

ELECTRIC AND MAGNETIC PROPERTIES OF OZONE BY MOLECULAR BEAM ELECTRIC RESONANCE SPECTROSCOPY

W.L. MEERTS, S. STOLTE and A. DYMANUS

Fysisch Laboratorium, Katholieke Universiteit, Nijmegen, The Netherlands

Received 16 July 1976

Molecular beam electric resonance spectroscopy has been used to investigate the $\Delta J = 0$, $\Delta M = \pm 1$ transitions of the 1_{11} , 2_{11} , 4_{04} and 4_{13} rotational states of ozone in the presence of external electric and magnetic fields. The data have been used to evaluate the electric dipole moment $\mu = 0.53373(7)$ D; the electric polarizability anisotropies $\alpha_{aa} - \alpha = 2.04(40)$ Å³ and $\alpha_{bb} - \alpha = -0.98(13)$ Å³; the molecular g -values $g_{aa} = -2.9877(9)$, $g_{bb} = -0.2295(3)$ and $g_{cc} = -0.0760(3)$; and the magnetic susceptibility anisotropies (in units of 10^{-6} erg/G² mole) $\chi_{aa} - \chi = 23.85(11)$ and $\chi_{bb} - \chi = 0.41(8)$. The molecular quadrupole moments obtained from the g -values and the magnetic susceptibility anisotropies are in satisfactory agreement with the results of ab initio calculations. The bulk susceptibility of ozone is estimated to be $\chi = 8.0 \times 10^{-6}$ erg/G² mole, using the theoretical value of the out-of-plane component of the second moment of the electronic charge distribution.

1. Introduction

The rotational spectrum of the ground state of ozone has been investigated quite intensively by many authors [1-3]. The structure of the molecule has been determined by Trambarulo et al. [1]. The oxygen nuclei form an isosceles triangle with an apex angle of 116.8° , and the two internuclear distances are 1.278 Å. Recently, Lichtenstein et al. [3] observed the microwave transitions up to the frequency of 320 GHz and recalculated the rotational spectrum up to $J = 40$. Several investigations yielded the electric dipole moment showing a wide spread of values from 0.49 D [4] to 0.58 D [2]. The most accurate value was found by Lichtenstein et al. $0.5324(24)$ D [3].

The rotational Zeeman effect has been observed by Pochan et al. [5] in the $3_{13} \rightarrow 4_{04}$ transition yielding the values of magnetic susceptibility anisotropies. These authors also determined the components of the molecular G -tensor by combining their results for the $3_{13} \rightarrow 4_{04}$ transition with those of Burrus [6] for the $0_{00} \rightarrow 1_{11}$ and $2_{02} \rightarrow 2_{11}$ transitions. The tensor components of the molecular quadrupole moment determined from these experimental g -factors and magnetic susceptibilities were not in agreement with the results of self-consistent field (SCF) calculations of Rothen-

berg and Schaefer [7]. This is quite surprising since a good agreement between SCF calculations and experiment was obtained for SO₂ [5,8,9].

In the present experiment we used the molecular beam electric resonance (MBER) method to investigate the $\Delta J = 0$ Stark and Stark-Zeeman transitions in ozone. The study was started to obtain an accurate value of the electric dipole moment and to investigate whether this moment shows a dependence on the rotational energy levels. Furthermore we determined the polarizability anisotropies of ozone. From the Zeeman splittings very accurate values of the molecular g -factors have been obtained, which may serve for a future determination of the sign of the electric dipole moment of ozone when accurate values for g -factors of a different isotopic species become available [10]. The present more accurate value of the electric dipole moment and the molecular g -factors agree with those of previous determinations [3,5]. No dependence of the dipole moment on the rotational quantum number was observed within the present experimental precision (0.00007 D). The Zeeman spectra also yielded values of magnetic susceptibility anisotropies which disagree with those found by Pochan et al. [5]. The molecular quadrupole moments calculated from the present molecular g -factors and magnetic susceptibil-

ity anisotropies show gratifying agreement with the SCF calculations [7]. Using the theoretical results for the out-of-plane component of the second moment of the electronic charge distribution (c^2) = 3.07 Å² [7] we estimated the bulk susceptibility to be 8.0(3) × 10⁻⁶ erg/G² mole. It is interesting to note that the bulk susceptibility of ozone is predicted to be paramagnetic.

