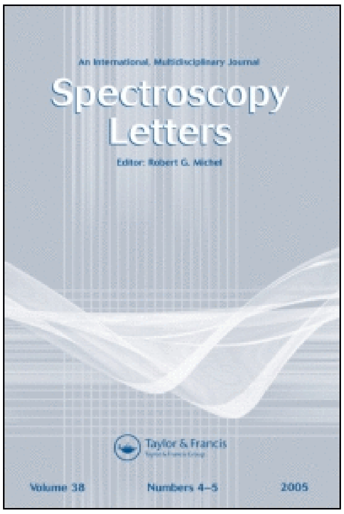

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K. Sunanda[a]; P. Saraswathy[a]; M. D. Saksena[a]
[a] Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India

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Electronic Transition Moment Variation in the $C^2\Pi-X^2\Sigma^+$ System of Boron Monoxide

K. Sunanda, P. Saraswathy and M. D. Saksena
Spectroscopy Division, Bhabha Atomic Research Centre, Trombay,
Mumbai, India

Abstract: The extensive band system belonging to the $C^2\Pi_r-X^2\Sigma^+$ transition of boron monoxide (BO) molecule lying in the vacuum ultraviolet region (150–230 nm) has been recorded in emission in a hollow cathode glow. A few new bands involving high v′ levels of C state have been observed. The Franck–Condon factors and r-centroids were computed for the C–X system. By correlating the measured intensities to theory, the (relative) variation of the C–X electronic transition moment with internuclear separation was examined.

Keywords: Boron oxide, Franck–Condon factor, vibronic intensity distribution

INTRODUCTION

Historically, the spectrum of boron monoxide (BO) has played an important role in the development of quantum theory; Mulliken [1] as early as in 1925 established experimentally for the first time the vibrational isotope effect and later verified the existence of zero-point energy in molecules. The reaction dynamics of the formation of BO in low-lying electronic states gained interest, following the suggestion of a possible lasing action in the $A^2\Pi_i-X^2\Sigma^+$ transition.[2,3] The electronic spectra of BO reported to date are identified to belong to α ($A^2\Pi_i-X^2\Sigma^+$:337–637 nm), β ($B^2\Sigma^+-X^2\Sigma^+$:214–330 nm), and γ ($C^2\Pi_r-X^2\Sigma^+$:150–230 nm) systems.[4–10] Configuration-interaction studies of the low lying electronic states of BO by Karna and Grein [11] suggested 16 stable states including four Rydberg states, out of which only four stable states

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Address correspondence to P. Saraswathy, Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India. E-mail: saras@barc.gov.in

($X^2\Sigma^+$, $A^2\Pi_i$, $B^2\Sigma^+$, and $C^2\Pi_r$) can so far be characterized experimentally. Investigation of the perturbing $C^2\Pi$ states has revealed the existence of few dark states like $^4\Sigma$, $^2\Sigma$, and $^2\Delta$, but so far no molecular constants for these states are known. Electronic transition moment variation with internuclear distance for the A–X and B–X, from experimentally measured intensity, is reported to be linearly increasing in the domain $1.24 \leq r \leq 1.42$ Å.[12]

In this paper, we report the vibrational studies carried out on the C–X system of BO molecule. The emission spectrum of BO has been recorded at a moderate resolution of 1.1 Å. We present, for the first time, the results of the quantitative study of the variation of the (relative) electronic transition moment with the internuclear separation for the C–X system.

