Rotational analysis of the $A^2\Pi_{3/2}$–$A'^2\Delta_{5/2}$ bands of LaS and evidence of interaction between the two spin components of the $A'^2\Delta$ state

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ABSTRACT

The emission spectra of the $A^2\Pi$–$A'^2\Delta$ transition of LaS have been reinvestigated using spectra recorded with the 1-m Fourier transform spectrometer of the National Solar Observatory at Kitt Peak. Sixteen bands involving the vibrational levels v' = 0–5 and v'' = 0–5 of the Δv = −1, 0 and 1 sequences of the $A^2\Pi_{3/2}$–$A'^2\Delta_{5/2}$ sub-band have been rotationally analyzed to derive an improved set of spectroscopic constants for the two states. Rotational perturbations have been observed near J = 171.5, 155.5, 134.5, 112.5, 85.5, and 43.5, respectively, in the v = 0, 1, 2, 3, 4, and 5 vibrational levels of the $A'^2\Delta_{5/2}$ state. These perturbations are caused by interaction between the $A'^2\Delta_{5/2}$ (v) and $A'^2\Delta_{3/2}$ ($v+2$) levels of the lower state.

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1. Introduction

The electronic spectra of LaS are known since 1970 when Marcano and Barrow [1] reported the first observation of bands in the 700–850 nm region in thermal emission and in absorption using a high temperature carbon tube furnace. These bands were assigned as the $B^2\Sigma^+$–$X^2\Sigma^+$ transition of LaS, and had strong similarity with the $B^2\Sigma^+$–$X^2\Sigma^+$ band system of LaO. The first spectroscopic constants of LaS were reported from a vibrational analysis of observed bands and a rotational analysis of the 0–0 band [1]. They also observed complex bands in the 400–450 nm region which remained unassigned. The 400–450 nm bands were later observed by Jones and Gole [2] by chemiluminescence from the reaction of lanthanum and carbonyl sulfide (OCS) and were assigned to the $C^2\Pi$-$X^2\Sigma^+$ transition of LaS. In another study, Winkel et al. [3] observed LaS spectra in the 1800–16 000 cm^{-1} region and obtained a vibrational analysis of the $A^2\Pi$-$X^2\Sigma^+$ and $B^2\Sigma^+$-$X^2\Sigma^+$ transitions. In a later study, Andersson et al. [4] recorded the higher resolution spectra of LaS in the same region and reported a rotational analysis of a number of bands of the two transitions. They also identified a new $A^2\Pi$-$A'^2\Delta$ transition in the 5000–5200 cm^{-1} region and reported a rotational analysis of a few bands. In the most recent study, He et al. [5] have performed an analysis of the hyperfine structure of the $B^2\Sigma^+$–$X^2\Sigma^+$ transition and reported the rotational, spin and hyperfine parameters for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states.

Transition metal containing molecules are important in astrophysics, and several metal oxides and sulfides have been identified in the spectra of cool stars. The spectra of S-type stars are characterized by absorption bands of LaO and ZrO molecules [6,7]. Some transition metal sulfides such as ZrS [8,9] and TiS [10,11] have also been found in the spectra of M- and S-type stars and there is a possibility that LaS may also be found.

In the previous study of the $A^2\Pi$–$A'^2\Delta$ transition, Andersson et al. [4] obtained a rotational analysis of a few bands using Fourier transform spectra recorded with 0.022 cm^{-1} resolution at Los Alamos National Laboratory. Their spectra were overlapped with broad water absorption lines and they obtained only a partial analysis of the 0–0 band of the $A^2\Pi_{1/2}$–$A'^2\Delta_{3/2}$ sub-band and the 0–0, 1–1 and 2–2 bands of the $A^2\Pi_{3/2}$–$A'^2\Delta_{5/2}$ sub-band. For the analysis of the $A^2\Pi_{3/2}$–$A'^2\Delta_{5/2}$ sub-band, they obtained measurements of the P, Q, R branches of the 0–0 band, Q and P branches of the 1–1 band and only the Q branch lines of the 2–2 band.

