Determination of electric dipole moments and transition probabilities of low-lying singlet states of CO

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Transitions from the $X\,^1\Sigma^+(v=0)$ ground state of the carbon monoxide molecule to the electronically excited $A\,^1\Pi(v=0)$, $B\,^1\Sigma^+(v=0)$, and $C\,^1\Sigma^+(v=0)$ states have been studied by 2-photon laser induced fluorescence spectroscopy. Accurate molecular constants for the B and C state have been determined. The electric dipole moments for all three electronically excited states have been deduced from the observed Stark effects. The dipole moments for the A, B, and C states are found to be 0.335 ± 0.013, 1.95 ± 0.03, and 4.50 ± 0.07 D, respectively. From the observed radiative lifetimes the transition probabilities of the B–A, B–X and C–B, C–A, and C–X transitions have been determined.

I. INTRODUCTION

Although spectroscopic studies of the CO molecule began more than a century ago it still is one of the most extensively studied diatomic molecules. Transitions between the $X\,^1\Sigma^+$ ground state and electronically excited singlet states have been observed in absorption[1,2] and recently in emission.[3] Transitions between electronically excited singlet states were observed in emission many years ago.[4] In recent years these transitions have been studied under high resolution using Fourier transform spectroscopy.[5,6] Many different laser excitation and detection schemes have also been applied to study electronically excited states[7–12] of the CO molecule.

Despite these extensive studies only little information is available on the electronic dipole moments of electronically excited singlet states. The only study up to now is by Fisher and Dalby[13] who observed the $B\,^1\Sigma^+(v'=0)$ $\rightarrow A\,^1\Pi(v''=0)$ and $C\,^1\Sigma^+(v'=0)\rightarrow A\,^1\Pi(v''=3)$ emission spectra in the presence of high electric fields. From the observed lineshifts the electric dipole moment for the three states involved could be determined. However, the lineshifts could only be observed at the maximum applied field and therefore the authors could not unambiguously conclude that the observed lineshifts were caused by the Stark effect, or as the authors state themselves: *"Calculations would be valuable in order to rule out the possibility that the experimental results observed here were due to some malevolent field induced perturbation rather than straightforward Stark effects."* Recently Cooper and Kirby[14] performed *ab initio* calculations for the lowest lying singlet states of CO and obtained values for the electric dipole moments of the A, B, and C state which agree to a reasonable extent with the experimental values of Fisher and Dalby.[13]

In the present experiment transitions from the electronic ground state $X\,^1\Sigma^+(v''=0)$ to the $A\,^1\Pi(v'=0)$, $B\,^1\Sigma^+(v'=0)$ and $C\,^1\Sigma^+(v'=0)$ states are studied in the presence of electric fields up to 30 kV/cm. To be able to observe the relatively small shifts and splittings of the rotational levels caused by the Stark effect a narrow bandwidth Fourier limited pulsed laser system is used.

The radiative lifetimes of the $B\,^1\Sigma^+$ and $C\,^1\Sigma^+$ states have been determined by many different techniques. The values reported for the radiative lifetimes disagree seriously with each other, especially for the C state, see, for example, the summary in Ref. 15. In the present study the radiative lifetime of the $B\,^1\Sigma^+$ state is determined directly from the decay of the observed laser induced fluorescence whereas the lifetime for the $C\,^1\Sigma^+$ state is determined from the width of the observed transitions. By making use of fluorescence trapping the transition probabilities from the B and C states to lower lying states are determined.

II. EXPERIMENT

A molecular beam is formed by expanding 3 atm neat CO through a pulsed valve, operated at 10 Hz, with an orifice of 0.5 mm. The molecular beam is collimated 25 mm downstream of the nozzle by a skimmer with an opening of 5 mm. During operation the background pressure in the vacuum chamber is well below 10^{-5} Torr. Two 45 mm diameter stainless steel electrodes spaced 9.7 mm apart are used to apply a static electric field up to 30 kV/cm perpendicular to the molecular beam axis. The center parts of the electrodes consist of a 15 mm diameter honeycomb structured grid, through which the laser induced fluorescence can be observed. Calculations have shown that the inhomogeneity of the electric field between the two electrodes due to the presence of the grids is less than 0.2%. Ground state $X\,^1\Sigma^+(v''=0)$ carbon monoxide is two-photon excited to the $A\,^1\Pi(v'=0)$, $B\,^1\Sigma^+(v'=0)$, or $C\,^1\Sigma^+(v'=0)$ state by a softly focused ($f=500$ mm) laser beam that crosses the molecular beam between the two electrodes 80 mm downstream of the nozzle. The laser induced fluorescence in the visible and uv region of the spectrum is collected through the grids of the electrodes by a quartz lens system and imaged onto a photomultiplier tube (EMI 9893B). An F/3.7 monochromator with a bandwidth of 1.8 nm can be placed in front of the photomultiplier to disperse this fluorescence. The vuv fluorescence is detected by a solar blind photomultiplier tube (EMI 9413) placed in the vacuum chamber. The signals

from the photomultipliers are processed by a digital oscilloscope (LeCroy 7400) and two boxcar integrators (SRS 250) interfaced with a personal computer.

