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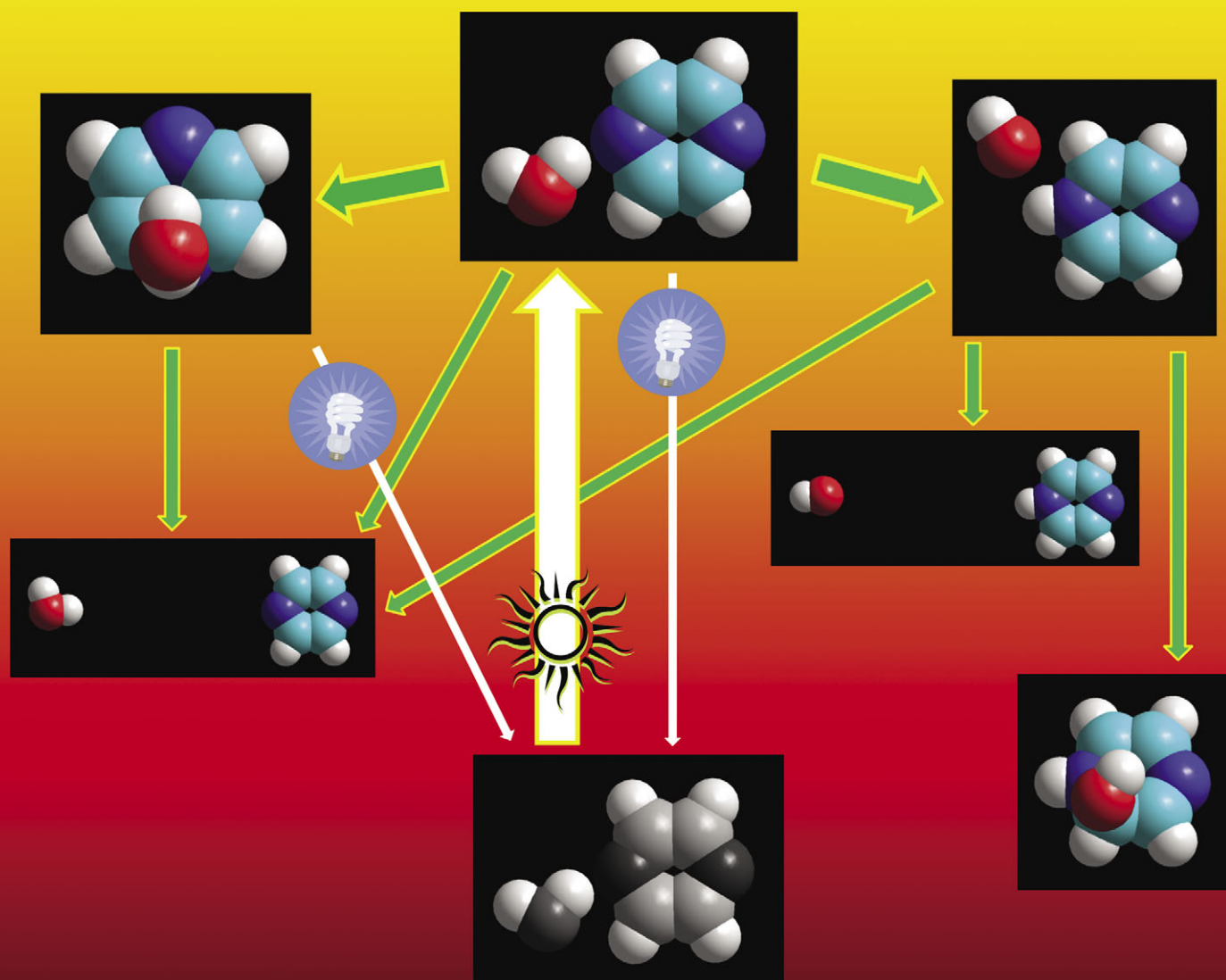
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PERSPECTIVE

Hydrogen bonding and reactivity of water to azines in their S_1 (n,π^*) electronic excited states in the gas phase and in solution†

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A unified picture is presented of water interacting with pyridine, pyridazine, pyrimidine, and pyrazine on the S_1 manifold in both gas-phase dimers and in aqueous solution. As (n,π^*) excitation to the S_1 state removes electrons from the ground-state hydrogen bond, this analysis provides fundamental understanding of excited-state hydrogen bonding. Traditional interpretations view the excitation as simply breaking hydrogen bonds to form dissociated molecular products, but reactive processes such as photohydrolysis and excited-state proton coupled electron transfer (PCET) are also possible. Here we review studies performed using equations-of-motion coupled-cluster theory (EOM-CCSD), multireference perturbation theory (CASPT2), time-dependent density-functional theory (TD-DFT), and excited-state Monte Carlo liquid simulations, adding new results from symmetry-adapted-cluster configuration interaction (SAC-CI) and TD-DFT calculations. Invariably, gas-phase molecular dimers are identified as stable local minima on the S_1 surface with energies less than those for dissociated molecular products. Lower-energy biradical PCET minima are also identified that could lead to ground-state recombination and hence molecular dissociation, dissociation into radicals or ions, or hydration reactions leading to ring cleavage. For pyridine.water, the calculated barriers to PCET are low, suggesting that this mechanism is responsible for fluorescence quenching of pyridine.water at low energies rather than accepted higher-energy Dewar-benzene based “channel three” process. Owing to (n,π^*) excitation localization, much higher reaction barriers are predicted for the diazines, facilitating fluorescence in aqueous solution and predicting that the as yet unobserved fluorescence from pyridazine.water and pyrimidine.water should be observable. Liquid simulations based on the assumption that the solvent equilibrates on the fluorescence timescale quantitatively reproduce the observed spectral properties, with the degree of (n,π^*) delocalization providing a critical controlling factor.

1. Introduction

Hydrogen bonding involving heteroaromatic rings such as those in azines and diazines plays an important role in the structure and function of many biological systems including DNA.^{1–3} Although hydrogen bonding to molecules in their ground electronic state has been widely investigated by different spectroscopic^{4–19} and theoretical^{1,19–54} methods, much less is known about hydrogen bonding to molecules in excited states. A major area of research focuses on situations in which various ground-state

isomeric structures are possible so that photoexcitation can induce proton-transfer reactions to modify the hydrogen-bonding pattern and hence other system properties.^{55–60} Excited-state studies of these systems are very fruitful as excitation changes the relative energies of the available tautomers, inducing photochemical reactions that can be monitored in great detail using time-resolved spectroscopies.

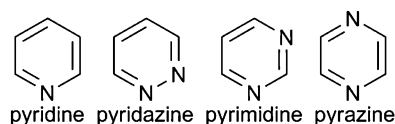
Typically,^{55–60} (π,π^*) or other excitations⁶¹ are utilized that do not explicitly involve the hydrogen-bonding electrons, and the chemical reactions transform between well-recognized ground-state hydrogen-bonding motifs. In the excited state, hydrogen bonds may be either weakened or enhanced depending on the details of the induced electronic rearrangement,^{45,57,62} with possible significant consequences.^{55–60,63,64}

There is, however, much interest in processes involving (n,π^*) excitations of the lone-pair electrons directly involved in hydrogen bonding, excitations that, in principle, should destroy an existing hydrogen bond.^{4,65–68} Here, we consider

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† Electronic ESI (ESI) available: wB97XD/6-311++G** and SAC-CI/6-31++G** or CCSD/6-31++G** calculated structures and energies for pyridine, pyridazine, pyridazine, and pyrazine as free molecules, after hydrogen additions, and in linear, π -linked, and PCET configurations with a single water molecule. See DOI: 10.1039/c2cp24040h

some of the simplest systems that can display such chemistry: the azines pyridine, pyridazine, pyrimidine, and pyrazine



interacting with water. For these, only *one* ground-state hydrogen-bonding motif is known, the linear hydrogen-bond between the electron-rich nitrogen atoms and water. However, *three* excited-state hydrogen-bonding motifs are identified, as well as species produced by proton-coupled electron transfer (PCET)^{69–73} including photohydration products. Study of these (n, π^*) excitations thus reveals fundamental properties of the very nature of hydrogen bonding.

