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Perturbation Effects on Molecular

and Resonance Pair Triplet Excited States

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by

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ABSTRACT OF THE DISSERTATION

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This thesis contains both theoretical (Chapters I, II and III) and experimental studies (Chapter IV). The aim behind the theoretical study is to examine the effect of various perturbations on the behavior of the lowest excited triplet states of molecules. The most prominent of these perturbations is the interaction of two identical molecules in an exciton type of energy transfer. The intermolecular potential between two molecules, one of which is in its first excited triplet state, leads to what is known as a triplet resonance pair whose behavior is studied in terms of the molecular triplet properties. Another interesting feature is the Stark effect on the triplet resonance pair and the electric field modification of such parameters as zero-field splittings, relative radiative power and populating rate constants of the zero-field levels. Furthermore, the relative orientation of the two interacting molecules is an important factor that is taken into account. The interaction of the triplet resonance pair bears some
limited resemblance (at least in the perturbation technique of calculations) to that in the singlet excited state. Furthermore, the behavior of such a pair largely depends on the coupling in the singlet manifold (via spin-orbit effects). As a result, a detailed discussion of the singlet resonance pair is of utmost necessity for full understanding of the problem.

The use of microwaves to modify the photochemical rate constant of a photoreactive molecular triplet is another aspect that is suggested as a means of isotope enrichment. Finally, heavy-atom substitution and its effect on the dynamic behavior of aromatic molecular triplets is investigated.

In Chapter I, equations describing the energy transfer process in singlet resonance pairs are derived by stationary and non-stationary perturbation techniques. The intermolecular potential responsible for such energy transfer is investigated in the dipole-dipole approximation as a function of relative orientation of the two molecules. Equations for the eigenfunctions and eigenvalues of the resonance pair both with and without applied electric field are derived. Furthermore, the transition moments and the polarization of emission of the singlet resonance pair states as a function of geometry and applied electric field are studied.

The second chapter starts by deriving equations for the matrix element of the intermolecular potential and spin-spin Hamiltonian of the triplet resonance pair. The effect of relative molecular orientation and the matrix elements of the applied electric field are also included. The six by six matrix is solved by matrix
diagonalization for a hypothetical pair of molecules having assumed zero-field splitting parameters as well as relative radiative power and $S_1 \rightarrow T_1$ intersystem crossing rate constants. Figs. 2-5 give the variation of the zero-field energies of the triplet resonance pair as a function of rotations of one of the molecules. Figs. 6-9 give that same dependence on the intermolecular potential $V_{12}$ and the electric field $F$. In the strong coupling limit ($V_{12} \gg D_1E = \text{zero-field splitting parameters}$) the geometric dependence obtained is in agreement with that derived by using an average spin-spin Hamiltonian (Ch. II, Ref. 18) and the zero-field splitting parameters $D_1^*$ and $E_1^*$ of one triplet resonance pair state are equal to those of the second. The high field limit results in the zero-field splitting parameters of the molecular triplet. From the coefficients of the resonance pair states and the molecular triplet's relative radiative power and intersystem crossing ratios, calculation of these quantities for the triplet resonance pair was also achieved and Figs. 10-18 show typical results including geometry dependence and electric field effects. Needless to say, the molecular parameters are extracted at high electric fields. To test the validity of our calculation, the naphthalene resonance pair was studied by similar methods and the zero-field parameters obtained in this work are in good agreement with experimental as well as theoretical (Tedder) values. It was further found that just as in molecular naphthalene, the top level of the two triplet resonance pair states is the most radiative. The chapter closes with a brief discussion of spin-lattice relaxation effects.

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In Chapter III, the feasibility of using microwaves resonant with the zero-field levels of photoreactive triplets, in order to bring about isotope enrichment of molecules containing isotopic species, is discussed. The method makes use of the fact that either the different triplet zero-field levels exhibit different photoreactivity (photochemical spin selectivity) or that the population of the triplet is appreciably changed by microwaves. The equations derived for monophotonic and biphotonic reactions indicate this fact. The isotope separation factor (given by the ratio of isotopic molecules before photochemical reaction over that after reaction) is derived as a function of light intensity, intersystem crossing ratios and decay constants of the zero-field levels. The equations show that isotope separation is effective at high light intensities only if the molecule is photchemically spin selective. At low and intermediate intensities large differences in the populations together with large anisotropies of the decay constants of the zero-field levels lead to favorable results even if spin-selectivity is not available. Statistical analysis shows that in molecules having one isotopic atom per molecule chances of observing the effect are improved over molecules with more than one such atom. Computer simulation on actual molecules as well as hypothetical cases was carried out to confirm the above conclusions.

In Chapter IV the effect of heavy atom substitution on the dynamic properties of the zero-field triplet levels in 9,10-dichlorophenanthrene and 1,2,3,4-tetrachloronaphthalene is experimentally determined. The results confirm that the 0-0 phosphorescence emission largely originating from the top two zero-field levels is
affected by spin-orbit coupling with $^1\sigma, \pi^*$ states and by static distortions of the heavy-atom substituents. The anisotropy of intersystem crossing to the triplet levels in those two molecules is similar to the parent aromatic molecules and is enhanced by the heavy-atom via enhancement of out-of-plane vibrations involved in spin-orbit vibronic coupling of the relevant $\sigma, \pi^*$ and $\pi, \pi^*$ states.