The Spectrum of Lanthanum Oxide: A Reanalysis of the Rotational Data

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A consistent set of improved rotational constants is derived for the $X^2\Sigma^+$, $A'^2\Delta_r$, $A^2\Pi_r$, $B^2\Sigma^+$, and $C^2\Pi_r$ electronic states of lanthanum oxide from the reanalysis of all available data. These constants are obtained from a global fit of the respective bands by a "Direct Approach" technique using complete Hamiltonian matrices for the description of Π and Δ states. In order to fit the lines accurately it is shown necessary to include centrifugal distortion effects in the spin-orbit interactions (A_J, A_J and A_{JJ} respectively in A', and A and C states) as well as in Λ-doubling (p_J, p_{JJ}, q_J in C state) and spin-rotation interactions (γ_J in B state).

More reliable values for the internal partition function and dissociation equilibrium constant of LaO are computed for temperatures between 1000 and 8000 K, by taking account of all the known electronic states and using present or recent values for the molecular parameters and dissociation energy.

I. Introduction

The spectrum of the lanthanum oxide molecule is of great interest in astrophysics in relation with stellar absorption. Indeed, the spectra of red variable stars of the S-type show LaO bands (see e.g., [1], [2]), particularly prominent at the minimum light, together with those of ZrO, YO and CeO, and numerous unidentified features [3]. Thus, a proper interpretation of such complex spectra necessitates precise laboratory measurements of the rotational line structure as well as valid sets of molecular parameters for the electronic states involved. Moreover, a correct understanding of the physical conditions prevailing in the atmospheres of those stars passes through theoretical abundance calculations for which reliable molecular thermochemical data (partition functions and equilibrium constants) are needed. In this respect, the knowledge of all the low-lying electronic states that actually exist is of prime importance. It is therefore the purpose of the present work to establish a consistent set of improved values for the molecular constants of LaO electronic states, derived from a reanalysis of all available rotational data, and to reestimate the internal partition function and dissociation equilibrium constant.

This work is a preparation of a further investigation of the LaO spectrum that we intend to do by means of high resolution Fourier transform spectrometry in the infrared spectral range (up to 3 μm), in the aim of observing transitions involving already known or new electronic states.

II. The Electronic Transitions of LaO

Seven electronic states of the LaO molecule, namely $X^2\Sigma^+$, $A'^2\Delta_r$, $A^2\Pi_r$, $B^2\Sigma^+$, $C^2\Pi_r$, $D^2\Sigma^+$, and $F^2\Sigma^+$, are known (Fig. 1) through the observation of six band systems ($F\rightarrow X$, $D\rightarrow X$, $C\rightarrow X$, $B\rightarrow X$, $C\rightarrow A'$, and $A\rightarrow X$) extending from ultraviolet to near-infrared spectral regions. Rotational analyses have been carried out on the $A\rightarrow X$ and $B\rightarrow X$ emission systems (0–1, 0–0, 1–0 bands) by Åkerlind [4], the ultraviolet emission systems ($F\rightarrow X$, $D\rightarrow X$) by Carette and Houdart [5]. Higher resolution works by Green [6], [7], [8] have dealt with the analyses of the $C\rightarrow X$ (0–0) and $C\rightarrow A'$ (0–0 and 1–1) bands. It is of interest to compare the spectrum of LaO with known spectra of the analogous molecules ScO, YO, and LuO. In all four

