CROSS-BEAM STUDIES OF CHEMILUMINESCENT REACTIONS OF METASTABLE ATOMS

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Molecular beam acceleration, using the high speed rotor technique originally devised by Bull and Moon[1], provides an excellent basis for generating supersonic beams of metastable atomic (or molecular) reagents, e.g. $Xe(^3P_{0,2})$, $Kr(^3P_{0,2})$..... $Hg(^3P_{0,2})$. A novel cross-beam system has been constructed[2] to study the chemiluminescent interaction of metastable atoms with molecular reagents, at collision energies tunable in the range $\leq$ 1.5 eV. It incorporates a carbon fibre composite shafted rotor, which is spun in a gas at low pressure (typically 10^{-4} Torr) at frequencies $\leq$ 4000 Hz, achieving tip speeds $\leq$ 2 km s^{-1}. The rotor, which is magnetically levitated and driven, propels a pulsed atomic beam through an electron bombarder, where a small proportion of the beam is excited into a metastable state. For example, the system generates pulses of metastable $Xe(^3P_{0,2})$ containing $\sim 10^5$ excited atoms/pulse at an average flux $\sim 10^{12}$ sr^{-1} s^{-1}. These intersect a nozzle beam of the molecular reagent at 90° and the chemiluminescence signals are monitored along the third perpendicular axis using photon counting and multichannel scaling techniques. A schematic diagram of the system is shown in fig. 1.

The technique is being used to study the molecular dynamics of a number of chemiluminescent reactions through the following types of observation.

a) Chemiluminescence spectra: for illustration, the fluorescence spectra generated under single collision conditions during the cross-beam interaction of $Xe(^3P_{0,2})$ with Br_2, CCl_4 and BrCN will be displayed at the Poster Session.

b) Fluorescence polarizations[3]: the anisotropy of the fluorescence, parallel and perpendicular to the relative velocity vector of the colliding beams, can be recorded as a function of the fluorescence wavelength and collision energy. Results for the fluorescence from XeBr* generated in the reaction

$$Xe(^3P_0) + Br_2 \rightarrow XeBr^* + Br \qquad (1)$$

and recorded at the 'primary' band at (280 ± 10)nm, are shown in fig. 2.

c) Excitation functions: results have been obtained for reaction (1) (see ref. 2(b)) and for the reaction of $Xe(^3P_{0,2})$ with BrCN (see fig. 3).

The observations provide information on the translational energy dependence of the total chemiluminescent reaction cross-section and of the energy disposal and the disposition of orbital and internal angular momenta in the separating products. In reaction (1) for example, the polarization of the fluorescence from $XeBr^*$, $p = (I_{/\!/} - I_{\perp})/(I_{/\!/} + I_{\perp})$, increases towards a limiting value $p \sim +\frac{1}{3}$ as the rotor speed increases (see fig. 2). The positive polarization, which has the same value at the 'primary' ($\sim$ 280 nm) and 'secondary' ($\sim$ 350 nm) bands, confirms the assignment of each component to transitions polarised parallel to the molecular axis, i.e. with $\Delta\Omega = 0$. The increasing anisotropy with increasing collision energy reflects the approach to spectator-stripping dynamics and in general, the observations reinforce the similarity of reaction (1) to the reaction of alkali metal atoms with halogens.[4] The measurement of polarization ratios at controlled collision energies and at selected wavelengths in the chemiluminescence spectrum is particularly advantageous, since it allows state selection in both the reagent and product channels.

1) T.H. Bull and P.B. Moon, Faraday Discussions, 17, 54, (1954)

2) (a) P.B. Moon, C.T. Rettner and J.P. Simons, J. Chem. Soc., Faraday II, 74, 630, (1978)

(b) M.R. Levy, C.T. Rettner and J.P. Simons, Chem. Phys. Letters, 54, 120, (1978)

3) The utility of fluorescence polarization measurements in cross-beam studies has been emphasised by

(a) D.A. Case, G.N. McClelland and D.R. Herschbach, Mol. Phys., 35, 541, (1978)

(b) C.D. Jonah, R.N. Zare and Ch. Ottinger, J. Chem. Phys., 56, 263, (1972)

