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MECHANISMS OF DEACTIVATION OF THE LOW-LYING ELECTRONIC STATES OF 2,2'-BIPYRIDIN

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ABSTRACT

The photophysical properties of 2,2'-bipyridine have been investigated in different solvents by means of lifetime measurements in the picosecond scale, quantum yield temperature dependence and quantum mechanical calculations.

INTRODUCTION

Despite the amount of investigations in the past, the photophysics of 2,2'-bipyridine (bip) is far from being completely understood. In fact, previous studies reached controversial results[1,2] and some authors claimed that this molecule fluoresces only when complexed[3]. We detected the emission spectra of bip in cyclohexane, 3-methyl pentane, methanol and water and measured the fluorescence lifetime in the picosecond time domain. The short lifetimes obtained were explained in terms of an efficient non radiative channel of deactivation involving mainly a triplet state isoenergetic with S_1.

RESULTS AND DISCUSSION

Repeated measurements in two laboratories with different sample purification and solution preparation gave reproducible emission spectra which excluded the presence of emitting impurities or complexes of bip in inert solvents and in alcohols. The excitation spectr were found consistent with these results. On the oth hand , in aqueous solutions we obtained emission an excitation spectra coincident with those of the com plex $Zn(bip)^{++}$, thus confirming previous results[3].

The lifetimes were measured using a single photo counting apparatus with instrumental resolution $\simeq$ 130 ps, which enables to calculate lifetimes of $\simeq$ 5 ps by deconvolution. Single exponential analysis wa successfully used in each case. The measured lifetim range from $\simeq$ 50 ps in alcoholic solutions to 160 ps inert solvents; the fluorescence quantum yields are the order of 5.10^{-4}.

Another kind of investigation, aimed at understand ing the mechanisms of deactivation of the emittin state, was carried out by measuring the variation fluorescence quantum yield with temperature. From the Arrhenius-like curves obtained the kinetic param eters extracted were $\phi = 1.5 \times 10^{-3}$, $A \simeq 10^{10}$ sec^{-1} $\Delta E = 0.65$ Kcal/mol for bip in 3MP and slightly dif ferent values for alcoholic solutions.

These parameters were interpreted as due to a quit favorable ISC process from the emitting state to local isoenergetic triplet. This hypothesis is consis tent both with recent flash-photolytic experiments[4] on the quantum yield of triplet formation and with the results of semi-empirical calculations. The latter were carried out using the CS-INDO CI method which proved particularly valid in describing the po-

tential energy surfaces relative to rotations around single bonds[5]. The wavefunctions so obtained allowed an estimate of the spin-orbit coupling between S_1 and a close lying triplet of appropriate symmetry. The fairly large value obtained for the spin-orbit integral is responsible for a very favourable ISC process, which appears practically independent of temperature. The other minor channel of non radiative deactivation of S_1 is due to the internal conversion process to S_0, induced by out of plane C-H bending modes of a_u symmetry, as indicated by the results of a vibronic coupling calculation on the modes of trans bip.

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