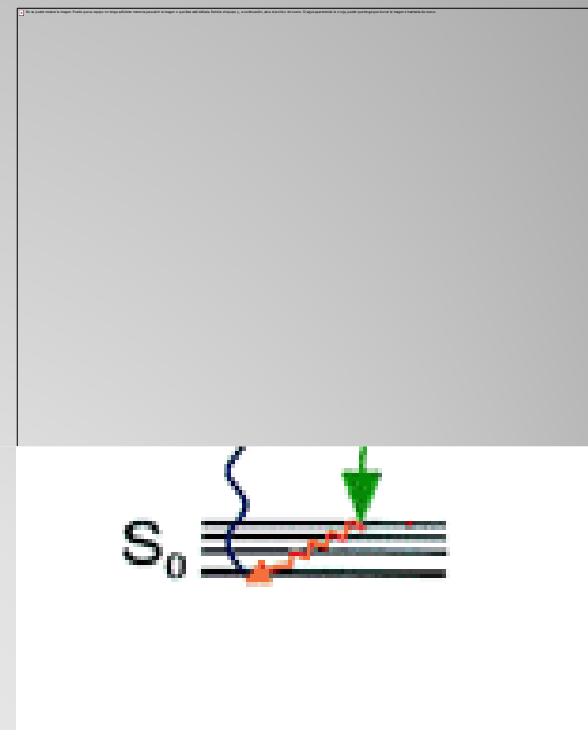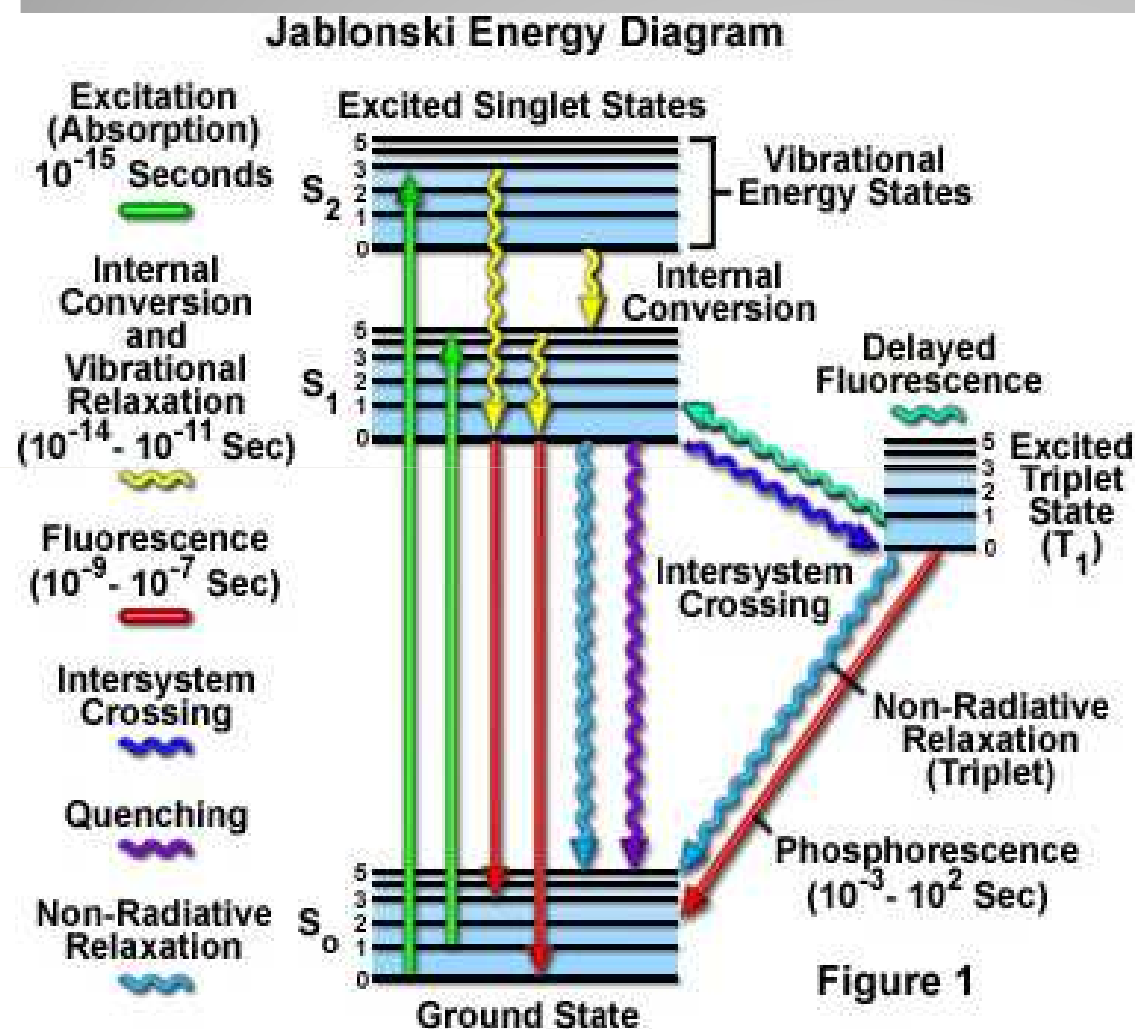# Computational Design of ESIPT Molecules and Some Related Photoelectronic Problems

