

FIG. 2. Schematic diagram of the occupation of the sites by hydrogen atoms in $\text{VH}_{0.77}$. s is the number of sites and X is the number of hydrogen atoms, which are normalized by the number of vanadium atoms. p is a occupation probability. The regions of slanting lines indicate the sites occupied by hydrogen atoms.

the O_{z1} site move gradually to the O_{z2} site with the increase of temperature without any abrupt change. This is probably because $\text{VH}_{0.59}$ has many vacant O_z sites.²

Component III is a component of small concentration and has longer T_2 values than the other two components, and this suggests that component III diffuses faster than the other two. Component III can be assumed to occupy the tetrahedral interstices in the metal atom lattice (T site), considering the fast diffusion of the hydrogen atoms on the T site in the α phase. Component III cannot be detected in $\text{VH}_{0.59}$, probably because the concentration is too small. Thus, the occupation probability

of the T site increases with the total concentration of hydrogen in the bct phase.

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Observation of the $\nu=3 \leftarrow 0$ band of $\text{SO}(X^3\Sigma^-)$ with a difference frequency laser

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The observation of the vibrational overtone bands of free radicals in absorption is generally difficult because of small transition dipole moments and low concentrations. In this letter, we report the detection of the $\nu=3 \leftarrow 0$ transitions of SO in the ground electronic state ($X^3\Sigma^-$) around $3 \mu\text{m}$ with a difference frequency laser spectrometer.¹⁻⁴

The SO radical was produced in an absorption cell by the reaction of a discharge product of oxygen with sulphur. The discharge current was about 10 mA and the O_2 pressure was about 100 Pa. The transition wave numbers were calibrated with NH_3 reference lines⁵ and the estimated absolute accuracy of our measurements was $\pm 0.002 \text{ cm}^{-1}$.

Figure 1 is an example of the absorption lines. Table I lists the observed transition wave numbers and their

assignments for the $\nu=3 \leftarrow 0$ band of ^{32}SO . The effective vibration-rotation Hamiltonian given in Ref. 6 was used in the least-squares fit of the data in Table I with $\nu=0$ state parameters held fixed at values of Ref. 7. The molecular constants for the $\nu=3$ state derived from our analysis are given in Table II along with the corresponding values of the $\nu=0^7$ and $\nu=1^8$ states. The standard deviation of the fit was 0.0007 cm^{-1} .

The parameters of Table II allow the equilibrium molecular constants of Table III to be extracted. Improved values were obtained for ω_e , $\omega_e x_e$, \tilde{B}_e , and α_e^B . New determinations were made for $\omega_e y_e$ and γ_e^B . The vibrational dependence of λ and γ agree with the more accurate values reported by Davies *et al.*⁹ and Tiemann.¹⁰ The constants λ_D and α_e^A were used to derive the internuclear distance dependence of

TABLE I. Observed wave numbers (in cm^{-1}) of the transition of the $v=3 \leftarrow 0$ band of $\text{SO}(X^3\Sigma^-)$.

J'	N'	J''	N''	Obs.	O-C ^a	J'	N'	J''	N''	Obs.	O-C ^a
5	4	6	5	3368.1887	-1	4	3	3	2	3380.2597	-3
3	4	4	5	3368.8437	-3	3	4	2	3	3381.0236	-5
4	3	5	4	3369.6928	-5	5	4	4	3	3381.4823	-9
2	3	3	4	3370.5695	-8	4	5	3	4	3382.4152	19
3	2	4	3	3371.1316	9	6	5	5	4	3382.7010	5
1	2	2	3	3372.3420	1	5	6	4	5	3383.7185	0
2	1	3	2	3372.4813	-3	7	6	6	5	3383.9003	2
1	1	2	2	3373.1431	0	6	6	5	5	3383.9427	-10
1	0	2	1	3373.7187	0	6	7	5	6	3384.9607	0
2	1	1	0	3377.8940	10	8	7	7	6	3385.0752	-2
2	2	1	1	3378.8191	10	7	7	6	6	3385.1393	3
3	2	2	1	3379.0513	-9	7	8	6	7	3386.1512	-5
2	3	1	2	3379.5179	6	9	8	8	7	3386.2230	5
3	3	2	2	3380.1505	-6	8	8	7	7	3386.2999	0

^aObserved minus calculated wave number in units of 10^{-4}cm^{-1} .