While reviewing the spectra of lanthanum-containing molecules recorded with the 1-m Fourier transform spectrometer of the National Solar Observatory (from the NSO archive), we found better near infrared thermal emission spectra of LaS recorded by S.P. Davis (now deceased). In this paper we report on a reanalysis of several bands of the $A^2\Pi_{3/2}$–$A'^2\Delta_{5/2}$ sub-band using these spectra, and observation of perturbations in the $A'^2\Delta_{5/2}$ component.

2. Experimental

The best spectrum of LaS was recorded on 01/17/1989 [spectrum #890117R0.001] by S. P. Davis in emission using a high temperature carbon tube furnace (King furnace). The LaS molecules were produced in thermal emission by vaporizing La$_2$S$_3$ at a tem-

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perature of ~2400 °C in an atmosphere of about 70–90 Torr of helium. The emission spectra in the 1850–9150 cm^{-1} region were recorded at a resolution of 0.01 cm^{-1} by co-adding 8 scans in about 2 h of integration. The spectrometer was equipped with a CaF$_2$ beam splitter, Si filter and InSb detectors. The spectrum observed in the 4600–5650 cm^{-1} region consists of bands belonging to the $\Delta v = -1$, 0, and 1 sequences of the A$^2\Pi$–A$'^2\Delta$ transition of LaS, in contrast to only the $\Delta v = 0$ sequence bands observed by Andersson et al. [4]. The strong rotational lines of the 0–0 band appear with a signal-to-noise ratio of about 50:1 and the measurement of strong and unblended rotational lines is expected to be better than ±0.002 cm^{-1}. The uncertainty of measurement in the higher vibrational bands is expected to be somewhat higher because of overlapping from rotational lines from the preceding bands. It was, therefore, decided to obtain a reanalysis of bands of this transition using the current spectrum. The line positions were extracted from the observed spectra using the WSPECTRA program (M. Carleer, Free University of Brussels) by fitting a Voigt line shape function to the individual spectral features. In addition to LaS bands, the spectra also contained emission bands of CO, C$_2$ and CN, which were present as impurities. The observation of these species as impurities is very common in carbon tube furnace experiments.

The spectra of impurity species consist of the $\Delta v = 2$ overtone bands of CO (3800–4362 cm^{-1}), the 0–0 band of the Ballik–Ramsay system of C$_2$ (5200–5660 cm^{-1}) and the $\Delta v = -1$ (5900–7220 cm^{-1}) and $\Delta v = -2$ (4300–5094 cm^{-1}) sequence bands of the A$^2\Pi_i$–X$^2\Sigma^+$ transition of CN. Since the rotational constants of these molecules are far larger than the constants of LaS, the presence of impurity molecules did not pose any problem in the analysis of LaS bands. We have used the measurements of near infrared CN lines [12] to calibrate the wavenumbers of the LaS lines. The LaS molecular lines were sorted into branches of different bands using a color Loomis program running on a PC computer.