2. Theory

The hamiltonian of an asymmetric rotor molecule in the Born–Oppenheimer rigid-rotor approximation with zero nuclear spins in an external field E and magnetic field B has the form

$$H = H_0 + H_R - \mu \cdot E - \frac{1}{2} E \cdot \alpha \cdot E - \mu_N \mathbf{B} \cdot \mathbf{G} \cdot \mathbf{J} - \frac{1}{2} \mathbf{B} \cdot \chi \cdot \mathbf{B}, \quad (1)$$

where H_0 and H_R represent the electronic-vibrational and rotational energies, respectively. These energies are not of interest in the present study and will not be discussed further. The other terms describe in the indicated order the Stark effect, the electric polarizability, the molecular Zeeman effect, and the magnetic susceptibility. The quantities which appear in eq. (1) are: J , the rotational angular momentum; μ , the electric dipole moment; α the polarizability tensor; μ_N , the nuclear magneton; \mathbf{G} , the rotational magnetic moment tensor; and χ , the magnetic susceptibility tensor. The Stark–Zeeman energies can be expressed in terms of coupling constant α_{J_τ} , g_{J_τ} , and χ_{J_τ} , for the electric polarizability anisotropy, the rotational magnetic moment and the susceptibility anisotropy, respectively. The relevant equations for the magnetic contributions can be found in ref. [11] while the third and fourth contributions to the energy of the $|J_\tau, M\rangle$ state can easily be deduced using the techniques described in refs. [11] and [12] resulting in

$$\begin{aligned} &(-\mu \cdot E) + \left(-\frac{1}{2} E \cdot \alpha \cdot E\right) = \mu^2 E^2 (\beta_{J_\tau}^0 + \beta_{J_\tau}^1 M^2) \\ &- \alpha_{J_\tau} E^2 [3M^2 - J(J+1)] / (2J-1)(2J+3). \quad (2) \end{aligned}$$

The coupling constants α_{J_τ} , g_{J_τ} , and χ_{J_τ} expressed in the components of the α , \mathbf{G} , and χ tensor along the principal axes are

$$\alpha_{J_\tau} = \sum_{g=a,b,c} \langle J_g^2 \rangle (\alpha_{gg} - \alpha) / J(J+1),$$

$$g_{J_\tau} = \sum_{g=a,b,c} \langle J_g^2 \rangle g_{gg} / J(J+1),$$

$$\chi_{J_\tau} = \sum_{g=a,b,c} \langle J_g^2 \rangle (\chi_{gg} - \chi) / J(J+1), \quad (3)$$

where $\langle J_g^2 \rangle$ is the average value of the squared rotational angular momentum along the g th principal inertial axis, and α and χ are the average electric and magnetic polarizabilities, respectively. The values of $\langle J_g^2 \rangle$ have been computed from the known reduced energies. As the trace of both the polarizability anisotropy tensor ($\alpha_{gg} - \alpha$) are zero, only two independent components may be determined for each tensor. So the Stark–Zeeman spectra are completely described by eight independent molecular constants: μ , $(\alpha_{aa} - \alpha)$, $(\alpha_{bb} - \alpha)$, g_{aa} , g_{bb} , g_{cc} , $(\chi_{aa} - \chi)$ and $(\chi_{bb} - \chi)$.

The first contribution to eq. (2) represents the quadratic Stark effect in the J_τ rotational state, obtained from a second order perturbation calculation:

$$\mu^2 E^2 (\beta_{J_\tau}^0 + \beta_{J_\tau}^1 M^2) = \sum_{J'_\tau \neq J_\tau} \frac{|\langle J_\tau M | -\mu \cdot E | J'_\tau M \rangle|^2}{E_{J_\tau} - E_{J'_\tau}}, \quad (4)$$

where $|J_\tau M\rangle$ are the eigenfunctions of the state corresponding to a rotational energy E_{J_τ} . The rotational wavefunctions used in this calculation were generated from the correct rotational hamiltonian formed on a basis of Wang wavefunctions. Since the second order Stark coefficients $\beta_{J_\tau}^0$ and $\beta_{J_\tau}^1$ depend rather strongly on the rotational spacings, the energies of the relevant levels for the low- J states used in the perturbation calculation were calculated from the experimental rotational transition frequencies tabulated by Lichtenstein et al. [3]. For the low rotational states of interest here this second order perturbation calculation should give Stark coefficients with an accuracy larger than the experimental precision of 1 part in 10⁴.

