Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

# Supporting Information



69451 Weinheim, Germany

# Nucleobase-Fluorobenzene Interactions: Hydrogen Bonding Wins Over $\pi$-Stacking.**

Roman Leist, Jann A. Frey, Philipp Ottiger, Hans-Martin Frey, Samuel Leutwyler*, Rafał A. Bachorz, and Wim Klopper*

The 2-pyridone·fluorobenzene (2PY·$n$-FB) clusters were synthesized and cooled in a 20 Hz pulsed supersonic expansion of Ne (1.5 bar) mixed with 0.2–1 % of the fluorobenzene (1,2,4,5-FB, 5FB: Aldrich, 99%, 6FB: Fluka 99%). 2PY (Aldrich, 97%) was placed in the nozzle and heated to 85-90°C. $S_1 \leftarrow S_0$ excitation was performed with UV pulses (0.2-0.5 mJ) from a frequency-doubled dye laser. Ionization pulses at 228 nm (1 mJ/pulse) were produced by sum-frequency mixing of 355 nm Nd:YAG laser light with 640 nm from a second dye laser. The ions were detected in a time-of-flight mass spectrometer. UV/UV holeburning was performed with an independently tunable dye laser (2 mJ/pulse) that preceded the excitation/ ionization lasers by 300 ns.

Furthermore, infrared (IR) depletion spectra were measured over the 2800-3600 $cm^{-1}$ range at 0.20 $cm^{-1}$ resolution. The IR pulses ($\sim$7 mJ/pulse) were produced by a LaserVision OPO/OPA system, pumped by a 10 Hz injection-seeded Nd:YAG laser. The depletion signals were monitored mass specifically at the $0_0^0$ bands of 2PY at 29,831 $cm^{-1}$, of 2PY·4FB at 30'189 $cm^{-1}$, of 2PY·5FB at 30'224 $cm^{-1}$ and of 2PY·6FB at the intense 30,019 $cm^{-1}$ band.

The population changes induced by IR depletion were measured by operating the UV excitation and ionization lasers at twice the repetition rate (20 Hz) of the IR laser while recording the difference in 2PY·$n$-FB ion signal. The IR spectra were measured in two overlapping sections of $\sim$500 $cm^{-1}$ width at a constant intensity level (7$\pm$1 mJ/pulse, unfocussed).

The IR depletion spectrum of bare 2-pyridone (Figure 5A) exhibits a "free" N-H stretching band at 3448 $cm^{-1}$. [29] Note the absence of C-H stretching bands in the 3000 $cm^{-1}$ region. In 2PY·4FB and 2PY·5FB, the N-H stretch vibrations shift by $-19$ and $-17$ $cm^{-1}$ to lower wavenumber, due to formation of the weak N-H$\cdots$F-C hydrogen bonds. Furthermore, intense infrared bands appear at 3028 $cm^{-1}$ for 2PY·4FB and at 3027 $cm^{-1}$ for 2PY·5FB (Figure 5B, C). These are the C-H stretching vibrations of the fluorobenzene moieties that are involved in the C-H$\cdots$O=C hydrogen bonds. These are calculated and observed to be $\sim$15 times more intense than the C-H stretches of the non-hydrogen-bonded C-H groups of 2-pyridone. All infrared intensities in Figure 5 are plotted relative to the calculated N-H stretch of 2-pyridone, calculated to be 160 km/mol. In the IR spectrum of 2PY·6FB (Figure 5D), the observed N-H stretch frequency agrees very well with that calculated for the "free" N-H stretch of the $\pi$-stacked complex. Note that no C-H vibrational band of the 2-pyridone moiety can be observed, as is expected for the $\pi$-stacked structure. The IR depletion spectra in Figure 5 confirm the hydrogen-bond connectivity of 2PY·4FB and 2PY·5FB and the absence of H-bonding in 2PY·6FB.

**Ab initio calculations**

The Hartree-Fock energy was computed in the augmented correlation-consistent polarized valence quadruple-zeta aVQZ (aug-cc-pVQZ [25, 26]) basis set. The second-order correlation energy was obtained in the same basis by means of the explicitly-correlated RI-MP2-R12 method, [23, 24] recently implemented in the TURBOMOLE program package. [30, 31] The correlation energy contributions at the coupled-cluster singles and doubles level (CCSD) were computed in the aVDZ basis. The perturbative triples (T) correction of CCSD(T) theory was computed in the slightly modified aVDZ' basis set (see below).

