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Measurement of the rotational spectrum of carbon monoxide in its metastable $a\,^3\Pi$ state by laser magnetic resonance

by RICHARD J. SAYKALLY† and KENNETH M. EVENSON
Time and Frequency Division, National Bureau of Standards,
Boulder, Colorado 80303, U.S.A.

and ELIZABETH R. COMBEN and JOHN M. BROWN
Physical Chemistry Laboratory, South Parks Road,
Oxford OX1 3QZ, England

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Three rotational transitions of CO in the $\Omega = 1$ and $\Omega = 2$ spin components of the metastable ($\tau \sim 7\,$ms) $a\,^3\Pi$ state have been measured by far infrared laser magnetic resonance spectroscopy of a positive column discharge. The L.M.R. spectra were analysed in terms of an effective hamiltonian to yield an improved set of molecular parameters.

1. INTRODUCTION

Far-infrared laser magnetic resonance (L.M.R.) spectra have been reported for three molecules in excited electronic states, viz. O_2 [1], NF [2] and PH [3] in their $a\,^1\Delta$ states. In each of these cases, radiative decay of the excited state is multiply forbidden and long radiative lifetimes ($>1\,$s) result. Consequently, it is relatively easy to generate molecules in these states in sufficient concentration for detection by the extremely sensitive L.M.R. method. In this paper we report far-infrared L.M.R. spectroscopy of an intracavity DC discharge to study pure rotational spectra of a molecule in a much shorter lived excited state—the $a\,^3\Pi$ state of CO—which has an average radiative lifetime of $7{\cdot}5 \times 10^{-3}\,$s [4].

The $a\,^3\Pi$ state, the lowest triplet state of CO, is situated 6 eV above the ground $^1\Sigma^+$ state. It decays through spin–orbit mixing with the isoconfigurational $A\,^1\Pi$ state, 8 eV above the ground state, giving rise to the well-known Cameron emission bands [5]. Lambda doubling intervals in the low-J states of the $\Omega = 2$ and $\Omega = 1$ spin components fall in the RF region and have been studied in a series of molecular beam electric resonance (MBER) experiments by Klemperer and his colleagues [6–12]. In that work, lambda-doubling transitions for both ^{12}CO and ^{13}CO were measured to about 1 kHz accuracy and fitted to the degenerate perturbation theory (DPT) model of Freed [13]. Precisely determined Stark shifts were used in conjunction with vibrational overlap integrals and zero-field eigenfunctions to determine the dipole moment of CO in the $a\,^3\Pi$ state ($\sim 1{\cdot}38\,$D) as a

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† National Research Council Postdoctoral Fellow. Present address: Department of Chemistry, University of California, Berkeley, California 94720, U.S.A.

function of internuclear distance†. Subsequent theoretical calculations of this property by several groups generated a good deal of controversy regarding the result [12, 14].

Saykally *et al.* [15, 16] measured the $J = 1 \leftarrow 0$ pure rotational transitions in the $\Omega = 0$ spin component of the $a\,{}^3\Pi$ state of CO for $v = 0$–4 by microwave spectroscopy in cryogenic glow discharges through mixtures of helium and carbon monoxide. Three isotopic species, ${}^{12}C^{16}O$, ${}^{13}C^{16}O$, and ${}^{12}C^{18}O$, were studied. These microwave transitions were analysed together with the RF lambda doublings measured in the Harvard beam experiments by least squares regression techniques in terms of a combined ${}^3\Pi$–${}^3\Sigma$ hamiltonian. The results of this work suggested shortcomings in the earlier treatments of the data. In particular, it was found that perturbations by the nearby $a'\,{}^3\Sigma$ state had to be included explicitly in the hamiltonian for all vibrational levels of the $a\,{}^3\Pi$ state in order to obtain a satisfactory fit producing physically realistic molecular parameters. Moreover, a recalculation of the Stark effects for the lambda doubling transitions showed that the $a'\,{}^3\Sigma$ state contributes substantially to these as well [16, 17]. In the previous analyses of the molecular beam results, perturbations from $a'\,{}^3\Sigma$ had been neglected for $v = 0$–3 of the $a\,{}^3\Pi$ state in both the zero-field hamiltonian and in the treatment of the Stark effect and subsequent extraction of the $a\,{}^3\Pi$ dipole moment function. It can be shown that these omitted perturbations account for the small J-variation in the dipole moments which had been originally attributed to centrifugal stretching effects. Inclusion of the Σ–Π perturbations in the Stark effect alters the shape of the resulting dipole moment function [17]. This result thus apparently explains the discrepancies between recent *ab initio* calculations of the $a\,{}^3\Pi$ dipole moment function and that obtained from the molecular beam studies.

