Rotational and vibrational analysis of the CaF $B^2\Sigma^+ - X^2\Sigma^+$ system

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A rotation–vibration analysis of the CaF $B^2\Sigma^+ - X^2\Sigma^+$ system is reported. Excitation spectra of CaF are recorded with a cw, 1 MHz bandwidth, dye laser combined with restricted-bandpass (2 Å) fluorescence detection. The accuracy of line measurements is 0.003 cm^{-1}. Nine bands in the $\Delta v = 0$ sequence are analyzed ($v'' = 0$–2, 8, 9, 12–15) and selected lines in four $\Delta v = -1$ bands ($v'' =$ 1–4) are used to obtain band origins needed for the vibrational analysis. The main constants (1σ error in parentheses) for the CaF $B^2\Sigma^+$ state are: $T_e = 18\,841.309(3)$ cm^{-1}, $B_e = 0.342604(7)$ cm^{-1}, $\omega_e = 572.405(36)$ cm^{-1}, $\alpha_e = 0.002630(6)$ cm^{-1}, $\omega_e x_e = 3.143(13)$ cm^{-1}, $R_e = 1.955$ Å. The $B^2\Sigma^+$ state is found to be in pure precession with $A^2\Pi$ with $l = 1$.

On présente une analyse rotation-vibration du système $B^2\Sigma^+ - X^2\Sigma^+$ de CaF. Les spectres d'excitation de CaF ont été obtenus en utilisant un laser à colorant, à onde continue et de 1 MHz de largeur de bande, en combinaison avec un détecteur de fluorescence à largeur de bande limitée (2 Å). La précision de la mesure des raies est de 0.003 cm^{-1}. Neuf bandes dans la série $\Delta v = 0$ sont analysées ($v'' = 0$–2, 8, 9, 12–15); et des raies choisies dans quatre bandes $\Delta v = -1$ ($v'' = 1$–4) sont utilisées pour obtenir les origines des bandes requises pour l'analyse vibrationnelle. Les principales constantes de l'état $B^2\Sigma^+$ sont (avec la valeur de l'écart σ entre parenthèses) : $T_e = 18\,841.309(3)$ cm^{-1}, $B_e = 0.342604(7)$ cm^{-1}, $\omega_e = 572.405(36)$ cm^{-1}, $\alpha_e = 0.002630(6)$ cm^{-1}, $\omega_e x_e = 3.143(13)$ cm^{-1}, $R_e = 1.955$ Å. On trouve que l'état $B^2\Sigma^+$ est en précession pure avec $A^2\Pi$ pour $l = 1$.

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Introduction

The first complete vibrational analyses of the CaF $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states were reported by Johnson (1) in 1929 followed by Harvey (2) in 1931. It was not until the advent of the tunable single mode dye laser, a lapse of over 40 years, that a correct rotational analysis of the $A^2\Pi - X^2\Sigma^+$ (0,0), (0,1), and (1,0) bands appeared in 1975 (3). Recent Microwave–Optical Double Resonance (MODR) experiments on the A–X system by Nakagawa *et al.* (4) and Optical–Optical Double Resonance (OODR) measurements involving the X, A, E, and E' states by Bernath and Field (5) improved the accuracy of the A and X state constants.

We present a complete rotational and vibrational analysis of the $B^2\Sigma^+ - X^2\Sigma^+$ system for selected bands of the $\Delta v = 0$ and -1 sequences up to $v' = 15$ and $v'' = 15$. Previous analyses of the system by Mohanty and Upadhya (6), Khanna and Dubey (7), and Nanda and Mohanty (8) are shown to be incorrect.

The B–X system spans the wavelength region 5145–5500 Å and consists of closely spaced bands comprising the $\Delta v = 0$, 1, and -1 sequences. Because the internuclear distances and potential curves are nearly identical for the two states, one finds only an intense $\Delta v = 0$ sequence and weaker $\Delta v = \pm 1$ sequences. The $\Delta v = 0$ and $+1$ bands display double heads shaded to the red (2) while the $\Delta v = -1$ bands appear to be headless. The double heads can be explained by the large spin–rotation constant of the $B^2\Sigma^+$ state, which has been determined from our analysis to be in pure precession with the $A^2\Pi$ state. The result is complete separation of the four main branches (P_1, P_2, R_1, and R_2 as expected for a $^2\Sigma$–$^2\Sigma$ transition) of each band. Nearly identical rotational constants for the X and B states result in bandhead to origin separations as large as 15 Å for the (0,0) band compared to 6 Å separations of successive bandheads in the $\Delta v = 0$ sequence. The large head–origin separations, combined with the small spacing of heads within a sequence, result in extensive band overlap which renders an analysis using classical spectroscopic techniques a formidable task. The main problem is to separate lines belonging to a single vibrational band and to correctly identify and number the rotational branches belonging to a particular band of a sequence. As an example, we observe for $v > 0$ in the $\Delta v = 0$ sequence typically 12 strong lines per reciprocal centimetre with Doppler widths (FWHM) on the order of 0.023 cm^{-1}. Usually strong lines from at least three different members of the $\Delta v = 0$ sequence can be found in 1 cm^{-1} of the spectrum.