$$\lambda = 157794.0(42) + 1.946(18) \times 10^5 \xi$$

$$- 1.816(184) \times 10^5 \xi^2 \text{ MHz},$$

where $\xi = (r - r_e)/r_e$. This function, along with the corresponding one for O_2 ,¹¹ has been plotted in Fig. 2. The internuclear variation of λ provides an excellent test for *ab initio* calculations of molecular parameters.¹²

Since the detection of H_3^+ by Oka² using difference frequency laser spectroscopy, the technique has been successfully applied to study the fundamental bands of other ions (HeH^+ ,³ NeH^{13}), and free radicals (NH_2 ,⁴ NH ,⁶ CH_3 ,¹⁴ SH^{15}). The observation of the $v=3 \leftarrow 0$ transition of SO illustrates the utility of the technique for the detection of unstable molecules that have no fundamental bands in the 2400–4400 cm^{-1} tuning range

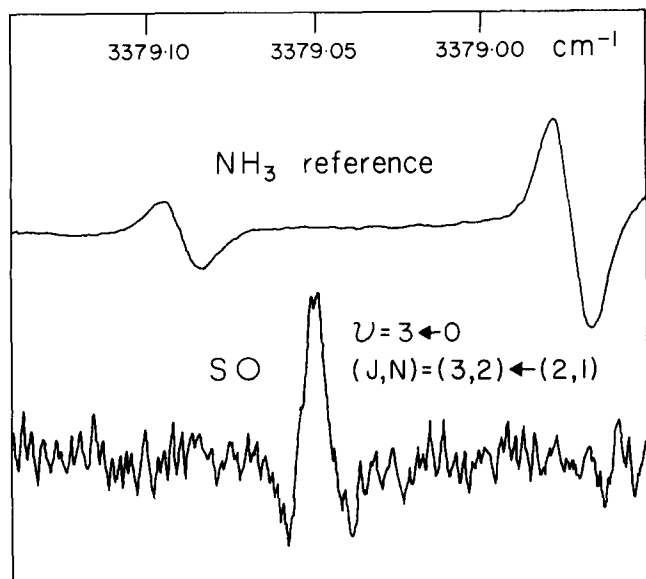


FIG. 1. The $(J, N) = (3, 2) \leftarrow (2, 1)$ transition of the $v=3 \leftarrow 0$ band of $\text{SO}(X^3\Sigma^-)$ at 3379.0513cm^{-1} obtained with Zeeman modulation. The reference lines of NH_3 were taken simultaneously with frequency modulation. The time constants were 400 ms. The effective path length was about 16 m.

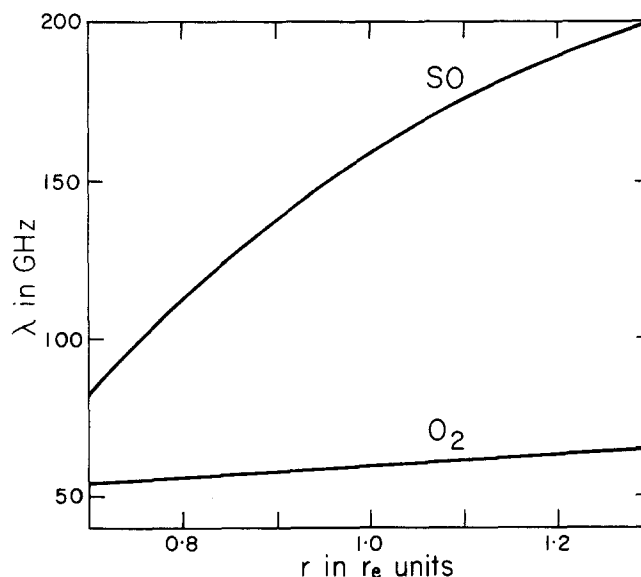


FIG. 2. The internuclear distance dependence of the "spin-spin" coupling constants of SO and O_2 .

TABLE II. Molecular constants of $\text{SO}(X^3\Sigma^-)$.^a

	$v=1 \leftarrow 0^b$	$v=2 \leftarrow 1^b$	$v=3 \leftarrow 0$
ν_0	1338.0089(4)	1125.3085(28)	3375.9852(7)
\tilde{E}_v	21523.5606(61)	21351.534(59)	21009.81(53)
λ_v	158254.388(35)	159190.9(40)	161127(20)
γ_v	-168.342(13)	-169.88(38)	-172.5(39)
D_v	0.033986(81)	0.033914(75)	0.03375 ^d
λ_D	0.1527(14)	0.151(16)	0.1465 ^d

^aAll units MHz except for ν_0 which is in cm^{-1} . Uncertainties are three times the standard deviation.