Furthermore, in the work of both the Klemperer group [6–12] and Saykally *et al.* [16] several molecular parameters were rather poorly determined, showing high correlations and irregular vibrational dependences. These problems suggested a need for more data, especially for precise measurements of different types of transitions, such as lambda doublings in the ${}^3\Pi_0$ component, cross-spin transitions and pure rotational transitions in the ${}^3\Pi_1$ and ${}^3\Pi_2$ components. In the present work, three such rotational transitions have been detected by far infrared laser magnetic resonance spectroscopy of CO in the $a\,{}^3\Pi$ state, which was generated in an intracavity d.c. discharge. These measurements have been analysed together with other existing data for the $v = 0$ state in terms of an effective hamiltonian for a molecule in a ${}^3\Pi$ state.

2. Experimental

The NBS-Boulder glow discharge laser magnetic resonance spectrometer has been described previously in connection with the L.M.R. detection of fine structure transitions in oxygen atoms [18] and pure rotational transitions in $a\,{}^1\Delta$ O_2 [1] and HBr^+ [19]. It consists of a 7·6 cm diameter quartz FIR gain cell pumped transversely by a 2·3 m Invar-stabilized CO_2 laser and separated from the sample region (5 cm diameter by 58 cm long) by a 13 μm polypropylene beam splitter set at the Brewster angle. The sample region is centred inside the bore of a 7·6 cm

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† $D \approx 3{\cdot}3356 \times 10^{-30}$ C m.

diameter by 33 cm long solenoid magnet cooled by liquid nitrogen and capable of providing field strengths up to 0·6 T with a homogeneity of 0·1 per cent over a 15 cm length. A DC glow discharge is maintained inside the sample region between a cylindrical copper anode and a water-cooled copper cathode located in a sidearm outside the laser cavity.

The total laser power inside the cavity is monitored with a liquid-helium cooled gallium doped germanium bolometer by coupling a variable fraction of the power out through a polyethylene window with a 5 mm diameter 45° cylindrical mirror adjusted to an optimum position in the laser mode pattern. The entire laser system is mounted on a vibration-isolated table. The power absorbed by a molecular transition tuned into coincidence with the laser frequency by the magnetic field is sine-wave modulated at 1 kHz by a solenoidal coil mounted coaxially within the magnet. The signal is detected by a lock-in amplifier and sent to a signal averager for processing and display. Because the magnetic field is directed along the laser axis, and is consequently always perpendicular to both the E and H fields of the laser, only σ-type transitions ($\Delta M_J = \pm 1$) can be observed.

The molecular parameters obtained by Saykally *et al.* [16], for $a\,^3\Pi$ $^{12}C^{16}O$ in the $v = 0$ state were used to calculate frequencies and Zeeman patterns of pure rotational transitions in the $^3\Pi_1$ and $^3\Pi_2$ spin components. Close coincidences were predicted for the $J = 6 \leftarrow 5$ and $J = 7 \leftarrow 6$ transitions in the $\Omega = 2$ component and cw far infrared laser lines at 458·9 μm (HCOOH) and 393·6 μm (HCOOH), respectively. A search for laser magnetic resonance spectra was carried out with these lines using an ambient temperature DC glow discharge through a mixture of 10 per cent CO in helium at a pressure of 133 Pa (1 Torr) to produce CO in the $a\,^3\Pi$ state. Both rotational transitions were readily observed with fairly good signal-to-noise ratios (30 : 1 for a 100 ms time constant) very near the predicted magnetic field positions.