3. Experiments and results

The molecular beam electric resonance apparatus used in the present experiment has been described in detail elsewhere [13]. A beam of about 90–100% pure ozone was generated from a low-pressure effusive-type

Table 1

Observed and calculated Stark transitions and Stark coefficients $C_{2\mu}$. All frequencies are in kHz, the Stark coefficients are in units of 10^{-3} kHz/(D V/cm)²

$J_{K_1K_2}$	Transition $ M\rangle \rightarrow M'\rangle$	$C_{2\mu}$	Observed frequency		C_4E^4 b)	ν_0 c)	ν_0 (obs) - ν_0 (calc)
			ν_2 a)	ν_1			
1 ₁₁	0 → 1	0.776899	1095.56	2191.11	-0.02	2191.13(23)	-0.07
2 ₁₁	1 → 2	0.609631	859.55	1719.02	-0.16	1719.18(23)	0.10
4 ₀₄	2 → 3	0.984864	1383.83	2766.97	-1.38	2768.35(23)	0.07
4 ₀₄	3 → 4	1.378809	1937.65	3875.07	-0.46	3875.53(23)	-0.06
4 ₁₃	2 → 3	0.269479	380.50	760.92	-0.16	761.08(23)	-0.02

a) ν_1 and ν_2 are the observed frequencies at $E = 3143.073$ (30) V/cm and 2222.488 (22) V/cm, respectively; experimental uncertainties are 50 Hz.

b) C_4E^4 : fourth order Stark shift at $E = 3143.073$ V/cm, calculated from ν_1 and ν_2 . The uncertainties in C_4E^4 are 220 Hz.

c) Experimental value of the pure second order Stark splitting at $E = 3143.073$ (30) V/cm.

source, operated at -155°C . The diameter of the beam forming orifice was 0.5 mm and the pressure in the source was estimated to be about 10 torr. An effusive rather than a nozzle source was used since pure ozone is self-exploding at pressures higher than 70 torr. The gas was fed from a five liter bulb through a stainless steel needle valve to the source. The beam intensity was monitored at the ion peak $m/e = 32$.

The ozone was prepared in a separate apparatus as described by Clough and Thrush [14]. Medical oxygen was passed through a Fischer ozone generator. The exit gas contained about 2.5 vol.% O_3 and was adsorbed selectively by a silica gel trap cooled to about -75°C . By pumping on the sample the additional amounts of oxygen were removed and the concentrated product was finally distilled into the reservoir flask up to a maximum pressure of 50 torr. The whole system was made of pyrex and teflon; and teflon or viton o-ring sealed valves were employed. No problems were encountered in maintaining a stable ozone beam for a few hours.

The instrumental linewidth was 2.2 kHz full width at half maximum. The observed frequencies involved the $\Delta J = 0$, $\Delta M = \pm 1$ transitions of the 1₁₁, 2₁₁, 4₀₄ and 4₁₃ rotational states. The typical signal-to-noise ratio was 15 at 1 s integration constant. The applied electric fields were 2.2 and 3.1 kV/cm. The Zeeman transitions were measured at magnetic fields of 1, 4, and 8 kG, while the electric field strength in the C-field region was 3.1 kV/cm.

As we did not perform a fourth order perturbation calculation of the Stark effect, we decided to deter-

mine the fourth order contributions experimentally. The observed frequency is expressible in a power series of the electric field E as:

$$\nu_1 = \nu(E) = C_2E^2 + C_4E^4 + \dots,$$

higher orders in E may be neglected. The transition frequency ν_2 , at an electric field of $(1/\sqrt{2})E$ is then

$$\nu_2 = \frac{1}{2} C_2E^2 + \frac{1}{4} C_4E^4.$$

The pure second order frequency $\nu_0 (= C_2E^2)$ is easily calculated from the experimental frequencies ν_1 and ν_2 by

$$C_2E^2 = \nu_0 = 4\nu_2 - \nu_1.$$

The observed Stark transitions ν_1 and ν_2 are given in table 1, together with the fourth order correction $C_4E^4 = 2(\nu_1 - 2\nu_2)$ and the frequencies ν_0 .

