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ELECTRIC AND MAGNETIC PROPERTIES OF CARBON MONOXIDE BY MOLECULAR-BEAM ELECTRIC-RESONANCE SPECTROSCOPY

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The molecular-beam electric-resonance method was used to investigate the Stark–Zeeman spectra of the $J = 1, v = 0$ state of CO. Along with the most abundant species $^{12}C^{16}O$ we studied the $^{13}C^{16}O$ and $^{12}C^{18}O$ molecules. The electric dipole moment, the magnetic g_J-factor, the magnetic susceptibility anisotropy, and the spin–rotation constant of carbon-13 were obtained. The experimental results were used to determine the polarity of the electronic charge distribution (C^-O^+ was found), the vibrational dependence of the electric dipole moment, and the molecular quadrupole moment.

1. Introduction

The carbon monoxide molecule has been subject of many investigations, both theoretical and experimental. A controversial point concerning the electronic structure was the sign of the electric dipole moment. The microwave experiments of Rosenblum et al. [1] on the rotational magnetic moments of several isotopic species of CO seemd to indicate a C^-O^+ polarity. Because questions were raised [2] concerning the interpretation of the data of Rosenblum et al. more accurate measurements of the sign and of the absolute values of the rotational magnetic moments of $^{12}C^{16}O$ and $^{13}C^{16}O$ have been performed by Ozier [3,4] using the molecular beam magnetic resonance (MBMR) method. However, even with the improved accuracy an unambiguous determination of the sign of the electric dipole moment could not be made [4]. Molecular orbital calculations of Nesbet [2] and by Huo [5] predicted a positive sign of the electric dipole moment (C^+O^-) whereas recent calculations of Billingsley and Krauss [6] using configuration interaction produce a negative sign (C^-O^+).

The absolute value of the electric dipole moment of $^{12}C^{16}O$ has first been obtained by Burrus [7] from Stark shifts of the $J = 1 \leftarrow 0$ rotational transitions yielding 0.112(5) D. A molecular beam electric resonance (MBER) investigation by de Leeuw [8,9] and more recently by Muenter [10] yielded for the rotationless electric dipole moment (μ_{el}) the value of 0.1096(2) and 0.10980(3) D, respectively. The dipole moment expansion function was obtained by Toth et al. [11] from infrared line intensity measurements in the 3–0 band. The vibrational dependence of the dipole moment calculated from this expansion function is quite large, about 10%.

The molecular quadrupole moment (θ) of CO has been obtained by a variety of experiments and the results cover a wide range of values. Stogryn and Stogryn [12] list values of the quadrupole moment from $|\theta| = 0.92 \times 10^{-26}$ esu cm^2, obtained by Smith [13] from microwave line broadening to $(-2.50 \pm 0.13) \times 10^{-26}$ esu cm^2 obtained by Buckingham [14] from a measurement of the induced birefringence. The value of θ calculated by Gustafson and Gordy [15] from the rotational g-factor and the magnetic susceptibility anisotropy is $(-2.0 \pm 1.0) \times 10^{-26}$ esu cm^2. A recent investigation of Buontempo et al. [16] of the far infrared absorption spectra of CO in Ar both in the gas and in the liquid phase yielded a value of $(1.9 \pm 0.1) \times 10^{-26}$ esu cm^2. The results of ab initio molecular orbital calculations vary from -1.80 to -2.23×10^{26} esu cm^2 [2,5,17].

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In the present work, the molecular beam electric resonance method has been applied for three isotopic species of CO: $^{12}C^{16}O$, $^{13}C^{16}O$ and $^{12}C^{18}O$. The $\Delta J = 0$ transitions in the $J = 1, v = 0$ state were investigated in an electric and magnetic field, yielding the electric dipole moment and the molecular magnetic moment for the three isotopic species, the anisotropy in the susceptibility of $^{12}C^{16}O$ and $^{12}C^{18}O$, and the carbon-13 spin–rotation constant in $^{13}C^{16}O$. The present results agree with earlier determinations wherever available. Thanks to the high accuracy of the relative values for the g-factor of the isotopes $^{12}C^{16}O$ and $^{12}C^{18}O$ we were able to determine unambiguously the negative (C^-O^+) polarity of the electric dipole moment. The vibrational dependence of the electric dipole moment was calculated from the observed values for the dipole moment in the different isotopes.

