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Laser-induced Fluorescence Spectroscopy of NiS: Identification of a Low-lying Electronic State

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Laser-induced fluorescence excitation spectra of jet-cooled NiS molecules were recorded in the energy range of $12200-13550$ cm^{-1}. Four vibronic bands with rotational structure have been observed and assigned to the $[12.4]^3\Sigma_0^- \text{-} X^3\Sigma_0^-$ transition progression. The relevant rotational constants, significant isotopic shifts, and (equilibrium) molecular parameters have been determined. In addition, the lifetimes of the observed bands have also been measured.

Key words: NiS, Laser-induced fluorescence, Isotopic shift

I. INTRODUCTION

Nickel containing complexes are important functional materials with various applications in catalysts [1], hydrogen storage alloys [2], nickel batteries [3, 4], and electrochemistry [5, 6]. Recently, nickel organic compounds such as nickel-containing enzymes and nickel thiolates have received increased attention in biochemistry. For instance, nickel-containing enzymes [7] were found to play an important role as synthetic models for environmentally and industrially significant enzymes like hydrogenases [8]. Considering the rich redox chemistry and structural diversity in supramolecular architectures, metal thiolates including nickel thiolates, have been extensively studied both experimentally and theoretically [9−11]. However, research on nickel thiolates with focus on the S-bridged molecular cage rather than the ubiquitous O- and/or N-bridged metallacrown [12, 13] is still quite limited [9−11, 14]. Therefore, sensitive spectroscopic investigations on the characterization of nickel-sulfur bond would be of great importance.

Unfortunately, the NiS radical is one of the most elusive diatomic group 10 metal chalcogenides. Only several ground and excited states of NiS have been characterized by theoretical and experimental studies over the past decades [15−21]. The ground state of NiS has been predicted to be the $^3\Sigma^-$ electric state [15, 16]. Recently, by employing a source-modulation microwave spectrometer, Okabayashi group has observed and analyzed the pure rotational spectrum of NiS in the region between 135 and 314 GHz [17]. The molecular parameters such as rotational, centrifugal distortion, and several fine structure constants were determined, which confirmed that the ground state was the $^3\Sigma^-$

electric state. Furthermore, the vibrational frequency ω_e'' and the anharmonic term $\omega_e\chi_e''$ were also derived from the determined molecular parameters. Bernath group has identified two low-lying electric states, $A^3\Pi_i$ and $[5.8]^1\Pi$, by means of Fourier transform (FT) emission spectroscopy in the near infrared [18]. Several vibrational bands were rotationally analyzed to determine the molecular parameters of both the ground state and the two low-lying states, and the obtained ground state spectroscopic constants agree well with the microwave work mentioned above.

In our laboratory several electronic states with term energies in the $15500-22000$ cm^{-1} range have been observed and identified using laser-induced fluorescence (LIF) technique [19−21]. Zheng *et al.* recorded the first LIF spectrum of NiS in the range of $495-555$ nm in a supersonic free jet expansion by reacting DC discharge-sputtering nickel atoms with CS$_2$ [19]. Six vibronic bands were tentatively assigned as $[17.4]^3\Sigma_0^-(v'=2-7)$-$X^3\Sigma_0^-(v''=0)$ transition. Recently, Wang *et al.* revisited the LIF excitation spectrum in combination with dispersed fluorescence (DF) measurements between 555 and 495 nm, and furthermore extended the laser frequency to a broader region, *i.e.*, $560-450$ nm [20]. Apart from the six vibrational bands reported by Zheng *et al.* [19], 29 new bands were observed. Several molecular constants for the excited state were determined by rotational analyses, moreover, the ω_e'' and $\omega_e\chi_e''$ values for the ground state were obtained through DF measurements. In the energy region of $15500-17200$ cm^{-1}, Zhen *et al.* reported 15 new vibrational bands of NiS [21]. Base on the spectroscopic data and lifetimes determined, the electronic configurations of the excited states were briefly discussed.

