

REACTION DYNAMICS OF ATOMS AND MOLECULES
USING THE PULSE CHARACTER OF SYNCHROTRON RADIATION

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1. Introduction

Synchrotron radiation (SR) is generally known as a pulsed, stable and tunable source of VUV radiation. These qualities are expected to be useful in studying spectroscopic and dynamic properties of highly excited atoms and molecules. The investigation has been carried out using mainly electron bombardment. Recently, however, several time-resolved measurements have been carried out using the pulse character of SR.^{1,2)} A reaction scheme actually has become much simpler using SR than electrons. An analysis of the experimental results thus becomes easier, and more reliable. Table 1 shows the pulse-to-pulse interval of SR and the corresponding experiments in single bunch operation at main facilities in the world.³⁾

The SOR-RING⁴⁾ at SRL-ISSP has recently been successful in single-bunch operation, where the time interval between two pulses is 58ns.⁵⁾ The first attempt at using the pulse character of SR from the SOR-RING has been successful recently and shown clearly that SR is a promising tool for studying reaction dynamics of state-specified highly excited atoms and molecules.²⁾

2. Time-Resolved Investigation of the De-excitation of Xenon Excimer by SF₆ and N₂²⁾

Time resolved fluorescence from vibrationally relaxed Xe₂^{*} (Ou⁺) excimer states has been observed in the selective excitation by SR pulses of Xe₂(Og⁺) van der Waals molecules in the presence of quencher molecules.

The apparatus is shown in Fig.1. Synchrotron radiation is dispersed by a 1.0m Seya-Namioka monochromator with a 600 line/mm grating. Dispersed light passes through an exit slit (2.5nm band pass for the maximum slit width) and enters a gas cell through a MgF₂ window. The fluorescence of the second continuum emission was measured by conventional single-photon counting with a delayed coincidence technique and accumulated in a MCA for several minutes.

The decay rate in the intensity of the second continuum emission was observed on the red-wing excitation of xenon gas with various partial pressures of a quencher molecule. The results are shown in Fig.2. The slope of the straight line gives the de-excitation rate constant of Xe₂^{*}(Ou⁺, low v) for SF₆ or N₂, respectively as $9 \times 10^{-10} \text{ cm}^3/\text{s}$ (300Å²) and $7 \times 10^{-12} \text{ cm}^3/\text{s}$ (2Å²). The magnitude of the obtained values shows a striking contrast with each other.

3. Fluorescence Lifetime Measurements of Liquid Hydrocarbons⁶⁾

An attempt of fluorescence lifetime measurements of liquid saturated hydrocarbons has been made with the following purposes: 1) To observe extremely weak fluorescence induced by SR pulses. The success in this observation will assure us of the usefulness of SR pulse character generally in measuring very weak signals from scientifically important systems. 2) To determine the fluorescent lifetime of liquid saturated hydrocarbons. The lifetime values have been obtained using a variety of pulsed excita-

tion sources; ordinary X-ray tubes, H₂ lamps, N₂ lasers, electron beams, etc.⁷⁾ The usefulness of SR in such measurements was expected earlier.⁸⁾ SR could be a new and the best excitation source whose energy can be selected continuously in the wide range of wavelength. This is the first attempt to measure the fluorescence lifetime of liquid saturated hydrocarbons by SR.

The experimental apparatus was almost the same as that in Fig.1. The sample purification method was similar to that used in the electron mobility measurements.⁹⁾ Fluorescence lifetime measurements were carried out at several excitation wavelength. In the case of cyclohexane, the FWHM of the fluorescence decay profile was only a little larger than that of the apparatus function, while in the case of bicyclohexyl two distinct fluorescence decay curves were observed as shown in Fig.3. The contribution of slow decay became larger in the wavelength region longer than about 180 nm. In the shorter wavelength region, the fluorescence showed only fast decay. It is a very interesting phenomenon although the reason is not known yet. As far as the signal intensity was concerned, it was clearly found that the SR light produced in the single bunch operation of the SOR-RING was strong enough for the present experiment dealing with the very weak fluorescence.

The fluorescence lifetime of sodium salicylate, a very useful wave-shifter or scintillator, has been tentatively measured using SR pulses. The result is shown in Fig.4. The obtained lifetime value, 4 nsec, is considerably shorter than those previously reported. Since this compound will be widely used also in the future for synchrotron radiation research, such measurements should be carefully carried out in detail.

