Available online at www.sciencedirect.com
ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 184 (2006) 250–264
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Origin of the strong effect of protic solvents on the emission spectra, quantum yield of fluorescence and fluorescence lifetime of 4-aminophthalimide

Role of hydrogen bonds in deactivation of S_1-4-aminophthalimide

Ewa Krystkowiak[a], Krzysztof Dobek[b], Andrzej Maciejewski[a,c,*]

[a] *Photochemistry Laboratory, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*
[b] *Quantum Electronics Laboratory, Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland*
[c] *Center for Ultrafast Laser Spectroscopy, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland*

Received 16 December 2005; received in revised form 11 April 2006; accepted 24 April 2006
Available online 8 June 2006

Abstract

The paper presents results of the spectral (absorption and emission) and photophysical study of 4-aminophthalimide (4-AP) in 1-chloro-*n*-alkanes (RCl) with which 4-AP interacts only nonspecifically, in hexafluoroisopropanol (HFIP) and dimethyl sulfoxide (DMSO) in which 4-AP forms only one type of hydrogen bond, and in water and deuterated water in which 4-AP forms both accepting and donating hydrogen bonds. Based on our solvatochromic data and independent literature data used for the determination of the energy of hydrogen bonds in the S_0 state, the energies of hydrogen bonds in the S_1-LE and S_1-ICT states of 4-AP were estimated. The results confirmed that, apart from 4-AP, there can be S_1-exciplexes (S_1-exc) formed as a result of strong hydrogen-bond formation between 4-AP molecules in the S_1-ICT state and the solvent molecules. In strongly protic solvents (e.g. HFIP) there can also be S_0-complexes (S_0-comp) in the ground state. The existence of solvent-dependent species of different character in the excited state forms the basis for explaining the origin of the large effects of protic solvents on the emission spectra, quantum yield of fluorescence, and fluorescence lifetime of 4-AP.
© 2006 Elsevier B.V. All rights reserved.

Keywords: 4-Aminophthalimide; Exciplex; Fluorescence; Solvatochromism; Hydrogen bond

1. Introduction

The presence of an electron donor group (e.g. amino, mono or di alkyl amino, methoxy) and an electron acceptor moiety (e.g. nitrile, nitro, carbonyl), especially if they are positioned along the same axis of the molecule, means that the electronic excitation of this molecule significantly changes the electron density distribution. This implies a significant change in the dipole moment (μ), as has been shown for a number of such molecules [1–8]. It is, however, most often disregarded that a change in the molecular electron density distribution leads to a significant change in the energy of the hydrogen bonds formed by it with the molecules in the direct neighbourhood of the donor group (D) and/or acceptor group (A) of this molecule. The probe molecule containing D and A groups forms hydrogen bonds with molecules of homogenous solvents or more complex systems e.g. microorganised ones, on condition that the solvent molecules are protic or contain a sufficiently electronegative heteroatom with a lone electron pair. Solvents with such properties are used in solvatochromic studies of all types, both steady-state and time-resolved, in order to get reasonably large shifts in probe's absorption and/or emission maxima. Alcohols and water are two of the commonly used solvents that form both types of hydrogen bonds of relatively high energy. Water is also frequently used as a solvent in studies of microorganised systems, e.g. micelles and cyclodextrines. In such systems the fundamental condition for a correct description of the properties of the probe in the microorganised systems is an accurate determination of the contribution of the probe–solvent non-specific and specific interactions (most often hydrogen bonds). It is

---

[*] Corresponding author. Tel.: +48 61 8291359; fax: +48 61 8658008.
E-mail address: iwonam@amu.edu.pl (A. Maciejewski).

1010-6030/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2006.04.022

necessary to have a picture of these interactions both, before and after the probe excitation. This information is most easily obtained from the experimentally observed spectral shifts in the probe's absorption and emission spectra. This shift depends on the energy of both types of probe–solvent interactions for the probe in its two electronic states involved in the transition under observation. Thus, it is very difficult to conclude on the basis of solvatochromic measurements alone whether the energy of the hydrogen bonds between the probe molecule and the solvent molecules is large enough for a complex to be formed between them. Moreover, solvatochromic results are usually presented as dependencies of the absorption spectral maxima ($\nu_{\max}^{\rm abs}$) and emission spectral maxima ($\nu_{\max}^{\rm em}$) on the solvent polarity expressed in one of the empirical polarity scales. However, the probe molecules, used for the establishment of these polarity scales, were involved with the solvents both in non-specific and also specific interactions. This means that the molecule under study often has spectral and photophysical properties that are too different from these of the reference compound for the empirical polarity scales to be useful [1–4,6–12]. In practice, this prevents a direct solvatochromic determination of the energies of both non-specific and specific probe–solvent interactions and a separation of their contributions. Therefore, it is also impossible to establish reliably which species, apart from the unexcited and excited probe are present in the system studied. In particular, it is vital to determine whether there are exciplexes in the S_1 state (S_1-exc) and/or ground state complexes (S_0-comp). Hence, quantitative conclusions cannot be made about on the changes in the concentrations of the unexcited and excited probe as a result of excitation or deactivation.

It has most often been assumed that the spectral and photophysical properties of the probes studied depend on the bulk polarity of their environments. However many authors have shown that probe molecules with D and A groups used in solvation studies often form hydrogen bonds with a number of different, especially protic, solvents. These phenomena have been studied, in particular, for some coumarines and their derivatives [13–28] and, in addition, for other compounds with D and/or A groups [15,16,29–52]. Excited-state hydrogen bond formation is more often an increase in the energy of hydrogen bonds ($E_{\rm HB}$) already present in the ground state of the probe as a result of the probe excitation. Apart from the emission and absorption spectra, excited-state hydrogen-bond formation is manifested first in the kinetics of the probe's emission decay and in changes in the probe's infrared and Raman spectra [18–21,27,36,44,53–57]. An analysis of the shape and position of the time resolved emission spectra of 4-aminophthalimide (4-AP) dissolved in sodium dodecyl sulfate micelles (SDS) was made in our laboratory [58,59]. The results showed that in addition to the 4-AP molecules, the micellar systems also contained S_1-exc which was formed between the 4-AP molecules and the surfactant or water molecules. The excitation of 4-AP leads to a significant increase in the energy of the hydrogen bonds made by the probe with the water molecules solubilized in the micelles. This leads to changes in the concentration equilibrium between the uncomplexed and complexed 4-AP molecules. Although the microorganised systems, including micelles, have complex properties, we have shown that in SDS micelles [58,59] it is possible to estimate the time in which the above equilibrium changes as well as to study the solvation dynamics resulting from non-specific interactions.

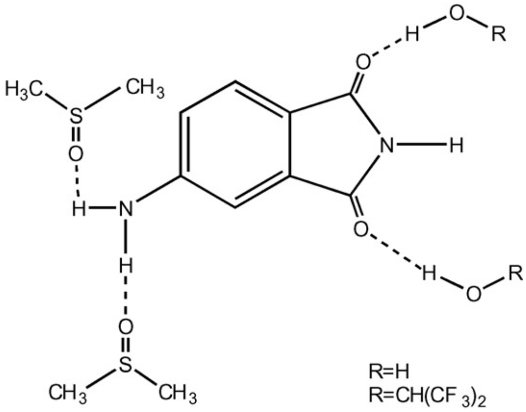

Fig. 1. The structure of the 4-AP molecule with the strongest hydrogen bonds formed in HFIP, H_2O and DMSO, whose energies change on excitation and deactivation of the 4-AP molecule.

The 4-AP molecule is often used as a probe in mono- and bicomponent solvents [60], in micellar systems [61–65] and other microorganised systems [66,67], in polymers, ionic solution, supercritial fluids, nanomaterials and biological systems [62,68–73]. It includes several chromophores with donor or acceptor properties capable of forming hydrogen bonds (see Fig. 1). A result of 4-AP excitation is a redistribution of charge, particularly large in the internal charge transfer state (S_1-ICT). As a consequence of this charge redistribution there is a significant change in the energy of the hydrogen bonds that are already present in the ground state [15,17,24,27,29,58,74,75]. Because all of these factors potentially come into play, they make it very difficult to understand (and interpret) the properties of 4-AP in its excited states. Strong dependencies of the $\nu_{\max}^{\rm em}$, fluorescence quantum yield ($\phi_{\rm F}$), and the lifetime ($\tau_{\rm F}$) of the 4-AP on the properties of its surroundings are reasons why this molecule has been used so often as a probe. Despite the large body of data collected from many studies [15,60,63,73–88], there are still many controversies as to the interpretation and origin of 4-AP's photophysical behaviour as influenced by the properties of its surrounding media.

Many authors assume that the large bathochromic shift of $\nu_{\max}^{\rm em}$ in polar solvents, which is much greater than $\nu_{\max}^{\rm abs}$, is a result of a large increase in the dipole moment of the 4-AP molecule after its excitation [4,63,88,89]. However, this interpretation seems unlikely on comparing the solvatochromic results obtained for 4-AP and 4-(dicyano-methylene)-2-methyl-6-(*p*-dimethylamino)styryl-4H pyran (DCM). The dipole moment of the DCM molecule in its ground state is $\mu_{S_0} = 6.2\,{\rm D}$, while in its excited state $\mu_{S_1} = 26\,{\rm D}$ [90]. The bathochromic solvent spectral shift ($\Delta\nu_{\max}^{\rm em}$) of the DCM emission spectral maximum on replacing a nonpolar solvent by the strongly polar acetonitrile (ACN) is $\sim 1400\,{\rm cm}^{-1}$ [91]. In contrast, for 4-AP, whose $\mu_{S_0} = 3.0$–$4.0\,{\rm D}$ and $\mu_{S_1} = 6.0$–$9.0\,{\rm D}$ [1,15,79,88,92], the replacement of a nonpolar solvent by H_2O gives $\Delta\nu_{\max}^{\rm em} > 5000\,{\rm cm}^{-1}$ (see below). H_2O is characterised by the Lippert–Mataga polarity function ($f(\varepsilon, n^2)$) value similar to that of ACN (for definition of $f(\varepsilon, n^2)$ see Refs. [1–3]) As has been shown by Ware et al. [74], Barbara et al. [85], Samanta et al. [65,67,79,80] and Aramendia et al. [75] the bathochromic shift is determined mainly by the protic properties of the solvent. These protic properties determine the energy of the hydrogen bonds formed between the solvent and the carbonyl groups of 4-AP in its S_1-ICT state. To a smaller degree $f(\varepsilon, n^2)$ affects the energy of the solvent non-specific interactions with the probe, which also leads to a bathochromic shift. Recently, Bhattacharyya et al. [93] have shown that the $\nu_{\max}^{\text{em}}$ of 4-AP in a dioxane-water mixture depends more strongly on the Kamlet–Taft hydrogen-bond parameter α [94–98], than on the Kamlet–Taft π^* parameter [95–100] which describes the proportion of specific and non-specific interactions in the system under study. In contrast to refs [74,75,85], the above authors have assumed that the amino and imino protons of 4-AP form stronger hydrogen bonds in its excited state than in its ground state. This leads to the large bathochromic $\nu_{\max}^{\text{em}}$ shift.

In the papers of Ware et al. [74] and Aramendia et al. [75] the significant decrease in ϕ_F and the shortening of τ_F observed for 4-AP in protic solvents was assigned to the formation of S_1-exc. The formation of this species was seen as the result of hydrogen bond formation between the carbonyl group of 4-AP in the S_1-ICT state and an H–O bond of the solvent molecule. According to Aramendia et al. [75] and Chapman and Maroncelli [70] the decay of 4-AP in neat protic solvents involves the participation of a few solvent molecules and leads to the formation of ensembles of excited complexes with different numbers of protic solvent molecules. Similarly, Yuan and Brown [81] attributed the observed decrease in the ϕ_F and τ_F of two 4-aminonaphthalimides derivatives in aqueous ethanol (relative to ethanol), to the quenching by the water molecules. The model involving quenching by multiple species was also evolved [101]. According to this model, these authors assumed that the quenching process must involve 7–8 molecules of H_2O and 18–20 molecules of D_2O.

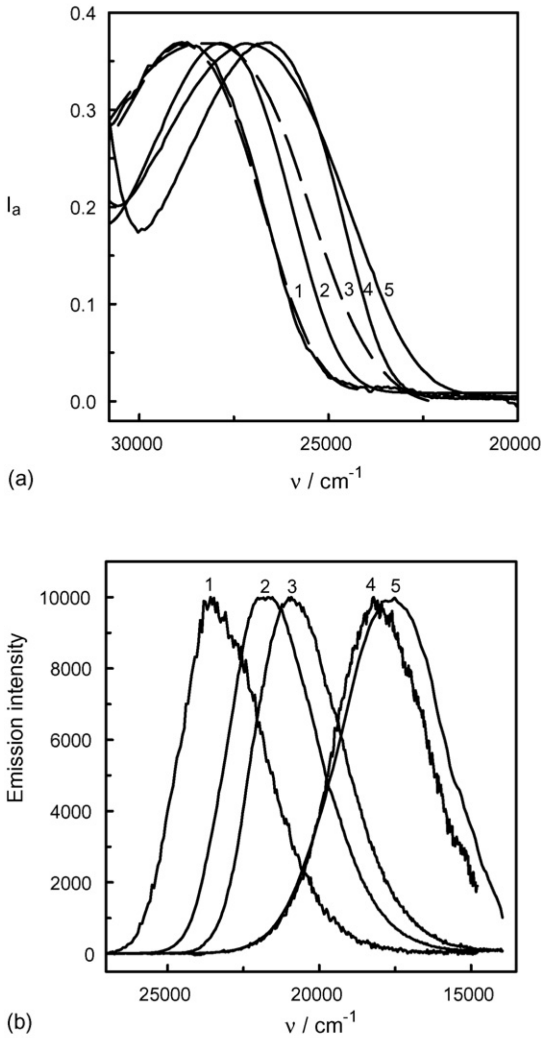

Fig. 2. (a) Normalized absorption, I_a (solid lines) and fluorescence excitation spectra (dashed lines) of 4-AP in selected solvents: (1) 1-chloropropane ($\lambda_{em} = 500$ nm), (2) ACN, (3) HFIP ($\lambda_{em} = 556$ nm), (4) DMSO, (5) H_2O. (b) Normalized fluorescence spectra of 4-AP in selected solvents: (1) 1-chloropropane, (2) ACN, (3) DMSO, (4) HFIP, (5) H_2O.