In order to be able to observe the relatively small shifts and splittings of rotational lines caused by the Stark effect a Fourier limited pulsed dye laser system is used to excite the CO molecules. Narrow bandwidth radiation of a cw single frequency ring dye laser (Spectra Physics 380D) operating on Stilbene 3 dye is amplified by a homebuilt four stage pulsed dye amplifier (PDA) system which is pumped by a frequency tripled Q-switched Nd:YAG laser (Quantel YG681-10C). The output of the PDA system is frequency doubled in a BBO crystal to yield 2.5 mJ uv radiation with an estimated bandwidth of 350 MHz. For relative frequency calibration the transmission fringes of a pressure and temperature stabilized Fabry–Perot interferometer with a free spectral range of 149.72±0.05 MHz are recorded. For absolute frequency calibration the absorption spectrum of the Te_2 molecule[16] is simultaneously recorded with the excitation spectrum.

III. RESULTS

A. Spectroscopic

The $B\ ^1\Sigma^+(v=0)$ state at 86 916 cm^{-1}, which is the first member of the $ns\sigma$ Rydberg series, was the subject of a former study[12] where only the lowest five rotational levels in the ground state were populated due to the strong rotational cooling in the molecular beam. In the present experiment the rotational temperature is increased to 10 K due to collisions of the CO molecules with the skimmer and as a result higher rotational levels are populated. The molecules are 2-photon excited from the $X\ ^1\Sigma^+(v''=0)$ ground state to the $B\ ^1\Sigma^+(v'=0)$ state via $\Delta J=0$ and $\Delta J=\pm 2$ transitions which are, however, 2 to 3 orders of magnitude weaker than the $\Delta J=0$ transitions. As a result only $\Delta J=2$ transitions from the lowest two rotational levels are observed. The $B\ ^1\Sigma^+(v'=0)\leftarrow X\ ^1\Sigma^+(v''=0)$ transition is recorded by detecting the strong fluorescence from the B state to the lower lying $A\ ^1\Pi$ state. The linewidth of the individual rotational transitions is 760 MHz and is largely determined by the bandwidth of the laser system. The observed line frequencies for the $B\ ^1\Sigma^+(v'=0)\leftarrow X\ ^1\Sigma^+(v''=0)$ transitions together with their assignments are listed in Table I. The observed transitions are fit to the following expression for a $^1\Sigma^+\leftrightarrow^1\Sigma^+$ transition:

$$\nu=T_0+B_0'J'(J'+1)-D_0'J'^2(J'+1)^2$$
$$-[B_0''J''(J''+1)-D_0''J''^2(J''+1)^2]. \quad (1)$$

Here B_0',D_0',J' and B_0'',D_0'',J'' refer to the upper state and the ground state, respectively. The rotational constants for the ground state are kept fixed in the least squares fit at the accurate values obtained by Guelachvili et al.[17] From the work of Amiot et al.[5] who performed a high resolution Fourier transform spectroscopy study on the $C\rightarrow B$ and $E\rightarrow B$ transitions it is known that the $J=4$ and $J=6$ levels in the B state are weakly perturbed. Transitions to these levels have therefore not been included in the least squares

TABLE I. Observed and calculated transition frequencies (both in cm^{-1}) of the $B\ ^1\Sigma^+(v'=0)\leftarrow X\ ^1\Sigma^+(v''=0)$ and the $C\ ^1\Sigma^+(v'=0)\leftarrow X\ ^1\Sigma^+(v''=0)$ transition.

Transition	$B\ ^1\Sigma^+(v=0)$ Observed	$B\ ^1\Sigma^+(v=0)$ Obs.–Calc.	$C\ ^1\Sigma^+(v=0)$ Observed	$C\ ^1\Sigma^+(v=0)$ Obs.–Calc.
$Q(0)$	86 916.149(3)	−0.001	91 919.066(3)	0.003
$Q(1)$	86 916.203(3)	0.001	91 919.105(3)	0.000
$Q(2)$	86 916.304(3)	0.000	91 919.188(3)	−0.001
$Q(3)$	86 916.456(3)	−0.002	91 919.312(3)	−0.002
$Q(4)$	86 916.646(3)[a]	−0.017	91 919.482(3)	0.001
$Q(5)$	86 916.918(3)	−0.001	91 919.693(10)	0.003
$Q(6)$	86 917.239(3)[a]	0.013	91 919.951(30)	0.010
$Q(7)$	86 917.588(3)	0.004		
$Q(8)$	86 917.993(3)	0.000		
$Q(9)$	86 918.453(3)	0.001		
$Q(10)$	86 918.961(3)	−0.001		
$Q(11)$	86 919.519(3)	−0.003		
$Q(12)$	86 920.130(3)	−0.002		
$Q(13)$	86 920.794(3)	0.002		
$Q(14)$	86 921.504(10)	0.003		
$S(0)$	86 927.839(3)	0.000	91 930.723(3)	−0.001
$S(1)$	86 935.682(3)	0.000	91 938.541(3)	0.001

