

TRIPLET 1-NITRONAPHTHALENE AND COMPETITIVE ENERGY AND ELECTRON TRANSFER REACTIONS WITH *TRANS*-STILBENE

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A time resolved resonance Raman (TR³) study of 1-nitronaphthalene (1NN) first triplet excited state in various solvents is combined with *ab initio* calculations to determine the nature and the geometry of this state in environments of different polarity. A transient absorption and TR³ study of the reactions of triplet 1NN with *trans*-stilbene (*tS*) in solution in both non-polar and polar solvents is reported. In polar solution, ³1NN acts as an electron acceptor whereas in non-polar solution only energy transfer to *tS* is observed. Moreover, at high concentrations of *tS*, the radical cation *tS*⁺ reacts with ground-state *tS* to form a dimer radical cation (*tS*₂)⁺. Differences between the Raman spectra of the monomeric and the dimeric radical cations are reported in the 1500–1650 cm⁻¹ region. The switch from energy to electron transfer when going from non-polar to polar solutions is discussed in terms of the Marcus–Hush theory of electron transfer.

Keywords: Raman; energy transfer; electron transfer; triplet state

TRIPLET 1-NITRONAPHTHALENE

Most aromatic nitro-molecules are known to be non-fluorescent and their excited states and photochemistry have been the subject of many studies [1]. Triplet 1NN is known to be formed quickly (< 25 ps)[2]

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and with a high yield (0.63 in EPA at 77 K)[3]. However the nature of this state is not clear from the literature; whilst some authors propose $\pi-\pi^*$ state [4], others an $n-\pi^*$ state [5], some even suggest that the lowest energy state switches from $n-\pi^*$ to $\pi-\pi^*$ with an increase of solvent polarity [1c].

The equilibrium ground state geometry of 1NN was determined using an *ab initio* RHF wavefunction with a 6-31 G(d, p) basis set and analytical gradients[6]. Harmonic frequencies were calculated analytically and were found to be in good agreement with the observed Raman frequencies. Equilibrium geometries and harmonic frequencies of the first two excited triplet states were determined using the configuration interaction singles (CIS) method. The calculated structures indicate that the main difference between ground and first triplet state is the change in angle between the C-NO₂ plane and the aromatic plane; 45° and 37° in the ground and first triplet state respectively. In each case, atomic charges on the NO₂ moiety were calculated to be ca. +0.5 (N) and -0.5 (both O) from a Mulliken population analysis. On the other hand, the second triplet state is characterised by a strong change in electron density on the atoms of the nitro group, now roughly 0 (N) and -0.2 (both O), accompanied by an important geometrical change in the NO₂ arrangement; whilst one C-N-O plane is almost perpendicular to the aromatic plane (with the oxygen atom above it), the other C-N-O makes a 48° angle with the aromatic plane (with the oxygen below it).

The calculations show that the lowest triplet state is of $\pi-\pi^*$ nature and the second triplet state, estimated to lie less than 0.1 eV above the former in the gas phase, is of $n-\pi^*$ type. However, the $n-\pi^*$ (T₂) state has a lower dipole moment (2.9 D) than the $\pi-\pi^*$ (T₁) state (4.9 D). Hence T₂ would not be expected to be stabilised relative to T₁ in a polar solvent. This is consistent with the TR³ data, where there was little difference in the Raman spectra in non-polar and polar solvents (Fig. 1) and the observed frequencies for the lowest triplet state were well in agreement with the calculated ones.

REACTIONS WITH *TRANS*-STILBENE

By exciting 1NN and *t*S solutions in carbon tetrachloride (CCl₄) and acetonitrile (MeCN) with a 355 nm laser pulse (3rd harmonic of a

