

LETTER

Experimental Determination of the Vibrational Constants of FeS($X^5\Delta$) by Dispersed Fluorescence Spectroscopy

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Based on previous laser-induced fluorescence excitation spectroscopy work, the vibrational constants of neutral FeS in the $X^5\Delta$ electronic state were obtained by directly mapping the ground-state vibrational levels up to $v''=3$ using conventional laser-induced dispersed fluorescence spectroscopy. The vibrational frequency of FeS($X^5\Delta$) (518 ± 5 cm^{-1}) agrees well with that reported in a recent PES measurement (520 ± 30 cm^{-1}) [J. Phys. Chem. A **107**, 2821 (2003)] which is the only one prior experimental vibrational frequency value for the $^5\Delta$ state of FeS. Careful comparisons of our experimental results and those documented in the literature (mainly from theoretical predictions) suggest that the ground state of FeS is $^5\Delta$ state.

Key words: FeS, Vibrational constant, Laser-induced dispersed fluorescence spectroscopy

Fe-S cluster (and complex) systems have been one of the major subjects of organometallic chemistry [1]. However, accurate calculations of large Fe-S systems are rather challenging [2]. As small sized Fe-S systems such as $\text{Fe}_2\text{S}_2^{-/0/+2+}$, FeS_n ($n=1-6$), and Fe_nS_m^- ($n=1-6$, $m=1-6$) can be accessed relatively easier and serve as a first step towards the understanding of the intrinsic physical properties and electronic structure of the active centers in the large sized Fe-S systems, they have received substantial attention from both theoretical [3-9] and experimental [10-13] sides.

It is noteworthy that even the electronic structure and chemical bonding of FeS, the smallest molecule with an iron sulfur bond, have not been well characterized thus far [12], and there remains much controversy about the nature of the electronic ground state of such a simple system as FeS [3]. Assuming a $^5\Sigma^+$ ground state, DeVore and Franzen reported a harmonic vibrational frequency ω_e'' of 540 cm^{-1} for FeS by means of matrix infrared spectroscopy [14]. Two decades later Bauschlicher and Maitre presented a comprehensive theoretical study on transition metal oxides and sulfides [8], as part of which a $^5\Delta$ ground state was proposed for FeS ($\omega_e''=521$ cm^{-1} calculated at the CASSCF/ICACPF level). A close ω_e'' of 502 cm^{-1} for FeS($^5\Delta$) was calculated at the B3LYP level by Glukhovtsev *et al.* [7]. By employing the CASSCF/ACPF basis set and the same active space as that in Ref.[8], Hübner *et al.* found a $^5\Sigma^+$ state

0.13 eV below the $^5\Delta$ state and a $^7\Sigma^+$ state 0.13 eV above the $^5\Delta$ state [6], and assigned the three closely spaced states to the first broad band in the photoelectron spectrum (PES) of FeS^- recorded by Zhang *et al.* [13]. The vibrational frequencies of the $^5\Sigma^+$ and $^5\Delta$ states were calculated to be 536 and 519 cm^{-1} , respectively [6]. Zhai *et al.* recently observed a vibrationally resolved PES spectrum of FeS^- , which revealed a long and well-resolved vibrational progression with an average spacing of 520 ± 30 cm^{-1} [12]; they attributed the transition X in their PES spectrum to the detachment of an electron from the anionic ground state $^6\Delta$ resulting in the formation of neutral FeS in its $^5\Delta$ ground state. In the meantime, a microwave spectrum of FeS was reported by Takano *et al.* who pointed out that the $^5\Delta$ is most probably the electronic ground state [11].

It should be mentioned here that Clima *et al.* recently performed *ab initio* computations at the B3LYP and CASSCF/CASPT2 levels, yielding a $^5\Sigma^+$ state lower in energy than the $^5\Delta$ state for FeS [3]. The vibrational frequencies of the $^5\Sigma^+$ and $^5\Delta$ states were calculated at the B3LYP level to be 529 and 513 cm^{-1} , respectively, and at the CASSCF/CASPT2 level to be 516 and 532 cm^{-1} , respectively [3]. In comparison with CASPT2, the B3LYP method has strength in predicting spectroscopic constants that generally agree well with experimental data (although it has major drawbacks in predicting the right ground state or any other energy differences). Hence, the B3LYP results (529 cm^{-1} for $^5\Sigma^+$ and 513 cm^{-1} for $^5\Delta$) of Clima *et al.* are relatively more reliable [3], which are generally in line with the CASSCF/ACPF results (536 cm^{-1} ($^5\Sigma^+$) and 519 cm^{-1} ($^5\Delta$)) of Hübner *et al.* [6].