[a]Not included in the least squares fit.

fit. The molecular constants resulting from the fit are given in Table II. For comparison the constants determined by Amiot et al.[5] are also included in this table. The agreement between our results and those of Amiot et al. is good, except for the rotational B_0 constant.

From the fit it can be concluded that the $J=4$ level of the B state is 0.017 cm^{-1} downshifted in energy and that the $J=6$ level is 0.013 cm^{-1} upshifted in energy. These observed perturbations are in excellent agreement with the experiments of Amiot et al. From the work of Tilford and Simmons[1] it is known that all three states $A\ ^1\Pi(v=19)$, $a'\ ^3\Sigma^+(v=37)$ and $e\ ^3\Sigma^-(v=28)$ are expected to lie within 20 cm^{-1} of the B state. The $a'\ ^3\Sigma^+(v=37)$ can be ruled out as perturbing state since an interaction between the $B\ ^1\Sigma^+$ state and the $a'\ ^3\Sigma^+$ is in first order forbidden by spin–orbit selection rules. The absence of a line shift for the $J=5$ level implies that the perturbations of the $J=4$ and $J=6$ levels result from two independent level crossings. Since the $A\ ^1\Pi(v=19)$ state could produce only one accidental level crossing this state can not be responsible for both observed perturbations. The $e\ ^3\Sigma^-(v=28)$ state, however, has two e parity components which both will

TABLE II. Molecular constants (in cm^{-1}) of the $B\ ^1\Sigma^+(v=0)$ and $C\ ^1\Sigma^+(v=0)$ state of CO.

		This work	Ref. 5
$B\ ^1\Sigma^+(v=0)$	T_0	86 916.150 1(16)	86 916.20(4)
	B_0	1.948 173(28)	1.948 11(2)
	D_0	6.90(27) · 10^{-6}	6.71(2) · 10^{-6}
$C\ ^1\Sigma^+(v=0)$	T_0	91 919.063 9(20)	91 919.11(4)
	B_0	1.943 425(97)	1.943 381(4)
	D_0	6.172 · 10^{-6} [a]	6.172(5) · 10^{-6}
	ν_{BC}	5 002.913 8(26)	5 002.909 4(6)

[a]Kept fixed in the least squares fit at the value determined by Amiot et al. (Ref. 5).

perturb the $B\,^1\Sigma^+(v=0)$ at different J values. Although the observed perturbations can not be fully analyzed, the directions of the level shifts indicate that the F_1, $N=3$, component of the $e\,^3\Sigma^-(v=28)$ state lies just above the $J=4$ level of the $B\,^1\Sigma^+(v=0)$ state and that the F_3, $N=7$, component lies just below the $J=6$ level. So it seems most probable that the $e\,^3\Sigma^-(v=28)$ state is the perturbing state although it cannot be excluded that also the $A\,^1\Pi(v=19)$ state is involved in one of the two perturbations.

The $C\,^1\Sigma^+$ state, which is the first member of the $np\sigma$ Rydberg series converging to the ground state of the ion, lies only 5000 cm^{-1} higher in energy than the $B\,^1\Sigma^+$ state and can therefore be observed with the same experimental setup as the B state. The $C\,^1\Sigma^+(v'=0)\leftarrow X\,^1\Sigma^+(v''=0)$ transition is recorded by detecting the fluorescence from the C state down to the A state in the region from 365 to 550 nm. The linewidths of the transitions to the C state are considerably larger than those of transitions to the B state, 1000 MHz instead of 760 MHz. The observed excitation frequencies and their assignments are listed in Table I. The highest observable rotational level in the C state is $J=6$. The difference with the B state, where the $J=14$ level could still be observed, is mainly due to the difference in branching ratio for fluorescence from both states down to the A state. The observed excitation frequencies have been fit to the expression (1) for a $^1\Sigma^+\leftrightarrow\,^1\Sigma^+$ transition. The molecular constants resulting from the least squares fit are listed in Table II together with the constants obtained by Amiot *et al.* There is a rather good agreement between the values for the rotational B_0 constant found in both experiments. The energy difference between the B and C states is determined from the term values of both states. The agreement with the value obtained by Amiot *et al.*, who observed the direct transitions between these two states, is satisfactory.

