Vibrational Dependence in the Molecular G- and Susceptibility-Tensors of Sulfur Dioxide

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The high field rotational Zeeman effect of SO_2 molecules in the first excited state of the bending vibration has been studied under high resolution. Within the experimental uncertainties no v-dependence is observed for the magnetic susceptibility anisotropies, and the observed v-dependence in the g-tensor elements appears to be essentially caused by the v-dependence of the rotational constants. If this finding may be generalized to all small amplitude vibrations, prospects for sign of the electric dipole moment determinations from rotational Zeeman effect studies of different isotopic species are brighter than expected hitherto.

Introduction

Sulfur dioxide was one of the first molecules whose pure rotational spectrum was studied by microwave spectroscopy [1] and with 148 citations [summer 1983] in the microwave bibliography compiled by Barbara Starck [2] it is one of the most thoroughly studied molecules. Since it is a comparatively heavy triatomic asymmetric top with several low J rotational transitions in the easily accessible frequency range between 7 and 40 GHz, it is also ideally suited to study the effect of small amplitude vibrations on the molecular parameters.

In the following we present the results of a rotational Zeeman effect investigation of sulfur dioxide in the first excited state of its bending mode ($\bar{\nu}_2 = 526\ \text{cm}^{-1}$).

Measurements and analysis of the data

The microwave spectrograph and high field electromagnet used in this work have been described before [3, 4]. The microwave spectrum of vibrationally excited SO_2 has been assigned and thoroughly analyzed by Morino and coworkers [5, 6]. We used the $2_{02} \rightarrow 1_{11}$ transition at 13457.352 MHz and the $3_{13} \rightarrow 4_{04}$ transition at 28138.393 MHz to study the rotational Zeeman effect under the selection rules $\Delta M = 0$ and $M = \pm 1$. The magnetic fields were close to 19 kGauss. Signal averaging was used to increase the S/N ratio. Typical linewidths were 120 to 150 kHz full width at half height with S/N ratios of 50 and better. In Table 1 we present the observed splittings.

For the analysis of the data the standard effective energy expression resulting from a first order perturbation treatment within the appropriate asymmetric top basis was used (see Eqs. III.11 and III.12 in ref. [4] or Eq. (28) in [7]). The terms included in our analysis are

$$\begin{aligned} &\langle J, K_- K_+, M | \hat{\mathscr{H}}_{\text{Zeeman}} | J, K_- K_+, M \rangle \\ &= -\mu_n H_z \cdot \frac{M}{J(J+1)} \sum_\gamma g_{\gamma\gamma} \langle | \hat{J}_\gamma^2 | \rangle - \tfrac{1}{2} \chi H_z^2 \\ &\quad - \frac{3M^2 - J(J+1)}{J(J+1)(2J-1)(2J+3)} \\ &\quad \cdot \sum_\gamma (\chi_{\gamma\gamma} - \chi) \langle | \hat{J}_\gamma^2 | \rangle , \end{aligned} \qquad (1)$$

$\mu_n = e\hbar/2m_p c$ = nuclear magneton; H_z = exterior magnetic field;
J = quantum number for the angular momentum of the molecular overall rotation;
M = quantum number for the angular momentum component in direction of the magnetic field;
$g_{\gamma\gamma}$ = diagonal elements of the molecular g-tensor ($\gamma = a, b, c$);
$\chi_{\gamma\gamma}$ = diagonal elements of the molecular magnetic susceptibility tensor ($\gamma = a, b, c$);
$\hat{J}_\gamma$ = operator corresponding to the angular momentum component in direction of the molecule fixed γ-axis measured in units of $\hbar$;
$\chi = (\chi_{aa} + \chi_{bb} + \chi_{cc})/3$ = "bulk susceptibility".

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Table 1. Observed and calculated shifts of the Zeeman satellites with respect to the zero field transition frequency. M_u and M_l designate the M-states for the upper and lower level, respectively. The frequencies are in Megahertz. Calculated shifts result from Eq. (1) and the optimized g-values and susceptibility anisotropies listed in Table 3.

Rotational transition zero field frequency magnetic field	M_l	M_u	Relative intensity	$\Delta \nu_{obs}$ [kHz]	$\Delta \nu_{calc}$ [kHz]	$\Delta \nu_{obs} - \Delta \nu_{calc}$ [kHz]
$2_{02} \rightarrow 1_{11}$ 13457.352 MHz 18875 Gauss	−1	−1	0.300	−3553	−3564.5	11.5
	0	0	0.400	6	1.2	4.8
	1	1	0.300	3605	3611.1	−6.1
$2_{02} \rightarrow 1_{11}$ 13457.352 kHz 19743 Gauss	−2	−1	0.300	−2220	−2220.1	0.1
	−1	0	0.150	1532	1534.6	−2.6
	0	1	0.050	5352	5337.9	14.1
	0	−1	0.050	−5265	−5260.7	−4.3
	1	0	0.150	−1551	−1558.3	7.3
	2	1	0.300	2191	2192.7	−1.7
$3_{13} \rightarrow 4_{04}$ 28138.393 MHz 18875 Gauss	−3	−3	0.083	1528	1522.7	5.3
	−2	−2	0.143	1041	1035.0	6.0
	−1	−1	0.179	532	533.5	−1.5
	0	0	0.190	22	18.1	3.9
	1	1	0.179	−504	−511.3	7.3
	2	2	0.143	−1047	−1054.5	7.5
	3	3	0.083	−1606	−1611.6	5.6
$3_{13} \rightarrow 4_{04}$ 28138.393 MHz 18875 Gauss	−3	−2	0.006	2976	2975.4	0.6
	−2	−1	0.018	2501	2495.0	6.0
	−1	0	0.036	1999	2000.7	−1.7
	0	1	0.060	1498	1492.6	5.4
	1	2	0.089	969	970.6	−1.6
	2	3	0.125	435	434.6	0.4
	3	4	0.167	−118	−115.2	−2.8
	−3	−4	0.167	77	77.3	−0.3
	−2	−3	0.125	−415	−417.6	2.6
	−1	−2	0.089	−922	−926.5	4.5
	0	1	0.060	−1450	−1449.2	−0.8
	1	0	0.036	−1980	−1985.8	5.8

