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Cavity Ring Down Laser Absorption Spectroscopy of NiI[†]

Tong-mei Ma, Ling Li, Joanne Wing Har Leung, Allan Shi Chung Cheung*

Department of Chemistry, The University of Hong Kong, Hong Kong

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The absorption spectrum of NiI between 445 and 510 nm has been investigated using the technique of laser vaporization/reaction with free jet expansion and cavity ring down laser absorption spectroscopy. Two new transitions namely, $[21.3]^2\Delta_{5/2}-X^2\Delta_{5/2}$ and $[21.9]^2\Pi_{3/2}-X^2\Delta_{5/2}$ systems were identified and studied. Spectra of both ^{58}NiI and ^{60}NiI isotopic molecules were observed. Equilibrium molecular constants for both electronic states are reported and the equilibrium bond length for the $[21.3]^2\Delta_{5/2}$ state and the $[21.9]^2\Pi_{3/2}$ state was respectively determined to be 2.431 and 2.481 Å.

Key words: Nickel monoiodide, Cavity ring down spectrum, electronic transition

I. INTRODUCTION

Spectroscopy of transition metal diatomic halides have been an active research area [1,2]. The importance of these metal halides ranges from catalysis [3], surface science [4] to astrophysics [2]. Furthermore, diatomic transition metal halides are simple systems that can provide insights into the role of the d orbitals in chemical bonding [5].

Nickel monohalides such as NiF and NiCl have attracted much attention in the last two decades; however, nickel monoiodide (NiI) has only recently been studied. Using laser vaporization/reaction free jet expansion and laser induced fluorescence spectroscopy, Tam *et al.* studied the near infrared and visible spectra of NiI between 588 and 770 nm [6,7]. The ground state was identified to be the $X^2\Delta_{5/2}$ state, which is different from other isovalent nickel monohalides: NiF, NiCl, and NiBr. In addition, five low-lying electronic states have also been studied and analyzed. Accurate vibrational and rotational constants of these electronic states were also reported. Zou and Liu performed *ab initio* calculations of the four nickel monohalides and their results were in good agreement with experimental observation [8].

In this work, we report the analysis of six electronic transition bands belonging to two new electronic transition systems recorded using the technique of laser vaporization/reaction free jet expansion and cavity ring down laser absorption spectroscopy (CRDS) [9]. Spectra of isotopic molecules: ^{58}NiI and ^{60}NiI were also observed and analyzed. Vibrational and rotational con-

stants for the two newly observed states are also reported.

II. EXPERIMENTS

NiI molecules were produced by the reaction of laser-ablated nickel atoms with methyl iodide (CH_3I) under supersonic free jet conditions and the spectrum was recorded using CRDS. Experimental apparatus used in this experiment and detailed procedures have been described in our earlier publications [10,11]. Only a brief description of the experimental conditions is given here. Pulses of 532 nm, 9 mJ, and 10 ns from a Nd:YAG laser were focused onto the surface of nickel metal rod to generate metal atoms. A pulsed valve with appropriate delay released a gas mixture of 3% CH_3I in helium to react with the vaporized metal atoms. The Nd:YAG laser-pulsed valve system was operated at 10 Hz. Tunable laser pulses in the region 440–510 nm were produced by a Nd:YAG pump-dye laser system. The linewidth of the dye laser was about 0.06 cm^{-1} and the typical energy used in this experiment was 1–3 mJ/pulse. The laser wavelength was calibrated using signals from an optogalvanic cell filled with argon and xenon gases. Two mirror sets and two laser dyes (Coumarin 460 and Coumarin 503) were necessary to cover the 440–510 nm wavelength region. The cavity ring down laser absorption signal was detected by a photomultiplier tube and fed to a preamplifier before forwarding to a digital oscilloscope and a computer for storage. It was found that shot-to-shot fluctuation of the cavity ring down absorption signal was severe, and a steady rotation of the metal rod was necessary to avoid ablating a particular surface for more than a few minutes. Averages of 10 laser shots per data point were necessary for maintaining good-signal-to-noise ratio in a spectrum. Spectral lines obtained were calibrated using values from the dye laser and converted to vacuum wavelength [12]. The es-

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*Author to whom correspondence should be addressed. E-mail: hrscsc@hku.hk

TABLE I Observed R head positions of the $[21.3]^2\Delta_{5/2}-X^2\Delta_{5/2}$ and $[21.9]^2\Pi_{3/2}-X^2\Delta_{5/2}$ transitions of NiI.