3. Results and discussion

We have obtained the rotational analysis of 16 bands of the A$^2\Pi_{3/2}$–A$'^2\Delta_{5/2}$ sub-band. We were able to identify P, Q and R branches in the 0–1, 1–2, 2–3, 3–4, 0–0, 1–1, 2–2, 3–3, 4–4, 1–0, 2–1, 3–2 and 4–3 bands. For the 4–5, 5–5 and 5–4 bands we could identify only Q and P branches. We have identified rotational lines up to $R(188.5)$, $P(193.5)$ and $Q(235.5)$ in the 0–0 band. Many lower J rotational lines (particularly for bands with higher v's) could not be identified because of weak intensity and strong overlapping from neighboring bands. For example in the 5–5 band, the R branch was completely overlapped, and the lower J rotational lines with $J < 45.5$ in the P branch and $J < 27.5$ in the Q branch were not identified. The Λ-doubling is not resolved in most of the bands except in the Q branch of the 0–0 band where lines are split into two components for $J > 180.5$. In total we have identified about 5000 rotational lines in 16 bands which have provided improved spectroscopic constants for the two electronic states. As will be discussed in the following section, we have observed local perturbations affecting all the vibrational levels of the A$'^2\Delta_{5/2}$ component. The rotational lines affected by perturbations were given lower weights or were de-weighted completely. We were not able to make much progress in the analysis of the A$^2\Pi_{1/2}$–A$'^2\Delta_{3/2}$ sub-band because of weak intensity and overlapping from the much stronger bands of the A$^2\Pi_{3/2}$–A$'^2\Delta_{5/2}$ sub-band. A portion of the $\Delta v = 0$ sequence is provided in Fig. 1 with the R-heads of a few bands marked and an expanded portion of the R branch of the 0–0 band is provided in Fig. 2. In this Figure some lower-J lines as well as some higher-J R-lines returning after forming the head have been marked.
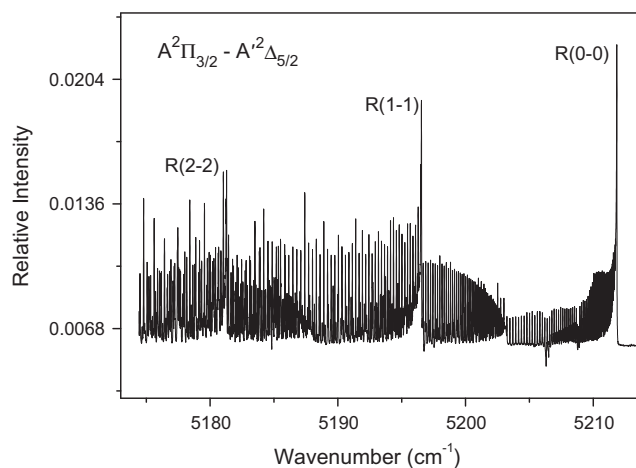

Fig. 1. A compressed portion of the A$^2\Pi_{3/2}$–A$'^2\Delta_{5/2}$ spectrum with the R-heads of a few $\Delta v = 0$ bands marked.
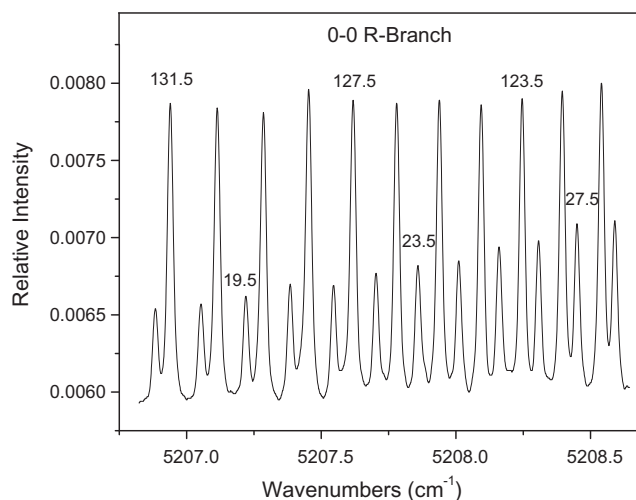

Fig. 2. An expanded portion of the R branch of the 0–0 band with some low-J lines marked as well as high-J lines returning after forming the band head.

The spectroscopic constants of the two states were determined by fitting the observed rotational lines using a simple term energy expression:

$$F_v(J) = T_v + B_v J(J+1) - D_v[J(J+1)]^2 \pm 1/2[p_{Dv}(J+1/2)^3] \qquad (1)$$

where ± signs refer to the e/f levels and the parity assignment in the 0–0 band was chosen arbitrarily. The rotational lines were given weights based on the signal-to-noise ratio, extent of blending, and effect of perturbations. In the fit, the T_0 value of the A$^2\Pi_{3/2}$ component was fixed at $T_0 = 11128.60572$ cm^{-1}, a value determined using the spectroscopic constants of Andersson et al. [4]. The spectroscopic constants obtained from the final fit are provided in Table 1. An effective Λ-doubling constant $p_{D0} = -1.560(88) \times 10^{-9}$ cm^{-1} was also determined for the $v = 0$ vibrational level of the A$^2\Pi_{3/2}$ component. The output of the final fit listing fitted constants, the observed transition wavenumbers and their obs.-calc. residuals are provided in Supplement 1. The supplement file is available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.o-hio-state.edu/jmsa_hp.htm). Our rotational constants agreed well with the constants of Andersson et al. [4]. The spectroscopic constants of the individual vibrational levels of the two states were

