

ELECTRIC AND MAGNETIC PROPERTIES OF OCS IN THE (01¹0) VIBRATIONAL STATE MEASURED BY MOLECULAR-BEAM ELECTRIC-RESONANCE SPECTROSCOPY

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The $\Delta J = 0$, l -doublet transitions in the first excited state of the bending vibration of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ have been investigated using the molecular-beam electric-resonance method. The l -doubling constant up to second order in $J(J+1)$ has been derived. The electric and magnetic properties obtained are the electric dipole moment and the magnetic constants g_{\perp} , $g_{\parallel} - g_{\perp}$, $g_{xx} - g_{yy}$, $\chi_{\perp} - \chi_{\parallel}$, and $\chi_{xx} - \chi_{yy}$.

1. Introduction

Measurements on $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ in the (01¹0) vibrational state have recently been performed by Maki [1] and by Hüttner and Morgenstern [2]. The latter authors determined the components g_{\perp} and g_{\parallel} of the magnetic moment tensor \mathbf{G} , and the anisotropy $\chi_{\parallel} - \chi_{\perp}$ of the magnetic susceptibility tensor χ , where the subscript (\parallel) and (\perp) refers to the component along and perpendicular to the molecular axis, respectively. The measurements of Maki [1] resulted in the determination of the l -doubling constant up to first order in $J(J+1)$. The present investigation was undertaken to improve accuracy of previous measurements and to determine some properties of the molecule which were either very poorly known or completely unknown. Among them is the electric dipole moment and the anisotropies ($g_{xx} - g_{yy}$, $\chi_{xx} - \chi_{yy}$) of the tensors \mathbf{G} and χ in the plane perpendicular to the molecular axis. We have used the molecular-beam electric-resonance (MBER) method which turned out to be ideally suited for investigation of phenomena associated with l -doubling in heavier triatomic molecules in spite of the rather unfavourable focusing properties of states with a first-order Stark effect. This comes from the high resolving power and sensitivity of the apparatus and possibility of selection of a large range of J -states whose l -doubling transitions cover a rather large and easily accessible frequency region. The MBER apparatus is described in full detail elsewhere [3, 4].

2. Theory

The hamiltonian used for the interpretation of the experimental results is

$$H = H_v + H_r + H_{rv} - \mu_{el} \cdot E - \frac{1}{2} E \cdot \alpha \cdot E - B \cdot G \cdot J - \frac{1}{2} B \cdot \chi \cdot B - \mu_{el} \cdot (v \times B). \quad (1)$$

In this expression H_v , H_r , and H_{rv} stand for the vibrational, the rotational and the rotation-vibration interaction part, respectively, of the hamiltonian. The terms four through seven describe the contribution to the molecular energy due to Stark effect, molecular polarizability, rotational Zeeman effect, and magnetic susceptibility, respectively. The last term is the Stark effect due to the transverse electric field generated by the translation of the

molecules in the external magnetic field. This term had to be included in the hamiltonian in order to explain the Zeeman spectra. The quantities of which the electric and magnetic contributions in eq. (1) are constructed, are indicated by generally accepted symbols; μ_{el} is the electric dipole moment, α is the electric polarizability tensor; v is the velocity of the molecule in the beam; E and B is the applied electric and magnetic field, respectively; J is the total angular momentum vector.

As wavefunctions for the calculation of the matrix elements of H we used eigenfunctions of $H_0 = H_r + H_v + H_{rv}$

$$|v_2 J l M \pm\rangle = 2^{-1/2} [|v_2 J l M\rangle \pm |v_2 J - l M\rangle], \quad (2)$$

where v_2 is the quantum number of the bending vibration, l represents the quantum number of the component of the angular momentum about the molecular axis, and M the magnetic quantum number. The quantum number l can take the values $-v_2, -v_2 + 2, \dots + v_2$; in the present case $l = -1$ or $+1$. $|v_2 J l M\rangle$ and $|v_2 J - l M\rangle$ are the well-known symmetric-top eigenfunctions [7].

The matrix elements of H_{rv} in the case $|l| = 1$ are known [5] to be

$$\langle v_2 J l M \pm | H_{rv} | v_2 J l M \pm \rangle = \pm \frac{1}{4} q_l (v_2 + 1) J(J+1), \quad (3)$$

where q_l is the l -doubling constant. The energies and transition frequencies in electric and magnetic fields are calculated using spherical tensor operator techniques.