Very recently we reported a laser-induced fluores-

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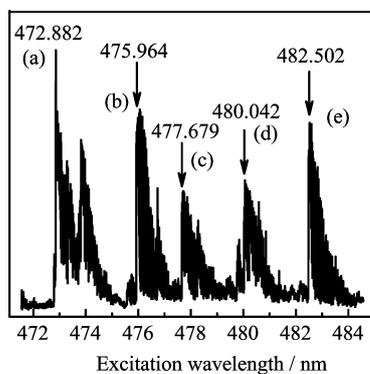


FIG. 1 The LIF excitation spectrum of FeS. The downward arrows indicate the band origin positions used for the excitation of the DF spectra. (a) $[19.32]\Omega'=5(v'=6)\leftarrow X^5\Delta_4(v''=0)$, (b) $[19.25]\Omega'=4(v'=9)\leftarrow X^5\Delta_4(v''=0)$, (c) $[19.42]\Omega'=4(v'=5)\leftarrow X^5\Delta_4(v''=0)$, (d) $[19.61]\Omega'=4(v'=4)\leftarrow X^5\Delta_4(v''=0)$, and (e) $[19.25]\Omega'=4(v'=8)\leftarrow X^5\Delta_4(v''=0)$.

cence (LIF) excitation spectrum of jet-cooled FeS molecules in the energy range $18900\text{--}21600\text{ cm}^{-1}$ [10], in which four parallel and one perpendicular vibronic transitions were identified with a common lower $^5\Delta_4$ electronic state. The determination of the lower state to be $^5\Delta_4$ was based on a careful rotational analysis of our LIF excitation spectrum. We notice that, apart from the earlier report who assumed a $^5\Sigma^+$ state [14], all the other available experimental works [10–13] claimed a $^5\Delta$ rather than a $^5\Sigma^+$ state for the electronic ground state of FeS. We also notice that, although a $^5\Sigma^+$ state has been theoretically predicted [3, 6] to be lower in energy than the $^5\Delta$ state that has been observed by means of a variety of spectroscopic techniques (including PES [12, 13], microwave [11], and LIF [10] spectroscopy), it is evident that the two states are indeed very closely spaced and the energy difference between them is well within the accuracy of the calculations. Additionally, as extensively discussed by Hübner *et al.* [6], computations for the particular system at hand, FeS, appear to be strongly basis set dependent.

We therefore cautiously hold that the electronic ground state of FeS may well be attributed to $X^5\Delta$. To further support this we present another experimental evidence by directly mapping the vibrational energy levels using conventional laser-induced dispersed fluorescence (DF) spectroscopy.

Our experiment was conducted on a home-built LIF/DF apparatus, details of which can be found elsewhere [10, 15]. Briefly, gaseous FeS molecules in their ground state were produced by the reaction of H_2S molecules (2% in Ar) with Fe atoms sputtered from a pair of pure iron pins under a molecular beam/pulsed DC discharge condition. The LIF 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.

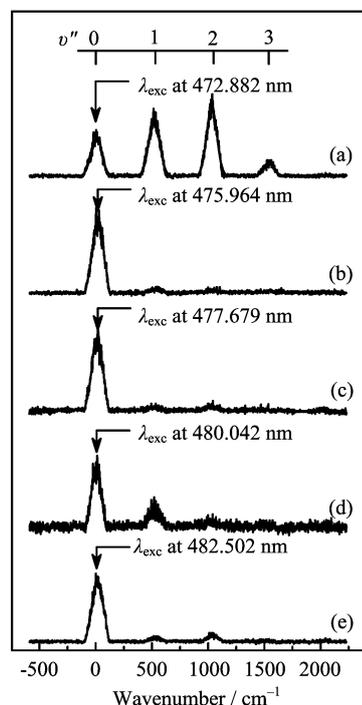


FIG. 2 The DF spectra of FeS recorded by using excitation wavelengths that are marked by downward arrows in Fig. 1. The vibrational numbering v'' for the $X^5\Delta$ state of FeS is indicated by ticks at the top. The red solid curve in (a) is the Gaussian fit of the four DF peaks. (a) $[19.32]\Omega'=5(v'=6)\leftarrow X^5\Delta_4(v''=0)$, (b) $[19.25]\Omega'=4(v'=9)\leftarrow X^5\Delta_4(v''=0)$, (c) $[19.42]\Omega'=4(v'=5)\leftarrow X^5\Delta_4(v''=0)$, (d) $[19.61]\Omega'=4(v'=4)\leftarrow X^5\Delta_4(v''=0)$, and (e) $[19.25]\Omega'=4(v'=8)\leftarrow X^5\Delta_4(v''=0)$.

The DF spectra were recorded by fixing the excitation laser wavelengths at the band origins obtained from the LIF excitation spectrum and scanning a monochromator (Zolix, Omni- λ 300) with a 1-mm-wide slit.

Figure 1 shows the LIF excitation spectrum obtained in the wavelength range of 471–485 nm. Based on a careful rotational analysis given in our previous work [10], the bands labeled in Fig. 1 have been assigned to the vibronic transitions, $[19.32]\Omega'=5(v'=6)\leftarrow X^5\Delta_4(v''=0)$, $[19.25]\Omega'=4(v'=9)\leftarrow X^5\Delta_4(v''=0)$, $[19.42]\Omega'=4(v'=5)\leftarrow X^5\Delta_4(v''=0)$, $[19.61]\Omega'=4(v'=4)\leftarrow X^5\Delta_4(v''=0)$, $[19.25]\Omega'=4(v'=8)\leftarrow X^5\Delta_4(v''=0)$, respectively. In the present DF measurements, the band origins of the five bands at 472.882 nm (21146.92 cm^{-1}), 475.964 nm (21009.99 cm^{-1}), 477.679 nm (20934.56 cm^{-1}), 480.042 nm (20831.51 cm^{-1}), and 482.502 nm (20725.30 cm^{-1}) were chosen to coincide with the excitation wavelengths; thus obtained DF spectra are displayed in Fig. 2, respectively.