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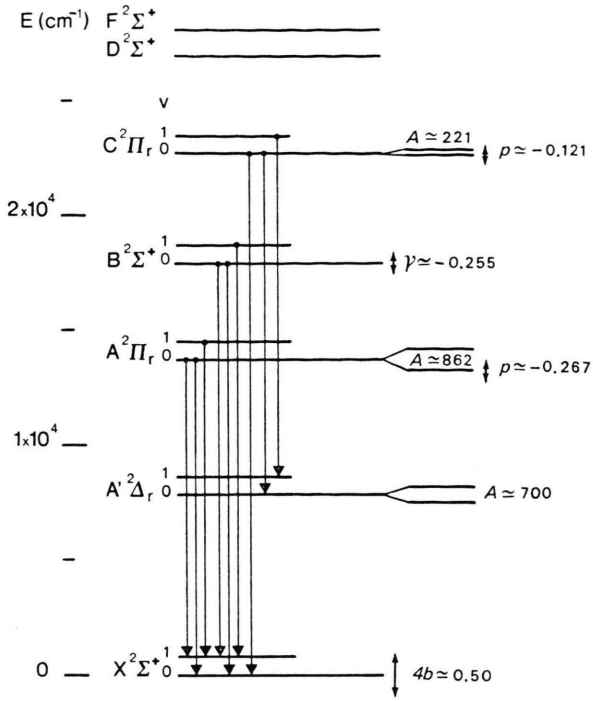

Fig. 1. The known electronic states of LaO and the rotationally analyzed transitions. The values of the parameters are in cm^{-1}.

molecules, transitions are observed involving a $^2\Sigma^+$ ground state. Except for YO with nuclear spin 1/2, the ground states belong to $b_{\beta S}$ coupling case, giving rise to two equidistant sublevels corresponding to $G = I + S = 3,\ 4$ ($I = 7/2,\ S = 1/2$). For ScO, YO, and LaO a regular $A^2\Pi$ state is observed, the energy of which is about 5000 cm^{-1} smaller than that of a $B^2\Sigma^+$ state. The observed values of the Λ-doubling p parameter in A state and spin-splitting γ parameter in B state are very close together in all three cases. It is a consequence of a tight interaction, of pure precession type, between A and B states, which are assumed to arise from the same 5p atomic configuration centered on the metal^{++} atom. Furthermore, the expected low-lying $^2\Delta_r$ electronic state, primarily from the metal dδ orbital, has been observed for ScO and YO via the $A' \rightarrow X$ forbidden transition [9] and LaO via the $C \rightarrow A'$ transition. This interpretation of the X, A', A, and B states as arising from the single unpaired electron centered on the metallic ion well explains the observed spectra, and particularly the high value for the Fermi contact term of hyperfine interaction in the ground state of pure "s-origin".

III. Reanalysis of the Rotational Data

All available rotational data concerning the visible and near-infrared spectrum of LaO have been reduced to a unique and consistent set of constants by using an elaborate "Direct Approach" technique. The method of calculation is based upon the original work of Athenour [10]. The data reduction consists of direct comparison between observed line wavenumbers and corresponding term value (or energy matrix eigenvalue) differences calculated from trial parameters. A non-linear least-squares procedure is then used and the parameters are improved until satisfactory agreement is obtained between measured and calculated line positions (see e.g., [11], [12]). The energy matrices used for the description of $^2\Pi$ and $^2\Delta$ states have been given previously [13]. The present work deals with the global treatment of the transitions indicated in Fig. 1 (note that no line positions are reported for the $A^2\Pi_{1/2} \rightarrow X^2\Sigma$ (1–0) subband). Owing to the unequal precisions achieved from the adjustment of the data from Åkerlind (Fig. 2a) or Green (Fig. 2b) it was necessary to employ a weighting procedure in the final simultaneous fit of the eight v-connected bands. A weight per branch in σ_b^{-2} was retained, σ_b^2 being the variance obtained in this branch from a separate fit of the bands with equal weights. Finally, line wavenumbers deviating by more than 3 standard deviations from their calculated value were removed and a new calculation cycle was executed.

In order to obtain an accurate reconstitution of the observed line wavenumbers it was found necessary to take account of centrifugal distortion effects in the spin-orbit interactions (A_J, A_J and A_{JJ}, respectively in A', and A and C states) as well as in Λ-doubling (p_J, p_{JJ}, q_J in C state) and spin-rotation interactions (γ_J in B state). On the other hand the parameter H did not appear significant in either state, within ± 2 standard deviation limits. The set of molecular constants so obtained (Table 1) allows to reproduce the measured lines to within a standard deviation of 0.049 cm^{-1} (the weighted standard deviation being 0.027 cm^{-1}).