The molecular quadrupole moment in the ground vibrational state of CO was obtained from the molecular g-factors and the anisotropies in the susceptibility. The result is $\theta = -1.95(4) \times 10^{-26}$ esu cm^2 with the center of mass as the origin of the coordinate system.

2. Theory

The hamiltonian for the interpretation of the MBER spectra of the investigated isotopic species of CO in an external electric field E and a magnetic field H may be written in the form:

$$H' = H_0 + BJ^2 - \boldsymbol{\mu}_{el} \cdot E - \tfrac{1}{2} E \cdot \boldsymbol{\alpha} \cdot E - g_I \mu_N J \cdot H - \tfrac{1}{2} H \cdot \chi \cdot H + c I \cdot J . \tag{1}$$

The average value of H_0 in eq. (1) gives the electronic and vibrational energies. These energies are *not* important in the present study and are not discussed further. The other terms describe the rotational energy, electric dipole contribution, electric polarizability, molecular Zeeman effect, magnetic susceptibility, nuclear Zeeman effect and spin–rotation interaction, respectively. The last contribution is only relevant for $^{13}C^{16}O$. The quantities which appear in eq. (1) are: B, the rotational constant; J, the rotational angular momentum; $\boldsymbol{\mu}_{el}$, the electric dipole moment; $\boldsymbol{\alpha}$, the polarizability tensor; g_J, the rotational gyromagnetic ratio; μ_N, the nuclear magneton; χ, the magnetic susceptibility tensor; I, the nuclear spin; and c the spin–rotation constant. The rotational magnetic moment μ_J is related to g_J by $g_J \mu_N = \mu_J / J$.

The matrix elements of the hamiltonian were calculated in the decoupled representation: $|JM_J\rangle|IM_I\rangle$, where I has only significance for $^{13}C^{16}O$. A computer program was used to calculate the matrix elements for the states $J = 0$ through 3 and to obtain the eigenvalues by diagonalization of the complete matrix. In this calculation the contribution of the Stark effect in the $J = 1$ state is correct up to fourth order $(\mu^4 E^4 / h^3 B^3)$.

The matrix elements are expressed in terms of coupling constants μ_{el}, $\alpha_\parallel - \alpha_\perp$, g_J, $\chi_\parallel - \chi_\perp$, and c. The subscript ($\parallel$) indicates the component of the relevant tensor along the molecular axis and ($\perp$) the component perpendicular to it. The relations between the coupling constants and the molecular properties and electronic charge distribution in the molecule are given in a previous paper [18].

3. Experiment and results

The molecular beam apparatus used has been described in details elsewhere [18]. Below only the experimental conditions relevant for the present work are discussed. A nozzle source was used with a diameter of 100 μm and backing pressure of 250 torr. The source was cooled to liquid nitrogen temperature. The beam intensities of $^{12}C^{16}O$, $^{13}C^{16}O$ and $^{12}C^{18}O$ were monitored at the parent ion peaks $m/e = 28$, 29 and 30, respectively. Commercial CO gas was used and the spectra of the two isotopic species $^{13}C^{16}O$ and $^{12}C^{18}O$ were investigated in their natural abundances. For all three isotopes the transitions observed were $J = 1, M_J = 0 \rightarrow J = 1, M_J = \pm 1$ ($\Delta M_I = 0$ in $^{13}C^{16}O$) in an electric field. The same transitions in combined electric and magnetic fields were performed only for the molecules $^{12}C^{16}O$ and $^{12}C^{18}O$. The applied electric fields were 4.7 and 6.3 kV/cm, corresponding to Stark shifts of about 175 kHz and 305 kHz, respectively. The value of the magnetic field used was about 8.4 kG. The full line width at half maximum was 1.5 kHz. Typical signal to noise ratio of these transitions was 80 for $^{12}C^{16}O$ and 3 for $^{13}C^{16}O$ and $^{12}C^{18}O$ at a time constant of 1 s.