Table 1
Spectroscopic constants (in cm^{-1}) of the $A^2\Pi_{3/2}$ and $A'^2\Delta_{5/2}$ states of LaS.

State	v	T_v	B_v	$D_v \times 10^8$
$A'^2\Delta_{5/2}$	0	5925.38786(17)	0.11323204(94)	3.1908(27)
	1	6350.80423(42)	0.11290120(94)	3.1962(28)
	2	6774.37504(54)	0.11256892(94)	3.1972(27)
	3	7196.09159(63)	0.11223739(94)	3.2038(28)
	4	7615.95755(73)	0.11190577(93)	3.2144(28)
	5	8033.9835(10)	0.11157040(94)	3.2153(28)
$A^2\Pi_{3/2}$	0	11128.60572[a,b]	0.11178226(94)	3.3001(27)
	1	11538.79050(41)	0.11144879(94)	3.3055(28)
	2	11947.16824(53)	0.11111449(94)	3.3110(28)
	3	12353.73649(64)	0.11077837(93)	3.3142(27)
	4	12758.48420(72)	0.11044176(94)	3.3203(28)
	5	13161.40839(89)	0.11010360(94)	3.3247(28)

Note: Numbers in parentheses are one standard deviation in the last digits quoted.
[a] Asterisk marks fixed value, determined from the constants of Andersson et al. [4].
[b] Constant $p_{D0} = -1.560(88) \times 10^{-9}$ cm^{-1} was also determined for the $A^2\Pi_{3/2}(v=0)$ level.

Table 2
Equilibrium spectroscopic constants (in cm^{-1}) of the $A'^2\Delta_{3/2}$ and $A^2\Pi_{5/2}$ states of LaS.

Constants	$A'^2\Delta_{5/2}$	$A^2\Pi_{3/2}$
T_e	5711.98573(86)	10922.83840(98)
ω_e	427.2665(12)	411.9840(18)
$\omega_e x_e$	0.92458(25)	0.89810(79)
$\omega_e y_e$	–	−0.001050(95)
B_e	0.11339869(87)	0.11194852(22)
$\alpha_e \times 10^4$	3.3193(28)	3.3223(17)
$\gamma_e \times 10^7$	–	−5.83(28)
r_e (Å)	2.3916159(92)	2.4070565(24)

Note: Numbers in parentheses are one standard deviation in the last digits quoted.

used to determine the equilibrium constants using the standard equations. The equilibrium constants of the two states are provided in Table 2. Our equilibrium constants (Table 2) agree well with the constants obtained by Andersson et al. [4], except for the T_e values.

This difference arises because of extra Ω-dependent terms in their energy level expressions [Eqs. (3), (5) of Ref. 4], compared to our expression. The contribution of these terms are about −0.2515 cm^{-1} and −0.7077 cm^{-1} for the $v = 0$ vibrational levels of the $A^2\Pi_{3/2}$ and $A'^2\Delta_{5/2}$ components, respectively. After correcting for the effect of the extra terms, their T_e values are changed to T_e ($A^2\Pi_{3/2}$) = 10922.8405 cm^{-1} and T_e ($A'^2\Delta_{5/2}$) = 5711.9933 cm^{-1}, which are also in very good agreement with our values of $T_e(A^2\Pi_{3/2})$ = 10922.83840(98) cm^{-1} and $T_e(A'^2\Delta_{5/2})$ = 5711.98573(86) cm^{-1} (Table 2).