Snezhana M. Bakalova, Jose Kaneti, Luis M. Frutos, Obis D. Castaño
(IOCCP, Sofia, Bulgaria; UAH, Alcala de Henares, Madrid, Spain)

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Varna, July 12 – 15, 2010

Luminescence and computational cycles

A simplified fluorescence cycle

19.7.2010 г.   2
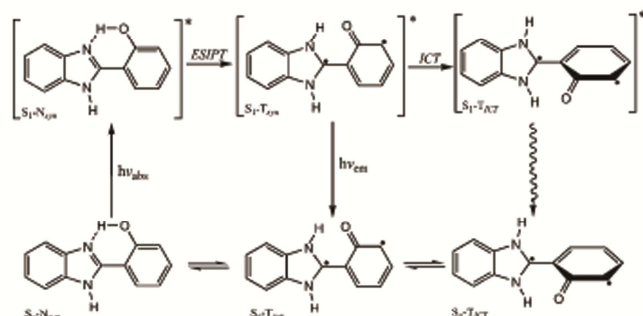
Figure 1. Structures of various HBI species in the ESIPT and ICT processes. From the TD-DFT results, the *o*-quinoid structures are presented for the tautomeric and ICT forms. The structures displayed here are only one of each of the Lewis structures, which do not present detailed structural and bonding characteristics. For details of the geometrical parameters and bonding, please see the main text.

Figure 9. PESs of the S_1 state of HBI in (a) ethanol and (b) cyclohexane as a function of the $N_6-C_1-C_2-C_3$ torsion angle and the pyramidalization angle centered at the C_1 atom. The energy of the S_1-T_{syn} state was chosen as the reference. The MEP from the S_1-T_{syn} state to the S_1-T_{ICT-i} state is depicted in red arrows; the MEP from the S_1-T_{syn} state to the S_1-T_{ICT-2} state is depicted in yellow arrows.

ESIPT (excited state internal proton transfer) is a process contributing to the visible dye brightness, and is normally manifested via large Stokes shifts, i.e. the emission is red-shifted with respect to absorption by 10^4 cm^{-1} and more, which has successfully been exploited in sensors, laser dyes, and nonlinear optoelectronic materials.

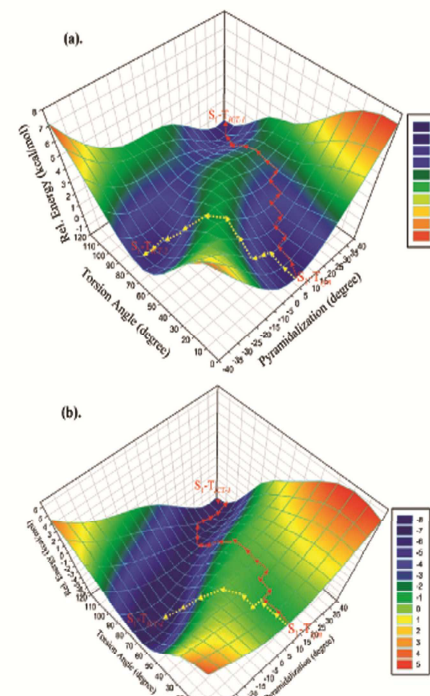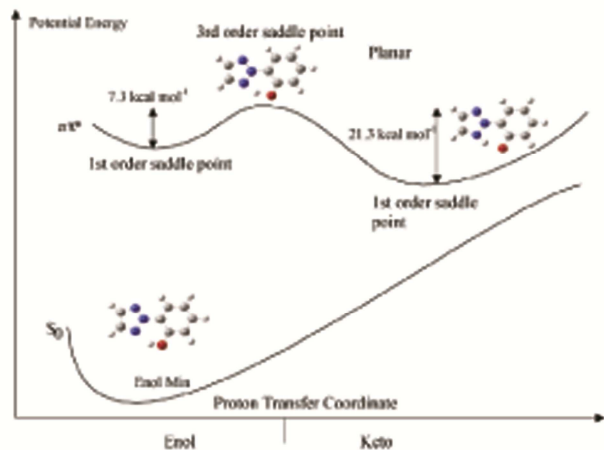# Photoprocesses in molecular excited electronic states