The $E\,^1\Pi(v=0)$ state, the first member of the $np\pi$ Rydberg series, lies only 1000 cm^{-1} higher in energy than the $C\,^1\Sigma^+(v=0)$ state. Transitions to this state should therefore also be observable with the present experimental setup. However, these transitions have not been observed. From the work of Letzelter *et al.*[18] it is known that the $v=0$ level of the $E\,^1\Pi$ state predissociates. Most probably due to the extra loss channel introduced by the predissociation, the transitions to the $E\,^1\Pi(v=0)$ state have not been observed.

B. Dipole moments

The electric dipole moments for the $A\,^1\Pi(v=0)$, $B\,^1\Sigma^+(v=0)$, and $C\,^1\Sigma^+(v=0)$ states are determined from the shifts and splittings of rotational levels in an electric field due to the Stark effect. The energy shift of a rotational level in an electric field in the presence of Λ doubling is in first-order given by

$$\Delta W = \sqrt{\left(\frac{E_\Lambda}{2}\right)^2 + (\mu E)^2 \left(\frac{M\Omega}{J(J+1)}\right)^2} - \frac{E_\Lambda}{2}. \qquad (2)$$

Here E_Λ is the energy difference between the two Λ doublet components, μ the permanent electric dipole moment, E

the applied static electric field, M the projection of the total angular momentum J on the electric field vector and Ω the projection of J on the internuclear axis. The first-order contribution is, however, zero for electronic states with $\Omega=0$, such as $^1\Sigma^+$ states. These states are described by the second-order Stark effect. The energy shift of a rotational level is then given by

$$\Delta W = \frac{(\mu E)^2}{2hB}\frac{J(J+1)-3M^2}{J(J+1)(2J-1)(2J+3)}. \qquad (3)$$

Here h is Planck's constant and B is the rotational constant of the electronic state involved. For states having $\Omega\neq0$ the second-order contribution is usually much smaller than the first-order contribution and can therefore be neglected.

In the present experiment transitions are induced from the electronic ground state $X\,^1\Sigma^+(v=0)$ to electronically excited states. The electronic ground state of CO has no first-order Stark effect and with a relatively small electric dipole moment of 0.1098 D[19] the splitting of the various M levels is in the order of a few MHz in electric fields up to 30 kV/cm. The observed Stark patterns are thus completely determined by the Stark splittings in the electronically excited states.

For the determination of the electric dipole moment of the $A\,^1\Pi(v=0)$ state, which exhibits a first-order Stark effect, the $Q(1)\,A\,^1\Pi(v'=0)\leftarrow X\,^1\Sigma^+(v''=0)$ transition is studied in the presence of an electric field. The molecules are 2-photon excited to the A state by a weakly focused laser beam polarized perpendicular to the electric field. The vuv fluorescence down to the ground state is then detected by a solar blind photomultiplier. The dipole moment of the $A\,^1\Pi(v=0)$ state can then directly be determined from the observed line splitting using Eq. (2) and taking into account the Λ doubling of 180 MHz for the $J=1$ level.[20] Figure 1 shows the $Q(1)$ transition in zero field and in an electric field of 15 kV/cm. At this field strength the $M\Omega=+1$ and $M\Omega=-1$ components are almost completely separated. The $M\Omega=0$ component is not observed due to selection rules. Unfortunately, the solar blind photomultiplier failed before measurements at higher electric fields and other rotational levels could be performed, which would yield a more accurate value for the dipole moment. The error in the electric dipole moment is now fully determined by the uncertainty in the observed splitting of the two components. The electric dipole moment for the $A\,^1\Pi(v=0)$ state was found to be 0.335±0.013 D. This value is a factor of two larger than the upper limit which was given by Fisher and Dalby[13] and is also considerably larger than the value calculated by Cooper and Kirby,[14] see Table III. It is, however, smaller than the value of 0.58 D calculated by Cooper and Langhoff.[21]