For the determination of the electric dipole moment from the second order coefficients C_2 , it is necessary to separate the polarizability contributions from these coefficients. It is seen from eq. (2) that

$$C_2E^2 = C_{2\mu}\mu^2E^2 + C_{2\alpha}\alpha_{J_T}E^2, \quad (5)$$

where

$$C_{2\mu} = \beta_{J_T}^1 (M_f^2 - M_i^2),$$

and

$$C_{2\alpha} = -3(M_f^2 - M_i^2)/(2J-1)(2J+3).$$

M_i and M_f being the quantum numbers of the initial and final states, respectively. The value of $C_{2\alpha}$ is exactly known for a given transition, while the values of

Table 2

Observed values of g_{J_T} and χ_{J_T} (in units of 10^{-6} erg/G² mole), and the expectation values $\langle J_a^2 \rangle$, $\langle J_b^2 \rangle$, and $\langle J_c^2 \rangle$, calculated under the assumption $\kappa = -0.96802$

Rotational state	g_{J_T} ^{a)}	χ_{J_T}	$\langle J_a^2 \rangle$	$\langle J_b^2 \rangle$	$\langle J_c^2 \rangle$
1 ₁₁	-1.5318(2)		1	0	1
2 ₁₁	-0.66359(10)	0.20(4)	1	4	1
4 ₀₄	-0.15035(2)	-12.37(6)	0.00292	9.63630	10.36078
4 ₁₃	-0.33239(9)	-4.03(10)	1.00052	14.43529	4.56418

a) The errors in g_{J_T} represent the relative errors, which have to be multiplied by two in order to obtain the absolute accuracies.

$C_{2\mu}$ (i.e., of $\beta_{J_T}^I$) have been evaluated using expression (4) as explained in the previous section. The numerical values of $C_{2\mu}$ used to obtain the electric dipole moment are given in table 1. The coupling constants α_{J_T} for all the levels investigated can be expressed in terms of two components of the $\alpha - \alpha$ tensor using eq. (3). Consequently the frequencies ν_0 of table 1 furnished five equations for three constants to be solved μ , $(\alpha_{aa} - \alpha)$, and $(\alpha_{bb} - \alpha)$. We found that those five values of ν_0 could be fitted within the experimental accuracies with one single value for the electric dipole moment. This indicates absence of any significant rotational dependence. The results of this fit are shown in table 1, and the fitted electric dipole moment and polarizability anisotropies are listed in table 3.

If in addition to the electric field a magnetic field

Table 3

Electric dipole moment, polarizability anisotropies, and the components of the molecular G-tensor and of the magnetic susceptibility anisotropy tensor χ . The electric dipole moment is listed in Debye units, the values of $\alpha_{gg} - \alpha$ are in units of A³, and the magnetic susceptibilities in units of 10^{-6} erg/G² mole

Quantity	Present work	Lichtenstein et al. [3]	Pochan et al. [5]
μ	0.53373(7)	0.5324(24)	
$\alpha_{aa} - \alpha$	2.04(40)		
$\alpha_{bb} - \alpha$	-0.98(13)		
$\alpha_{cc} - \alpha$	-1.03(42)		
g_{aa}	-2.9877(9) ^{a)}		-2.968(35)
g_{bb}	-0.2295(3)		-0.228(7)
g_{cc}	-0.0760(3)		-0.081(6)
$\chi_{aa} - \chi$	23.85(11)		32.7(19)
$\chi_{bb} - \chi$	0.41(8)		-5.8(17)

a) The errors indicated on the g -factors represent the absolute inaccuracies.

