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Laser-induced Fluorescence and Dispersed Fluorescence Spectroscopy of NiB: Identification of a New $^2\Pi$ State in 19000−22100 cm^{-1}

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The laser-induced fluorescence excitation spectra of jet-cooled NiB radicals have been recorded in the energy range of 19000−22100 cm^{-1}. Eleven bands have been assigned to the $[20.77]^2\Pi$-$X^2\Sigma^+$ transition system for the first time. The dispersed fluorescence spectra related to most of these bands have been investigated. Vibrationally excited levels of the ground electronic state, with v'' up to 6, have been observed. In addition, the lifetimes for almost all the observed bands have also been measured.

Key words: NiB, Laser-induced fluorescence, Dispersed fluorescence, Direct current discharge

I. INTRODUCTION

Since metal borides are believed to play important roles in a variety of fields, such as catalysis [1] and surface chemistry [2], they have received increased attention in recent years. As the simplest building blocks of the very complex metal borides, the diatomic transition metal borides (DTMB) have drawn more interest from both theoretical [3, 4] and experimental [5−8] sides. Compared to their hydride counterparts, the spectroscopic data of DTMB remain quite meager. To the best of our knowledge, only a few DTMB including RhB [5, 6], IrB [7], and NiB [8] have very recently been spectroscopically characterized. In view of the current situation that the theoretical calculations on electronic structure and bonding of DTMB [3, 4] considerably precede information available from the spectroscopic investigations, more experimental corroboration on DTMB is apparently required. While a pioneering experimental work has recently been reported on the $[19.7]^2\Sigma^+$-$X^2\Sigma^+$ band system of NiB [8], spectroscopic data on this particular species remain far from being complete. In this work, we report on the identification of a new electronic band system of NiB, *i.e.*, that of $[20.77]^2\Pi$-$X^2\Sigma^+$, by means of laser-induced fluorescence (LIF) and dispersed fluorescence (DF) spectroscopy. We further measured the lifetimes of almost all the observed bands.

II. EXPERIMENTS

The experimental setup has been described in detail elsewhere [9]. Briefly, the NiB molecules were produced by the reaction of B_2H_6 molecules with the nickel atoms sputtered from a pair of pure nickel pins under a pulsed DC discharge condition. The B_2H_6 sample gas seeded in argon (about 0.5%) at a stagnation pressure of 555.5 kPa passed through a pulsed nozzle (General valve Co.) with an orifice diameter of 0.5 mm into the vacuum chamber. The nickel pins were used for DC discharging, the B_2H_6/Ar gas was fixed in a Teflon disk and set at a spacing of around 1 mm. The background pressure of the vacuum chamber was 270 and 2.7 mPa, with and without operation of the free jet, respectively.

The light source was a tunable dye laser (Lumonics, HT-500) pumped by a Nd:YAG laser (Spectra Physics, GCR-190). The output of the pulsed dye laser (linewidth about 0.1 cm^{-1}, pulse duration about 5 ns) was introduced into the vacuum chamber and crossed the jet flow perpendicularly about 3 cm downstream from the point of discharge.

The excitation spectrum was recorded by monitoring the total fluorescence as a function of laser wavelength. No attempt was made to normalize the spectral intensity against the laser power. The DF spectra were obtained by holding fix the probe laser frequency at or near a strong R-head and scanning the monochromator (Zolix, Omni-λ 300) whose slit was set at about 1 mm. For lifetime measurements, a digital oscilloscope (Tektronix, TDS308) was used to record the fluorescence signal averaged over 256 laser shots. The relative time delays among the nozzle, the laser, and the DC discharge were controlled by a home-made pulsed multi-channel delay generator. Laser wavelength was calibrated by a wavemeter (Coherent, WaveMaster 33-2650).

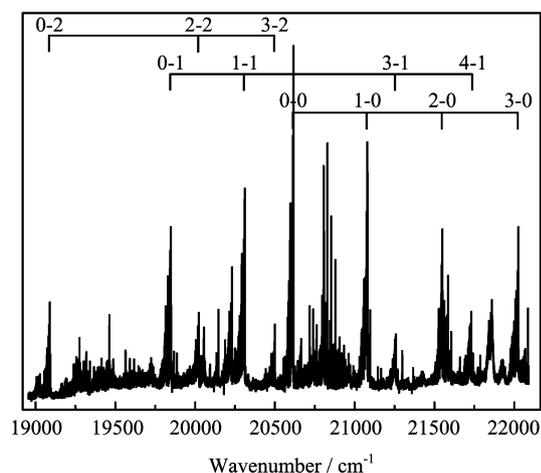*Author to whom correspondence should be addressed. E-mail: yangchen@ustc.edu.cn