The $B\,^1\Sigma^+$ and $C\,^1\Sigma^+$ states both exhibit a second order Stark effect. In the presence of an electric field the $J=0$ level will shift in energy by an amount of $\Delta W = -[(\mu E)^2/6hB]$. The $J=1$ level will split into two components, $|M|=1$ and $M=0$, which are separated by $[3(\mu E)^2/20hB]$. In the present experiment the electric dipole moments for the B and C states are determined by measuring this shift and splitting as a function of the elec-
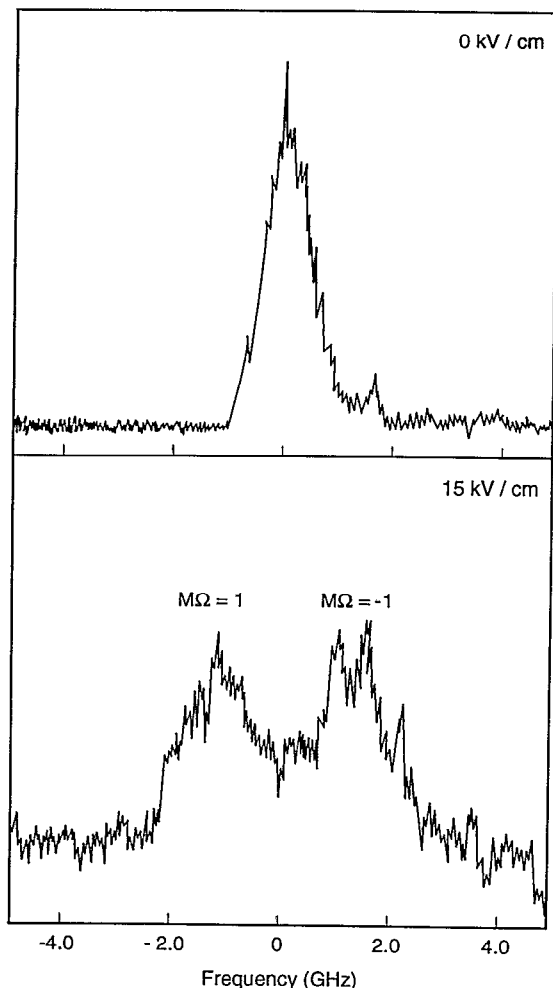
FIG. 1. Recording of the $Q(1)$ A $^1\Pi(v'=0)\leftarrow X$ $^1\Sigma^+ v''=0$ transition at zero field and at an electric field of 15 kV/cm.
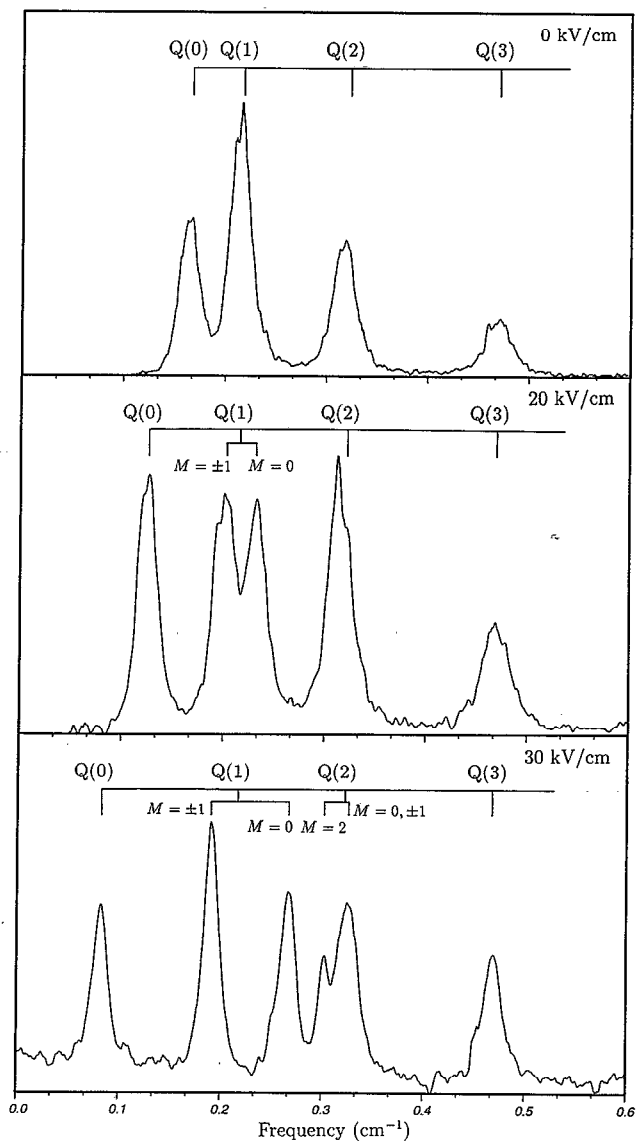

FIG. 2. Part of the observed Q branch of the B $^1\Sigma^+(v'=0)$ $\leftarrow X$ $^1\Sigma^+(v''=0)$ transition as a function of the electric field in the excitation region.

tric field. Figure 2 shows a part of the Q branch of the B $^1\Sigma^+(v'=0)\leftarrow X$ $^1\Sigma(v''=0)$ transition. The shift and splitting become observable at electric fields of 15 kV/cm and higher. At the maximum applied field of 30 kV/cm the splitting of the $J=2$ level becomes observable. In Fig. 3 the observed shift for the $J=0$ level and the splitting for the $J=1$ level are plotted as a function of the square of the electric field. As can be seen the observed Stark patterns are very well described by the second-order Stark effect, Eq. (3). From the measurements an electric dipole moment of 1.95 ± 0.03 D is obtained for the B $^1\Sigma^+(v=0)$ state. For the C $^1\Sigma^+(v=0)$ state a much larger value of

4.50±0.07 D is obtained. In these cases the error is determined by the uncertainty in the distance between the two electrodes. The value found for the electric dipole moment of the B state is considerably larger than the value found by Fisher and Dalby[13] but smaller than the value calculated by Cooper and Kirby,[14] see Table III. For the C state the agreement with the result of Fisher and Dalby is excellent. The value for the electric dipole moment calculated by Cooper and Kirby for the C state is also slightly too large.