is applied each Stark transition splits into two Stark-Zeeman components. The splittings are determined by the rotational g_{J_T} -factors, whereas the shifts of the average Stark-Zeeman transitions with respect to the Stark transition yield magnetic susceptibility anisotropies. The weighted averages of the observed g_{J_T} and χ_{J_T} values from measurements at 1, 4 and 8 kG are given in table 2, together with the expectation values of $\langle J_g^2 \rangle$ necessary to evaluate the components of the G- and χ -tensor along the principal inertial axes of the molecule. The relative errors in the rotational g_{J_T} -factors are mainly determined by the frequency determination of the Zeeman splittings. The magnetic field was known to within 3 parts in 10^4 , which is equal to the absolute uncertainties in the g_{J_T} -factors. To obtain the expectation values of $\langle J_g^2 \rangle$, κ has been taken from Lichtenstein et al. [3]: $\kappa = -0.96802$. The coupling constants of table 2 were used to determine the components of the G- and the χ -tensor along the principal inertial axes of the molecule. The results are given in table 3, which also lists results of the most recent investigations.

The present more accurate values of the electric dipole moment and the components of the G-tensor agree with the results of the previous experiments. However, the values obtained for the components of the magnetic susceptibility deviate well outside the given uncertainties from the experimental results of Pochan et al. [5]. The discrepancies originate most probably from the overlap of the Zeeman components of the $\Delta M = \pm 1$ transitions in the experiments of Pochan et al.

4. Discussion

The molecular quadrupole moments in the principal axes system (θ_{gg}) have been calculated from the g -factors and magnetic susceptibilities as obtained in the present work using relations given by Flygare and Benson [15]. The results together with the experimental values obtained by Pochan et al. [5] and the theoretical values from a self-consistent field calculation [7] are listed in table 4. The theoretical quadrupole moment tensor elements of the SCF calculation show a satisfactory agreement with the present experimental values.

The second moment of the electronic charge distribution can be related to the known molecular structure and the components of the tensors \mathbf{G} and χ [15]. The second moments of the electronic charge distribution are defined by

$$\langle g^2 \rangle = \langle 0 | \sum_i g_i^2 | 0 \rangle,$$

where g represents one of the principal inertia axes a , b , c ; g_i is the component of the position vector of the i th electron along the g th inertial axis, and $\langle 0 || 0 \rangle$ indicates an expectation value in the ground electronic state. The experimental and theoretical anisotropies in the second moment of the electronic charge distribution listed in table 4, are found to be in excellent agreement. The ab initio second moments are among the most accurately predicted properties obtained in the calculation of Rothenberg and Schaefer [7].

Table 4

Molecular quadrupole moments and anisotropies in the second moment of the electronic charge distribution as obtained in the present experiments, together with the results of previous observations [5] and of a SCF calculation [7]. The quadrupole moments are in units of 10^{-26} esu cm^2 , and the second moments are in \AA^2

Quantity	Present work	Pochan et al. [5]	Rothenberg et al. [7]
θ_{aa}	-1.37(18)	-17.1(52)	-2.14
θ_{bb}	-0.80(13)	9.2(47)	0.36
θ_{cc}	2.17(22)	7.9(79)	1.78
$\langle a^2 \rangle - \langle b^2 \rangle$	16.67(3)		16.91
$\langle b^2 \rangle - \langle c^2 \rangle$	2.80(3)		2.59
$\langle c^2 \rangle - \langle a^2 \rangle$	-19.47(3)		-19.50

Since our anisotropies in the second moments are in very close agreement with the SCF results it looks plausible to use the theoretical value for $\langle c^2 \rangle = 3.07 \text{\AA}^2$ [7] to determine the other two components of the second moment from the experimental results of table 4. The result is $\langle a^2 \rangle = 22.54 \text{\AA}^2$, $\langle b^2 \rangle = 5.87 \text{\AA}^2$.

The diagonal elements in the paramagnetic susceptibility (χ_{gg}^p) tensor can also be obtained from the molecular structure and the molecular g -factors [15]. Using the present results for the g -factors the results for the paramagnetic susceptibilities are: $\chi_{aa}^p = 69.80(2)$, $\chi_{bb}^p = 117.07(3)$, and $\chi_{cc}^p = 104.30(5)$, all in units of 10^{-6} erg/G² mole.

