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Lifetime of vibrational levels of the $A\ ^2\Pi$ and $B\ ^2\Sigma^+$ states of CO^+

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The radiative lifetimes of the $A\ ^2\Pi$ ($v' = 1$–5) and $B\ ^2\Sigma^+$ ($v' = 0$–2) states of CO^+ have been measured by means of the delayed coincidence method. Excitation has been performed by a pulsed electron beam incident on CO. For the lifetime measurements of vibrational levels of the $A\ ^2\Pi$ state, particular attention has been paid to collisional quenching and electrostatic repulsion. The results of these measurements are $3.25 \pm 0.4\ \mu$s ($v' = 1$), $3.04 \pm 0.17\ \mu$s ($v' = 2$), $2.79 \pm 0.15\ \mu$s ($v' = 3$), $2.56 \pm 0.15\ \mu$s ($v' = 4$), and 2.38 ± 0.16 ($v' = 5$). For the $B\ ^2\Sigma^+$ state measurements, no pressure dependence over a range 1–40 mTorr has been observed; the lifetimes are found to be 53.8 ± 0.8 ns ($v' = 0$), 58.1 ± 0.8 ns ($v' = 1$), and 63.3 ± 1.0 ns ($v' = 2$).

INTRODUCTION

The electronic emission spectra of CO^+ arises mainly from the decay of the $A\ ^2\Pi$ and $B\ ^2\Sigma^+$ states. The de-excitation of the $A\ ^2\Pi$ state produces the *comet tail* system ($A\ ^2\Pi \rightarrow X\ ^2\Sigma^+$). The $B\ ^2\Sigma^+$ state de-excitation gives the first negative ($B\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$) and the Baldet–Johnson ($B\ ^2\Sigma^+ \rightarrow A\ ^2\Pi$) systems.

Different authors[1–8] have measured the lifetimes of several vibrational levels of the $A\ ^2\Pi$ state. In most of the works the values have been deduced by extrapolation towards zero pressure in a Stern–Volmer plot. The results of these measurements show in many cases important discrepancies not only in the lifetime values but in the pressure dependence, too. The main reason for these disagreements is the long lifetime of the positive ions in this state (~3 μs). Möhlmann and de Heer[6] first found that, besides the pressure dependence, the apparent lifetime of the population depends on the current and the width of the excitation electron pulse. Curtis and Erman[7] pointed out that in the measurements of lifetimes of long-lived ions after pulsed excitation of a static gas target, ions escape out of the viewing region due to the electrostatic repulsion. Because of this phenomenon, the viewed light intensity decays more quickly than the level population and may even exhibit a nonexponential decay. This effect increases with the ion density produced by the excitation pulse. Evidently, in the limit of zero ion density this effect disappears. This limit can be approached by decreasing the electron current or the gas pressure.

The $B\ ^2\Sigma^+$ state lifetime measurements do not present these kinds of experimental difficulties. However, the first measurements[9,10] were in total disagreement. This prompted new experiments[2,3,11–15] giving results that disagree by 24% for the $v' = 0$ level,[2,3,13] and by 35% for the $v' = 1$ level.[3,13] For the level $v' = 2$, four measurements exist that range from 38.8 ± 4[9] to 59.4 ± 6.1 ns.[11] The remaining discrepancies in the lifetime values of the vibrational levels of both states have prompted this work, intended to contribute to the existing literature new experimental data.

EXPERIMENTAL PROCEDURE

The experimental technique is based on the delayed coincidence method. The experimental setup has been described previously in other work.[16,17] The ionization and excitation of the molecules have been performed by a pulsed electron beam 6 mm in diameter with energy ranging from 50 to 200 eV. For the measurement of the $A\ ^2\Pi$ lifetimes, the pulse width was 1.1 μs and the cutoff time was 15 ns. In the case of the measurement of the $B\ ^2\Sigma^+$ lifetimes, the pulse width was 170 ns and the cutoff time was 4 ns. In both cases, the repetition frequency was 10 kHz. To choose the spectral bands of interest, a 0.25 m Jarrell-Ash monochromator has been used. The optical resolution was 4 Å in the visible region and 2 Å in the ultraviolet. Photons were detected with a 56 UVP photomultiplier of U(S13) spectral response. The decay of the $A\ ^2\Pi$ levels was studied in a 12 μs time range using a time-to-amplitude converter especially designed for this work.[17] The decay of the $B\ ^2\Sigma^+$ levels was studied in an 800 ns time range.[17] In both cases a multichannel pulse-height analyzer was used to classify and store the data.

