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Electronic states and spectra of BiS

K.D. Setzer, F. Meinecke, E.H. Fink *

Physikalische Chemie-Fachbereich C, Bergische Universität Wuppertal, D-42097 Wuppertal, Germany

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NIR/VIS emission spectra of BiS were measured in the 5800–25 000 cm^{-1} region with a Fourier-transform spectrometer. BiS was produced by reaction of bismuth and sulfur vapor and excited by energy transfer from metastable oxygen $O_2(a^1\Delta_g)$ in a fast-flow system. The spectrum of BiS was found to be closely related to that of the previously studied BiO radical [O. Shestakov et al., J. Mol. Spectrosc. 190 (1998) 28–77]. Five transitions connecting the Ω-components of the first three excited states, $A^4\Pi(A_13/2, A_21/2)$, $B^2\Pi(B_11/2)$, and $C^4\Sigma^-(C_11/2, C_23/2)$, with the components of the strongly split ground state, $X^2\Pi(X_11/2, X_23/2$, have been observed and analyzed.

1. Introduction

In the course of studies of NIR emission spectra of diatomic radicals with low-lying electronic states which may be excited in chemical reactions or by energy transfer processes from metastable energy carriers like $O_2(a^1\Delta_g)$ or $NF(a^1\Delta)$ [1], we have reported a detailed study of the UV/VIS/NIR spectrum of the BiO radical [2]. BiO was found to have an $X^2\Pi_r$ ground state with large spin-orbit splitting of 7088 cm^{-1}. On the addition of Bi_x vapor to microwave-discharged oxygen, $E \rightarrow E$ energy transfer from $O_2(a^1\Delta_g)$ populating $BiO(X_2{}^2\Pi_{3/2})$ and subsequent energy pooling processes lead to excitation of BiO states up to above 30 000 cm^{-1} [2–6]. The NIR emission spectrum observed from this system is dominated by the intense fine structure transition $X_2{}^2\Pi_{3/2} \rightarrow X_1{}^2\Pi_{1/2}$ of BiO in the 6400–7400 cm^{-1} region. Strong perturbation of the vibrational structure of the $X_23/2$ state for levels $v' \geqslant 5$ showing up in this spectrum and the observation of a number of new states and transitions of BiO stimulated a detailed *ab initio* theoretical study of the BiO molecule by Alekseyev et al. [7]. The results of this work allowed safe assignments of all experimentally observed new states and transitions. In particular, the perturbation of the $X_2{}^2\Pi_{3/2}, v' \geqslant 5$ vibrational levels was explained by an avoided crossing of the $X_2{}^2\Pi_{3/2}$ and $A_1{}^4\Pi_{3/2}$ potential curves.

In subsequent experimental work, the analogous $X_23/2 \rightarrow X_11/2$ fine structure transitions were observed for BiS and BiSe but not for BiTe [8,9]. In BiS and BiSe the perturbation of the vibrational structure of the $X_23/2$ states was found to occur at steadily lower v' levels. These findings were explained by further theoretical work [10,11] which included *ab initio* calculations of BiS states up to 20 000 cm^{-1} above the ground state [10].

The first spectroscopic observation of BiS in the gas phase was made by Barrow et al. [12] who assigned an extensive absorption system in the 500–800 nm region to an $A^2\Pi_{1/2} \leftarrow X^2\Pi_{1/2}$ transition. Later Patiño et al. [13] studied the A–X system by laser induced fluorescence and reported on the analysis of strong hyperfine structure splitting of the $A \leftarrow X$ lines. Ahmed [14] measured LIF spectra of BiS in argon matrices. He observed three band series which he assigned to transitions from new states B, C and D at 18 400 cm^{-1}, 20 652 cm^{-1} and 21 206 cm^{-1}, respectively, to the ground state.

Recently, we have reported on the analysis of low-resolution FT emission spectra of the $X_2 \rightarrow X_1$ fine structure transition of BiS and on a joint analysis of a high-resolution spectrum of the 0-0 band of this transition and of millimeterwave measurements of rotational transitions in the X_1 ground state [9]. The latter analysis has yielded a complete set of rotational and hyperfine splitting parameters for the $X^2\Pi, v = 0$ ground state of BiS which were compared with the results of previous analogous work on BiO [15].

In the present paper we report on measurements and analyses of emission spectra of BiS in the wavenumber range of 8000–25 000 cm^{-1}. Five transitions were found in this range four of which have not been observed in the gas phase before.

2. Experimental

The experimental setup and procedures used for measuring the NIR/VIS emission spectra of BiS have been described in previous work on BiO [2] and BiS [9]. Chemiluminescence from the $Bi_x/S_x/O_2(a^1\Delta_g)$ system was measured with a high-resolution Fourier-transform spectrometer (Bruker IFS 120 HR) equipped with a liquid-nitrogen cooled Ge detector (Applied Detector Corp. Model

* Corresponding author. Address: Physikalische Chemie-Fachbereich C, Bergische Universität Wuppertal, Gauss-Strasse 20, D-42097 Wuppertal, Germany. Fax: +49 202 4392505.
E-mail address: fink@uni-wuppertal.de (E.H. Fink).

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403 S) or a photomultiplier (Hamamatsu type R 928 or R 666-10). Broad-band and short-wave-pass interference filters were used to suppress part of the emissions in order to reduce the statistical noise of the detectors. The wavenumber scale of the spectrometer was calibrated by use of emission lines of the $a \rightarrow X$ band of molecular oxygen near 1260 nm as secondary standards. The precision of the measured wavenumbers is on the order of one tenth of the spectral resolution used in the experiments.