^bFrom Ref. 8.

^cFrom Ref. 7. Fixed in our fit of the $v=3 \leftarrow 0$ band.

^dFixed to values obtained by linear extrapolation of $v=0$ and 1 parameters.

TABLE III. Equilibrium molecular constants of $\text{SO}(X^3\Sigma^-)$.^a

ω_e	1150.766 (11)	$\omega_e x_e$	6.3950 (75)	$\omega_e y_e$	0.0100 (14)
\tilde{B}_e	21 609.865 (85)	α_e^B	172.80 (21)	γ_e^B	0.390 (93)
λ_e	157 794.0 (42)	α_e^λ	-915 (10)	γ_e^λ	10.5 (39)
γ_e	-167.52 (59)	α_e^γ	1.7 (10)		

^aAll units are MHz except for vibrational constants which are in cm^{-1} . Each parameter $X_v (= B_v, \lambda_v, \text{ or } \gamma_v)$ was represented by a power series expansion $X_v = X_e - \alpha_e^X (v + \frac{1}{2}) + \gamma_e^X (v + \frac{1}{2})^2$.

of the apparatus.

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Frequency distribution function for benzene

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There is considerable interest in the use of organic materials particularly benzene as neutron moderators. To theoretically study neutron scattering from any material, it is essential to have a good model for the frequency distribution function (FDF) $g(\xi)$, ($\xi = \hbar\omega/k_B$ is the phonon energy measured in Kelvin, \hbar is the Planck's constant divided by 2π , ω is the angular frequency, and k_B is the Boltzmann constant). Recently Malik and Kothari suggested a method for obtaining the FDF directly from the observed temperature variation of the specific heat at constant volume.^{1,2} This method is based on the so-called "unfolding technique" developed in Reactor Physics.³⁻⁶

If $C_v(T)$ is the (measured) specific heat of a substance (per mole) at temperature T , then the integral equation to be solved for the FDF is⁷

$$C_v(T) = \frac{3N_0 k_B}{T^2} \int_0^{\theta_D} \frac{\xi^2 \exp(\xi/T)}{[\exp(\xi/T) - 1]^2} g(\xi) d\xi, \quad (1)$$

where N_0 is the Avogadro's number and θ_D is the Debye temperature. Here $g(\xi)$ is normalized to unity. Equation (1) may be written as a linear integral equation of the first kind:

$$Y(t) = \int_a^b K(t, s) X(s) ds \quad (a \leq t \leq b), \quad (2)$$

where $K(t, s)$ is the kernel and is assumed to be well behaved in the domain of integration. $Y(t)$ is a known function. This equation can be solved by an iterative

procedure. For details see Ref. 2.

Using the observed values of $C_v(T)$ for benzene^{8,9} in the temperature range 0–210 K, we have calculated the

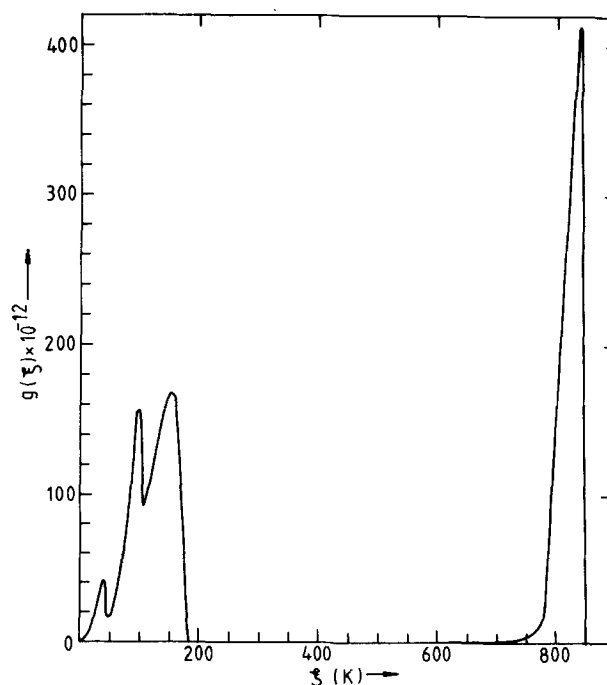


FIG. 1. Calculated frequency distribution function of benzene.