In this work we extended the LIF excitation spectrum of jet-cooled NiS to the red region of $12200-13550$ cm^{-1}. Four vibronic bands with fine rotational structure have been recorded for the

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first time and assigned to the electronic transition $[12.4]^3\Sigma_0^-\,(v'=0-3)$-$X^3\Sigma_0^-\,(v''=0)$. The rotational constants, the signification isotopic shifts as well as the lifetimes of the observed bands have also been determined.

II. EXPERIMENTS

The production of a cold molecular beam sample of NiS was similar to that used previously for other Ni-containing molecules [20−23]. Briefly, the NiS molecules were produced by reaction of H_2S molecules with the nickel atoms sputtered from nickel pin electrodes. The H_2S sample gas seeded in argon (∼5%) at a stagnation pressure of ∼550 kPa passed through a pulsed nozzle (General Valve Co.) with the orifice 0.5 mm diameter into the vacuum chamber. A pair of nickel pin electrodes used for DC discharging the mixed H_2S/Ar gas was fixed in a Teflon disk with a spacing of ∼2.5 mm locating at ∼2.0 mm downstream from the nozzle, and was supplied with a pulsed high voltage from a home-made power supply. By using a molecular pump (KYKY, FF-160/620N) and a mechanical pump as the fore pump, the background pressure was ∼40 and ∼0.2 mPa, with and without operation of the free jet, respectively.

A tunable dye laser (Sirah, PRSC-LG-18) pumped by a Nd:YAG laser (Spectra Physics, GCR-190, repetition rate of 10 Hz) was used to excite the jet-cooled NiS molecules. To cover the energy region used, the LDS751 and LDS722 dyes were used by employing dimethyl sulfoxide as a solvent. The output of the pulsed dye laser with approximately 1 mJ (pulse duration ∼8 ns, line width ∼0.1 cm^{-1}) was introduced into the vacuum chamber and crossed the jet flow perpendicular at ∼3.5 cm downstream from the point of DC discharge. The frequency of the laser was calibrated by a commercial wavemeter (Coherent, WaveMaster 33-2650) with a resolution of 0.016 cm^{-1}.

The LIF excitation spectra were recorded by monitoring the total fluorescence from the NiS molecular beam. The fluorescence signal was detected by a photomultiplier tube (PMT, Beijing Hamamatsu, CR105) and digitized by an A/D card and then transferred to a personal computer. The relative time delays among the nozzle, the discharge, the laser and the signal were controlled by a home-made four channel digital delay/pulse generator. A digital oscilloscope (Tektronix, TDS3032B) was used to record the fluorescence signal averaged 128 laser shots when the lifetimes of the electronic transitions were measured. No attempt was made to normalize the spectral intensity against the laser power.

III. RESULTS AND DISCUSSION

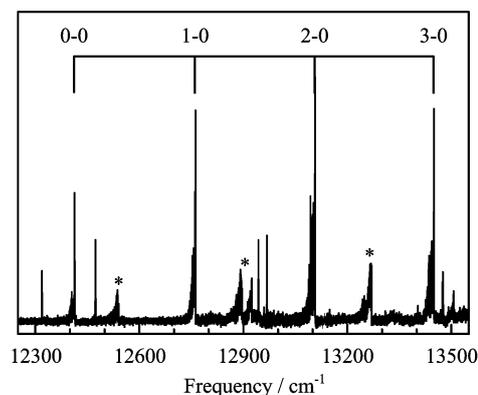The LIF excitation spectrum of the jet-cooled NiS radicals was recorded in the energy region of