Figure 1. Potential energy profiles for ground and ππ* states with the geometry constrained to be planar. Geometries given in Supporting Information (Energies relative to 3rd order saddle-point).
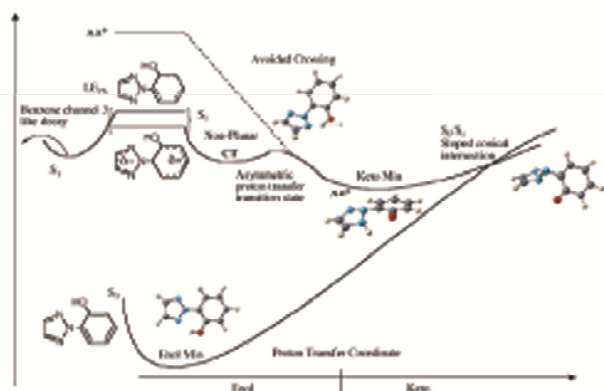

Figure 2. Schematic representation of the ground and ππ* excited-state potential energy surfaces along the proton-transfer coordinate in the full space of nuclear coordinates. The reaction pathway involves an intertwining of the three excited states and the ground state. Geometries given in Table 4.

M. Robb *et al., J. Am. Chem. Soc.* **2004**, *126*, 2912-2922, have shown that ESIPT is often accompanied by inter-system crossings, known to occur at intersections of potential energy surfaces of two or more excited molecular electronic states of the same, or different spin symmetry. These conical intersections not only result in protothropic tautomerism, but also bring significant molecular deformations in the 3D-space.
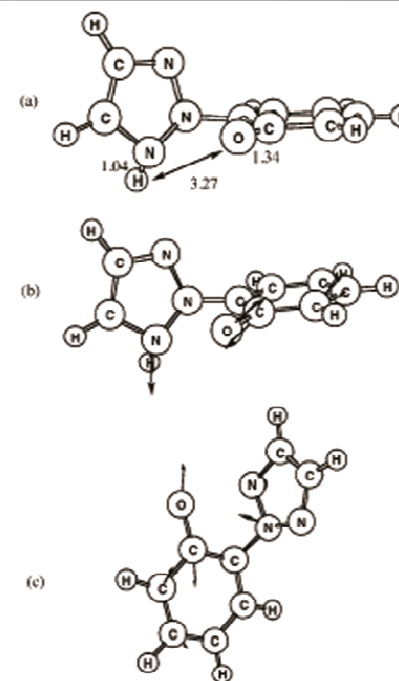

Figure 6. S_0/S_1 (ππ*) conical intersection responsible for ultrafast deactivation of excited-state species. (a) Optimized with CAS(10,8)/6-31G*. (b) Derivative coupling vector. (c) Gradient difference vector. (All bond lengths in Ångstroms).
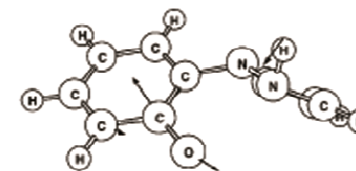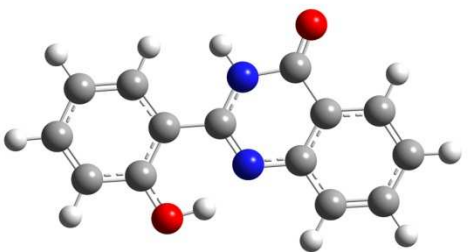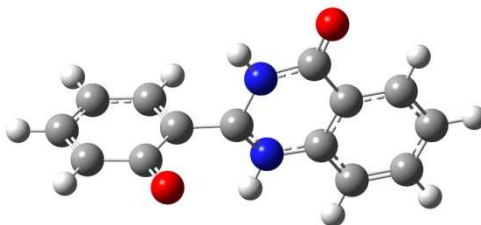

