energy D_e for each external turning point r, using fixed C_n and exchange energy constants. After that a mean value for the dissociation energy has been calculated using the values for D_e obtained for each r value.

In our case, we start with theoretical C_n coefficients from Tang et al. [12] for the $X\ ^1\Sigma_g^+$ electronic ground state and from Bussery and Aubert-Frécon [13] for the (1) $^1\Pi_g$ electronic excited state, being their numerical values varied in order to adjust the experimental points in a non-linear fit using (2) to represent the long range part of the potential energy curve. The choice of these two sets of C_n constants have been done considering that: a) the C_n coefficients calculated by Tang et al. [12] have been used in NaLi [14] and RbCs [15] with very good results, and b) the Bussery and Aubert-Frécon [13] calculated coefficients were the same used by Barrow et al. and was not so different from the previous calculated coefficients.

The expansion (2) is truncated to $n = 6, 8, 10$ for the $X\ ^1\Sigma_g^+$ electronic ground state, and to $n = 3, 6$ for the (1) $^1\Pi_g$ electronic excited state, by the reasons explained above.

The second reason to perform these new calculations concerns basically the $X\ ^1\Sigma_g^+$ electronic ground state. Following observations from molecular states that arise from pairs of S atomic states, an empirical relation between C_{10}, C_8 and C_6 coefficients, has been suggested by LeRoy [16];

$$C_{10} \approx \frac{4}{3} (C_8)^2/C_6. \qquad (4)$$

This relation has already been used to correct, successfully, the C_{10} values in the NaLi molecule [14]. It can be observed, and we will return later to this point, that both set of C_n constants used by Barrow et al. [1] in their calculations do not match this empirical relation.

3. Results

The exchange energy term

Considering, as explained above, that the exchange energy must be introduced in our calculations, a functional form should be chosen in order to represent it. A single exponential form like,

$$E_{\text{exc}} = A e^{-ar}, \qquad (5)$$

proposed by Mason and Monchick [17] is the most commonly used. Here A and a are adjustable constants and r is the internuclear distance. For the electronic states of alkaline metal diatomics, formed by atoms in the S state, an analytical functional form has been proposed by Smirnov and Chibisov [18]. For homonuclear species this function takes the form:

$$E_{\text{exc}} = \mathscr{A} r^\gamma e^{-\delta r}, \qquad (6)$$

where $\mathscr{A}$, γ and δ are adjustable parameters.

In a first step the functional form (5), representing the exchange energy, has been used combined with multi-polar expansion (2) for both states. For both electronic states the fit of the $V(r)$ potential energy values has been performed using the following procedure:

Firstly all the coefficients were left free and the calculations performed. As departure parameters D_e values for each electronic state from Barrow et al. [1], the Tang et al. [12] theoretical values for C_6, C_8 and C_{10} coefficients for the $X\,^1\Sigma_g^+$ electronic ground state, the theoretical values from Bussery and Aubert-Frécon [13] for C_3 and C_6 for the (1) $^1\Pi_g$ excited state and the theoretically calculated values for A and a from Konowalow and Rosenkrantz [19], for both states, have been used.

Secondly, D_e, C_6, C_8 and C_{10} parameters for the $X\,^1\Sigma_g^+$ electronic ground state, or D_e, C_3 and C_6 for the (1) $^1\Pi_g$ excited state, have been held fixed with the values obtained in the first step and A and a calculated as free parameters.

After that A and a have been held fixed with the values obtained in the second step, for each electronic state, and D_e and C_6 for the $X\,^1\Sigma_g^+$ electronic ground state and D_e and C_3 for the (1) $^1\Pi_g$ excited electronic state, fixed with values calculated in the first step. C_8 and C_{10} for the $X\,^1\Sigma_g^+$ state and C_6 for the (1) $^1\Pi_g$ state are then left free to calculations.

Finally, D_e and C_6 for the $X\,^1\Sigma_g^+$ ground state and D_e and C_3 for the (1) $^1\Pi_g$ state are left free, and all other coefficients fixed with their last obtained values, for each state.

