Effect of microhydration on the resonances of pyridine and thymine

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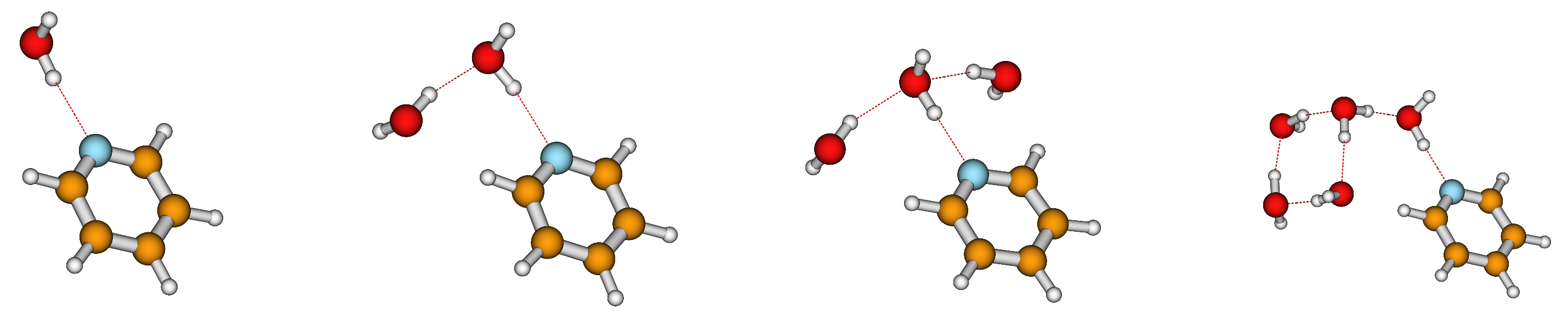
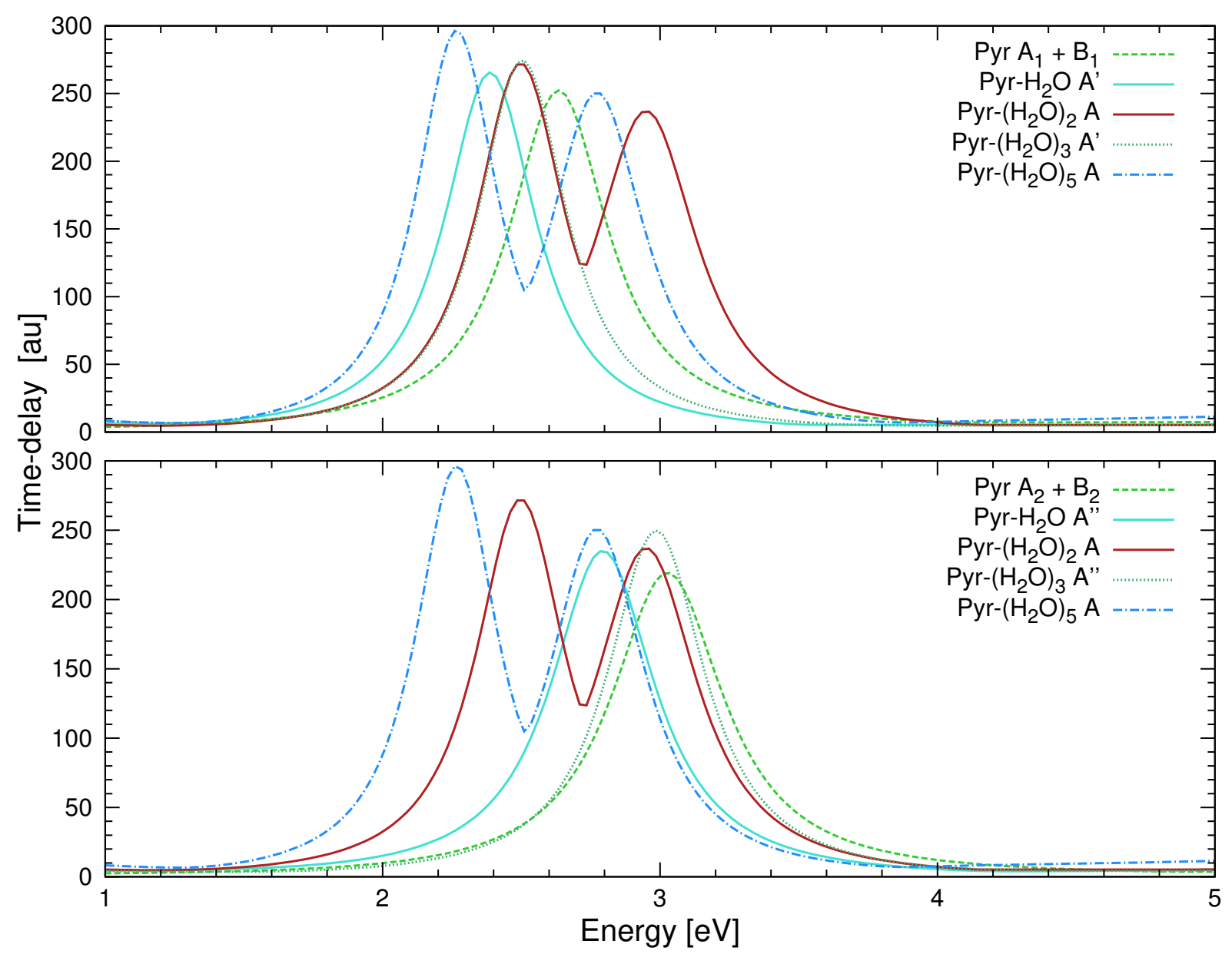
Introduction

