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Mechanisms of Deactivation of the Low-Lying Electronic States of 2,2'-Bipyridine

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The photophysical properties of 2,2'-bipyridine have been investigated in different solvents by means of lifetime measurements on the picosecond scale, quantum yield temperature dependence, and CS-INDO CI calculations. Both experimental and theoretical results indicate that in inert solvents the very low fluorescence quantum yield of this molecule is due to a very effective intersystem crossing to a local triplet state. The picture emerging from these data helps to gain insight into the elusive photophysical behavior of this compound.

Introduction

Like other azaaromatics, 2,2'-bipyridine (hereafter bpy) shows a tiny fluorescence emission in inert solvents which can be hardly detected. In fact, it has been claimed that the molecule does not fluoresce in inert solvents, whereas its protonated adducts luminesce, the amount and type of emission depending on the pH of the solutions.¹ Harriman² first reported on the fluorescence of bpy in cyclohexane and stressed its very low quantum yield and subnanosecond lifetime. Phosphorescence occurs at low temperature with a rather large quantum yield. Other difficulties encountered while characterizing the photophysics of the isolated molecule arise from its ability in complexing ions like Zn^{2+} , giving species with a very high quantum yield of fluorescence.³ Moreover, emission and absorption studies as a function of the

concentration in different solvents⁴ have shown that formation of aggregates can very likely take place. In the same range of concentration experiments of two-photon excitation have also been reported.⁵

In this paper we report the results of a reinvestigation of the photophysics of bpy based on fluorescence lifetime measurements with picosecond resolution in different solvents, on the temperature dependence of the fluorescence quantum yield, and on semi-empirical calculations on the relevant potential curves of the excited states of the free molecule. A critical analysis of previously reported preliminary lifetime measurements in cyclohexane⁶ is also made.

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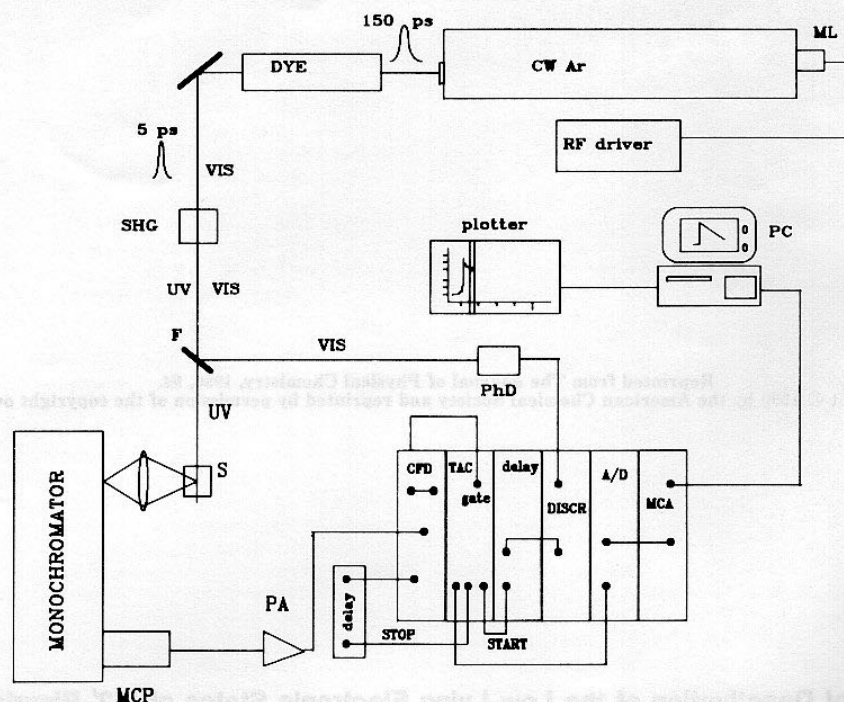
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From the structural point of view, bpy presents two important features that reflect on its elusive photophysical properties. The first one is the presence of relatively close-lying $n\pi^*$ and $\pi\pi^*$ excited states which can be coupled vibronically by out-of-plane vibrations with subsequent modification of the potential energy surface and mixed spectral and photophysical properties. This effect has long been recognized for azaaromatics, and it is known as the "proximity effect".⁷ It is well-known that the solvent plays an important role in this effect by influencing the energy gap between the states involved and largely differentiating bpy from the parent molecule, biphenyl. The second important feature is the presence of a single bond connecting two azaaromatic moieties, with the possibility of rotation of the rings to reach the minimum-energy conformation with relatively small barriers to be overcome. Related to this feature is the presence of rotamers with different possible spectral and photophysical properties. The presence of rotational isomers (conformers) has recently been evidenced for many ethylenic-substituted molecules⁸⁻¹⁰ as well as for 2,2'-binaphthyl.¹¹

