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Laser Excitation Spectrum of the $\tilde{A}^2A'(004) \leftarrow \tilde{X}^2A''(000)$ Band of HSO Radical

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The dye laser excitation spectrum of the $\tilde{A}^2A'(004) \leftarrow \tilde{X}^2A''(000)$ vibronic band of HSO was observed and analyzed in the frequency range from 17132 to 17182 cm^{-1}. 414 spectral lines were assigned to an ordinary c-type transition and 21 lines to an axis-switching transition. The rotational constants of HSO in the $\tilde{A}^2A'(004)$ state were used to calculate the inertia defect of 0.518 u Å^2 for this state. A relatively large dependence of the centrifugal distortion constant on the vibrational quantum number was also found.

The HSO radical is expected to play an important role in various oxidations, for example, that of hydrogen sulfide. Recently, spectroscopic studies on this radical have been made by several workers[1–4] and the existence of this radical in gas phase has been established.

Schurath *et al.*[1] observed the chemical luminescence spectrum of $\tilde{A}^2A' \leftarrow \tilde{X}^2A''$ band of HSO and DSO, and deduced some vibrational frequencies: $\nu_3'(\mathrm{HSO})=702$, $\nu_3''(\mathrm{HSO})=1013$, $\nu_3'(\mathrm{DSO})=702$, $\nu_3''(\mathrm{DSO})=1030$ cm^{-1} for the SO bond stretching, and $\nu_2'(\mathrm{DSO})=600$ and $\nu_2''(\mathrm{DSO})=770$ cm^{-1} for the bending vibration.

Kakimoto *et al.*[2] observed the laser excitation spectrum of the $\tilde{A}^2A'(003) \leftarrow \tilde{X}^2A''(000)$ vibronic transition of HSO and determined the rotational constants and centrifugal distortion constants precisely.

Ohashi *et al.*[3] determined the structural parameters of HSO in the ground and the excited states by combining the rotational constants of HSO and DSO; they also estimated an approximate force field. For the $\tilde{X}^2A''$ ground state, they determined a simple valence force field by using the observed centrifugal distortion constants of HSO. The force field reproduced fairly well the fundamental frequencies obtained by Schurath *et al.*, the centrifugal distortion constants, and the inertia defects of HSO and DSO. For the $\tilde{A}^2A'$ excited state, however, they could not obtain a satisfactory force field by applying the same procedure as they had used for the ground state. The centrifugal distortion constants may depend strongly on the vibrational quantum numbers in this case. The failure in determining the force field for the excited state is considered to originate from the v-dependence of the centrifugal distortion constants.

In the present study, $\tilde{A}^2A'(004) \leftarrow \tilde{X}^2A''(000)$ band of HSO was observed and analyzed with the intention of obtaining further information on the centrifugal distortion constants and the inertia defects.

Experimental

The experimental setup for recording the laser excitation spectrum was similar to that used by Kakimoto *et al.*,[2] except that the dye laser was a ring laser (Spectra Physics, Model 380A) and the frequency scanning was in 200 MHz mode-hopping. The present measuring system for the excitation spectrum of unstable molecules has been fully described elsewhere.[5]

The wavenumber determination of spectral lines was made by using iodine lines as standard. The precision was about 0.02 cm^{-1}, which was about ten times worse than that obtained by Kakimoto *et al.*[2] because of the mode-hopping.

The generation of the HSO radical was made in the following reaction system:

$$\mathrm{C_2H_5SH + O_2}\ \text{(MW discharge)},$$

where partial pressures measured with a Pirani gauge were 30 mTorr (1 Torr = 133.322 Pa) for C_2H_5SH and 100 mTorr for O_2. The laser output power was about 100 mW.