Because of the weak Stark effect the Zeeman and Stark splittings are comparable already at relatively low magnetic field strengths. This results in a level crossing between the $J = 1, M_J = 0$ and $M_J = 1$ states when the magnetic field has a proper value for a given electric field. Due to this crossing the state selection obtained by the first quadrupole may be disturbed by Majorana transitions [19] in such a way that only one of the two ($M_J = 0 \rightarrow M_J = 1$ and $M_J = 0 \rightarrow M_J = -1$) Stark–Zeeman transitions was observable. It was found experimentally that by adjusting the voltages on the buffer fields between the C-field and the two quadrupole state selectors [18] both Stark–Zeeman transitions could be observed in $^{12}C^{16}O$. The situation for $^{12}C^{18}O$ was similar to that of $^{12}C^{16}O$ and the same setting was used. However, because of the nuclear Zeeman effect of carbon-13, the crossings of the Stark–Zeeman levels are more complicated in $^{13}C^{16}O$. We did not succeed in observing any of the four possible transitions of $^{13}C^{16}O$ in a magnetic field of 8.4 kG. Only at a very low field of 35 G Stark–Zeeman transitions were observable for this molecule.

The transitions of $^{13}C^{16}O$ and $^{12}C^{18}O$ in only electric as well as in electric and magnetic fields were measured relative to those of $^{12}C^{16}O$. This method allowed an accurate measurement of the relative values of the electric dipole moment and of the molecular g-factors of the different isotopes species. The accuracies in the relative values were determined by the errors in the frequency determination (50–100 Hz) and resulted in an uncertainty of 4 parts in 10^4 and 5 parts in 10^5 for the relative electric dipole moment and the g-factor, respectively. The absolute uncertainty in the electric dipole moment of 1 part in 10^3 was determined by the accuracy of the electric field measurement. The magnetic field was known to within 2 parts in 10^4, which is equal to the absolute error in the g_J-factor.

The physical constants used to evaluate our data were those recommended by Cohen and Taylor [20]. The values of the rotational constants B we used were (in MHz) 57635.5 [7]; 55100.7 [1] and 54891.1 [1] for $^{12}C^{16}O$, $^{13}C^{16}O$ and $^{12}C^{18}O$, respectively. The polarizability anisotropy has been taken from Bridge and Buckingham [21] $\alpha_\parallel - \alpha_\perp = 0.532$ Å^3, and was assumed to be the same for all isotopic species.

The results of the present work given in table 1 are found to be in agreement with the results of previous investigators. The spin–rotation coupling constant (c) in $^{13}C^{16}O$ was obtained from the splitting of the Stark transition $M_J = 0, M_I = \pm\frac{1}{2} \rightarrow M_J = \pm 1, M_I = \pm\frac{1}{2}$ into two lines for each value of $M_J M_I$. This splitting in the strong field approximation (Stark effect $\gg c$) is equal to c. As we were not able to distinguish in our spectrometer between $\Delta M_J = +1$ and $\Delta M_J = -1$ transitions, the two spectral lines of $^{13}C^{16}O$ in electric field may be assigned in two ways, yielding a different sign for c. So it might be expected that only the absolute value of the c constant can be obtained from the present results. However, because the Stark effect was comparable to the hyperfine structure in $^{13}C^{16}O$ (interme-

Table 1
Observed electric and magnetic properties of the molecules $^{12}C^{16}O$, $^{13}C^{16}O$ and $^{12}C^{18}O$ ($v = 0, J = 1$)

Quantity	$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	Ref.
μ_{el}(rel.)	1.0000	1.0027(4)	1.0027(4)	P.I. [a]
μ_{el}(D)	0.1097(1)			P.I.
	0.10980(3)			[10]
g_J(rel.)	1.00000		0.95275(5)	P.I.
g_J	−0.26895(5)	−0.2595(30) [b]	−0.25625(5)	P.I.
	−0.26890(10)			[3]
		−0.25691(20)		[4]
	−0.26910(50)	−0.25704(50)	−0.25622(50)	[1]
$\chi_\parallel - \chi_\perp$($10^{-6}$ erg/G^2 mole)	−8.262(12)		−8.242(20)	P.I.
	−8.2(9)			[15]
c(kHz)		32.70(12)		P.I.
		32.59(15) [c]		[4]

[a] P.I. stands for present investigation.

[b] From a measurement at a magnetic field of 35 G.

[c] The value of the spin–rotation constant of Ozier et al. [4] has been converted to the present sign convention.

diate case) the absolute value of c and the value of μ_{el} found for a negative spin–rotation constant, $c = -40.4$ kHz, and $\mu_{el} = 0.10893$ D, are markedly different from those given in table 1 (positive c constant). The value of the electric dipole moment corresponding to a negative c constant would lead to an unrealistic vibrational dependence of the electric dipole moment (see below) for $^{13}C^{16}O$ as compared with reliable results for the other isotopes. Although the spectrum of $^{13}C^{16}O$ alone does not allow determination of the sign of the spin–rotation constant, assignment of a positive sign (in agreement with Ozier et al. [4]) looks well justified.