Owing to the strong difference of emission of the isolated molecule with respect to water adducts and complexes with Zn^{2+} ions, special care was used in the preparation of the solutions. 2,2'-Bipyridine (Merck, pro analysis) was purified by repeated sublimation. 3-Methylpentane (3-MP) (Carlo Erba, R.P.E.) was chromatographed on activated silica gel and then dried over an-

Corrected emission and excitation spectra were recorded on a Perkin-Elmer MPF44-B spectrofluorimeter equipped with a DCSU-2 differential corrected spectra unit.

The fluorescence quantum yields in 3-MP and methanol at room temperature were obtained by using naphthalene and biphenyl in cyclohexane as standards ($\phi = 0.23$ and 0.18, respectively) and optically thin solutions, compatible with the low emission quantum yield of bpy, according to a procedure described elsewhere.¹³ Refractive index and inner filter effect corrections were made.

The temperature dependence of the luminescence intensity was measured with reference to the room-temperature value. Low temperatures were maintained by means of a Thor C610 nitrogen flow cryostat equipped with a Thor 3030 temperature controller (uncertainty ± 2 K).

The lifetime measurements were performed with the time-correlated single photon counting technique (SPC).^{6,12} Although

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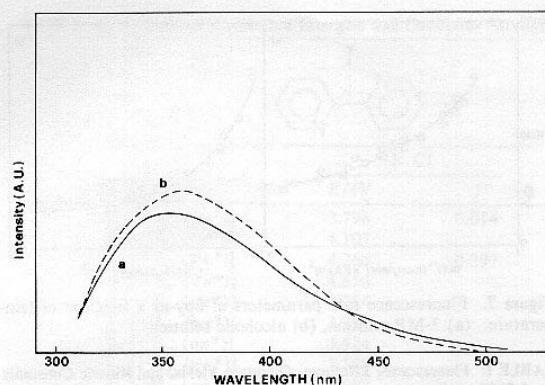


Figure 2. Emission spectra of bpy in 3-MP at 298 K, $\lambda_{exc} = 275$ nm (a) and in methanol solution, $\lambda_{exc} = 280$ nm (b).

a detailed description of the picosecond spectrometer used in the measurements is beyond the scope of this paper, a brief outline of the principles of the technique is in order. The essential experimental setup is shown in Figure 1.

Every photon statistically emitted from the sample is put into coincidence with the exciting pulse of a train of pulses emitted from a dye laser synchronously pumped by a CW Ar laser working in the mode-locked regime. The time interval between excitation and emission is converted into amplitudes in a time-to-amplitude (TAC) converter and fed to a multichannel analyzer (MCA) for display and storage. The key operation for a good instrumental resolution is the reduction of the jitter between the time of arrival at the TAC of the amplified and discriminated fluorescence signal from the photomultiplier (acting as stop signal of the conversion process) and the discriminated signal (start of the conversion) from the fast photodiode (PhD) collecting a diverted small portion of the laser pulse train.