Harju et al. [86,87] and Bhattacharyya et al. [77] suggested that the remarkable sensitivity of 4-AP′s photophysical properties to protic solvents originates from the fact that in these solvents 4-AP undergoes ultrafast solvent-mediated proton transfer. The emission, then, originates from the proton-transferred species. The abrupt decrease in the ϕ_F and τ_F of 4-AP in protic solvents was attributed by these authors to the reduction in the S_1–S_0 energy gap in the proton-transferred species. A significant increase in ϕ_F and τ_F in D_2O relative to H_2O was ascribed by Bhattacharyya et al. [77] to a decrease in the nonradiative $S_1 \rightarrow S_0$ internal conversion rate in 4-AP upon deuteration of the imino proton. However, it should be noted that for 4-AP derivatives in which the hydrogen atom of the imino group has been replaced by *n*-alkyl group, their emission properties remain as sensitive to protic solvents as those of 4-AP [80]. The substituted *n*-alkyl group excludes the formation of proton-transferred species and the participation of the above process in deactivation. Taking into account these results, Bhattacharyya in his later work assumed that in 4-AP derivatives with *n*-alkyl groups the proton transfer occurred between the amino group and the carbonyl group of 4-AP with the participation of two molecules of water used as a solvent [12]. Valeur [3] assumed that the decrease in ϕ_F of 4-AP in protic solvents is the result of an increase in the rate constant of the intersystem crossing due to hydrogen bond formation with the solvent molecule.

Based on results of the ϕ_F in benzene, in the presence and absence of ethanol (Ref. [16], see Figs. 2 and 3), Inoue et al. have concluded that no 4-AP fluorescence quenching takes place as a result of hydrogen bond formation with this solvent. This is in spite of the normally effective interaction of 4-AP with ethanol. If such a quenching via hydrogen bonding takes place, it occurs at such a low rate constant ($0.24 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$) that it effectively does not participate in the deactivation of 4-AP in the S_1-ICT state. It should be noted that the rate constant of 4-AP quenching in Ref. [16] has been determined from the steady-state measurements, assuming that the emission comes exclusively from 4-AP in the S_1-ICT state. The emission spectra presented by Inoue et al. [16] reveal significant changes in

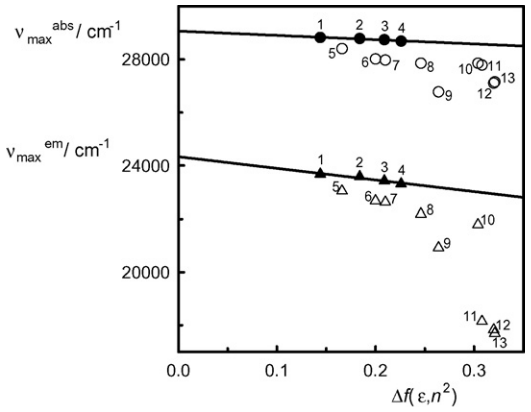

Fig. 3. The solvatochromic plot of ν_{max}^{abs} (circle) and ν_{max}^{em} (triangle) as a function of $\Delta f = ((\varepsilon - 1)/(2\varepsilon + 1)) - ((n^2 - 1)/(2n^2 + 1))$ of 4-AP in selected solvents: (1) 1-chlorodecane, (2) 1-chlorohexane, (3) 1-chlorobutane, (4) 1-chloropropane, (5) diethyl ether, (6) ethyl acetate, (7) THF, (8) octanenitrile, (9) DMSO, (10) ACN, (11) HFIP, (12) H_2O, (13) D_2O.

ν_{max}^{em} and a broadening of the emission spectra with increasing concentrations of ethanol. This indicates the presence of more than one emitting species. These authors have also found that the fluorescence decay of 4-AP in protic solvents depends on the emission wavelength and could be fitted by double exponential functions. These data independently support the notion that there are two emitting species present. Hence, these results show that the rate constant of 4-AP quenching by ethanol, obtained by Inoue et al. [16] from the steady-state emissions, should be carefully interpreted.

Interesting results on 4-AP and 4-amino-*N*-methylphthalimide (NM-4-AP), were reported by Topp et al. [102,103] who studied the properties of these molecules and their van der Waals complexes with acetonitrile and hydrogen-bonded molecules (e.g. water) under jet-cooled conditions. They showed that hydrogen-bonded interactions greatly stabilize the excited states of 4-AP and NM-4-AP. Of particular interest is that a cluster of only a few water molecules exhibits almost all of the red shift observed between the isolated molecule and the condensed phase. However, the red shift observed for the clusters of two conformers of 4-AP with single water molecules under jet-cooled conditions is significantly smaller than that in the corresponding acetonitrile cluster. This interesting result could not be predicted from the known condensed-phase behaviour where water gives much larger red shifts than do acetonitrile and other aprotic solvents. Therefore, it is not possible to use directly the results obtained for 4-AP under jet-cooled conditions for the interpretation of solvatochromic and photophysical properties of 4-AP in solution.

The above differences in interpretations of the results suggest that the large effect of the surroundings on the ν_{max}^{em}, ϕ_F, and τ_F of the 4-AP molecule is not yet fully explained. In summary the literature gives three main reasons for the effect: (i) an increase in μ_{S_1} relative to μ_{S_0} (considering only ν_{max}^{em}) [4,63,88,89], (ii) formation of much stronger hydrogen bonds in the S_1-ICT than in the S_0 state [3,9,74,79] and (iii) formation of an emitting enol form of 4-AP [77,87] as the result of a proton transfer from the imino or amino groups to the carbonyl group of 4-AP with the involvement of one or two protic solvent molecules.

On studying the emission of 4-AP in micellar systems [58,59], we assumed that the second reason (ii) was mainly responsible for the strong effect of the surroundings on the 4-AP emission. This assumption was made on the basis of the above-mentioned literature and on our own studies. This hypothesis lead to the most reliable and reasonable interpretation of the results in micellar systems. Since the properties of microorganised systems are very complicated, this assumption had to be verified for 4-AP in simple surroundings (monocomponent solvent). Hence the main objective of the current paper is to find the reason for the strong dependence of ν_{max}^{em}, ϕ_F and τ_F for the 4-AP molecule on the properties of the solvent. We show and discuss the results of solvatochromic and photophysical measurements on the 4-AP molecule interacting with a few selected solvents, from non-specific (1-chloro-*n*-alkanes, RCl) to specific (hexafluoroisopropanol, HFIP and dimethyl sulfoxide, DMSO). Based on our measurements and independent data, we estimated the energy of hydrogen bonds formed by this solute in the locally excited singlet state (S_1-LE) and in the S_1-ICT state with specifically interacting solvents. We also propose a scheme for the deactivation of the excited 4-AP molecule in solvents with differing properties. All these data lead to an interpretation of the complex dependencies of ν_{max}^{em}, ϕ_F, and τ_F on the properties of the surrounding media of the 4-AP molecule. In addition, because of similar behaviour seen in other probe molecules containing electron donor and electron acceptor groups, the results presented in our article and their interpretation can be applied to investigations of other probe molecules in homogeneous and micro-heterogeneous systems.

2. Experimental

2.1. Materials

4-AP (Aldrich) was purified by recrystallization from methanol. 1-Chloropropane (99%) (Aldrich), 1-chlorohexane (99%) (Aldrich), 1-chlorodecane (98%) (Aldrich), 1-chlorohexadecane (98%) (Fluka) were additionally dried over molecular sieve (A3). 1-Chlorobutane 99.5% (anhydrous) (Aldrich) was used as received, or when necessary, it was additionally dehydrated. DMSO anhydrous (Aldrich), DMSO-d_6 (Aldrich), HFIP for spectroscopy (Fluka), ACN anhydrous (Aldrich), tetrahydrofurane (THF) for fluorescence (Merck), diethyl ether for fluorescence (Merck), ethyl acetate for fluorescence (Merck), octanenitrile (97%) (Aldrich), D_2O (Aldrich) were used as received. H_2O was distilled and deionised. When necessary the samples were deoxygenated by bubbling dried oxygen-free helium through them for at least 5 min.

2.2. Experimental setup

Absorption spectra were measured on a Jasco V-550 spectrometer. Steady-state emission measurements were made on a modernized MPF-3 spectrofluorimeter with a single photon counting system [104]. An argon ion-pumped, tunable, modelocked Ti:sapphire laser was also used as an excitation source for the steady-state fluorescence measurements. The picosecond laser system and time-correlated single-photon counting (TCSPC) detection systems used to measure fluorescence lifetimes with picosecond precision have been previously described in detail [105–107].

3. Results and discussion

3.1. The solvatochromic studies

The choice of solvents for the solvatochromic study should allow for an accurate and separate determination of non-specific and specific interactions in the experimentally observed solvent spectral shifts of $\nu_{\max}^{\mathrm{abs}}$ and $\nu_{\max}^{\mathrm{em}}$. The main criterion was whether the solvent interacts exclusively via non-specific interactions with the solute or whether it forms in addition hydrogen bonds with the solute.

In our opinion, the best solvents, that interact only non-specifically with 4-AP, are the 1-chloro-*n*-alkanes (RCl). They do not form hydrogen bonds as their Kamlet–Taft hydrogen-bond donating and accepting abilities are $\alpha = 0$ and $\beta = 0$ [95–97]. They do not have π-electrons, they do not have a charge-transfer character; and their higher-order interactions – in particular the quadrupole ones – can be neglected [108]. Moreover, the same structure of the solvent molecules, with the chlorine atom always at the same position attached to the *n*-alkane chain of different lengths, should ensure that the Onsager model [1–4] of non-specific solute–solvents interactions should be valid [109–111]. Although the range of $f(\varepsilon, n^2)$ values for RCl used (from 0.11 for 1-chlorohexadecane to 0.23 for 1-chloropropane) is not very wide, it should be enough to extrapolate the dependencies of $\nu_{\max}^{\mathrm{abs}}$ and $\nu_{\max}^{\mathrm{em}}$ on $f(\varepsilon, n^2)$. It should be emphasised that the RCl have not been hitherto used in solvatochromic studies, except for a few cases when 1-chlorobutane was used in the study along with many other solvents.

The second group of solvents are those that specifically interact with 4-AP. In order to study the properties and energy of each type of hydrogen bond made by the 4-AP molecule (see Fig. 1) separately and to possibly form other species, it was necessary to use solvents capable of forming hydrogen bonds of *one of type exclusively*. The hydrogen bonds formed by the N–H bonds of the 4-AP molecule with electronegative heteroatoms of the solvent molecules have been studied in dimethylsulfoxide (DMSO), characterised by $\beta = 0.76$, and $\alpha = 0$ [95–97]. Determination of the change in the energy (ΔE_{HB}) of the hydrogen bonds, involving exclusively the oxygen atom and/or the carbonyl groups of 4-AP, required the use of solvents characterised by $\alpha \gg 0$ and $\beta = 0$. This condition is satisfied for HFIP whose $\alpha = 1.96$ and $\beta = 0$ or TFE whose $\alpha = 1.51$ and $\beta = 0$ [95–97]. The polyfluorinated alcohols appear to be an interesting group of solvents exhibiting properties distinct from those of other hydrogen-bonding protic solvents [112–122] and references therein. This is a consequence of the electron-withdrawing ability of the CF_3 group, which decreases the basicity and nucleophilicity of the oxygen atom but increases the acidity of the hydrogen atom of the hydroxyl group. The independently determined parameter SB was used to evaluate the suitability of TFE versus HFIP for these studies. SB is a measure of the solvent basicity (similar to β). It is much higher for TFE ($\mathrm{SB} = 0.107$) than for HFIP ($\mathrm{SB} = 0.014$)[1] [124]. Thus, to make sure that no hydrogen bonds will be formed between the solvent and the amino group of 4-AP, HFIP was chosen for the study. This solvent forms strong hydrogen bonds through its O–H bond as directly determined by the experimental and calculated values of E_{HB} [113–116,121,122,125] and as also seem in the results of absorption and emission solvatochromic measurements [41,51,113,126,127]. HFIP and DMSO are capable of forming hydrogen bonds of only one type, and they do not associate,[2] i.e. they do not form dimers or higher mers, in contrast to the majority of hydrogen-bond forming solvents. The molecules of HFIP and DMSO have approximately spherical shape and similar size ($r_{\mathrm{HFIP}} = 0.55$ Å, $r_{\mathrm{DMSO}} = 0.51$ Å) [97]. Their sizes are also similar to the molecules of the RCl used (1-chloropropane and 1-chlorobutane). Therefore, it could be assumed that Onsager's reaction-field model satisfactorily describes the non-specific interactions of 4-AP with HFIP and DMSO.

