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Fluorescence excitation and excited state intramolecular relaxation dynamics of jet-cooled methyl-2-hydroxy-3-naphthoate

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Two distinct $S_0 \rightarrow S_1$ fluorescence excitation spectra of methyl-2-hydroxy-3-napthoate (MHN23) have been obtained by monitoring fluorescence separately in the short (~410 nm) and long (~650 nm) wavelength emission bands. The short wavelength fluorescence is assigned to two MHN23 conformers which do not undergo excited state intramolecular proton transfer (ESIPT). Analysis of the 'long wavelength' fluorescence excitation spectrum, which arises from the proton transfer tautomer of MHN23 indicates an average lifetime of $\tau \geqslant 18 \pm 2$ fs for the initially excited states. Invoking the results of Catalan et al. [J. Phys. Chem. A, **1999**, *103*, 10921], who determined the N tautomer to decay predominantly via a fast non-radiative process, the limit of the rate of intramolecular excited proton transfer in MHN23 is calculated as, $k_{pt} \leqslant 1 \times 10^{12}\ s^{-1}$.

1. Introduction

The present work on the fluorescence excitation spectra of jet-cooled methyl-2-hydroxy-3-naphthoate (MHN23) supplements earlier work on the excited state intramolecular proton transfer of the jet-cooled napthol derivatives 1-hydroxy-2-naphthaldeyde [1] and 2-hydroxy-1-naphthaldehyde [2]. MHN23 is the naphthalene equivalent of methyl salicylate (MS), a molecule which exhibits one of the most extensively studied excited state intramolecular proton transfer processes [3–6]. MHN23 undergoes an excited state intramolecular proton transfer (ESIPT) analogous to that which occurs in MS. However, MHN23 has not been as extensively studied as MS and its photophysics is still not fully understood.

Bergmann et al. [7] conducted the first study of MHN23 in solution and observed the S_1 absorption band at ~375 nm in dioxane solution. The authors established the presence of an intramolecular hydrogen bond in MHN23. Dual fluorescence emission in MHN23, was first observed by Naboikin et al. [8]. In Ref. [8], an emission at ~410 nm and a Stokes shifted (~9000 cm^{-1}) emission at ~650 nm were observed. The long wavelength emission was subsequently ascribed to the keto tautomer of MHN23 (Fig. 1) by Woolfe and Thistlethwaite [9]. Law and Shoham [10] reported an intrinsic fluorescence quantum yield of 0.7% of MHN23 in methylcyclohexane at room temperature. Catalan et al. [11] have conducted the most recent study of MHN23 and its structural isomers methyl 1-hydroxy-2-naphthoate and methyl 2-hydroxy-1-naphthoate. Absorption, emission, and excitation spectra of MHN23 in solution and in the gas phase were measured. A theoretical study of the molecule was also conducted. The DFT B3LYP/6-31G** ground state energies of four MHN23 conformers were computed and the N tautomer (see Fig. 1) was found to be the dominant ground state species. Upon excitation to the S_1 state, ESIPT in the N tautomer is driven by increases in the acidity and basicity of the hydroxyl and carbonyl groups, respectively. Catalan et al. [11] concluded that proton transfer occurs with a yield of only ca. $\Phi_{pt} \sim 0.018$, across a potential energy barrier of ~1.5 kcal/mol in the S_1 state. Radiative decay of the keto tautomer produces the observed 650 nm fluorescence band. A biexponential decay with lifetimes of 14.5 ns and 2.9 ns were observed by Catalan et al. [11] in the short wavelength fluorescence emission at 410 nm. The two fluorescence components were tentatively assigned to the HB and NHB conformers (see Fig. 1). No component of the short wavelength fluorescence was ascribed to the N tautomer which was explained to decay predominantly via an efficient non-radiative process. Intersystem crossing to a triplet state was proposed as a possible N tautomer decay mechanism.

MHN23 has not previously been studied in a supersonic jet. In this publication, the photophysics of MHN23 is investigated, through fluorescence excitation measurements of jet-cooled MHN23. Two distinct excitation spectra were obtained by monitoring the fluorescence in the short (~410 nm) and long (~650 nm) wavelength emission bands.