The method we used in our experiments involves

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excitation of the CaF B–X system by scanning a cw, narrow band (< 1 MHz), single-mode dye laser over consecutive 1 cm^{-1} intervals and detecting the resultant fluorescence through a moderate resolution monochromator functioning as a narrow bandpass filter (typically 2 Å spectral width). The method described is similar to that employed by Demtröder (9) and Linton (10) used in the analyses of NO_2 and YO spectra, respectively. Two important advantages of narrow band detection vs. total fluorescence detection are: (*1*) elimination of detected scattered laser light and chemiluminescence which results in enhanced signal-to-noise ratio in the excitation spectrum, and (*2*) in the case of the CaF B–X system, the excitation spectrum of the Δv band of interest is simplified by exclusion of other bands simultaneously excited by the laser.

Experimental

CaF was produced in a Broida-type oven (11) by the reaction of SF_6 with calcium metal vapor produced by heating calcium metal in an alumina crucible and entraining the vapor in flowing argon at pressures typically 1–2 Torr. The Ca–SF_6 reaction is very exothermic with an estimated enthalpy of −36.5 kcal/mol (12, 13). As a result, high vibrational levels of the X state were significantly populated. This allowed us to observe, in a broad band dye laser (1 Å FWHM bandwidth) excitation spectrum, bandheads from the $\Delta v = 0$ bands as high as $v'' = 25$. Insufficient single line fluorescence intensity limited single-mode dye laser excitation to levels not much higher than $v'' = 15$ in the $\Delta v = 0$ sequence.

B–X fluorescence was excited by a Coherent Radiation Model 599-21 dye laser (< 1 MHz bandwidth) operated with rhodamine 110 dye pumped by 4 W all lines from a CR-3 argon ion laser. It was necessary to adjust the pH of the dye solution, which is normally pH 6, up to pH 7 in order to achieve single mode operation in the wavelength region 5296–5380 Å. The pH of the dye solution was increased by the addition of a commercial pH 10 buffer solution containing a mixture of potassium hydroxide and potassium carbonate in water. The buffer solution was slowly added to the circulating glycol–dye solution until a final single mode output power of 20 mW from the dye laser at 5296 Å was achieved. The resultant CaF B–X fluorescence is dispersed through a Spex Model 1802 monochromator and detected by a dry ice cooled Hamamatsu R818 photomultiplier tube operated at 600 V.

Excitation spectra for the $\Delta v = 0$ sequence were obtained selectively, two branches of a given vibrational band at a time. The single mode dye laser was scanned through the selected branches (e.g., R_1 and R_2) in 1 cm^{-1} intervals and fluorescence was detected exclusively in the other main branches (e.g., P_1 and P_2) which arise from the desired v' and restricted range of N', J' levels. The monochromator wavelength setting and the spectral band width were adjusted to eliminate extraneous lines from other (v', v'') transitions and yet allow a large enough bandwidth to observe a sufficient number of rotational lines over several 1 cm^{-1} scans without the need for frequent readjustment of the wavelength setting. For $\Delta v = -1$ sequence excitation scans, the monochromator was set to detect fluorescence in a rotational branch of the corresponding $\Delta v = 0$ sequence band which is much stronger than that in $\Delta v = \pm 1$ bands. The fluorescence excitation spectrum is calibrated with respect to I_2 $B0_u^+ - X^1\Sigma_g^+$ lines (14) by simultaneously recording I_2 and CaF excitation spectra along with etalon fringes from a 750 MHz free spectral range semi-confocal Fabry-Perot. This allows the line positions to be measured to a relative precision of ± 0.002 cm^{-1} and an absolute accuracy of ± 0.003 cm^{-1}. The absolute wave numbers of the line positions and band origins listed here have *not* been corrected by subtraction of 0.0056 cm^{-1} as suggested by Gerstenkorn and Luc (15).

Results

A list of the measured line positions fitted to obtain molecular constants from the $\Delta v = 0$ and −1 bands appears in the Appendix. It should be noted that the lines indicated as blended, in most cases, involve accidental overlap between similar N members of different F_1 and F_2 branches (e.g., P_1 and P_2) both belonging to the same vibrational band. An ordinary absorption or emission spectrum would exhibit far more blends than our selectively detected fluorescence excitation spectra. The few exceptions to this blend-only-within-a-vibrational-band rule involve the (0,0), (1,1), (1,2), and (2,3) bands. Laser excitation in the (0,0) and (1,1) bands produces extremely bright fluorescence. The monochromator spectral bandwidth was adjusted to 2 Å for the (1,1) band. At this setting, a small amount of leakage of (0,0) fluorescence was unavoidable. This posed no problem in the analysis of the excitation spectrum of the (1,1) band.