Absorption spectra, fluorescence excitation spectra, and emission spectra of 4-AP in selected solvents are presented in Fig. 2. These spectra show that there is a much larger solvent effect for $\nu_{\max}^{\mathrm{em}}$ (Fig. 2b) than for $\nu_{\max}^{\mathrm{abs}}$ (Fig. 2a). This is consistent with earlier results [66,77,79,89]. Table 1 gives the most important spectral results for 4-AP in selected solvents with relevant solvent properties also presented. There were no detectable changes in absorption or emission spectra within the range of 4-AP concentrations used (10^{-5} to 10^{-4} M).

3.1.1. The effect of non-specific interactions on the spectral shift

Since even small amounts of water in 4-AP solutions of RCl and other aprotic solvents affected $\nu_{\max}^{\mathrm{abs}}$ and, in particular, $\nu_{\max}^{\mathrm{em}}$, it was necessary to dry the solvents used (see e.g. Ref. [128]). Dehydrations were carried out until no changes (within experimental error) in the positions of the maxima of the longest wavelength bands in the absorption or fluorescence-excitation spectra and the emission spectra were observed. This corresponded to a water concentration in RCl lower than 10^{-2} M.

Solvatochromic measurements on 4-AP were performed in five different RCl solvents. In 1-chloropropane and 1-chlorobutane in which the solubility of 4-AP was relatively high, good quality absorption spectra were measured. Their shape was the same as that of fluorescence excitation spec-

---

[1] It is also confirmed by the results of [123], showing that TFE is more effective in solvating cations than HFIP.

[2] The lack of associates formation is evidenced by a significantly lower viscosity of HFIP ($\eta = 1.58$ cP) than that of 2-propanol ($\eta = 2.04$ cP) in spite of much greater size of the HFIP molecule. For comparison: the viscosity of perfluoroalkanes is 2.3–2.4 times greater than that of alkanes because of the greater size of the molecules of the former. Analogously, the lack of associates formation by DMSO ($\eta = 1{,}99$ cP) is evidenced by an over 5 times lower viscosity than that of CH_3SO_3H ($\eta = 10.5$ cP), which forms hydrogen bonds among their molecules, while the size of the molecules of both compounds is similar.

Table 1
Spectral properties of 4-AP in anhydrous solvents of different properties, in H_2O and in D_2O

Solvent	$\nu_{\max}^{\mathrm{abs}}$ (cm^{-1})	$\nu_{\max}^{\mathrm{em}}$ (cm^{-1})	$\Delta\nu_{\max}^{\mathrm{abs-em}}$ (cm^{-1})	$f(\varepsilon, n^2)$	ε[a]	n[a]	α[a]	β[a]
C_3H_7Cl	28680[b]	23310	5370	0.226	8.588	1.388	0	0
DMSO[c]	26770	20920	5850	0.264	46.45	1.477	0	0.76
HFIP	27780[d]	18150	9630	0.308	16.62	1.277	1.96	0.00
H_2O	27100	17830	9270	0.320	78.0	1.333	1.17	0.47
D_2O	27150	17690	9460	0.320	78.06	1.328		

n is the refraction coefficient and ε is the dielectric constant.

[a] From Ref. [97].

[b] $\nu_{\max}^{\mathrm{abs}}$ were determined also from fluorescence excitation spectra.

[c] The same $\nu_{\max}^{\mathrm{abs}}$ and $\nu_{\max}^{\mathrm{em}}$ values were obtained in DMSO-d_6.

[d] $\nu_{\max}^{\mathrm{abs}}$ were determined only from fluorescence excitation spectra.

tra (after conversion into the total intensity of absorbed light, I_a). The positions of the maxima of these two bands were also the same (Table 1 and Fig. 2a). In all RCl solvents used, the shapes of the fluorescence-excitation spectra of 4-AP were the same. The signal-to-noise ratio of absorption spectra of 4-AP in 1-chlorohexane, 1-chlorodecane, and 1-chlorohexadecane[3] were because of the low solubility of 4-AP in these RCl. Therefore, the values of $\nu_{\max}^{\mathrm{abs}}$ (Fig. 3) of 4-AP in 1-chlorohexane and 1-chlorodecane were determined from the more accurate measurements of the fluorescence-excitation spectra.

The same shape of the 4-AP emission spectra was observed in all the RCl solvents used (see Footnote 3). This means that in each solvent the transition in the 4-AP molecule occurred between the same electronic states. The polarities of 1-chlorobutane and 1-chloropropane are relatively high with $f(\varepsilon, n^2)$ equal to 0.209 and 0.226, respectively. Based on previous results [26,74,87,93,129] it is reasonable to assume that the emitting state is only the S_1-ICT state, at least for $f(\varepsilon, n^2) > 0.14$. In RCl solvents, there is a very small effect of $f(\varepsilon, n^2)$ on $\nu_{\max}^{\mathrm{abs}}$ as shown by the small change in absorption energy of $\Delta\nu_{\max}^{\mathrm{abs}} = 470\,\mathrm{cm}^{-1}$ when f changes by $\Delta f(\varepsilon, n^2) = 0.30$ (see Fig. 3). Therefore, it can be assumed that the energy of the non-specific interactions of 4-AP with the RCl solvents is only slightly larger in its absorbing S_1-LE state than in its ground state. This means that as a result of the $S_0 \rightarrow S_1$-LE transition, the value of the dipole moment of 4-AP is not much larger than its value in the ground state, i.e. $\mu_{S_0} = 3.0$–$4.0\,\mathrm{D}$ [1,15,88]. This result is in full agreement with the very small (nearly 1 D) increase in the dipole moment of NM-4-AP determined from the integrated electrooptical emission measurements, by Nemkovich et al. [26] in cyclohexane. From this it can be surmised that in a nonpolar solvent, the emission of NM-4-AP from its S_1-LE state will be different than in more polar solvents where the probe molecule emits from its S_1-ICT state [26].

The solvatochromic plot of the 4-AP emission data in RCl (see Fig. 3) shows that the non-specific interactions in the S_1-ICT state of 4-AP are significantly stronger than in the absorbing S_1-LE state. This is shown by the significantly larger effect of $f(\varepsilon, n^2)$ on $\nu_{\max}^{\mathrm{em}}$ than on $\nu_{\max}^{\mathrm{abs}}$. $\Delta\nu_{\max}^{\mathrm{em}}$ is equal to $1310\,\mathrm{cm}^{-1}$ for $\Delta f(\varepsilon, n^2) = 0.30$ compared to $470\,\mathrm{cm}^{-1}$ for absorption. The absorption measurements of 4-AP and, in particular, the study of solvent effects on $\nu_{\max}^{\mathrm{abs}}$ involve the transition from the relaxed ground state to the locally excited Franck–Condon state, $S_0^{\mathrm{rel}} \rightarrow S_1^{\mathrm{FC}}$-LE. In contrast emission measurements and the study of solvent effects on $\nu_{\max}^{\mathrm{em}}$ involve the transition from the relaxed excited state to the Franck–Condon ground state, S_1^{rel}-ICT $\rightarrow S_0^{\mathrm{FC}}$. As shown from fluorescence polarisation measurements [130] on the fairly rigid molecules of aminophthalimides, the absorption and emission transition moments are parallel, and it can be assumed that there is no essential difference between the directions of the dipole moments in the Franck–Condon (μ_e^{FC}) and the relaxed (μ_e^{rel}) 4-AP excited state. Taking this into account, Nemkovich et al. [26] have shown that the values of μ_e^{FC} and μ_e^{rel} in the S_1-ICT states of NM-4-AP and 3-AP are almost equal (see Table 2), so also the distribution of electron density in these states is very similar. By extrapolation it can be assumed that the situation is similar for the S_0 state of 4-AP. Thus, when determining the dipole moment of 4-AP in its S_1-ICT state ($\mu_{S_1\text{-ICT}}$), the differences between the Frank-Condon and the relaxed states of 4-AP can be neglected. This will be important in the discussion of the solvatochromic and photophysical results of 4-AP. The solvatochromic measurements of 4-AP emission in RCl permit determination of $\mu_{S_1\text{-ICT}}$. Based on the results reported by Nemkovich et al. [26], we can assume that the cavity radii are the same and the vectors are collinear in the S_0, S_1-LE, and S_1-ICT states [130]. Taking into account that $\mu_{S_0} = 3.0$–$4.0\,\mathrm{D}$[4] of 4-AP and that in RCl the effect of $f(\varepsilon, n^2)$ on $\nu_{\max}^{\mathrm{em}}$ is 2.8 times greater than on $\nu_{\max}^{\mathrm{abs}}$, it can be assumed that $\mu_{S_1\text{-ICT}} = 8.4$–$11.2\,\mathrm{D}$.[5]

A large Stokes shift is observed for the approximately rigid 4-AP molecules in RCl ($\Delta\nu_{\max}^{\mathrm{abs-em}} > 5100\,\mathrm{cm}^{-1}$, Table 1 and Fig. 4). This confirms that the transition observed in the absorption spectra ends in the S_1-LE state and that the transition in emission spectra starts from the S_1-ICT state.

The non-specific solvent interactions with the excited states of 4-AP are not strong enough to lead to complex formation

---

[3] The slight dependence of $\nu_{\max}^{\mathrm{em}}$ position on λ_{exc} observed for emission spectra of 4-AP in 1-chlorohexadecane prevented the use of this RCl in quantitative solvatochromic measurements.

[4] These values are most often reported, but it is possible to find $\mu_{S_0} = 5.1$ [66] or 5.3 [79].

[5] It is worth noting that although most often it is assumed that for 4-AP in S_1-ICT the value of $\mu_{S_1\text{-ICT}}$ is ~6.0 D, from independent solvatochromic measurements a value of 8.3–9.0 D was obtained [78,88].

Table 2
The contributions of non-specific interactions (NS) and hydrogen bonds (HB) for 4-AP in selected solvents as determined from the solvatochromic absorption and emission measurements

Solvent	$\nu_{\max}^{\text{abs}}(f(\varepsilon, n^2))$ (cm^{-1})	$\Delta\nu_{\text{shift}}^{\text{abs}}$(NS) (cm^{-1})	$\Delta\nu_{\text{shift}}^{\text{abs}}$(H-bond) (cm^{-1})	$\nu_{\max}^{\text{em}}(f(\varepsilon, n^2))$ (cm^{-1})	$\Delta\nu_{\text{shift}}^{\text{em}}$(NS) (cm^{-1})	$\Delta\nu_{\text{shift}}^{\text{em}}$(H-bond) (cm^{-1})
C_3H_7Cl	28680	370	0	23310	1020	0
DMSO	28640	410	1870	23180	1150	2260
HFIP	28560	490	780	22980	1350	4830
H_2O	28550	500	1450	22930	1400	5100

The parameters $\nu_{\max}^{\text{abs}}(f(\varepsilon, n^2))$, $\Delta\nu_{\text{shift}}^{\text{abs}}$(H-bond), $\nu_{\max}^{\text{em}}(f(\varepsilon, n^2))$ and $\Delta\nu_{\text{shift}}^{\text{em}}$(H-bond) are defined in the text, the parameters $\Delta\nu_{\text{shift}}^{\text{abs}}$(NS) and $\Delta\nu_{\text{shift}}^{\text{em}}$(NS) bring information on the contributions of non-specific interactions to $\nu_{\max}^{\text{abs}}$ and $\nu_{\max}^{\text{em}}$ for 4-AP in a given solvent relative to $\nu_{\max}^{\text{abs}}$ and $\nu_{\max}^{\text{em}}$ for $f(\varepsilon, n^2) = 0$. The experimental $\nu_{\max}^{\text{abs}}$ and $\nu_{\max}^{\text{em}}$ values and the most important properties of the solvents are given in Table 1; $\nu_{\max}^{\text{abs}}(f(\varepsilon, n^2) = 0) = 29\,050\,\text{cm}^{-1}$, $\nu_{\max}^{\text{em}}(f(\varepsilon, n^2) = 0) = 24\,330\,\text{cm}^{-1}$ (see Fig. 3).

with the solvent molecules. This is true even though the energy of non-specific interactions with the S_1-ICT state of 4-AP is greater than with the S_1-LE state because of the significantly larger dipole moment of 4-AP in its S_1-ICT state. The above conclusion in consistent with the small value of the non-specific interaction energy of 4-AP molecules in their S_1-ICT state with individual molecules of the solvent. This interaction energy was estimated from calorimetric data and theoretical calculations for molecules of similar properties [131] and also from solvatochromic measurements of 4-AP in RCl (Fig. 3). The resulting values is less than 100 cm^{-1} per solvent molecule assuming that the first solvation layer has at least 10 solvent molecules and that the interaction energy of 4-AP with each of them is similar.