Electron scattering from biological molecules has been investigated for at least a couple of decades [1]. One of the most significant applications is in the study of biological radiation damage, where electron-induced dissociative electron attachment (DEA) can lead to DNA strand breaks [2]. DEA is initiated by the formation of a resonance or transient negative ion. Work until recently has mainly concentrated on gas phase/isolated molecules. However, biological radiation damage occurs in a condensed environment where all molecules with a biological function are surrounded other particles, mainly by water.

Small clusters are being investigated to understand the effect of hydration on electron induced molecular processes.

Pyridine-$(H_2O)_n$





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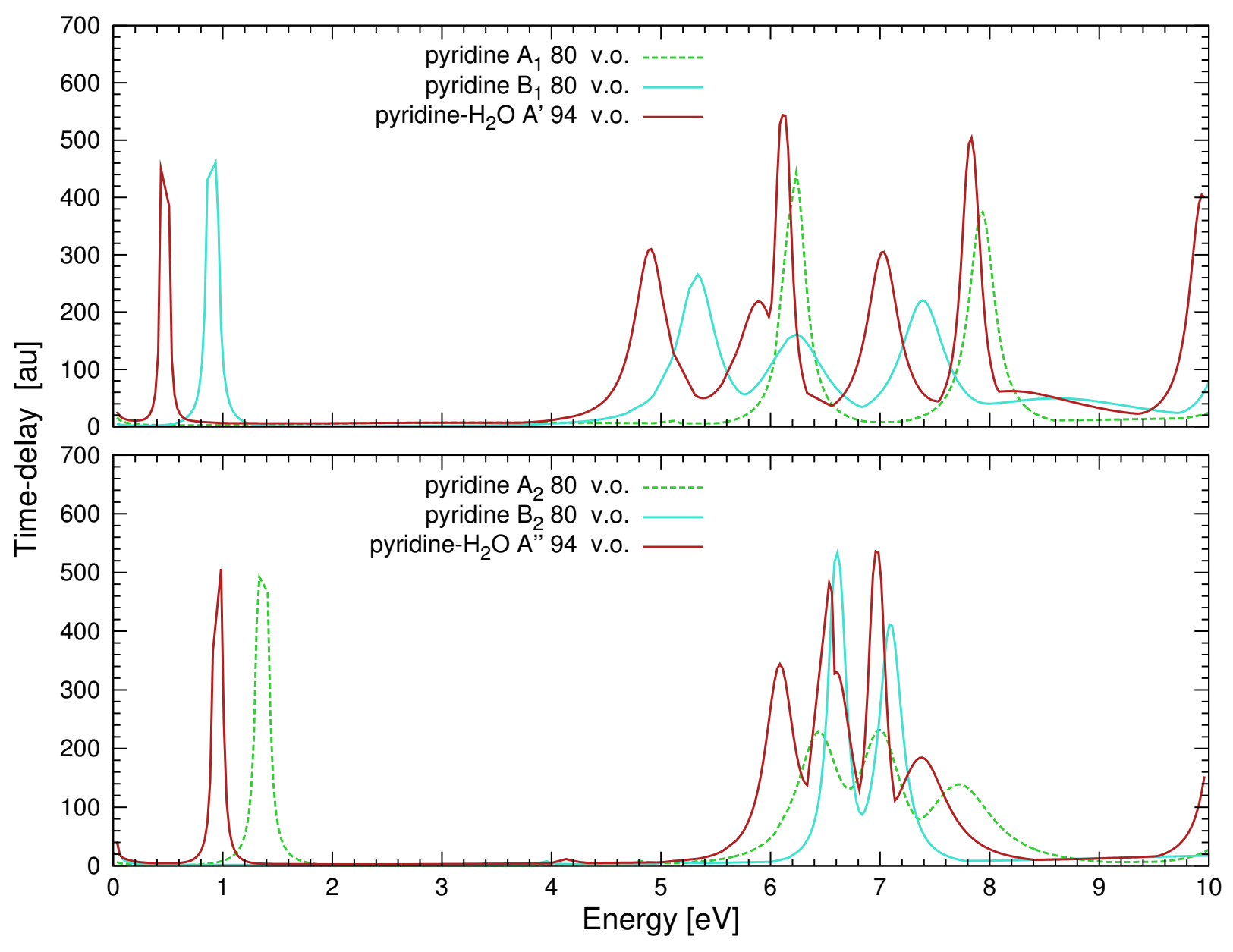
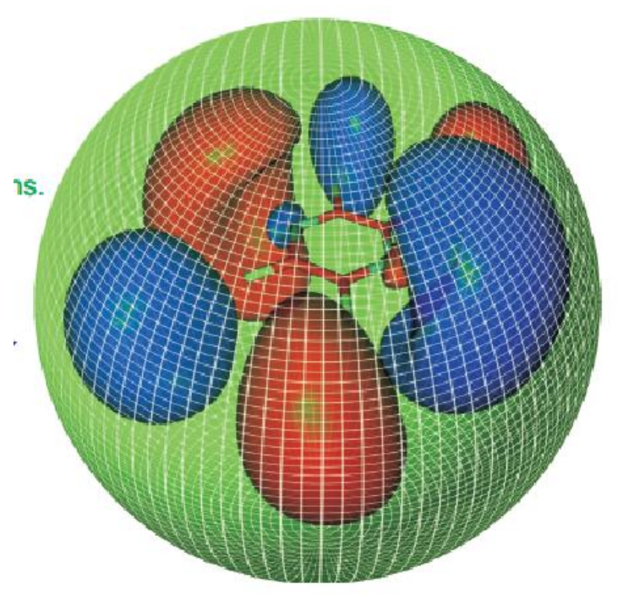


CC

- Direct effects stronger than (destabilizing) indirect effects
- **Stabilization** of shape resonances in all Pyridine-$(H_2O)_n$ clusters.
- Size of shift linked to dipole moment of cluster and connected with energy of orbital to which the electron binds
- Lowest shape resonance is more stabilized than second one; explained by orbital density
- Core-excited resonances are all stabilized

$1\pi^*$ and $2\pi^*$ orbitals of pyridine.

