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QUANTUM-RESOLVED DYNAMICS OF HALOGENS AND INTERHALOGENS AND STUDIES OF NF AND PF RADICALS

Kinetic studies of ground and excited states of NF and PF radicals were carried out to determine radiative lifetimes, branching ratios, and quenching rate constants. Similar studies were performed on the diatomic halogens and interhalogens in order to identify and study the dynamics of ground and excited states in order to evaluate the laser potential of these species.

Highlights of major achievements of the program include the following:

The reaction H plus NF(a) has been shown to yield N ²D + HF. The formation of excited molecular states from the H + NF2 reaction has been investigated. The reaction has been shown to give NF(a) with a branching ratio greater than or equal to 0.9. Intense N_2 (B-A) and Lyman-Birge-Hopfield emission is believed due to the formation of the relevant excited states in the highly excergic reaction of N 2D atoms with NF(a). N 2D + H₂ is believed to be the precursor reaction of triplet and singlet states of NH. The lifetime of NF(b) has been determined using a pulsed discharge technique. NF(b) is formed by the reaction of Ar $^{3}P_{2,0}$ metastables with NF3 or N2F4. The first study of state-to-state vibrational transfer in excited Brf(B) was reported. State-selective chemistry of the NCl free radical has been investigated using collision-free mass spectrometry. The precursor of ground state NC1 (X triplet sigma) and excited state NCl (a singlet delta, b singlet sigma) is the rapid excergic reaction Cl + N_3 = NCl + N_2 . While ground state NCl does not react at 298K with Clo. excited state NCl(b) forms NClo by reaction with Clo in an expergic step. Radiative lifetimes and quenching data have been determined for the A singlet pl and b prime triplet pl states of SnO.

Among the results of this research program are the scientific reports listed below.

 "Non-Reversed Source of Br Atom Resonance Radiation and its Application to the Measurement of Br Atom Concentrations," M.A.A. Clyne and D.J. Smith, J. Chem. Soc. Faraday II <u>74</u>, 263 (1978).

2. "Quantum-Resolved Dynamics of Excited States. Part 1. Predissociation in the B $^{3}\pi$ (O+) State of BrF," N.A.A. Clyne and I.S. McDermid, J. Chem. Soc. Faraday II, <u>74</u>, 644 (1978).

3. "Quantum-Resolved Dynamics of Excited States. Part 2. Stable Levels of the B $^{3}\pi$ (Q+) State of BrF," M.A.A. Clyne and I.S. McDermid, J. Chem. Soc. Faraday II, <u>74</u> 664 (1978).

4. "Studies of BrCl by Laser-Induced Fluorescence. Part 1. Excitation Spectra and Predissociation in the Excited B $^3\pi$ (0+) State," M.A.A. Clyne and I.S. McDermid, J. Chem. Soc. Faraday II, <u>74</u>, 796 (1978).

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5. "Studies of BrCl by Laser-Induced Fluorescence. Part 2. State-Selected Kinetics in the Excited B 3 $_{\rm II}$ (0+) State of BrCl," M.A.A. Clyne and I.S. McDermid, J. Chem. Soc. Faraday 11, <u>74</u>, 807 (1978).

6. "Quantum-Resolved Dynamics of Excited States. Part 3. Collision-Free Lifetimes of BrF(B)," N.A.A. Clyne and I.S. McDermid, J. Chem. Soc. Faraday II, <u>74</u>, 1376 (1978).

7. "Kinetic Spectroscopy in the Far Vacuum Ultraviolet. Part 5. Oscillator Strengths for the 3s, 4s, 5s, 3d, and 4d $^{4}P_{J} = 2p^{3} \frac{4Sg}{2}$ Transitions in Atomic Nitrogen," N.A.A. Clyne, S. Jaffe, and P.D. Whitefield, J. Chem. Soc. Farraday II, 76, 369–382 (1980).

B. "Laser-Induced Fluorescence of the BO and BO₂ free radicals," N.A.A. Clyne and N.C. Heaven, Chem. Phys. <u>51</u>, 299-309 (1980).

9. Reactions Forming Electronically Excited Free Radicals. III. Formation of Excited Molecular States in the H + NF₂ Reaction," C.T. Cheah, M.A.A. Clyne, J. Photochem. <u>15</u>, 21–35 (1981).

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