In Fig. 2(a), the displacements of the four peak maxima with respect to the position marked with a downward arrow (indicating the excitation wavelength of 472.882 nm), read 0, ~ 515 , ~ 1027 , and

$\sim 1535\text{ cm}^{-1}$, respectively. The emission with the shortest wavelength was found to be at $\sim 472.882\text{ nm}$, exactly equivalent to the wavelength used for excitation, which implies that this peak should correspond to the $[19.32]\Omega'=5(v'=6)\rightarrow X^5\Delta_4(v''=0)$ transition [10]. Hence, we anticipate that the remaining three peaks in Fig.2(a) may correspond to the $[19.32]\Omega'=5(v'=6)\rightarrow X^5\Delta_4(v''=1-3)$ transitions. Fitting the above displacement values into the customary Eq.(1) yields the harmonic vibrational frequency ($\omega_e''=518\pm 5\text{ cm}^{-1}$) as well as the anharmonicity constant ($\omega_e\chi_e''=1.7\pm 0.2\text{ cm}^{-1}$) for the $X^5\Delta_4$ state of FeS.

$$G(v'') = \omega_e'' \left(v'' + \frac{1}{2} \right) - \omega_e\chi_e'' \left(v'' + \frac{1}{2} \right)^2 \quad (1)$$

The ω_e'' value we obtained directly from our DF measurements turned out to agree well with both the calculated ones (*e.g.*, 521 cm^{-1} (CASSCF/ICACPF) [8], 519 cm^{-1} (CASSCF/ACPF) [6], 513 cm^{-1} (B3LYP) [3], and 502 cm^{-1} (B3LYP) [7]) and the recent PES measurement ($520\pm 30\text{ cm}^{-1}$) [12]. In addition, based on the recent microwave spectroscopic data ($B_e''=6106.16\text{ MHz}$ and $D_e''=3.9529\text{ kHz}$) [11], the ω_e'' value is estimated to be about 506 cm^{-1} . All this agreement lends support to the assignment of our DF spectrum shown in Fig.2(a).

Unlike the DF spectrum shown in Fig.2(a) which arises from a $[\Omega'=5]-^5\Delta$ type transition, the remaining four DF spectra shown in Fig.2 (b)–(e) all correspond to a $[\Omega'=4]-^5\Delta$ type transition. Nevertheless, they all exhibit vibrational spacings that are almost identical to those observed in Fig.2(a) although some of the spectral features are quite weak (but discernable). This indicates that all the DF spectra in Fig.2 bear a common lower electronic state ($X^5\Delta$) and in turn further validates the vibrational constants we derived in this work.

Interestingly, one can readily detect that (i) the intensity patterns of the DF spectra shown in Fig.2 (b)–(e) reassemble one another (all with a predominant emission to the $v''=0$ level) while differ dramatically with that of the DF spectrum shown in Fig.2(a), and (ii) for all the DF spectra shown in Fig.2, no emissions to the levels with $v''\geq 4$ were observed. All this may result from different Franck-Condon coefficients for the four $[\Omega'=4](v')-X^5\Delta(v'')$ and the one $[\Omega'=5](v')-X^5\Delta(v'')$ vibronic transitions.

To summarize, based on our previous work [10] we obtained the harmonic vibrational frequency ($\omega_e''=518\pm 5\text{ cm}^{-1}$) and the anharmonicity constant ($\omega_e\chi_e''=1.7\pm 0.2\text{ cm}^{-1}$) of neutral FeS in the $X^5\Delta$ electronic state by directly mapping the ground-state vibrational levels up to $v''=3$ using conventional laser-induced dispersed fluorescence spectroscopy. The vibrational frequency of FeS ($X^5\Delta$) we obtained ($518\pm 5\text{ cm}^{-1}$) is in good agreement with (yet more

accurate than) that reported in a recent PES measurement ($520\pm 30\text{ cm}^{-1}$) [12] which is the only one prior experimental value. It is also helpful to point out that almost all the reported vibrational frequency values for the $^5\Delta$ state (calculated or measured) are basically around 520 cm^{-1} or below [3, 6–8, 11, 12], while those for the $^5\Sigma^+$ state appear to be larger (*e.g.*, 540 cm^{-1} (matrix infrared spectroscopy) [14], 536 cm^{-1} (CASSCF/ACPF) [6], and 529 cm^{-1} (B3LYP) [3]), which strongly supports that what we observed in the DF spectra and the LIF excitation spectrum [10] is indeed the $^5\Delta$ state, an electronic state we would cautiously suggest as the ground state of FeS.

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