Calculations



We have used the R-matrix method [3] as implemented in the UKRmol+ suite [4].
The method is based on the separation of space into an inner and an outer region, divided by a sphere of radius *a*. In the inner region, exchange and correlation are taken into account.
The R-matrix is built at the boundary between the two regions.
In the outer region, a set of coupled differential equations is solved, using the R-matrix as boundary condition. Matching its solutions to the asymptotic form of the radial wavefunction describing the free electron, K-matrices are obtained and, from them, the relevant observables [3].
The resonances are located investigating the largest eigenvalue of the time-delay:

$$\mathbf{Q}(E) = i\hbar \mathbf{S}\frac{d\mathbf{S}}{dE}$$

where the S-matrices are obtained from the R-matrix calculations.
All calculations have been performed using a cc-PVDZ basis. Unless otherwise stated, the calculations are performed at the Static-Exchange (SE) level with partial waves l <7.

References

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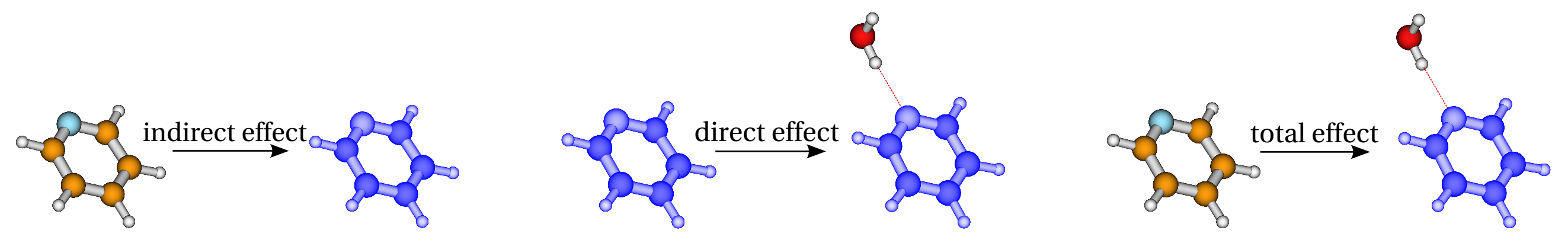
[4] http://ccpforge.cse.rl.ac.uk/gf/project/ukrmol-in/, /ukrmol-out/
[5] T. C. Freitas *et al* 2013 *J. Chem. Phys.* **138** 174307
[6] M. Smyth, J. Kohanoff, and I. Fabrikant 2014 *J. Chem. Phys.* **140** 184313
[7] J. Kočišek, A. Pysanenko, M. Fárník, and J. Fedor 2016 *J. Phys. Chem. Lett.* **7** 3401