1. Rotational Analysis

The absolute numbering of the rotational branches was established by a procedure involving combination differences between the F_1 and F_2

TABLE 1. $X^2\Sigma^+$ rotational constants in reciprocal centimetres

	B_v''		$D_v'' \times 10^7$	
v''	Experimental*	Exp. − cal.	Experimental*	Exp. − cal.
0	0.342488	−0.000002	4.50†	0.07
1	0.340050	0.000001	4.50†	0.02
2	0.337621(16)	0.000000	4.50†	−0.02
8	0.323300(17)	−0.000014	4.73(4)	−0.06
9	0.320969(6)	−0.000005	4.73‡	−0.10
12	0.313929(53)	0.000097	5.04§	0.08
13	0.311781(13)	0.000045	5.04(4)	0.03
14	0.309413(35)	−0.000044	5.04§	−0.01
15	0.307128(24)	−0.000063	5.04§	−0.05

*Uncertainties in parentheses represent one standard deviation.
†Fixed to D_0'' in ref. 5.
‡Fixed to D_8'' in fit of line positions.
§Fixed to D_{13}'' in fit of line positions.

TABLE 2. $B^2\Sigma^+$ rotational constants in reciprocal centimetres

	B_v'		$D_v' \times 10^7$	
v''	Experimental*	Exp. − cal.	Experimental*	Exp. − cal.
0	0.341285(3)	−0.000006	4.65(2)	−0.03
1	0.338677(2)	0.000003	4.75(2)	0.03
2	0.336074(17)	0.000005	4.75†	−0.01
8	0.320691(15)	−0.000014	5.01(3)	0.02
9	0.318172(8)	−0.000016	4.95(3)	−0.08
12	0.310594(57)	−0.000118	5.25‡	0.10
13	0.308284(12)	0.000039	5.25(4)	0.06
14	0.305750(31)	−0.000041	5.25‡	0.02
15	0.303311(30)	−0.000038	5.25‡	−0.02

*Uncertainties in parentheses represent one standard deviation.
†Fixed to D_1' in fit of line positions.
‡Fixed to D_{13}' in fit of line positions.

component lines of a $\Delta N = +1$ or -1 branch. The first combination difference between a $P_1(N)$ and $P_2(N)$ line is (ref. 16, p. 249)

$$[1] \quad \Delta\nu_{12}{}^{P}(N) = \Delta\gamma N - \tfrac{1}{2}(\gamma' + \gamma'')$$

while, between $R_1(N)$ and $R_2(N)$ lines, it is

$$[2] \quad \Delta\nu_{12}{}^{R\,(N)} = \Delta\gamma N + \tfrac{1}{2}(3\gamma' - \gamma'')$$

In both cases the *second combination difference* is equal to $\Delta\gamma$, the difference between the upper and lower state spin–rotation constant. For the B–X transition of CaF, $|\gamma'| \gg |\gamma''|$ and to a first approximation the second difference equals γ'. For the A state $p < 0$ (refs. 3–5) and, if the A and B states are in pure precession, this requires that $\gamma' < 0$. In other words, the $P_2(N)$ (or $R_2(N)$) line is always to the blue of the $P_1(N)$ (or $R_1(N)$) line. The variation with N of the separation between consecutive rotational lines belonging to the same F_i branch is, in this case, very small compared to that of the $\Delta N = 0$ combination difference since $|\Delta B| \ll |\gamma'|$. With knowledge that γ' is negative and larger in magnitude than γ'' and ΔB, one may quickly identify pairs of F_i branches (e.g., P_1 and P_2) from a set of consecutive excitation spectra. The appropriate γ' obtained from second differences is substituted into either [1] or [2] to establish an absolute rotational numbering for both branches.

The line positions for each band of the $\Delta v = 0$ sequence were fit to standard expressions for the energy levels of a $^2\Sigma - {}^2\Sigma$ transition (ref. 16, p. 249) by a nonlinear, weighted, least-squares procedure. The rotational and band origin constants obtained from the fits for the X and B states are listed in Tables 1–4. In the fits involving the (0,0) and (1,1) bands the B_v'' and γ'' constants were fixed to the values reported in ref. 4 while the D_v'' constant was fixed to the value given in ref. 5. The calculated B_v values were obtained by a weighted least-squares fit to the expression

$$[3] \quad B_v = B_e - \alpha_e(v + 1/2) + \gamma_e(v + 1/2)^2$$

and for D_v to the expression

$$[4] \quad D_v = D_e + \beta_e(v + 1/2)$$

A complete fit of the $\Delta v = -1$ bands was not

TABLE 3. The $B^2\Sigma^+$ spin-rotation constants as a function of vibrational level in reciprocal centimetres

	γ_v	
v	Experimental*	Exp. − cal.†
0	−0.04581(3)	−0.00003
1	−0.04607(2)	0.00002
2	−0.04642(6)	−0.00001
8	−0.04860(3)	−0.00003
9	−0.04897(3)	−0.00000
12	−0.05019(3)	0.00002
13	−0.05063(2)	0.00002
14	−0.05115(3)	−0.00006
15	−0.05149(6)	0.00006

*Uncertainties in parentheses represent one standard deviation.
†Calculated from the weighted least-squares fit of γ_v, $\gamma_v = -0.04562(3) - 0.00030(1)(v + 1/2) - 0.0000050(7)(v + 1/2)^2$.