MATERIALS AND METHODS

To record the C–X band system of BO molecule, earlier workers have used both microwave and hollow cathode (HC) excitations. In our case, the use of HC run at high currents (500 mA) helped us to record the entire system in the region 1400–3200 Å with good intensity. Anhydrous boric oxide (B_2O_3) was loaded in the stainless steel cathode, and the neon flow was adjusted using a needle valve to obtain a steady glow. To get the best excitation condition, different rare gases like argon and helium were also tried as buffer gases. Though spectra appeared with good intensity with argon, the presence of strong atomic lines of argon overlapping the weak vibrational band-heads made the vibrational assignment difficult. With helium, the hollow cathode glow was difficult to sustain at low pressures, and for high pressures of helium, BO spectra appeared weak and broadened. Neon was found to be a better buffer gas for exciting the BO spectra. To obtain an intense spectrum of BO, the neon flow had to be kept at low pressure (~1–2 Torr); at high pressures of neon, the bands of BO were found to be broadened. The spectrum was recorded on a 1-m normal incidence vacuum monochromator (Acton VM521, Acton Research Corp., USA), having a resolution of ~1.1 Å using 1200 grooves/mm grating blazed at 1500 Å. The detector was photomultiplier tube (PMT) (9635QB) with a sodium salicylate–coated window kept in front. The absolute quantum efficiency of sodium salicylate for exciting radiation between 400 and 3400 Å is about 65% and is almost constant. An in-house assembled data acquisition system (DAS) was used for scanning the spectrum and to collect the data. A lithium fluoride window was used at the entrance slit, and the monochromator was pumped through a turbo molecular pump to maintain a vacuum of about 10^{-5} mbar inside. The hollow cathode lamp was coupled directly to the entrance port of the monochromator without any focusing devices. Boron atomic lines served as standard for wavelength calibration. In order to study the variation of the electronic transition moment, the height of the bands was approximated as the band intensity.

RESULTS AND DISCUSSION

Vibrational Structure

Figure 1 shows an overview of the observed band system of BO in the 1500–2500 Å region. As seen from the figure, the extensive system of bands belong to $C^2\Pi-X^2\Sigma^+$ transition overlapped on the longer wavelength region by some bands of the β system. The wave number of the band-heads were fitted to a least-squares program to yield the vibrational constants of the $C^2\Pi$ state with an overall standard deviation of $\sim 5\,\mathrm{cm}^{-1}$. The vibrational analysis could be extended to bands involving $v' = 10$ in the C state. The resulting vibrational constants agreed with those reported by previous workers.[10] The band-heads along with their vibrational assignments are listed in Table 1. The newly observed bands are marked with an asterisk in Table 1. Although we obtained bands involving $v' = 10$ levels, the $\omega'_e y'_e$ value of the C state could not be determined very precisely. From the Birge–Sponer plot, the C and X states dissociation energy values were computed to be $39{,}900\,\mathrm{cm}^{-1}$ and $60{,}510\,\mathrm{cm}^{-1}$, respectively. These values suggest that the $C^2\Pi$ state correlates diabatically with $[B(^2P) + O^*(^1S)]$ and $X^2\Sigma^+$ into $[B(^2P) + O(^3P)]$.

Intensity Distribution

The reinvestigation of the C–X system was taken up to correlate the relative variation of the electronic transition moment with internuclear separation *r*. The C–X system of BO is rather extensive, so the net electronic transition intensity is distributed among many vibronic transitions. A quantitative

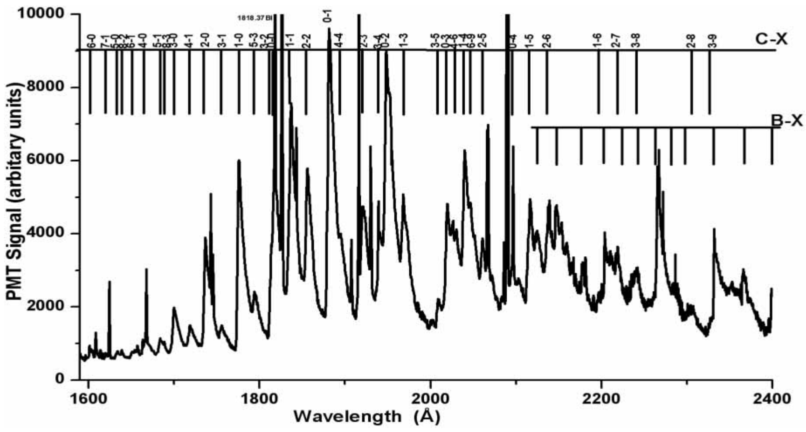

Figure 1. $C^2\Pi_r-X^2\Sigma^+$ band system of BO.

