PICOSECOND RAMAN INVESTIGATION OF THE STRUCTURE AND REACTIVITY OF 4,4'-BIPYRIDINE IN THE S_1 STATE

G. BUNTINX^{a,*}, L. BUSSOTTI^a, V. DE WAELE^a,
C. DIDIERJEAN^a and O. POIZAT^b

^a *Laboratoire de Spectrochimie Infrarouge et Raman (LASIR),
UPR 2631, Centre d'Etudes et de Recherches Lasers et Applications,
Université de Lille I, Bât C5, 59655 Villeneuve d'Ascq cedex, France;*

^b *Laboratoire de Spectrochimie Infrarouge et Raman (LASIR),
UPR 2631, 2 rue H. Dunant, 94320 Thiais, France*

(Received 17 April 1997)

The lowest excited singlet state (S_1) of 4,4'-bipyridine (44BPY) has been studied in water and methanol by using pump-probe time-resolved resonance Raman spectroscopy in the picosecond time domain. Spectroscopic evidence for a disymmetric S_1 structure with localization of the electronic excitation in one of the two pyridyl rings is given. The fast formation of the N-hydro radical 44BPYH[•] from the S_1 state is clearly observed in methanol.

Keywords: Time-resolved Raman; 4,4'-bipyridine; excited state; picosecond; photochemistry

1. INTRODUCTION

The photoexcitation of 4,4'-bipyridine (44BPY) in alcohols yields the N-hydro radical 44BPYH[•] with a double, slow and fast, kinetics [1]. The slow component corresponds to a process of H-atom abstraction by the triplet T_1 state ($\pi\pi^*$) of 44BPY from the solvent ($k \leq 10^6 \text{ M}^{-1} \text{ s}^{-1}$) via the homolytic break of the CH bond in position α to the OH group. From recent sub-picosecond transient absorption

*Corresponding author.

data, we proposed [2] that the fast process of 44BPYH[•] formation arises in the S_1 state of 44BPY, within a H-bonded $^144\text{BPY}^*$ -alcohol complex, and results from H-atom abstraction or concerted H^+/e^- transfer from the OH bond of the H-bonded alcohol. This conclusion was partly stated from the observation that, in alcohol-hexane and alcohol-acetonitrile binary solutions with various alcohol mole fractions, the yield of 44BPYH[•] production is proportional to the amount of H-bonded 44BPY molecules in the S_0 state. However, several points remain unclear. First, the S_1 state and 44BPYH[•] radical absorption bands being almost superposed, the S_1 origin of the radical could not be demonstrated clearly. On the other hand, the formation of 44BPYH[•] has been observed in *n*-hexane but not in water, which is in contradiction with the above mechanism. We have undertaken pump-probe picosecond Raman measurements of the 44BPY in solution with the aim of:

- characterizing the vibrational properties and the structure of the S_1 state as a function of the solvent.
- confirming that S_1 is the radical precursor in the fast process.
- obtaining more detailed information on the mechanism of this fast process.

2. RESULTS AND DISCUSSION

We have used a pump-probe experimental system including a 1 kHz regeneratively amplified Ti:Sapphire laser running in the picosecond regime (2.2 ps) and pumping a narrow-band OPG – OPA device (B.M. industries). The two following sets of pump-probe wavelengths were used: 253/380 nm and 266/580 nm (crosscorrelation FWHM $\sim 3\text{--}4$ ps).

The S_1 state of 44BPY is characterized by two strong absorptions at ~ 580 and ~ 380 nm and its lifetime varies from 11.5 ps in methanol to 41 ps in acetonitrile [2]. Figure 1 presents time-resolved resonance Raman spectra recorded 6 ps after pumping of 44BPY (10^{-3} M) in water using probe excitations at 380 and 580 nm. At longer time delay, we observe the decay of these spectra and the simultaneous appearance of new bands which correspond to the T_1 state. The evolution is completed within 100 ps. It is likely ascribable to the

dynamics of the intersystem crossing and thus the spectra in Figure 1 characterize the S_1 state of 44BPY. The detailed analysis of the Raman activity and assignment established by analogy with the ground state molecule for several isotopomers provides strong evidence of an asymmetrical S_1 structure with the excitation localized mainly on one of the two rings. The inter-ring bond appears to be only weakly affected by the $S_0 \rightarrow S_1$ transition. *Ab initio* calculations are currently in progress to give a more quantitative insight in the S_1 structure of 44BPY.

In methanol and ethanol, the S_1 spectra observed at short time are similar to those found in water. At longer time delay, the spectra show

FIGURE 1 Picosecond time-resolved resonance Raman spectra of photoexcited 44BPY in water. Pump 253 nm/probe 380 nm and pump 266 nm/probe 580 nm, delay 6 ps.

the decay of the S_1 state and the appearance of 44BPYH $\bullet$. The S_1 decay and radical rise kinetics are similar. This result demonstrates definitively that S_1 44BPY is the precursor of the 44BPYH $\bullet$ radical. Spectra of 44BPYH $\bullet$ recorded in isotopically labelled alcohols show that, as in the case of the T_1 state, the mechanism of formation of the radical from the S_1 state involves an homolytic break of a CH bond in position α to the OH group with a surprising high rate constant.

References

- [1] Poizat, O., Buntinx, G., Valat, P., Wintgens, V. and Bridoux, M. (1993). *J. Phys. Chem.*, **97**, 5905.
- [2] Buntinx, G., Naskrecki, R. and Poizat, O. (1996). *J. Phys. Chem.*, **100**, 19380.