A reasonably low jitter, i.e., a good instrumental resolution, has been obtained by using a microchannel plate constant fraction discriminator (CFD). The TAC was operated in the coincidence mode in which the excitation pulse arrives first at the gate opened by a signal originating in the CFD and generated by the fluorescence signal. Both the start and the stop signals are delayed to allow every start photon (laser) to be associated with its stop photon (emission). In terms of SPC language this is a direct configuration.

Typical values of the parameters of the measure were as follows: instrumental resolution ≈ 130 ps, which enables to calculate lifetimes of about 50 ps by deconvolution; repetition rate, 76 MHz, i.e., one pulse of 5-ps width every ≈ 13 ns; average power at the sample, a few milliwatts of UV light; $\lambda_{exc} \approx 280$ nm (duplicated R6G emission at 560 nm); λ_{em} chosen by a monochromator according to the emission maxima, typically $\lambda_{em} \approx 350$ nm.

The instrumental decay curve used in the convolution of the true decay curve was obtained from the Raman signal of the solvent at ≈ 310 nm or, alternatively, from the elastically scattered photons.

The accumulated decay curves were transferred via RS232 serial interface to a personal computer for data processing. Typical decay curves for bpy in cyclohexane and MeOH are reported in Figures 4 and 5, respectively.

Single-exponential analysis was successfully used in each case. The fastest decays required to be deconvoluted with the excitation function according to a standard nonlinear iterative procedure.¹⁴ The quality of the fits was checked by the residual distribution plot and the χ^2 test. The kinetic parameters, deduced from the Arrhenius-like function of the fluorescence yields vs the temperature, were also calculated by standard iterative nonlinear algorithms.

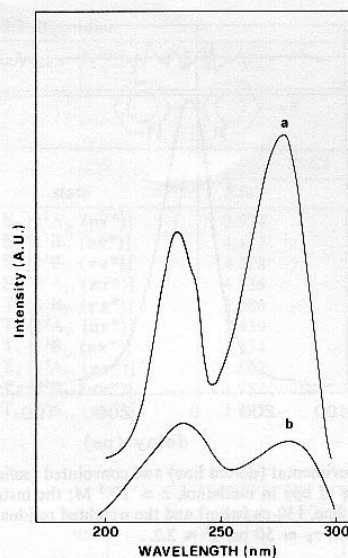


Figure 3. Absorption (a) and excitation spectrum ($\lambda_{em} = 370$ nm) of bpy in alcoholic solution, MeOH-EtOH (1:1).

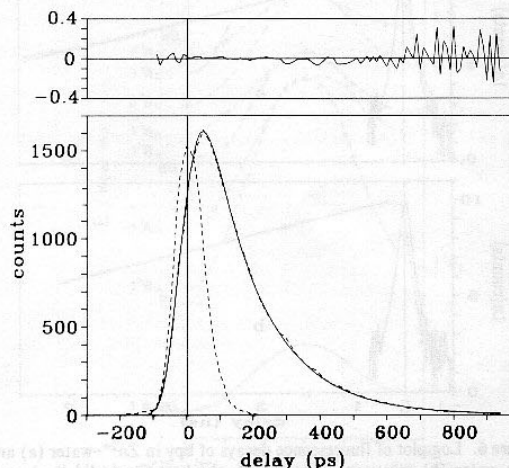


Figure 4. Experimental (dotted line) and convoluted (solid line) decay of fluorescence of bpy in cyclohexane, $c \approx 10^{-5}$ M; instrumental response (dotted line, 110-ps fwhm) and weighted residual plot (upper part) are shown; $\tau_F = 160 \pm 5$ ps, $\chi^2 = 1.1$.

