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QUEEN MARY COLL LONDON (ENGLAND) DEPT OF CHEMISTRY F/G 7/4  
KINETIC STUDIES INVOLVING ELECTRONICALLY-EXCITED INTERHALOGENS --ETC(U)  
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
The following areas are covered: (a) kinetics of chemiluminescent reactions involving excited B states of halogens and interhalogens; (b) measurement of halogen atom concentrations; (c) studies of halogens and interhalogens by laser-induced fluorescence. Citations to 26 papers are given.		

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SUMMARY OF WORK

*Kinetic Studies Involving Electronically-Excited Interhalogens and Halogens*

1. Senior Research Personnel: Dr. I. S. McDermid; Dr. J. P. Liddy; Dr. E. Martinez; Professor S. Toby; Professor S. Jaffe; Dr. D. J. Smith.
2. Junior Research Personnel: Mr. P. D. Whitefield; Mr. M. C. Heaven.
3. Abstract of Objectives and Accomplishments

(a) Kinetics of chemiluminescent reactions involving excited B states of halogens and interhalogens.

The kinetics of the chemiluminescent atom-recombination reactions  $\text{Cl} + \text{Br} + \text{M} \rightarrow \text{BrCl} (\text{B}) + \text{M}$ ,  $\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 (\text{B}) + \text{M}$  and  $\text{Br} + \text{Br} + \text{M} \rightarrow \text{Br}_2 + \text{M}$  have been determined. Branching ratios for forming the excited states were determined; all lie in the range 0.01 to 0.1.

The kinetics of the chemiluminescent reaction of  $\text{Br}_2$  with  $\text{OClO}$  have been studied. The overall reaction was characterized as a branched-chain process. The branching ratio for forming excited  $\text{BrCl} (\text{B})$  is  $> 0.05$ .

New spectroscopic data on the B and X states of  $\text{BrCl}$  are reported.

(b) Measurement of halogen atom concentrations

Methods based on atomic resonance absorption and fluorescence have been developed for measuring  $\text{Br}$  and  $\text{Cl}^2\text{P}_{3/2}$  and  $^2\text{P}_{1/2}$  atom concentrations over a wide range of densities, and in mixtures of different halogen atoms. The variation of oscillator strength within the  $(n+1)s - np^5$  resonance multiplets has been exploited in wavelength-resolved atomic resonance studies.

(c) Studies of halogens and interhalogens by laser-induced fluorescence (LIF)

A state-of-the-art narrow-band, pulsed dye laser has been used to study the quantum-resolved dynamics of excited  $\text{B}^3\Pi(0^+)$  states of  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{BrCl}$ ,  $\text{BrF}$ ,  $\text{IF}$ ,  $\text{ICl}$  and  $\text{IBr}$  and the  $\text{A}^3\Pi(1_u)$  state of  $\text{Br}_2$ . The first observation of quantum-resolved LIF is described for all of these molecules other than  $\text{Br}_2 (\text{B})$ . The first direct determinations of radiative lifetimes by LIF is described for the B states of  $\text{Cl}_2$ ,  $\text{BrF}$ ,  $\text{Br}_2$ ,  $\text{IF}$  and for the A state of  $\text{Br}_2$ . Detailed studies of predissociation dynamics are reported. Measurements of rate constants for electronic quenching, collisional predissociation and ro-vibrational transfer are reported. In most cases, quenching of the B states is slow, but vibrational transfer is fast, thus favouring the B-X transitions as electronic-transition laser candidates.

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