FIG. 1 Survey LIF excitation spectrum of NiB in the energy range of $19000-22100$ cm^{-1}. Eleven observed vibronic bands indicated by ticks are assigned to the $[20.77]^2\Pi$-$X^2\Sigma^+$ transition system. Additional weak bands are present in this region, but they cannot be assigned due to their weak intensity. The spectrum contains also the bands arising from the BH molecules (between the 0-0 and 1-0 bands) and from the NiB molecules that have been reported by Walter *et al.* [8].
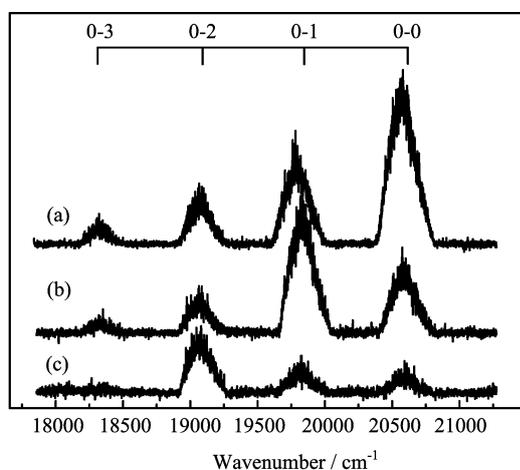

FIG. 2 DF spectra of ^{58}Ni^{11}B obtained using the three probe laser wavelengths of (a) λ_{probe}=20616.69 cm^{-1} for the 0-0 band, (b) λ_{probe}=19848.32 cm^{-1} for the 0-1 band, and (c) λ_{probe}=19089.43 cm^{-1} for the 0-2 band, respectively. The bands of these DF spectra are indicted by ticks and labeled accordingly.

III. RESULTS AND DISCUSSION

Figure 1 shows a survey LIF excitation spectrum of NiB in the energy range of $19000-22100$ cm^{-1}. Apart from the spectral features arising from ^{58}Ni^{11}B, some arising from its isotopic species were also observed. Natural abundance ratio of ^{58}Ni to ^{60}Ni is about 3:1 and ^{11}B to ^{10}B is about 4:1, so the abundance of ^{58}Ni^{11}B:^{60}Ni^{11}B:^{58}Ni^{10}B:^{60}Ni^{10}B is about

TABLE I The $T_v(^{58}$Ni^{11}B) and Δv values (in cm^{-1}) of the identified bands of the $[20.77]^2\Pi_{3/2}$-$X^2\Sigma^+$ transition system with some "extra" unidentified bands. The lifetimes and isotopic shifts of these bands. The isotopic shifts: $\Delta v(^{58}$Ni^{10}B)=$T_{\text{R-head}}(^{58}$Ni^{11}B)$-T_{\text{R-head}}(^{58}$Ni^{10}B) and $\Delta v(^{60}$Ni^{11}B)=$T_{\text{R-head}}(^{58}$Ni^{11}B)$-T_{\text{R-head}}(^{60}$Ni^{11}B).

$v'-v''$	T_v (^{58}Ni^{11}B)	$\Delta v(^{58}$Ni^{10}B)	$\Delta v(^{60}$Ni^{11}B)	τ/ns
0-0	20611.93	−		139(2)
1-0	21075.45	−17.2	1.9	143(2)
2-0	21545.58	−30.8		178(1)
3-0	22022.38	−43.8		160(1)
0-1	19843.44		−2.1	132(2)
1-1	20306.58		−0.4	114(2)
3-1	21253.60			159(1)
4-1	21736.45			161(1)
0-2	19084.96	62.3	−4.3	113(1)
2-2	20019.03		−1.7	167 (1)
3-2	20495.63			163 (1)
	20054.08			
	20224.74 [8]	−18.29		481(2)
	20662.27			
	21600.02			151(3)
	21726.42			265(3)

The 1σ errors are given in parentheses in unit of the last digits quoted.

0.58:0.22:0.15:0.05. Eleven bands shown in Fig.1 can be classified into three progressions with regular energy intervals. Since the band origin (T_e) lies at 20770.88 cm^{-1}, we assigned them to a new transition band system of $[20.77]^2\Pi$-$X^2\Sigma^+$ by convention of using the band origin in square brackets to label the upper electronic state.