The same magnetic field regions were monitored with the glow discharge shut off, and as expected, the spectra disappeared. Approximately 10 mTorr of oxygen, air, and water vapour were than added separately to the helium/CO discharge to test for the possibility of the spectra being due to impurities. Oxygen and water vapour reduced the size of the signals substantially, while air had a smaller attenuating effect. The discharge region of the laser cavity was cooled to near 77 K by flowing liquid nitrogen through 1/4″ teflon tubing wound along the laser inside the solenoid magnet. The cooling actually reduced the size of the signals, in contrast to the microwave experiments on metastable CO, where liquid nitrogen cooling was essential for observing any signals [16]. This is not altogether unexpected, since the $\Omega = 2$ spin state is approximately 80 cm^{-1} above the $\Omega = 0$ state and higher J states are being monitored, thus offsetting the effect of condensing out certain molecules (CO_2, C_3O_2) produced in the discharge which quench the $a\,^3\Pi$ state [16]. The variation of the signal strength with discharge current was studied and proved to be approximately linear, as in the microwave study [16]. The optimum pressure and composition were about 100 Pa of roughly 10 per cent CO in helium. The L.M.R. spectra observed with laser lines at 393·6 μm and 458·9 μm are shown in figures 1 and 2. Unexpected spectra resulting from the $J = 7 \leftarrow 6$ transitions in the $\Omega = 0$ spin component were also observed with the 458·9 μm line and will be described later.

The flux densities of the resonances observed with both laser lines were measured by the following procedure. A precision calibrated shunt with a resistance

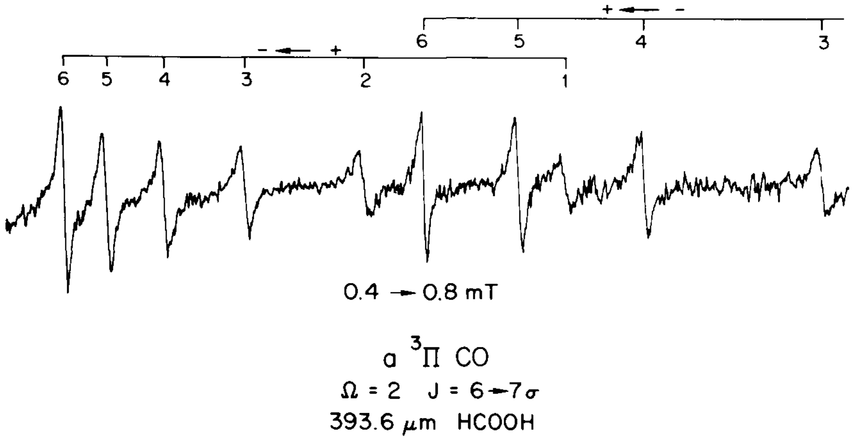

Figure 1. L.M.R. spectrum of $a\,^3\Pi$ CO observed in a discharge through a 10 per cent mixture of CO in helium at a total pressure of 100 Pa with a 300 ms time constant.

of 1·000 Ω was connected in series with the solenoid and placed in a temperature controlled oil bath. Since there are no ferromagnetic materials in the vicinity of the magnet, the magnetic field density is strictly proportional to the DC current in the windings and there is no hysteresis when the current is swept. A programmable digital voltmeter was connected to monitor the voltage drop across the shunt. A nuclear magnetic resonance gaussmeter was used to map out the magnetic field inside the solenoid and to establish the calibration between the voltage drop across the shunt and the flux density in the homogeneous region of the magnetic field. This relationship was found to be linear over the entire range of magnetic fields available (0·0 to 0·6 Tesla). By simply reading the digital voltmeter, the magnetic field could be reproducibly determined to within 2×10^{-5} T. This provided a very convenient and accurate way to measure the L.M.R.