4. Discussion

4.1. *The sign of the electric dipole moment*

It was shown by Townes et al. [22] that the sign of the electric dipole moment can be obtained from the isotopic dependence of the molecular g_J-factor. The appropriate equation is

$$hg_J(2)/2\pi B_2 - hg_J(1)/2\pi B = -2\boldsymbol{\mu}_{el}\cdot \boldsymbol{d}\,, \qquad (2)$$

where $g_J(i)$ and B_i ($i = 1, 2$) is the g_J-factors and rotational constant, respectively, of the isotopic species i; $\boldsymbol{d}$ is the displacement vector of the center of mass of isotope 2 referred to the center of mass of isotope 1. Eq. (2) is deduced by assuming that the intermolecular distances and the electronic charge distributions are the same in both isotopes. Furthermore vibrational effects are neglected. The values of μ_{el} calculated from the presently observed relative g_J-factors of $^{12}C^{16}O$ and $^{12}C^{18}O$ is $\mu_{el} = -0.07(2)$ D, corresponding to a C^-O^+ polarity of the electronic charge distribution. The vibrational correction on the evaluation of μ_{el} from eq. (2) was estimated to be 6%, which lies well within the uncertainty in μ_{el} as determined from eq. (2). This estimate was obtained using eq. (4) given in ref. [18] and the theoretical results for g_J from Stevens and Karplus [23]. The absolute value of μ_{el} found in this way is quite acceptable in view of the approximation made in the derivation of eq. (2).

4.2. *The vibrational dependence of the electric dipole moment of CO*

The expectation value of the electric dipole moment in a given vibrational–rotational state can be expanded as a Taylor series in B_e/ω_e where B_e and ω_e are the rotational constant and vibrational frequency, respectively, for the equilibrium distance (r_e). As $B_e/\omega_e = 8.9 \times 10^{-4}$ for CO we can neglect the terms involving powers of $(B_e/\omega_e)^n$ for $n > 2$. The following equation is then obtained for the expectation value of μ_{el} [24, 25, 18]

$$\langle\mu_{el}\rangle_v = \mu_e + (B_e/\omega_e)\{-3a_1 r_e(\partial\mu/\partial r)|_{r=r_e} + r_e^2(\partial^2\mu/\partial r^2)|_{r=r_e}\}(v+\tfrac{1}{2})\,, \qquad (3)$$

where μ_e, $(\partial\mu/\partial r)|_{r=r_e}$ and $(\partial^2\mu/\partial r^2)|_{r=r_e}$ is the electric dipole moment, the first and the second derivative, respectively, with respect to the internuclear separation r evaluated at the equilibrium distance r_e; $a_1 = -(1 + \alpha_e\omega_e/6B_e^2)$ is a Dunham potential constant [25]. Assuming that the Born–Oppenheimer approximation is valid, the electronic wavefunction and subsequently the dipolar properties of the molecule are not influenced by the change in vibration. In this approximation the difference in the expectation values of the electric dipole moments for two isotopic species A and B is then:

$$\langle\mu_{el}\rangle_{v,A} - \langle\mu_{el}\rangle_{v,B} = (v+\tfrac{1}{2})(B_e/\omega_e)_A \times \{-3a_1 r_e(\partial\mu/\partial r) + r_e^2(\partial^2\mu/\partial r^2)\} \times \{(m_{red,A}/m_{red,B})^{1/2} - 1\}\,. \qquad (4)$$

Herein m_{red} is the reduced mass of a molecule. It is clear from eq. (4) that the relative dipole moments of $^{13}C^{16}O$ and $^{12}C^{18}O$ with respect to $^{12}C^{16}O$ should both be larger or both be smaller than unity. The experimental values of the relative dipole moment are 1.0027(4) for $^{12}C^{18}O$ and 1.0027(4) or 0.9930(4) for $^{13}C^{16}O$ assuming a positive or a negative value for the carbon-13 c-constant, respectively. This has led to the conclusion of a positive sign for the spin–rotation constant discussed in the previous section.

