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by

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Radiative Lifetimes of Ions from Electron-Photon Coincidence Measurements*

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New threshold electron-photon coincidence measurements are presented which enable one to directly measure the lifetimes and fluorescence quantum yields of selected vibronic states of ions. Results are given for the ($v_1$00) v_1 = 0,1,2,3 states and a combination state of the $\tilde{A}$ state and for the $\tilde{B}$ (000) state of CO_2^+.

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Here we present threshold electron-photon coincidence measurements of molecular ions which permit a direct measurement of the radiative lifetimes of individual vibronic states. We filter out the electrons with zero kinetic energy, since the ions in coincidence with these electrons have the internal energy given by the incident photons, a technique we developed previously /1/. Any measurements carried out in coincidence with these resonance electrons are state selected to the state prepared by the primary photons. We now observe that also secondary photons are scattered from the photoionization region, which, by coincidence with threshold electrons can now be assigned to the vibronic state so selected. These secondary photons are due to transitions from the $\tilde{A}$ and $\tilde{B}$ state of CO_2^+, to the ground $\tilde{X}$ state of CO_2^+, hence this is now the direct analogue to fluorescence detection in neutral molecules. State selected fluorescence means here that a fluorescence photon from an ion is counted only when a threshold electron has been detected. By this means the origin of the fluorescence photons is unambiguously determined.

In the present work, the fluorescence lifetimes for CO_2^+ $\tilde{A}$ $({}^2\Pi_u;\ v_1 = 0,1,2,3;\ v_2 = v_3 = 0)$ and CO_2^+ $\tilde{B}({}^2\Sigma_u;\ 000)$ were determined. The individual vibronic states of CO_2^+ were prepared in a photoionization experiment using dispersed continuum radiation from the storage ring DORIS at DESY in Hamburg, Germany /3/. The coincidence system has been previously described /2/ where, for the present experiments, a photomultiplier served to detect the fluorescence photons. In this previous work, the vibrational energy levels of the $\tilde{X}$, $\tilde{A}$, $\tilde{B}$ and $\tilde{C}$ states were determined by

threshold electron spectroscopy /1/ and the fragmentation of CO_2^+ in the $\tilde{C}$ state by threshold electron-ion coincidence measurements. A schematic diagram of the system is shown in figure 1. In the experiment, the photon wavelength is set to excite a particular vibronic state of the ion. A threshold electron pulse serves to start a time-to-amplitude converter (TAC) and a fluorescence photon to stop it. The coincidence pulses obtained from the TAC were stored in a pulse height analyser. The component electron and fluorescence photon signals as well as the incident (exciting) photon intensity were stored simultaneously. From these data both the radiative lifetime and the quantum yield of the ionic states can be determined. At the low signal levels observed, the coincidence signal follows the equation

$$n(t)dt = \left[A \cdot \exp\,(-\tau/t) + B \right] dt$$

where A is proportional to the true coincidence count, B the random coincidence count and τ is the radiative lifetime. A least squares analysis was used to fit the data to this equation.

Figure 2 shows a typical coincidence spectrum obtained by this method; in particular emission from the $\tilde{A}(100)$ state of CO_2^+ measured in coincidence with threshold electrons from this state. The radiative lifetimes determined here are given in Table 1 along with their standard deviations. As seen in Table 1, the radiative lifetimes of CO_2^+ $(\tilde{A})$ in $v_1 = 0,1,2$ and 3 for $v_2 = v_3 = 0$ exhibit no distinct trend. It is possible, however, that a dependence of lifetime on the vibrational state exists but is very small. For example, from experiments on N_2 and H_2 it was also found /4/ that the lifetimes of different vibrational states differed by only a fraction of a nanosecond.

The radiative lifetime observed for the $\tilde{B}$ state is significantly different from that of the $\tilde{A}$ state. This finding here is in contrast to the results of electron impact experiments where state selection is done in the emission and where the $\tilde{A}$ and $\tilde{B}$ states of CO_2^+ yielded lifetimes of 113± 12 and 118± 12 nsec. respectively /5/. The present method of state selection via threshold electron-photon coincidence measurements rules out the possibility of cascading from states above the one being studied. Such cascading may have lead to an averaged value in the above electron impact phasefluorimetry experiments. The total emission from the ion has also been determined in unselected ion-photon coincidence measurement at 584 Å in which an average value of 120 nsec was obtained /6/. The only other reported value for the lifetime of the $\tilde{B}$ state was obtained in a photoelectron spectroscopy experiment in which coincidence measurements gave a tentative value of 150 nsec /7/.

Another interesting example is the pumping of a Rydberg state at 691.4 Å which also produced threshold electrons followed by photons from the closest lying ion state. At this high energy several overtone-combination bands in the $\tilde{A}$ state would be possible. It is interesting that the lifetime of this state (165 nsec) is significantly longer then those of the other states observed perhaps because this state is an unfavorable combination of vibrational quanta with respect to possible final states.

The quantum yields given in Table 1 were obtained assuming a value

of 1.0 for the $\tilde{A}$ (000) state - an evidently reasonable assumption since, at the pressure measured no other decay channels are observed. There is no significant difference between the quantum yields of the various $\tilde{A}$ state transitions. The yield of the $\tilde{B}$ state is smaller, due to the fact that the emission was filtered to reject wavelengths below 3300 Å. Direct fluorescence transitions from $\tilde{B}$ to higher excited vibrational levels of the $\tilde{X}$ state lie outside the Franck-Condon region, as can be seen from the threshold electron /2/ or photoelectron spectrum of these states. Hence the observed red shifted light is most likely produced from ions which have crossed to the $\tilde{A}$ state prior to emission. The quantum yield could then be taken as a measure of this crossing yield, and hence constitutes a possible method for separating these two processes /8/.