FIG. 1 The survey LIF exaction spectrum of NiS in 12200−13600 cm^{-1}. Four observed vibronic bands assigned to the $[12.4]^3\Sigma_0^-\,(v'=0-3)$-$X^3\Sigma_0^-\,(v''=0)$ transitions are indicated by ticks. The bands with asterisks were conjectured to the spectra of NiSH.
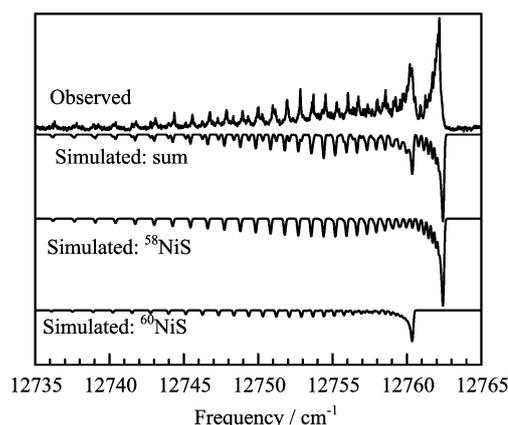

FIG. 2 Rotationally resolved LIF excitation spectrum of the $[12.4]^3\Sigma_0^-$-$X^3\Sigma_0^-$(2, 0) band of NiS. The upper trace is the observed spectrum, while the lower three traces are the simulated spectra for the ^{58}NiS and ^{60}NiS bands and their sum.

12200−13550 cm^{-1}. The survey spectra with four vibronic bands along with the assignments are presented in Fig.1. The spectral features of all the four bands are very similar to each other, and the observed bands except the (0, 0) band possess a weak subband rotational structure in common, which can be interpreted as the isotopic shifts between the NiS isotoplogues. Among the five naturally occurring isotopes of nickel, the two most abundant are ^{58}Ni (68.08%) and ^{60}Ni (26.22%). The spectral features associated with the two isotoplogues, ^{58}NiS and ^{60}NiS, can be readily identified in Fig.2. The relation of the isotopic shift and the vibrational parameters of the upper/lower state can be given by the equation

$$\Delta\nu \;=\; (1-\rho)\omega'_e\left(v'+\frac{1}{2}\right)-(1-\rho^2)\cdot$$

TABLE I Spectroscopic constants for the $[12.4]^3\Sigma_0^- - X^3\Sigma_0^-$ transition bands of NiS.

v', v''	^{58}NiS		^{60}NiS		Isotopic shift/cm^{-1}		Lifetime/μs
	T_v/cm^{-1}	B_v/cm^{-1}	T_v/cm^{-1}	B_v/cm^{-1}	Observed	Calculated	
0, 0	12411.279(13)	0.18874(5)			0.0	−0.459	2.357(10)
1, 0	12760.431(22)	0.18733(5)	12758.588(27)	0.18561(6)	1.843	2.052	2.332(8)
2, 0	13105.521(16)	0.18564(5)	13101.754(22)	0.18357(6)	3.767	3.607	2.352(9)
3, 0	13448.234(26)	0.18469(7)	13442.670(23)	0.17889(11)	5.564	5.583	2.340(14)

$$\omega_e\chi_e'\left(v'+\frac{1}{2}\right)^2 - \left[(1-\rho)\omega_e''\left(v''+\frac{1}{2}\right) - \right.$$
$$\left. (1-\rho^2)\omega_e\chi_e''\left(v''+\frac{1}{2}\right)^2\right] \tag{1}$$

where $\Delta\nu$ is denotes the isotopic shift between ^{58}NiS and ^{60}NiS, ρ^2 is the ratio of the reduced mass, *i.e.*, μ/μ^* (μ and μ^* being the reduced mass of ^{58}NiS and ^{60}NiS, respectively), $v'(v'')$ is the vibrational quantum number of the excited (ground) states, $\omega_e'(\omega_e'')$ and $\omega_e\chi_e'(\omega_e\chi_e'')$ are the vibrational constants of the ^{58}NiS isotopologue for the excited (ground) states. Because the NiS molecular beam under investigation was well cooled down and vastly populated in their ground state due to an ~100 μs expansion from the discharge zone to the detection zone, the v'' value was held fixed to zero. The vibrational constants for the ground state were taken from the previous microwave study [17], and the ω_e' value was set as the rough spacing of the observed bands. By using those three parameters, ω_e'', $\omega_e\chi_e''$, and ω_e' (where $\omega_e\chi_e'$ sets as zero), the v' can be roughly determined with the aid of the observed isotopic shifts in comparison with the calculated values by using Eq.(1). Based on this isotopic-shift analysis, the four predominant spectral features shown in Fig.1 can be unambiguously assigned to the vibronic (3-0, 0) bands of the $[12.4]^3\Sigma_0^- - X^3\Sigma_0^-$ transition progression.