The value of the Λ-doubling q parameter in $A^2\Pi(v=0)$ level, though roughly determined, is found close to the expected one ($q = 4B^2/\Delta E = -1.0 \times 10^{-3}$ cm^{-1}) in the unique perturber approximation. Then, the value of the Λ-doubling o

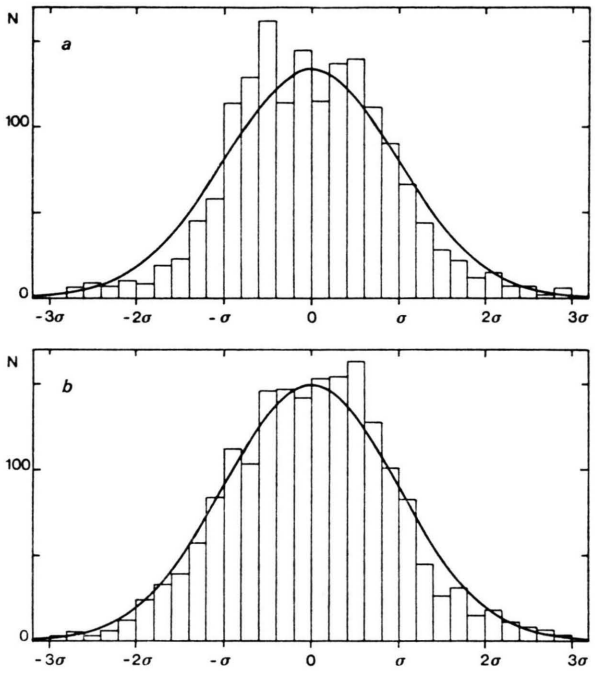

Fig. 2. Histogram of the distribution of the residuals between observed and calculated line wavenumbers. The solid curve is a normal distribution

$$\phi(x) = \frac{n\,l}{\sigma\sqrt{2\,\pi}} \exp\left[-\frac{1}{2}\left(\frac{x}{\sigma}\right)^2\right], \quad \text{with:}$$

a) $n = 1654$, $l = \sigma/5$, $\sigma = 0.0454$ cm^{-1} for A, B→X bands [4].
b) $n = 1858$, $l = \sigma/5$, $\sigma = 0.0224$ cm^{-1} for C→X, A′ (0-0) bands [6], [7].

parameter derived from $o = (A/8B)p \cong -75$ cm^{-1} is certainly reliable. Because of their correlation, the quantities o, ν_0 and A cannot be obtained independently from the fit. Only the effective values

$$A_{\text{eff}} = A - o \quad \text{and} \quad \nu_{0\,\text{eff}} = \nu_0 + \frac{o}{2}$$

are accessible. Thus, the large value of o has a significant effect, yielding the true values $A \cong 787.5$ cm^{-1} and $\nu_0 \cong 13104.5$ cm^{-1}. As already pointed out [7], an apparent increase with N of the hyperfine splitting was observed $\Delta\nu_H = 0.4840(76) + 0.00033(13)N$ in X($v = 0$) level, whose interpretation needs further attention [14].

A summary of the equilibrium molecular parameters inferred from present or recent works is given in Table 2.

Table 1. Rotational constants (in cm^{-1}) for the X, A′, A, B, and C electronic states of LaO *.