Archetypal studies of hydrogen bonding to (n, π^*) excited states include absorption and fluorescence studies which culminated in the work of Baba, Goodman, and Valenti,⁴ computations pioneered by Del Bene,^{20–24} supersonic molecular jet spectroscopy pioneered by Bernstein *et al.*,^{8,9} and the photohydration study of Wilzbach and Rausch.⁷⁴ These studies reveal how the hydrogen-bonding environment interacts with the spectroscopic transition, the energetic of the interaction, and the ensuing dynamical processes following excitation.

2. Analytical dipole-interaction models for the effect of solvent on vertical transition energies

In 1966 Baba, Goodman, and Valenti⁴ studied the absorption and fluorescence spectra of pyridine and the diazines in dilute solution in a variety of hydrogen-bonding and non-hydrogen-bonding solvents. They found that the hydrogen bond formed between pyridine in its ground electronic state and solvent molecules gives a large blue shift in the (n, π^*) absorption transition but only small changes in the corresponding fluorescence spectrum, see Table 1. Dielectric solvation theories^{29,75–78} express these solvent shifts as

$$\Delta U = -\frac{2\varepsilon - 2}{2\varepsilon + 1} \frac{1}{a^3} \boldsymbol{\mu}_i \cdot (\boldsymbol{\mu}_i - \boldsymbol{\mu}_f) - \frac{2n^2 - 2}{2n^2 + 1} \frac{1}{a^3} |\boldsymbol{\mu}_i - \boldsymbol{\mu}_f|^2$$

where $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_f$ are the dipole moment vectors of the initial and final states solvated outside a cavity of radius a by a material of dielectric constant ε and refractive index n . This equation expresses the solvent shift in terms of linear and quadratic responses to the change in dipole moment $\boldsymbol{\mu}_f - \boldsymbol{\mu}_i$ upon excitation. As the coefficient of the linear term is much larger

than that for the quadratic one, and as only the linear term can give rise to a blue shift, Baba *et al.* qualitatively interpreted the experimental data as indicating a large dipole moment (*ca.* 3 D) in the ground state and a small, perhaps oppositely polarized, dipole moment in the excited state. By comparing the deduced dipole moments in hydrogen-bonding and non-hydrogen-bonding solvents of similar polarity, they observed that the ground-state dipole moment is considerably enhanced by hydrogen-bonding whereas the excited-state dipole moment is not. This additional dipole term was then assumed to be a diagnostic for hydrogen bonding and hence it was concluded that the hydrogen bonding is broken in the (n, π^*) singlet excited state of pyridine.

A similar analysis was also performed⁴ for the diazines pyridazine, pyrimidine, and pyrazine, with a 50% larger ground-state dipole moment attributed to pyridazine due to small angle (60°) between the two local nitrogen lone-pairs. However, pyrazine by symmetry has no dipole moment yet a substantial absorption solvent shift is still observed, indicating that more terms than just the molecular dipole moment need to be included in the analysis. Nevertheless, the observed large absorption blue shifts and concurrent small fluorescence shifts were interpreted as indicating that the hydrogen bond is also broken in the excited states of the diazines.⁴

3. Explicit hydrogen-bonding model for the effect of solvent on vertical transition energies

The dimers of pyridine and the azines with water were first studied using computational methods^{20–23} by Del Bene during the 1970's. She showed that for pyridine the vertical excitation energy increased on hydrogen bonding by more than the ground-state hydrogen-bond dissociation energy; her results are given in Table 1 (blue shifts) and 2 (hydrogen bond energies of formation). Hence, even if the hydrogen-bond in the excited state was as strong as it is in the ground state, then the complex would still dissociate. For pyrazine, the calculated blue shift paralleled the observations of Baba, Goodman, and Valenti⁴ in being about half of that for the other molecules, indicating that the computational methods successfully include electrostatic interactions beyond the dipolar term manifest in eqn (1). However, the hydrogen-bond energy is calculated to be only slightly less for pyrazine than for the other molecules, so that for pyrazine the ground-state hydrogen-bond energy is actually

Table 1 Observed and calculated shifts in the vertical absorption and emission energies (eV) of azines in dilute solution and in complexes with water molecule(s)

System	Absorption						Emission	
	Obs ^h	ZHRSS	Del Bene ⁱ	EOM-CCSD	CASPT2	TD-B3LYP	Obs ^h	ZHRSS
Pyridine-H ₂ O		0.32 ^a	0.22	0.19 ^e	0.24 ^e	0.16 ^e		
Pyridine(aq)	0.3–0.4	0.43 ^a						
Pyridazine-H ₂ O			0.09					
Pyridazine(aq)	0.47	0.51 ^d					0.09	0.08 ^d
Pyrimidine-H ₂ O			0.11	0.11 ^f	0.24 ^f	0.10 ^f		
Pyrimidine(aq)	0.33 ± 0.04	0.42 ^b					–0.07	–0.04 ^b
Pyrazine-H ₂ O	0.07	0.15 ^c	0.04	0.06 ^g				
Pyrazine(aq)	0.20–0.25	0.25 ^c					0.09	0.04 ^c

^a Ref. 27. ^b Ref. 29. ^c Ref. 30. ^d Ref. 31. ^e Ref. 43. ^f Ref. 44. ^g Ref. 45. ^h Ref. 4. ⁱ Ref. 21.

less than the absorption blue shift. Hence it is not so clear as to whether pyrazine/water would be stable in the excited-state. Further, pyrimidine and pyridazine are intermediate between pyridine and pyrazine and hence these simple molecules could display rich excited-state hydrogen-bonding chemistry.