A typical observed rotationally resolved LIF excitation spectrum is displayed in the upper part of Fig.2. Note that the strong head and the weak subband were interpreted as the ^{58}NiS and ^{60}NiS isotopologues. As expected, the ratios of the relative intensities for the two bands coincide with the natural abundant ratios of the two predominant NiS isotopologues, *i.e.*, ^{58}NiS:^{60}NiS≈3.0:1.0. The spectral features for all the observed bands have similar rotational structure: a strong R head and separated P branches, which imply a Σ-Σ electronic transition. The simulated spectra for the ^{58}NiS and ^{60}NiS bands were also displayed in the lower part of Fig.2, which match nicely with the observed spectrum, and then the rotational assignment for this band can be obtained. For the (0, 0) band, the simulation for the main isotopologue, ^{58}NiS, can only be given because of a severe spectral congestion of the weak subband as a result of a rather small isotopic shift.

Once the vibrational and rotational assignments of all the bands were determined, a set of molecular parameters can be obtained through a least-squares fitting procedure. The energies were modeled using the expression,

$$F(J) = T_v + B_v[J(J+1)] - D_v[J(J+1)]^2 \tag{2}$$

where T_v is the band origin, B_v the rotational constant, and D_v the centrifugal distortion. The parameters for the ground state were taken from the microwave work [17] and held fixed in our simulation. The D_v values for the excited states were also fixed as the ground state. The least-squares fit was accomplished by the PGO-PHER program [24]. The obtained molecular parameters are listed in Table I.

The equilibrium spectroscopic constants for this low-lying state can be obtained by the following equation,

$$\nu(v', v'') = T_e + \omega_e'\left(v'+\frac{1}{2}\right) - \omega_e\chi_e'\left(v'+\frac{1}{2}\right)^2 -$$
$$\left[\omega_e''\left(v''+\frac{1}{2}\right) - \omega_e\chi_e''\left(v''+\frac{1}{2}\right)^2\right] \tag{3}$$
$$B_v = B_e + \left(v+\frac{1}{2}\right)\alpha_e \tag{4}$$

where T_e is the electronic state energy term, ω_e and $\omega_e\chi_e$ are the vibrational constants, B_e and α_e are the equilibrium rotational and vibrational-rotational coupling constant, respectively. The obtained equilibrium constants are presented in Table II.

As mentioned above, the theoretical isotopic shifts can be determined from Eq.(1) by using the equilibrium parameters presented in Table II when the ground-state constants taken from Ref.[17] were held fixed. As a result, the observed and calculated shifts are presented in Table I, and the comparison of the two values is illustrated in Fig.3. The theoretical isotopic shift values are in agreement with the observed ones, which further confirms that the obtained spectroscopic constants are reliable and the assignments are reasonable.

Furthermore, considering that the NiS molecules were produced in a very low concentration under a supersonic jet condition in our experiments and hence, in several microseconds, the expansion of those molecules is reasonably close to a collision-free process, the lifetime of the excited state can be derived from an exponential fit of the fluorescence decay traces. Therefore, the lifetimes for all the vibrational levels of the excited state

TABLE II Equilibrium parameters for the $[12.4]^3\Sigma_0^-$ state of NiS.