Transition	Band	^{58}NiI	^{60}NiI
$[21.3]^2\Delta_{5/2}-X^2\Delta_{5/2}$	(0, 0)	21328.93	21329.21
	(1, 0)	21547.75	21545.54
	(2, 0)	21762.69	
$[21.9]^2\Pi_{3/2}-X^2\Delta_{5/2}$	(0, 0)	21990.03	21990.38
	(1, 0)	22202.36	22200.29
	(2, 0)	22408.12	

estimated absolute accuracy of measured spectral lines is about $\pm 0.2 \text{ cm}^{-1}$.

III. RESULTS AND DISCUSSION

The cavity ring down laser absorption spectrum of NiI in the blue green region between 445 and 510 nm was recorded. Two transitions: $[21.3]^2\Delta_{5/2}-X^2\Delta_{5/2}$ and the $[21.9]^2\Pi_{3/2}-X^2\Delta_{5/2}$ systems were observed and analyzed.

A. The $[21.3]^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition

Three vibronic transition bands were recorded for this system. Strong R heads are readily identified and assigned. The band head positions were listed in Table I. The three bands were assigned as the (0, 0), (1, 0), and (2, 0) bands. Amongst the observed bands, the (0, 0) band was recorded with better signal-to-noise ratio and the rotational structure was partially resolved. Figure 1 shows the band head region of the (0, 0) band of the $[21.3]^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition. It is easily noticed that the R head of the minor ^{60}NiI isotope lies very close (about 0.3 cm^{-1}) to the major ^{58}NiI isotope, which provides evidence for assigning it as the (0, 0) band. Strong R and P branches are easily identified and the rotational quantum number was assigned using ground state combination differences. The rotational intensity distribution fits nicely to a $\Delta\Lambda=0$ transition.

Unlike the other transitions studied [6,7], due to insufficient resolution we were not able to identify the first line in each branch. In general, when both upper and lower states conform to good Hund's cases (a) coupling scheme, subband transition with $\Delta\Lambda=\Delta\Omega$ are stronger in intensity. The so far observed NiI transitions are consistent with this expectation. Since the ground state is $X^2\Delta_{5/2}$ state, the upper electronic state is assigned to be $^2\Delta_{5/2}$ state, therefore, transition is assigned as the $[21.3]^2\Delta_{5/2}-X^2\Delta_{5/2}$ system. The observed line positions were fit to a standard expression [13]. Since ground state molecular constants were accurately determined [6], they were held fixed in the least squares fit. The obtained upper state molecular constants are

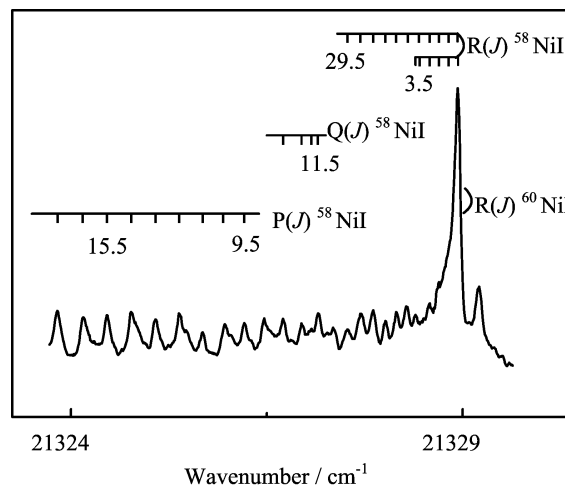


FIG. 1 Cavity ring down absorption spectrum of the (0, 0) band of the $[21.3]^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition of NiI.