All single-point energy calculations were corrected for basis-set superposition error (BSSE) by the Boys-Bernardi full counterpoise method. [32] The equilibrium geometries, harmonic frequencies, and RI-MP2-R12 energies were obtained with TURBOMOLE, [30] the CCSD [33] and CCSD(T) [34] energies with MOLPRO. [35] The structures were optimized at the RI-MP2 (resolution-of-the-identity second-order Møller-Plesset perturbation theory) level [23] with the aVTZ (augmented correlation-consistent polarized valence triple-zeta [25, 26]) basis set. Convergence thresholds were $10^{-8}$ a.u. for the energy and $10^{-6}$ a.u. for the gradient. All calculations

were carried out in the frozen-core approximation. The harmonic vibrational frequencies and zero-point vibrational energies (ZPVE) were evaluated at the RI-MP2 level with the aVDZ basis. [25, 26]

Alternatively to eqn. (1), both the CCSD and the contributions from perturbative triple excitations were evaluated in the aVDZ′ basis, in which the most diffuse $d$ functions of the aVDZ basis of C, N, O, and F are removed. The contributions to the total energy are evaluated as:

$$E = E^{\mathrm{aVQZ}}_{\mathrm{Hartree\text{-}Fock}} + \Delta E^{\mathrm{aVQZ}}_{\mathrm{RI\text{-}MP2\text{-}R12}} + \Delta E^{\mathrm{aVDZ'}}_{\mathrm{CCSD}} + \Delta E^{\mathrm{aVDZ'}}_{\mathrm{CCSD(T)}} \quad (2)$$

Table 1 shows that removal of the diffuse function increases the $\pi$-stacked binding energies of both 2PY·4FB and 2PY·5FB by ∼2.9 kJ/mol, that is, the $\pi$-stacked binding energies are more sensitive to the basis set size.

We calculated the vertical electronic excitation energies of the 2PY·$n$FB complexes using the RI-CC2 (resolution-of-the-identity approximate second-order coupled-cluster) method [36] at the RI-MP2/aVTZ equilibrium ground-state geometries, using the augmented correlation-consistent polarized valence triple-zeta (aVTZ) basis set. Table 2 shows the computed vertical electronic excitation energies.

Table 2: Vertical excitation energies (in $\mathrm{cm}^{-1}$) calculated at the CCS, CIS(D) and CC2 levels in the aug-cc-pVTZ basis (invoking the RI and FC approximations, at the RI-MP2/aVTZ geometries). The CC2 values are plotted in Figure 1.

| Complex | Isomer | CCS | CIS(D) | CC2 |
|---|---|---|---|---|
| 2-pyridone | | 41,779 | 36,564 | 35,001 |
| 2PY·1,2,4,5-tetrafluorobenzene | H-bonded | 42,125 | 36,675 | 35,075 |
| 2PY·pentafluorobenzene | H-bonded | 42,163 | 36,752 | 35,121 |
| 2PY·1,2,4,5-tetrafluorobenzene | $\pi$-stacked | 41,593 | 36,377 | 34,628 |
| 2PY·pentafluorobenzene | $\pi$-stacked | 41,557 | 36,077 | 34,433 |
| 2PY·hexafluorobenzene | $\pi$-stacked | 41,715 | 36,234 | 34,506 |

The $S_0 \rightarrow S_1$ transitions of *both* the H-bonded and $\pi$-stacked forms are $\pi\pi^*$ excitations on 2PY, dominated by the excitation from the highest occupied $\pi$ molecular orbital (HOMO) to the lowest unoccupied $\pi^*$ orbital (LUMO) (Figure 6B). The calculated transition energies for the H-bonded and $\pi$-stacked geometries are marked by vertical bars in Figure 1. The $S_0$, $S_1$ and $S_2$ potential energy curves (Figure 6A) are very similar, with calculated minima at 3.22, 3.21 and 3.20 Å, respectively. The RI-CC2 calculations also predict very small excited-state orbital overlaps between the 2PY and 6FB moieties and negligible delocalization or charge-transfer character for both electronic transitions, which rules out an interpretation of the broad bands of 2PY·6FB (Figure 1) in terms of absorption to an exciplex state.