4. Interaction between the $A^2\Delta_{5/2}$ (v) and $A^2\Delta_{3/2}$ ($v + 2$) levels

Rotational analysis of the $A^2\Pi_{3/2}$–$A'^2\Delta_{5/2}$ sub-band indicates that all of the observed vibrational levels of the $A'^2\Delta_{5/2}$ state are affected by local perturbations. The $v = 0, 1, 2, 3, 4,$ and 5 vibrational levels of the $A'^2\Delta_{5/2}$ spin component are locally perturbed near $J = 171.5, 155.5, 134.5, 112.5, 85.5,$ and 43.5, respectively. The spin–orbit coupling constant of the $A'^2\Delta$ state of LaS has been determined as $A = 410.8$ cm^{-1} by Andersson et al. [4], indicating that the $A'^2\Delta_{5/2}$ component is about 821.6 cm^{-1} higher than the $A'^2\Delta_{3/2}$ component. The $A'^2\Delta_{5/2}$ state vibrational constant is 427.2665 cm^{-1}. Assuming a similar vibrational constant for the $A'^2\Delta_{3/2}$ component suggests that the $A'^2\Delta_{5/2}(v)$ levels are close to the $A'^2\Delta_{3/2}(v+2)$ vibrational levels and observed perturbations are the result of interactions between these two levels. The vibrational term values (T_v) of the $A'^2\Delta_{3/2}$ levels were calculated using our vibrational constants $\omega_e = 427.2665$ cm^{-1}, $\omega_e x_e = 0.9246$ cm^{-1}, and $T_0 = 5104.474$ cm^{-1} as reported by Andersson et al. [4]. This calculation provides approximate term values of 5105, 5530, 5954, 6375, 6795, 7213, 7629, and 8043 cm^{-1} for the $v = 0, 1, 2,$ 3, 4, 5, 6, and 7 vibrational levels of the $A'^2\Delta_{3/2}$ spin component. The experimental term values of the $v = 0, 1, 2, 3, 4,$ and 5 vibrational levels of the $A'^2\Delta_{5/2}$ state are 5925, 6351, 6774, 7196, 7916, and 8034 cm^{-1}, respectively. A comparison of the term values of the two spin components indicates that the $v = 0, 1, 2, 3, 4,$ and 5 vibrational levels of the $A'^2\Delta_{5/2}$ state are located below the $v = 2, 3, 4, 5, 6,$ and 7 vibrational levels of the $A'^2\Delta_{3/2}$ state by 29,
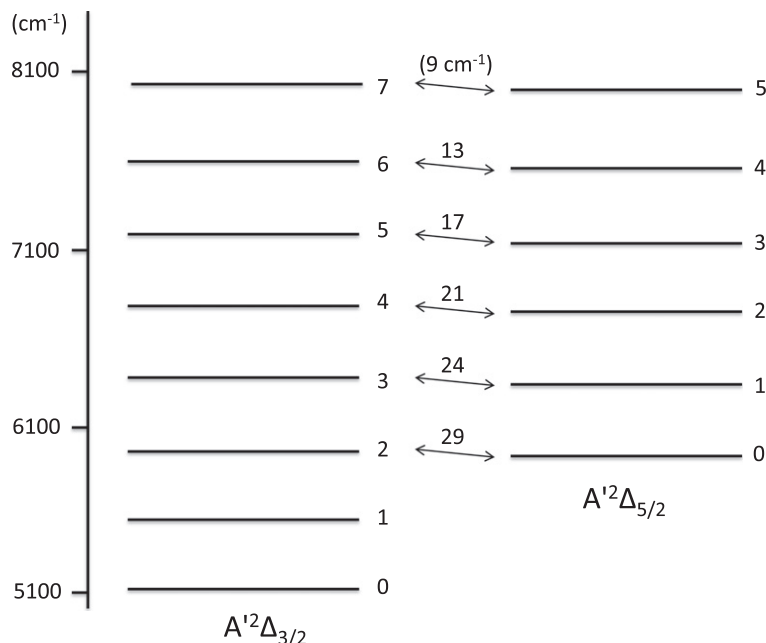

Fig. 3. A schematic energy level diagram showing interaction between the $A'^2\Delta_{5/2}$ (v) and $A'^2\Delta_{3/2}$ ($v+2$) vibrational levels of LaS.