It is not possible to determine the sign of the dipole moment from the Stark measurements. Since the values of the electric dipole moment calculated by Cooper and Kirby are relatively close to the experimentally determined values it can be assumed that the signs of the electric dipole
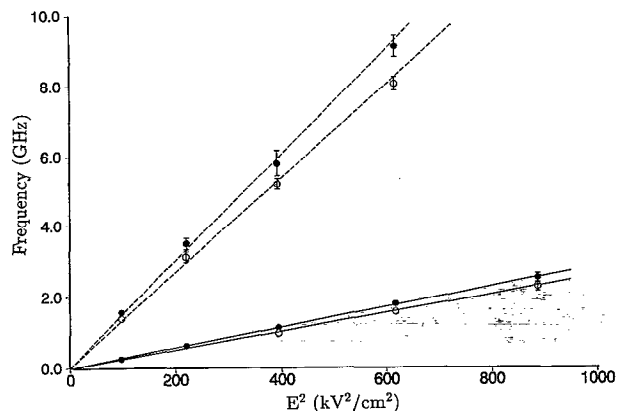
TABLE III. Electric dipole moments (in Debye) of electronically excited states of CO. The signs of the dipole moments are taken from the work of Cooper and Kirby (Ref. 14). A positive value indicates polarity C$^+$O$^-$.

	This work	Ref. 13	Ref. 14
A $^1\Pi(v=0)$	0.335(13)	<0.15(5)	0.19
B $^1\Sigma^+(v=0)$	1.95(3)	1.60(15)	2.79
C $^1\Sigma^+(v=0)$	−4.50(7)	−4.52(35)	−5.34

FIG. 3. Observed shift of the $J=0$ level (filled dots) and splitting of the $J=1$ level (open dots) for the $B\,^1\Sigma^+(v=0)$ state (solid line) and for the $C\,^1\Sigma^+(v=0)$ state (dashed line) as a function of the square of the electric field.

TABLE IV. Radiative lifetimes (in ns) and transition probabilities (in 10^7 s^{-1}) of the $B\,^1\Sigma^+(v=0)$ and $C\,^1\Sigma^+(v=0)$ state.

		This work	Ref. 22	Ref. 15
$B\,^1\Sigma^+(v=0)$	τ	29.8(12)	23(3)	33.5
	τ_{trap}	68.0(27)	72(3)	—
	$A_{B\to X}$	1.90(10)	3.0(6)	1.052
	$A_{B\to A}$	1.45(6)	1.39(6)	1.935
$C\,^1\Sigma^+(v=0)$	τ	0.48(12)	2.2(8)	1.47
	τ_{trap}	58.8(23)	36(2)	—
	$A_{C\to X}$	207(52)	42(17)	67.13
	$A_{C\to A}$	0.55(15)	2.8(1)	0.514
	$A_{C\to B}$	0.12(5)		0.391

moments are equal to those calculated by Cooper and Kirby.

C. Transition probabilities

The transition probabilities from the B and C state to the lower lying A state and the ground state can be deduced from the observed radiative lifetimes. The radiative lifetime for the B state is related to the transition probabilities by

$$1/\tau = A_{B\to X} + A_{B\to A}. \tag{4}$$

Here $A_{B\to X}$ and $A_{B\to A}$ are the transition probabilities from the $B\,^1\Sigma^+(v=0)$ to all the vibrational levels in the ground state and the $A\,^1\Pi$ state, respectively. At relatively high CO densities fluorescence trapping between the B and the ground state can occur. The observed lifetime, τ_{obs}, which is in this case larger than the actual radiative lifetime is related to the transition probabilities by

$$1/\tau_{\text{obs}} = (1-g)A_{B\to X} + A_{B\to A}. \tag{5}$$

Here g is the fraction of the $B\to X$ fluorescence that is reabsorbed by ground state molecules. At high densities this fraction becomes equal to the relative vibrational transition probability for the $B\,^1\Sigma^+(v'=0)\to X\,^1\Sigma^+(v''=0)$ transition and the observed lifetime approaches a constant value τ_{trap}. By measuring the lifetime of the B state at low and high densities the transition probabilities from the B state to the ground state and the A state can be determined.