3.1.2. The effect of specific interaction (hydrogen bonds) on the spectral shifts

It was possible to extract the contributions of the specific interactions between 4-AP and the hydrogen bonding solvents HFIP and DMSO out of the overall solute–solvent interactions. This was accomplished on the basis of solvatochromic plots for absorption spectra, fluorescence-excitation spectra, and emission spectra of 4-AP in RCl and with the information on $\nu_{\max}^{\text{abs}}$ and $\nu_{\max}^{\text{em}}$ measured in HFIP and DMSO. The procedure used to determine the energy ΔE_{HB} of the hydrogen bonds between the solvent and the solute in two different electronic states was based on an analysis of the solvatochromic dependencies of $\nu_{\max}^{\text{abs}}$ and $\nu_{\max}^{\text{em}}$ on the polarity function $f(\varepsilon, n^2)$ of the solvents used. An analogous determination was made for the dipole moment in the excited state. The first step of the procedure required a determination of the contribution of the non-specific interactions *only* using the experimentally observed solvent spectral shifts, both in the absorption spectra and the emission spectra of the solute studied. The results of the solvatochromic study in the RCl solvents interacting only non-specifically can be approximated by straight lines (see Fig. 3). It was assumed that these lines describe the effect of non-specific solute–solvent interactions on the values of $\nu_{\max}^{\text{abs}}$ and $\nu_{\max}^{\text{em}}$, not only in the RCl solvents but also in other solvents that make hydrogen bonds with 4-AP, as long as these solvents satisfy the other assumptions of the Onsager reaction field model of interactions with solute molecule. The distance between $\nu_{\max}^{\text{abs}}$ and/or $\nu_{\max}^{\text{em}}$ values and the straight line describes the change in the energy of the hydrogen bonds (ΔE_{HB}) formed by 4-AP molecule in a given solvent. The bathochromic shift of $\nu_{\max}^{\text{abs}}$ and/or $\nu_{\max}^{\text{em}}$ (the corresponding points below the line), means that this energy is greater in the excited state. The value of ΔE_{HB} between two electronic states, $\Delta\nu_{\text{shift}}^{\text{abs}}$(H-bond) and $\Delta\nu_{\text{shift}}^{\text{em}}$(H-bond), is determined from simple equations (1) and (2):

$$\Delta\nu_{\text{shift}}^{\text{abs}}(\text{H-bond}) = \nu_{\max}^{\text{abs}}(f(\varepsilon, n^2)) - \nu_{\max}^{\text{abs}}, \tag{1}$$

$$\Delta\nu_{\text{shift}}^{\text{em}}(\text{H-bond}) = \nu_{\max}^{\text{em}}(f(\varepsilon, n^2)) - \nu_{\max}^{\text{em}}, \tag{2}$$

where $\nu_{\max}^{\text{abs}}$ and $\nu_{\max}^{\text{em}}$ are the experimental positions of the maxima of the absorption and the steady-state fluorescence spectra of the solute in a solvent forming hydrogen bonds with this molecule. $\nu_{\max}^{\text{abs}}(f(\varepsilon, n^2))$ and $\nu_{\max}^{\text{em}}(f(\varepsilon, n^2))$ are the values of the predicted maxima of the absorption and the steady-state fluorescence spectra, respectively, of the solute in this solvent. These latter two quantities correspond to non-specific interactions only (from the straight line in the solvatochromic plot).

The experimentally observed position of $\nu_{\max}^{\text{abs}} = 27\,780\,\text{cm}^{-1}$ in HFIP relative to $\nu_{\max}^{\text{abs}}(f(\varepsilon, n^2)) = 28\,560\,\text{cm}^{-1}$ obtained from the solvatochromic plot for 4-AP in RCl for $f(\varepsilon, n^2) = 0.308$ (Fig. 3) indicates a bathochromic shift of absorption spectra, thus the value $\Delta\nu_{\text{shift}}^{\text{abs}}$(H-bond) for 4-AP in this solvent

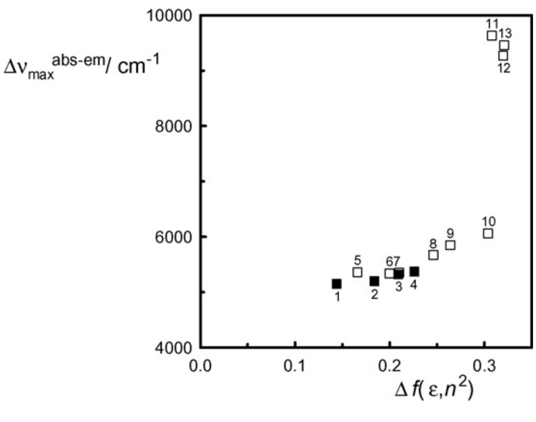

Fig. 4. The solvatochromic plot of the $\Delta\nu_{\max}^{\text{abs-em}}$ dependence on $\Delta f = ((\varepsilon - 1)/(2\varepsilon + 1)) - ((n^2 - 1)/(2n^2 + 1))$ of 4-AP in selected solvents: (1) 1-chlorodecane, (2) 1-chlorohexane, (3) 1-chlorobutane, (4) 1-chloropropane, (5) diethyl ether, (6) ethyl acetate, (7) THF, (8) octanenitrile, (9) DMSO, (10) ACN, (11) HFIP, (12) H_2O, (13) D_2O.

is 780 cm^{-1}.[6] These data imply that the energy of the hydrogen bonds is 780 cm^{-1} larger in the S_1-LE state than in S_0. This is a result of a relatively small increase in the electron density on the oxygen atoms of the carbonyl groups immediately after excitation of the 4-AP molecule.

There is a significant bathochromic shift of $\nu_{\mathrm{max}}^{\mathrm{em}} = 18\,150\,\mathrm{cm}^{-1}$ for 4-AP in HFIP relative to $\nu_{\mathrm{max}}^{\mathrm{em}}(f(\varepsilon, n^2)) = 22\,980\,\mathrm{cm}^{-1}$ for $f(\varepsilon, n^2) = 0.308$ from the solvatochromic results in RCl (Fig. 3). This implies that $\Delta\nu_{\mathrm{shift}}^{\mathrm{em}}(\text{H-bond}) = 4830\,\mathrm{cm}^{-1}$. It means that E_{HB} in the S_1-ICT state is much larger than E_{HB} in the S_0 or S_1-LE states. For the two excited states the ratio is large $\Delta\nu_{\mathrm{shift}}^{\mathrm{em}}(\text{H-bond})/\Delta\nu_{\mathrm{shift}}^{\mathrm{abs}}(\text{H-bond}) = 4830\,\mathrm{cm}^{-1}/780\,\mathrm{cm}^{-1} = 6.2$. The reason for such a large ratio must be that there is significant charge transfer, in the transition from the S_1-LE to the S_1-ICT state, which goes from the donor part of the 4-AP molecule to the oxygen atoms of its carbonyl groups. It is expected that the formation of such a strong hydrogen bond should lead to formation of a S_1-exciplex,[7] (S_1-exc(1)) with high efficiency.

The position of $\nu_{\mathrm{max}}^{\mathrm{abs}} = 26\,770\,\mathrm{cm}^{-1}$ in DMSO relative to $\nu_{\mathrm{max}}^{\mathrm{abs}}(f(\varepsilon, n^2)) = 28\,640\,\mathrm{cm}^{-1}$ evaluated at $f(\varepsilon, n^2) = 0.264$ (Fig. 3) indicates a relatively strong bathochromic shift of the absorption spectra of 4-AP as a result of the excitation $S_0 \rightarrow S_1$-LE. It is over twice as large as that in HFIP. The computed value of $\Delta\nu_{\mathrm{shift}}^{\mathrm{abs}}(\text{H-bond}) = 1870\,\mathrm{cm}^{-1}$. This means that, on average, each of the two hydrogen bonds N–H···O=S in the S_1-LE state is 935 cm^{-1} stronger than the hydrogen bonds in the S_0 state.[8] Taking into account the results of theoretical calculations of the changes in electron density within the 4-AP molecule as a result of its excitation [75], this change of E_{HB} can be interpreted as resulting from a decrease in the electron density on the two hydrogen atoms of the NH_2 group.

In DMSO $\Delta\nu_{\mathrm{shift}}^{\mathrm{em}}(\text{H-bond}) = 2260\,\mathrm{cm}^{-1}$, therefore, the two hydrogen bonds of the same type in the S_1-ICT state are 1130 cm^{-1} stronger than the hydrogen bonds in the S_0 state. This is a result of a lower electron density on the hydrogen atoms of the amino group in the S_1-ICT state than in the S_0 state. In contrast to the behaviour in HFIP, the two bathochromic shifts of $\nu_{\mathrm{max}}^{\mathrm{abs}}$ and $\nu_{\mathrm{max}}^{\mathrm{em}}$ of 4-AP in DMSO are similar to each other (Fig. 3). These results lead to an important conclusion that the energy of the hydrogen bonds formed between DMSO with 4-AP in its S_1-LE state is similar in energy to the analogous hydrogen bond with 4-AP in its S_1-ICT state. Thus, the transition from S_1-LE to S_1-ICT is not accompanied by changes in the electron density on the two hydrogen atoms of the NH_2 group. As a consequence, there is also no change in the concentration of 4-AP forming an S_1-exciplex (S_1-exc(2)) via the N–H···O=S hydrogen bonds with DMSO molecules.

We also performed solvatochromic measurements of NM-4-AP in DMSO. The values of $\Delta\nu_{\mathrm{shift}}^{\mathrm{abs}}(\text{H-bond})$ and $\Delta\nu_{\mathrm{shift}}^{\mathrm{em}}(\text{H-bond})$ in this solvent are by about 200 cm^{-1} (for the former) and 50 cm^{-1} (for the latter), respectively, smaller for NM-4-AP than for 4-AP. Also in HFIP, H_2O and D_2O, the values of $\Delta\nu_{\mathrm{shift}}^{\mathrm{abs}}(\text{H-bond})$ and $\Delta\nu_{\mathrm{shift}}^{\mathrm{em}}(\text{H-bond})$ are very similar for both aminophthalimides. Thus it can be concluded that the imino group of 4-AP forms hydrogen bonds of very similar energy in the S_0, S_1-LE and S_1-ICT states. Although the spectral and photophysical properties of NM-4-AP and their comparison to those of 4-AP will be a subject of a separate work [133], the solvatochromic data are presented here because of the contradictory interpretation of the role of the imino groups in the emission solvatochromic data and deactivation of 4-AP [77,80,86,87]. Thus, our results show that after excitation of the 4-AP molecule, the proton transfer does not take place with the involvement of a protic solvent from the imino group to the oxygen atom of the carbonyl group.

We can also comment briefly on the solvatochromic results for 4-AP dissolved in ethers, esters, and nitriles. It is often assumed that these solvents interact through non-specific interactions only, and hence, they are often used for the determination of the dipole moments of probes in their excited states from solvatochromic measurements. However, as shown by the experimental values of $\nu_{\mathrm{max}}^{\mathrm{abs}}$ and $\nu_{\mathrm{max}}^{\mathrm{em}}$ obtained for 4-AP in these solvents (Fig. 3), in each of the solvents there are similar bathochromic shifts of the maxima of their long-wavelength band in the absorption spectra and emission spectra, relative to its positions in the spectra taken in RCl. It is not surprising taking into account that for these solvents $\beta \approx 0.40$–0.55 [96,97,112,134], thus they can form hydrogen bonds (analogously as DMSO) with the N–H bonds of the 4-AP molecule.

For the sake of illustration we also present the 4-AP Stokes shift dependence on the $f(\varepsilon, n^2)$ value of the solvents used (Fig. 4). The character of the dependence reflects a significant effect of hydrogen bonds on the value of $\Delta\nu_{\mathrm{max}}^{\mathrm{abs-em}}$, observed in protic solvents. However, the presence of hydrogen bonds between 4-AP and aprotic solvents (DMSO, nitriles, ethers) is almost undetectable because of the similar values of E_{HB} in the S_1-LE and the S_1-ICT excited states. Therefore, in order to detect hydrogen bonds and to determine their ΔE_{HB} (also regarding that different excited states are observed in absorption spectra and emission spectra), solvatochromic results should be

---

[6] The absorption spectrum of 4-AP in HFIP significantly differs from the absorption spectra taken in the other solvents (Fig. 2), in particular in the shape in the long-wavelength region. The reason for the differences most probably is the formation of the complex of 4-AP···$(\mathrm{HFIP})_n$ in the ground state (S_0-comp), where $n \geq 1$, because of a relatively high value of E_{HB} of the hydrogen bonds made by HFIP and the molecules including carbonyl group [113,115,116,121,122]. That is why the fluorescence excitation spectra measured in HFIP for the emission wavelength $\lambda_{\mathrm{em}} = 550$–$650$ nm were used for determination of $\nu_{\mathrm{max}}^{\mathrm{abs}}$ in HFIP. The shape of these fluorescence excitation spectra is very similar to that of the 4-AP absorption bands in the other solvents not forming S_0-comp, and the value of $\nu_{\mathrm{max}}^{\mathrm{abs}} = 27\,780\,\mathrm{cm}^{-1}$ determined from fluorescence excitation spectra in HFIP is practically independent of λ_{em} in the range 550–650 nm, so in the range of S_1-exc(1) emission. This S_1-exc(1) appears as a result of formation of a strong hydrogen bond by 4-AP in the S_1-ICT state and HFIP. Unfortunately, we do not know a solvent whose value of α would be lower than that of HFIP, so that the hydrogen bonds made with 4-AP in the S_0 state would be weak enough not to form the S_0-comp and whose basicity would be low enough not to form weak hydrogen bonds with the H–N bonds of the amino group.