The lifetime measurements of the $A\ ^2\Pi$ levels have been carried out using the *comet tail* transitions. In this work special care has been taken to avoid the distortion effects due to space charge. For this purpose, the influence of the gas pressure and the electron beam current has been studied. For currents higher than 30 μA and pressures higher than 10 mTorr, nonexponential decay curves have been observed. This agrees qualitatively with results of Curtis and Erman.[7] For the measurement of the lifetimes of the levels, small electron beam currents (0.5–5 μA) and pressures lower than 25 mTorr have been used. Under these conditions, we have obtained exponential decay curves, and the corresponding lifetimes were not dependent on the electron beam current. This behavior shows that, for these small currents, the ion density is small enough that the ion drift out of the viewing region may be neglected. In Fig. 1, several decay curves of the level $v' = 3$ are plotted. These results were obtained in the above-mentioned experimental conditions by using different pres-

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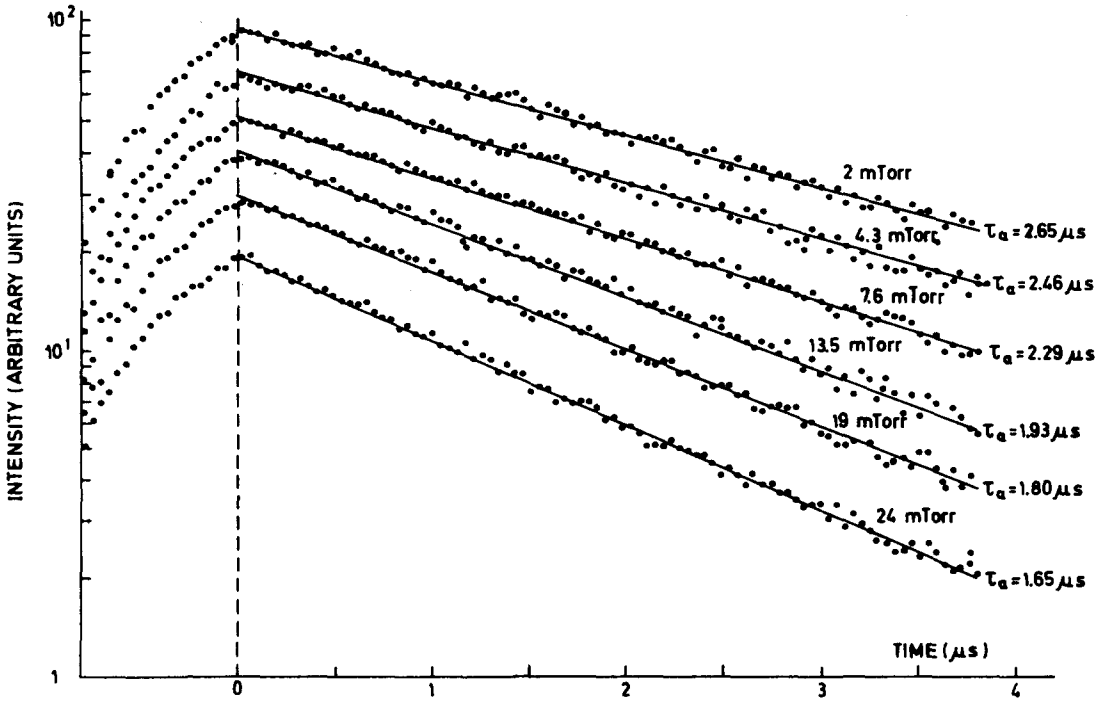

FIG. 1. Decay curves of the vibrational level $v' = 3$ of the $A\,^2\Pi$ electronic state of CO^+ obtained at different pressures and with an electron current of 0.5 μA. τ_a indicates the apparent lifetime of the levels.

sures. In Fig. 2, the Stern–Volmer diagram corresponding to this level is shown. The plot of $1/\tau_a$ versus pressure is linear as expected from only collisional deexcitation effects.

To measure the lifetimes of $B\,^2\Sigma^+$ levels, the transitions of the first negative system have been used. In this case all of the decay curves were single exponential. No dependence on the electron beam current in the range 0.5–60 μA and no pressure dependence in the range 1–40 mTorr have been found, nor were they expected for the short lifetime (~ 60 ns) of these levels. Figure 3 shows typical decay curves obtained in this work.