The radiative lifetime of the B state is measured for several rotational levels. In order to make sure that fluorescence trapping does not occur, a mixture of 2% CO in argon is used. The observed laser induced fluorescence has been fit to a single exponential decay. The radiative lifetime for the $B\,^1\Sigma^+(v=0)$ state was found to be 29.8 ± 1.2 ns, independent of the rotational level. This value is in agreement with most of the published results, see for example the summary in Ref. 15.

In order to measure the lifetime of the B state at a high CO density the skimmer is removed and the molecules are excited closer to the nozzle. To make sure that fluorescence

trapping occurs the lifetime was measured as a function of the distance between the excitation region and the nozzle. For a distance smaller than 4 cm, a constant lifetime, τ_{trap}, of 68.0 ± 2.3 ns was found. In order to calculate the transition probabilities the relative vibrational transition probability of the $B\,^1\Sigma^+(v'=0)\to X\,^1\Sigma^+(v''=0)$ transition has to be known. Unfortunately, the relative vibrational transition probability for this transition has not been determined experimentally. To determine the transition probabilities we have calculated the relative vibrational transition probabilities. In a first step the RKR potential energy curves for both electronic states are calculated from their molecular constants. In a second step the Schrödinger equation is solved numerically for these potentials and the overlap integral for the vibrational wave functions is calculated using the R-dependent transition moment function for the $B\leftrightarrow X$ transition given by Kirby and Cooper.[15] As a result we find that 0.990 of the fluorescence is emitted to the $v''=0$ level in the ground state. The transition probabilities for the $B\,^1\Sigma^+(v'=0)$ to the $X\,^1\Sigma^+(v'')$ and to the $A\,^1\Pi(v'')$ states can now be determined. The results are listed in Table IV. For comparison the values obtained by Dotchin et al.,[22] who performed lifetime measurements on electronically excited states using a proton beam as excitation source, and the calculated values of Kirby and Cooper[15] are also included in this table. The agreement with these experimentally and calculated values is quite satisfactory.

The values found for the radiative lifetime of the $C\,^1\Sigma^+(v=0)$ state vary strongly, from <1.5 to 50 ns. This large discrepancy between the different measurements may be due to several experimental factors such as cascading effect and fluorescence trapping which tend to increase the apparent lifetime and unreliable extrapolations to zero pressure in cell experiments due to the absence of data at sufficiently low pressures. In the present experiment all these effects can be avoided. The radiative lifetime was at first instance determined by monitoring the laser induced fluorescence from the $C\,^1\Sigma^+(v=0)$ state to the A state. From this measurement it is concluded that the radiative lifetime of the C state is considerably shorter than the 5 ns response time of our electronics.

If the lifetime of the C state is shorter than 1 ns it will result in an observable broadening of the lines in the excitation spectrum. As mentioned in Sec. III A the linewidth
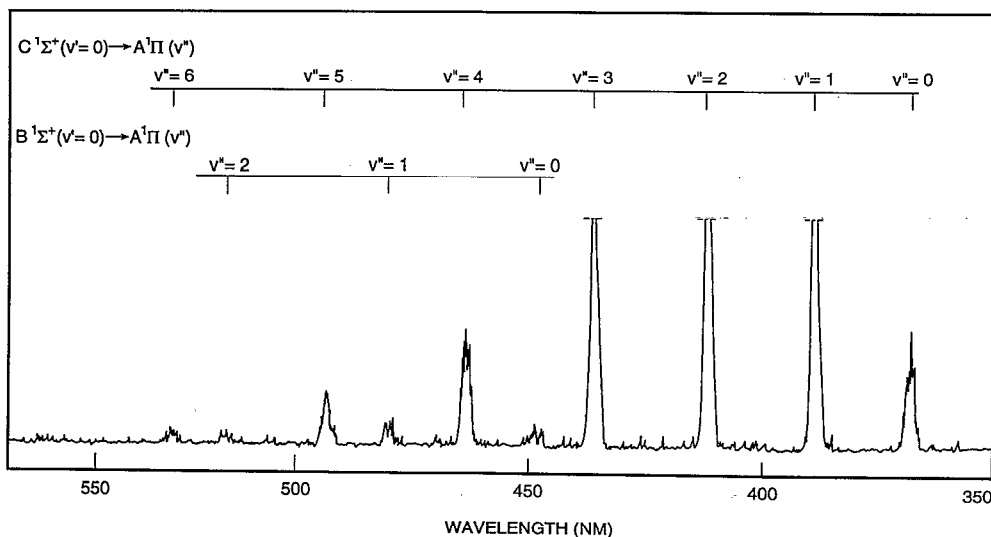
FIG. 4. Dispersed fluorescence spectrum after excitation to the $J=0$ level of the $C\,^1\Sigma^+(v=0)$ state.