TABLE 4. The $B^2\Sigma^+$–$X^2\Sigma^+$ band origins in reciprocal centimetres

	ν_0	
v', v''	Experimental*	Exp. − cal.
0, 0	18 833.139(1)	0.002
1, 1	18 816.442(1)	−0.002
2, 2	18 799.293(1)	−0.002
8, 8	18 687.260(2)	0.000
9, 9	18 667.146(1)	0.004
12, 12	18 604.478(2)	0.003
13, 13	18 582.841(0)	−0.001
14, 14	18 560.852(1)	0.001
15, 15	18 538.513(1)	0.002
0, 1	18 250.296(7)	0.002
1, 2	18 239.343(3)	−0.001
2, 3	18 227.890(2)	0.001
3, 4	18 215.937(2)	0.000

*Uncertainties in parentheses represent one standard deviation.

performed due to the insufficient number of lines recorded. Instead, the $\Delta v = -1$ band origins were determined by averaging the difference

$$\nu_0(v',v'') = \nu(N)_{\text{measured}} - F_i'(N') + F_j''(N'')$$

using the rotational constants obtained from the $\Delta v = 0$ band fits.

The γ' constants for the B state are listed in Table 3. The calculated γ_v constants were obtained by a weighted least-squares fit to the empirical expression

$$[5] \quad \gamma_v = \gamma_1 + \gamma_2(v + 1/2) + \gamma_3(v + 1/2)^2$$

For the X state we did not observe any significant vibrational dependence of the spin–rotation constant. From a trial fit of the (13,13) band, a $\gamma'' = 0.0012 \pm 0.0004\,\text{cm}^{-1}$ was determined. A high precision value for $\gamma'' = 0.001287 \pm 0.000007\,\text{cm}^{-1}$ was measured for $v'' = 0$ by Bernath *et al.* (17) using the technique of intermodulation spectroscopy on the A–X (0,0) band. Therefore, we concluded that the vibrational dependence of γ'' can be ignored and its value was fixed to 0.0013 in all subsequent fits.

2. Vibrational Analysis

The vibrational constants for the X and B states were obtained from a weighted least-squares fit of the $\Delta v = 0$ and -1 band origins to the expression

$$[6] \quad T_v = T_e' + \omega_e'(v' + 1/2) - \omega_e''(v'' + 1/2) - \omega_e'x_e'(v' + 1/2)^2 + \omega_e''x_e''(v'' + 1/2)^2 + \omega_e'y_e'(v' + 1/2)^3 - \omega_e''y_e''(v'' + 1/2)^3$$

A summary of the molecular constants for both states is presented in Table 5.

3. Estimates of α_e, D_e, β_e, γ_e, and $\omega_e y_e$

In addition to the molecular constants listed in Table 5 obtained from the various fits for the X and B states, estimates are also included for the constants α_e, D_e, β_e, γ_e, and $\omega_e y_e$ for both states. Because these particular constants can be expressed in terms of B_e, α_e, ω_e, and $\omega_e x_e$, using relationships derived by Dunham and certain assumed model potentials, the estimates, especially for α_e, β_e, and $\omega_e y_e$, provide a means to determine whether the fitted constants have reasonable values.

The α_e and D_e constants were estimated using the standard Pekeris (18) and Kratzer (ref. 16, p. 103) relations, respectively. The β_e constants were calculated using the Dunham expression (19)

$$[7] \quad \beta_e \simeq -Y_{12} = (12B_e^4/\omega_e^3) \times (19/2 + 9a_1 + 9a_1^2/2 - 4a_2)$$

The Dunham a_1 and a_2 coefficients were computed using [8] and [9] respectively, listed below.

$$[8] \quad a_1 = -\alpha_e\omega_e/6B_e^2 - 1$$

$$[9] \quad a_2 = 5a_1^2/4 - 2\omega_e x_e/3B_e$$

But in order to calculate γ_e and $\omega_e y_e$ from [10] and [11], respectively,

$$[10] \quad \gamma_e \simeq Y_{21} = (6B_e^3/\omega_e^2)[5 + 10a_1 - 3a_2 + 5a_3 - 13a_1a_2 + 15(a_1^2 + a_1^3)/2]$$

$$[11] \quad \omega_e y_e \simeq Y_{30} = (B_e^2/2\omega_e)[10a_4 - 35a_1a_3 - 17a_2^2/2 + 225a_1^2a_2/4 - 705a_1^4/32]$$

it was necessary to obtain expressions for the

TABLE 5. Equilibrium molecular constants for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states in reciprocal centimetres*

	$X^2\Sigma^+$		$B^2\Sigma^+$	
	Fit	Calculated	Fit	Calculated
T_e	0	—	18 841.309(3)	—
ω_e	588.633(36)	—	572.405(36)	—
$\omega_e x_e$	2.908(13)	—	3.143(13)	—
$\omega_e y_e$	0.0081(15)	0.010(2)	0.0095(15)	0.012(2)
B_e	0.343715(7)	—	0.342604(7)	—
α_e	0.002453(5)	0.002300(6)	0.002630(6)	0.002494(6)
γ_e	0.0000062(4)	0.0000069(14)	0.0000063(4)	0.0000073(16)
$D_e \times 10^7$	4.21(5)	4.6878(6)	4.66(3)	4.9094(7)
$\beta_e \times 10^9$	6.13(42)	0.11(14)	3.93(56)	0.69(17)
R_e (Å)	—	1.952	—	1.955

*Uncertainties in parentheses represent one standard deviation.

