LUMINESCENCE STUDIES WITH SPECIAL REFERENCE TO BIMOLECULAR
PHENOMENA

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ABSTRACT

Bimolecular transitions in oxygen were investigated theoretically. It is shown that relative intensities of the bimolecular transitions can be predicted without invoking any type of bonding between a pair of oxygen molecules. The influence of vibronic perturbations in inducing transition probability was assessed. The luminescence of oxygen pair following the optical excitation of one of the double molecule transitions is partially investigated.

Emission spectra of s-tetrazine and pyrazine were studied under collision free conditions. Absorption spectrum of s-tetrazine was assigned to be due to one allowed and one forbidden transition. It was shown that these two transitions are within 300 cm^{-1} of each other - an unusual case. Luminescence of s-tetrazine was analyzed in great detail and the rates of radiative and non-radiative transitions were computed for free s-tetrazine and for s-tetrazine in presence of foreign gases.

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I Bimolecular Transition

Work Completed

Oxygen in the liquid and the solid state and at high pressures in the gaseous state show bimolecular absorption, in which two molecules are simultaneously excited by a single photon. While this phenomenon can be expected to be present in other systems, it is only in oxygen the bimolecular electronic transitions have been studied in depth experimentally. This is because the forbidden transitions in oxygen are located in the near infra-red and the frequencies of the bimolecular transitions fall in the transparent visible region. The five electronic transitions that are clearly characterized are:

- A. $^3\Sigma_g^- \rightarrow ^1\Delta_g + ^3\Sigma_g^- \rightarrow ^3\Sigma_g^-$
- B. $^3\Sigma_g^- \rightarrow ^1\Sigma_g^+$
- C. $^1\Delta_g \rightarrow ^1\Delta_g$
- D. $^1\Delta_g \rightarrow ^1\Sigma_g^+$
- E. $^1\Sigma_g^+ \rightarrow ^1\Sigma_g^+$

In spite of the extensive experimental work and the importance of bimolecular phenomena in the energy transfer processes in condensed media, rigorous theoretical studies on these bimolecular transitions have been lacking before. Systematic attempts have been made to develop a fairly general theory of the bimolecular transitions in oxygen.

The details of the calculations and the results are published.^{1,2} The theory gives a satisfactory agreement with the experimentally measured transition probabilities.

The following is abstracted from the published work:

- A. "A fairly general theory of the relative intensities of the transitions $^1\Delta_g \leftarrow ^3\Sigma_g^-$ and $^3\Sigma_g^- \leftarrow ^1\Delta_g$ in oxygen is given. The theory rests on the postulate that the terms in the above transitions mix with other bimolecular terms due to the intermolecular forces. Intermolecular exchange is shown to be essential for a successful interpretation of these transitions. Calculations are done neglecting the intermolecular overlap, but including all the electrons in the theory. All the allowed interactions, in the absence of intermolecular overlap, are considered in the theory. No assumption regarding the geometry of the $O_2 \dots O_2$ pair is made. The theory predicts that relative oscillator strengths of the above two transitions (former to latter) should be 1.20. This is in excellent agreement with the experimental results. Theoretical predictions are shown to be unaffected when the intermolecular overlap is included in the calculations. The above results are derived from the ratios of interactions and thus are independent of approximations commonly used in the evaluation of integrals."
- B. "A general theory of the oscillator strengths of the three bimolecular transitions, $^3\Sigma_g^+ \leftarrow ^3\Sigma_g^-$, $^1\Sigma_g^+ \leftarrow ^3\Sigma_g^-$, and $^1\Sigma_g^+ \leftarrow ^1\Sigma_g^-$, in oxygen is given. The intensity of these three transitions is assumed to be derived from the allowed transitions due to mixing of the electronic terms through the intermolecular interaction. The theoretical techniques developed in Paper I of this series are used. No particular geometry for the $O_2 \dots O_2$ pair is assumed. All electrons are included in the theory and all the interactions, allowed in the absence of intermolecular overlap, are considered. Two

experimentally significant points emerge from this work.

(1) Each of these three transitions should be considerably weaker than either of the two transitions $^1\Delta_g \rightarrow ^3\Sigma_g^-$ and $^1\Delta_g \rightarrow ^1\Delta_g$ discussed in Paper I. This is because while the latter transitions can borrow from several allowed transitions, including the strongly-allowed $\pi-\pi$ transitions, the former can borrow only from transitions involving $\pi-\sigma$ excitation which are expected to be at higher energy and to have relatively small oscillator strengths. (2) The relative oscillator strengths of these three transitions considered here agree fairly well with experiments."

The main conclusions from these studies are:

- (i) No particular binding between oxygen molecules need be invoked for the bimolecular transitions to be allowed and that van der Waals or weak dispersion forces are sufficient for inducing the bimolecular transition probability.
- (ii) The bimolecular transitions are electric dipole transitions.
- (iii) Further theoretical study of the intensities of the bimolecular transitions as a function of pressure would give a detailed description of intermolecular potentials in the excited states.