Del Bene's original minimal basis set, small CI calculations provided a direct link between observed (n,π^*) solvent shifts in solution and hydrogen-bonding properties of gas-phase dimers. Since then, much effort has been spent in providing improved computational estimates of the blue shifts and interaction energies for the diazines^{27–33,39–46,79–81} and other azines,^{82–84} and previous estimates obtained using coupled-cluster theory (CCSD⁸⁵), complete-active-space self-consistent field theory with 2nd-order perturbative corrections (CASPT2),⁸⁶ equation-of-motion coupled-cluster (EOM-CCSD) theory,⁸⁷ and time-dependent density-functional theory (TD-TFT) using the B3LYP density functional^{88,89} are also given in Tables 1 and 2.^{43–45}

In addition, new results are also presented obtained using CCSD, symmetry-adapted-cluster configuration-interaction (SAC-CI),⁹⁰ EOM-CCSD, and the wB97XD density functional.⁹¹ The coupled-cluster based calculations use CCSD for all ground-state properties. Excited-state geometries are optimized using SAC-CI but reported are excited-state single-point energies obtained at these geometries using EOM-CCSD; this approach provides continuous potential-energy surfaces and is labelled "EOM/SAC". A further improved scheme would involve the use of third-order perturbation corrections to these single-point energies, EOM-CCSD(T), as this

method is known to produce accurate transition energies for azines.⁹² For the DFT calculations, the wB97XD functional is chosen as it contains both long-range and dispersion corrections, as required for studying problems of this type;^{93–98} also, it is a method that is likely to be useful for studying azines in biological and other environments. All calculations are performed using GAUSSIAN-09⁹⁹ with the 6-311++G** basis set for wB97XD and the 6-31++G** basis set for the coupled-cluster calculations; triple-zeta basis sets like 6-311++G** are known to give converged results for azine transition energies¹⁰⁰ while the smaller double-zeta basis is large enough to give accurate results with either no or else partial correction for basis-set superposition error.^{43–45,101,102} Analytical gradients are used in all geometry and frequency calculations performed herein, and all newly optimized structures and energies are provided in Electronic Supporting Information (ESI).† Calculations reviewed from previous papers typically used analytical gradients for EOM-CCSD calculations and numerical gradients for TD-DFT and CASPT2 geometries and frequencies.

From the results in Tables 1 and 2, it can be seen that Del Bene's early estimates for the blue shift are close to modern ones but the strengths of the ground-state hydrogen bonds were originally somewhat underestimated. These corrections undermine to some extent the simplistic argument originally presented, however, and so it is clear that a deeper fundamental understanding is to be found. The vertical solvent shift is determined within the first 10's of fs of excited-state dynamics following excitation¹⁰³ and so does not reveal the nature of the long-time product in either the gas-phase cluster or aqueous environments, and the energy distributed into intramolecular and intermolecular vibrations (the "reorganization energy") as a result of vertical excitation must be considered. We shall return to these issues later, but first we consider a critical issue stressed in Del Bene's original analysis:²¹ whether or not the (n,π^*) excitation is localized or delocalized in the diazines.

4. Excitation localization and delocalization

The analysis of Baba, Goodman, and Valenti⁴ is incomplete in that it does not properly address the issue of the localization/delocalization of the (n,π^*) excitation over the two nitrogen atoms, an effect first pointed out by Del Bene.²¹ For pyridine, only one (n,π^*) excitation is possible, but when two heteroatoms are included in the one aromatic molecule it is possible that (n,π^*) excitation influences just one of the heteroatoms or else simultaneously influences them both. If both are affected then the molecule will retain its symmetry but if it affects only one of a symmetry-related pair then spontaneous symmetry lowering will occur; in these situations, the excitation is said to be *delocalized* or *localized*, respectively. Interestingly, this effect leads to quantum entanglement of the nuclear and electronic motions, and effect that could possibly be exploited for quantum computing.¹⁰⁴

Localization *versus* delocalization is indeed a general phenomenon throughout chemistry. The classic localized system is the pyramidal distortion in ammonia: this produces a double-well potential-energy surface with minima corresponding to the two localized configurations, as opposed to the delocalized planar transition-state structure. The classic delocalized system is benzene, this molecule displaying six equivalent C–C bond

Table 2 Calculated adiabatic energies of interaction between azines in their S_0 , lowest (n,π^*) , and lowest (π,π^*) states and a water molecule, in eV, as first evaluated in the 1976 by Del Bene²¹ and by modern state of the art methods

State	Method	Pyridine	Pyridazine	Pyrimidine	Pyrazine
S_0	Del Bene	−0.20	−0.21	−0.18	−0.16
Linear	CCSD ^a	−0.31		−0.27	−0.21
	CASPT2 ^a	−0.27		−0.31	
	B3LYP ^a	−0.29		−0.26	−0.23
	wB97XD ^b	−0.33	−0.35	−0.31	−0.29
	CCSD ^b	−0.30	−0.32	−0.29	−0.27
(n,π^*)	EOM-CCSD ^a	−0.05		−0.19	−0.18
	CASPT2 ^a	−0.02		−0.14	
	TD-B3LYP ^a	−0.10		−0.21	−0.16
	TD-wB97XD ^b	−0.14 ^c	−0.18	−0.29	−0.26
	EOM/SAC ^d	−0.07	−0.19	−0.20	−0.23
(n,π^*)	EOM-CCSD ^a	−0.25		−0.12	−0.04
	CASPT2 ^a	−0.22		−0.09	−0.14
	TD-B3LYP ^a	−0.14		−0.14	−0.05
	TD-wB97XD ^b	−0.28	−0.19	−0.23	
	EOM/SAC ^d	−0.17		−0.15	−0.23
(π,π^*)	TD-wB97XD ^b	−0.96	−0.21	−0.40	−0.66
	PCET ^e	−1.06	−0.59	−0.74	−0.95
	EOM-CCSD ^a	−0.26			−0.24
Linear	TD-wB97XD ^b	−0.35	−0.36	−0.31	−0.32

^a Basis sets 6-31G* (pyrimidine) and 6-31++G** (water) for pyrimidine-water,⁴⁴ aug-CC-pVDZ for water-pyridine,⁴³ and aug-CC-pVDZ for water-pyrazine,⁴⁵ all with 50% BSSE correction; numerical derivatives used for TD and CASPT2 calculations. ^b 6-311++G** basis set. ^c The planar structure is a transition state linking the symmetrically related π -cloud bonded structures. ^d EOM-CCSD/6-31++G** energies at SAC-CI/6-31++G** optimized geometries. ^e The PCET singlet-state energies are corrected for the difference between TD-wB97XD (or EOM-CCSD) and open-shell wB97XD (or CCSD) calculations for the corresponding triplet states.

lengths rather than a double-minimum potential connecting two localized cyclohexatriene-type Kekulé structures. Typically systems can be classified as localized/delocalized based on whether or not a double-well potential-energy surface is produced,¹⁰⁴ but there also exists a class of systems for which a double-well potential does exist but is insufficiently deep to support zero-point vibration, so the intermediary regime is in itself unique. The forces that drive localization can be internal within a molecule (*e.g.*, those in ammonia) or can be induced by environmental interactions such as hydrogen-bonding, with then the timescales of the solvent motion compared to the double-well vibrational dynamics becoming critical.¹⁰⁵ Some experiments (*e.g.* traditional X-ray crystallography) can take too long to perform and so give an averaged apparent delocalized structure to a system that displays equilibrium between the two localized isomers. So, while the localization/delocalization concept is very powerful in describing the chemical and physical properties of molecules, its analysis always requires care.

It is often stated that some “molecule” is either “localized” or “delocalized”, but this is a misleading description. Double-well Born-Oppenheimer potential-energy surfaces can always be expressed in terms of two simpler but interacting diabatic harmonic potential-energy surfaces, and delocalized molecules like benzene always have an associated low-energy excited-state potential-energy surface. It is very common that molecular properties cannot be interpreted adequately without explicit consideration of both potential-energy surfaces,¹⁰⁴ thus directly embodying effects of the breakdown of the Born-Oppenheimer approximation. So at best it can be stated that pairs of potential-energy surfaces are localized or delocalized, and in general different pairs of surfaces for the same molecule may exhibit different types of behaviour. Then these pairs can intersect each other, leading to very complex excited-state phenomena containing many transition states and conical intersections.