State		$v = 0$	$v = 1$
$X^2\Sigma^+$	T	0	812.676 (69)
	B	0.351728 (28)	0.350368 (75)
	$D \times 10^6$	0.2579 (24)	0.2667 (94)
	$4b$	0.5005 (36)	0.469 (14)
$A'^2\Delta_r$	T	7818.9132 (45)	t
	A	700.2858 (72)	a
	$A_J \times 10^3$	0.27106 (83)	0.231 (28)
	B	0.242953 (28)	0.341514 (60)
	$D \times 10^6$	0.2712 (22)	0.2603 (69)
$A^2\Pi_r$	T	13066.951 (11)	13824.166 (10)
	A	862.434 (22)	862.434
	$A_J \times 10^3$	0.3095 (97)	0.31
	$A_{JJ} \times 10^8$	− 0.77 (12)	
	B	0.346162 (82)	0.344564 (63)
	$D \times 10^6$	0.2741 (78)	0.2891 (80)
	p	− 0.26743 (24)	− 0.267
	$q \times 10^4$	− 0.96 (100)	− 0.96
$B^2\Sigma^+$	T	17837.345 (30)	18567.613 (69)
	B	0.340500 (64)	0.338936 (82)
	$D \times 10^6$	0.2914 (80)	0.285 (13)
	γ	− 0.25508 (50)	− 0.25474 (32)
	$\gamma_J \times 10^6$	− 0.17 (11)	
$C^2\Pi_r$	T	22729.5399 (35)	14936.2074 (42) + t
	A	221.4056 (63)	924.1779 (88) − a
	$A_J \times 10^3$	0.3777 (15)	0.345 (28)
	$A_{JJ} \times 10^9$	0.402 (98)	
	B	0.350241 (27)	0.348871 (60)
	$D \times 10^6$	0.2680 (23)	0.2587 (69)
	p	− 0.12059 (20)	− 0.12025 (11)
	$p_J \times 10^6$	0.202 (82)	
	$p_{JJ} \times 10^{10}$	− 0.232 (76)	
	$q \times 10^3$	− 0.180 (12)	− 0.1903 (52)
	$q_J \times 10^8$	− 0.39 (17)	

* Numbers in parentheses represent two standard deviations (in units of the last figure). In the final fit, the values of A, A_J, p, and q in $A(v = 1)$ level have been set equal to those found for $A(v = 0)$ level (owing to the non-observation of the $A^2\Pi_{1/2} \rightarrow X^2\Sigma(1 - 0)$ subband).

Table 2. Summary of the equilibrium molecular parameters (in cm^{-1}) for the X, A′, A, B, and C states of LaO *.

	T_e	ω_e	$\omega_e x_e$	B_e	α_e	r_e(Å)
$X^2\Sigma^+$	0	817.22	2.206	0.35241	0.00136	1.8262
$A'^2\Delta$	7842.61	770.11	2.798	0.34367	0.00144	1.8493
$A^2\Pi$	13094.53	762.09	2.230	0.34696	0.00160	1.8405
$B^2\Sigma^+$	17878.66	734.59	2.064	0.34128	0.00156	1.8558
$C^2\Pi$	22740.38	795.84	2.796	0.35093	0.00137	1.8301

* The values for ω_e and $\omega_e x_e$ are from Schoonveld and Sundaram [15]; the mean values found in the two Ω-components are given for A′, A, and C states.

IV. Partition Function and Equilibrium Constant

Vardya [16] proposed partition functions and equilibrium constants for ScO, YO, and LaO based upon the contribution of the X, A and B states. Since then, the A′ state has been observed, and a significant change in these quantities may be expected because of its large electronic degeneracy and low excitation energy in the case of LaO. So, more reliable values for the internal partition have been computed by summing the weighted Boltzmann factors over all the known electronic levels of LaO according to the method described by Tatum [17]. The large spin-splitting of the A′ state has been taken into account by separate summation for the two substates, with electronic statistical weight 2 (instead of 4) for each. The contribution of A′ state to the partition function is found as large as 20 and 43% for $T=5000$ and 8000 K, respectively. On the other hand the contribution of A state becomes significant only for high temperatures while more excited states have a negligibly small influence.

The dissociation equilibrium constant for the reaction $AB \rightleftarrows A + B$ at a given temperature can be obtained from the expression

$$\log_{10} K_p(T) = -\frac{5040.39}{T} D_0^0 + \frac{5}{2}\log_{10} T + \frac{3}{2}\log_{10}\mu + \log_{10}\frac{Q_A Q_B}{Q_{AB}} + 4.41405,$$

where $K_p(T)$ is in dyne/cm², T is in °K, μ is the reduced mass of the molecule in a.m.u. and D_0^0 the dissociation energy in eV. The value $D_0^0 = 8.24$ eV was admitted for LaO from the works of Ames, Walsh, and White [18], Smoes, Drowart, and Verhaegen [19], Gole and Chalek [20]. Atomic partition functions were calculated by classical methods.