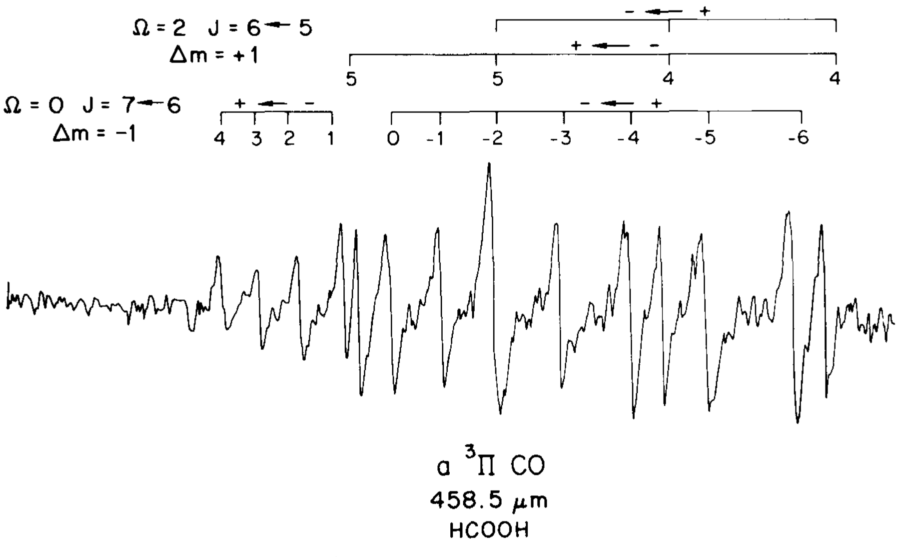

Figure 2. L.M.R. spectrum of $a\,^3\Pi$ CO observed with the same conditions as in figure 1. Note that transitions in both $\Omega = 2$ and $\Omega = 0$ spin components appear.

Table 1. The measured L.M.R. spectra of $v = 0$, $a\,^3\Pi$ CO.

Parity	M_J	Flux density, B/mT	$\dfrac{\nu_L - \nu_{calc}}{\text{MHz}}$	$\dfrac{\partial\nu/\partial B}{\text{MHz/mT}}$ †
458·5 μm		(ν_L = 653821·4 MHz)	$^3\Pi_2$, $J = 6 \leftarrow 5$	
+ ← −	6 ← 5	368·13	1·8	4·04
− ← +	6 ← 5	403·98	2·9	4·05
+ ← −	5 ← 4	447·59	−2·2	3·32
− ← +	5 ← 4	490·90	−1·6	3·33
+ ← −	4 ← 3	576·54	5·2	2·58
− ← −	4 ← 3	628·02	−3·3	2·60
458·5 μm		$^3\Pi_0$, $J = 7 \leftarrow 6$		
+ ← −	3 ← 4	331·94	0·5	2·34
+ ← −	2 ← 3	342·17	1·1	2·28
+ ← −	1 ← 2	352·87	1·0	2·21
+ ← −	0 ← 1	364·01	0·1	2·14
+ ← −	−1 ← 0	376·58	0·2	2·07
+ ← −	−2 ← −1	390·23	0·2	2·00
+ ← −	−3 ← −2	403·98	−1·9	1·92
+ ← −	−4 ← −3	421·70	0·6	1·84
+ ← −	−5 ← −4	439·17	−0·6	1·76
+ ← −	−6 ← −5	459·68	0·0	1·68
+ ← −	−7 ← −6	482·59	0·3	1·59
393·6 μm		(ν_L = 761606·5 MHz)	$^3\Pi_2$, $J = 7 \leftarrow 6$	
− ← +	7 ← 6	50·25	−0·1	3·27
− ← +	6 ← 5	57·56	0·3	2·86
− ← +	5 ← 4	67·12	0·2	2·45
− ← +	4 ← 3	80·55	0·2	2·04
− ← +	3 ← 2	100·92	0·5	1·63
+ ← −	7 ← 6	110·92	0·5	3·28
+ ← −	6 ← 5	126·54	−0·1	2·87
− ← +	2 ← 1	134·19	−0·2	1·27
+ ← −	5 ← 4	147·43	−0·4	2·46
+ ← −	4 ← 3	176·77	−0·7	2·05
− ← +	1 ← 0	201·78	−0·7	0·80
+ ← −	3 ← 2	220·90	−0·9	1·64
+ ← −	2 ← 1	294·99	−1·1	1·22