A careful analysis for the isotopic shifts as well as the DF spectra of these bands confirmed our such assignments. The obtained isotopic shifts for some bands are listed in Table I, while for the rest bands heavy spectral congestion prevented us from obtaining their isotopic shifts. The observed isotopic shift values are in good agreement with the calculated ones that use the data of the equilibrium constants (see Table II) for the ground and the $[20.77]^2\Pi$ state of ^{58}Ni^{11}B.

The DF spectra of NiB are shown in Fig.2 and Fig.3. Figure 2 shows the DF spectra of the 0-0, 0-1, and 0-2 bands, which indicate that our assignments are correct and consistent with the vibrational intervals of the $[20.77]^2\Pi$ and the ground state. The DF spectra of the isotopic species ^{58}Ni^{11}B and ^{58}Ni^{10}B of the 1-0 band have also been recorded, as shown in Fig.3, from which a clear "blue shift" can be observed. The "bule shift" value is consistent with the isotopic shifts listed in Table I.

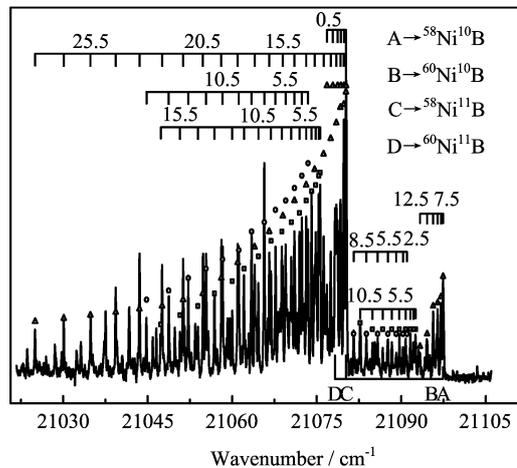Figure 4, as an example, shows the rotation-

TABLE II Equilibrium constants (in cm^{-1}) for states of ^{58}Ni^{11}B (The 1σ errors are given in parentheses in unit of the last digits quoted).

	T_e	ω_e	$\omega_e\chi_e$	B_e
Electronic state ([20.77]$^2\Pi_{3/2}$)	20770.88 (0.15)	457.05 (0.15)	-3.25 (0.10)	0.520 (0.03)
Ground state ($X^2\Sigma$)		779.20 (0.05)	5.25 (0.05)	0.620 (0.03)
		778 [8]	4.9 [8]	0.6321 [8]
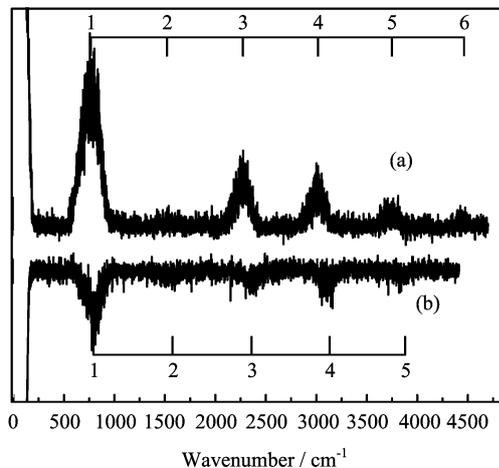
FIG. 3 DF spectra obtained using the two probe laser wavelengths of (a) λ_{probe} (R-head of ^{58}Ni^{11}B)=21079.79 cm^{-1} for the 0-1 band and (b) λ_{probe} (R-head of ^{58}Ni^{10}B)=21096.60 cm^{-1} for the 0-1band. Vibrational levels ($v''\leq6$) of the ground state are labeled.

FIG. 4 Rotationally resolved LIF excitation spectrum of the 1-0 band of the [20.77]$^2\Pi$-$X^2\Sigma^+$ transition of NiB. Rotational assignments are indicated in ticks. The spectrum is very dense and lines from different branches as well as the three other isotopic species overlap with each other. The ticks labeled A, B, C, D indicate the R head of the four species of ^{58}Ni^{10}B, ^{60}Ni^{10}B, ^{58}Ni^{11}B, and ^{60}Ni^{11}B, respectively.