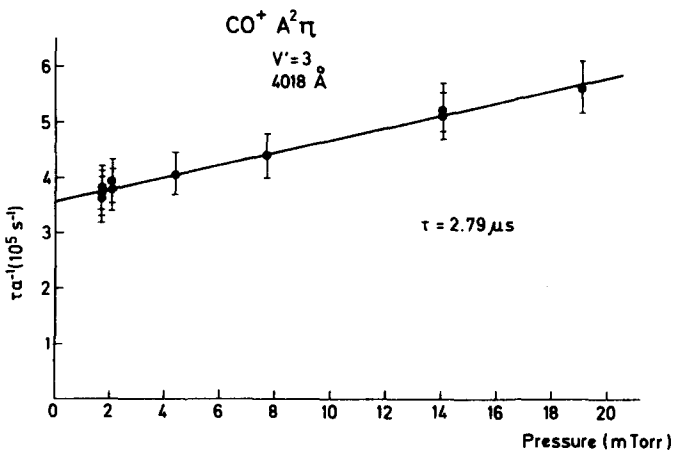

FIG. 2. Stern–Volmer plot of the vibrational level $v' = 3$ of the electronic $A\,^2\Pi$ state. τ_a indicates the apparent lifetime of the levels.

EXPERIMENTAL RESULTS AND DISCUSSION

$A\,^2\Pi$ state

The radiative lifetimes obtained for the $A\,^2\Pi$ state in the present experiment are shown in Table I. As can

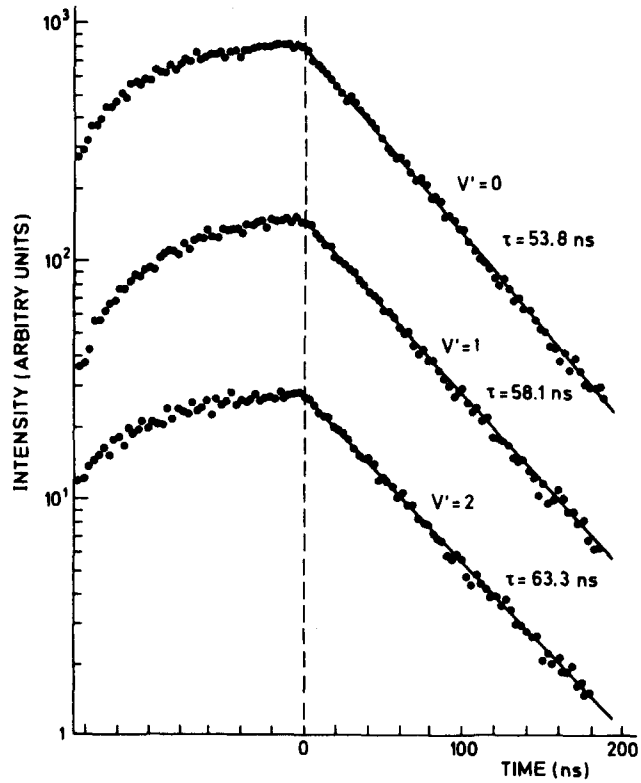

FIG. 3. Decay curves of the vibrational levels of the $B\,^2\Sigma^+$ electronic state of CO^+.

TABLE I. Radiative lifetime (μs) of the vibrational levels of the $A\,^2\Pi$ state of CO^+.

		Vibrational quantum number (v')				
		1	2	3	4	5
Present work	$v''=0$[a]	3.25±0.4	3.04±0.17	2.79±0.15	2.56±0.15	2.38±0.16
Reference 1	$v''=0$	2.61±0.20	2.48±0.21	2.36±0.15	2.22±0.13	2.11±0.13
	$v''=1$	2.95±0.22	2.74±0.21			
Reference 2	$v''=0$	2.60±0.10	2.46±0.10	2.22±0.12	2.11±0.10	2.04±0.15
	$v''=1$	3.09±0.12	2.81±0.12	...		
Reference 3	$v''=0$	...	...	...	2.60±0.50	...
Reference 4	$v''=0$	...	...	2.78±0.19	2.63±0.18	...
	$v''=1$	3.49±0.24				
Reference 5	$v''=0$	3.97±0.12	4.11±0.27	3.16±0.57	3.95±0.09	...
Reference 6	$v''=0,1$	3.58±0.18	3.09±0.15	2.85±0.14	2.69±0.13	2.58±0.13
Reference 7	$v''=0$		2.85±0.2			
Reference 8		3.8±0.5	3.1±0.7			