Dunham a_3 and a_4 coefficients. Approximate expressions for a_3 and a_4 in terms of a_1 and a_2 were derived by Jordan *et al.* (20) from a method, using Padé approximants, to construct potential curves for ionic molecules. The expressions for a_3 and a_4, obtained from ref. 20, are

[12] $a_3 \simeq 2a_1a_2 - a_1^3$

[13] $a_4 \simeq a_2^2 + a_1^2 a_2 - a_1^4$

With the exception of the β_e constants, reasonable agreement is obtained between estimated and fitted constants.

Discussion

The rotational analysis of the B–X system indicates that the $A^2\Pi$ and $B^2\Sigma^+$ states are in pure precession. From the value of $p = -0.04454$ cm^{-1} reported in ref. 5 for the $v = 0$ level of the A state, the ratio of γ_0/p_0 ($\gamma = -0.04581$ cm^{-1} for $v = 0$ of the B state) is 1.029 and the pure precession relation holds to within 3%. A value of $l = 1.04$ for the B state is obtained by substituting γ_1 from [5], T_e for the B state, and the A state B_e, T_e, and spin–orbit constants from ref. 4 into the vibration-independent term of the Van Vleck pure precession relation. Thus, it seems that the $A^2\Pi$ and $B^2\Sigma^+$ states originate from the $3p$ complex of the calcium ion as suggested in refs. 5 and 21.

The X state vibrational constants reported in ref. 5 were poorly determined since they incorporated bandhead data from Johnson (1) in their weighted least-squares fit. It is not surprising that there are differences between the two sets of constants, illustrating that raw bandhead data from ref. 1 must be treated with caution.

Franck–Condon factors were calculated for all sequences up to $v = 20$ using standard RKR (22) and FC (23) computer programs. The Franck–Condon factors for the $\Delta v = 0$ and ± 1 sequences are displayed in Table 6. As expected, the $\Delta v = 0$ sequence is the most intense followed by weaker $\Delta v = \pm 1$ sequences. The ratio

$$\frac{I_{\Delta v=+1} + I_{\Delta v=-1}}{2I_{\Delta v=0}}$$

changes from 0.0023 for $v = 1$ to 0.30 at $v = 19$ so the vibrational structure becomes appreciably less diagonal as v increases.

We observed no sharp bandhead structure for the $\Delta v = -1$ sequence, in contrast to the $\Delta v = 0$ sequence. A closer look at the rotational constants for both states explains this observation. The bandhead to band origin separation is inversely proportional to ΔB. For the $\Delta v \geq 0$ sequences ΔB is always negative, resulting in red degraded rota-

TABLE 6. Franck–Condon factors for the $\Delta v = -1$, 0, and +1 sequences of the $B^2\Sigma^+$–$X^2\Sigma^+$ transition

v''	$q_{v''-1,v''} \times 10^2$	$q_{v'',v''}$	$q_{v''+1,v''} \times 10^2$
0	—	0.999	0.137
1	0.134	0.995	0.333
2	0.321	0.991	0.596
3	0.566	0.985	0.938
4	0.877	0.977	1.37
5	1.26	0.968	1.89
6	1.72	0.956	2.52
7	2.25	0.943	3.26
8	2.88	0.928	4.12
9	3.59	0.910	5.10
10	4.40	0.890	6.22
11	5.29	0.867	7.46
12	6.27	0.842	8.83
13	7.35	0.815	10.3
14	8.51	0.785	11.9
15	9.74	0.753	13.7
16	11.1	0.718	15.5
17	12.4	0.681	17.4
18	13.8	0.642	19.4
19	15.3	0.601	21.4
20	16.8	0.558	—

tional branches. This is not the case for the $\Delta v < 0$ sequences. For a given sequence one can write

$$\Delta B = \Delta B_e - \alpha_e'\Delta v - \Delta\alpha_e(v'' + 1/2) + \ldots$$

For the B–X system $\Delta\alpha_e > 0$ and $\Delta B_e < 0$. The above equation reveals that for $\Delta v < 0$ sequences, a sign reversal of ΔB will occur at some value of v. Because α_e' is slightly larger than ΔB_e, the reversal will occur at fairly low v. Thus, the bandhead pattern in a $\Delta v < 0$ sequence is violet shaded heads for low v, becoming headless at a particular v, followed by red shaded heads for high v. For the $\Delta v = -1$ sequence, the bandhead to band origin separation for the (0,1) band is already fairly large, approximately 15 Å, and increases steadily to infinity as ΔB approaches zero. This occurs near the (7,8) band. From then on, the bandheads are shaded to the red and a steady decrease in bandhead to band origin separation is expected. The bandhead intensity is diminished considerably because the population of the very high N levels where the head occurs is essentially zero. This, combined with closely spaced sequence bands, results in the nonoccurrence of a sharp bandhead structure.

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Appendix

In addition to the blended lines within a band, a few blends between bands were present. The $P_2(6)$ line of the (1,1) band was blended with $P_1(28)$ of the (0,0) band. For the (1,2) and (2,3) bands the only inter-band blends were those of $R_2(1)$ to $R_2(4)$ lines of the (1,2) band with $R_2(17)$ to $R_2(20)$ of the (2,3) band.