Results and Discussion

The excitation spectrum of the HSO radical was recorded in the spectral range of 17132 to 17182 cm^{-1}. The spectrum observed in the present work corresponds to a vibronic band of $\tilde{A}^2A'(004) \leftarrow \tilde{X}^2A''(000)$ and obeys a c-type rotational selection rule. The assignment of the spectral lines could be done easily by using a simulation spectrum calculated from the determined ground state constants[4] and the assumed upper state constants. Most of the observed lines could be assigned; 414 lines were assigned to ordinary c-type transitions. Besides these transitions, 21 lines were assigned to $\Delta K_a=0$ and $+2$ type transitions allowed by axis switching,[6] because the H–S–O angle in the excited state is smaller by about 11° than that in the ground state.

The following Hamiltonian was used in the least squares analysis:

$$H = H_{\mathrm{rot}} + H_{\mathrm{cd}} + H_{\mathrm{sr}}, \tag{1}$$

$$H_{\mathrm{rot}} = AN_a^2 + BN_b^2 + CN_c^2, \tag{2}$$

$$\begin{aligned} H_{\mathrm{cd}} = {} & -\Delta_N N^4 - \Delta_{NK} N^2 N_a^2 - \Delta_K N_a^4 \\ & - 2\delta_N N^2 (N_b^2 - N_c^2) \\ & - \delta_K [(N_b^2 - N_c^2) N_a^2 + N_a^2 (N_b^2 - N_c^2)], \end{aligned} \tag{3}$$

$$H_{\mathrm{sr}} = \varepsilon_{aa} N_a S_a + \varepsilon_{bb} N_b S_b + \varepsilon_{cc} N_c S_c, \tag{4}$$

for both the upper and lower states. In the above analysis, the ground state constants were fixed to the values determined by Endo *et al.*[4] in the microwave measurements.

In Table 1, the obtained molecular constants for $\tilde{A}^2A'(004)$ of HSO are given. The rms deviation between the observed and calculated wavenumbers is

TABLE 1. MOLECULAR CONSTANTS OF HSO (MHz)

Constants	$\tilde{A}^2A'(004)$	$\tilde{A}^2A'(003)$[a]
A	293446(78)	291862(16)
B	16834.7(54)	16934.7(17)
C	15666.0(60)	15802.1(17)
Δ_N	0.0585(51)	0.0483(22)
Δ_{NK}	3.80(29)	3.318(38)
Δ_K	56.7(87)	39.9(18)
δ_N	0.0003(72)	0.00506(58)
δ_K	8.0(25)	4.01(41)
ε_{aa}	16578(869)	17854(165)
ε_{bb}	129(36)	87(32)
ε_{cc}	−345(36)	−352(32)
ν_0/cm^{-1}	17168.2116(44)	16483.0252(13)

a) Ref. 2.

Values in parentheses are 2.5 times the standard deviation and apply to the last digits.

0.015 cm^{-1}. In Fig. 1, the observed spectrum is compared with the simulated one, which was calculated from the obtained constants. In the present calculation of the simulated spectrum, the axis-switching effect was not taken into account, because the axis-switching angle is very small($\theta_T=1.65°$). The good agreement between the observed and simulated spectra indicates that (1) the observed band is free from any perturbation and (2) the spectral lines attributable to other bands of HSO or to other species than HSO do not exist in the observed spectral region (17132 to 17182 cm^{-1}).

The inertia defect for the $\tilde{A}^2A'(004)$ state was obtained to be 0.518 u Å^2 from the determined rotational constants. The value for the $\tilde{A}^2A'(000)$ state was deduced to 0.074 u Å^2 by extrapolation from 0.407 u Å^2 for the (003) state[2)] and 0.518 u Å^2 for the (004) state.

Using the force constants given in Table 5 of Ref. (3), values of the inertia defect for the $\tilde{A}^2A'(000)$, $\tilde{A}^2A'(003)$, and $\tilde{A}^2A'(004)$ states of HSO were calculated to be 0.088, 0.192, and 0.226 u Å, respectively. Thus, the calculated value of the (000) state agreed well with the extrapolated value, but the agreement between the calculated and observed values was poor for the (003) and (004) states.