Table 1. Band-heads of the C–X system of BO molecule

v′-v″	$\lambda_{v',v''}$(Å)	$\nu_{v',v''}$(cm^{-1})	I_{obs}	I_{cal}	FCF	$r_{centroid}$
0–0	1816.48	55051.53	5.2	6.44	0.129	1.2608
0–1	1880.00	53191.49	10.0	10.0	0.278	1.2943
0–2	1947.14	51357.37	9.3	7.45	0.285	1.3277
0–3	2018.87	49532.66	3.1	3.50	0.185	1.3612
0–4	2094.51	47743.86	1.6	1.16	0.084	1.3952
1–0	1774.93	56340.25	6.7	8.09	0.241	1.2375
1–1	1835.54	54479.88	2.9	3.40	0.140	1.2707
1–3	1967.19	50833.93	1.9	1.30	0.102	1.3384
1–4	2039.08	49041.72	3.9	1.92	0.206	1.3713
1–5	2115.47	47270.82	2.7	1.19	0.175	1.4050
1–6	2196.45	45528.01	—	—	0.009	1.4396
2–0	1735.69	57613.97	4.0	5.55	0.245	1.2147
2–2	1854.88	53911.84	2.7	1.39	0.116	1.2814
2–3	1919.26	52103.41	2.5	0.84	0.097	1.3134
2–5	2060.15	48540.15	0.9	0.42	0.091	1.3822
2–6	2136.67	46801.80	1.0	0.62	0.182	1.4153
2–7	2218.11	45083.43	0.8	0.38	0.153	1.4498
2–8	2304.11	43400.70	—	—	0.008	1.4857
3–0	1698.98	58858.84	1.7	2.77	0.180	1.1923
3–1	1754.12	57008.64	0.9	0.51	0.045	1.2252
3–2	1813.31	55147.77	1.2	0.86	0.105	1.2586
3–4	1939.48	51560.21	0.6	0.49	0.113	1.3244
3–5	2008.37	49791.62	0.5	0.18	0.056	1.3553
3–8	2240.19	44639.07	—	—	0.173	1.4605
3–9	2327.17	42970.65	—	—	0.126	1.4966
3–10	2419.70[a]	41327.10	—	—	0.057	1.4968
4–0	1663.99	60096.51	0.6	1.13	0.107	1.1702
4–1	1717.45	58225.86	0.7	0.95	0.124	1.2030
4–3	1832.65	54565.79	—	—	0.088	1.2696
4–4	1894.15	52794.13	—	—	0.037	1.3002
4–6	2029.84	49264.97	—	—	0.105	1.3668
4–9	2262.86[a]	44179.17	—	—	0.140	1.4722
4–10	2351.40[a]	42526.23	—	—	0.159	1.5015
5–0	1631.59	61289.91	0.2	0.39	0.055	1.1484
5–1	1682.52	59434.66	0.5	0.76	0.144	1.1816
5–3	1792.80	55778.67	—	—	0.081	1.2479
5–7	2051.40[a]	48746.48	—	—	0.074	1.3786
6–0	1600.97	62462.13	—	—	0.025	1.1266
6–1	1649.85	60611.57	0.16	0.74	0.115	1.1602
6–6	1936.37	51643.02	—	—	0.062	1.3234
6–9	2147.45[a]	46566.86	—	—	0.093	1.4219
7–1	1619.65[a]	61741.73	—	—	0.074	1.1390
8–2	1637.94[a]	61052.29	—	—	0.105	1.1511
8–3	1688.03[a]	59240.65	—	—	0.052	1.1828
9–3	1656.93[a]	60352.58	—	—	0.089	1.1629
10–3	1627.50[a]	61443.93	—	—	0.094	1.1430

[a] New bands.

