

ARTICLE

Laser-induced Fluorescence Excitation Spectrum of NiS in 15500–17200 cm^{-1} †

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The laser-induced fluorescence excitation spectrum of jet-cooled NiS molecule has been recorded in the energy range of 15500–17200 cm^{-1} . Fifteen bands have been assigned as three transition progressions: $[15.65]^3\Pi_1(v'=0-4)-X^3\Sigma_0^-(v''=0)$, $[15.69]^3\Sigma_0^-(v'=0-4)-X^3\Sigma_0^-(v''=0)$, and $[15.81]^3\Pi_1(v'=0-4)-X^3\Sigma_0^-(v''=0)$. Spectroscopic constants for the three newly identified electronically excited states have been determined for the first time. In addition, the lifetimes for most observed vibronic bands have also been measured.

Key words: NiS, Laser-induced fluorescence spectrum, DC discharge

I. INTRODUCTION

Transition-metal sulfides have found a variety of applications in many fields, such as those related to lubricants, support materials, superconductors, and gas sensors for pollution monitoring and control [1,2]. They have also been proposed as catalysts that could have promoted metabolism in the early development of life on Earth [3].

The 3d transition-metal sulfides have been the subject of extensive experimental and theoretical studies [4–9]. Although the spectroscopic database for their ground and electronically excited states keeps growing, it remains far from being complete. Such an incompleteness is even apparent for nickel monosulfide (NiS), in that only the ground state and one excited state of this species have hitherto been characterized [10,11]. A first spectroscopic study of NiS was recently carried out by means of laser-induced fluorescence (LIF) technique by Zheng *et al.* who reported six vibrational bands assigned to the $[17.4]^3\Sigma_0^-(v'=2-7)-X^3\Sigma_0^-(v''=0)$ transitions [10]. By employing a source-modulation microwave spectrometer, Takuya *et al.* observed the rotational spectrum of NiS in the region between 135 and 314 GHz [11]. Their spectral analyses yielded the molecular constants, such as the rotational, centrifugal distortion, and several fine-structure constants for the $X^3\Sigma_0^-$ ground state of NiS.

In this work, we report on the LIF excitation spectrum of ^{58}NiS and ^{60}NiS in the energy range of 15500–17200 cm^{-1} . We observed fifteen vibronic

bands which were assigned to the $[15.65]^3\Pi_1(v'=0-4)-X^3\Sigma_0^-(v''=0)$, $[15.69]^3\Sigma_0^-(v'=0-4)-X^3\Sigma_0^-(v''=0)$, and $[15.81]^3\Pi_1(v'=0-4)-X^3\Sigma_0^-(v''=0)$ transitions, respectively. Our rotational analyses for these bands yielded the molecular constants of the three newly identified electronically excited states. Furthermore, we also carried out a measurement of lifetimes for almost all the observed bands.

II. EXPERIMENTS

The experimental setup has been described in detail elsewhere [12]. Briefly, the NiS molecules were produced by the reaction of H_2S molecules with the nickel atoms sputtered from a pair of pure nickel pins under a pulsed DC discharge condition. The H_2S sample gas seeded in argon ($\sim 2\%$) at a stagnation pressure of ~ 556 kPa passed through a pulsed nozzle (General valve Co.) with an orifice diameter of 0.5 mm into the vacuum chamber. The nickel pins used for DC discharging the $\text{H}_2\text{S}/\text{Ar}$ gas were fixed in a Teflon disk, and set at a spacing of ~ 1 mm. The background pressure of the vacuum chamber was ~ 0.4 Pa and ~ 4 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 ~ 0.2 cm^{-1} , pulse duration ~ 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. For lifetime measurements, a digital oscilloscope (Tektronix, TDS308) was used to

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record the fluorescence signal averaged over 256 laser shots. The relative time delays among the nozzle, the laser, and the discharge were controlled by a home-made pulsed multi-channel delay generator. Laser wavelength was calibrated by a wavemeter (Coherent, WaveMaster 33-2650).