The last three stages have been repeated for each electronic state, until a convergence was reached for all determinations. Table 3a show the results for the electronic ground state $X\,^1\Sigma_g^+$. The results for the (1) $^1\Pi_g$ electronic excited state are shown in Table 4a.

Table 3. Dissociation energy value D_e, van der Waals coefficients C_n, exchange energy parameters for the $X\,^1\Sigma_g^+$ electronic ground state calculated as explained in the text

	a	b	c	d	e
$D_e(\text{cm}^{-1})$	6022.11 $\pm$ 0.04	6022.09 $\pm$ 0.04	6022.6 $\pm$ 1.0	6022.6 $\pm$ 1.0	
$C_6(\text{cm}^{-1}\,\text{Å}^6)$	7.300×10^6	7.297×10^6	8.18×10^6	8.10×10^6	7.277×10^6
$C_8(\text{cm}^{-1}\,\text{Å}^8)$	1.476×10^8	1.487×10^8	1.39×10^8	2.21×10^8	1.498×10^8
$C_{10}(\text{cm}^{-1}\,\text{Å}^{10})$	0.416×10^{10}	0.410×10^{10}	0.26×10^{10}	0.26×10^{10}	0.404×10^{10}
$A(\text{cm}^{-1})$	1.730×10^6		7.57×10^4	7.57×10^4	
$a(\text{Å}^{-1})$	1.552		1.226	1.226	
$\mathscr{A}(\text{cm}^{-1})$		3.316×10^5			
γ		1.630			
$\delta(\text{Å}^{-1})$		1.770			
R_L	1.394	1.353	1.101	0.431	1.310

Table 4. Dissociation energy value D_e, van der Waals coefficients C_n, exchange energy parameters for the (1) $^1\Pi_g$ electronic excited state calculated as explained in the text

	a	b	c	d
$D_e (\text{cm}^{-1})$	22990.90 $\pm$ 0.09	22993.6 $\pm$ 1.0	22993.6 $\pm$ 1.0	
$C_3 (\text{cm}^{-1}\,\text{Å}^3)$	2.052×10^5	2.11×10^5	2.16×10^5	2.034×10^5
$C_6 (\text{cm}^{-1}\,\text{Å}^6)$	12.225×10^6	12.78×10^6	14.00×10^6	12.94×10^6
$A (\text{cm}^{-1})$	7.567×10^4	5.42×10^5	5.42×10^5	
$a(\text{Å}^{-1})$	1.294	1.226	1.226	

In a second step the expression (6) has been used to represent the exchange energy in the electronic ground state. In this case the fitting procedure differs from the last one by the addition of a previous stage. Since no numerical value for $\mathscr{A}$, γ and δ have been furnished by Smirnov and Chibisov [18] (or at least comprehensible ones), departure values for these parameters have been obtained in the following way: the D_e value from Barrow et al. [1], C_6, C_8 and C_{10} from Tang et al. [12] have been held fixed in expression (2) combined with expression (6) to represent the exchange energy and $\mathscr{A}$, γ and δ calculated as free parameters. These values are then placed as departure values and the fitting procedure is developed as described when expression (5) is used to represent the exchange energy. The results of this fitting are shown in Table 3b.

The uncertainties in C_6 for the $X\,^1\Sigma_g^+$ electronic ground state and in C_3 for the (1) $^1\Pi_g$ excited electronic state are estimated to be 5%, while the higher coefficients C_n and exchange energy constants may have large errors for both states.

From Table 3a and b, it can be observed that the difference in the dissociation energy values for the $X\,^1\Sigma_g^+$ electronic ground state, obtained when using different exchange energy formulas, differs only by 0.02 cm^{-1}. The calculated standard deviation for the D_e values in the final iteration was about 0.04 cm^{-1} in both procedures, showing that the observed discrepancy between these two values is in the range of the calculated standard deviation.

It can be observed, by comparing the results presented in Table 3a and b, that the different representation of the exchange energy leads to quite the same results for D_e and C_n coefficients.