study of C(v′)–X(v″) vibronic intensity distribution and correlation to theory helped us to map the variation of the electronic transition moment. The vibronic intensity, I(v′,v″) is given by

$$I(\mathrm{v}', \mathrm{v}'') = K(\nu_{\mathrm{v}',\mathrm{v}''}/\nu_e)^4 \ |<\mathrm{v}'|M(r)|\mathrm{v}''>|^2 \ \exp[-hcG'(\mathrm{v})/kT], \qquad (1)$$

where $\nu_{\mathrm{v}',\mathrm{v}''}$ is the band origin (approximated by the band-head positions), ν_e is the system origin, K is a constant of proportionality, and $M(r) = <C^2\Pi| - 2^{-1/2}(M_x + iM_y)|X^2\Sigma^+>$ is the r-dependent electronic transition moment. M_x and M_y refer to the molecule fixed components of the electric dipole moment operator M. An initial value for vibrational temperature T ($\sim$3320 K), governing the population distribution for upper state, was estimated by plotting $\ln(I_{\mathrm{v}',\mathrm{v}''}/(\nu_{\mathrm{v}',\mathrm{v}''}/\nu_e)^4 q_{\mathrm{v}',\mathrm{v}''})$ versus $G(\mathrm{v}')$. In studies of this kind, it is usual to invoke the r-centroid approximation originally due to Fraser[13] and improved by Turner and Nicholls.[14] The squared vibronic transition moment $|<\mathrm{v}'|M(r)|\mathrm{v}''>|^2$ then reduces to $q_{\mathrm{v}',\mathrm{v}''}\ |M(r_{\mathrm{v}',\mathrm{v}''})|^2$ where $q_{\mathrm{v}',\mathrm{v}''}$ is the Franck–Condon factor and $r_{\mathrm{v}',\mathrm{v}''}$ is the r-centroid. For fitting of the vibronic intensities, a polynominal of M in the form $M(\xi) = 1 + a_1\xi + a_2\xi^2\ldots$, where $\xi = (r - r_{00})/r_{00}$ (r_{00} being the r-centroid for the 0–0 band) was used. The final set of constants T, a_1, a_2, and so forth, were estimated through an iterative procedure that minimized the sum of the squared deviations. The potential energy curves for the $C^2\Pi$ and $X^2\Sigma^+$ states, the vibrational wave functions, and the matrix elements $<\mathrm{v}'|r^n|\mathrm{v}''>$ for $n = 0, 1, 2\ldots$ required for solving Eq. (1) were generated using the TRAPRB program developed by Jarmain and Mc Callum[15] and program LEVEL 6.0 obtained from Le Roy.[16] The molecular parameters needed for these computations were taken from Mal'tsev et. al.[9] The peak height at the position of the R-head above the corresponding background was measured and taken as the observed intensities I(v′,v″). The orders of the other experimental artifacts like nonuniformity in the spectral response and finite band pass of the monochromator[17] are assumed to be constant in the region of the calculation. It turned out that because of the limited accuracy of our experimental intensities, only the linear coefficient a_1 could be meaningfully determined. The final fit gave the following results:

$$T = 3200 \pm 100\,\mathrm{K}$$

$$M(r) = (1 + 2.26 r_{\mathrm{v}',\mathrm{v}''})1.10 \le r \le 1.50\,\mathrm{A} \ \text{ with } \ r_{00} = 1.2608$$
$$\text{and } \mathrm{K} = 40.1. \qquad (2)$$

In this limit of restricting $M(\xi)$ to the linear term, the result of the determination of $M(r)$ as outlined was found to be equivalent to using the r-centroid approximation.[13] In Table 1, the intensities calculated with Eq. (1) and Eq. (2) are compared with the observed values. Franck-Condon factors (FCFs) and r-centroids computed are also listed. During the calculation of the band intensities, the correction for the overall generic behavior of the monochromator and PMT response of the spectral region has been taken into account. But for want of an absolute calibrated vacuum ultra violet (VUV) intensity source from 1500 Å to 2500 Å, the absolute intensity value as a function of wavelength could not be corrected, which could account for a maximum of ± 15% error. Discrepancies in some bands could also be attributed to overlapping of the sequence bands. The observed intensities conform closely to the theoretical values, which independently corroborates their assignments to the C–X system.

CONCLUSIONS

The vibrational structure in the $C^2\Pi_r$–$X^2\Sigma^+$ transition of boron mono-oxide was studied and the system extended to $v' = 10$ in the C state. The FCFs and r-centroids for the band system were computed. The measured vibronic intensity distribution and its theoretical elucidation suggest a linearly increasing variation of the C–X transition moment with internuclear separation over the range $1.10 \leq r \leq 1.50$ Å.

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