Discussion and Conclusions

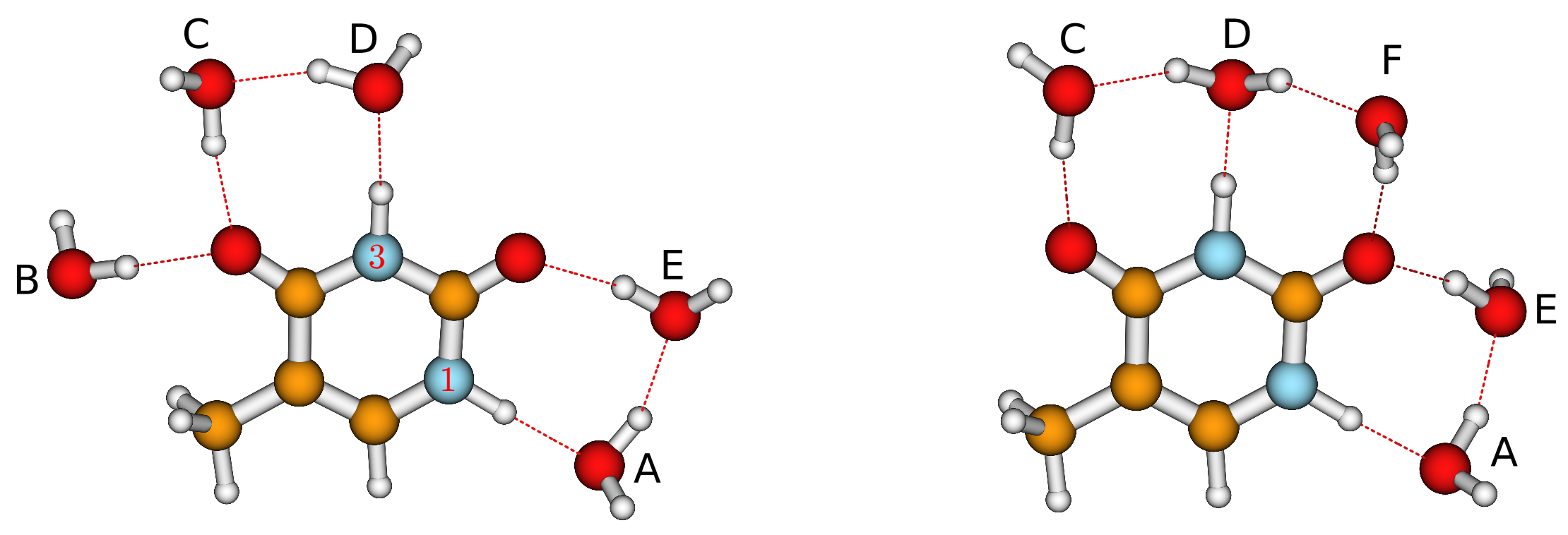
Direct and indirect effects



'Natural' colours symbolise molecule in its isolated, ground state, equilibrium geometry; the blue colour indicates molecule in the optimized geometry of the cluster.