References

- 1) O. Dutuit, R. A. Gutcheck and J. le Calvé, *Chem. Phys. Letters* **58**, 66 (1978); H. D. Wenck, S. S. Hasnain, M. M. Nikitin, K. Sommer, G. Zimmerer and D. Haaks, *ibid.*, **66**, 138 (1979); O. Dutuit, M. C. Castex, J. le Calvé and M. Lavollée, *J. Chem. Phys.*, **73**, 3107 (1980); T. D. Bonifield, F. H. K. Rambow, G. K. Walters, M. V. McCusker, D. C. Lorentz and R. A. Gutcheck, *ibid.*, **72**, 2914 (1980).
- 2) Y. Hatano, M. Ohno, N. Kouchi, H. Koizumi, A. Yokoyama, G. Isoyama, H. Kitamura and T. Sasaki, *Chem. Phys. Lett.*, **84**, 454 (1981).
- 3) Y. Hatano, KEK Report "Proc. Meeting on Pulse Structure of SR and its Applications" ed. by Y. Hatano and T. Ohta, KEK 81-16 (1982), p.32.
- 4) T. Miyahara, H. Kitamura, S. Sato, M. Watanabe, S. Mitani, E. Ishiguro, T. Fukushima, T. Ishii, Shi. Yamaguchi, M. Endo, Y. Iguchi, H. Tsujikawa, T. Sugiura, T. Katayama, T. Yamakawa, Se. Yamaguchi and T. Sasaki, *Particle Accelerators*, **7**, 163 (1976).
- 5) H. Kitamura, G. Isoyama, A. Uchida, S. Sato and T. Yamakawa, *Activity Report of SRL-ISSP-1979*, 95 (1980).
- 6) N. Kouchi, K. Shinsaka, Y. Nakamura, M. Toriumi, H. Koizumi, T. Tezuka, N. Takahashi, M. Ukai, S. Yano, G. Isoyama, Y. Hatano and T. Sasaki, *Activity Report of SRL-ISSP-1980*, 46 (1981).
- 7) Y. Katsumura, S. Tagawa and Y. Tabata, *Radiat. Phys. Chem.*, in press.
- 8) T. Wada and Y. Hatano, *J. Phys. Chem.*, **81**, 1057 (1977).
- 9) T. Wada, K. Shinsaka, H. Namba and Y. Hatano, *Can. J. Chem.*, **55**, 2144 (1977).

Table 1. SR Pulse Structure and the Experiments in Single Bunch Operation

Facilities	Pulse-to-Pulse Interval(nsec)	Fluorescence	TOF
ACO	73	Hemoglobin, fluorescein naphthol, NO, CO, etc. Xe ₂ [*] , Biologically important compounds	Ion dissociation H ₂ ⁺ , O ₂ ⁺ , H ₂ O ₂ ⁺ , etc.
DORIS	1000	Kr ₂ [*] , Xe ₂ [*] , Solids XeF ₂ [*] , XeF ₂ [*] , etc.	
SPEAR	780	Xe [*] , Kr [*] , Xe ₂ [*] Proteins (Polarized SR)	Solid surface Ion desorption Angle resolved electrons
SOR-RING	58	Xe ₂ [*] de-excitation Solid scintillation Liquid hydrocarbons Electronic quenching of radicals	
PF	624		
NSLS (VUV)	170		
UVSOR	170		

* Pulse width = $\sim 10^2$ psec

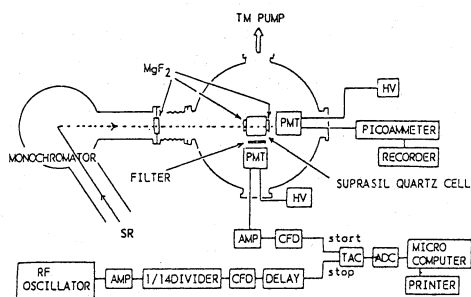


Fig.1. Schematic diagram of the apparatus

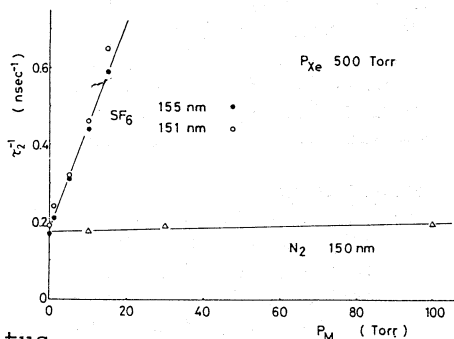


Fig.2. Observed decaying rates of the second continuum emission under red-wing excitation as a function of the pressure of SF₆ and N₂.

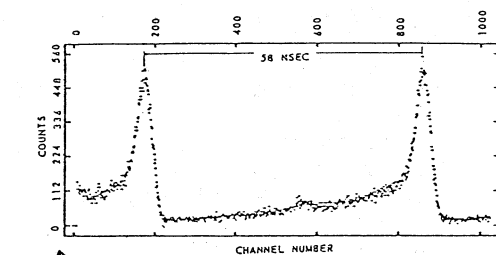
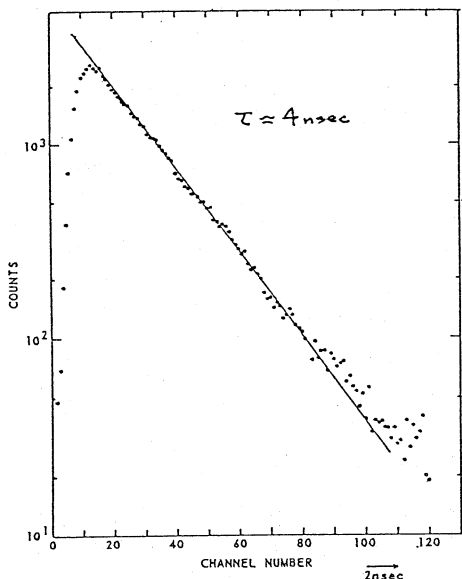


Fig.3. Time-resolved fluorescence of liquid bicyclohexyl at 230 nm excitation (17°C).
 Fig.4. Observed fluorescence decay of sodium salicylate.