Damping term in multipolar expansion

Finally, a damping function $f_n(r)$ has been introduced in the calculations. It was strongly suggested [20] that in order to avoid the divergence in the multipolar expansion, $\Sigma_n\,C_n/r^n$, at smaller values of r, a damping function is necessary. In this case the long range development takes the form

$$V(r) = D_e - \sum_i f_n(r)\frac{C_n}{r^n} - E_{\mathrm{exc}}. \qquad (7)$$

The choosed functional form used to represent the damping function $f_n(r)$, in our case, is the same used by Demtröder et al. [21] and Fellows et al. [15] and it is represented by:

$$f_n = [1 - e^{-\alpha(r - n\beta)}]^n, \qquad (8)$$

where α and β are adjustable constants, n is the multipolar order and r is the internuclear distance. The exchange energy E_{exc} is represented by the functional form of expression (5). The choice of this expression, rather than the other one, has been done simply by the fact that this function have less adjustable parameters than (6) and can represent quite well the exchange energy, as been shown above.

The external turning points for the $X\,^1\Sigma_g^+$ and (1) $^1\Pi_g$ electronic states of the Na$_2$ molecule listed in Tables 1 and 2, respectively, have been fitted now using expression (7), being $f_n(r)$ represented by expression (8) in the following way:

Firstly the values of D_e, C_6, C_8, C_{10}, A and a for the $X\,^1\Sigma_g^+$ electronic ground state and D_e, C_3, C_6, A and a for the (1) $^1\Pi_g$ electronic state have been held fixed in the values obtained without damping functions and α and β calculated as free parameters.

After that the same procedure used in the calculations performed without damping functions has been performed. It means, freezing some parameters and keeping free others up to a convergence is reached. When the damping functions are used, van der Waals coefficients can be extended up to $n = 12$ for the $X\,^1\Sigma_g^+$ electronic ground state and $n = 8$ for the (1) $^1\Pi_g$ electronic excited state [15, 21]. The results obtained when using damping functions in the fitting can be found in Table 5, for both electronic states. This results will be discussed in more details in the next sections.

4. Discussion

The $X\,^1\Sigma_g^+$ electronic ground state

As discussed above, an empirical relation linking C_6, C_8 and C_{10} coefficients has already been pointed by Le Roy [16] for the electronic ground states of diatomics molecules. In Table 3 this empirical relation is represented by the ratio R_L that means

$$R_L = \frac{C_6\,C_{10}}{(C_8)^2}.$$

Table 5. Dissociation energy values D_e, van der Waals C_n coefficients, exchange energy parameters A and a, calculated using expression (7) for $X\,^1\Sigma_g^+$ and (1) $^1\Pi_g$ electronic states. The values of α and β parameters of the damping function $f(n)$ are listed in this Table for each electronic state

$X\,^1\Sigma_g^+$		(1) $^1\Pi_g$	
D_e(cm^{-1})	6022.13 $\pm$ 0.03	D_e(cm^{-1})	22990.88 $\pm$ 0.04
C_6(cm^{-1} Å^6)	7.303 × 10^6	C_3(cm^{-1} Å^3)	2.050 × 10^5
C_8(cm^{-1} Å^8)	1.475 × 10^8	C_6(cm^{-1} Å^6)	12.225 × 10^6
C_{10}(cm^{-1} Å^{10})	0.416 × 10^{10}	C_8 (cm^{-1} Å^8)	7.363 × 10^8
C_{12}(cm^{-1} Å^{12})	0.164 × 10^{12}		
A(cm^{-1})	1.730 × 10^6	A(cm^{-1})	7.567 × 10^4
a(Å^{-1})	1.581	a(Å^{-1})	1.222
α(Å^{-1})	0.755	α(Å^{-1})	0.697
β(Å)	0.482 × 10^{-1}	β(Å)	0.321 × 10^{-1}
R_L	1.395		

Following expression (4), R_L should be approximately equal to 1.33.

Now the theoretical C_n values used by Barrow et al. [1] to calculate the $X\,^1\Sigma_g^+$ electronic ground state dissociation energy can be compared with the results obtained in this work for the same electronic state. In Table 3, column a, are presented the C_6, C_8 and C_{10} values obtained in the direct fit using expression (2), truncated to $n = 6, 8$ and 10, with formula (5) to represent the exchange energy E_{exc} and in column b the same truncated expression with formula (6) to represent the exchange energy, as explained above.