Results

Emission Spectra. Emission and excitation fluorescence spectra of N_2 -purged or deaerated as well as O_2 -purged solutions of bpy in apolar (cyclohexane, 3-MP) and polar (methanol, methanol-ethanol 1:1 mixture) were obtained. Figure 2a shows the emission spectrum in 3-MP at 298 K and $\lambda_{exc} = 275$ nm. The general feature of this spectrum, unstructured and having a maximum around 350 nm, remains unchanged on cooling. We observed also that the O_2 -saturated solutions showed, after light irradiation of some hours, the growth of a broad, intense emission, red-shifted with respect to that of freshly prepared samples. A similar effect was not observed in deaerated or N_2 -purged solutions. The fluorescence spectrum of bpy in methanol or in the alcoholic mixture (Figure 2b, $T = 298$ K, $\lambda_{exc} = 280$ nm) shows a weak emission peaking around 365 nm, and a slight blue shift was observed by decreasing the temperature. Our measurements conflict with previous results on the photophysical properties of the molecule in alcohols. Harriman² indicated a larger quantum yield and a longer fluorescence lifetime (see below), whereas Grabowski et al.³ suggested that not only the emission in water

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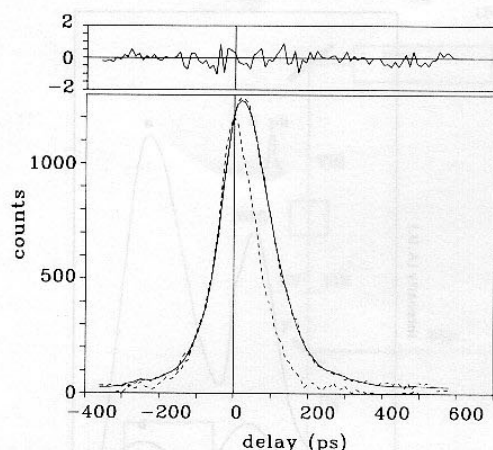


Figure 5. Experimental (dotted line) and convoluted (solid line) decay of fluorescence of bpy in methanol, $c \approx 10^{-5}$ M; the instrumental response (dotted line, 130-ps fwhm) and the weighted residual plot (upper part) are shown; $\tau_F \approx 50$ ps, $\chi^2 = 2.2$.

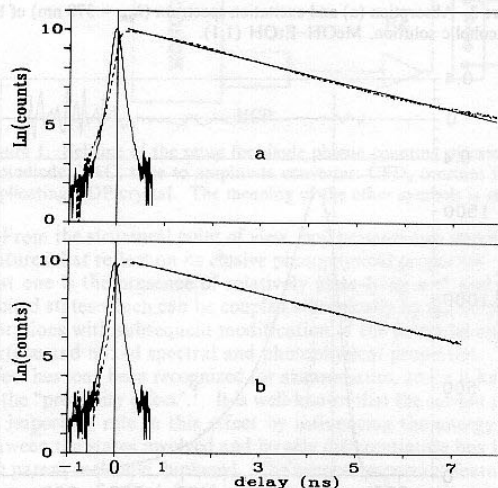


Figure 6. Log plot of fluorescence decays of bpy in Zn^{2+} -water (a) and pure water (b) solutions, $c = 10^{-5}$ M; the best fits (solid line) were obtained with linear least squares; $\tau_F = 1625 \pm 20$ ps (a), $\tau_F = 1640 \pm 20$ ps (b).

should be ascribed to the $\text{Zn}(\text{bpy})^{2+}$ complex but also that detected in alcohols, as these solvents are contaminated by the metal ions extracted by the glass wall of the containers. However, repeated measurements on samples of different origin in two laboratories confirm the photophysical behavior here described for the species present in solution. Moreover, a comparison between the spectra reported (Figures 2b and 3a,b) and the emission and excitation spectra of the $\text{Zn}(\text{bpy})^{2+}$ complex in methanol allowed us to exclude the presence of Zn^{2+} as an impurity in our solvents and to unequivocally assign the observed band to free bpy in solution. This conclusion is supported by the much shorter lifetime of the emission. On the contrary, we agree with Grabowski³ in assigning to the complex the only strong, detectable, emission in water, on the basis of emission and excitation spectra as well as fluorescence lifetime, found to be exactly coincident with those of $\text{Zn}(\text{bpy})^{2+}$.