The only nonvanishing matrix elements for the case $E \neq 0, B = 0$ are

$$\langle v_2 J l M \pm | H_{ST1} | v_2 J l M \mp \rangle = [-M/J(J+1)] \mu_{el} E, \quad (4)$$

and

$$\langle v_2 J l M \pm | H_{ST1} | v_2 J \pm 1 l M \pm \rangle = \frac{-\mu_{el} E}{(J+1)} \left[\frac{J(J+2)(J+M+1)(J-M+1)}{(2J+3)(2J+1)} \right]^{1/2}, \quad (5)$$

where l is set equal to 1 and H_{ST1} represents the fourth term of eq. (1). The fifth term, H_{ST2} gives the following small (≈ 100 Hz at $E = 400$ V/cm) contribution to the energy

$$\begin{aligned} \langle v_2 J l M \pm | H_{ST2} | v_2 J l M \pm \rangle \\ = -E^2 \frac{3M^2 - J(J+1)}{2(2J+3)(2J-1)J(J+1)} \{ 2[\frac{1}{5}J(J+1) - 1] (\alpha_{\perp} - \alpha_{\parallel}) \pm \frac{1}{2} \delta_{\parallel 1} J(J+1) (\alpha_{xx} - \alpha_{yy}) \} - \frac{1}{2} E^2 \alpha_{av}. \end{aligned} \quad (6)$$

Herein $\alpha_{\parallel} = \alpha_{zz}$, the component of α along the molecular axis, $\alpha_{\perp} = \frac{1}{2}(\alpha_{xx} + \alpha_{yy})$, and $\alpha_{av} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$. The contribution of matrix elements of H_{ST2} for which $\Delta J = 1, 2$ can be neglected in the present case.

The magnetic contributions to the energy can be expressed by the matrix elements

$$\begin{aligned} \langle v_2 J l M \pm | H_M | v_2 J l M \pm \rangle = -B \frac{M}{J(J+1)} [J(J+1) g_{\perp} + (g_{\parallel} - g_{\perp}) \pm \frac{1}{4} \delta_{\parallel 1} J(J+1) (g_{xx} - g_{yy})] \\ - B^2 \frac{3M^2 - J(J+1)}{2(2J+3)(2J-1)J(J+1)} \{ 2[\frac{1}{3}J(J+1) - 1] (\chi_{\perp} - \chi_{\parallel}) \pm \frac{1}{2} \delta_{\parallel 1} J(J+1) (\chi_{xx} - \chi_{yy}) \} - \frac{1}{2} B^2 \chi_{av}, \end{aligned} \quad (7)$$

and

$$\langle \nu_2 J 1 M + | H_M | \nu_2 J 1 M - 1 \rangle = -\frac{1}{2} \mu_{e1} \nu B [(J+M)(J-M+1)]^{1/2} / J(J+1). \quad (8)$$

In these expressions H_M represents the last three terms of eq. (1). The first- and second-order terms of H_M give the result of eq. (7), the third the result of eq. (8). Higher-order contributions to the energy matrix are neglected here.

Diagonalization of the energy matrices yields energies of the M -sublevels. The frequencies of the electric dipole transitions between these sublevels are obtained from selection rules $\Delta M = 0, \pm 1$.

3. Results and discussion

The $\Delta J = 0, l$ -doublet transition frequencies of $J = 1$ through 12, with no external electric and magnetic fields applied, are given in table 1. From the frequencies ν the q_l values as a function of J are derived from [7]

$$\nu = q_l(J)J(J+1). \quad (9)$$

The $q_l(J)$'s were fit by a least-squares computer program to the expression

$$q_l(J) = q_v + \mu_v J(J+1) + \Delta H J^2(J+1)^2. \quad (10)$$

The resulting constants q_v , μ_v and ΔH are given in table 2. The reported errors for q_v and μ_v represent two standard deviations. In the present case ΔH had a too large uncertainty to be significant, only an upper limit for $|\Delta H|$ can be given. Our values for q_v and μ_v did not change significantly when ΔH was set equal to zero, only the errors became somewhat smaller. From a recalculation of the measurements of Maki [1], it became obvious that the values for q_v and μ_v are not included in the quoted error regions if ΔH is also treated as a variable. As also q_v is not and μ_v is hardly in agreement with our values it is obvious that the errors for q_v and μ_v given by Maki are too small or ΔH had to be included also in his fit.

Stark measurements were performed at electric fields of 50, 100, 200, and 400 V/cm on the $J = 1, 2$, and 3 transitions to check the theory and to investigate if a J -dependence of the electric dipole moment could be measured. For the evaluation of the data we used: $\alpha_0 - \alpha_1 = 4.63(6) \times 10^{-24} \text{ cm}^3$ [6], the rotational constant $A = 6088.75 \text{ MHz}$ [7], and the centrifugal constant $D = 1.31 \text{ kHz}$ [7]. The electric dipole moment of OCS in the $(01^1 0)$ state (μ_1) was measured relative to that of the ground vibrational state (μ_0). The accuracy of this relative $\mu_{e1} (= \mu_1 / \mu_0)$ is fully determined by the short time accuracy of the voltage standard (Fluke 335A) which is better than 1×10^{-5} . The absolute value of μ_{e1} of the $(01^1 0)$ state is calculated using the value of μ_{e1} of the (000) state of ref. [3].