TABLE II Molecular constants for the $[21.3]^2\Delta_{5/2}$ and $[21.9]^2\Pi_{3/2}$ states of ^{58}NiI (cm^{-1}).

Parameter	$[21.3]^2\Delta_{5/2}$	$[21.9]^2\Pi_{3/2}$
T_0	21327.88(1) ^a	21989.1
B_0	0.07158(2) ^a	0.0687
T_1	21546.9	22201.5
B_1	0.0712	0.0684
T_2	21761.8	22407.4
B_2	0.0709	0.0681
T_e	21216.9	21880.5
ω_e	223.1	218.9
$\omega_e\chi_e$	2.05	3.25
B_e	0.07171	0.06885
α_e	0.0003	0.0003
$r_e/\text{\AA}$	2.431	2.481

^a Molecular constants were obtained by least squares fitting of line positions.

listed in Table II. For the (1, 0) and (2, 0) bands, the rotational structure in these bands was modeled using the diatomic simulation program PGOPHER [14]. The lower state constants were taken from Tam *et al.* [6] and a rotational temperature of 60 K was used. The upper state rotational constants B and band origins were obtained by comparing the simulated transition contour to experimental measurements. These constants and the equilibrium molecular constants are reported in Table II.

B. The $[21.9]^2\Pi_{3/2}-X^2\Delta_{5/2}$ transition

Only 660 cm^{-1} above the (0, 0) band of the $[21.3]^2\Delta_{5/2}-X^2\Delta_{5/2}$ transition, we have recorded an-

other three bands with very different transition intensity distribution. All these three bands have weak R branch and relatively strong P and Q branches, which is consistent with the transition pattern of a $\Delta\Lambda=-1$ transition. The R head of these bands are also summarized in Table I. Similar to the discussion earlier for the $[21.3]^2\Delta_{5/2}-X^2\Delta_{5/2}$ system, the transition intensity for the subband transition with $\Delta\Omega=\Delta\Lambda=-1$ is usually stronger, the upper state of this system was thus assigned to be the $[21.9]^2\Pi_{3/2}$ state. Due to relatively large laser linewidth of our pulsed dye laser (about 0.06 cm^{-1}) and low signal-to-noise ratio, the recorded spectrum shows only partially resolved rotational structure. Similar to the analysis of the earlier vibronic bands, the rotational structure within the vibrational bands was modeled in a Hund's case (a) basis using the simulation PGOPHER program [14]. The obtained band origins and rotational constants, and the equilibrium molecular constants are all listed in Table II.

C. Discussion

Vibrational quantum number assignment of vibronic transition bands observed can be confirmed by examining the isotopic relationships. For the two newly observed electronic states, the $\Delta G_{1/2}$ for the $[21.3]^2\Delta_{5/2}$ and $[21.9]^2\Pi_{3/2}$ states of ^{58}NiI were determined to be 218.8 and 212.4 cm^{-1} respectively. Using isotopic relationships [11] and the values from ^{58}NiI , the $\Delta G_{1/2}$ for ^{60}NiI were calculated to be 216.5 cm^{-1} for the $[21.3]^2\Delta_{5/2}$ state and 210.0 cm^{-1} for the $[21.9]^2\Pi_{3/2}$ state. These values are in excellent agreement with experimental measurements of 216.3 cm^{-1} for the $[21.3]^2\Delta_{5/2}$ state and 210.0 cm^{-1} for the $[21.9]^2\Pi_{3/2}$ states respectively. In addition, the calculated isotopic displacement of the $v=1$ level for the $[21.3]^2\Delta_{5/2}$ and the $[21.9]^2\Pi_{3/2}$ states are 2.23 and 2.09 cm^{-1} , which is also in excellent agreement with the experimental determination of 2.21 and 2.07 cm^{-1} respectively.