Improvement of the force field was tried by adding the present value of inertia defect to the reported data.

(1). A valence force field was determined by using inertia defects for the (003) and (004) states of HSO and for the (003) state of DSO, and ν_3(HSO), ν_2(DSO), and ν_3(DSO). The obtained force constants, and the frequencies and inertia defects reproduced by these force constants, are summarized in column (1) of Table 2. As seen from the table, the agreement between observed and calculated values is good for vibrational frequencies of HSO and DSO, but the calculated values of inertia defects were too small, compared with the observed values. The contribution of the frequencies to the determination of the force field was thus dominant and that of the inertia defect was small. Indeed, the force field could not be determined by using data of inertia defects only.

TABLE 2. FORCE CONSTANTS, VIBRATIONAL FREQUENCIES, AND INERTIA DEFECTS FOR $\tilde{A}^2A'$ STATE

		Calculated values		Observed values
		(1)	(2)	
	F_{11}[a)]/mdyn Å^{-1}	4.36700	4.36700	
	F_{22}/mdyn Å^{-1}	0.30437	0.25117	
	F_{33}/mdyn Å^{-1}	2.98064	3.31768	
HSO	ν_1/cm^{-1}	2754	2754	[2769][b)]
	ν_2/cm^{-1}	842	781	[828][b)]
	ν_3/cm^{-1}	679	702	702(5)[b)]
	Δ(003)/u Å	0.203	0.410	0.407(5)[c)]
	Δ(004)/u Å	0.241	0.514	0.518(17)[d)]
DSO	ν_1/cm^{-1}	1978	1978	[1978][b)]
	ν_2/cm^{-1}	594	548	600(10)[b)]
	ν_3/cm^{-1}	707	735	702(10)[b)]
	Δ(003)/u Å	0.131	0.131	0.388(7)[e)]

a) Fixed. b) Ref. 1. c) Ref. 2. d) Present work. e) Ref. 3.

Values in brackets are estimated ones.

(2). A force field was determined by using ν_3 (HSO) and Δ(003) and Δ(004) of HSO. These force constants are listed in column (2) of Table 2, together with other constants deduced from this field. In this case, close agreement between the calculated and observed values of inertia defect for HSO was obtained, but the calculated value of the inertia defect for DSO is still smaller than the observed value.

The force field, determined by data of HSO only, reproduced fairly well all the constants except Δ(003) for DSO (see column (2) in Table 2). The discrepancy of Δ(003) for DSO is considered to originate from non-diagonal components of the force field, but these can not be obtained because of lack of data. There may be some other perturbations which have an effect to this constant, but it is difficult to make these problems clear until the measurements on the (012) and (021) states are carried out.

For the centrifugal distortion constants, the obtained value in the (004) state clearly differs from that in the (003) state, in spite of the wide experimental errors (Table 1). Therefore, it can be said that the centrifugal distortion constant depends on the vibrational quantum number. This v-dependence is surely the main reason why the reasonable force field for the $\tilde{A}^2A'$ state could not be obtained from the centrifugal distortion constants. Essentially, the force field for the $\tilde{A}^2A'$ state must be determined from the centrifugal distortion constants for the vibration-free (000) state, which can be obtained by extrapolation of values of the (004) and (003) states. But the precision of obtained distortion constants is not high enough to allow us to extrapolate. The centrifugal distortion constants for the (000) state were calculated by using the force field of column (2) in Table 2, the values are $\Delta_N=0.0369$, $\Delta_{NK}=1.064$, $\Delta_K=16.592$, $\delta_N=0.00256$,