Table 3. Internal partition function and dissociation equilibrium constant for LaO.

T(K)	Q_{LaO} $\times 10^{-4}$	$\log_{10} K_P$ (dyne/cm²)
1000	0.5753	− 29.9892
1250	0.8174	− 21.5240
1500	1.1039	− 15.8540
1750	1.4367	− 11.7853
2000	1.8193	− 8.7204
2250	2.2561	− 6.3270
2500	2.7528	− 4.4053
2750	3.3160	− 2.8279
3000	3.9530	− 1.5096
3250	4.6716	− 0.3912
3500	5.4801	0.5698
3750	6.3871	1.4044
4000	7.4015	2.1362
4250	8.5324	2.7832
4500	9.7893	3.3596
4750	11.1814	3.8763
5000	12.7184	4.3424
5250	14.4099	4.7650
5500	16.2658	5.1501
5750	18.2958	5.5025
6000	20.5099	5.8264
6250	22.9182	6.1252
6500	25.5306	6.4017
6750	28.3573	6.6584
7000	31.4085	6.8974
7250	34.6945	7.1206
7500	38.2255	7.3295
7750	42.0120	7.5254
8000	46.0644	7.7096

The internal partition function and logarithmic dissociation equilibrium constant of LaO are given in Table 3 for temperatures in the range 1000—8000 K. For practical application the equilibrium constant can be approximated as a function of $\theta = 5040.39/T$ by the following polynomial ($\sigma = 0.004$)

$$\log_{10} K_p = 13.430 - 9.2536\,\theta + 0.28666\,\theta^2 - 0.049114\,\theta^3 + 0.3457 \times 10^{-2}\,\theta^4.$$

[1] P. C. Keenan, Astrophys. J. **107**, 420 (1948).
[2] W. P. Bidelman, Astrophys. J. **117**, 377 (1953).
[3] S. Wyckoff and R. E. S. Clegg, Monthly Notices Roy. Astron. Soc. **184**, 127 (1978).
[4] L. Åkerlind, Ark. Fys. **22**, 65 (1962).
[5] P. Carette and R. Houdart, C. R. Acad. Sci. Paris Ser. B **272**, 595 (1971).
[6] D. W. Green, J. Mol. Spectrosc. **38**, 155 (1971).
[7] D. W. Green, Canadian J. Phys. **49**, 2552 (1971).
[8] D. W. Green, J. Mol. Spectrosc. **40**, 501 (1971).
[9] C. L. Chalek and J. L. Gole, J. Chem. Phys. **65**, 2845 (1976).
[10] C. Athenour, Ph. D. thesis, University of Nice (1975).
[11] R. Bacis, D. Cerny, J. d'Incan, G. Guelachvili, and F. Roux, Astrophys. J. **214**, 946 (1977).
[12] D. Cerny, R. Bacis, G. Guelachvili, and F. Roux, J. Mol. Spectrosc. **73**, 154 (1978).
[13] A. Bernard, R. Bacis, and P. Luc, Astrophys. J. **227**, 338 (1979).
[14] R. Bacis, R. Collomb, and N. Bessis, Phys. Rev. **8**, 2255 (1973).
[15] L. Schoonveld and S. Sundaram, Astrophys. J. Suppl. **27**, 307 (1974).
[16] M. S. Vardya, Astron. Astrophys. **5**, 162 (1970).
[17] J. B. Tatum, Pub. Dom. Astrophys. Obs. Victoria, **13**, 1 (1966).
[18] L. L. Ames, P. N. Walsh, and D. White, J. Chem. Phys. **71**, 2707 (1967).
[19] S. Smoes, J. Drowart, and G. Verhaegen, J. Chem. Phys. **43**, 732 (1965).
[20] J. L. Gole and C. L. Chalek, J. Chem. Phys. **65**, 4384 (1976).