[a] v'' indicates the lower vibrational quantum number of the transition used to measure the lifetime.

be seen, our lifetime values decrease with the vibrational quantum number (v'), as can be deduced theoretically from the Franck–Condon factors of the *comet tail* system[18] and assuming no dependence of the electronic transition moment on the internuclear distance.[19]

In Table I the results of other authors are shown for comparison. Our results do not agree with early measurements performed using a pulsed electron beam[1] and the phase-shift method.[2] On the other hand, in these works there is no mention of any dependence of the lifetime on the electron beam intensity. The results obtained using a radio frequency discharge[5] do not show the expected lifetime dependence on the vibrational quantum number.

Our results are in good agreement, within the experimental errors, with those of Refs. 6 and 7 where a pulsed electron beam was used. In both cases the authors have carried out a study of the influence of space charge on the measurements. In order to avoid this distortion effect, two different methods have been employed. The authors of Ref. 6 have used low pressures (≤ 1 mTorr). In the work of Ref. 7 an additional low energy electron current has been used to neutralize the space charge. The method of the present work is somewhat different and depends on using very low electron excitation currents.

It is important to point out that our results are in good agreement with those of time-of-flight experi-

TABLE II. Radiative lifetime (ns) of the vibrational levels of the $B\,^2\Sigma^+$ state of CO^+.

	Vibrational quantum number (v')			
	0	1	2	Experimental method
Present work	53.8±0.8	58.1±0.8	63.3±1.0	Electron pulsed beam
Reference 9	39.5±3	39.5±3	38.8±4	Electron pulsed beam
Reference 10		101±5[a]		Electron pulsed beam
Reference 11	53.4	57.9±0.8	59.4±1.1	Phase shift
Reference 2	46±8	47	45	Phase shift
Reference 3	45±5	45±5		Time of flight
Reference 12	51.0±0.7	52.2±1.8		Pulsed discharge
Reference 13	58.6±0.7	64.1±0.8		Proton pulsed beam
Reference 14	54±5	50±5	52±6	Time of flight
Reference 15	54.3±1.8[a]			Electron–photon coincidence

[a] Average value over v'.

ments[3,4] which were free of space charge influence and with the lifetime values obtained by observing directly the time-resolved fluorescence following selective laser excitation.[8]

$B\,^2\Sigma^+$ state

The results of the lifetime measurements for the $B\,^2\Sigma^+$ state are shown in Table II, where we have compared our values with previous work. From our results, we can deduce that the lifetimes of the vibrational levels of this electronic state increase as the vibrational quantum number increases. Most other authors agree with this qualitative result. Our lifetime values do not agree with those of the first measurements performed by Lawrence[9] using the phase-shift method and by Schwenker[10] using a pulsed electron beam. However, our values are in good agreement with those of phase-shift measurements of Hesser.[11] The lifetime values given in Refs. 2, 3, and 12 are lower than ours and those of Ref. 13 are higher. Nevertheless, taking into account the experimental errors, no large discrepancy appears to exist. The results of the time-of-flight measurements of Ref. 14 are in agreement for the $v'=0$ level. The lifetime measurement of Smith *et al.*[15] obtained by using the electron–photon coincidence method is in good agreement with our values. In their experiment, no photon selection of the first negative system is performed. Their lifetime result is primarily due to the $v'=0$ level decay since most of the first negative emission arises from this level. Finally, we must note that in Refs. 2 and 13 the authors report a pressure dependence that we have not found in the pressure range of the present experiment.

SUMMARY

The radiative lifetimes of the $A\,^2\Pi$ and $B\,^2\Sigma^+$ vibrational levels have been measured. The effect of the space charge on the lifetime measurement of the $A\,^2\Pi$ levels of CO^+ has been observed. In order to avoid this distortion effect, a small electron beam current has been used. The present results are in good agreement with time-of-flight measurements[3,4] with pulsed electron beam values[6,7] and with selective laser excitation results.[8] In the measurement of the lifetime of $B\,^2\Sigma^+$ levels, no secondary effects have been observed. The present results agree with those obtained by means of very different experimental techniques as the phase-shift method[11] and the electron–photon coincidence method.[15]

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