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Laser spectroscopy of the $\tilde{A}^2A' - \tilde{X}^2A''$ system for the HSO radical

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ABSTRACT

Rotationally resolved spectra of the $\tilde{A}^2A' - \tilde{X}^2A''$ system for the HSO radical were observed by laser induced fluorescence spectroscopy. The radical was produced in a discharged supersonic jet of a gas mixture of dimethyl disulfide and O_2 diluted in Ar. The observed spectra were assigned to ro-vibronic transitions of the $K_a' \leftarrow K_a'' = 0 \leftarrow 1, 1 \leftarrow 0$, and $2 \leftarrow 1$ subbands of $\tilde{A}(00v_3') - \tilde{X}(000)$ with $v_3' = 0$–8, and those of $\tilde{A}(013) - \tilde{X}(001)$, yielding the rotational and spin–rotation interaction constants for the excited electronic state. For the vibronic origin band, the band origin and the rotational constants are determined to be $T_v = 14383.2533(28)\ \mathrm{cm}^{-1}$, $A = 287316(33)$, $(B + C)/2 = 16712.8(48)$, and $(B - C)/2 = 532.0(70)$ MHz. Dispersed fluorescence spectra of the HSO radical were also observed, where the fundamental vibrational frequencies of the ν_1 and ν_2 modes for the $\tilde{X}$ state have been determined experimentally for the first time.

1. Introduction

The HSO radical is one of the important species in atmospheric chemistry, since it plays significant roles in H_2S oxidation processes, yielding atmospheric H_2SO_4. The HS radical is considered to be oxidized by the following reactions [1–3],

$$HS + O_3 \rightarrow HSO + O_2 \tag{1}$$

$$HS + NO_2 \rightarrow HSO + NO. \tag{2}$$

On the other hand, the HSO radical is reduced by O_3,

$$HSO + O_3 \rightarrow HS + 2O_2. \tag{3}$$

Because the reactions (1) and (3) are regarded as an ozone depletion cycle [4,5], a number of theoretical studies [6–8] of the HSO radical have been reported so far.

In 1978 Schurath et al. have observed the $\tilde{A}^2A' - \tilde{X}^2A''$ system of HSO by chemiluminescence spectroscopy [9]. They have observed vibronic bands with prominent ν_3 progressions of HSO for the $\tilde{A}$ state, where emissions up to $v_3' = 7$ were observed. For high resolution studies of the $\tilde{A}$ state, rotationally resolved laser induced fluorescence (LIF) spectra for the vibronic bands of $\tilde{A}\ (00v_3') - \tilde{X}\ (000)$, with $v_3' = 3$ and 4, have been observed by Kakimoto et al. and Satoh et al., respectively [10,11]. For the DSO radical, Ohashi and co-workers have observed bands with $\tilde{A}\ (003)$, $\tilde{A}\ (021)$, $\tilde{A}\ (012)$, $\tilde{A}\ (022)$ and determined the molecular constants for these bands [12–14]. Fluorescence lifetimes of $\tilde{A}\ (00v_3')$, with $v_3' = 1$, 3, 4, 7 and 8, have been measured by Kawasaki et al. [15]. The lifetimes showed systematic decrease with increasing the upper state vibrational quantum number, v_3', because the vibrational levels of the $\tilde{A}$ state approach to the dissociation limit as the energies are increased. In spite of these studies, however, there are no reports for high resolution spectroscopic studies of the vibronic origin band of the $\tilde{A} - \tilde{X}$ system.

Endo et al. have observed pure rotational spectra by mm-wave spectroscopy for the ground electronic state, and determined accurate molecular constants including the hyperfine coupling constants for the HSO and DSO radicals in 1981 [16]. Sears and McKellar have observed the ν_3 band for the $\tilde{X}$ state, and determined the rotational constants using laser magnetic resonance spectroscopy in the 10 μm region [17]. They have also searched for the ν_2 band below 1100 cm^{-1}, but failed to observe it. They concluded that their failure to observe the band was attributed to the fact that the transition dipole moment was considerably small or the ν_2 band was located above 1100 cm^{-1}.

In this study, we have observed vibronic bands of the $\tilde{A}\ (00v_3') - \tilde{X}\ (000)$ system with $v_3' = 0$–8 and $\tilde{A}\ (013) - \tilde{X}\ (001)$ for HSO using an LIF spectrometer in combination with a pulsed-discharge nozzle (PDN), yielding the rotational constants and the spin–rotation interaction constants for the excited electronic state. We have also observed dispersed fluorescence (DF) spectra for the HSO and DSO radicals, and determined the fundamental vibrational frequencies for the $\tilde{X}$ state.