III. RESULTS AND DISCUSSION

Figure 1 shows a survey LIF excitation spectrum of NiS in the energy range of 15500–17200 cm^{-1} . Apart from the spectral features arising from ^{58}NiS , those arising from its isotopic molecule ^{60}NiS were also observed (natural abundance ratio of ^{58}Ni over ^{60}Ni is about 3:1). Since all the NiS molecules in the detection zone are in their ground state after having expanded for $\sim 60 \mu\text{s}$ from the discharge zone, we can conclude that all the observed vibronic bands should originate from the ground state of NiS.

As in NiO [13], the $X^3\Sigma^-$ ground state of NiS can be described by Hund's case (a) with the spin-spin coupling constant $\lambda_0=1087.5(24)$ GHz [11]. Among the three ground substates $^3\Sigma_{0e}^-(\Omega=0)$, $^3\Sigma_{1e}^-(\Omega=1)$, and $^3\Sigma_{1f}^-(\Omega=1)$, the latter two locate about 70 cm^{-1} above the former one. Our spectral analysis indicates that all the observed spectra originate from the $v''=0$ level of the lowest $^3\Sigma_{0e}^-$ substate. No spectral features associated with the two upper substates as well as hot bands could be found.

The fifteen bands shown in Fig.1 can be classified into three progressions with regular energy intervals, among which two types of transition are

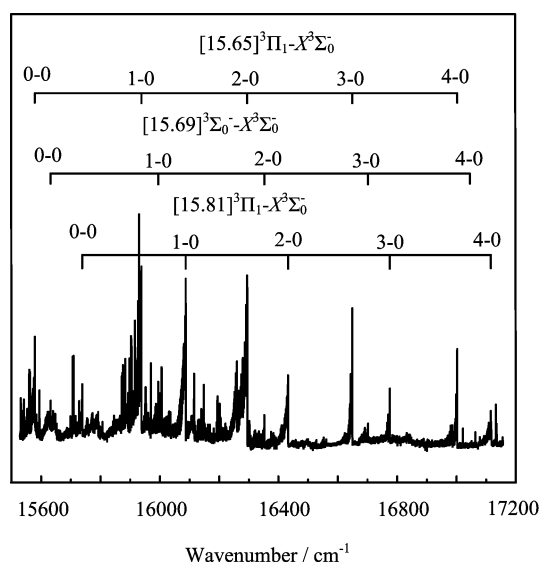


FIG. 1 The survey LIF excitation spectrum of NiS in the energy range of 15500–17200 cm^{-1} . Fifteen observed vibronic bands indicated by ticks were assigned to three transition progressions.

involved: two Π - Σ ($\Delta\Lambda=1$) type transitions and one Σ - Σ ($\Delta\Lambda=0$) type transition in between. The band origins (T_e) of the three progressions lie at about 15650, 15699, and 15815 cm^{-1} , respectively. By convention of using the band origin in square brackets to label the upper electronic state, we assigned the three progressions as $[15.65]^3\Pi_1(v'=0-4)-X^3\Sigma_0^-(v''=0)$, $[15.69]^3\Sigma_0^-(v'=0-4)-X^3\Sigma_0^-(v''=0)$, and $[15.81]^3\Pi_1(v'=0-4)-X^3\Sigma_0^-(v''=0)$, respectively. A careful analysis for the isotopic shifts as well as the rotational lines of these bands confirmed our such assignments. The obtained spectroscopic constants for the fifteen rotationally resolved transition bands and the molecular equilibrium constants of ^{58}NiS are listed in Tables I and II.