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Table 1

Lifetimes τ and quantum yields ϕ_f for fluorescence emission of CO_2^+ vibronic states

	present work		phase shift method /5/	Photon-energetic PE coincid./7/	Photon-ion* coincid. /6/
	τ (nsec)	ϕ_f	τ	τ	τ
$\tilde{A}$(000)	102 ± 8	1.0	113 ± 12		$\tilde{A}$ + $\tilde{B}$: 120
(100)	100 ± 8	1.13	109		
(200)	102 ± 8	0.96	109	120	
(300)	113 ± 10	1.06	111		
($v_1v_2v_3$)	165 ± 10	1.06			
$\tilde{B}$(000)	138 ± 12	0.34	118 ± 12	(150)	

*The fluorescence quantum yield for $\tilde{A}$ reported in ref. 6 has slightly an other meaning and cannot be compared directly.

References

1. W.B. Peatman, T.B. Borne and E.W. Schlag, Chem. Phys. Lett. 3, 492 (1969)

   T. Baer, W.B. Peatman and E.W. Schlag Chem. Phys. Lett. 4, 243 (1969)
2. R. Frey, B. Gotchev, O.F. Kalman, W.B. Peatman, H. Pollak and E.W. Schlag, Chem. Phys. 21, 89 (1977)
3. V. Saile, M. Skibowski, W. Steinmann, P. Gürtler, E.E. Koch and A. Kozevnikov, Applied Optics 15, 2559 (1977)
4. R.E. Imhof and F.H. Read, J. Phys. B, 4, 1063 (1971)
5. J.E. Hesser, J. Chem. Phys. 48, 2518 (1968)
6. J.H.D. Eland, M. Devoret and S. Leach, Chem. Phys. Lett. 43, 97 (1976)
7. M. Bloch and D.W. Turner, Chem. Phys. Lett. 30, 344 (1975)
8. J.A.R. Samson, J.L. Gardner and J.E. Mentall, J. Geophys. Res. 77, 5560 (1972)

   E.P. Gentieu and J.E. Mentall, J. Chem. Phys. 64, 1376 (1976)

   P. Gauacq, M. Horani, S. Leach and J. Rostas, Can. J. Phys. 53, 2040 (1975)

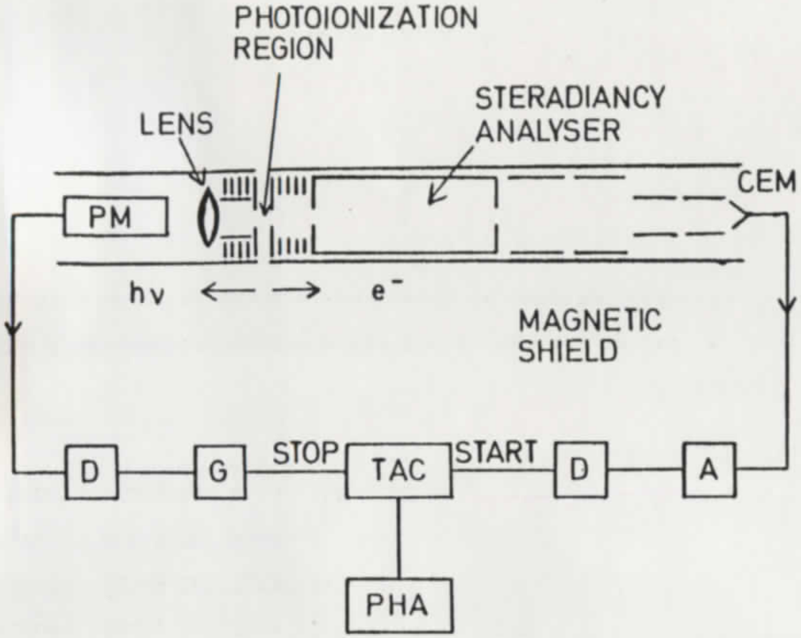

Fig. 1 Experimental set up, PM Photomultiplier CEM Channel electron multiplier, D Discriminator, G Gate and Delay, A Amplifier, TAC Time to Amplitude Converter, PHA Pulse Heigh Analyzer

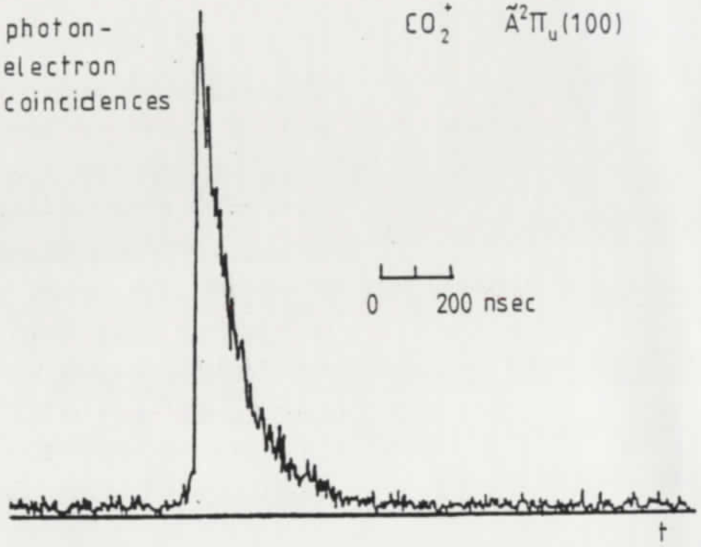

Fig. 2 Photon-Threshold electron coincidence curve showing the radiative decay of the $\tilde{A}$ (100) state of CO_2^+. The mean lifetime is 100 nsec.