Fluorescence Quantum Yields and Lifetimes. Lifetime measurements were performed in the picosecond range in different solutions: cyclohexane, methyl alcohol, water, Zn^{2+} -water solution. Owing to the possibility of aggregate formation,⁴ typical concentrations were $(1-2) \times 10^{-5}$ M. The average time of accumulation of the decay curves was about 15 min for nonaqueous solutions and about 1 min for aqueous solutions, due to the very

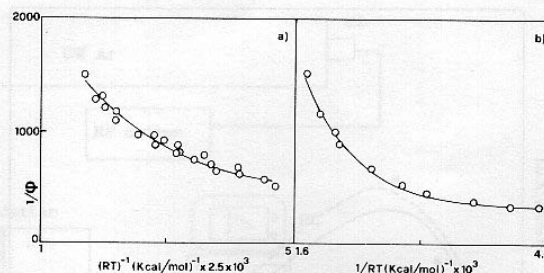


Figure 7. Fluorescence rate parameters of bpy as a function of temperature: (a) 3-MP solution, (b) alcoholic solution.

TABLE I: Fluorescence Lifetimes, Quantum Yields, and Kinetic Constants for 2,2'-Bipyridine

	τ_F , ps	ϕ_F	A , s^{-1}	ϕ_0	ΔE , kcal/mol
cyclohexane	160				
3-MP	160	6×10^{-4}	9×10^9	1.5×10^{-3}	0.65
MeOH	≈ 50	5×10^{-4}			
MeOH-EtOH (1:1)		5×10^{-4}	$>10^{10}$	1.2×10^{-3}	1.77

different quantum yields of fluorescence of the samples. Similar decay curves from pure water and water- $\text{Zn}(\text{bpy})^{2+}$ solutions were accumulated in almost the same time. The lifetimes obtained after the nonlinear least-squares fitting with a single-exponential function were also very similar (see Figure 6).

This supports the conclusion reached above that the observed emission from the pure water and the Zn^{2+} -water solutions both originate in the strongly emitting $\text{Zn}(\text{bpy})^{2+}$ complex. This emission is so strong that a full decay curve can be easily accumulated to many decades of signal even with very diluted solutions.

In fact, the very preliminary finding of a longer lifetime in diluted cyclohexane solution,⁶ i.e., $<10^{-6}$ M, could be due to a very small amount of Zn^{2+} complex probably present also in the solutions of nonaqueous solvents stored for some time in glass bulbs and not immediately used. This was witnessed also by a weak, longer lasting, emission accompanying the main, shorter living, emission in more concentrated solutions.

Fluorescence quantum yields and lifetimes of bpy at room temperature in polar and apolar solvents are reported in Table I.

The temperature dependence of the fluorescence quantum yield in 3-MP was investigated in the range 298–90 K. Below 100 K a strong phosphorescence band appears, overlapping the red tail of the fluorescence. The experimental points were found to obey the following equation:

$$1/\phi_F(T) = 1/\phi_0 + A' \exp(-\Delta E/RT) \quad (1)$$

where ϕ_0 is the term independent of T , $A' = A(s^{-1})\tau_0/\phi_0$, with the A frequency factor, and ΔE is the activation energy for radiationless processes.

The accuracy of the parameters ϕ_0 , ΔE , and A , calculated by (1), is dependent on the large uncertainty affecting the measurements of the quantum yields, due to their low value. Corrections made to include the effects of the volume and refractive index variations with the temperature were substantially ineffective on the quality of the fit. Another source of error derives, in this case, from the shape of the calculated curve not showing, into the investigated temperature range, the typical plateau (see Figure 7a). The averaged kinetic parameter values given in Table I were finally extracted from a series of independent experiments, carried out on several different samples. To calculate the frequency factor A , we have made the reasonable assumption that the temperature dependence of the lifetime follows a trend parallel to that observed for the quantum yield. (This appears satisfied in the case of single emitting species and k_R independent of T .) Moreover, we have assumed the same τ_F in cyclohexane and 3-MP. Then we can write

$$A'\phi_0/\tau_0 = A'\phi_F/\tau_F (T = 298 \text{ K}) = A \quad (2)$$

1B_u state through the b_g modes. Indeed, an estimate of the activity of 818 cm^{-1} (the most active b_g mode) made by means of the orbital following method²¹ leads to a value of the borrowed oscillator strength equal to that permitted. The presence of vibronically active modes in the region between the $n\pi^*$ and $\pi\pi^*$ electronic system has been confirmed by the detection of a diffuse band of overall A_g symmetry in the two-photon spectrum in solution.⁵