24, 21, 17, 13, and 9 cm^{-1}, respectively. This shows that A$'^2\Delta_{5/2}$ ($v = 0$) interacts with A$'^2\Delta_{3/2}$ ($v = 2$) vibrational level, A$'^2\Delta_{5/2}$ ($v = 1$) interacts with A$'^2\Delta_{3/2}$ ($v = 3$) vibrational level and so on. There are no other electronic states in the vicinity of the A$'^2\Delta$ state which could be responsible for these perturbations. A comparison of the term values of the A$'^2\Delta_{3/2}$ and A$'^2\Delta_{5/2}$ components is provided in the schematic energy level diagram provided in Fig. 3. The J values at which perturbations occur, decrease with increasing v values since the two interacting levels become closer with increasing v. We have also calculated the rotational term values, $T_v(J)$, of the A$'^2\Delta_{3/2}$ component using the experimental spectroscopic constants of the $v = 0$ vibrational level [4] and estimated constants for the higher vibrational levels. These calculations confirm the interactions. Similar perturbations have been observed in the A$'^2\Delta_{5/2}$ spin component of the isovalent LaO by Bernard and Vergès [13], which were explained as due to interaction between the A$'^2\Delta_{5/2}$ (v) and A$'^2\Delta_{3/2}$ ($v + 1$) vibrational levels.

5. Summary

The emission spectra of the A$^2\Pi$–A$'^2\Delta$ near infrared transition of LaS have been reinvestigated at high resolution. A rotational analysis of 16 bands with vibrational levels $v' = 0$–5 and $v'' = 0$–5 has been obtained and improved spectroscopic constants have been obtained for the two states. Rotational perturbations have been observed in all the vibrational levels ($v = 0$–5) of the A$'^2\Delta_{5/2}$ spin component. These perturbations occur as a result of interaction between the A$'^2\Delta_{5/2}$ (v) and A$'^2\Delta_{3/2}$ ($v + 2$) vibrational levels.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jms.2013.02.004.

References

[1] M. Marcano, R.F. Barrow, J. Phys. B 3 (1979) L121–L123.
[2] R.W. Jones, J.L. Gole, Chem. Phys. 20 (1977) 311–318.
[3] R.J. Winkel Jr., S.P. Davis, M.C. Abrams, Appl. Opt. 35 (1996) 2874–2878.
[4] N. Andersson, S.P. Davis, G. Edvinsson, R.J. Winkel Jr., Phys. Scripta 64 (2001) 134–139.
[5] S.G. He, W.S. Tam, J.W.-H. Leung, A.S.-C. Cheung, J. Chem. Phys. 117 (2002) 5764–5769.
[6] P.C. Keenan, Astrophys. J. 107 (1948) 420–421.
[7] P.C. Keenan, P.C. Boeshaar, Astrophys. J. Suppl. 43 (1980) 379–391.
[8] R.R. Joyce, K.H. Hinkle, L. Wallace, M. Dulick, D.L. Lambert, Astrophys. J. 116 (1998) 2520–2529.
[9] J. Jonsson, B. Lindgren, A.G. Taklif, Astron. Astrophys. 246 (1991) L67–L68.
[10] K.H. Hinkle, D.L. Lambert, R.F. Wing, Mon. Not. R. Astron. Soc. 238 (1989) 1365–1379.
[11] J. Jonsson, O. Launila, B. Lindgren, Mon. Not. R. Astron. Soc. 258 (1992) 49–51.
[12] R.S. Ram, L. Wallace, P.F. Bernath, J. Mol. Spectrosc. 263 (2010) 82–88.
[13] A. Bernard, J. Vergès, J. Mol. Spectrosc. 201 (2000) 172–174.