With the values for the relative electric dipole moments from table 1 in combination with eq. (4) we found

$$\mu_e = -0.123(2)\,\mathrm{D}\,,$$

and

$$(B_e/\omega_e)\{-3a_1 r_e(\partial\mu/\partial r) + r_e^2(\partial^2\mu/\partial r^2)\} = 0.026(3)\,\mathrm{D}\,.$$

The errors indicated are determined by the uncertainties in the experimental values, while the results for each pair of isotopes agree within those errors.

With the above results the vibrational dependence of $\langle\mu\rangle_v$ is given by

$$\langle\mu_{el}\rangle_v = -0.123 + 0.026\,(v + \tfrac{1}{2})\,.$$

Toth et al. [11] obtained from infrared intensity measurements for the dipole moment expansion

$$M(r) = M_0 + 3.10(r - r_e) - 0.14(r - r_e)^2$$
$$- 2.30(r - r_e)^3\,,$$

where $M(r)$ is in debye. Since the experiments of Toth et al. were not able to determine an independent value for M_0, they adopted Burrus' [7] value of -0.112 D. The above equation can be rewritten as [25]

$$\langle M(r)\rangle_v = M_0 + 0.025\,(v + \tfrac{1}{2})\,.$$

The vibrational dependence of the dipole moment as obtained in the present work and by Toth et al. are in excellent agreement. An experimental value of the electric dipole moment in one of the excited vibrational states would allow a more direct determination of both μ_e and the vibrational part of μ_{el}. It is unfortunately not possible to observe MBER spectra of CO in an excited vibrational state with the present sensitivity of the spectrometer.

4.3. The molecular quadrupole moment

The relation originally derived by Ramsey [19] was applied to calculate the molecular quadrupole moment of CO:

$$\theta = -(4m/e)(\chi_\parallel - \chi_\perp) + h\mu_N g_J/2\pi B$$
$$+ me \sum_k Z_k r_k^2/m_k\,.$$

In this equation m and e are the electronic mass and proton charge, respectively; m_k and Z_k are the mass and the charge of the kth nucleus, respectively. With the experimental values of g_J and $\chi_\parallel - \chi_\perp$ from table 1 the result is $\langle\theta\rangle_{v=0} = -1.93(4)$ and $-1.97(4)$ for $^{12}C^{16}O$ and $^{12}C^{18}O$ respectively, in units of 10^{-26} esu cm^2. In the calculation the vibrational corrections to g_J as discussed in ref. [18] were included using the results of Stevens and Karplus [23] to obtain the first derivative of g_J to the internuclear separation. Other experimental results for θ are in the same units $-2.50(13)$ [14], $-2.0(10)$ [15] and $-1.9(1)$ [16]. The values for θ from molecular orbital calculations are given in table 2.

4.4. Comparison of experimental results with results from ab initio calculations

The present experimental results are summarized in table 2 along with results of ab initio calculations. The most extensive calculations have been performed by Stevens and Karplus [23] who evaluated the magnetic properties of CO at four different internuclear

Table 2
Calculated and observed electric and magnetic properties of the CO molecule. All calculated results are reported for the equilibrium distance, unless otherwise specified

	Nesbet [2]	Huo [5]	Billingsley and Krauss [6]	Billingsley and Krauss [17]	Stevens and Karplus [23]	Observed [a]
μ_{el}(D)	0.379	0.274	-0.151 [b]		0.268	$-0.1097(1)$
θ (10^{-26} esu cm^2)	-1.79	-2.14		-2.23 [b]		$-1.94(4)$
g_J					-0.2424	$-0.26895(5)$
$\chi_\parallel - \chi_\perp$ (10^{-6} erg/G^2 mole)					-6.973	$-8.262(12)$
χ_{av}^p (10^{-6} erg/G^2 mole)					18.334	19.01(2)
c in $^{13}C^{16}O$ (kHz)					31.56	32.70(12)

[a] Observed values are all of $^{12}C^{16}O$ except the c-constant.

[b] Vibrationally averaged value, $v = 0$ state.

distances using an extended coupled Hartree–Fock method. Their results show rather good agreement with the experimental ones. The only exception is the value of the electric dipole moment. The results for the electric dipole moment obtained by Nesbet [2], by Huo [5] and by Billingsley and Krauss [6] also disagree with the experiments. The latter authors obtained, however, the correct sign. The results of all ab initio calculations for the molecular quadrupole moment show rather good agreement with the present result.

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