For pyridine, pyrazine, pyridazine, and pyrimidine, the first excited state is (n,π^*) but there exists close-lying (π,π^*) states that cross at accessible energies to vertically excited molecules. One then needs to consider not only whether the two (n,π^*) states in diazines are localized/delocalized but also the possibility of distortions localizing the excitation of nearby (π,π^*) states as well as the possibility of nearby conical intersections amongst the (π,π^*) manifold.^{74,106–110} In the singlet manifold, the low-energy excited (π,π^*) states all appear to be delocalized, and all simple rules for understanding the spectroscopy of aromatic molecules are based on this assumption. This is not the case in the triplet manifold, however, as revealed through the calculated potential-energy surfaces shown in Fig. 1.

For benzene,¹¹¹ the lowest energy triplet state $^3B_{1u}$ has a double-well structure in vibrational mode ν_{8a} (e_{2g}), with this excited state interacting strongly with the higher-energy excited state $^3E_{1u}$. (Note that this is a distinctly different mode from the Kekulé mode (ν_{14}) that connects the ground state with the lowest-energy singlet excited state, $^1B_{2u}$.¹¹²) For the diazines, mode 8a becomes totally symmetric and gives rise to two quite different high-symmetry structures on the lowest triplet surface. Vertical excitation occurs at zero displacement of this mode and so we see that the (π,π^*) excited states fall considerably in energy away from vertical excitation. The consequences of this

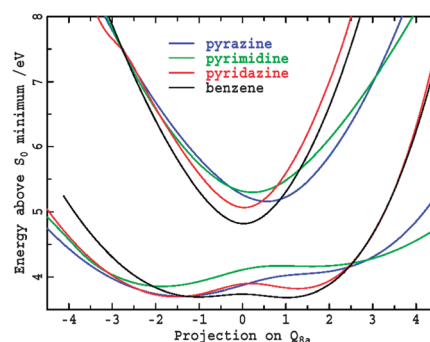


Fig. 1 Calculated EOM-CCSD/cc-pVDZ potential-energy surfaces for benzene, pyrazine, pyrimidine, and pyridazine as a function of displacement (in units of the zero-point displacement length) the vibrational mode 8a. This mode has e_{2g} symmetry in benzene and produces a symmetric double-well potential but for the azines this mode becomes totally symmetric. The state symmetries are $^3B_{1u}$ (lower) and $^3B_{3u}$ (upper) for benzene, 3B_2 for pyridazine, 3A_1 for pyridazine, and $^3B_{1u}$ for pyrazine.

are profound, with *e.g.*, pyridine showing an extremely complex lowest triplet potential-energy surface with these two (π,π^*) states crossing the (n,π^*) state.¹¹³ Further, the lowest (n,π^*) state interacts strongly with an upper (π,π^*) state, causing it to distort into a “boat” configuration.¹¹³ The phosphorescence spectrum of pyridine is thus very different to its singlet to triplet absorption spectrum, a spectrum that took 40 years to interpret.¹¹³ Understanding hydrogen bonding to the triplet manifold in these molecules is thus a very challenging task.

For the singlet manifold, Table 3 shows the observed and calculated (using EOM-CCSD) point-group symmetries of pyridine,¹¹³ pyridazine,^{114–116} pyrimidine,⁴⁷ and pyrazine^{117,118} in their ground states and also their first excited singlet (n,π^*) state. Pyridine also undergoes an out-of-plane “boat” distortion in the excited state,^{113,119} an effect which is critical to the understanding of the molecule’s photochemistry.^{74,106–108,119} The full ground-state symmetry is clearly preserved for pyrazine^{117,118,120} and pyrimidine,^{47,121} indicating that the (n,π^*) excitation remains delocalized in the excited state. Pyridazine, however, requires special consideration.

From an experimental perspective, pyridazine has been the most difficult diazine to assign owing to its very complex first singlet absorption spectrum. In 1996 we qualitatively interpreted this as arising through strong vibronic coupling involving a

Table 3 Observed and calculated symmetries of the ground-state vibrational density for the S_1 (n,π^*) excited electronic state of pyridine,^{113,119} pyridazine,^{114–116} pyrimidine,^{47,121} and pyrazine^{117,118,120}

Molecule	Obs	EOM-CCSD	CASPT2	TD-B3LYP	TD-wB97XD ^d
Pyridine	C_s	C_s^e	C_s^e	C_{2v}	C_s^e
Pyridazine	C_{2v}	C_{2v}^a			C_{2v}
Pyrimidine	C_{2v}	C_{2v}	C_{2v}	C_s	C_s^b
Pyrazine	D_{2h}	D_{2h}		D_{2h}	D_{2h}^c

^a Predicts shallow double wells in a_2 , b_1 , and b_2 modes that do not support zero-point vibration.¹¹⁴ ^b Predicts shallow double well in a b_2 localizing in-plane distortion that does not support zero-point vibration.

^c Predicts shallow double minimum in out-of-plane b_{3g} mode that does not support zero-point vibration. ^d This work, 6-311++G** basis set.

^e Non-planar “boat” structure induced by b_1 distortion.

vibrational mode that could induce localization, ν_{6b} , acting between two closely spaced electronic states, 1B_1 and 1A_2 .³¹ However, Fischer and Wormell¹¹⁴ later provided the first quantitative interpretation of key aspects of the observed spectra by expanding this scenario to include as an essential feature the effects of totally symmetric mode ν_{6a} , making manifest a low-lying conical intersection between 1B_1 and 1A_2 . EOM-CCSD electronic-structure calculations verified the critical aspects of this model, indicating that 1B_1 and 1A_2 reverse in order between vertical excitation (1B_1 lower) and adiabatic excitation (1A_2 lower).¹¹⁴ All computational methods considered indicate that the 1B_1 surface is not stable but instead has an imaginary b_2 vibration frequency. Distortion of the 1B_1 surface along this mode reduces the symmetry from C_{2v} to C_s , circling around the conical intersection towards C_{2v} symmetry again at the 1A_2 S_1 -surface minimum. wB97XD predicts the 1A_2 structure to be the global minimum of S_1 . However, EOM-CCSD predicts the 1A_2 structure distorts along a_2 , b_1 , and b_2 modes,¹¹⁴ but none of these distortions are sufficiently deep to support zero-point vibration and hence the vibrational density of the S_1 state is still predicted to have C_{2v} symmetry. Subsequent EOM-CCSD calculations by Anh *et al.* depict a contradictory energy scenario,^{115,116} suggesting that rather the b_2 well is very deep. However, these calculations predict a reorganization energy of $5714\text{ cm}^{-1} = 0.71\text{ eV}$, grossly inconsistent with the observed value¹¹⁴ of 0.37 eV (see later in Table 6). Our current EOM-CCSD calculations vindicate the original EOM-CCSD results of Fischer and Wormell, results which are consistent with the basic experimental data. It is hence clear that the (n,π^*) excitation is delocalized in pyridazine. Most interestingly, however, we note that the issue of localization/delocalization in this case is not dominated by the excitations from the two lone pair orbitals to a common π^* orbital but rather by the excitations from just the upper lone-pair orbital to two nearly degenerate π^* orbitals.