of the transitions to the C state is substantially broader than that of the transitions to the B state. In order to obtain the radiative lifetime of the C state, the extra line broadening due to the short lifetime of the C state is determined. In a first step the isolated $S(0)$ and $S(1)$ transitions to the B state are fit to a Voigt profile in order to determine the the contribution of instrumental effects to the Lorentzian part of the linewidth. Next the $S(0)$ and $S(1)$ transitions of the $C \leftarrow X$ system are fit to a Voigt profile. The Lorentzian contribution to the linewidth is 330 MHz larger for the transitions to the C state, whereas the Gaussian contribution is the same as for the transitions to the B state. To make sure that the observed line broadening is not due to saturation of the $C \leftarrow X$ transition or due to fast ionization the laser power has been varied. Since no power dependence of the linewidth has been observed it is concluded that the line broadening is due to the short radiative lifetime of the C state. The extra contribution of 330 ± 80 MHz to the linewidth corresponds to a lifetime for the $C\,^1\Sigma^+(v=0)$ state of 0.48 ± 0.12 ns. This value for the lifetime of the C state is considerably shorter than the previously determined values for the lifetime.

The $C\,^1\Sigma^+(v=0)$ state can fluoresce to the $X\,^1\Sigma^+$, $A\,^1\Pi$, and $B\,^1\Sigma^+$ state. The calculations by Kirby and Cooper[15] show that although the transition frequency for the $C \rightarrow B$ transition is much smaller than that of the $C \rightarrow A$ transition the probabilities for both transitions are almost equal. Since the potential energy curves of the B and C states are almost identical, nearly all the fluorescence from the $C\,^1\Sigma^+(v=0)$ state will be to the $v=0$ level of the $B\,^1\Sigma^+$ state. The fluorescence from this level to the ground state and the electronically excited A state can then be detected. In order to determine the branching ratio for the $C \rightarrow A$ and $C \rightarrow B$ transitions the dispersed fluorescence spectrum is recorded. Figure 4 shows the dispersed fluorescence spectrum after populating the $J=0$ level of the $C\,^1\Sigma^+(v=0)$ state. Clearly two distinct branches are observed, one due to transitions from the $C\,^1\Sigma^+(v=0)$ state

to the vibrational levels of the A state and the other due to transitions from the $B\,^1\Sigma^+(v=0)$ state to the A state. The branching ratio for the $C \rightarrow A$ and the $C \rightarrow B$ transitions can be determined from the observed intensity ratio of the two branches, after correction for the wavelength dependence of the detection system. Taking into account the branching ratio for the $B \rightarrow X$ and the $B \rightarrow A$ transitions, see Table IV, we find a branching ratio for the transitions from the $C\,^1\Sigma^+(v=0)$ to the A state of 0.82 ± 0.06 and to the B state of 0.18 ± 0.06.

To be able to determine the absolute transition probabilities, the lifetime of the C state is determined at CO densities at which fluorescence trapping occurs. The apparent lifetime is found to be $\tau_{\text{trap}} = 58.8 \pm 2.3$ ns. In order to derive the transition probabilities from the observed lifetimes, the relative vibrational transition probabilities for the $C \leftrightarrow X$ transition are calculated, since no experimental values for the relative vibrational transition probabilities are available for this transition. In these calculations an R-dependent transition moment for the $C \leftrightarrow X$ transition is assumed as is given by Kirby and Cooper.[15] As a result we find that the relative vibrational transition probability for the $C\,^1\Sigma^+(v'=0) \leftrightarrow X\,^1\Sigma^+(v''=0)$ transition is equal to 0.995. Using the previously determined branching ratios for the transitions to the A and B states, the transition probabilities can be determined. The results are given in Table IV. It has to be noticed that these values for the transition moments of the $C \rightarrow A$ and $C \rightarrow B$ transitions depend strongly on the calculated value of g, and can thus easily change if experimentally a different value for the relative vibrational transition probability is found. There is a clear difference between the values determined in the present study and those determined by Dotchin et al.,[22] see Table IV. This difference is mainly due to the difference in the lifetime found for the C state. The agreement with the calculated values of Kirby and Cooper[15] is satisfactory only for the value of the $C \rightarrow A$ transition.

IV. SUMMARY

Transitions from the electronic ground state of the CO molecule to the electronically excited $A\,^1\Pi(v=0)$, $B\,^1\Sigma^+(v=0)$, and $C\,^1\Sigma^+(v=0)$ states have been studied at high resolution in a molecular beam employing a Fourier limited pulsed laser system. Accurate molecular constants are obtained for the B and C states. The weak perturbations observed in the B state are attributed to interactions with the $e\,^3\Sigma^-(v=28)$ state. The electric dipole moments of the electronically excited states have been determined from the observed Stark effects. The transition probabilities of the B and C state to lower lying states could be deduced from the observed lifetimes of these two states.

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