As far as the triplet states are concerned, the lowest state of $\pi\pi^*$ nature is calculated at energy lower than the first $n\pi^*$ in the trans conformation and with a small energy difference with respect to the cis conformation. This result appears in agreement with the data recently detected by ODMR spectroscopy at 1.8 K.²²

Discussion

The photophysical parameters extracted from the experiments show that bpy has a very effective nonradiative mechanism of deactivation. Knowledge of the triplet quantum yield in apolar solvents ($\phi_T = 0.83$, obtained by flash photolytic experiments in cyclohexane²³) allows for a more detailed discussion on the nonradiative deactivation channels of S_1 in this case. This large quantum yield of triplet formation is in agreement with the strong phosphorescence observed in cyclohexane² and in the Shpol'skii matrix.²² The high value of frequency factor obtained from the Arrhenius curve in apolar solvent thus points to an upper limit of a spin-forbidden process rather than to a spin-allowed process, as inferred for biphenyl.²⁴ These features clearly show that the main nonradiative process from S_1 is an ISC process, probably favored by the presence of two nitrogen atoms. In this respect, bipyridine resembles much more pyrazine and pyrimidine, for which the ISC from S_1 has been proved to be very effective,²⁵ than the mononitrogenated parent, pyridine.²⁶ The relatively high rate of the ISC process is consistent with the results of calculations, which locate at least three triplets of $\pi\pi^*$ nature in the region

of S_1 , i.e., T_4 , T_5 , and T_6 . Taking into account that of most favorable symmetry (3B_u) and orbital nature, namely T_5 , we get as a result of a qualitative estimate of the spin-orbit coupling^{27,28} the value of 8.5 cm^{-1} and $k_{ISC} \approx 7 \times 10^9\text{ s}^{-1}$. This value fits well the experimental value of $k_{tr} \approx 1/\tau_F = 6.4 \times 10^9\text{ s}^{-1}$, obtained at room temperature. The presence of a local triplet with favorable energy would also justify the observed very smooth dependence of k_{tr} on temperature ($\Delta E = 0.6\text{ kcal/mol}$). The relatively large barriers calculated in the potential energy curves of S_1 for the interring rotation indicate that conformational changes in this state are improbable. The features of the photophysics of bpy in alcoholic solutions do not differ markedly from those in inert solvents, except for a shorter lifetime and a further increase of the preexponential factor (Table I). The lack of data on the triplet quantum yield and the larger uncertainty on the fluorescence lifetime (Figure 5) and quantum yield in these solvents do not allow for quantitative conclusions on the mechanisms of deactivation. However, the similarity of the emission spectra in two solvents (Figure 2), the value of the preexponential factor, and the improbable large enhancement of the internal conversion rate when the S_1 energy remains constant²⁹ also seem to indicate a prevailing ISC process in this case.

Conclusions

The detection of the fluorescence emission on the picosecond scale allowed us to determine τ_F for bipyridine in cyclohexane and in methanol. An Arrhenius plot of the fluorescence quantum yields vs the reciprocal of the temperature was used to gain information about the main mechanisms of radiationless deactivation of the lowest excited singlet state. In inert solvents the main deactivation channel was found to be an ISC to a local triplet, and this conclusion is in agreement both with previous experimental results and with the indications of a semiempirical calculation. The complex problem of bpy in water in the absence of inorganic ions, as well as a quantitative determination of the triplet quantum yield in alcoholic solutions, needs further investigation.

Registry No. 2,2'-Bipyridine, 366-18-7.

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