[7] We use the term S_1-exciplex for the excited complex of (S_1-4-AP···S_0-solvent) also when it was formed as a result of the excitation of S_0-complex, according to Ref. [132].

[8] The presence of individua with one hydrogen bond N–H···O=S and 4-AP molecules not forming hydrogen bonds in the S_1 state in the solution cannot be excluded.

presented in the form of dependencies of $\nu_{\max}^{\mathrm{abs}}$ and $\nu_{\max}^{\mathrm{em}}$ on $f(\varepsilon, n^2)$ (see Fig. 3).

A similar method for the determination of the contributions of non-specific interactions and hydrogen bonds has been proposed by Maroncelli et al. [15] for 16 different solutes in 1-propanol, however they adopted the Kamlet–Taft approach. In this paper these authors show that for a majority of the solutes studied, including 4-AP and NM-4-AP, the hydrogen bonds made by these solutes with 1-propanol make a significant contribution to the solvent spectral shift. This had hitherto been often neglected, assuming that in the processes of solvating molecules with both acceptor and donor groups, the non-specific interactions play the main role. To study exclusively the non-specific interactions between the solute and the solvent, Maroncelli et al., chose eight aprotic solvents. As has been shown in our paper (see Fig. 3 and Table 2) six of them characterised by $0.4 \leq \beta \leq 0.76$, including DMSO, make hydrogen bonds of the acceptor type with the majority of the solutes studied. Since Maroncelli et al. [15] did not take this into account the contributions of hydrogen bonding to the solvent spectral shifts that they calculated were probably underestimated.

3.1.3. *Energy of hydrogen bonds formed by 4-AP*

Solvatochromic results permit only the determination of ΔE_{HB} between two electronic states. Therefore, determination of E_{HB} made by 4-AP in the excited states requires the knowledge of E_{HB}, formed by 4-AP in its ground state. Unfortunately, we have not found any literature (calorimetric, theoretical calculation, etc.) data on the energy of the interaction of 4-AP (or similar molecules e.g. NM-4-AP) in the S_0 state, with HFIP, DMSO, H_2O, and other solvents which could be used for an estimation of E_{HB} made by N–H bonds from the amino groups or oxygen atoms from the carbonyl groups of 4-AP with the solvents molecules. Therefore, in order to estimate the E_{HB} made between the oxygen atom from the carbonyl group of 4-AP in the S_0 state and the O–H bond from HFIP, we used the experimental result of $E_{\mathrm{HB}} = 2500\,\mathrm{cm}^{-1}$ for the hydrogen bond formed between the carbonyl oxygen atom of flavone in the ground state and HFIP (in the 1:1 complex) [122]. Since 4-AP is a rigid aromatic molecule with a similar dipole moment in its ground state and a similar the size to flavone, we assume that this approximation is adequate.[9] Because of a similar distribution of electron density on the two carbonyl groups of 4-AP in its S_0 state [75], it can be assumed that E_{HB} of the bond made by them is similar.

Taking into account that the 4-AP molecule includes two carbonyl groups whose oxygen atoms have two lone electron pairs, there is the possibility for the formation of more than one hydrogen bond. It is usually assumed that the solute and solvent form a single hydrogen bond although it has been shown in a number of works [78,137–142] that the carbonyl group can form two such bonds. Topp et al. [102,103] have shown in a supersonic jet experiment that two carbonyl groups of 4-AP are able to form hydrogen bonds both in the S_0 and S_1 state. Unfortunately, to the best of our knowledge, there are no experimental or theoretical data for 4-AP and/or similar compounds that would describe the number and energy of hydrogen bonds formed by two carbonyl groups in solution. Taking into account the energies of hydrogen bonds formed between the oxygen atom and π-electrons of the carbonyl group of several ketones (including anthrone) with H–O bond in methanol [143] as well as of acetone or cyclohexanone and the H–O bond in the *p*-cresol molecule [142], we can assume by analogy that in the interaction of 4-AP in the S_1-ICT state with HFIP the hydrogen bonds formed via the n-electron pair of oxygen atoms are significantly stronger than via π-electrons of the carbonyl group.

Table 3
Total energy of hydrogen bonds of a given type $\left(E_{\mathrm{HB}}^{\Sigma},\ \mathrm{cm}^{-1}\right)$ formed by the 4-AP molecule in different electronic states with DMSO, HFIP and H_2O[a]

State	DMSO	HFIP	H_2O	
	N–H···O=S	C=O···H–O	N–H···O=H_2	C=O···H–O–H
S_0	1090 (5.4)	5000 (25.0)	670 (3.4)	2960 (14.8)
S_1-LE	2960 (14.8)	5780 (29.0)	1830 (9.2)	3420 (17.2)
S_1-ICT	3350 (16.8)	9830 (49.2)	2070 (10.4)	5820 (29.0)

The values in parentheses are $E_{\mathrm{HB}}^{\Sigma}/k_{\mathrm{B}}T$.

[a] Similar values of E_{HB} can be assumed for D_2O in view of very similar solvatochromic results in D_2O and H_2O and the values of $f(\varepsilon, n^2)$ in these solvents.

The E_{HB} of hydrogen bonds between 4-AP in its S_1-LE state with HFIP was determined from the estimated E_{HB} value of the hydrogen bond formed by 4-AP in the S_0 state and ΔE_{HB} obtained from the absorption spectra. An analogous determination of E_{HB} between 4-AP in its S_1-ICT state and HFIP was obtained from emission spectra in HFIP (Fig. 3). The total values of E_{HB} in the S_1-LE and S_1-ICT states being a sum of energies of all hydrogen bonds in the system made with the strong protic solvent were computed to be 5780 and $9830\,\mathrm{cm}^{-1}$, respectively (see Table 3).[10] A comparison of the E_{HB} values for 4-AP in the S_1-ICT and S_0 states shows that $E_{\mathrm{HB}}(S_1\text{-ICT})/E_{\mathrm{HB}}(S_0) \approx 2.0$ (or ∼1.7 relative to S_1-LE). Since the 4-AP molecules in the S_1-ICT state form such strong hydrogen bonds, it can be expected that practically all the 4-AP molecules in this state form S_1-exc(1) with HFIP. Taking into account that in the conditions

---

[9] The significant differences in the properties of HFIP and carbon tetrachloride as solvents are the reason why the value of $E_{\mathrm{HB}} \sim 2500\,\mathrm{cm}^{-1}$, assumed for 4-AP in the S_0 state in HFIP should be treated as approximate. As it has been shown, e.g. in [121,135,136], the influence of the solvent on E_{HB} and in consequence on S_0-complex formation efficiency is significant.

[10] In the hitherto discussion we have disregarded the effect of hydrogen bonds that can be formed by alone electron pairs of nitrogen atoms from amine and imine group with the H–O bonds of HFIP or H_2O. It is assumed that excitation of the 4-AP molecule to S_1-LE and particularly to S_1-ICT, leads to a decrease in the electron density on the nitrogen atom of amino group so weakening of its hydrogen bond. However, according to literature data [113] the relevant change in E_{HB} may be small relative to the value of E_{HB} in the S_0 state. Therefore, it can be assumed that taking into regard the change in the energy of this hydrogen bond leads to still higher values of E_{HB} formed by the carbonyl groups in the S_1-ICT state, which however, has no significant effect on the interpretation results proposed.

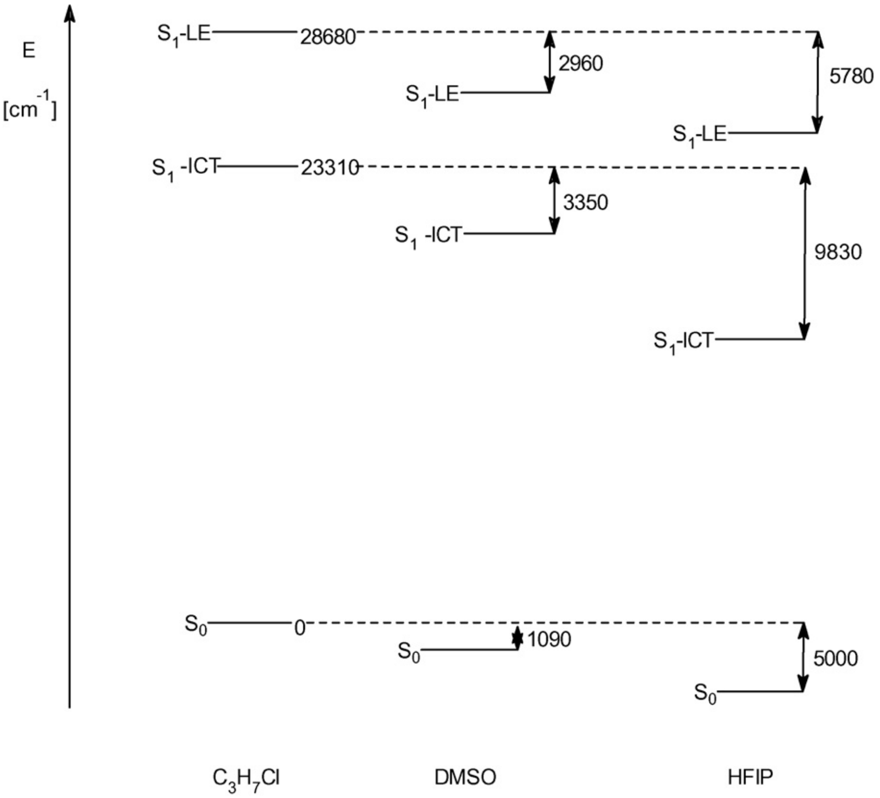

Fig. 5. The scheme of electronic levels of 4-AP in 1-chloropropane (non-specific interactions), DMSO and HFIP (non-specific interactions and hydrogen bonds); the energy values given correspond to $\nu_{\max}^{\text{abs}}$ (S_1-LE) and $\nu_{\max}^{\text{em}}$ (S_1-ICT); the relatively small differences in the energy of nonspecific interactions of 4-AP with the three solvents are disregarded.

of spectral and photophysical measurements (at room temperature) the mean energy per a single degree of freedom is $(1/2)k_BT \approx 100\,\text{cm}^{-1}$ (where k_B is the Boltzmann constant, T is the temperature in Kelvin) the above data imply that the energy for a single hydrogen bond (E_{HB}^1) for 4-AP in its S_1-ICT state in HFIP is equal to about $25k_BT$. In additional taking into account the value of E_{HB}^1 in the S_0 state (Table 3), it can be assumed that a significant fraction of the 4-AP molecules dissolved in HFIP are able to form a complex in the ground state (S_0-comp) with this solvent.

Estimations were also made of the energies of the hydrogen bonds between DMSO's oxygen and the amino group (N–H) of 4-AP in its S_0 state. These energies were estimated from the independent measurements on compounds that differ from 4-AP but which have the same hydrogen-bond forming N–H bonds (or n-alkyl amino groups) and which have similar values of their dipole moments in their S_0 state [144]. The energy E_{HB} determined for the hydrogen bonds formed between DMSO and amino groups of cytosine and guanine and their methyl and ethyl derivatives is 3.1 or 1.55 kcal/mol for a single N–H bond [144]. From these data, the two hydrogen bonds made between DMSO and the amino groups of the 4-AP molecule in its S_0 state should have a total value of $E_{\text{HB}}^{\Sigma} \sim 1090\,\text{cm}^{-1}$ (i.e. for one hydrogen bond $E_{\text{HB}}^1 \approx 545\,\text{cm}^{-1}$). Therefore, the energy of the hydrogen bond formed by the 4-AP molecule in the S_0 state with DMSO molecules is too low to enable formation of a complex in the ground state. From the solvatochromic results on the $S_0 \rightarrow S_1$-LE transition, the total E_{HB} of the bond formed between DMSO and the N–H bonds of the amino group of 4-AP in its S_1-LE state increases by $\sim 1870\,\text{cm}^{-1}$ relative to S_0 (Fig. 3). The total value of E_{HB}^{Σ} in S_1-LE is therefore, about $2960\,\text{cm}^{-1}$, which means that the energy of a single hydrogen bond N–H···O=S is $E_{\text{HB}}^1 \approx 1480\,\text{cm}^{-1}$. The value of E_{HB} ($\sim 7k_BT$) for a single hydrogen bond in this state indicates that there is a possibility to form an S_1-exc(2) between 4-AP and one or two of the DMSO molecules. The value of E_{HB} for the two N–H···O=S hydrogen bonds in S_1-ICT states is $E_{\text{HB}}^{\Sigma} = 3350\,\text{cm}^{-1}$ ($1675\,\text{cm}^{-1}$ per a single bond). This value is very similar to that in the S_1-LE state. Therefore, as mentioned earlier, as a result of the transition from S_1-LE to S_1-ICT, the concentration of S_1-exc(2) is practically the same as indicated by the very small value of $E_{\text{HB}}(S_1\text{-ICT})/E_{\text{HB}}(S_1\text{-LE}) \approx 1.1$.