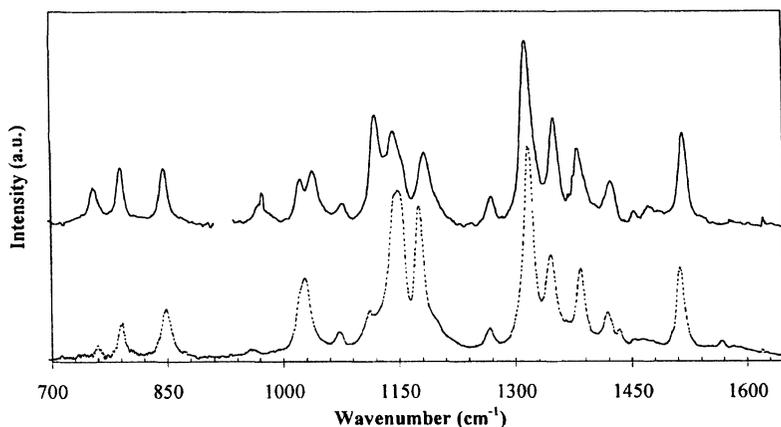


FIGURE 1 TR³ spectra of triplet INN in CCl₄ (---) and MeCN (—).

Continuum 8000 Nd:YAG), we obtained the triplet INN species, characterised [7] by a main absorption band at 540 nm (CCl₄) or 580 nm (MeCN). We then observe a quenching of this species and the rise of absorption bands peaking below 380 nm (CCl₄) and at 470 nm followed, at high *tS* concentrations, by a shift towards 465 nm (MeCN). These absorptions are characteristic of the triplet excited state of *tS* [8], its radical cation [9], and a dimeric species formed by reaction of *tS*⁺ with ground state *tS* [9] respectively. The absence of *tS*⁺ in non-polar solution was confirmed by a TR³ experiment performed with a probe laser beam at 480 nm (Continuum SunliteTM OPO). Similarly, we observed by TR³ spectroscopy the formation of the dimer radical cation of *tS* in MeCN solution (Fig. 2). The radical cation *tS*⁺ is characterised in the 1500–1650 cm⁻¹ range by two bands at 1570 and 1607 cm⁻¹ as well as a shoulder at ca 1590 cm⁻¹, whereas the shoulder is absent from the vibrational spectrum of (*tS*₂)⁺ and also the band at 1607 cm⁻¹ is more intense relative to the band at 1570 cm⁻¹ for the *tS*⁺. These observations are consistent with calculations of the vibrational frequencies of the radical ions of various stilbenes [10] and a recent Raman study of *tS* monomeric and dimeric cations produced by UV irradiation in boric acid matrices [11].

Using the formalism of Marcus–Hush theory to describe the rate of electron transfer [12], and Rehm–Weller theory to estimate the free

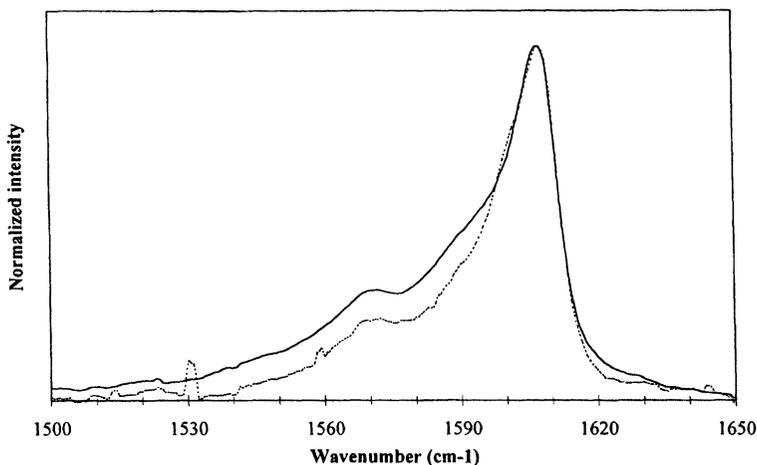


FIGURE 2 Normalised TR³ spectra of 1NN (2mM) + *t*S (3mM) in MeCN at time delays 50 ns (—) and 1 μs(---). Pump 360 nm, probe 480 nm.

energy (ΔG) of the electron transfer reaction and the solvent reorganisation energy [13], we can show that the experimental observations can be explained simply [14]. In CCl₄, $\Delta G = 0.50$ eV and the reaction is thermodynamically unfavourable. In MeCN, $\Delta G = -0.07$ eV and $\Delta G^\ddagger = 0.14$ eV and the reaction is possible.

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