A full description of the experimental apparatus was presented in [1] and will not be repeated here. Experimental details pertaining to specific measurements are also given in the figure captions.

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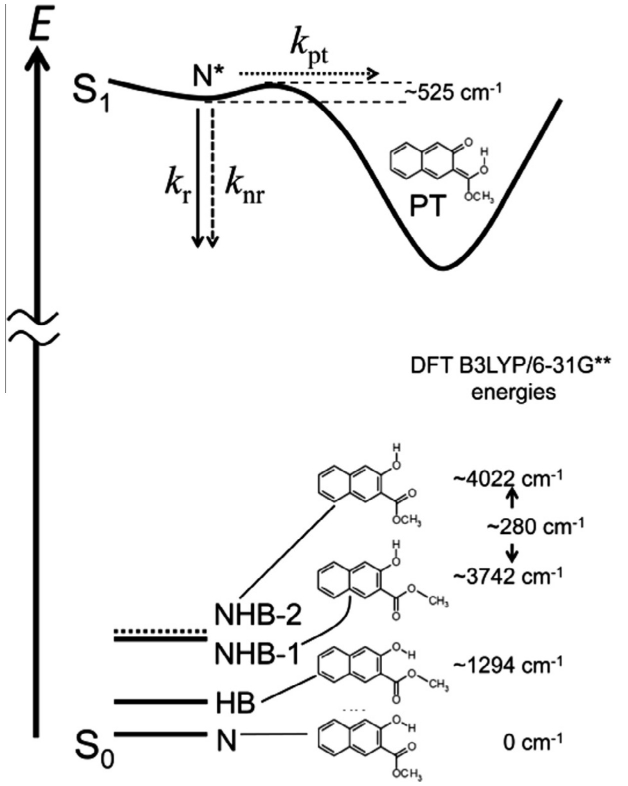

Fig. 1. Chemical structures of the MHN23 conformers, the nomenclature was adapted from Ref. [11] and also the relative separation of calculated ground state energies (DFT B3LYP/6-31G**) of the conformers, which will provide arguments in the spectral assignments and discussion in Section 2. The N tautomer is the dominant ground state species and the proton transfer (PT) tautomer (keto) is formed after ESIPT of the N tautomer [11]. (N)HB = (non)hydrogen bonded. The decay rates k_r (radiative), k_{nr} (non-radiative) and k_{pt} (proton transfer) of different processes which are discussed in Section 2.3 are also shown.

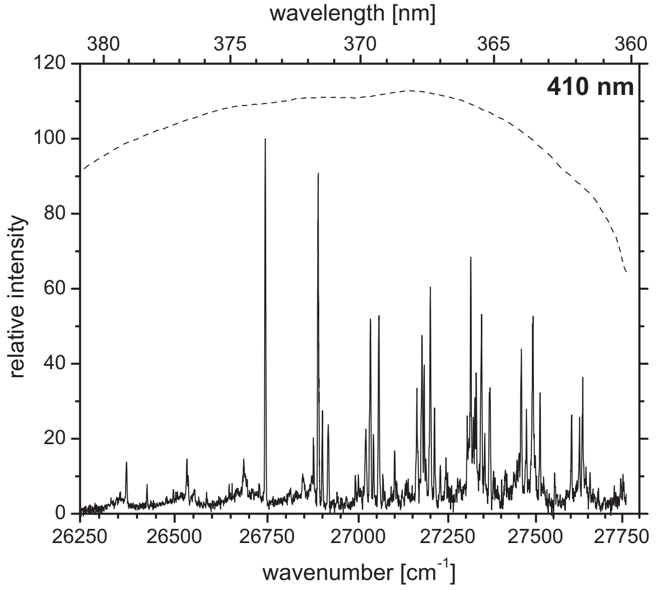

Fig. 2. $S_1 \leftarrow S_0$ excitation spectrum of the $S_1 \rightarrow S_0$ short wavelength fluorescence (~410 nm) of jet-cooled MHN23. The fluorescence was collected through a 435 nm (FWHM ~40 nm) interference filter. The dashed line indicates the relative excitation power (laser power ~1.5 mJ per pulse in maximum at ~27250 cm^{-1} (dye: frequency doubled emission of Styryl 8). The spectrum has been scaled to the varying laser power [1]. Carrier gas was argon at a stagnation pressure of 760 mbar.