Always, delocalization of the (n,π^*) excitation in the diazines indicates that one half of an electron is taken from each nitrogen and transferred into the π^* system. The breaking of the hydrogen bond between pyridine and water when one of the two lone-pair electrons is removed seems intuitively obvious, but what is the effect of removing just a half of an electron going to be? Possibilities include (i) the excitation being drawn onto just one of the two nitrogens as a result of the hydrogen bonding, lowering the molecular symmetry and, in solution, breaking the hydrogen bond to this nitrogen only, (ii) the excitation remaining delocalized and in solution both hydrogen bonds break, and (iii) the excitation remains delocalized but the two weakened hydrogen bonds remain. Clearly option (i) is fully consistent with the experimental observations of Baba, Goodman, and Valenti,⁴ but the other options may also be feasible. In 1966 at the time of their analysis, through-bond intramolecular interactions were undiscovered and only localized excited states were expected, and indeed it was believed¹²² at the time that the diazines had localized (n,π^*) excited states.

5. Molecular hydrogen-bonded motifs

Hydrogen-bonded structures of pyridine and the diazines with water have been identified in both the ground-state S_0

(using the CCSD, CASPT2, BLYP, and wB97XD methods) and in the first (n,π^*) excited state S_1 (using the EOM-CCSD, TD-B3LYP, TD-wB97XD, and CASPT2 methods), and representative structures are sketched in Fig. 2. In both states, traditional linear hydrogen bonded structures formed to nitrogen lone-pair orbitals are identified. However, in the excited state, structures with hydrogen bonds to the aromatic π system are also prevalent, structures that closely resemble ground-state hydrogen bonds formed between water and say benzene or fluorobenzene;^{8,51,123–125} of these, the lowest-energy structures are found with the closest water hydrogen atom nearest to a ring nitrogen atom and so the hydrogen bonds appear to be formed to the nitrogen π orbital.

Key geometrical descriptors of these structures, the CNC bond angles (optimized^{43–45,114} using CCSD, EOM-CCSD, or, in this work, SAC-CI) are given in Table 4. Adding a hydrogen-bonded water molecule to one of the two nitrogens in a diazine breaks the inherent symmetry (Table 3) and hence the two CNC bond angles become different. This difference is less than 1° for hydrogen-bonds to the ground states. However, in the excited state it increases to 4° in pyrazine, 12° in pyrimidine, and 16° in pyridazine. This quantifies the driving force for localization in each diazine and reflects key qualitative observed spectroscopic features including the low-lying conical intersection of pyridazine and the large resonance interaction of pyrazine.

The hydrogen-bond energies for these structures are given in Table 2. Always the linear hydrogen bond is found to be the most stable structure for the ground state, as is expected, but for the excited state either this structure can remain the most stable or else the hydrogen bond to the π system may be the most stable. CCSD/6-31++G** predicts strong ground-state linear hydrogen bonding energies in the range of 0.27 to 0.32 eV, reducing in the excited state as calculated by EOM/SAC-CI to 0.07 eV for pyridine and from 0.19 eV to 0.23 eV for the diazines. The intermediate values for the diazines arise as a result of full or partial (n,π^*) -excitation localization onto the non-interacting nitrogen.

Pyridine and the diazines thus reveal three different excited-state hydrogen bonding motifs: for pyridine, a strong hydrogen bond to the π system, for pyrimidine and pyridazine strong linear hydrogen bonds to fully symmetry-broken species, and for pyrazine a strong

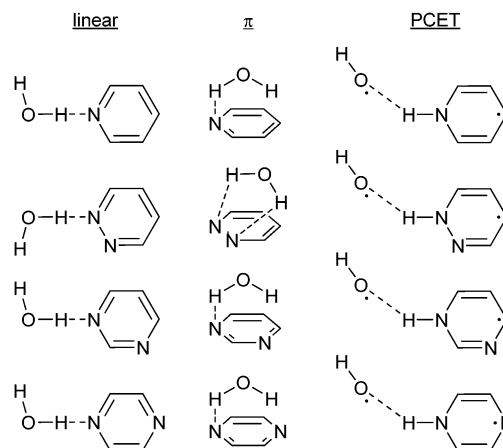


Fig. 2 Generic types of molecular hydrogen-bonding structures identified by azine–water dimer calculations.

Table 4 EOM-CCSD CNC bond angles (°) in the equilibrium structure of pyridine,⁴³ pyrimidine,⁴⁴ and pyrazine,⁴⁵ as well as SAC-CI/6-31++G** CNN angles (°) for pyridazine calculated for isolated molecules and for molecules hydrogen-bonded (HB) to one water

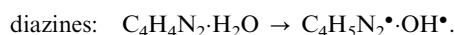
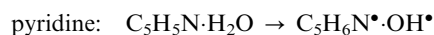
Molecule	Gas phase		Linear HB		HB to π S_1
	S_0	S_1	S_0	S_1	
Pyridine	116	129	118	122	127
Pyridazine	2 @ 119	2 @ 127 ^b	120 ^a , 119	117 ^a , 133	126, 127
Pyrimidine	2 @ 115	2 @ 123	116 ^a , 115	118 ^a , 130	118 ^a , 130
Pyrazine	2 @ 115	2 @ 121	116 ^a , 115	118 ^a , 122	122 ^a , 125

^a This N hydrogen bonded to water. ^b 127° for the ¹A₂ global surface minimum, 123° for the ¹B₁ transition state. EOM-CCSD for pyridazine¹¹⁶ 127° for (¹A₂) and 123° (¹B₁).

linear hydrogen bond to a molecule with only partially localized (n, π^*) excitation.

6. Excited-state intermolecular proton transfer

Sobolewski and Domcke have described products of excited-state intramolecular and intermolecular proton transfer (PCET) reactions for pyridine.ammonia and other hydrogen-bonded azines.⁷¹ These processes are facilitated by partial charge transfer from the proton donor to the electron donor that accompanies both (n, π^*) and (π, π^*) transitions; they are known as electron-driven proton-transfer (EDPT) reactions. We consider PCET in the 1 : 1 complexes of pyridine and the diazines with water, see Fig. 2, both in the gas phase and in aqueous solution, looking at both local-minimum structures and transition states from linear hydrogen-bonded species. These structures are singlet biradicals resulting from the photochemical reactions



Both the EOM/SAC and TD-wB97XD methods are used in these analyses. These calculations are particularly difficult as the PCET ground states are multi-configurational charge-transfer species, and the transition states involve weak orbital interactions with large imaginary frequencies that link structures differing significantly in many more than two geometrical variables. Ideally multireference configuration-interaction calculations would be preferable, but these present significant practical difficulties associated with the need for continuity of the active space. The single-reference methods that are used instead are found to be adequate for all investigated structures except the PCET minima themselves. For these structures we apply a correction obtained by evaluating the corresponding triplet-state energies using both time-dependent excited-state and open-shell ground-state techniques, adding the obtained difference to the time-dependent-calculated singlet-state energies. As the effect of out-of-plane distortions on azine singlet and triplet states is known to be quite different, these calculations are restricted to planar geometries. In ESI† results are also given for many structures and energies of non-planar linear hydrogen bonded and PCET species, revealing that relaxation of this restriction usually lowers energies by a small amount; the main text

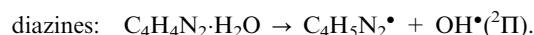
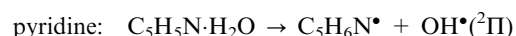
focuses on only reliable results that depict the general qualitative scenario.

As well as gas-phase calculations, liquid-state reactivity is also modelled. Equilibrium solvation corrections for aqueous solution are applied using the COSMO¹²⁶ self-consistent reaction field (SCRF) dielectric-continuum model. These corrections are evaluated based on the triplet open-shell ground-state electronic structures rather than through the use of TD-DFT or EOM-CCSD calculations based on closed-shell reference configurations. In particular, this is to avoid convergence problems associated with investigating charge-neutral PCET excited states based on charge-transfer closed-shell ground-state structures.