† Calculated value obtained using the parameter values in table 4.

spectra. The flux densities for the L.M.R. transitions given in table 1 were measured in this manner with a conservatively estimated precision of 5×10^{-5} T by centring the laser on its gain curve, setting the field at the inflection point of the first derivative lineshape, and reading the digital voltmeter. The limitation in accuracy of these measurements does not come from the field measurements themselves, but rather from the drift of the laser frequency due to length changes of the FIR cavity from temperature drifts.

3. ANALYSIS

The L.M.R. data for carbon monoxide in the $v = 0$ level of the $a\,^3\Pi$ state have been analysed in terms of the effective hamiltonian

$$H_{eff} = H_{SO} + H_{SS} + H_{SR} + H_{rot} + H_{LD} + H_Z, \tag{1}$$

Table 2. Part of the matrix representation of the Zeeman hamiltonian for a molecule in a $^3\Pi$ state.

	$^3\Pi_{0\pm}$	$^3\Pi_1$	$^3\Pi_2$
$^3\Pi_{0\pm}$	$-g_r \mu_B B_0 M_J$	$\frac{\mu_B B_0 M_J}{J(J+1)} \sqrt{(2x)}\{\frac{1}{2}(g_S + g_r + g_l) \mp \frac{1}{2}(g_l' - g_r^{e\prime})\}$	$\mp \frac{1}{2} g_r^{e\prime} \mu_B B_0 M_J \times [x(x-2)]^{1/2}/J(J+1)$
$^3\Pi_1$		$\frac{\mu_B B_0 M_J}{J(J+1)} \{g_L' - g_r[J(J+1) - 1] \mp \frac{1}{2} g_r^{e\prime} J(J+1)\}$	$\frac{\mu_B B_0 M_J}{J(J+1)} \sqrt{[2(x-2)]} \times \{\frac{1}{2}(g_S + g_r + g_l)\}$
$^3\Pi_2$			$\frac{2\mu_B B_0 M_J}{J(J+1)} \{g_L' + g_S + g_r[2 - \frac{1}{2}J(J+1)]\}$

In this matrix, x stands for $J(J+1)$ and the notation is taken from [25]. The section of the matrix shown is diagonal in J and M_J and is expressed in terms of parity conserving combinations of case (*a*) basis functions. The upper and lower sign choice refer to *e* and *f* levels respectively; for a triplet state *e* levels have parity $(-1)^J$.

where the various contributions on the right-hand side of (1) describe, in turn, the spin orbit coupling, the spin–spin dipolar interaction, the spin–rotation interaction, the rotational kinetic energy and its centrifugal distortion, the lambda-type doubling terms, and the Zeeman interaction. The detailed forms of all but the last term have been given by several authors [13, 20–23]. We have adopted the N^2 formulation described by Brown, Colbourn, Watson and Wayne [24]. The explicit matrix representation in a Hund's case (*a*) basis set has been given by Brown and Merer [23]. The Zeeman hamiltonian is taken from the work of Brown, Kaise, Kerr and Milton [25] on molecules in $^2\Pi$ states. No additional terms are required for molecules in $^3\Pi$ states within the accuracy implicit in that paper and the present measurements. The part of the matrix representation of H_Z diagonal in J for a $^3\Pi$ state is given in table 2, using the same basis set and phase convention as Brown and Merer [23]. It has recently been demonstrated [26] that an effective hamiltonian of the form in equation (1) is quite adequate to fit the lambda-type doubling frequencies of CO measured by molecular beam electric resonance [6, 7] to within their experimental accuracy and is preferable to the more cumbersome form derived by direct fourth order degenerate perturbation theory [13].