To first order, the relation of the isotopic shift ($\Delta\nu$) and the vibrational parameters of the upper and lower states is given: [14]

$$\Delta\nu = (1 - \rho) \left[\omega'_e \left(v' + \frac{1}{2} \right) - \omega''_e \left(v'' + \frac{1}{2} \right) \right] \quad (1)$$

where $\Delta\nu$ denotes the isotopic shift between ^{58}NiS and ^{60}NiS , ρ equals $[\mu(^{58}\text{NiS})/\mu(^{60}\text{NiS})]^{1/2}$ with μ being the reduced mass of NiS. According to the Eq.(1), the vibrational quantum numbers v' of the upper states can be determined by using the known ω''_e value (507.227 cm^{-1}) of the ground state [11] and the observed vibrational intervals of the upper state. Based on this analysis, the fifteen bands were assigned to be the three transition progressions from the $v''=0$ level of the $X^3\Sigma_0^-$ ground state to the $v'=0-4$ levels of each upper state, as indicated by ticks in Fig.1. The assignments of the fifteen bands as well as the corresponding band origins (T_v) are given in Table I.

The isotopic shifts of almost all the observed bands are also given in Table I. The observed isotopic shift values are in good agreement with the calculated ones (see Table I), which further confirms that our assignments are reasonable and the obtained spectroscopic constants are reliable.

Figure 2 shows the rotationally resolved LIF excitation spectrum for the 3-0 band of the progression with band origin (T_e) at $\sim 15650 \text{ cm}^{-1}$, as shown in Fig.1. 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 upper excited state can thus be determined as a $^3\Pi_1$ state. We assigned this progression as the $[15.65]^3\Pi_1(v'=0-4)-X^3\Sigma_0^-(v''=0)$ transitions.

In Fig.2(a), the observed rotational lines belonging to the P, Q, and R branches for ^{58}NiS and to the Q branch for ^{60}NiS are indicated by ticks with corresponding J numbers. The lower part of Fig.2 shows the simulated rotational spectrum, which matches nicely with the observed one shown in the upper part of Fig.2. A least-squares fit was employed to derive the rotational constants and the band origin (T_v) of the upper $[15.65]^3\Pi_1$

TABLE I Spectroscopic constants (cm^{-1}) for the three rotationally resolved transition bands of ^{58}NiS . The isotopic shift $\Delta\nu = T_v(^{58}\text{NiS}) - T_v(^{60}\text{NiS})$.

| Electronic state | $v'-v''$ | T_v | $B_v \times 10^3$ | $D_v \times 10^6$ | $\Delta\nu(\text{obs.})$ | $\Delta\nu(\text{cal.})$ | $\tau/\mu\text{s}$ |
|------------------------|----------|----------|-------------------|-------------------|--------------------------|--------------------------|--------------------|
| [15.65] $^3\Pi_1$ | 0-0 | 15577.28 | 180.3 | 2 | -0.50 | -0.43 | 2.71 |
| | 1-0 | 15936.17 | 178.3 | 3 | 2.00 | 1.69 | 2.69 |
| | 2-0 | 16293.42 | 175.8 | 2 | 3.80 | 3.78 | 2.73 |
| | 3-0 | 16647.81 | 175.5 | 1 | 5.58 | 5.85 | 1.89 |
| | 4-0 | 17001.38 | 174.3 | 4 | 7.65 | 7.90 | 1.67 |
| [15.69] $^3\Sigma_0^-$ | 0-0 | 15629.36 | | | | | |
| | 1-0 | 15994.76 | 188.3 | 3 | 1.84 | 1.71 | 1.66 |
| | 2-0 | 16350.61 | 187.5 | 1 | 3.90 | 3.77 | 2.37 |
| | 3-0 | 16700.52 | 186.1 | 2 | 5.80 | 5.77 | 1.57 |
| | 4-0 | 17049.56 | | | | | |
| [15.81] $^3\Pi_1$ | 0-0 | 15737.60 | 184.2 | 3 | -0.38 | -0.46 | 2.48 |
| | 1-0 | 16086.36 | 182.5 | 2 | 1.70 | 1.59 | 2.51 |
| | 2-0 | 16431.26 | 180.4 | 4 | 3.40 | 3.61 | 2.79 |
| | 3-0 | 16774.23 | 179.6 | 2 | 5.47 | 5.60 | 2.40 |
| | 4-0 | 17115.26 | 176.7 | 1 | 7.28 | 7.55 | 2.29 |