Work Partially Completed

1. The Franck-Condon factors for the oxygen bimolecular transitions are anomalous. These transitions show strong (0",0') and (0",1') bands in absorption. The rest of the bands are either quite weak or not present in the spectrum. One normally expects a smooth variation of the Franck-Condon factors with the vibrational quantum number.

In our calculations it was found that the geometric configuration of oxygen pairs that give the maximum energy of stability is not the same as the configuration in which the transitions are allowed. Therefore, these transitions can be expected to show characteristics of forbidden transitions that become allowed through vibronic perturbation. In the case of oxygen pairs these vibrations could also be the intermolecular vibrations (phonons). Work is partially completed in assessing the influence of the intermolecular vibrations and the intramolecular vibration of oxygen in inducing the transition probability. The possibility of oxygen vibration of $\approx 1400 \text{ cm}^{-1}$ inducing an electric dipole transition probability has not been mentioned in literature. From our preliminary calculations, this path seems to be a very significant one.

2. Experimental work was undertaken in which the bimolecular transitions, particularly (C), were excited optically. The aim is to measure the life-times and quantum yields for these processes from the observed photoluminescence. These experiments are very inconclusive due to the extreme weakness of the signals (assuming we are observing proper signals). More recently we acquired a nitrogen laser and built a dye laser. We are in the process of repeating the photoluminescence experiments with the dye laser as an excitation source and a box-car integrator as a signal averager.

The aim of this experiment is to correlate the observed life-times and quantum yields with the inter and intramolecular processes: (i.e.) radiative processes and the nonradiative processes such as "dissociation" of the oxygen pair.

II Nonradiative Transitions in Azines

In recent years there has been a resurgence of interest in the study of nonradiative transitions in molecules. Most of the current research is theoretical and only a few experimental investigations that have a direct bearing on the theory have been reported.^{3,4} The need for a clear understanding of the non-radiative processes for explaining and predicting various photo-biological and photochemical processes has been recognized.

Work Completed

1. The luminescence of s-tetrazine was studied under collision-free conditions. Excitation was done with radiation of narrower wavelength spread than the vibrational widths of s-tetrazine absorption. In my opinion, studies with comparable resolution (in polyatomic systems) are not available except in the case of benzene. The details of the work are published now⁵ and the following abstract is taken from the published work.

"Fluorescence of s-tetrazine in the collision-free region resulting from excitation into (0',0'') and three sequence bands has been investigated. The quantum efficiency of emission from the four corresponding vibronic levels has been determined. A marked variation in the quantum efficiency from level to level and within the envelopes of vibrational bands is found. The quantum yields do not show a systematic decrease or increase with the energy of the vibronic levels. Quenching of the resonance fluorescence by 3-methylpentane and argon has been studied. Bimolecular processes--vibrational deactivation and quenching of total fluorescence--are found to be very inefficient. The number of hard-sphere collisions

needed for these processes ranged from 50 to several hundred depending on the vibronic level.

2. In connection with the above work on nonradiative transitions we undertook to assign the vibrational structure of the visible absorption of s-tetrazine. From the molecular orbital theory, we expect eight $n\text{-}\pi^*$ transitions in the visible and ultraviolet region. Six of these transitions are forbidden, but could be allowed through vibronic coupling or other mechanisms. The absorption spectrum (in the visible) consists of unusually sharp vibrational bands. The principle progression involves 700 cm^{-1} excited state vibration.

Careful analysis of the spectrum revealed the existence of two states, $^1B_{3u}$ and 1A_u within 300 cm^{-1} of each other. Transition to the second state is allowed through vibronic mixing.

I do not know any well-documented cases of two electronic levels (in molecules with well-resolved spectra) as close to each other as in this case. Therefore, this absorption spectrum would offer a unique opportunity to study the vibronic and other coupling mechanisms in great detail.

The main conclusions from this work are:

- (i) Nonradiative transitions are very efficient even in the absence intermolecular interactions.
- (ii) Rate of nonradiative transitions critically depend on the vibronic level of the electronic transition.
- (iii) Rate of nonradiative transitions may also depend on the rotational substructure of the vibronic level.
- (iv) Vibrational relaxation in the excited electronic state in the vapor phase is quite inefficient even at relatively high pressures (150 torr) of foreign gases.

Work Partially Completed

The emission spectrum of pyrazine in the vapor phase in the collision-free region was studied. Both phosphorescence (with steady state illumination) and fluorescence (with steady state illumination and pulsed excitation with a nitrogen laser) were investigated. The emission spectrum of this molecule gives an excellent example for intersystem crossing without the aid of intermolecular perturbation. The analysis of the existing emission data will be completed in future.

References

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LIST OF PUBLICATIONS

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1. V. G. Krishna, J. Chem. Phys. 50, 792 (1969).
2. V. G. Krishna and T. Cassen, J. Chem. Phys. 51, 2140 (1969).
3. G. K. Vemulapalli and T. Cassen, J. Chem. Phys. 56, 5120 (1972).