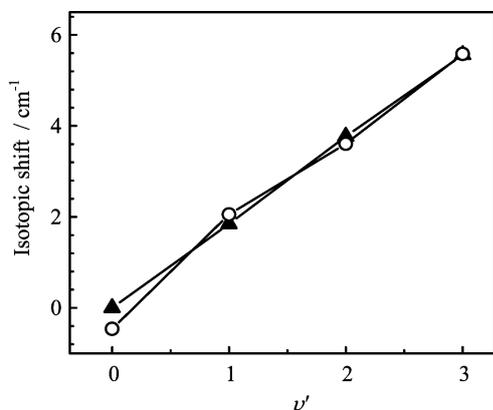|		T_0/cm^{-1}	$\omega_e/\mathrm{cm}^{-1}$	$\omega_e\chi_e/\mathrm{cm}^{-1}$	B_e/cm^{-1}	$\alpha_e\times10^4/\mathrm{cm}^{-1}$	$r_e/\text{Å}$
$[12.4]^3\Sigma_0^-$	^{58}NiS	12488.811(65)	352.03(77)	1.61(19)	0.18937(23)	13.8(10)	2.143
	^{60}NiS		347.67	1.13	0.19109(200)	33.6(76)	2.154
$X^3\Sigma_0^-$ [17]	NiS		507.227(35)	2.30418(38)	0.2124534(15)	14.909(2)	1.962
$X^3\Sigma_0^-$ [18]	^{58}NiS		512.68(23)	3.610(92)	0.2124516(62)	11.831(54)	1.962
$X^3\Sigma_0^-$ [20]	NiS		506(5)	2.29(65)			

FIG. 3 The comparison between the observed and the calculated isotopic shifts of the $[12.4]^3\Sigma_0^-$-$X^3\Sigma_0^-$ (v'=0) bands of NiS, where v' is the vibronic quantum number of the excited state. The triangles denote the observed shifts and the circles show the calculated values.

FIG. 4 A typical fluorescence decay trace recorded for the (2, 0) band R head of the $[12.4]^3\Sigma_0^-$-$X^3\Sigma_0^-$ transition progression. The circles denote the experimental data, while the solid curve is the exponential fit of the decay trace.

were measured by recording the fluorescence signal decay traces as a function of delay time. The decay signal was averaged over 128 laser pulses at the selected wavelength. A typical decay trace of the fluorescence resulting from the (2, 0) band of the $[12.4]^3\Sigma_0^-$-$X^3\Sigma_0^-$ transition progression for the ^{58}NiS radical is displayed in Fig.4. The obtained lifetimes presented in Table I are on approximately the same time scale (~2.3 μs) for different vibrational levels, which may provide complementary information about this low-lying electronic state of NiS.

IV. CONCLUSION

The jet-cooled laser-induced fluorescence excitation spectrum of NiS has been recorded in the red band. Four new vibronic bands in the energy range of 12200−13550 cm^{-1} have been assigned to the $[12.4]^3\Sigma_0^-$(v'=0−3)-$X^3\Sigma_0^-$(v''=0) transition progression by comparing the theoretical and experimental isotopic shifts. All the bands were rotationally analyzed and the molecular parameters of the upper state were evaluated. In addition, the lifetimes of the observed bands were measured by monitoring the fluorescence signal under the collision-free condition.
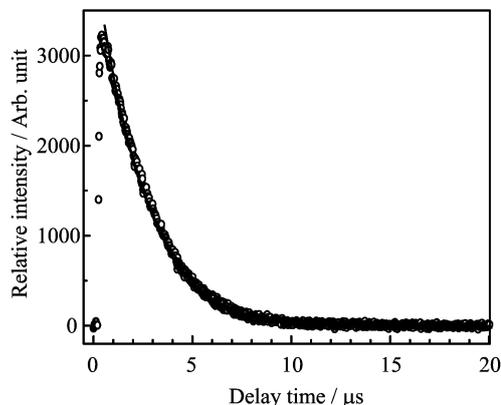
V. ACKNOWLEDGMENTS

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