

### III. MOLECULAR ENERGY TRANSFER AND SPECTROSCOPY\*

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#### RESEARCH OBJECTIVES AND SUMMARY OF RESEARCH

##### 1. Resonance Fluorescence Spectroscopy

a. The fluorescence of iodine vapor excited by the 5145 Å line of the Argon ion laser has been assigned as originating primarily from  $V' = 43$ . Bands arising from molecules that have gained or lost as many as eight vibrational energy quanta, on account of collisions with added foreign gases, have been observed in emission.

b. The fluorescence of iodine vapor excited by the 5086 Å line of the cadmium arc has been identified as originating primarily from  $V' = 50$  and 55. In these high levels, quenching by collisional release of the excited iodine atom becomes a significant process. The high quenching efficiencies are observed to compete effectively with vibrational energy transfer.

c. The spectroscopic analysis of the visible absorption system of iodine has been extended further toward the dissociation limit, in order to aid in the interpretation of fluorescence spectra. The long-range attractive potential between the iodine atoms appears to have an  $R^{-5}$  dependence, which is attributed to quadrupole interactions.

d. The magnetic quenching of the iodine vapor fluorescence has been reanalyzed, in collaboration with Dr. E. Wasserman of Bell Telephone Laboratories, Inc. The vibrational dependence of the quenching probability maps out the dissociative potential; also, an independent determination of the vibrational dependence of the collision-induced self-quenching cross section is obtained.

e. A calculation of transition probabilities for the collision-induced predissociation quenching mechanism is being carried out. The probability is found to be proportional to the polarizability of the quenching partner, in agreement with observations.

The extension of this work will involve measurement of the depolarization of fluorescence excited by the Argon ion laser, in order to determine the extent of molecular reorientation accompanying inelastic collisions. Photon counting techniques will be applied to the measurement of weak fluorescence signals. Since the radiative lifetime is an important parameter in these systems, we shall apply excitation by pulsed dye lasers to redetermine this quantity. Other systems that can be investigated in this way include  $O_2$  (particularly the  $^{17}O^{18}O$  isotope) excited by the mercury 1849 Å line, TlI as an example of a polar molecule, and a possible variety of small polyatomic molecules. Some further theoretical calculations of vibrational energy transfer are planned,

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### (III. MOLECULAR ENERGY TRANSFER AND SPECTROSCOPY)

appropriate to closely spaced levels with large inelastic probabilities. The problem of vibrational energy transfer in the presence of quenching may also be investigated with the use of an optical potential model.

#### 2. Optical Double Resonance

a. Saturation of a vibrational absorption band in sulfur hexafluoride by high-power infrared radiation from a carbon dioxide laser has been measured, and interpreted in terms of a four-state linear kinetic model. The results give some insight into the relaxation processes occurring in the gas, and also predict a population of excited vibrational states under irradiation adequate to carry out double-resonance spectroscopy and molecular-beam scattering experiments. The last are being carried out in collaboration with Professor John Ross. Additional work needs to be carried out on the response of these systems to pulsed radiation.

b. Two double-resonance experiments are being readied. One involves infrared pumping and infrared absorption in sulfur hexafluoride itself; other possibilities include boron trichloride and ethylene. The second involves infrared pumping and ultraviolet absorption in propynal vapor.

c. Band contour analysis of the  $\nu_3$  absorption in sulfur hexafluoride at  $940\text{ cm}^{-1}$  is being carried out in order to assign the rotational levels that are pumped by infrared laser radiation.

#### 3. Faraday Rotation Quenching

Work is beginning on the pressure effects on the intensity of magneto-optic rotation (Faraday effect). A theoretical analysis of the relation between collision parameters and intensities will be carried out first, followed by an experimental investigation of these effects in such systems and iodine monochloride, glyoxal, etc.

#### 4. Dye Solution Lasers

Some earlier work carried out in collaboration with Dr. M. Bass of Raytheon Research Corporation indicated time-dependent behavior of the output of dye solution lasers, which gave information about relaxation processes involving dye molecules in solution; for example, the vibrational relaxation time can be as long as  $10^{-8}$  sec for the lower levels of cryptocyanine dyes. We plan to continue and extend this work here. We are also investigating the absorption and emission spectra of these dyes at  $4.2^\circ\text{K}$  to try to clarify the homogeneous and inhomogeneous contributions to the observed spectral widths.

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