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LIFETIMES OF Xe EXCIMER LEVELS*

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Rare-gas excimers have attracted considerable recent attention as the working media for ultraviolet lasers, but the basic dynamic radiation parameters of these systems are not well characterized. For example, in the Xe₂* molecule, which lases at 1700Å, the lifetimes of the 0_u and 1_u excited states are not accurately known, and conflicting values have been reported. Discrepancies have arisen because most measurements to date have been indirect owing to the lack of a suitable pulsed light source. In this note we report the first direct measurements of the fluorescence lifetimes of these levels using pulsed synchrotron radiation as a light source and monochromatized, time-resolved fluorescence detection.

The characteristic synchrotron radiation pulse structure at the Stanford Synchrotron Radiation Laboratory (0.4 nsec width, 780 nsec repetition time) was used as a time base for time-resolved spectroscopy. The apparatus is described elsewhere. Fluorescence detection was done with the aid of a toroidal mirror which focused fluorescent radiation on the entrance slit of a GCA/McPherson 218 monochromator. Single photon counting was carried out using an EMR 510G photomulti-
plier tube and standard pulse-counting techniques. These studies were done at ambient temperature, 294K, and at a pressure of 68 Torr.

The relevant electronic potential curves are shown in Fig. 1a. Absorption of monochromatized synchrotron radiation by van der Waals' molecules in the ground state yields the upper excimer state(s). At the resolution used for this study (8.7Å in excitation) it is possible to irradiate selectively below, at, or above the dissociation energy of a given excimer state, but resolution in the fluorescence spectrum of fine structure within a vibronic manifold is not possible. Others\textsuperscript{12,13} have found a broad fluorescence spectrum, with peaks near 1510Å and 1700Å; which are termed the "first continuum" and "second continuum", respectively. We qualitatively reproduced their spectra, though our excitation wavelength was 1508Å and our fluorescence channel band pass was 50Å (see Fig. 1b). By exciting at 1508Å (\( \geq 2kT \) below the \( {}^3P_2 \) atomic resonance), we have been able to avoid much of the complexity associated with atomic metastable production\textsuperscript{12} and extracted the relevant lifetimes, reported below.

Figure 2 shows time-resolved fluorescence decay curves taken at energies that emphasize the two continua separately. Only a single, short-lived (\( \tau = 2.1 \) nsec) component is observed at the first continuum wavelength of 1514 ± 25Å (Fig. 2a), corresponding to decay of \( O^+_u \) molecules.\textsuperscript{2,8} Since no long component is observed, we infer that the \( 1_u \rightarrow X0_g^+ \) and conversely the \( X0_g^+ \rightarrow 1_u \) transitions are practically forbidden at the 4-5Å internuclear separation of the van der Waals' molecule.\textsuperscript{2} The \( 1_u \rightarrow X0_g^+ \) radiative transition occurs at closer distances (3.4Å) as discussed below, but becomes a dipole forbidden \( {}^3P_2 - {}^1S_0 \) transition in the
separated atoms.

Fluorescence at the second continuum energy yields two decay components (Fig. 2b; the shorter component is depicted more clearly on an expanded time scale in Fig. 2c). We assign these two components to decay of the $0^+_u$ level (6.9 nsec) and the $1_u$ level (112 nsec), respectively, in agreement with other workers.

On excitation at 1508Å, the $Xe_2(0^+_u)$ level can decay either radiatively or via collisions:

$$Xe_2(0^+_u, \text{ high } v) \xrightarrow{k_1} Xe_2(0^+_g) + hv(1500\text{Å})$$

(1)

$$Xe + Xe_2(0^+_u, \text{ high } v) \xrightarrow{k_2} Xe + Xe_2(0^+_u \text{ or } 1_u, \text{ low } v)$$

(2)

The observed lifetime of 2.1 nsec is of course derived from the composite of these two processes: $\tau^{-1} = \tau_1^{-1} + \tau_2^{-1}$. Pressure-dependent studies are planned to separate the two effects.

The two-component decay evident in the second continuum fluorescence is consistent with the above processes, together with radiative decay of the products of Eq. (2). The measured lifetime of the $1_u$ level, at the second continuum energy, $\tau_4 = k_4^{-1} = 112$ nsec, is a lower limit: when pressure-dependent data becomes available, extrapolation to zero pressure will probably yield a longer lifetime. The same comment applies to the $0^+_u$ lifetime at 1690Å, viz. $\tau_3 = k_3^{-1} = 6.9$ nsec. Both of these values are in fairly good agreement with the values of Keto, Gleason, and Walters$^2$ which were measured by the use of electron excitation at 30 atm. pressure. Pressure dependent data on this system are still required, however, in order to fully understand the decay kinetics.
Again, we expect both the $O_u^+$ and $l_u$ lifetimes to be somewhat longer as $P \to 0$. For comparison, we note that Pitzer and co-workers\textsuperscript{14} have calculated $\tau_3 = 5.6 \text{ nsec}$ on a relativistic pseudopotential model. The comparable atomic lifetime of the $^3P_1$ state is $3.46 \text{ nsec.}$\textsuperscript{10} A very simple calculation assuming frozen orbitals shows that this must be equal to the molecular lifetime at the same energy: with a $v^3$ correction the $O_u^+$ lifetime would thus have a lower limit of $5.3 \text{ nsec}$, close to our result.

In summary, through combined use of a monochromator on the fluorescence channel and time-resolved measurements, we have spectrally separated different emissions and temporally separated components that are spectrally non-resolvable, in this case the $O_u^+$ and $l_u$ fluorescence.
REFERENCES

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FIGURE CAPTIONS.

Figure 1. a) Potential curves for the relevant electronic levels in Xe₂.
   after Fink and Comes. 12
   b) Fluorescence spectrum of Xe₂.

Figure 2. Decay curves following excitation of Xe₂ at 1508Å:
   a) in the first continuum;
   b) and c) in the second continuum.
   In (c) the time scale is expanded to show the O⁺ lifetime.
Fig. 2

(a) \( \lambda_{\text{ex}} = 1508 \, \text{Å} \)
\( \lambda_{\text{fl}} = 1514 \, \text{Å} \)
\( P_{\text{Xe}} = 68 \, \text{Torr} \)
\( \tau_3 = 2.1 \, \text{nsec} \)

(b) \( \lambda_{\text{ex}} = 1508 \, \text{Å} \)
\( \lambda_{\text{fl}} = 1690 \, \text{Å} \)
\( P_{\text{Xe}} = 68 \, \text{Torr} \)
\( \tau_3 = 6.9 \, \text{nsec} \)
\( \tau_4 = 112 \, \text{nsec} \)

(c)
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