The units are reciprocal centimetres and it is recommended (15) that a correction of 0.0056 cm^{-1} be subtracted from all lines. The numbers in parentheses are (observed − calculated) in units of 10^{-3} reciprocal centimetres. The asterisk indicates a blended line.

TABLE A1. Measured line positions

Band	N	R_1	R_2	P_1	P_2
(0, 0)	10	18 840.256(2)	18 840.792(−2)	—	—
	11	18 840.886(1)	18 841.473(0)*	18 825.232(−6)	—
	12	18 841.507(−7)*	18 842.147(−2)*	18 824.501(−2)	18 825.041(−5)
	13	18 842.147(6)*	18 842.818(−5)*	18 823.767(0)	18 824.355(−2)
	14	18 842.764(−1)*	18 843.496(2)	18 823.026(−2)	18 823.665(0)
	15	18 843.390(4)	—	—	18 822.972(1)*
	16	—	—	—	18 822.281(6)*
	17	—	—	18 820.799(2)	—
	18	—	—	—	18 820.876(1)
	26	—	18 851.339(0)	18 813.984(1)	—
	27	—	18 851.972(−3)	18 813.216(1)	—
	28	18 851.216(−3)	18 852.609(1)	18 812.450(5)*	18 813.741(0)
	29	18 851.799(−3)	—	18 811.669(−3)	18 813.016(0)
	30	18 852.380(−2)	—	18 810.899(2)	18 812.288(0)
	31	18 852.960(1)	—	—	18 811.558(0)
	34	—	—	18 807.780(6)	—
	35	—	—	18 806.988(0)	—
	36	—	—	18 806.202(2)	18 807.875(2)
	37	—	—	18 805.408(−1)	18 807.128(−2)
	38	—	—	—	18 806.386(2)
	39	—	—	—	18 805.635(−1)
(1, 1)	5	—	18 820.630(0)	18 812.922(3)	18 813.133(−1)
	6	18 820.962(2)	18 821.311(−3)	18 812.199(−3)	18 812.454(−10)*
	7	18 821.587(−7)*	18 821.995(−1)	18 811.481(−1)	18 811.787(−4)
	8	—	18 822.675(1)	18 810.760(1)	18 811.115(0)
	9	18 822.855(1)	—	18 810.037(3)	18 810.438(1)
	10	—	—	18 809.314(9)*	18 809.759(2)
	11	—	—	18 808.574(−1)	18 809.075(2)
	12	—	—	18 807.842(1)	18 808.386(−1)
	13	18 825.341(3)	18 826.021(−3)*	—	18 807.699(0)
	14	18 825.951(−1)	18 826.684(−1)	—	—
	15	18 826.562(−1)	18 827.340(−3)	—	—
	16	18 827.170(−1)	18 827.997(−1)	—	—
	17	18 827.773(−2)	18 828.648(−2)	18 804.135(1)	—
	18	18 828.378(1)	18 829.301(2)	18 803.386(1)	—
	19	18 828.973(−3)	18 829.947(2)	18 802.635(2)	18 803.514(3)
	20	18 829.572(1)	18 830.587(−1)	18 801.881(2)	18 802.804(0)
	21	18 830.165(1)	18 831.226(−2)	18 801.121(0)	18 802.095(1)
	22	18 830.750(−3)	—	18 800.363(2)	18 801.382(1)
	23	18 831.336(−3)	—	18 799.597(−2)	18 800.668(2)
	24	—	—	—	18 799.949(1)
	25	—	—	—	18 799.230(2)
	28	—	18 835.617(0)	—	—
	29	—	18 836.232(1)	—	—
	30	18 835.351(0)	18 836.842(0)	—	—
	31	18 835.911(0)	18 837.448(−1)	—	—
	32	18 836.468(0)	—	—	—
	33	18 837.022(1)	—	—	—
	34	18 837.570(0)	—	—	—
(2, 2)	5	18 803.138(1)	18 803.447(1)	—	—
	6	18 803.766(0)	18 804.125(2)	—	—
	7	18 804.392(−1)	18 804.794(−3)	—	—
	8	18 805.013(−3)	18 805.462(−6)	—	—
	9	18 805.629(−7)	—	18 792.916(2)	18 793.323(2)
	10	—	—	18 792.190(2)	18 792.643(0)
	11	—	—	18 791.462(4)	18 791.961(0)
	12	18 807.474(−2)	—	18 790.726(0)	18 791.274(−2)
	13	18 808.083(0)*	18 808.772(−1)	18 789.992(2)	18 790.587(−1)
	14	18 808.686(0)	18 809.426(2)	—	18 789.898(1)
	15	18 809.287(1)	18 810.073(1)	—	18 789.203(−1)*
	16	18 809.886(3)	—	—	—
	21	—	—	18 783.995(−3)	—

TABLE A1 (*Continued*)