Based on the results of solvatochromic measurements on 4-AP and the calculated value of E_{HB} in its S_0 state [113,121,122,125,144], a scheme can be constructed for the electronic levels of 4-AP in its S_0, S_1-LE, and S_1-ICT states in selected solvents: 1-chloropropane, DMSO and HFIP (Fig. 5). From a comparison of the energies of 4-AP in its S_0 and S_1 states (Fig. 5 and Table 3), it can be concluded that the hydrogen bonds made between the 4-AP molecule and DMSO and HFIP have great effect on energy decreases, in particular, in the S_1-ICT state. The non-specific interactions of 4-AP with DMSO

Table 4
Photophysical properties of 4-AP in selected anhydrous, aerated solvents, in H_2O and in D_2O

Solvent	ϕ_F	τ_F (ns)	k_F ($\times 10^7$ s^{-1})	k_{nr} ($\times 10^7$ s^{-1})	E_{S_1} (cm^{-1})[a]	Most important fluorescent individual
C_3H_7Cl	0.69; 1.0[b]	12.5; 17.9[b]	5.52; 5.59	<0.1	23310	S_1-4-AP
ACN	0.63[c]; 0.96[b,d]	14[c]; 21.3[b,e]	4.50	0.19	21790	S_1-4-AP[f]
DMSO	0.83[g]; 0.91[b]	17.5; 19.2[b]	4.74[h]	0.47	20920	S_1-4-AP, S_1-exc(2)
HFIP	0.053; 0.065[b,e]	2.3; 2.8[b]	2.30	33.4	18150	S_1-exc(1)
D_2O	0.12; 0.045[c]	5.4; 5.7[i]	2.22	16.3	17690	S_1-exc(1)
H_2O	0.022; 0.014[d]; 0.01[c]	1.05; 1.2[i]	2.10	93.1	17830	S_1-exc(1)

[a] E_{S_1} is taken from the position of the emission maximum of 4-AP in the S_1-ICT state, S_1-exc(1) and S_1-exc(2).

[b] In deoxygenated solution.

[c] From Ref. [79].

[d] From Ref. [89].

[e] Calculated from the relation $\phi_F(\text{deox}) = \phi_F\tau_F(\text{deox})/\tau_F$, and $\tau_F(\text{deox}) = \tau_F\phi_F(\text{deox})/\phi_F$, where ϕ_F(deox) and τ_F(deox) are the quantum yield of fluorescence and fluorescence lifetime for 4-AP in deoxygenated solution.

[f] S_1-exc(2) is also present but at a lower concentration than in DMSO.

[g] The same ϕ_F value was obtained in DMSO-d_6.

[h] For aerated and deoxygenated solution.

[i] From Ref. [77].

and HFIP are relatively not much stronger than those with 1-chloropropane, both in the S_0 and S_1 states.[11] The results show that the experimental solvent spectral shifts, both in absorption spectra and in emission spectra, at the transition between S_0 and S_1-LE or S_1-ICT are determined mainly by the increases in E_{HB} in the excited states and not by an increase in their dipole moment. This effect is surprisingly large, which means that the results interpreted under the assumption that practically the total spectral shift was due to the non-specific interactions, neglecting the hydrogen bonds, must be treated with caution [1,4,88].

Taking into account the solvatochromic results of absorption and emission spectra for 4-AP in HFIP and DMSO, it was possible to propose a quantitative interpretation of the spectral shift recorded for 4-AP in H_2O (using α and β values of these three solvents). In this solvent the 4-AP molecule forms hydrogen bonds of donor type (as in DMSO) and acceptor type (as in HFIP). The values of E_{HB} estimated for 4-AP in its S_0, S_1-LE, and S_1-ICT states in H_2O are presented in Table 3.

The calculated E_{HB} given in Table 3 should be treated as approximate. However, on the basis of these data obtained for a complex solute–solvent system containing both donor and acceptor hydrogen bonds, it is possible to infer the formation of species other than 4-AP molecules.

The occurrence of hydrogen bonds between the excited 4-AP molecule and trifluoroethanol (TFE) molecules, leading to formation of 1:1 complex, is indicated by the rotation dynamic measurements [145], quite independently of our solvatochromic results. Rotation of 4-AP in TFE is significantly slower than would be expected on the basis of the correlation established in the other solvents that are not able to form hydrogen bonds.

3.2. The photophysical studies

In order to determine the properties of the 4-AP molecules in their excited states and, in particular, to explain the reasons for the strong dependence of $\nu_{\max}^{\text{em}}$, ϕ_F, and τ_F [66,77,79] on solvent properties, photophysical measurements were performed in the same solvents as were used in the solvatochromic studies. Quantum yields of 4-AP fluorescence were measured by a relative method using quinine sulfate in 0.1N H_2SO_4 ($\phi_F = 0.52$) as the standard. The results of ϕ_F and τ_F, for 4-AP in aerated solvents (some solvents were also deoxygenated) are presented in Table 4. Also Table 4 presents the radiative rate constant, $k_F = \phi_F\tau_F^{-1}$, and the rate constant of radiationless deactivation, $k_{nr} = (1 - \phi_F)\tau_F^{-1}$, of 4-AP in selected solvents. The lifetime of 4-AP in the S_1-ICT state is relatively long, $\tau_{S_1\text{-ICT}} \approx 20$ ns (in the oxygen-free solution), both in RCl and in the aprotic, more polar, solvents (ACN, DMSO). 4-AP in its S_1-ICT state is strongly quenched by highly protic solvents (e.g. calculated from Stern–Volmer relation the bimolecular quenching rate constant (k_S) for HFIP in 1-chloropropane is high, $k_S > 5 \times 10^9$ M^{-1} s^{-1}).[12] In order to determine the values of ϕ_F and τ_F for 4-AP in such solvents, it was necessary to decrease the amount of water to a concentration below 10^{-3} M!

As found in earlier works [66,77,79], there was a strong dependence of ϕ_F and τ_F for 4-AP on the solvent properties. In deoxygenated 1-chloropropane and 1-chlorobutane, the value of $\phi_F \approx 1.0$ was obtained. A similarly high, but somewhat lower, value of ϕ_F was obtained in DMSO. The smallest values of ϕ_F and the shortest τ_F were obtained in protic solvents capable of

---

[11] Using the solvatochromic plots of 4-AP in RCl (Fig. 3) it can be shown that at the transition $S_0 \rightarrow S_1$-LE the energy decrease is about 60 cm^{-1} as a result of non-specific interactions of 4-AP with DMSO and about 170 cm^{-1} at the transition S_1-ICT $\rightarrow S_0$ relative to 4-AP with 1-chloropropane. Analogously, in HFIP the energy decrease is about 130 cm^{-1} at $S_0 \rightarrow S_1$-LE and about 360 cm^{-1} at S_1-ICT $\rightarrow S_0$.

[12] Because of too low water solubility in RCl it was impossible to determine the quenching rate constant of 4-AP in the S_1-ICT state by water. Therefore, HFIP was used as a quencher forming similarly strong hydrogen bonds. Taking into regard very similar spectral and photophysical properties of 4-AP in these solvents we can assume that the quenching rate constants of 4-AP in the S_1-ICT state by these two solvents are similar.

forming of hydrogen bonds: HFIP, H_2O, and D_2O. In H_2O and D_2O, the values of ϕ_F are twice as large as the earlier results 0.01 and 0.045 [66,79][13], respectively. The values of τ_F (1.1 and 5.4 ns) in H_2O and D_2O, respectively are very similar to those obtained in an earlier work.

It should be noted that the k_F values vary in the range between 2.2×10^7 and $5.5 \times 10^7\,s^{-1}$, reaching the highest value in 1-chloropropane, while in HFIP, H_2O and D_2O the value of k_F is 2.5 times lower. From the solvatochromic results in RCl, it is seen that the excited 4-AP molecule in its S_1-ICT state deactivates exclusively through intramolecular processes. The value of $\phi_F = 1.0$ in RCl indicates that practically the only deactivation pathway of 4-AP from its S_1-ICT state is via fluorescence, characterised by $k_F = 5.5 \times 10^7\,s^{-1}$. Since the contributions from the processes of internal conversion and intersystem crossing in the deactivation are negligible, the rate constants of these processes must be much lower than k_F!

The photophysical results for 4-AP in HFIP, H_2O, and D_2O are very interesting and consistent. In all these solvents practically the same value of $k_F \approx 2.25 \times 10^7\,s^{-1}$ was obtained (Table 4). As mentioned earlier, 4-AP in the S_1-ICT state forms very strong hydrogen bonds with these solvents (Table 3). Thus, it can be assumed that after formation of hydrogen bonds in these solvents only S_1-exc(1) is present. Therefore, the k_F values in these solvents describe the radiative properties of this species. The value of k_F for S_1-exc(1) is 2.5 times lower than that for 4-AP in its S_1-ICT state. It should be noted that a similar decrease in k_F is observed in strongly protic solvents for other aromatic molecules containing a carbonyl and a nitro group [51,146] capable of forming hydrogen bonds with the solvent molecules. In protic solvents the values of ϕ_F and τ_F are significantly lower than their corresponding values for 4-AP in its S_1-ICT state in RCl. This decrease in ϕ_F and τ_F is more pronounced the greater the total energy of the interaction between 4-AP in its S_1-ICT state and its surroundings. In HFIP, ϕ_F is 15 times lower than in 1-chloropropane while τ_F is 6 times shorter. In H_2O, ϕ_F is 45 times lower, and τ_F is 17 times shorter than in 1-chloropropane.

The process of internal conversion dominates in deactivation of S_1-exc(1), and it is responsible for a significant decrease in the experimental value of ϕ_F in the protic solvents in which 4-AP makes strong hydrogen bonds ($C{=}O\cdots H{-}X$). Similar to earlier studies on excited molecules [147–149], that considered to the energy gap law [150], the rate constant of internal conversion (k_{IC}) for S_1-exc(1) strongly depends on the S_1–S_0 energy gap ($\Delta E(S_1–S_0)$). Unfortunately, the scarcity of data on S_1-exc(1) makes it impossible to discuss the dependence of k_{IC} on $\Delta E(S_1–S_0)$ in more quantitative terms. The influence of $\Delta E(S_1–S_0)$ on k_{IC} explains why the shortest lifetime of S_1-exc(1) is seen in H_2O, in which the energy of the S_1-exc(1) ($E_{S_1\text{-exc}(1)}$) is the smallest because of the presence of the two types of hydrogen bonds. On the other hand, the approximately 5.7 times lower value of k_{IC} of 4-AP in D_2O compared to H_2O [9][14] despite the same value of $E_{S_1\text{-exc}(1)}$, may be the result of the decrease in the Franck–Condon factors, caused by the decrease in the frequency of the accepting modes from $\nu_{O–H} \approx 3500\,cm^{-1}$ (in H_2O) to $\nu_{O–D} \approx 2500\,cm^{-1}$ (in D_2O). This interesting finding is a direct confirmation not only for the formation of S_1-exc(1) as a result of a strong hydrogen bond formation, but it also proves that S_1-exc(1) undergoes internal conversion with the involvement of this bond, which is in consistence with an earlier proposition [58,59,74,75].

Finally, it is instructive to discuss the photophysical results obtained in aprotic solvents capable of forming hydrogen bonds with the N–H bonds of the amino group (and probably also the imino group). The values of ϕ_F and τ_F for 4-AP dissolved in these solvents are similar to those obtained in RCl (Table 4). Although there are no experimental data from time-resolved measurements that could directly prove the formation of S_1-exc(2), the relatively high value of $E^1_{HB} \approx 1500\,cm^{-1}$ for the single hydrogen bond ($N{-}H\cdots O{=}S$) in DMSO (Table 3), both in the S_1-LE and S_1-ICT states, suggests that it does form readily. An indirect confirmation of S_1-exc(2) formation is the fact that the values of $k_F \approx 4.6 \times 10^7\,s^{-1}$ in DMSO and ACN are lower than in RCl, $k_F \approx 5.5 \times 10^7\,s^{-1}$. The monoexponential decays of the emissions in DMSO, ACN, and RCl, all three having similar values of τ_F, can be explained by assuming that the deactivations of 4-AP in its S_1-ICT state and of S_1-exc(2) are almost exclusively determined by the fluorescence, and, furthermore, the values for k_F of both species are similar. Slightly faster overall nonradiative decay in these solvents than in RCl can be the result of an increase in the rate constants $k_{S_1S_0}$ for the internal conversion $S_1\text{-ICT} \rightarrow S_0$ for 4-AP due to a decrease in the value of $\Delta E(S_1–S_0)$ as well as the contribution of radiationless processes in S_1-exc(2) deactivation. Because of the greater value of E_{HB}, seen as a greater bathochromic shift of ν^{em}_{max} in DMSO than in ACN (see Table 1 and Fig. 3), these processes should play a greater role in the deactivation of 4-AP in the former solvent.

3.3. Scheme of 4-AP deactivation

Based on the results presented of the solvatochromic and photophysical measurements and independent data (E_{HB} in the S_0-state of 4-AP in DMSO and HFIP), we propose a scheme for the excited-state deactivation of 4-AP in solvents of different properties. Rate constants, k^y_x, refer to the processes described on the left.