The calculated PCET complex energies, as well as the activation energy required to make these complexes from the linearly hydrogen-bonded (LIN) adiabatic (n, π^*) and/or (π, π^*) minima are given in Table 2 and 5, while Fig. 3 presents these and other results in graphical form.

The results obtained indicate that the PCET structures of the S_1 (n, π^*) excited states are lower in energy than the identified azine-water hydrogen-bonded motifs. The radicals sit in the π^* LUMO orbitals of the chromophores and in the co-linear sp σ orbitals of the hydroxy radicals. Asymptotically, these structures dissociate into OH• radicals in their ² Σ state that lie¹²⁷ 4.03 eV (calculated values are wB97XD: 3.69 eV, and CCSD: 4.14 eV) above the ² Π ground state, but the strong interaction¹²⁷ of the ² Σ state with its neighbouring radical compensates at short distances. Also, linearly hydrogen-bonded (π, π^*) states facilitate PCET processes that directly produce PCET complexes involving OH•(² Π). Explicit optimized structures for these species have not been generated and would most likely involve non-planar character, but we find that at the (n, π^*) optimized transition-state (TS) and local-minima PCET structures, the corresponding (π, π^*) states are within 0.1 eV of the (n, π^*) ones. These calculations thus indicate that initial (n, π^*) or (π, π^*) character would be lost during the production of PCET species.

Fig. 3 also shows that the calculations depict dissociation of the PCET biradical complexes into ground-state radicals as an exothermic process (over some small uncalculated barrier), making



The ground-states of the PCET dimeric complexes are predicted to be the zwitterionic proton-transfer structures

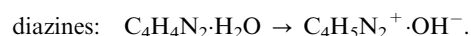
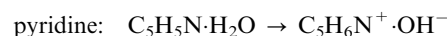


Table 5 Calculated energies of activation (ΔE^\ddagger) and conversion (ΔE) in eV of (n, π^*) or (π, π^*) excited linear hydrogen-bonded species to PCET biradical species in the gas phase

	Method	Pyridine	Pyridazine	Pyrimidine	Pyrazine
(n, π^*) ΔE^\ddagger	TD-wB97XD	0.21	0.57	0.68	0.78
(n, π^*) ΔE	TD-wB97XD	−0.82	−0.03	−0.11	−0.43
(n, π^*) ΔE	EOM/SAC	−0.99	−0.40	−0.54	−0.72
(π, π^*) ΔE^\ddagger	TD-wB97XD	0.46	0.09	0.34	0.35

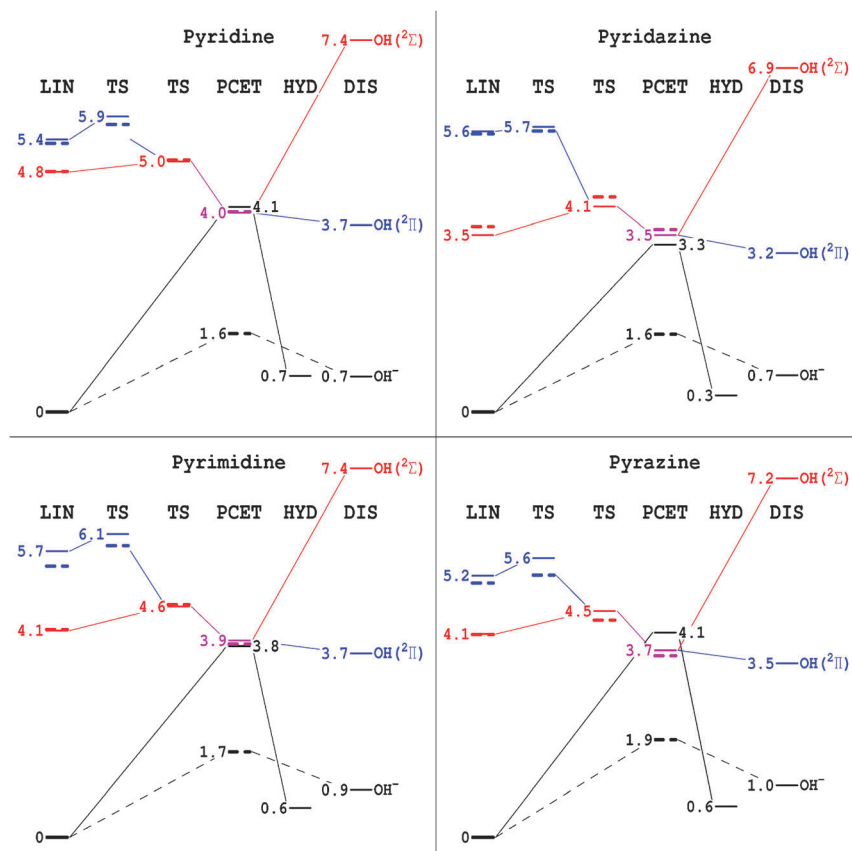


Fig. 3 wB97XD/6-311++G** calculated energies (in eV) for linear hydrogen-bonded structures (LIN), transition states (TS), PCET complexes, photohydrated azines (HYD), and dissociation products (DIS) for photoinduced chemical reactions involving PCET for the ground state (black), (n,π^*) state (red, purple), and lowest (π,π^*) state (blue, purple), both in the gas phase (solid lines) and in solution (dashed lines).

In the gas phase these are high-energy species, and all calculations predict very small differences between the energies of these zwitterions and the PCET complexes, indicating the presence of conical intersections between the ground and excited states of the complexes,⁷¹ see Fig. 3. Hence the PCET species can also lead to very rapid internal conversion to the ground state and hence molecular dissociation of the azine-water complex.⁷¹

7. Photodynamics of gas-phase complexes with water

The previous section considered PCET reactions of gas-phase azine-water dimers and identified two generally open reactive pathways: proton transfer followed by radical dissociation, and proton transfer followed by internal conversion to the ground state and hence molecular dissociation. Historically, excited-state dynamics of azines has not focused on such PCET pathways but rather on the question as to whether or not the excitation provides enough energy to directly dissociate the hydrogen bond. In the 1970s Del Bene^{20–23} using small configuration-interaction calculations with a minimal basis set argued that sufficient energy was deposited during the excitation directly into the hydrogen-bond stretch motion to dissociate azine hydrogen bonds. If this were not the case then there arises the possibility of forming metastable excited-state

species, and in any case computationally resolving the fate of excited dimers would require extensive dynamics calculations on high-quality interacting potential-energy surfaces.¹²⁸ Here we focus on the possible existence of metastable complexes.

Del Bene's^{20–23} original calculations, along with modern high-level assessments, are reported in Table 6 (gas-phase reorganization energies compared to experiment) and 7 (cluster photochemical dissociation energies). High-level calculations depict a complex scenario. For pyridine, pyrimidine, and pyrazine, Table 7 gives the energy change on hydrogen-bond dissociation for three processes: (1) vertical excitation, with no relaxation of intramolecular energy into intermolecular motion, (2) vertical excitation with full energy relaxation allowed, and (3) 0–0 excitation with full energy relaxation allowed. All calculations predict that these molecules after vertical excitation can dissociate exothermically only if full relaxation is allowed. They also predict that the hydrogen bonds in *all* molecules are *stable* following 0–0 excitation to molecular dissociation to form a water molecule and an excited-state azine.