(c) J.L. Kinsey, Ann. Revs. Phys. Chem., 28, 349, (1977)

4) M.F. Golde in "Gas Kinetics and Energy Transfer", Vol. 2, Chem. Soc. Specialist Per. Reps., 123, (1977)

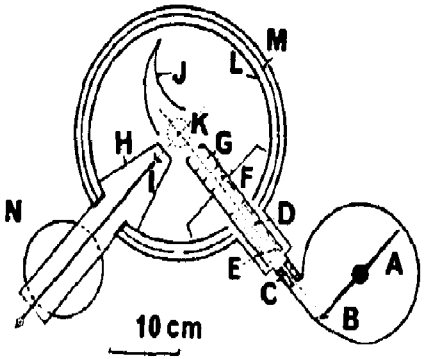

Fig. 1a Apparatus: horizontal cross section. A rotor; B line of He/Ne laser; C collimation; D exciter grid; E exciter filaments; F ion deflector; G light baffles; H liquid nitrogen-cooled cross-beam bulkhead; I cross-beam nozzle source; J Wood's horn; K photomultiplier position (above); L cold shield; M radiation shield; N differentially pumped cross-beam vessel.

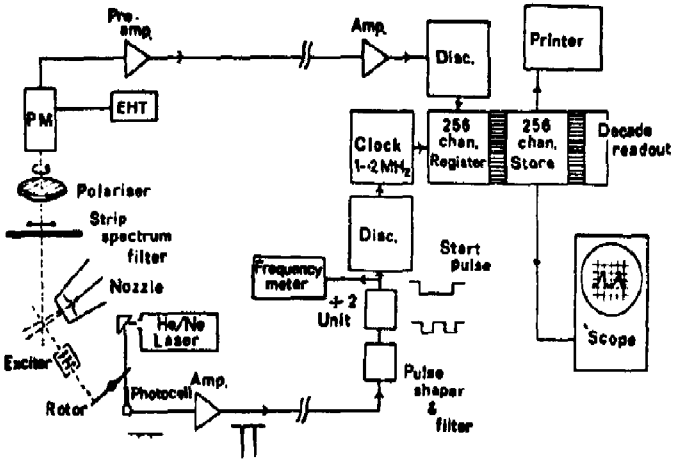

Fig.1b. Block diagram of data collection system

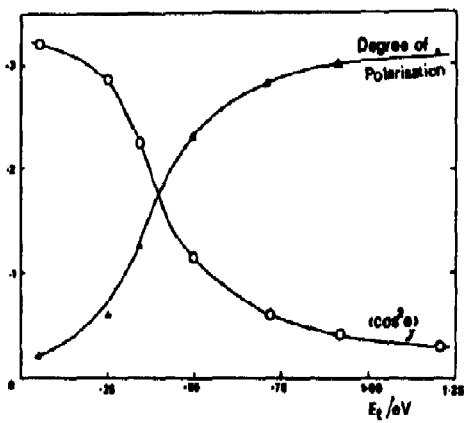

Fig.2. Polarization of fluorescence from $XeBr^*$.

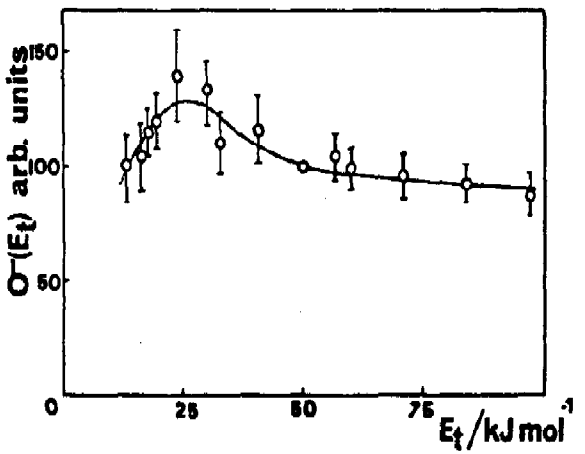

Fig.3. Excitation function for CN(B→X) fluorescence from $Xe(^3P_{0,2})$ + BrCN.