Band	N	R_1	R_2	P_1	P_2
(2, 2)	22	—	—	18 783.236(0)	18 784.260(−3)
	23	—	—	—	18 783.543(−2)
	24	—	—	—	18 782.830(5)
(8, 8)	16	—	—	18 675.924(4)*	—
	17	—	—	18 675.169(3)	18 675.988(−3)*
	18	—	—	18 674.404(−3)	18 675.280(−1)
	19	—	—	18 673.645(2)	18 674.566(−1)
	20	—	18 700.157(−1)	18 672.874(1)	18 673.846(−2)
	21	—	18 700.711(0)	—	18 673.122(−1)
	22	18 700.089(2)	18 701.256(−3)	—	18 672.392(−2)
	23	18 700.580(1)	18 701.798(−2)	—	—
	24	18 701.067(2)	18 702.334(−2)	—	—
	25	18 701.546(1)	18 702.868(1)		
	26	18 702.020(0)	—	—	
	27	18 702.490(1)	—	—	—
	28	18 702.955(3)	—	—	—
	44	18 709.540(−3)	—	—	—
	45	18 709.899(−3)	—	—	—
	46	18 710.256(1)	—	18 651.061(3)	—
	47	18 710.600(−1)	—	18 650.149(1)	—
	48	18 710.941(1)	—	18 649.231(−1)	—
	49	18 711.273(0)	—	18 648.307(−4)	18 650.737(4)
	50	18 711.601(1)	—	18 647.385(0)	18 649.860(4)
	51	18 711.921(2)	—	18 646.449(−4)	18 648.974(0)
	52	—	—	—	18 648.086(−1)
	53	—	—	—	18 647.195(1)
	54	—	—	—	18 646.295(−1)
(9, 9)	11	—	18 674.733(−2)	18 659.527(0)	—
	12	18 674.651(0)	18 675.328(−1)	18 658.799(0)	18 659.377(−2)
	13	18 675.190(1)	18 675.912(−4)	18 658.069(3)*	18 658.694(−2)
	14	18 675.719(−1)	—	—	18 658.010(3)*
	15	18 676.243(−2)	—	—	18 657.320(7)*
	31	—	18 685.481(5)	—	—
	32	—	18 685.948(−1)	—	—
	33	—	18 686.414(−2)	—	—
	34	—	18 686.876(−1)	—	—
	35	—	18 687.331(0)	18 640.546(2)	—
	36	18 685.901(5)*	18 687.781(2)	18 639.683(−1)	—
	37	18 686.284(−3)	18 688.221(0)	18 638.818(−1)	18 640.657(2)
	38	18 686.671(−1)	—	—	18 639.833(−2)
	39	18 687.052(2)	—	—	18 639.008(−1)
	40	—	—	—	18 638.177(−1)
(12, 12)	10	18 610.662(3)	18 611.247(−3)	—	—
	11	18 611.179(−1)	18 611.820(−2)	—	—
	12	18 611.693(−1)	18 612.386(−2)	—	—
	13	18 612.201(−1)	18 612.946(−1)	—	—
	14	18 612.703(1)	18 613.500(1)	—	—
	15	18 613.197(1)	18 614.044(0)	—	—
	16	18 613.687(5)	—	—	—
	35	—	—	18 577.716(1)	—
	36	—	—	18 576.833(1)	—
	37	—	—	18 575.941(−1)	18 577.825(2)
	38	—	—	18 575.045(−1)	18 576.982(4)
	39	—	—	18 574.144(1)	18 576.126(−1)
	40	—	—	18 573.233(−1)	18 575.271(2)
	41	—	—	—	18 574.402(−3)
	42	—	—	—	18 573.535(1)
(13, 13)	2	18 584.591(−1)	18 584.773(0)	—	—
	3	—	18 585.391(−3)	—	—
	4	18 585.726(2)	18 586.010(1)	—	—
	5	18 586.283(3)	18 586.617(1)	—	—

TABLE A1 (*Continued*)

