

## MAGNETIC SWITCHING IN RADIATIONLESS TRANSITIONS

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The disposition of energy in a molecule after optical excitation is a major question in photochemistry and is still inadequately understood. Magnetic effects on the fluorescence from singlet excited states represent an interesting method of studying the behaviour of the excited state. The magnetic field is used as a molecular probe to provide new kinds of information about configuration, properties of eigenstates and molecular processes.

Most experiments performed in the gas phase are of the type like magnetic resonance, where the interaction with paramagnetic molecules is studied, and which are commonly in the electronic ground state. Another type of experiments are magnetic induced dichroism or magnetic induced circular double refraction, in which paramagnetic molecular states are identified and  $g$ -values could be determined. Further techniques are levelcrossing experiments and the Hanle effect, which lead to interference effects in the fluorescence intensity from levels which become degenerate or are split due to Zeeman interaction in a Magnetic field.

Another type of the influence of a magnetic field on excited states of molecules in the gas phase is the quenching of

fluorescence in the presence of a static magnetic field. This has only been observed for a few molecules like  $I_2$ ,  $NO_2$ ,  $CS_2$  and glyoxal. Whereas in the case of  $I_2$  and  $NO_2$  paramagnetic states are involved there in the case of  $CS_2$  and glyoxal the primary excited state is a singlet. Since these states are magnetically insensitive, the influence of the magnetic field results from the mixing with another magnetically active state and offers a new possibility of learning something about the interaction with such a state, which in the case of  $CS_2$  and glyoxal are probably the triplet states showing the magnetic sensitivity. In addition, due to its molecular size, glyoxal represents an intermediate type system in radiationless processes. This is characterized by a low density of states and therefore intersystem crossing is only observed in the presence of collisions, which gives another interesting possibility of studying these kinds of radiationless processes.

We studied glyoxal because it is often used as a test molecule for theoretical models and because its lowest excited states are well known. Experimentally one finds a quenching of fluorescence in the magnetic field and simultaneously an increase of phosphorescence, which clearly shows the enhancement of intersystem crossing from the singlet to the triplet state. The magnetic field effect shows a pressure dependence and vanished at zero pressure. The magnetic field effect can therefore be understood as an increase of the rate of intersystem crossing. From experiments with different molecules

as collisions partners and from the pressure dependence it is seen that the increase of the intersystem crossing depends on the nature of the collision partner in a benign way. It also does not change upon deuteration of the glyoxal molecule. Due to this uniform enhancement the collisions can be seen not to influence the spin orbit coupling, but rather transfer the energy difference between the excited singlet and triplet states. Different from other molecules, which also show a fluorescence quenching in a magnetic field, in the case of glyoxal the magnetic field effect occurs already at low fields and saturates at a field strength of 1 kG. A phenomenological description of the magnetic field dependence could be made with a Brillouin type function which gives a value of about 400 Gauss for the characteristic field strength which is equivalent to an energy in the order of the zero field splitting of the triplet sublevels. The direct spin orbit coupling in glyoxal vanishes and only the  $T_x$  and  $T_y$  sublevels are populated via a vibronic spin orbit coupling at zero field. In the presence of a magnetic field the zero field substates will be transferred to field dependent states which can be described as linear combinations of the zero field states. The total intersystem crossing rate constant is the sum of the rates to the individual states. The summation over all states shows that the total rate cannot change in a magnetic field. From this it is clear that the magnetic field has to open a new channel for intersystem crossing. At higher fields the spin system is no longer coupled to the molecular frame but rather to the external field. This is similar to the Paschen-Back effect in atomic

systems when the magnetic field exceeds the L - S coupling. The high field regime in glyoxal is reached when the field strength exceeds the triplet spin-spin dipole interaction which occurs at about 1 kG, after which this magnetic field effect can be described as a molecular Paschen-Back effect. From then on no further change of intersystem crossing should occur. In the high field case where the spin system is decoupled from the molecular frame more triplet sublevels can be reached due to the fact that the selection rules for the zero field case are no longer valid and different vibrations can act as promoting modes.