The total magnetic susceptibility χ_{gg} along any axis, which is a sum of the diamagnetic χ_{gg}^d and the paramagnetic χ_{gg}^p components, can be calculated using the second moments of the electronic charge distribution. The diamagnetic susceptibility can be directly obtained from these second moments [15]. The components along the principal inertial axes of the total magnetic susceptibility obtained in this way are: $\chi_{aa} = 31.9(1)$, $\chi_{bb} = 8.4(1)$ and $\chi_{cc} = -16.2(2)$, in units of 10^{-6} erg/G² mole. The errors indicated are based on the assumption of zero error in $\langle c^2 \rangle$. The average or bulk susceptibility obtained from these results, $\chi = 8.0(3) \times 10^{-6}$ erg/G² mole, is quite surprising as ozone is showing a paramagnetic behaviour. This is in disagreement with the near zero value of the bulk susceptibility for ozone found by Laine [16]. However, a zero value for χ may be obtained from the present experimental results by assuming that all the components of the second moment of the electronic charge distribution are 0.95\AA^2 larger, hence being $\langle a^2 \rangle = 23.49 \text{\AA}^2$, $\langle b^2 \rangle = 6.82 \text{\AA}^2$ and $\langle c^2 \rangle = 4.02 \text{\AA}^2$. A more accurate determination of the bulk susceptibility of ozone is needed to check our assumptions and conclusions.

The theoretical value of the electric dipole moment as obtained by Rothenberg and Schaefer [7], 0.82 D, is in poor agreement with the observed electric dipole moment, 0.53373 D, whereas the calculations of Petrongolo et al. [17] yielded $\mu = -0.48$ D, which agrees much better. The latter calculation is based on the LCAO SCF MO method with Slater orbitals as basis. A negative sign of the electric dipole moment is predicted from the calculations of ref. [17] and it would be interesting to obtain this sign experimentally from an accurate measurement of the molecular

g-factors in a different isotopic species of ozone [10]. Unfortunately measurements on isotopic species of ozone in natural abundance are beyond the present sensitivity of our MBER spectrometer, while production of enriched ozone gas is a rather costly enterprise.

Acknowledgement

The authors like to thank Professor J. Reuss for suggesting the experiment.

References

- [1] R. Trambarulo, S.N. Gosh, C.A. Burrus and W. Gordy, *J. Chem. Phys.* 21 (1953) 851.
- [2] R.H. Hughes, *J. Chem. Phys.* 21 (1953) 959.
- [3] M. Lichtenstein, J.J. Gallagher and S.A. Clough, *J. Mol. Spectrosc.* 40 (1971) 10.
- [4] G.L. Lewis and C.P. Smyth, *J. Amer. Chem. Soc.* 61 (1939) 3063.
- [5] J.M. Pochan, R.G. Stone and W.H. Flygare, *J. Chem. Phys.* 51 (1969) 4278.
- [6] C.A. Burrus, *J. Chem. Phys.* 30 (1959) 976.
- [7] S. Rothenberg and H.F. Schaefer, *Mol. Phys.* 21 (1971) 317.
- [8] S. Rothenberg and H.F. Schaefer, *J. Chem. Phys.* 53 (1970) 3014.
- [9] A.W. Ellenbroek and A. Dynanus, *Chem. Phys. Lett.* 42 (1976) 303.
- [10] C.H. Townes, G.C. Dousmanis, R.L. White and R.F. Schwartz, *Discussions Faraday Soc.* 19 (1955) 56.
- [11] W. Hüttner and W.H. Flygare, *J. Chem. Phys.* 47 (1967) 4137.
- [12] C.H. Townes and A.L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).
- [13] F.H. de Leeuw and A. Dynanus, *J. Mol. Spectrosc.* 48 (1973) 427.
- [14] P.N. Clough and B.A. Thrush, *Chemistry and Industry* 47 (1966) 1971.
- [15] W.H. Flygare and R.C. Benson, *Mol. Phys.* 20 (1971) 225.
- [16] P. Laine, *Ann. Phys.* 3 (1935) 461.
- [17] C. Petrongolo, E. Scrocco and J. Tomasi, *J. Chem. Phys.* 48 (1968) 407.