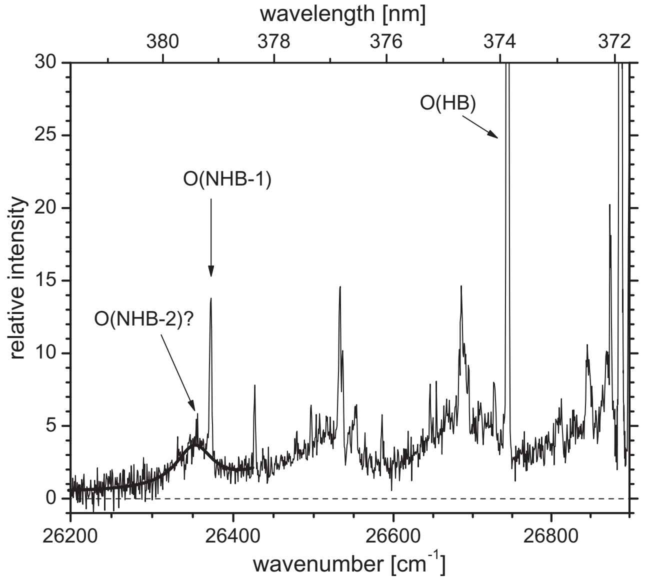

Fig. 3. Low energy part of the $S_1 \leftarrow S_0$ fluorescence excitation spectrum of MHN23 (short wavelength fluorescence, ~410 nm). The positions of the origins of the HB (26743.7 cm^{-1}) and NHB-1 (26372.7 cm^{-1}) are marked with arrows. A weak feature at (26356.0 cm^{-1}) at a slightly lower energy than O(NHB-1) may be the origin of the NHB-2 conformer (tentative). Solid line between 26200 and 26450 cm^{-1}: Lorentzian fit to data (see text).

MHN23 ($C_{12}H_{10}O_3$, m.p. = 73–75 °C, minimum purity 98%) was purchased from Sigma Aldrich and used without further purification.

2. Fluorescence excitation spectra of MHN23

2.1. Short wavelength emission

The excitation spectrum of the $S_1 \leftarrow S_0$ electronic transition of jet-cooled MHN23, obtained by monitoring the short wavelength fluorescence (~410 nm, collected through an interference filter centered at 435 nm) is shown in Fig. 2. The excitation spectrum was measured from 24096 to 27778 cm^{-1} with spectral resolution of ~0.07 cm^{-1} (FWHM of laser bandwidth) [1]. Spectral features were observed between ~26300 cm^{-1} and 27778 cm^{-1}. The spectrum consists of two distinct patterns of narrow lines with different intensities and a broad ("humped") structure, all following similar progressions as discussed in the next section (cf. also Fig. 3). The observed narrow features were assigned to the HB and one of the NHB ground state conformers of MHN23. The nature of the broad structure is not clear as of yet. In the following, the vibrational assignments will be described and discussed on basis of our own calculations and the results by Catalan and co-workers [11].

2.1.1. Vibrational assignments

The strongest spectral feature occurs at 26744 cm^{-1} and is likely to be an origin of one of the MHN23 conformers (the relative intensity of the spectrum was normalized to 100 arb. units based on this line, Fig. 2). A series of weaker features appear on the low energy side of this strong origin (see Fig. 3), which did not change when different carrier gases (argon or xenon rather than helium) were used for the supersonic expansion. Therefore these weak features cannot be based on van der Waals complexes of MHN23 with atoms of the expansion gas. The expected small changes in rotational temperature caused by different carrier gases at similar stagnation pressures did also not change the shape of the weak