We have written a computer program to calculate the eigenvalues and eigenfunctions of H_{eff}, for a given set of molecular parameters. This program can be used both to predict the form of a fixed frequency magnetic resonance spectrum and to fit measured resonances to determine molecular parameters. Using the best available parameters, accurate predictions were made of the spectra likely to be associated with the 458·5 and 393·6 μm laser lines. The observed spectra were assigned on the basis of these predictions as Zeeman components of the $^3\Pi_2$, $J = 6 \leftarrow 5$ and $^3\Pi_0$, $J = 7 \leftarrow 6$ transitions (468·5 μm) and the $^3\Pi_2$, $J = 7 \leftarrow 6$ transition (393·6 μm). The observation of CO in the $^3\Pi_0$ component is of interest since the diagonal matrix elements of the Zeeman hamiltonian are very small for

Table 3. Zero-field transition frequencies for $v = 0$, $a\,^3\Pi\ ^{12}C^{16}O$.

	Transition J	Parity	Experimental frequency, ν/MHz	$\frac{\nu_{obs} - \nu_{calc}}{kHz}$
$^3\Pi_2$	2	$- \leftarrow +$	7·351(1)†, ‡	1·1§
	3	$+ \leftarrow -$	34·064(1)	2·4
	4	$- \leftarrow +$	92·907(1)	3·4
	5	$+ \leftarrow -$	194·080(1)	2·1
	6	$- \leftarrow +$	343·486(1)	−3·5
	7	$+ \leftarrow -$	542·591(2)	−4·7
	8	$- \leftarrow +$	789·259(2)	5·0
$^3\Pi_1$	1	$+ \leftarrow -$	394·065(1)	0·5
	2	$- \leftarrow +$	1150·065(3)	−1·3
$^3\Pi_0$	$1 \leftarrow 0$	$- \leftarrow +$	92889·86(9)‖	−193
	$1 \leftarrow 0$	$+ \leftarrow -$	92499·14(4)	34

† The figure in parenthesis represents the estimated experimental uncertainty (2σ), in units of the last quoted decimal place.

‡ Experimental lambda-doubling frequencies from Wicke *et al.* [10].

§ Calculated value using the parameter values in table 4.

‖ Experimental rotational frequencies from Saykally [16].

Table 4. Molecular parameters for $v = 0$, $a\,^3\Pi$ CO†.

	This work‡		MBER§
A	41·4464(24) cm^{-1}		41·415(5)
B	50416·39(19)		50395·1(30)
λ	899·4(*F*)	$(-3/2C)$	899(134)
$(o + p + q)$	26009·85(*F*)	(C^{δ})	25958(80)
$(p + 2q)$	169·350(23)	$2(B_1^+ - B_1^-)$	83·7(20)
q	1·55851(70)	$2(B_0^+ - B_0^-)$	1·54(8)
γ	59·7(47)		26·8(70)
D	0·1933(23)		0·1829
g_r	$-0{\cdot}77(33) \times 10^{-3}$		—
g_l	$-0{\cdot}2266 \times 10^{-3}$(*F*)		—
g_S	2·0020(*F*)		—
g_L	1·000(*F*)		—

Correlation Matrix

	A	γ	B	D	g_r	$(p + 2q)$	q
A	1·000000						
γ	−0·995166	1·000000					
B	0·961384	−0·977725	1·000000				
D	0·959141	−0·972591	0·986829	1·000000			
g_r	0·916623	−0·934361	0·928968	0·911323	1·000000		
$(p + 2q)$	0·816553	−0·759625	0·655715	0·668467	0·628397	1·000000	
q	0·920234	−0·932102	0·944052	0·957411	0·871601	0·596361	1·000000

† All values in MHz unless otherwise noted. Figures in parentheses denote one standard deviation.

‡ *F* denotes parameters fixed at values from [9]. *g* factors are unitless and were fixed at estimated values [25].

§ From [7]. See discussion. Values are given for combinations of parameters which correspond to those used in the present paper.

rotational levels in this state (see table 1). However the $^3\Pi_0$ and $^3\Pi_1$ basis states are quite significantly mixed by Coriolis effects (L uncoupling) for $J = 6$ and 7 and the molecule therefore has a sizeable magnetic moment in these levels.