Based on the results found in the previous section, such excited-state species would be metastable to PCET processes. However, the activation energies ΔE^\ddagger for PCET processes on the S_1 surface given in Table 5 are quite large for the diazines (0.6 to 0.8 eV), indicating that PCET production would be reasonably slow. In contrast, for pyridine-water ΔE^\ddagger is calculated to be just 0.2 eV, a small barrier that could be overcome by either

Table 6 Observed and calculated monomer reorganization energies (eV) for the lowest singlet excited state (n,π^*) of pyridine,¹¹³ pyridazine,³¹ pyrimidine,⁴⁷ and pyrazine^{117,118}

Molecule	Obs.	EOM-CCSD	CASPT2	TD-B3LYP	TD-wB97XD ^a	EOM/SAC ^a
Pyridine	0.43	0.49	0.55	0.43	0.46	0.43
Pyridazine	0.37 ^b				0.43	0.36
Pyrimidine	0.35	0.44	0.42	0.42	0.45	0.42
Pyrazine	0.15	0.14		0.12	0.12	0.10

^a This work. ^b From gas-phase spectrum.¹¹⁴

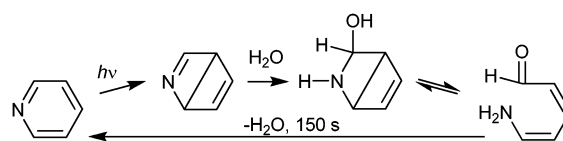
available excess energy or else by proton tunnelling through the barrier. A significant feature of the diazines is that excitation localization forces (n,π^*) onto the nitrogen that is not hydrogen bonded, destabilizing PCET transition states. Reaction from an initially linearly hydrogen-bonded excited state to form a PCET complex then requires changes in OH and NH bond lengths and angles as well as re-hybridization of both nitrogens in the diazine.

Wanna, Menapace and Bernstein^{8,9} have studied the hydrogen bonded clusters of the diazines with alkanes, NH_3 and H_2O in molecular beams using two-colour time-of-flight mass spectroscopy and fluorescence-excitation spectroscopy. They did not observe diazine-water clusters in the mass spectrometer following 0–0 excitation, but pyrazine.water in the beams was detected using fluorescence excitation spectroscopy. However, under similar conditions, clusters of diazines with alkanes, ammonia, and other proton donors are usually observed in the mass spectrometer.^{6,8,9} These results thus indicate that clusters form but either dissociate or else lose their energy after excitation but before ionization. As energy loss by collisional de-excitation is unlikely, dissociation of the complex on a time-scale faster than the fluorescence lifetime is suggested for pyrimidine.water and pyridazine.water; in the gas phase these lifetimes are 320 ps for pyrazine (owing to $S_1 \rightarrow S_0$ conversion),^{129,130} and 2200 ps for pyrimidine (owing to $S_1 \rightarrow T_1$ conversion).¹²⁹ However, an analogous dissociation process for pyrazine.water would need to be slow on the timescale of pyrazine emission (110 ps owing to $S_1 \rightarrow T_1$ conversion¹²⁹) as emission is observed from pyrazine.water.

An alternative explanation, however, is that pyrimidine.water and pyridazine.water are stable in S_1 but just emit weakly to be observed in molecular-beam experiments. Table 7 predicts that 0–0 excitation of azine-water complexes is below the barrier for molecular dissociation, whereas Table 5 predicts that the activation energy for PCET from pyrazine.water is less than that for pyrimidine.water and pyridazine.water and so cannot explain the observation of fluorescence from pyrazine.water and the lack of fluorescence from the other two. The calculations thus suggest that emission from pyrimidine.water and pyridazine.water should in fact be observable.

Fluorescence from pyridine in aqueous solution is not observed, and our dimer calculations suggest that PCET processes could be responsible; note that Fig. 3 also shows results for dimer energetics corrected for aqueous solution using dielectric continuum models, and the calculated effects on the PCET process are small. However, pyridine in the gas phase is known to undergo complex photodynamical processes^{74,106–109} in which (n,π^*) excitation 1600 cm^{-1} above the 0–0 line accesses the conical intersection between the (π,π^*) state and the ground state to form a

Dewar-benzene type structure in a process known as “channel three”.¹¹⁰ Further, in aqueous solution following (π,π^*) excitation, pyridine undergoes photohydration through the cycle⁷⁴



and the same long-lived enamine aldehyde is also observed following (n,π^*) excitation.¹³¹ It is usually assumed that the same mechanism operates following both (n,π^*) and (π,π^*) excitation, this being possible only if the additional energy provided by the solvation blue shift provides the 1600 cm^{-1} energy deficit observed for this process in the gas phase. However, energy released from the excited-state cleavage of the hydrogen bond is unlikely to find its way in high yield into ring vibrational modes of pyridine, and so an alternative mechanism for the observed chemical processes at low excitation energy may be required. PCET could provide such a mechanism.

Transfer of energy near the conical intersection from excited-state PCET complexes to the ground state is recognized to lead to ground-state recombination and hence molecular dissociation of gas-phase dimers.⁷¹ In addition, we find that another barrierless process following internal conversion to the ground state is attack of the hydroxide ion on the azine ring, leading to the reaction cycle.

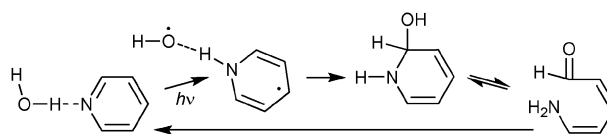
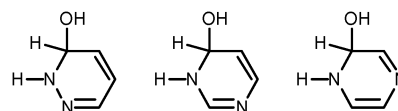


Fig. 3 also gives results for the reaction in the gas phase of PCET complexes after internal conversion to the ground state for pyridine as well as for the possible diazine photohydration products:



For all azines, calculations thus predict that PCET complexes can decompose into not only separated ions, radicals, and neutrals but also can lead to relatively stable photohydration products. If the cyclic alcohol (or some tautomerized derivative) is observed following excitation of pyridine at the low-frequency tail of its S_1 band in aqueous solution or in clusters in molecular beams, evidence supporting PCET would be obtained.

8. Photodynamics in aqueous solution

In aqueous solution, fluorescence is observed from all diazines,⁴ indicating that the excited states are stable in solution for relatively long times. Calculations modelling solvation using dielectric continuum modes predict similar energetics for PCET reactions to that predicted in the gas phase (see Fig. 3), attributing the necessitated slow rates for this process to the large activation energy caused by excitation

Table 7 Excess energy (eV) available for excited-state molecular dissociation of azine-water complexes with retention of the azine excitation for vertical and 0–0 excitation, with and without energy relaxation from intramolecular motions^{43–45}

Molecule	Vert. excitation, no relaxation			Vertical excitation, with relaxation			0–0 excitation, with relaxation		
	EOM-CCSD	CASPT2	B3LYP	EOM-CCSD	CASPT2	TD-B3LYP	EOM-CCSD	CASPT2	TD-B3LYP
Pyridine·H ₂ O	−0.01	0.07	−0.02	0.42	0.50	0.41	−0.14	−0.16	0.01
Pyrimidine·H ₂ O	−0.08	−0.01	−0.08	0.27	0.34	0.27	−0.12	−0.06	−0.13
Pyrazine·H ₂ O	−0.07			0.08			−0.07		

localization in (n,π*)-excited hydrogen bonded diazines. The calculations also suggest that a second feature may be important, however. In aqueous solution, the zwitterionic ground-state associated with the excited-state PCET species is strongly stabilized, as shown in Fig. 3, removing the conical intersection from ready access. Hence excited-state PCET species may be long lived and could exist in equilibrium with orthodox hydrogen-bonded species. In any case it is clear that the observed fluorescence from diazines in water arises from molecules that have not undergone photochemical reactions. We proceed assuming that fluorescence from the diazines arises subsequent to equilibration of the solvent to the change distribution of the S₁ state, and, even though competitive chemical processes render this scenario as merely hypothetical, for comparison we also consider pyridine using similar techniques.