The chemical bonding in transition metal containing diatomic molecules is appropriately described by using the molecular orbital (MO) approach [5]. The low-lying electronic states of NiI have been discussed using an MO energy level diagram [6,7]. The two newly observed electronic states could also be understood using such MO diagram. The following electronic configurations can be considered:

$$2\sigma^2 2\pi^4 1\delta^3 \quad X^2\Delta_i \quad (1)$$

$$2\sigma^1 2\pi^4 1\delta^3 3\sigma^1 \quad {}^2\Delta_i, {}^2\Delta_i, {}^4\Delta_i \quad (2)$$

$$2\sigma^2 2\pi^3 1\delta^3 3\sigma^1 \quad (2)^2\Pi_i, {}^4\Pi_i, (2)^2\Phi_i, {}^4\Phi_i \quad (3)$$

$$2\sigma^2 2\Pi^2 1\delta^4 3\sigma^1 \quad {}^2\Sigma^+, {}^2\Sigma^-, {}^2\Delta, {}^4\Sigma^- \quad (4)$$

The $[21.3]^2\Delta_{5/2}-X^2\Delta_{5/2}$ and the $[21.9]^2\Pi_{3/2}-X^2\Delta_{5/2}$ transitions observed in this work are likely to arise from the promotion of an electron from the 2σ MO and 2π to

TABLE III Observed electronic states of NiI.

State	$r_e/\text{\AA}$	ω_e/cm^{-1}	Configuration
$X^2\Delta_{5/2}$	2.3479 ^a	276.67 ^b	$2\sigma^2 2\pi^4 1\delta^3$
$A^2\Pi_{3/2}$	2.3484 ^a		$2\sigma^2 2\pi^3 1\delta^4$
$[13.3]^2\Sigma^+$	2.4608	237.24	$2\sigma^2 2\pi^2 1\delta^4 3\sigma^1$
$[13.9]^2\Pi_{3/2}$	2.4834	235.09	$2\sigma^2 2\pi^3 1\delta^3 3\sigma^1$
$[14.0]^2\Phi_{7/2}$	2.4680	233.91	$2\sigma^2 2\pi^3 1\delta^3 3\sigma^1$
$[14.6]^2\Delta_{5/2}$	2.5081	230.5	$2\sigma^1 2\pi^4 1\delta^3 3\sigma^1$
$[21.3]^2\Delta_{5/2}$	2.431	223.1	$2\sigma^1 2\pi^4 1\delta^3 3\sigma^1$
$[21.9]^2\Pi_{3/2}$	2.481	218.9	$2\sigma^2 2\pi^3 1\delta^3 3\sigma^1$

^a r_e refers to r_o .

^b $\Delta G_{1/2}$.

the 3σ MO respectively. The inverted states are from the unfilled δ^3 configuration. The observed bond length of the $[21.3]^2\Delta_{5/2}$ state is larger than the ground state, which is consistent with the expectation of taking an electron from the 2σ bonding orbital to the slightly antibonding 3σ orbital. The bond length of the $[21.3]^2\Delta_{5/2}$ state is also larger than the ground state, which also reflects the removal of an electron for the bonding 2π MO to the 3σ antibonding orbital. Table III lists the observed electronic states of NiI. It is easily noticed that the transitions studied so far involved the promotion of an electron from either the 2σ , 2π , or 1δ orbital to the 3σ orbital. Since the 3σ orbital is slightly antibonding in nature, it is consistent that the bond length of the excited states studied are longer than the $X^2\Delta_{5/2}$ and the $A^2\Pi_{3/2}$ states. Zou and Liu performed extensive theoretical calculations of the NiI molecule, many low-lying electronic states in the near infrared and the visible regions were presented but no transition in the ultra-violet region was predicted in their work [8].

The electronic configurations (1)–(4) give rise to many electronic states and the spin-orbit components of these electronic states are quite far apart due to large spin-orbit interaction, it is expected that these low lying electronic states can give rise to many electronic transitions between the ground $X^2\Delta_{5/2}$ and the $A^2\Pi_{3/2}$ states. The observed transitions are mainly located in the near infrared region, a comparison of the electronic states studied for nickel monoiodide to other nickel monohalides such as NiF and NiCl indicates that more electronic transitions should lie in the visible and ultraviolet regions between 15000 and 21000 cm^{-1} . We have work in progress to record laser induced fluorescence spectrum of NiI in this spectral region.

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