3. Observed spectra and analyses

Fig. 1 shows a medium-resolution (0.5 cm^{-1}) spectrum of BiS observed in the wavenumber range 7800–13 200 cm^{-1} through a 1.3 μm short-pass filter. Actually all measured spectra consist of superpositions of BiS and BiO bands. Therefore, each experiment was started by measuring spectra of the pure BiO chemiluminescence under exactly the same conditions as used for the subsequent BiS experiments. These BiO spectra were used to subtract the BiO background emissions from the BiS/BiO spectra. The resulting BiS spectrum shown in Fig. 1 consists of short sequences of red-degraded bands with heads in the R-branches and thus is quite similar to the $A_2{}^4\Pi_{1/2} \rightarrow X_1{}^2\Pi_{1/2}$ spectrum of BiO observed at somewhat larger wavenumbers [2]. Based on this similarity and the theoretical calculations of Lingott et al. [10] the spectrum is assigned to the corresponding $A_2{}^4\Pi_{1/2} \rightarrow X_1{}^2\Pi_{1/2}$ transition of BiS. Assuming then that the regularly spaced strongest bands belong

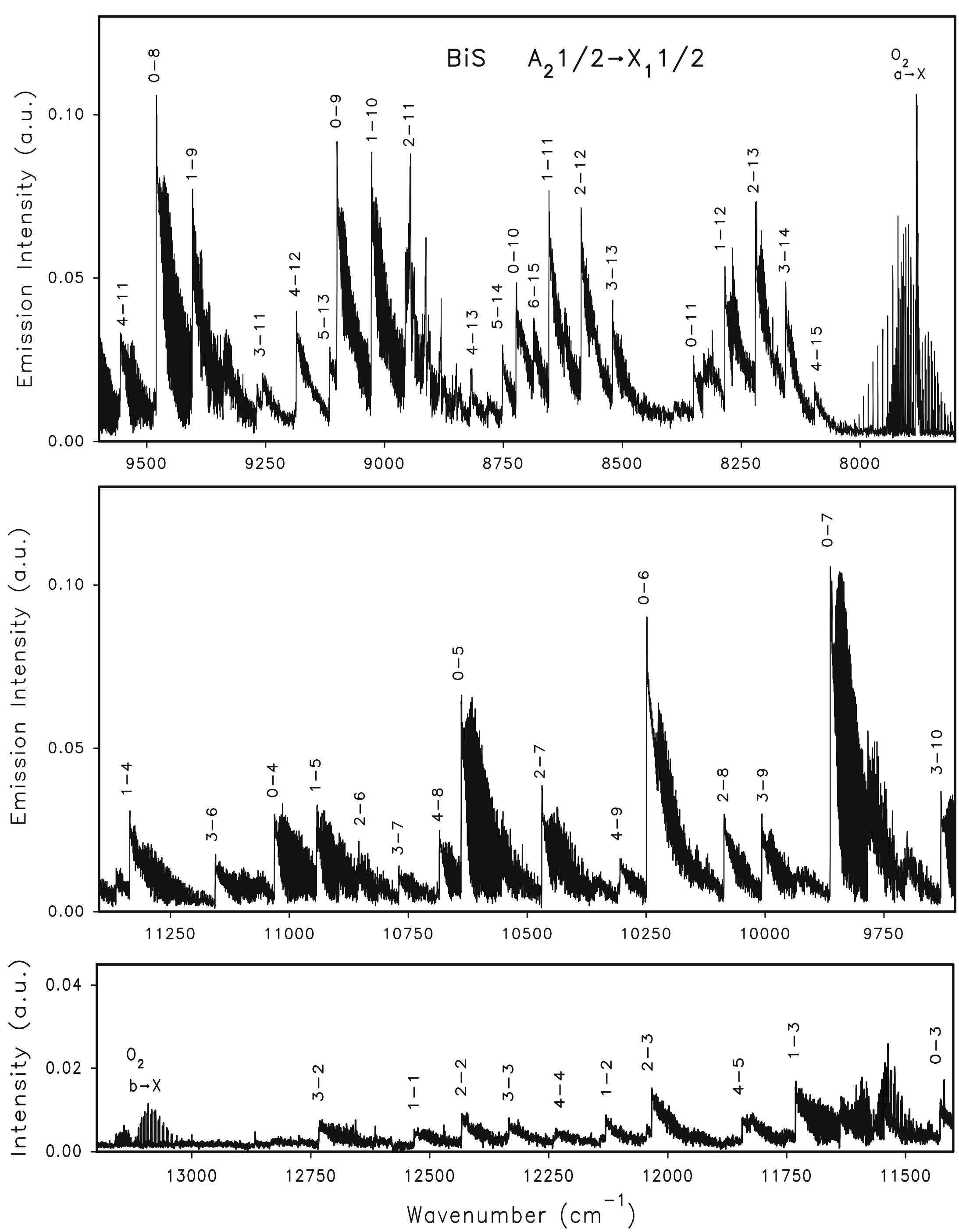

Fig. 1. Spectrum of the $A_2 1/2 \rightarrow X_1 1/2$ transition of BiS. The spectral resolution is 0.5 cm^{-1}.