Columns c and d show the values from Barrow et al. [1] article. In column c the dissociation energy value D_e has been calculated using the C_6 and C_8 values from [19], the C_{10} value from [13] and the A and a values from [19] by inversion of (2) with (5) to represent the exchange energy, as explained in Section 2a. Column d shows D_e value obtained by inversion of (2) when using the C_6, C_8, C_{10}, A and a values from [19] listed in this column. Finally, column e shows the C_6, C_8, C_{10} values calculated by Tang et al. [12] in order to compare with the previous values.

It can be observed that the R_L value obtained when using the constants from columns a and b, calculated in this work, are very near to the LeRoy's prediction of 1.33, as so do the R_L value obtained when using Tang et al. [12] values listed in column e.

Taking into account the dispersion constants C_6, C_8 and C_{10}, which has been used in Barrow's article [1] for dissociation energy calculations, it can also be observed that the obtained R_L ratios are far from 1.33 value for column c and still farther from this value for values in the column d.

In column b, where the expression (6) is used to represent the exchange energy in (2), the R_L value is closer 1.33 than the value obtained by using the C_n coefficients from column a. This fact shows that the exchange energy is better described by the functional form of (6). Nevertheless, the discrepancy between these R_L values, in columns a and b, is not extremely high showing that the functional form (5) can represent quite well the exchange energy too.

The exchange energy coefficients, A and a, obtained in this work can be now compared with those theoretically calculated by Konowalow and Rosenkrantz [19]. These last values have been used by Barrow et al. [1] to calculate the dissociation energy of the $X\,^1\Sigma_g^+$ electronic ground state, as explained in Sect. 2a, and are listed in columns c and d. From this comparison it can be observed:

- The A value obtained in our calculations is higher than the one theoretically calculated. This can be explained by considering that actually this coefficient carries the contribution from the higher order dispersion terms $(n > 10)$, neglected in the development (2).
- The a coefficient obtained in our calculations shows the same order of magnitude of the calculated one [19] listed in columns c and d.
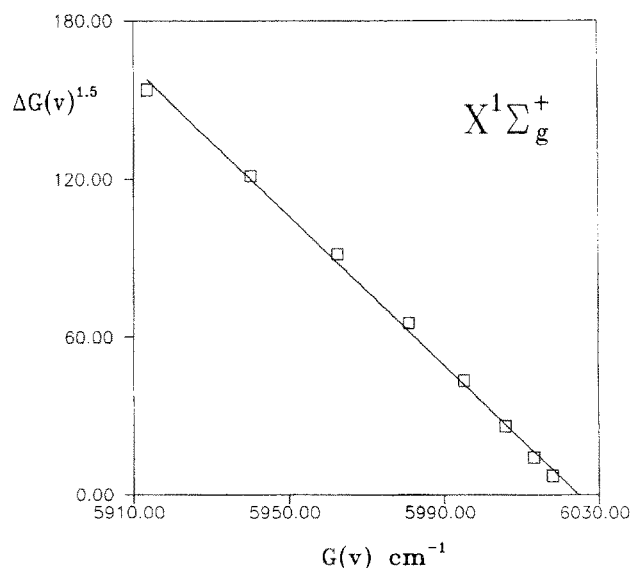

Fig. 1. $(\Delta G(v))^{1.5}$ plotted against $G(v)$ for levels of $X\,^1\Sigma_g^+$, after LeRoy-Bernstein theory

In order to verify our results, a LeRoy-Bernstein plot [4] has been performed, using the function:

$$\Delta G(v) = \frac{\bar{H}_n}{\mu^{1/2} C_n^{1/n}} [D_e - G(v)]^{\frac{n+2}{2n}}$$
$$= K_n [D_e - G(v)]^{\frac{n+2}{2n}}, \tag{9}$$

with $n = 6$, as leading term. The result is shown in Fig. 1. The D_e and C_6 values obtained from this figure are 6024.8 cm^{-1} and 7.45×10^6 cm^{-1} Å^6, respectively. The difference between the values obtained in this work and those calculated by the LeRoy-Bernstein theory can be easily explained by the simple fact that the experimental points used in the fitting are still below the LeRoy's limit r_{lim}. This can be observed in Fig. 1 where the plot of $(\Delta G(v))^{1.5}$ against $G(v)$ is not quite linear, and a precise extrapolation is difficult. In spite of this, the obtained values are not far from the calculated ones.