Band	N	R_1	R_2	P_1	P_2
(13, 13)	6	18 586.827(−1)	18 587.215(−1)	—	—
	7	18 587.370(1)	18 587.808(−1)	18 578.175(2)	18 578.513(1)
	8	18 587.904(1)	—	18 577.475(0)	18 577.865(−1)
	9	—	—	18 576.769(−1)	18 577.209(−4)
	10	—	18 589.547(1)	18 576.059(1)	18 576.550(−3)
	11	18 589.465(2)	18 590.110(−1)	18 575.341(2)	18 575.885(−1)
	12	18 589.969(0)	18 590.667(−1)	18 574.612(−1)	18 575.213(1)
	13	18 590.467(0)	18 591.220(1)	18 573.875(−6)*	18 574.529(−2)
	14	18 590.958(0)	—	18 573.148(7)*	18 573.853(10)*
	15	18 591.443(1)	18 592.299(1)	18 572.398(3)	18 573.148(−1)*
	16	—	—	—	18 572.448(0)
	17	18 592.388(0)	—	—	—
	18	18 592.848(−2)	18 593.855(−6)	—	—
	19	18 593.304(−1)*	18 594.367(−1)	—	—
	20	18 593.751(−1)	18 594.867(0)	—	—
	21	18 594.191(−1)	18 595.359(0)	—	—
	22	18 594.624(−1)	—	—	—
	23	18 595.050(0)	—	—	—
	24	18 595.469(1)	—	—	—
	28	18 597.065(1)	18 598.590(−5)*	—	—
	29	18 597.445(1)	18 599.028(1)	—	—
	30	18 597.816(−1)	18 599.453(2)	—	—
	31	18 598.181(−1)	—	—	—
	32	18 598.541(2)	—	—	—
	33	18 598.888(−1)	—	—	—
	34	18 599.229(−2)	—	—	—
	35	18 599.564(−1)	—	—	—
	40	—	—	18 551.507(0)	—
	41	—	—	18 550.582(0)	—
	42	—	—	18 549.649(−1)	—
	43	—	—	—	18 550.921(1)
	44	—	18 604.581(0)	—	—
	45	—	18 604.888(0)	—	—
	46	—	18 605.190(3)	—	—
	47	—	18 605.479(1)	—	—
	48	—	18 605.760(−1)	—	—
	49	—	18 606.035(0)	—	—
	50	—	18 606.300(−1)	—	—
(14, 14)	8	—	—	18 555.516(3)	—
	9	—	—	18 554.811(1)	18 555.257(0)
	10	—	—	18 554.101(2)	18 554.602(3)
	11	—	—	18 553.381(−1)	18 553.934(0)
	12	—	—	18 522.657(0)	18 533.258(−3)
	13	—	—	—	18 552.579(−3)
	14	—	—	18 551.192(7)*	—
	15	—	—	18 550.444(5)*	18 551.192(−9)*
	21	—	18 573.188(−1)*	—	—
	22	—	18 573.651(−10)*	—	—
	23	18 572.840(−2)	18 574.126(0)	—	—
	24	18 573.246(−1)*	18 574.582(−1)	—	—
	25	18 573.651(7)*	18 575.032(0)	—	—
	26	18 574.034(2)	18 575.480(7)*	—	—
	27	18 574.414(1)	18 575.905(−2)*	—	—
	28	18 574.788(1)	18 576.328(−5)	—	—
	29	18 575.152(0)	—	—	—
	30	18 575.500(−9)*	18 577.164(4)*	—	—
	31	18 575.866(7)*	18 577.564(2)	—	—
	32	18 576.196(−4)	18 577.956(0)	—	—
	33	18 576.533(−1)	18 578.344(2)	—	—
	34	—	—	—	—
	35	18 577.164(−12)*	—	—	—

TABLE A1 (*Concluded*)

Band	N	R_1	R_2	P_1	P_2
(15, 15)	6	—	18 542.810(1)	—	—
	7	18 542.943(2)	18 543.389(1)	—	—
	8	18 543.459(0)	—	—	—
	9	18 543.967(−3)*	18 544.521(−2)*	—	—
	10	18 544.476(3)*	18 545.078(−1)	—	—
	11	18 544.968(−1)	18 545.625(−2)	—	—
	12	18 545.453(−3)	18 546.167(−1)	—	—
	13	18 545.937(1)	18 546.703(3)	—	—
	14	18 546.410(2)	—	—	—
	16	—	—	18 527.380(1)	—
	17	—	—	18 526.618(0)	18 527.491(1)
	18	—	—	18 525.847(−2)	18 526.776(2)
	19	—	—	18 525.072(0)	18 526.049(−1)
	20	—	—	—	18 525.319(0)
	21	—	—	—	18 524.580(−1)
(0, 1)	8	—	18 256.750(−12)	—	—
	9	18 256.990(−6)	18 257.485(−4)	—	—
	10	18 257.678(−1)	18 258.227(7)	—	—
	11	18 258.381(17)	—	—	—
(1, 2)	1	18 240.658(5)*	18 240.773(3)*	—	—
	2	18 241.315(4)	18 241.471(−4)*	—	—
	3	18 241.971(0)	18 242.176(−7)*	—	—
	4	18 242.631(−2)	18 242.875(−17)*	—	—
	5	18 243.298(1)	18 243.601(−3)	—	—
(2, 3)	5	18 231.806(0)	18 232.118(3)*	—	—
	6	18 232.466(−2)	18 232.823(2)*	—	18 224.038(0)
	7	18 233.124(−1)	18 233.531(2)	18 223.089(−1)	18 223.404(2)
	8	18 233.784(−2)*	18 234.235(−3)	—	—
	9	—	18 234.948(−1)	—	—
	17	—	18 240.697(3)	—	—
	18	18 240.489(0)	18 241.415(−4)	—	—
	19	18 241.167(−1)	18 242.147(2)*	—	—
	20	18 241.847(−1)	18 242.876(4)*	—	—
	21	18 242.526(−3)	—	—	—
	22	18 243.210(−1)	—	—	—
(3, 4)	10	18 223.089(8)*	18 223.636(3)	—	—
	11	18 223.744(6)	18 224.338(0)	—	—
	12	18 224.398(2)	—	—	—
	21	—	18 231.449(0)	—	—
	22	—	18 232.165(−1)	—	—
	23	18 231.708(3)	18 232.882(−2)	—	—
	24	18 232.378(2)	18 233.601(−2)	—	—
	25	18 233.048(1)	18 234.321(−1)	—	—
	26	18 233.724(5)	—	—	—
	27	18 234.395(3)	—	—	—

*Blended line.