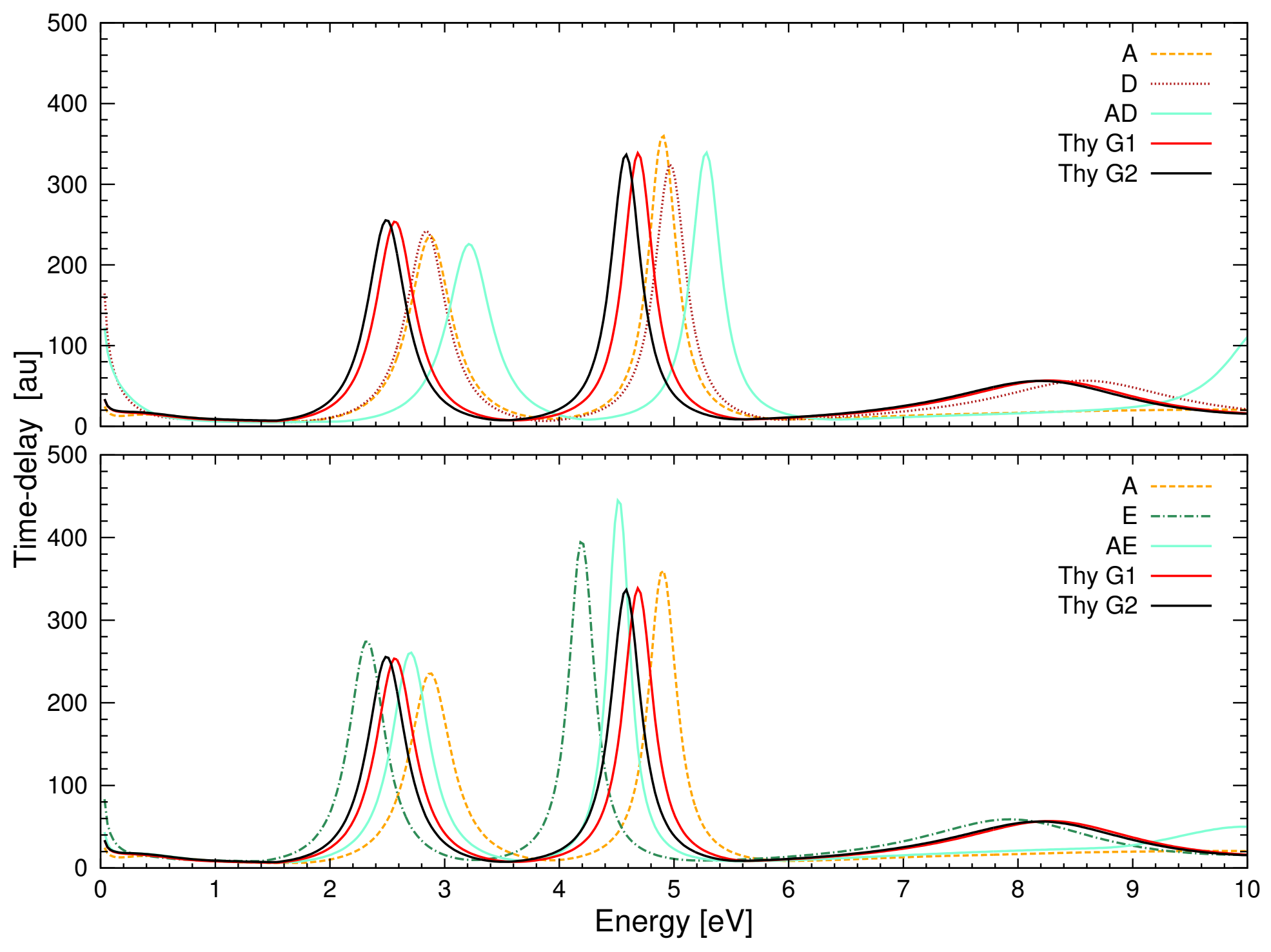
- Microhydration effects can be understood in terms of an indirect (change to the molecule's geometry) and direct (actual effect of the hydrogen-bonding) contribution
- Calculations confirm the findings of Freitas *et al.*[5]:
  - water acting as hydrogen donor stabilizes resonance, water acting as acceptor destablizes it
  - effect is approximately additive
- Effect of each H_2O molecule depends weakly on the binding site
- Effect is different for different resonances in the system
- Full effect of polarization still needs to be understood