(a) In the sufficiently polar solvents interacting only non-specifically with 4-AP:

$$S_0 \xrightarrow{h\nu} S_1\text{-LE}, \tag{i}$$

$$S_1\text{-LE} \rightarrow S_1\text{-ICT}, \quad k^{\text{LE–ICT}}_{S_1}. \tag{ii}$$

---

[13] Measurements of ϕ_F in H_2O and D_2O have been many times repeated for different 4-AP concentrations and different λ_{exc}, obtaining values very similar to those given in Table 4.

[14] It should be noted that a very similar deuteration effect has been observed for NM-4-AP in H_2O and D_2O [133]. It confirms that the imino group is not responsible for the deactivation of the 4-AP molecule.

In these solvents the only deactivation process of S_1-LE is (ii).

The deactivation of S_1-ICT occurs in the processes (iii)–(v):

$$S_1\text{-ICT} \xrightarrow{h\nu'} S_0, \quad k_F^{ICT}, \tag{iii}$$

$$S_1\text{-ICT} \rightarrow S_0, \quad k_{IC}^{ICT}, \tag{iv}$$

$$S_1\text{-ICT} \rightarrow T_1\text{-ICT}, \quad k_{ISC}^{ICT}, \tag{v}$$

where T_1-ICT corresponds to 4-AP in the triplet ICT state.

As for S_1-ICT $\phi_F \approx 1.0$, therefore $k_F^{ICT} \gg k_{IC}^{ICT} + k_{ISC}^{ICT}$.

(b) In sufficiently polar aprotic solvents with electronegative heteroatom(s) and in protic solvents, in addition to the intramolecular processes mentioned in (a), another process also occurs

$$S_1\text{-ICT} + (S_0\text{-solv})_n \rightarrow S_1\text{-exc}(x), \quad k_S^{ICT}, \quad n \geq 1, \tag{vi}$$

where $x \equiv 1$ or 2 in protic and aprotic solvents, respectively.

Process (vi) in monocomponent solvents is a pseudo-first-order reaction.

The deactivation of S_1-exc(x) occurs in processes (vii)–(viii):

$$S_1\text{-exc}(x) \rightarrow S_0\text{-comp}(x), \quad k_{IC}^{exc(x)\text{—}comp(x)}, \tag{vii}$$

and/or

$$S_1\text{-exc}(x) \xrightarrow{h\nu''} S_0\text{-comp}(x), \quad k_F^{exc(x)}. \tag{viii}$$

(c) In strong protic solvents, e.g. in HFIP, additional processes occur:

$$S_0\text{-4-AP} + (S_0\text{-solv})_n \rightarrow S_0\text{-comp}(1), \quad n \geq 1, \tag{ix}$$

$$S_0\text{-comp}(1) \xrightarrow{h\nu} S_1\text{-comp}(1). \tag{x}$$

The steady-state and time-resolved emission measurements results do not allow for a differentiation between S_1-exc(1) and the excited complex (S_1-comp(1)), therefore, we have assumed that the deactivation of the latter species, similar to S_1-exc(1), occurs through processes (vii)–(viii), according to Ref. [151].

4. Conclusions

This paper presents results on the spectral (absorption and emission) and photophysical studies of 4-AP molecules in a range of solvents. The results of the solvatochromic study of this probe, presented above, are to our knowledge the first obtained with the use of solvents from the group of 1-chloro-*n*-alkanes (RCl) (with $\alpha = \beta = 0$). In these solvents, irrespective of the complexity of the properties of the molecule studied, only non-specific solvent–solute interactions take place. That is why a change in the maxima of the absorption and emission spectra versus the Lippert–Mataga polarity function, $f(\varepsilon, n^2)$, for 4-AP provides quantitative information on the changes in the energy of the non-specific interactions and on changes in the dipole moment as a result of the electronic transitions of this probe.

Based on literature data for the energy of the hydrogen bonds made by carbonyl groups and N–H bonds of a few aromatic molecules in their S_0-states with HFIP and DMSO, the energy of the hydrogen bonds formed by 4-AP in its ground state in these solvents was determined. From the same data and the results of absorption and emission solvatochromic plots in RCl, the values of E_{HB} were determined for 4-AP in the excited states S_1-LE and S_1-ICT in HFIP and in DMSO (by computation also in H_2O). Thus, we were able to decide whether E_{HB} of the hydrogen bonds in the S_0 and in the excited states was high enough to permit not only the presence of 4-AP molecules but also its complexes (in S_0) and exciplexes (in S_1) with the solvent molecules.

The solvatochromic results in this study show that when using 4-AP as a probe, ethers, esters, and nitrile cannot be employed as solvents if it is assumed that these solvents are engaged only in non-specific interactions with 4-AP (this is also true for many other probes with donor and acceptor groups). This is clearly seen by the bathochromic positions of the maxima in the absorption and emission spectra of 4-AP in these solvents, relative to their positions in the spectra of the 1-chloro-*n*-alkanes.

The example of the 4-AP molecule, containing both a donor and an acceptor group, has shown that its electronic excitation significantly changes the energy of the hydrogen bonds that this molecule forms. Despite complexity of the spectral and photophysical properties of 4-AP (in particular, the formation of several types of hydrogen bonds), it was possible to identify the possible species present in the system and to estimate the changes in their concentrations at the 4-AP transition between two electronic states.

The high value of E_{HB} determined in highly protic solvents (Tables 3 and 4) from the solvatochromic emission study (Fig. 3) clearly indicates that the emission observed in these solvents cannot come from the 4-AP molecule in its S_1^{rel}-ICT state but must come from S_1-exc(1), appearing as a result of formation of strong hydrogen bonds between 4-AP in this state and the solvent molecules (HFIP, TFE, H_2O, D_2O).

Acknowledgements

The authors wish to thank MSc Julia Józkowiak for skilful assistance in the experimental work, Dr. Jacek Kubicki for helpful discussions and Dr Gordon L. Hug and MSc Maria Spychalska for helpful in manuscript preparation. Financial support within the KBN (State Committee for Scientific Research), project 2 P03B 015 24 is gratefully acknowledged. Thanks are also due to the Foundation for Polish Science for financial support within the project SUBIN 25/2004. The dynamic measurements were performed at the Centre for Ultrafast Laser Spectroscopy at the A. Mickiewicz University, Poznań, Poland.

References

[1] P. Suppan, N. Ghoneim, Solvatochromism, The Royal Society of Chemistry, Information Services, 1997.
[2] J.R. Lakovicz, Principles of Fluorescence Spectroscopy, 2nd ed., Kluwer Academic/Plenum Publisher, New York, 1999.
[3] B. Valeur, Molecular Fluorescence, Wiley/VCH Publishers, 2002.

[4] N.G. Bakshshiew, Solvatochromism, Leningradskij Gosudarstwiennyj Univiersitiet, Leningrad, 1989.

[5] R.B. Cundall, R.E. Dale, Time Resolved Fluorescence in Biochemistry and Biology, NATO ASI Series A: Life Science, vol. 69, Plenum Press, New York, 1983.

[6] K. Dimroth, C. Reichardt, T. Siepmann, F. Bohlmann, Liebigs Ann. Chem. 661 (1963) 1.

[7] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, VCH, Weinheim, 1988.

[8] C. Reichardt, Chem. Rev. 94 (1994) 2319.

[9] K. Kalyanasundaram, Photochemistry in Microheterogeneous Systems, Academic Press, New York, 1987.

[10] K. Kalyanasundaram, Photophysical probes for microenvironments, in: V.V. Ramamurthy (Ed.), Photochemistry in Organized Constrained Media, vol. 2, VCH Publishers, New York, 1991, pp. 39–77.

[11] A. Mallaris, Adv. Colloid Interf. Sci. 27 (1987) 153.

[12] K. Bhattacharyya, in: V. Ramamurthy, K.S. Schanze (Eds.), Organic Molecular Photochemistry, Marcel Dekker, New York, 1999, 283 pp.

[13] A. Declemy, C. Rulliere, P. Kottis, Chem. Phys. Lett. 101 (1983) 401.

[14] A. Declemy, C. Rulliere, P. Kottis, Chem. Phys. Lett. 133 (1987) 448.

[15] C.F. Chapman, R.S. Fee, M. Maroncelli, J. Phys. Chem. 99 (1995) 4811.

[16] A. Morimoito, T. Yatsuhashi, T. Shimada, L. Biczok, D.A. Tryk, H. Inoue, J. Phys. Chem. 105 (2001) 10488.

[17] T. Lopez Arbeloa, F. Lopez Arbeloa, M.J. Tapia, I. Lopez Arbeloa, J. Phys. Chem. 97 (1993) 4704.

[18] R.W. Yip, Y.-X. Wen, Can. J. Chem. 69 (1991) 2142.

[19] R.W. Yip, Y.-X. Wen, A.G. Szabo, J. Phys. Chem. 97 (1993) 10458.

[20] F. Tschirschwitz, E.T.J. Nibbering, Chem. Phys. Lett. 312 (1999) 169.

[21] E.T.J. Nibbering, F. Tschirschwitz, C. Chudoba, T. Elsaesser, J. Phys. Chem. A 104 (2000) 4236.

[22] R. Królicki, W. Jarzęba, M. Mostafavi, I. Lampre, J. Phys. Chem. A 106 (2002) 1708.

[23] F. Morlet-Savary, C. Ley, P. Jaques, J.P. Fouassier, J. Phys. Chem. A 105 (2001) 11026.

[24] T. Gustavsson, L. Cassara, V. Gulbinas, G. Gurzadyan, J.-C. Mialocq, S. Pommeret, M. Sorgius, P. van der Meulen, J. Phys. Chem. A 102 (1998) 4229.

[25] B.B. Raju, S.M.B. Costa, Phys. Chem. Chem. Phys. 1 (1999) 3539.

[26] N.A. Nemkovich, W. Baumann, H. Reis, N. Detzer, J. Photochem. Photobiol. A: Chem. 89 (1995) 127.

[27] T. Yatsuhashi, Y. Nakajima, T. Shimada, H. Tachibana, H. Inoue, J. Phys. Chem. A 102 (1998) 8657.

[28] R.S. Moog, D.L. Bankert, M. Maroncelli, J. Phys. Chem. 97 (1993) 1496.

[29] R.S. Moog, N.A. Burozski, M.M. Desai, W.R. Good, C.D. Silvers, P.A. Thompson, J.D. Simon, J. Phys. Chem. 95 (1991) 8466.

[30] J. Herbich, J. Waluk, R.P. Thummel, C.-Y. Hung, J. Photochem. Photobiol. A: Chem. 80 (1994) 157.

[31] T. Okada, I. Karaki, N. Mataga, J. Am. Chem. Soc. 104 (1982) 7191.

[32] A.J. Bengino, E. Ahmed, M. Berg, J. Chem. Phys. 102 (1998) 9304.

[33] S. Yamaguchi, H. Hamaguchi, J. Phys. Chem. A 104 (2000) 4272.

[34] M.M. Martin, Chem. Phys. Lett. 35 (1975) 105.

[35] T. Yatsuhashi, H. Inoue, J. Phys. Chem. A 101 (1997) 8166.

[36] H. Miyasaka, A. Tabata, S. Ojima, N. Ikeda, N. Mataga, J. Phys. Chem. 97 (1993) 8222.

[37] A. Morimoito, T. Yatsuhashi, T. Shimada, S. Kumazaki, K. Yoshihara, H. Inoue, J. Phys. Chem. A 105 (2001) 8840.

[38] T.W. Ebbesen, C.A. Ghiron, J. Phys. Chem. 93 (1989) 7139.

[39] J. Herbich, M. Kijak, A. Zielińska, R.P. Thummel, J. Waluk, J. Phys. Chem. A 106 (2002) 2158.

[40] J. Figueras, J. Am. Chem. Soc. 93 (1971) 3255.

[41] R. Nakagaki, N. Kitamura, J. Aoyama, H. Ohtsubo, J. Photochem. Photobiol. A: Chem. 80 (1994) 113.

[42] M.M. Martin, Chem. Phys. Lett. 43 (1976) 332.

[43] L. Biczok, T. Berces, H. Linschitz, J. Am. Chem. Soc. 119 (1997) 11071.

[44] H. Inoue, M. Hida, N. Nakashima, K. Yoshihara, J. Phys. Chem. 86 (1982) 3184.

[45] K. Foshimi, K. Kikuchi, H. Kokubun, J. Photochem. 5 (1976) 457.

[46] S. Das, K.G. Thomas, R. Ramanathan, M.V. George, P.V. Kamat, J. Phys. Chem. 97 (1993) 13625.

[47] A. Krychenko, Y. Stepanczenko, J. Waluk, J. Phys. Chem. A 104 (2000) 9542.

[48] I. Guilford Jones, Z. Feng, W.R. Bergmark, J. Phys. Chem. 98 (1994) 4511.

[49] R. Rusakowicz, G.W. Byers, P.A. Leermakers, J. Am. Chem. Soc. 93 (1971) 3263.

[50] C. Cazeau-Dubroca, G. Nouchi, M.B. Brahim, M. Pesquer, D. Garse, P. Cazeau, J. Photochem. Photobiol. A: Chem. 80 (1994) 125.

[51] A. Cser, K. Nagy, L. Biczok, Chem. Phys. Lett. 360 (2002) 473.

[52] N. Ikeda, H. Miyasaka, T. Okada, N. Mataga, J. Am. Chem. Soc. 105 (1983) 5206.