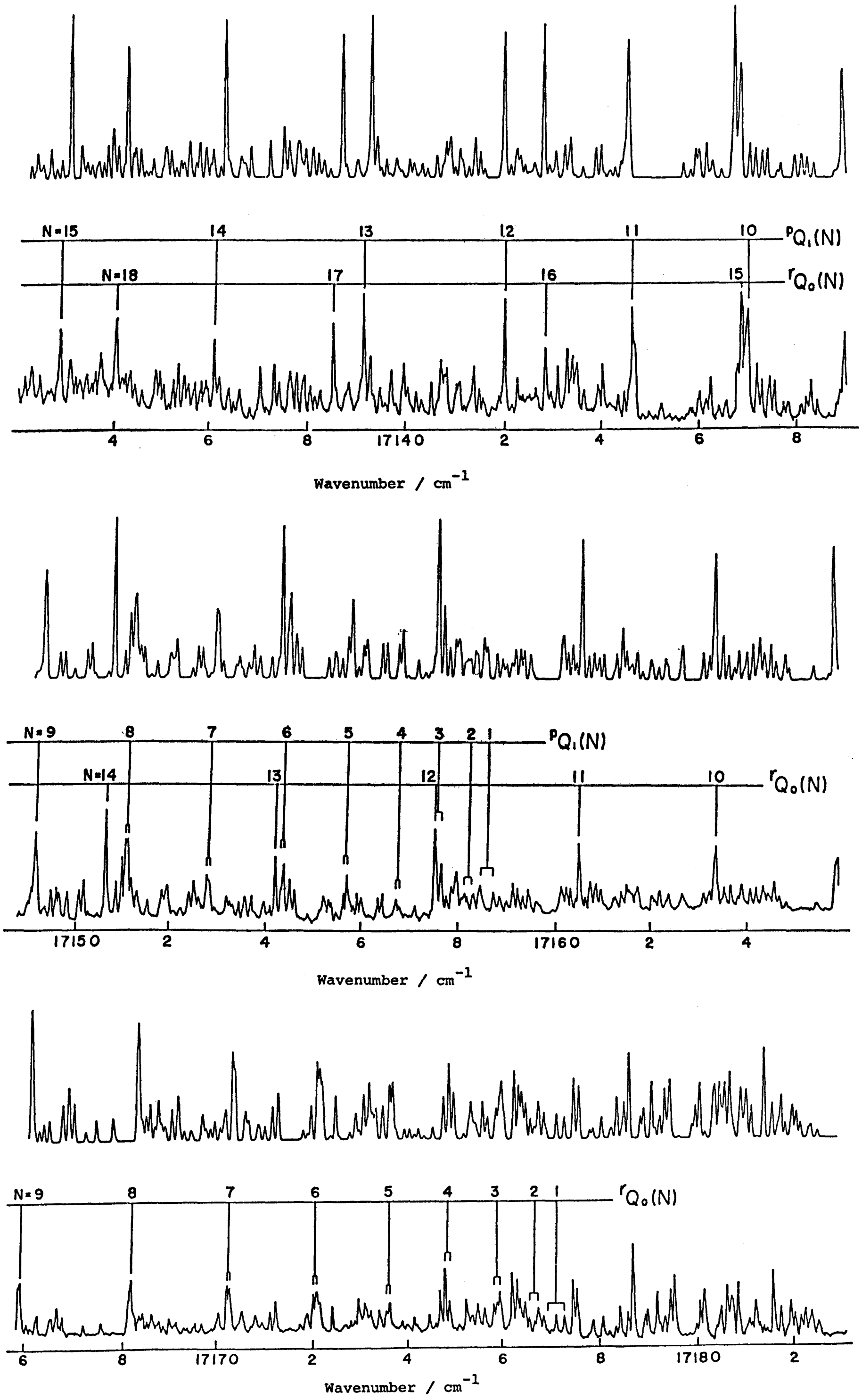

Fig. 1. Observed (bottom) and simulated (top) spectrum of the HSO $\tilde{A}^2A'(004)$ $\tilde{X}^2A''(000)$ band.

and δ_K=0.660 MHz.

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