With the present sensitivity of the apparatus no J -dependence of the electric dipole moment could be measured and the most accurate Stark effect measurements were performed at an electric field of 400 V/cm. The resulting μ_{e1} is given in table 2. The error in μ_{e1} is determined mainly by the error in μ_{e1} for the vibrational ground state. The latter error is determined almost completely by the inhomogeneity of the electric field [3].

Zeeman spectra for the $J = 3, 4$, and 5 transitions have been measured at a magnetic field of about 8.5 kG. Each transition in a J -state splits into $2J$, $\Delta M = -1$ and $\Delta M = +1$ transitions, and into $2J + 1$, $\Delta M = 0$ transitions. The $\Delta M = 0$ transitions could not be observed as separate lines at this (maximum available) field. The last term of eq. (1) gives some line broadening because of velocity distribution of the molecules in the beam. This broadening made resolution of the transitions for $J = 1$ and $J = 2$ impossible at 8.5 kG. At lower fields the separations of the $\Delta M = \pm 1$ lines were too small to resolve. The same difficulty was experienced for J -states higher than $J = 5$ at maximum field.

Table 1

Measured and calculated l -doubling frequencies of OCS in the (01¹0) vibrational state for $J = 1$ through 12

J	Obs. freq. (kHz)	Calc. freq. (kHz)	Obs.-calc. (kHz)	Exp. error (kHz)
1	12 722.88	12 722.81	0.07	0.10
2	38 168.36	38 168.32	0.04	0.10
3	76 336.32	76 336.34	-0.02	0.10
4	127 226.48	127 226.55	-0.07	0.10
5	190 838.50	190 838.54	-0.04	0.10
6	267 171.86	267 171.80	0.06	0.10
7	356 225.85	356 225.71	0.14	1.00
8	457 999.60	457 999.57	0.03	0.10
9	572 492.46	572 492.55	-0.09	0.20
10	699 703.55	699 703.73	-0.18	0.20
11	839 632.20	839 632.09	0.11	0.20
12	992 276.00	992 276.53	-0.53	2.00

Table 2

Electric and magnetic properties of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ in the (01¹0) vibrational state; PI in the last column stands for present investigation

Quantity	(01 ¹ 0) state	(000) state	Ref.
q_v (kHz)	6361.413(5)		PI
	6361.31(5)		[1]
	6393(13)		[8]
	6344(18)		[9]
μ_v (Hz)	-4.27(5)		PI
	-4.20(3)		[1]
$ \Delta H $ (Hz)	$< 8 \times 10^{-4}$		PI
μ_{el} (D)	0.70423(3)		PI
		0.71515(3)	[3]
	0.7019(8)		[10]
	0.704		[11]
μ_{el} (relative)	0.98473(1)	1.00000	PI
g_{\perp}	-0.02930(4)*		PI
	-0.0285(6)		[2]
		-0.028839(6)	[3]
$g_{\parallel} - g_{\perp}$	0.0905(5)*		PI
	0.0895(21)		[2]
$g_{xx} - g_{yy}$	0.00023(2)*		PI
$\chi_{\perp} - \chi_{\parallel}$ (kHz/kG ²)	2.38(10)**		PI
	2.00(25)		[2]
		2.348(3)	[3]
$\chi_{xx} - \chi_{yy}$ (kHz/kG ²)	-0.03(3)**		PI

*(**) Errors are two (five) standard deviations.

The magnetic field strength was determined from the two known transitions of $\nu_2 = 0$ which were measured before and after each line or each group of lines of $\nu_2 = 1$. The magnetic constants derived from the frequencies with help of a least squares computer program are listed in table 2. The transverse Stark effect term of eq. (1) $-\mu_{el} \cdot (\nu \times B)$ caused a shift of the spectral lines of about 3 kHz (at 8 kG) for $J = 3$ and therefore this term is needed to explain the spectra.

From the calculated magnetic energies [eqs. (7) and (8)] it can be seen that it is not possible to identify the spectral lines uniquely if the sign of either $g_{xx} - g_{yy}$ or $\chi_{\perp} - \chi_{\parallel}$ is not known. We assumed $\chi_{\perp} - \chi_{\parallel}$ to have the same sign as in the (000) state, which fixes also the sign of $g_{xx} - g_{yy}$. The present values of g_{\perp} , $g_{\parallel} - g_{\perp}$, and $\chi_{\parallel} - \chi_{\perp}$ do essentially agree with the less accurate results of Hüttner and Morgenstern [2]. The anisotropy $g_{xx} - g_{yy}$ is determined for the first time, for $\chi_{xx} - \chi_{yy}$ in fact only an upper limit could be determined. The well established value of $g_{xx} - g_{yy}$ indicates a slight (about 1%) asymmetry of the two perpendicular motions of the molecules in the bending mode of vibration.

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