Table 2. Expectation values from the squared angular momentum components calculated from the rotational constants given in [5] (see Table 3). Values are in units of $\hbar^2$ and are rounded after the fifth decimal.

$J K_- K_+$	$\langle\vert\hat{J}_a^2\vert\rangle$	$\langle\vert\hat{J}_b^2\vert\rangle$	$\langle\vert\hat{J}_c^2\vert\rangle$
1 1 1	1.00000	0.00000	1.00000
2 0 2	0.00064	2.95572	3.04364
3 1 3	1.00039	2.47277	8.52684
4 0 4	0.00960	9.33860	10.65180

The expectation values for the squared angular momentum components which enter into Eq. (1) were calculated from the rotational constants (see Table 3) as described in [8]. Those which are of relevance here are given in Table 2. In Table 3 we present the g-values and magnetic susceptibility anisotropies which result from a least squares fit to the Zeeman splittings listed in Table 1. Also given in Table 3 are the corresponding ground state values obtained by Pochan, Stone and Flygare [9] and Ellenbroek and Dymanus [10] respectively.

Discussion

As a basis for the subsequent discussion we recall the theoretical rigid rotor expression for the g-tensor elements (see Chapt. IV in [4] for a detailed derivation):

$$g_{aa} = \frac{m_p}{I_{aa}} \left[\sum_{n}^{\text{nuclei}} Z_n (b_n^2 + c_n^2) + \frac{2}{m} \sum_{v}^{\text{ex. el. states}} \frac{|\langle v | \hat{L}_a | 0 \rangle|^2}{E_0 - E_v} \right], \tag{2}$$

m_p = proton mass; m = electron mass;

I_{aa} = moment of inertia about the principal inertia a-axis;

Z_n = atomic number of n-th nucleus;

b_n, c_n = b- and c-coordinates of n-th nucleus with respect to the principal inertia axes system;

Table 3. Observed g-values and magnetic susceptibility anisotropies of SO_2 in the ground state [9, 10] an in the first excited state of the ν_2-bending mode ($\bar{\nu}_2 = 526$ cm^{-1}). The susceptibility anisotropies are given in units of 10^{-6} erg G^{-2} mol^{-1}. Also given are the corresponding effective rotational constants from the work of Morino et al. [5]. In the last column at right we have listed extrapolated g-values, which are calculated as the ground state values weighted with the quotient of the corresponding rotational constants. They result from Eq. (2) under the assumption that the expression within the brackets is vibrationally independent i.e. that the effect of vibrational changes in the positive charge distribution is counterbalanced by the corresponding changes in the negative charge distribution.

	Ground state from [9]	 from [10]	Excited state $v_2 = 1$	Extrapolated g-values
g_{aa}	−0.6037(5)	−0.6043(3)	−0.61540(44)	−0.6160(3)
g_{bb}	−0.1161(2)	−0.11634(12)	−0.11697(18)	−0.1164(1)
g_{cc}	−0.0882(4)	−0.08865(10)	−0.08884(18)	−0.0885(1)
$2\chi_{aa} - \chi_{bb} - \chi_{cc}$	6.4(5)	5.58(12)	5.43(37)	
$2\chi_{bb} - \chi_{cc} - \chi_{aa}$	3.1(3)	3.60(9)	3.82(32)	
A/MHz	60778.79		61954.69	
B/MHz	10318.10		10320.28	
C/MHz	8799.96		8783.96	

E_0, E_ν = Eigenvalues of the electronic fixed center Schrödinger equation;
$\hat{L}_a$ = operator corresponding to the a-component of the electronic angular momentum.

The perturbation sum runs over the excited electronic states.

From (2) g_{aa} is proportional to the rotational constant $A = h/8\pi^2 I_{aa}$). The faster the molecule rotates at given angular momentum, the larger is the corresponding g-value. Therefore, observing that the g-values in Table 3 behave similar as the rotational constants, it is tempting to assume that their vibrational dependence is largely given by the vibrational dependence in the rotational constant i.e. that the vibrational corrections to the nuclear and electronic contributions in the bracket will almost cancel.

We therefore multiply the ground state g-values with weight factors $A_{0,1,0}/A_{0,0,0}$ etc., and indeed we find that the g-values observed for the $v_2 = 1$ state may be reproduced that way within the experimental uncertainties. This was not the case in formaldehyde where a fairly strong Coriolis coupling between the ν_5 and ν_6-states causes an "anomalous" vibrational dependence in the g-values and the rotational constants [11, 12]. If the observation made here for SO_2 could be generalized to all small amplitude vibrations, sign of the electric dipole moment determinations from experimental g-values of different isotopic species should be possible without the necessity to study also the vibrational dependence. The quotients $g_{aa,0}/A_0$ etc. which are used in such dipole moment determinations should then come sufficiently close to the quotients of the corresponding equilibrium values.

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