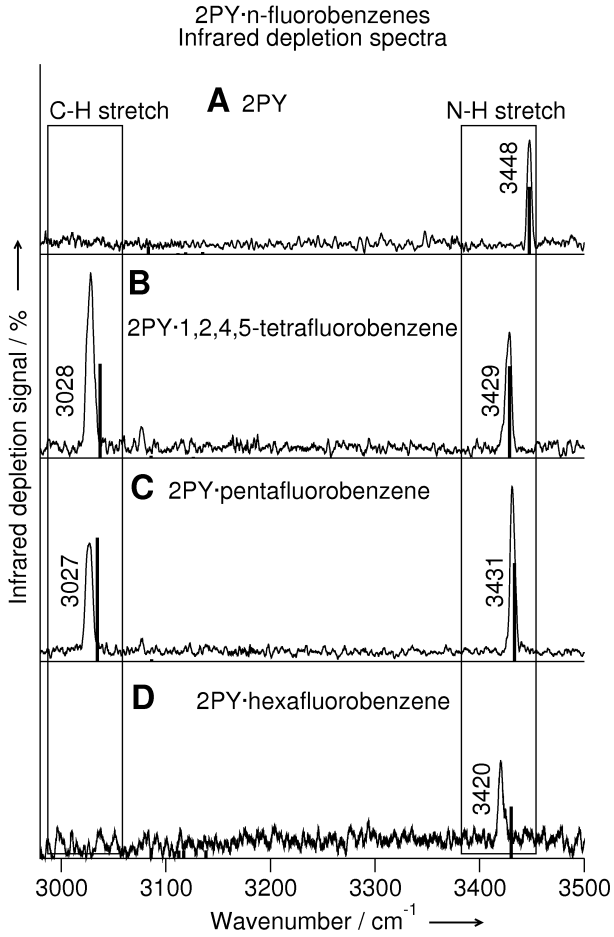


Figure 5: Infrared-ultraviolet (IR(UV) depletion spectra of (A) 2-pyridone, (B) 2PY·4FB, (C) 2PY·5FB, (D) 2PY·6FB. Vertical bars indicate the N-H stretch and C-H stretch infrared bands (RI-MP2/aVDZ, scaled by 0.960 to correct for anharmonicity). The strong C-H stretching bands in B and C are diagnostic for C-H$\cdots$O=C hydrogen bonds of 2PY·4FB and 2PY·5FB, note the absence of such bands in the spectra of (A) and (D).

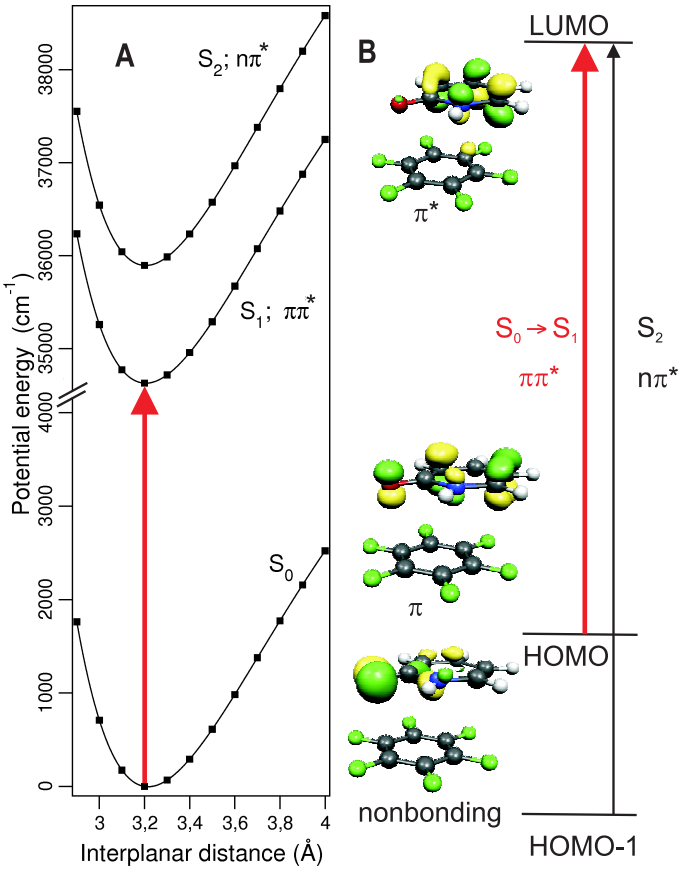


Figure 6: (A) Calculated $S_0$, $S_1$ and $S_2$ state intermolecular potentials of $\pi$-stacked 2PY-hexafluorobenzene, as a function of the interplanar distance. (B) The HOMO-1, HOMO and LUMO molecular orbitals and electronic $S_0 \rightarrow S_1$ ($\pi\pi^*$) and $S_0 \rightarrow S_2$ ($n\pi*$) electronic transitions. The vertical red arrow indicates the $\pi\pi^*$ excitation, see Figure 1.