[53] R. Laenen, C. Rauscher, A. Laubereau, Chem. Phys. Lett. 283 (1999) 7.

[54] H. Graener, T.Q. Ye, A. Laubereau, J. Chem. Phys. 90 (1989) 3413.

[55] M. Rini, A. Kummorow, J. Dreyer, E.T.J. Nibbering, T. Elsaesser, Faraday Discuss. 122 (2002) 27.

[56] J.D. Simon, Acc. Chem. Res. 21 (1988) 128.

[57] Z.R. Grabowski, K. Rotkiewicz, W. Rettig, Chem. Rev. 103 (2003) 3899.

[58] A. Maciejewski, J. Kubicki, K. Dobek, J. Phys. Chem. B 107 (2003) 13986.

[59] A. Maciejewski, J. Kubicki, K. Dobek, J. Phys. Chem. B 109 (2005) 9422.

[60] E. Laitinen, K. Salonen, T. Harju, J. Chem. Phys. 104 (1996) 6138.

[61] G. Saroja, A. Samanta, J. Chem. Soc., Faraday Trans. 92 (1996) 2697.

[62] G. Saroja, B. Ramachandram, S. Saha, A. Samanta, J. Phys. Chem. B 103 (1999) 2906.

[63] A. Datta, D. Mandal, S.K. Pal, S. Das, K. Bhattacharyya, J. Mol. Liq. 77 (1998) 121.

[64] P. Sen, S. Mukherjee, A. Halder, K. Bhattacharyya, Chem. Phys. Lett. 385 (2004) 357.

[65] G. Saroja, A. Samanta, Chem. Phys. Lett. 246 (1995) 506.

[66] T. Soujanya, T.S.R. Krishma, A. Samanta, J. Phys. Chem. 96 (1992) 8544.

[67] T. Soujanya, T.S.R. Krishma, A. Samanta, J. Photochem. Photobiol. A: Chem. 66 (1992) 185.

[68] D. Lengeler, K. Weisz, Tetrahedron Lett. 42 (2001) 1479.

[69] R. Karmakar, A. Samanta, J. Am. Chem. Soc. 123 (2001) 3809.

[70] C.F. Chapman, M. Maroncelli, J. Phys. Chem. 95 (1991) 9095.

[71] J. Gawroński, F. Kazmierczak, K. Gawrońska, U. Rychlewska, B. Norden, A. Holmen, J. Am. Chem. Soc. 120 (1998) 12083.

[72] A. Datta, S. Das, D. Mandal, S.K. Pal, K. Bhattacharyya, Langmuir 13 (1997) 6922.

[73] S. Sen, D. Sukul, P. Dutta, K. Bhattacharyya, J. Phys. Chem. A 105 (2001) 10635.

[74] W.R. Ware, S.K. Lee, G.J. Brant, P.P. Chow, J. Chem. Phys. 11 (1971) 4729.

[75] D.E. Wetzler, C. Chesta, R. Fernandez-Prini, P.F. Aramendia, J. Phys. Chem. A 106 (2002) 2390.

[76] S.M. Arriwo, E.J. Heilweil, J. Phys. Chem. 100 (1996) 11975.

[77] S. Das, A. Datta, K. Bhattacharyya, J. Phys. Chem. A 101 (1997) 3299.

[78] S. Aich, C. Raha, S. Basu, J. Chem. Soc., Faraday Trans. 93 (1997) 2991.

[79] T. Soujanya, R.W. Fessenden, A. Samanta, J. Phys. Chem. 100 (1996) 3507.

[80] G. Saroja, A. Samanta, J. Chem. Soc., Faraday Trans. 94 (1998) 3141.

[81] D. Yuan, R.G. Brown, J. Phys. Chem. A 101 (1997) 3461.

[82] K. Bhattacharyya, B. Bagchi, J. Phys. Chem. A 104 (2000) 10603.

[83] N. Nandi, K. Bhattacharyya, B. Bagchi, Chem. Rev. 100 (2000) 2013.

[84] M.F. Vitha, J.D. Weeckwerth, K. Odland, V. Dema, P.W. Carr, J. Phys. Chem. 100 (1996) 18823.

[85] V. Nagarajan, A.M. Brearley, T.-J. Kang, P.F. Barbara, J. Chem. Phys. 86 (1987) 3183.

[86] T.O. Harju, A.H. Huizer, C.A.G.O. Varma, Acta Chem. Scand. 49 (1995) 829.

[87] T.O. Harju, A.H. Huizer, C.A.G.O. Varma, Chem. Phys. 200 (1995) 215.

[88] P. Suppan, J. Chem. Soc., Faraday Trans. 1 (83) (1987) 495.

[89] D. Noukakis, P. Suppan, J. Lumin. 47 (1991) 285.

[90] M. Glasbeek, H. Zhang, Chem. Rev. 104 (2004) 1929.

[91] P. Mehlen, H. Zhang, A.M. Jonkman, M. Glasbeek, J. Phys. Chem. 100 (1996) 5367.
[92] Y. Hagan, D. Pillowol, P. Suppan, Chem. Phys. Lett. 139 (1987) 499.
[93] S. Mukherjee, K. Sahu, K. Roy, S.K. Mondal, K. Bhattacharyya, Chem. Phys. Lett. 384 (2004) 128.
[94] R.W. Taft, M.J. Kamlet, J. Am. Chem. Soc. 98 (1976) 2886.
[95] M.J. Kamlet, J.L.M. Abboud, M.H. Abraham, R.W. Taft, J. Org. Chem. 48 (1983) 2877.
[96] M.H. Abraham, Chem. Soc. Rev. 22 (1993) 73.
[97] J. Marcus (Ed.), The Properties of Solvents, Wiley, Chichester, UK, 1998.
[98] M.J. Kamlet, J.L.M. Abboud, R.W. Taft, Prog. Phys. Org. Chem. 13 (1981) 485.
[99] C. Laurence, P. Nicolet, M.T. Dalati, J.L.M. Abboud, R. Notario, J. Phys. Chem. 98 (1994) 5807.
[100] M.J. Kamlet, J.L.M. Abboud, R.W. Taft, J. Am. Chem. Soc. 99 (1977) 6027.
[101] R.A. Moore, J. Lea, G.W. Robinson, J. Phys. Chem. 89 (1985) 3648.
[102] B.A. Pryor, P.M. Palmer, P.M. Andrews, M.B. Berger, T. Troxler, M.R. Topp, Chem. Phys. Lett. 271 (1997) 19.
[103] Y. Chen, M.R. Topp, Chem. Phys. 283 (2002) 249.
[104] M. Milewski, W. Augustyniak, A. Maciejewski, J. Phys. Chem. A 102 (1998) 7427.
[105] J. Karolczak, D. Komar, J. Kubicki, M. Szymański, T. Wróżowa, A. Maciejewski, Bull. Pol. Acad. Sci. Chem. 47 (1999) 4.
[106] J. Karolczak, D. Komar, J. Kubicki, T. Wróżowa, K. Dobek, B. Ciesielska, A. Maciejewski, Chem. Phys. Lett. 344 (2001) 154.
[107] T. Wróż, B. Ciesielska, D. Komar, J. Karolczak, A. Maciejewski, J. Kubicki, Rev. Sci. Instrum. 75 (2004) 3107.
[108] D.V. Matyushov, G.A. Voth, J. Chem. Phys. 111 (1999) 3630.
[109] M. Maciejewski, Chem. Phys. Lett. 163 (1989) 81.
[110] M. Lamotte, J. Joussot-Dubien, J. Chem. Phys. 2 (1973) 245.
[111] M. Lamotte, R. Lasclaux, A.M. Merte, J. Joussot-Dubien, Faraday Discuss. Chem. Soc. 58 (1974) 253.
[112] R.S. Drago, M.S. Hirch, D.C. Ferris, C.W. Chronister, J. Chem. Soc., Faraday Trans. 2 (1994) 219.
[113] R. Nakagaki, I. Aoeama, K. Shimuzu, M. Akagi, J. Phys. Org. Chem. 6 (1993) 261.
[114] K.F. Purcell, J.A. Stikeleather, S.D. Bruk, J. Am. Chem. Soc. 91 (1969) 4019.
[115] A.V. Iogansen, G.A. Kurkchi, V.M. Furman, S.E. Glazonov, S.E. Odinokov, J. Appl. Spectr. USSR 33 (1980) 460.
[116] A.V. Iogansen, G.A. Kurkchi, V.M. Furman, S.E. Glazonov, S.E. Odinokov, J. Appl. Spectr. USSR 33 (1980) 302.
[117] B. Allard, A. Casadevall, C. Largeau, Nouv. J. Chim. 4 (1980) 539.
[118] N. Mathivanan, F. Cozens, R.A. McClelland, S. Steenken, J. Am. Chem. Soc. 114 (1992) 2198.
[119] Y. Chen, B. Liu, M.D. Barkeley, J. Am. Chem. Soc. 117 (1995) 5608.
[120] L. Eberson, M.P. Hartshorn, O. Persson, J. Chem. Soc., Perkin Trans. 2 (1995) 1735.
[121] A.V. Iogansen, Spectrochim. Acta, Part A 55 (1999) 1585.
[122] A. Kivinen, J. Murto, S. Liljequist, S. Vaara, Acta Chem. Scand. A 29 (1975) 911.
[123] M.A. Matesich, J. Knoefel, H. Feldman, D.F. Evans, J. Phys. Chem. 77 (1973) 366.
[124] J. Catalan, C. Diaz, V. Lopez, P. Perez, J.-L.G. de Paz, J.G. Rodriguez, Liebigs Ann. (1996) 1785.
[125] D. Banerjee, A.K. Chandra, M. Banerjee, B. Bagchi, J. Mol. Struct. 343 (1995) 167.
[126] P.K. Das, G.L. Hug, Photochem. Photobiol. 36 (1982) 455.
[127] A. Kuboyama, Y. Sato, H. Arano, Bull. Chem. Soc. Jpn. 49 (1976) 3685.
[128] C. Cazeau-Dubroca, S. Ait Lyazidi, G. Nouchi, A. Peiriqua, P. Cazeau, Nouv. J. Chim. 10 (1986) 337.
[129] T.G. Kim, M.F. Wolford, M.R. Topp, Photochem. Photobiol. 2 (2003) 576.
[130] A.M. Sarzshevski, A.N. Sevchenko, Anisotropiya Pogłoshcheniya i Ispuskaniya Molecul (Absorption and Emission Anisotropy of Molecules), Izdatelstvo BGU, Mińsk, 1971, 331 pp.
[131] P. Haberfield, D. Rosen, I. Jasser, J. Am. Chem. Soc. 101 (1979) 3196.
[132] F. Brouwer, Structural aspects of exciplex formation, in: J. Waluk (Ed.), Conformational Analysis of Molecules in Excited States, Wiley/VCH, 2000.
[133] K. Dobek, E. Krystkowiak, A. Maciejewski, in preparation.
[134] M.J. Kamlet, R.W. Taft, J. Am. Chem. Soc. 98 (1976) 377.
[135] A.D. Sherry, K.F. Purcell, J. Am. Chem. Soc. 94 (1972) 1853.
[136] D.J.W. Grant, T. Higuchi, Techniques of Chemistry Series, vol. XXI, Wiley/Interscience, New York, 1990 (Chapters 4–6).
[137] T. Cairns, G. Eglinton, D.T. Gipson, Spectrochim. Acta A 20 (1964) 31.
[138] L. Joris, P.v.R. Schleyer, J. Am. Chem. Soc. 90 (1968) 4599.
[139] H. Fritzsche, Spectrochim. Acta 21 (1965) 799.
[140] A.T. Shulgin, H.O. Kerlinger, Chem. Commun. (1966) 249.
[141] S.D. Christan, B.M. Keenan, J. Phys. Chem. 78 (1974) 432.
[142] K.B. Whetsel, R.E. Kagarise, Spectrochim. Acta 18 (1962) 315.
[143] E.M. Arnett, L. Joris, E. Mitchell, T.S.S.R. Murty, T.M. Gorrie, P.v.R. Schleyer, J. Am. Chem. Soc. 92 (1970) 2365–2377.
[144] R.C. Fort, T.R. Lindstrom, J. Phys. Chem. 75 (1971) 3963.
[145] J.A. Ingram, R.S. Moog, N. Ito, R. Biswas, M. Maroncelli, J. Phys. Chem. B 107 (2003) 5926.
[146] S. Lin, W.S. Struve, Photochem. Photobiol. 54 (1991) 361.
[147] A. Maciejewski, R.P. Steer, Chem. Rev. 93 (1993) 57.
[148] G. Burdziński, J. Kubicki, A. Maciejewski, R.P. Steer, S. Velate, E.K.L. Yeow, Photochemistry and photophysics of highly excited valence states of polyatomic molecules: nonalternant aromatocs, thioketones and metalloporphyrins, in: Ramamurthy (Ed.), Organic Photochemistry and Photophysics, vol. 14, Taylor & Francis, 2005, 1 pp.
[149] E.M. Kober, J.V. Caspar, R.S. Lumpkin, T.J. Meyer, J. Phys. Chem. 90 (1986) 3722.
[150] R. Engelman, J. Jortner, J. Mol. Phys. 18 (1970) 145.
[151] J. Prochorow, R. Siegoczyński, Chem. Phys. Lett. 3 (1969) 635.