All the available high resolution data for CO in the $v = 0$ level of the $a\,^3\Pi$ state have been used to determine the parameters of the effective hamiltonian in a weighted least-squares fit. The weights were taken as the inverse squares of the estimated experimental uncertainty with the L.M.R. measurements assigned an uncertainty of 2 MHz. All of the major parameters of H_{eff} were determined in this way. Two other parameters, λ and $(o + p + q)$, were constrained to the values from the optical [27] spectrum and three of the g factors were estimated by well-established methods [25]. The quality of the fit was highly satisfactory, as judged from the residuals in table 1 for the magnetic resonance data in table 3 for the zero field data. The standard deviation of the fit measured relative to the experimental uncertainty was 0·841. The values for the parameters determined in the fit are given in table 4. An even better fit was obtained when the third lambda-doubling parameter $(o + p + q)$ was also allowed to vary from the value determined by optical spectroscopy [27]. However, since there are no data which depend directly on this parameter, the parameter set obtained in this way showed unacceptably high correlations for the present set of measurements.

4. Discussion

The level of agreement between the parameters determined in this work with those from the MBER studies is generally good, as is evident in table 4. We have chosen the parameter set of Wicke *et al.* [11] for comparison, rather than the results of Field *et al.* [5], because it relates more directly to that used here. The spin rotation constant (γ) is a factor of three smaller than that of Wicke *et al.* [11]. This is a result of allowing the spin–orbit constant (A) to vary in the fit. It should be noted that A is determined here exclusively from high resolution data with ten times higher precision than obtainable from analysis of optical data [5, 11]. While the two sets of parameters in table 4 exhibit satisfactory agreement, one should not expect all parameters to show such behaviour, since the truncated sets of perturbation parameters employed in the MBER analysis produce, in effect, a contact transformation of the hamiltonian, and a corresponding set of correlated parameters which is not well-defined. This is the disadvantage inherent in the explicit perturbation theory approach, which is alleviated by using an appropriate effective hamiltonian, as was done in the present analysis.

One of the ultimate goals of this work on the $a\,^3\Pi$ state of CO is to obtain a significant, interpretable, and uncorrelated set of molecular parameters. In order to achieve this, more data are clearly needed. In particular, measurement of lambda doubling transitions in the $\Omega = 0$ component, as well as the spin-forbidden $\Delta\Omega \neq 0$ transitions, will permit A and the lambda doubling term $(o + p + q)$ to be determined precisely.

One experimental observation deserves further comment. Efforts were recently made at Berkeley to measure rotational spectra of $a\,^3\Pi$ CO by L.M.R., using the intracavity transverse discharge system employed for L.M.R. studies of molecular ions (HBr^+, HCl^+, HF^+, OH^+, H_2O^+) [28–32] and atomic ions (C^+, N^+) [33, 34]. However, none of the spectra reported here were observed with the Berkeley system. A probable explanation is that the transverse discharge corresponds more to a negative glow, with a very low electron temperature ($T_e <$ 1 eV), while the longitudinal discharge used in the present work is a positive column, with T_e being in the range 1–10 eV. Since the $a\,^3\Pi$ state of CO lies 6 eV above the ground state, it is probably not produced effectively in the cooler transverse discharge.

REFERENCES

[1] SCALABRIN, A., SAYKALLY, R. J., EVENSON, K. M., RADFORD, H. E., and MIZUSHIMA, M., 1981, *J. molec. Spectrosc.*, **89**, 344.

[2] DAVIES, P. B., and TEMPS, F., 1981, *J. chem. Phys.*, **74**, 6556.

[3] DAVIES, P. B., RUSSELL, D. K., SMITH, D. R., and THRUSH, B. A., 1979, *Can. J. Phys.*, **57**, 522.

[4] JAMES, T. C., 1971, *J. chem. Phys.*, **55**, 4118.

[5] FIELD, R. W., TILFORD, S. G., HOWARD, R. A., and SIMMONS, J. D., 1972, *J. molec. Spectrosc.*, **44**, 347.