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2. Experiment

2.1. Observation of LIF spectra

Since the experimental set-up has been described previously in Ref. [18], only a brief explanation is given here. The HSO radical was produced in a supersonic jet using a gas mixture of 10% O_2 diluted in Ar, passed through a reservoir filled with dimethyl disulfide, CH_3SSCH_3. When we used a sample gas mixture of 5% H_2S and 10% O_2 diluted in Ar as a precursor, the intensities of the observed spectra for HSO were much weaker, *c.a.* 1/5, than the case of using dimethyl disulfide. However, the DSO radical was produced using a gas mixture of 5% D_2S and 10% O_2 diluted in Ar. The sample gas was discharged by applying a 2500 V pulse for HSO and 1500 V for DSO in the PDN [19,20] and the stagnation pressure was kept at 6.0 atm. A dye laser (Lamda Physik, SCANMATE 2E) pumped by a 355 or 532 nm output of a Nd^{3+}:YAG laser (Spectra Physics, Lab. 170) was employed. Coumarin 480, Coumarin 500, Rhodamine 6G, Rhodamine B, DCM, and LDS 698 dyes were used for the operation of the dye laser to cover the wavelength region from 485 to 697 nm. The line width of the laser is *c.a.* 0.1 cm^{-1} without an etalon and is *c.a.* 0.02 cm^{-1} when the etalon is installed in the resonator. The experimental accuracy of the frequency measurement is estimated to be 0.005 cm^{-1}, when the etalon is used. The visible light beam was crossed to the jet at 2.8 cm downstream from the PDN. The fluorescence from the excited state of the HSO radical was collected by two planoconvex lenses located at right angles to the directions of the laser beam and the supersonic jet. The fluorescence was detected by a photomultiplier tube (PMT), Hamamatsu R3896. Absolute frequency calibration was accomplished by simultaneously recording the I_2 absorption spectrum. For the measurements of DF spectra, the fluorescence was dispersed with a 0.5 m monochromator (SPEX, 500 M) with a typical slit width of the monochromator at 0.4 mm. The resolution of the monochromator is thus *c.a.* 40 cm^{-1}, and the estimated accuracy of the frequency measurement is 5 cm^{-1}.

2.2. Ab initio calculations

Ab initio calculations, at the multi-reference configuration interaction, MRCI, and the restricted coupled cluster with single and double excitation with noniterative perturbational treatment of triple excitation, RCCSD(T), levels of theories, have been performed to obtain the molecular geometries and the vibrational frequencies in the $\tilde{X}$ and $\tilde{A}$ states of HSO. The polarized valence quadruple-zeta correlation-consistent bases set with diffuse functions, aug-cc-pVQZ, have been used in the calculations. All the *ab initio* calculations were performed by the MOLPRO 2006.1 package [21]. In the MRCI calculations, orbitals from $6a'$ to $12a'$, $2a''$ and $3a''$ are selected as active orbitals for the multi-configuration self-consistent field, MCSCF, calculations, and the same number of orbitals are taken into account for the MRCI calculations. The vibrational frequencies of the $\tilde{A}$ state were calculated at the geometry optimized at the same level of theory. For the DSO radicals, *ab initio* calculations at the RCCSD(T)/aug-cc-pVQZ level of theory were performed to estimate the vibrational frequencies of the $\tilde{X}$ state.

3. Results and analysis

3.1. LIF spectra

Rotationally resolved LIF spectra of $\tilde{A}\ (00v_3') - \tilde{X}\ (000)$ with v_3' = 0–8, and $\tilde{A}\ (013) - \tilde{X}\ (001)$ were observed in the region from 503 to 697 nm for the HSO radical. The fluorescence lifetimes of all the observed bands show nonexponential decays, presumably due

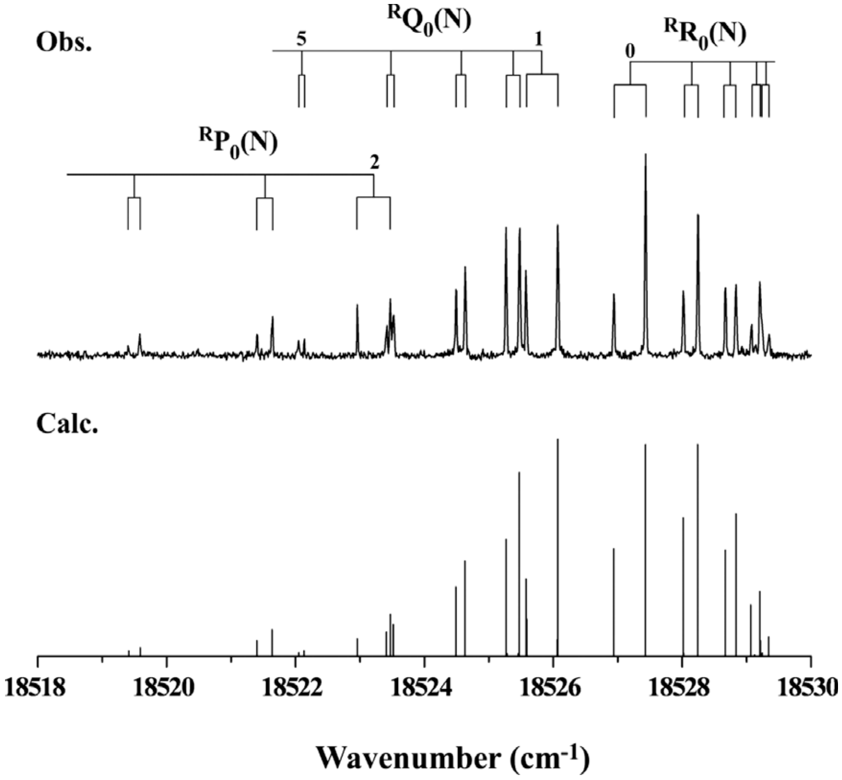

Fig. 1. Rotationally resolved LIF spectrum of $\tilde{A}\ (006) - \tilde{X}\ (000)$ for the HSO radical. The observed spectrum shows doublet structures due to the spin–rotation interaction. Sticks illustrate the line positions for the calculated ones assuming the rotational temperature of 6 K.