TABLE II Equilibrium constants (cm^{-1}) for the three electronic states of ^{58}NiS .

| Electronic state | T_e | ω_e | $\omega_e\chi_e$ | $B_e \times 10^3$ | $\alpha_e \times 10^3$ | $D_e \times 10^6$ |
|------------------------|-------------|------------|------------------|-------------------|------------------------|-------------------|
| [15.65] $^3\Pi_1$ | 15650.31(2) | 360.96(2) | 1.01(1) | 181.5(2) | 2.3(2) | 2 |
| [15.69] $^3\Sigma_0^-$ | 15699.45(2) | 367.99(1) | 2.64(3) | 190.1(3) | 1.1(4) | 3 |
| [15.81] $^3\Pi_1$ | 15815.91(3) | 350.59(1) | 1.26(1) | 185.2(4) | 1.8(3) | 3 |

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

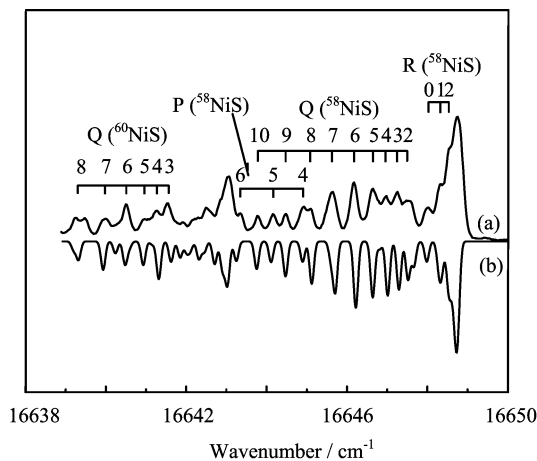


FIG. 2 Rotationally resolved LIF excitation spectrum of the [15.65] $^3\Pi_1(v'=3)$ - $X^3\Sigma_0^-(v''=0)$ transition of NiS. (a) the experimental spectrum and (b) the simulated spectrum.

state, as listed in Table I. The rotational energy term value of the upper state used in the simulation was given: [14]

$$F_v(J) = B_v J(J+1) - D_v [J(J+1)]^2 \quad (2)$$

The line shape was convoluted with a Lorentzian

function and the rotational distribution was assumed to be Boltzmann (incorporated with a Hönl-London factor) with a rotational temperature of ~ 50 K. The molecular constants of the $X^3\Sigma_0^-$ ground state ($B_0=6351.4222$ MHz, $D_0=4478.99$ Hz) were taken from Ref.[11]. It should be noted here that in our previous report on the [17.4] $^3\Sigma_0^-(v'=2-7)$ - $X^3\Sigma_0^-(v''=0)$ transition bands of NiS [10], the rotational constant and bond length for the $v''=0$ level of the $X^3\Sigma_0^-$ ground state were determined as $B_0=0.182$ cm^{-1} and $r_0=2.1195$ Å. There is obviously too much difference between these values and those ($B_0\approx 0.212$ cm^{-1} and $r_0\approx 1.9625$ Å) reported in Ref.[11]. Our recent reinvestigation on the LIF spectrum of NiS in the energy range of 17000–23000 cm^{-1} indicated that the values given in Ref.[10] are incorrect, therefore we used the rotational constant reported in Ref.[11] for the spectral fitting in the present work.

The electronic state energy term T_e , the vibrational frequency ω_e , and some other equilibrium spectroscopic constants for the [15.65] $^3\Pi_1$ state were also calculated as follow [14]:

$$\nu_0(v', v'') = T_e + \omega'_e (v' + 1/2) - \omega_e \chi'_e (v' + 1/2)^2 - [\omega''_e (v'' + 1/2) - \omega_e \chi''_e (v'' + 1/2)^2] \quad (3)$$