The (1) $^1\Pi_g$ electronic excited state

Our results for the direct fitting of experimental points using expression (2), combined with expression (5) to represent the exchange energy, are shown in Table 4a. In order to compare, column b shows the dissociation energy value obtained by Barrow et al. [1] by inversion of equation (2) when using the values of C_3 and C_6 from Bussery and Aubert-Frécon [13] and the theoretical values of A and a from Konowalow and Rosenkrantz [19], listed in the same column. In column c the dissociation value obtained in the same way is shown, when using C_3, C_6, A and a values theoretically calculated by Konowalow and Rosenkrantz [19] listed in this column. The theoretical values for C_3 and C_6 obtained by Vigné-Maeder [24] are shown in column d of the same Table.
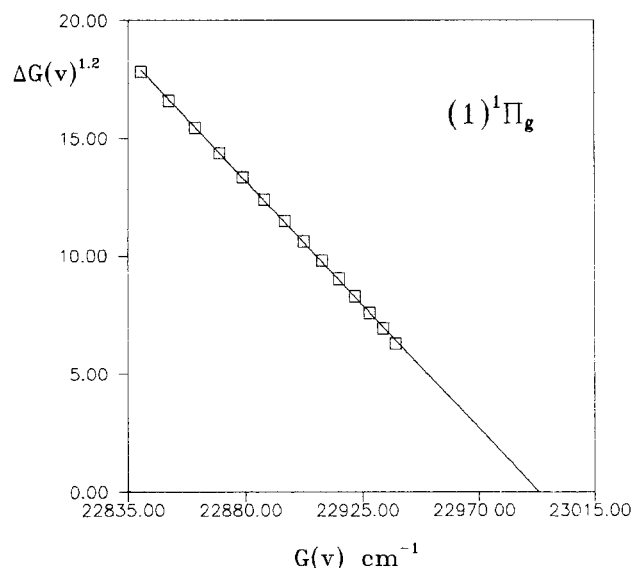
Fig. 2. $(\Delta G(v))^{1.2}$ plotted against $G(v)$ for levels of (1) $^1\Pi_g$, after LeRoy-Bernstein theory

Now, some points can be considered. It can be observed that the dissociation energy value obtained in the present calculations is quite lower than that obtained by Barrow et al. [1]. The C_3 and C_6 coefficients obtained theoretically and shown in this Table are in a good agreement with those calculated in this article. The A and a values, theoretically calculated by Konowalow and Rosenkrantz [19], are in reasonably good accordance with the corresponding ones obtained in this work, showing the same order of magnitude, in spite of the A value obtained being lower than the theoretically calculated one.

In order to obtain more information about the dissociation energy value for the (1) $^1\Pi_g$ electronic state, a LeRoy-Bernstein plot has been performed for this state, in the same way as performed to the X $^1\Sigma_g^+$ ground state, using expression (9) with $n=3$ as leading term. From Fig. 2, $D_e = 22993.3$ cm^{-1} and $C_3 = 2.53 \times 10^5$ cm^{-1} Å^3 values can be deduced. For the same reason as for the X $^1\Sigma_g^+$ electronic ground state, considering that the experimental points are below LeRoy's limit, a lack of agreement can be found between the D_e and C_3 values calculated in this work, and those obtained by LeRoy-Bernstein plot. This cames from the fact that the approximation here is extremely long, ≈ 55 cm^{-1}, as may be seen from Fig. 2. The estimates done in this plot, lead to a somewhat higher C_3 value, and thus to lower values of K_3, fitting to higher value of the dissociation limit. The same happened in the analysis of the X $^1\Sigma_g^+$ electronic ground state, where LeRoy's plot gave a higher values for the dissociation energy and C_6 constant when the extrapolation is long.