[6] FREUND, R. S., and KLEMPERER, W., 1965, *J. chem. Phys.*, **43**, 2422.

[7] STERN, R. C., GAMMON, R. H., LESK, M. E., FREUND, R. S., and KLEMPERER, W., 1970, *J. chem. Phys.*, **52**, 3467.

[8] GAMMON, R. H., STERN, R. C., and KLEMPERER, W., 1971, *J. chem. Phys.*, **54**, 2151.

[9] GAMMON, R. H., STERN, R. C., LESK, M. E., WICKE, B. G., and KLEMPERER, W., 1971, *J. chem. Phys.*, **54**, 2136.

[10] WICKE, B. G., FIELD, R. W., and KLEMPERER, W., 1972, *J. chem. Phys.*, **56**, 5758.

[11] WICKE, B. G., KLEMPERER, W., and FIELD, R. W., 1975, *J. chem. Phys.*, **62**, 3544.

[12] WICKE, B. G., and KLEMPERER, W., 1975, *Molec. Phys.*, **30**, 1021.

[13] FREED, K. F., 1966, *J. chem. Phys.*, **45**, 4214.

[14] NORBECK, J. M., MERKEL, R. R., and CERTAIN, P. R., 1977, *Molec. Phys.*, **34**, 589.

[15] SAYKALLY, R. J., DIXON, T. A., ANDERSON, T. G., SZANTO, P. G., and WOODS, R. C. (in preparation).

[16] SAYKALLY, R. J., 1977, Ph.D. Thesis, University of Wisconsin.

[17] WOODS, R. C. (unpublished results).

[18] SAYKALLY, R. J., and EVENSON, K. M., 1979, *J. chem. Phys.*, **71**, 1564.

[19] SAYKALLY, R. J., and EVENSON, K. M., 1979, *Phys. Rev. Lett.*, **43**, 515.

[20] HEBB, M. H., 1936, *Phys. Rev.*, **49**, 610.

[21] MILLER, T. A., and FREUND, R. S., 1973, *J. chem. Phys.*, **58**, 2345.

[22] BROWN, J. M., KOPP, I., MALMBERG, C., and RYDH, B., 1978, *Phys. scripta*, **17**, 55.

[23] BROWN, J. M., and MERER, A. J., 1979, *J. molec. Spectrosc.*, **74**, 488.

[24] BROWN, J. M., COLBOURN, E. A., WATSON, J. K. G., and WAYNE, F. D., 1979, *J. molec. Spectrosc.*, **74**, 294.

[25] BROWN, J. M., KAISE, M., KERR, C. M. L., and MILTON, D. J., 1978, *Molec. Phys.*, **36**, 553.

[26] STEIMLE, T. C., and BROWN, J. M., 1985, *J. chem. Phys.*, **82**, 1618.

[27] DIEKE, G. H., and MAUNCHLY, J. W., 1933, *Phys. Rev.*, **43**, 12.

[28] RAY, D., LUBIC, K. G., and SAYKALLY, R. J., 1982, *Molec. Phys.*, **46**, 217.

[29] HOVDE, D. C., SCHÄFER, E., STRAHAN, S. E., FERRARI, C. A., RAY, D., LUBIC, K. G., and SAYKALLY, R. J., 1984, *Molec. Phys.*, **52**, 245.

[30] GRUEBELE, M., MÜLLER, R. P., and SAYKALLY, R. J., 1986, *J. chem. Phys.*, **84**, 2489.

[31] STRAHAN, S., MÜLLER, R. P., and SAYKALLY, R. J., 1986, *J. chem. Phys.* (in the press).

[32] SAYKALLY, R. J., 1985, *Chemistry in Britain*, February, pp. 159–161.

[33] COOKSY, A., HOVDE, D. C., and SAYKALLY, R. J., 1986, *Astrophys. J.* (in the press).

[34] COOKSY, A., BLAKE, G., and SAYKALLY, R. J., 1986, *Astrophys. J.* (in the press).