$$B_v = B_e - (v + 1/2) \alpha_e \quad (4)$$

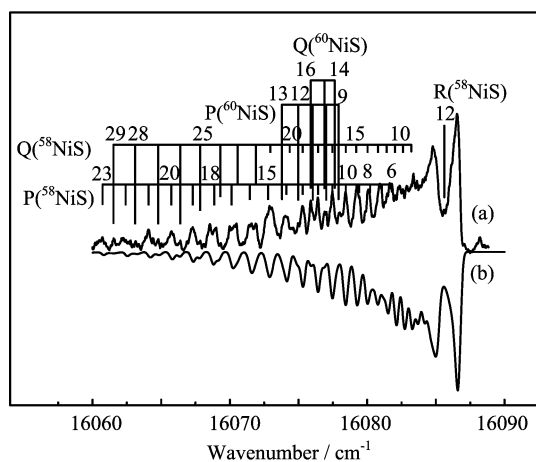


FIG. 3 Rotationally resolved LIF excitation spectrum of the $[15.81]^3\Pi_1(v'=1)-X^3\Sigma_0^-(v''=0)$ transition of NiS. (a) the experimental spectrum and (b) the simulated spectrum.

The calculated equilibrium constants are summarized in Table II.

It is worth noting that the obtained rotational constants B_v of the $[15.65]^3\Pi_1$ state are not linearly dependent on v' (see Eq.(4)), which may imply that the $v'=3$ and $v'=4$ vibrational levels of the $[15.65]^3\Pi_1$ state are perturbed by other adjacent states. This may explain why the lifetimes we measured decrease at the $v'=3$ and $v'=4$ levels, as discussed below. Therefore, the B_e and α_e values of the $[15.65]^3\Pi_1$ state were derived by using the rotational line positions for only the 0-0, 1-0, and 2-0 bands. The obtained values are given in Table II.

In Fig.3, the LIF rotational spectrum for the 1-0 band of the $[15.81]^3\Pi_1-X^3\Sigma_0^-$ transition progression is shown. Similar to the analysis given above, we obtained the spectroscopic constants for the observed five bands and the equilibrium constants for the $[15.81]^3\Pi_1$ state, as listed in Tables I and II. In contrast to the case for the $[15.65]^3\Pi_1(v'=0-4)-X^3\Sigma_0^-(v''=0)$ transition bands described above, the obtained rotational constants B_v for the $[15.81]^3\Pi_1(v'=0-4)-X^3\Sigma_0^-(v''=0)$ transition bands are found to be linearly dependent on v' .

For the remaining progression with band origin (T_e) at $\sim 15699 \text{ cm}^{-1}$, as shown in Fig.1, we found that unlike the two $\Pi-\Sigma$ type transitions discussed above, this progression should be attributable to a $\Sigma-\Sigma$ type transition. As an example, Figure 4 exhibits the rotational spectrum for the 2-0 band of this progression. The $\Sigma-\Sigma$ type transition can be verified by the fact that the Q branch vanishes in this spectrum. According to the transition selection rules in Hund's case (a), the upper state of this progression can be determined to be $^3\Sigma_0^-$. The obtained spectroscopic constants and the equilibrium constants are listed in Tables I and II, in which the data for the 0-0 and 4-0 bands are not given because of their very weak spectral line intensities.

Furthermore, we measured the lifetimes of almost all the observed bands by recording the decay traces of

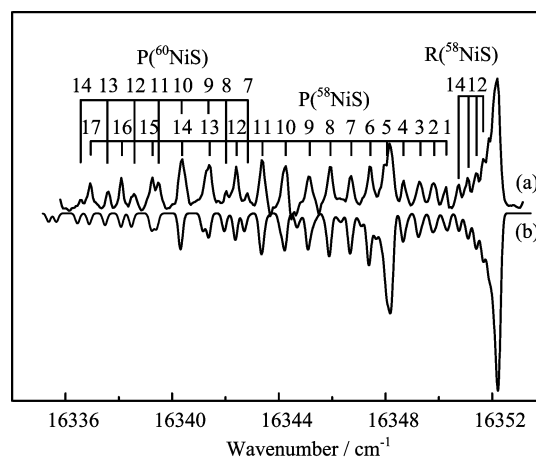


FIG. 4 Rotationally resolved LIF excitation spectrum of the $[15.69]^3\Sigma_0^-(v'=2)-X^3\Sigma_0^-(v''=0)$ transition of NiS. (a) the experimental spectrum and (b) the simulated spectrum.