But it is interesting to note that if the previously obtained dissociation energy value for the X $^1\Sigma_g^+$ electronic ground state is taken, 6022.1 cm^{-1}, and to this value is added the energy of the Na $3s$ $^2S_{1/2} \leftarrow 3p$ $^2P_{3/2}$, limit of the (1) $^1\Pi_g$ electronic state, the dissociation energy

of this last electronic state corresponds to 22995.5 cm^{-1}. This value is still above the value obtained by the LeRoy-Bernstein plot, considered high, as discussed in the last paragraph. More interesting is if recently calculated values for C_3 and C_6 constants by Hadinger and Aubert-Frécon [25] are used in an inversion of (2), a mean value of 23050 ± 5 cm^{-1} can be deduced!

In our point of view there are two possibilities that explain this paradox. The first one is that some errors in the estimation of the turnings points at these very large distances of the (1) $^1\Pi_g$ potential can be the source of this problem, as suggested by Barrow et al. The second one is that the (1) $^1\Pi_g$ electronic state could be extremely perturbated in this long range region, leading to some confuse estimates of the dissociation energy as well as C_n constants.

The damping terms applied to both states

In order to improve the calculated values for both states, damping terms were used as discussed in Section 3b. For the X $^1\Sigma_g^+$ electronic ground state, the potential energy is described by the multipolar expansion combined with the damping function as represented in expression (7).

Here, some points must to be considered. As it has been observed by Weickenmeier et al. [21], the inclusion of higher second order terms C_n/r^n up to at least $n=12$ in expression (7) is necessary for the X $^1\Sigma_g^+$ electronic ground state, in order to obtain a better representation of the long range part of the potential energy curve. For this reason the C_{12} terms has been calculated using the recurrence relation proposed by Tang et al. [12]:

$$C_{(2n+4)} = \left(\frac{C_{(2n+2)}}{C_{2n}}\right)^3 C_{(2n-2)} \qquad (10)$$

using the values of C_6, C_8 and C_{10} listed in Table 3a. The value of $C_{12} = 0.164 \times 10^{12}$ cm^{-1} Å^{12}, calculated by Equation (10), has been held fixed in the calculations.

Using the same argument, the term C_8 has been used in expression (7), in the (1) $^1\Pi_g$ development. As departure value the C_8 constant theoretically calculated by Bussery and Aubert-Frécon have been used and held fixed in the calculations. The results, for both electronic states are shown in Table 5.

5. Conclusion

In this paper a direct fitting of the external turning points of the electronic states of the Na$_2$ molecule, the X $^1\Sigma_g^+$ and the (1) $^1\Pi_g$, using the experimental data reported by Barrow et al. [1] is performed. Our obtained results show a very good agreement with the previous theoretical ones, but some comments should be made, for each electronic state.

For the X $^1\Sigma_g^+$ electronic ground state the direct fitting of experimental turning points, including exchange energy and damping correction, shows that a more accu-

rate value for the dissociation energy value could be attained. Nevertheless, the obtained errors for the D_e value seems to us extremely low. For this reason, and by comparison between D_e values obtained in Tables 3a, b and V, a new value for the $X\,^1\Sigma_g^+$ electronic ground state dissociation limit could be set to 6022.10 ± 0.5 cm^{-1}.

Regarding the $(1)\,^1\Pi_g$ electronic state, the problem is more delicate. As explained above, the dissociation energy calculated in this work for this electronic state is, in our point of view, lower than the expected value. It can be considered that the 22990.9 ± 0.1 cm^{-1} is a lower limit and the 22995.5 cm^{-1} value obtained in Section 4b is a higher limit for the dissociation energy. By this reason it is preferable to set the dissociation energy value of the $(1)\,^1\Pi_g$ electronic state as 22993 ± 6 cm^{-1}. More experimental work should be performed in this electronic state in order to obtain a more accurate value for the dissociation energy.

As final comment, it can be seen in spite of being a weak method to determine long range parameters in potential energy curve [22, 23], the method of direct fitting of the turning points is stil the only way to obtain interaction parameters in that internuclear distance range where the exchange energy cannot be neglected. This article shows that, with some care, this method can be applied not only to electronic ground states but to excited states too.

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