Many computational methods are now available for simulating excited states of molecules dissolved in liquids. The electronic and geometrical structure of pyridine and the diazines in their (n,π*) excited states in clusters and in aqueous solution have been simulated by Karelson and Zerner,^{79,80} Zeng, Hush and Reimers,^{27–32} Gao and Byun,³³ Almeida *et al.*,³⁹ Mennucci,⁴¹ Cossi and Barone,⁴⁰ and de Monte *et al.*⁴⁶ using combinations of semi-empirical INDO/S^{39,79,80} or AM1³³ methods with continuum solvation models,^{79,80} QM/MM methods,^{33,81,132} analytical all-atom electrostatic methods,^{27,29–32} time-dependent density functional theory,^{40,41} and the continuum solvation model COSMO¹²⁶ in combination with multi-reference configuration interaction with singles and doubles (MR-CISD).⁴⁶ With the development of excited-state DFT liquid simulation techniques^{133,134} and density-functionals that can treat dispersion accurately, this type of approach looks very promising for the future. Alternate fragment-orbital methods^{135,136} are also promising.

Our approach,^{27–32,82–84} called the Zeng-Hush-Reimers solvent-shift model (ZHRSS), has been to parameterize AMBER¹³⁷-based molecular-mechanics force fields using multi-reference configuration-interaction calculations.³⁰ This method is very robust, having *e.g.* been used to describe a range of electron-transfer spectra of inorganic complexes,^{32,48,138–141} and has the advantage of being able to include large liquid samples, as is necessary to describe long-range spectroscopic and energetic effects, at a level that permits both the evaluation of ground-state and excited-state thermodynamic quantities *and* the evaluation of spectroscopic properties.

Thermodynamic data calculated using ZHRSS for pyridine and the diazines in dilute aqueous solution is compared to experimental data in Table 8. The calculated enthalpies of solvation ΔH range from −14 to −19 kcal mol^{−1} and somewhat uniformly overestimate the observed values of −12 to −15 kcal mol^{−1}, while the calculated and observed excess volumes of solvation ΔV are in

all good agreement. As ΔH and ΔV are both very sensitive to the details of the potential-energy functions used in the simulations, these results indicate that the *ab initio*-derived force fields appear quite realistic. Also given in the table are the numbers of hydrogen bonds formed to the solute at equilibrium in both its ground and excited states. For the ground state, these numbers are close to expectations, although 2.2 rather than 2 water molecules are predicted to be bound to pyrimidine. However, for S₁, quite different results are found for each solute: pyridine retains its hydrogen bonded water molecule, but the coordination is through the π-cloud rather than the nitrogen lone pair, no hydrogen bonding remains for pyridazine, one localized hydrogen bond remains for pyrimidine, and for pyrazine only one half of a hydrogen bond remains. The results for pyrimidine and pyrazine directly parallel those from the high-level dimer calculations reported earlier in Table 2 and 4: for pyrimidine, the full excitation localization found for the dimer leads directly to the calculated solution-phase structure, while for pyrazine, the identified significant retention of excitation delocalization in the dimer leads to the calculated significant weakening of the hydrogen bonds to both nitrogens in solution.

Table 1 shows that the solvent shifts in aqueous solution for absorption and emission closely parallel the observed ones and hence the ZHRSS calculations provide an atomistic description for the observed phenomena. Also, spectral shifts calculated by the same method for just the dimeric complexes with a single water molecule are given in this table, but corresponding experimental data is available only for pyrazine. The calculated dimer shift of 0.15 eV is 60% of the calculated solution solvent shift of 0.25 eV whereas the observed dimer value of 0.07 eV is just one third of the observed solution value of 0.20–0.25 eV. This suggests that ZHRSS overestimates short-range effects and underestimates those from long-range, an effect that may be largest for pyrazine and stem from the high level of treatment needed to properly describe the localizing effect of hydrogen bonding on this molecule. For pyridine, ZHRSS predicts an even larger relative contribution from the hydrogen-bonded water.

Table 8 Calculated and observed equilibrium structural properties for dilute solutions of pyridine and the diazines in aqueous solution for pyridine,²⁷ pyridazine,³¹ pyrimidine,^{26,28,29} and pyrazine³⁰

Molecule	ΔH (kcal mol ^{−1})		ΔV (cm ³ mol ^{−1})		N–H coord. number	
	ZHRSS ± 2	obs.	ZHRSS ± 9	obs.	S ₀	S ₁
Pyridine	−13.6	−11.9			1	1
Pyridazine	18.5	−14.9	65	70	2.0	0.1
Pyrimidine	−16.9	−14.3	67	69	2.2	1.0
Pyrazine	−16.2	−11.8	69	71	2.0	0.5

For the solvent shift in aqueous solution, the results of ZHRSS are in good agreement with those from the latest DFT SCRF cluster analyses of QM/MM solvent structures.¹³²

9. Conclusions

While the effects of excitation on hydrogen bonding are often related to subtle changes that occur in the electron distribution of the base induced by transitions remote from hydrogen-bonding sites, we consider gross effects caused by (n,π^*) excitations that directly remove electrons from hydrogen bonds. Such excitations have traditionally been viewed as simply breaking the associated hydrogen bonds. However, we show that the picture is much more complex than this. In some circumstances, the bonding is indeed significantly weakened in the excited state, becoming non competitive compared to other options in condensed phases or leading to direct dissociation of gas-phase complexes. However, the enhanced π electron density after excitation can give rise to new motifs for strong hydrogen bonds to the excited state so that the existing bonds simply rearrange into a different structure rather than break. Also, excitation localization in chromophores acts to protect hydrogen bonds from breakage.

Molecular hydrogen-bonded species for pyridine and all the diazines with water are predicted to exist in the S_1 state, contrary to the simplistic notion that hydrogen bonds are simply broken in the excited state. However, PCET reactions are identified that lead exothermically to hydrogen transfer and subsequent dissociation into radicals in both the gas-phase and in solution; these species can also lead to $S_1 \rightarrow S_0$ internal conversion and hence either molecular dissociation on the ground-state surface or else photohydration reactions producing relatively stable new chemical species. The activation energy for PCET is calculated to be accessibly low for pyridine, possibly providing an explanation for the observation of photohydration products in solution at energies below the known thresholds for alternative processes of isolated pyridine. Detectable molecular intermediates involved in this mechanism are identified. However, the analogous PCET activation energies for the diazines are calculated to be much higher as a result of (n,π^*) excitation localization in diazine-water complexes, reducing the rates of PCET reactions to be less than the fluorescence lifetimes of the solvated diazines. The calculations fully support the observation of fluorescence from pyrazine-water dimers in molecular beams and suggest that similar fluorescence from pyrazine-water and pyrimidine-water should also be observable.

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