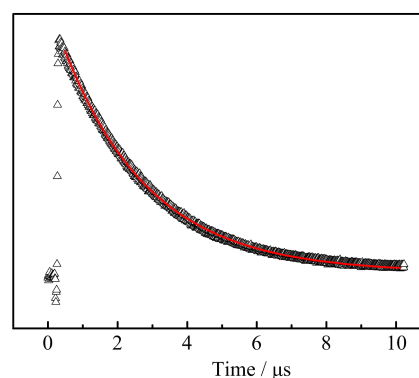


FIG. 5 A typical fluorescence decay trace of $[15.81]^3\Pi_1(v'=0)-X^3\Sigma_0^-(v''=0)$ band of NiS. The red trace is an exponential fit of the fluorescence decay, the black trace is an experimental fluorescence decay. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.

the time-resolved LIF signal. Such measurements provide complementary information about the three newly identified electronic states. In the present study, the fluorescence decay signal was averaged over 256 laser shots at a selected wavelength. Figure 5 shows a typical decay trace of the fluorescence resulting from the $[15.81]^3\Pi_1(v'=0)-X^3\Sigma_0^-(v''=0)$ transition. Considering that the NiS molecules in this experiment were produced in a very low concentration under a supersonic jet condition and the expansion of the NiS 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 in approximately the same time scale (2.0–3.0 μs) for different vibronic bands. Those with lifetimes of 1.0–2.0 μs may imply that they are perturbed by other states.

The binding in NiS is found to be quite similar to that of NiO, the energy separations between the $^3\Sigma^-$, $^3\Pi$, and $^3\Sigma^+$ states agree between NiS and NiO to $\sim 400\text{ cm}^{-1}$ [15]. The $X^3\Sigma^-$ ground state of both NiO and NiS has been determined to be of the similar electronic configuration of (core)($3\pi^4$)($4\pi^2$)($1\sigma^4$)($9\sigma^2$) [15–17]. As in the case for NiO [17], the electronic configuration of the $^3\Sigma^-$ state of NiS we observed can be attributable to that of (core)($3\pi^2$)($3\pi^1$)($4\pi^2$)($4\pi^1$)($1\sigma^4$)($9\sigma^2$). Since the two $^3\Pi$ states of NiS lie energetically close to the $^3\Sigma^-$ state, two possible electronic configurations for the two $^3\Pi$ states may be (core)($3\pi^4$)($4\pi^2$)($4\pi^1$)($1\sigma^2$)($1\sigma^1$)($9\sigma^2$) and (core)($3\pi^4$)($1\sigma^2$)($1\sigma^1$)($9\sigma^2$)($4\pi^2$)($4\pi^1$), according to a recent calculation using density functional theory [16]. Further theoretical and experimental investigations are required to identify the electronic configuration of NiS.

IV. CONCLUSION

We have presented the jet-cooled laser-induced fluorescence excitation spectrum of NiS in the energy range of 15500–17200 cm^{-1} . Fifteen vibronic bands were observed and rotationally analyzed, all of which were reported for the first time. Vibrational and rotational analyses indicated that the fifteen bands can be assigned to the $[15.65]^3\Pi_1(v'=0-4)-X^3\Sigma_0^-(v''=0)$, $[15.69]^3\Sigma_0^-(v'=0-4)-X^3\Sigma_0^-(v''=0)$, and $[15.81]^3\Pi_1(v'=0-4)-X^3\Sigma_0^-(v''=0)$ transitions. The molecular constants of the three newly identified electronic states were derived, and the isotopic shifts were determined. In addition, the lifetimes of most observed bands were measured under the collision free condition. On the basis of the spectroscopic data and lifetime measurement, the electronic structures of these electronic states are discussed.

V. ACKNOWLEDGMENTS

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