ally resolved LIF excitation spectrum for the 1-0 band, which involves four isotopic species. We label the position of R head of the four isotopic species A, B, C, and D. The isotopic shift $\Delta v(^{60}\text{Ni}^{11}\text{B})=T_{\text{R-head}}(^{58}\text{Ni}^{11}\text{B})-T_{\text{R-head}}(^{60}\text{Ni}^{11}\text{B})$ is so small that the spectral features arising from the two species overlap very tightly, and the abundance of ^{60}Ni^{10}B is low, we therefore cannot give the rotational analysis for ^{60}Ni^{11}B and ^{60}Ni^{10}B. The rotational assignments for ^{58}Ni^{11}B and ^{58}Ni^{10}B are listed in Table III. No fine structures were found for the rotational lines of the P, Q, and R branches. The intensity of the P branch is weaker than that of the Q and R branches, implying that this transition belongs to the case with $\Delta\Lambda=+1$ and $\Delta\Omega=+1$. The first lines for P, Q, and R branches are P(2.5), Q(1.5), and R(0.5), respectively. The upper excited state can thus be determined as a $^2\Pi_{3/2}$ state. We tried to use Hund's case (a) or case (b) to describe the ground $X^2\Sigma^+$ state and the upper excited [20.77]$^2\Pi$ state, but it turned out not to yield reasonable results. We therefore used the conventional rotational energy formula $F(J)=BJ(J+1)-D[J(J+1)]^2$ [10] to fit the rotational lines, and the determined molecular constants are listed in Table II.

Furthermore, we measured the lifetimes of almost all

the observed bands by recording the decay traces of the time-resolved LIF signal. The fluorescence decay signal was averaged over 256 laser shots at a selected wavelength. Considering that the NiB molecules in this experiment were produced in a very low concentration under a supersonic jet condition and the expansion of the NiB molecules is reasonably close to a collision free process, we derived the lifetimes of the excited states from an exponential fit of the fluorescence decay traces without deconvolution of the system response function. The fitted lifetime values are listed in Table I, which are approximately the same time scale (about 150 ns) for different vibronic bands.

The electronic configuration of the ground state has been determined to be (core)$(7\sigma^2)(8\sigma^2)(3\pi^4)(1\delta^4)(9\sigma^1)$ [3, 4, 8]. Two possible electronic configurations for the $^2\Pi$ state are (core)$(7\sigma^2)(8\sigma^2)(3\pi^3)(1\delta^4)(9\sigma^2)$ and (core)$(7\sigma^2)(8\sigma^2)(3\pi^4)(1\delta^4)(4\pi^1)$ [4]. However, for the [20.77]$^2\Pi$ state reported in the present work, we cannot unambiguously determine to which configuration this newly observed state belongs. To clarify the electronic structure of NiB, more detailed theoretical calculations and high-resolution spectroscopic studies are required.

TABLE III Assigned rotational lines of the 1-0 band of NiB in cm^{-1}.

| | ^{58}Ni^{11}B | | | ^{58}Ni^{10}B | | |
J	Q	P	R	Q	P	R
0.5			21076.824			
1.5	21075.616		21077.885	21092.540		
2.5	21075.379	21073.472	21078.712	21092.193	21091.019	
3.5	21074.824	21072.357	21079.274	21091.635	21090.319	
4.5	21074.097	21071.055	21079.847	21090.788	21089.108	
5.5	21073.135	21069.492	21080.218	21089.672	21087.634	
6.5	21071.940	21067.691	21080.191	21088.341	21085.818	
7.5	21070.493	21065.701	21079.807	21086.720	21083.820	21097.424
8.5	21068.810	21063.451	21079.205	21084.884		21097.060
9.5	21066.890	21061.161	21078.481	21082.725		21096.460
10.5	21064.646	21058.303	21077.485			21095.669
11.5	21062.106	21055.356	21076.230			21094.594
12.5	21060.014	21052.212	21074.624			21093.344
13.5	21056.860	21048.739	21073.126			
14.5	21053.917	21044.800	21071.057			
15.5	21050.736		21068.985			
16.5	21047.313		21066.578			
17.5			21063.979			
18.5			21060.977			
19.5			21058.068			
20.5			21054.816			
21.5			21051.290			
22.5			21047.558			
23.5			21043.554			
24.5			21039.333			
25.5			21034.838			
26.5			21030.103			
27.5			21025.018			

IV. CONCLUSION

A new electronic transition band system of NiB, $i.e.$, that of [20.77]$^2\Pi$-$X^2\Sigma^+$, has been identified in the energy range of $19000-22100$ cm^{-1} for the first time by means of laser-induced fluorescence and dispersed fluorescence spectroscopy. The molecular constants of the [20.77]$^2\Pi$ state were derived, and part of its isotopic shifts were determined. In addition, the lifetimes of almost all the observed bands were measured under the collision free condition.

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