Thymine-$(H_2O)_n$



ABCDE geometry from *Smyth et al.* [6]; ACDEF geometry

Thy-$(H_2O)_n$

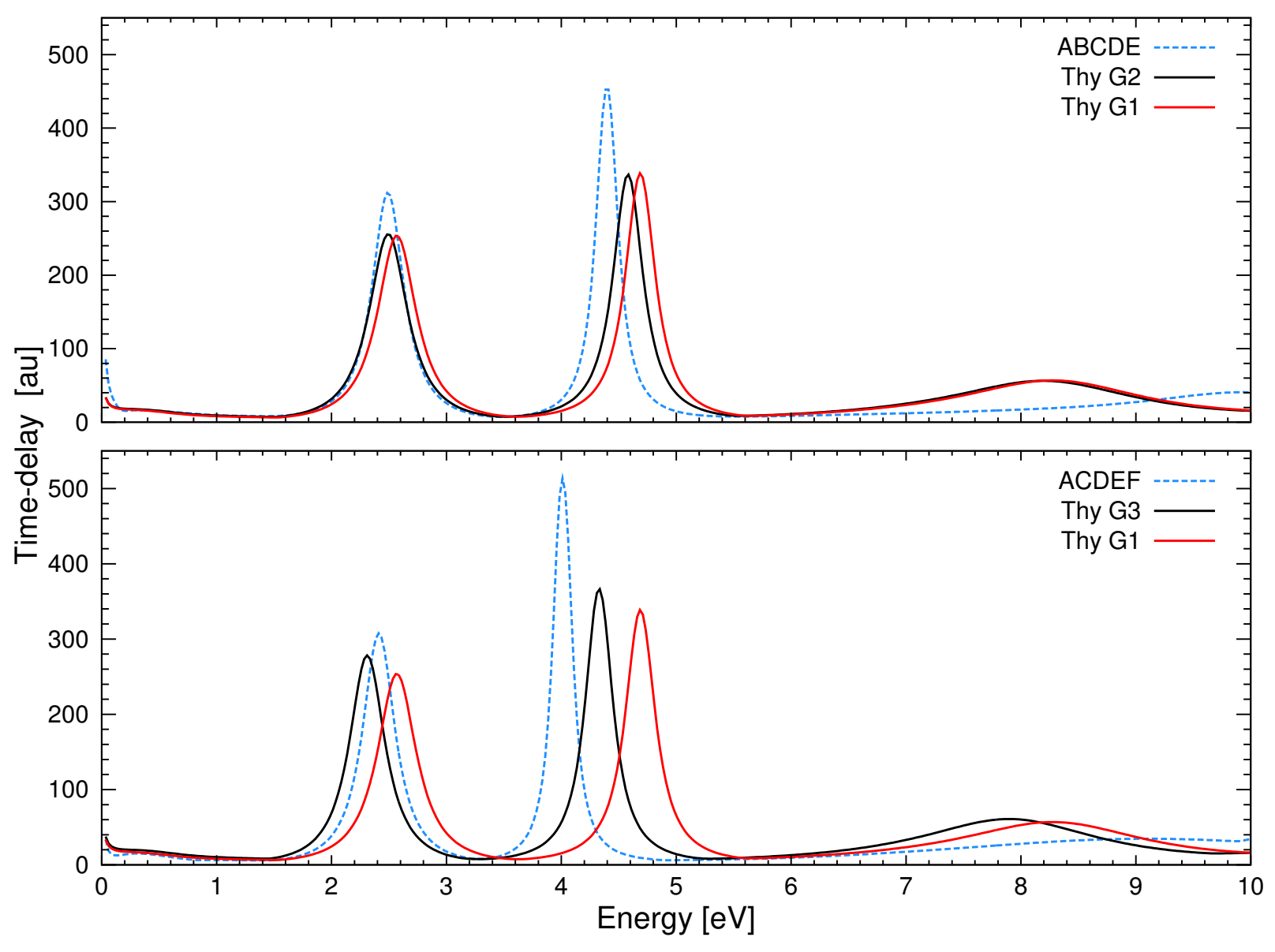


- Effect of additional waters is approximately additive
- Indirect effect is small and similar for all clusters
- Effect is different for different resonances
- For some clusters we see destabilizations.

Letters (A, B, AE...) indicate attachment position of water molecule. Thy G1: thymine in its equilibrium geometry. Thy G2 and Thy G3, thymine in the geometry it has in the ABCDE and ACDEF clusters respectively.

Thy-$(H_2O)_5$

- DEA calculations [6] based on resonance stabilization predict an increase in H loss for Thy-$(H_2O)_5$
- Experiments for microhydrated uracil /thymine [7] show complete quenching of H loss
- Size of shift of two lowest π^* resonances is similar to the change in the HF orbital energies
- The σ^* orbitals that should describe the σ^* resonances involved in H loss change significantly: they no longer describe electronic density around the N_1 or N_3 bonds
- The quenching observed experimentally could be linked to significant modification of the σ^* rather than π^* resonances



- Resonances stabilized for both clusters but by different amounts
- Larget resonances shift < 0.7 eV
- Indirect effect different for different clusters but similar for both resonances
- Direct effect destabilizes first resonances and stabilizes second
- Both direct and indirect effects are stronger in ACDEF cluster than in ABCDE

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