Figure 7. Gradient at optimized IRD on S_0 surface. This corresponds to the ground-state relaxation channel and involves CO and OH stretching, leading to the regeneration of the enol form. The gradient of the IRD on S_1 is very similar which is indicative of a sloped-conical intersection topology.
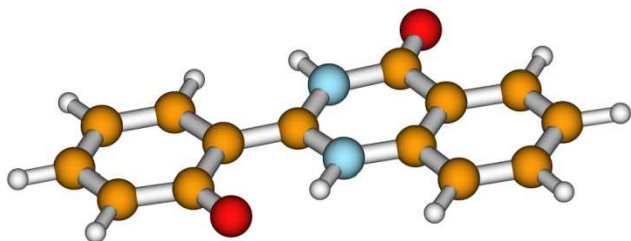
Photoprocesses in molecular excited electronic states

S0

S1

```
S0 : -794.71992
T1 : -794.63212
T2 : -794.58837  conical
S1 : -794.58836  intersection
CAS SCF(10,10)/6-31G*
```

The planar "quinoid" form is not a minimum on either the S0, or the S1 DFT surface. On the S1 surface, however, the "quinoid" form shows a perpendicular minimum… CAS finds a planar quinoid structure, which is a S1 – T2 conical intersection.

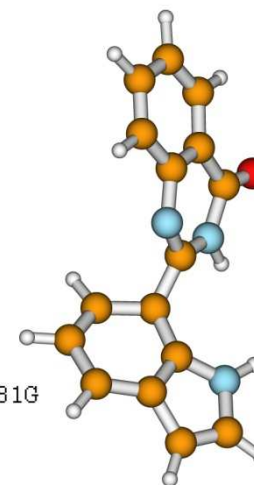# 2-(2'-Hydroxyphenyl)-quinazolinone CASSCF & MP2 CASSCF

S0

S1-T1 conical intersection
`MP2 CAS(10,10)/6-31G`

Sx intersection seam
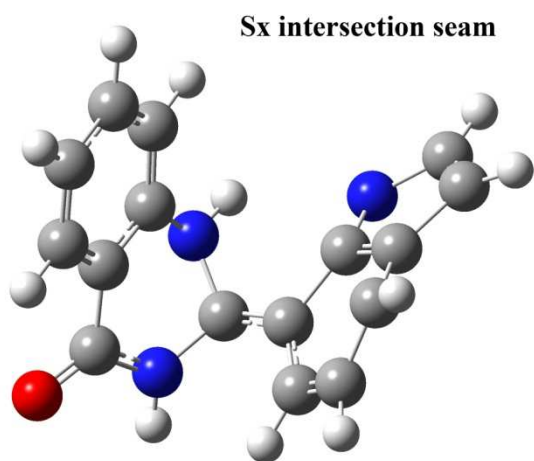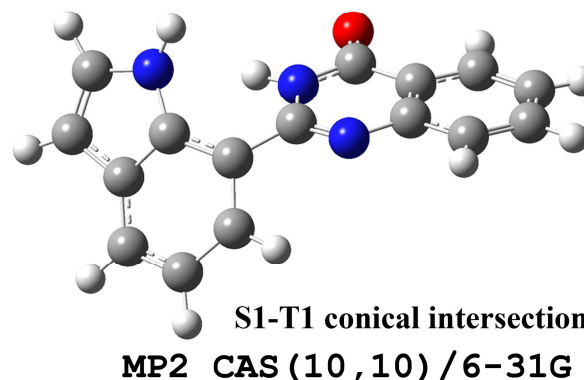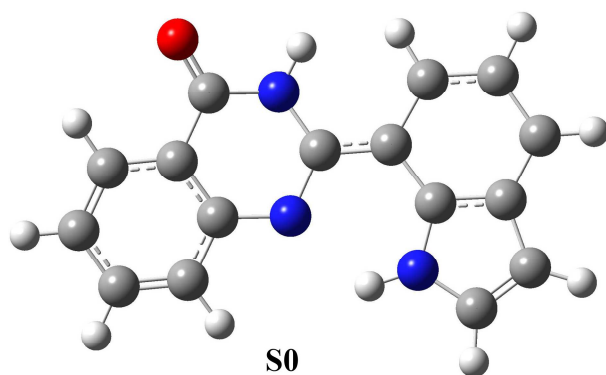
The molecule has a stable S0 "quinoid" tautomer, DFT.

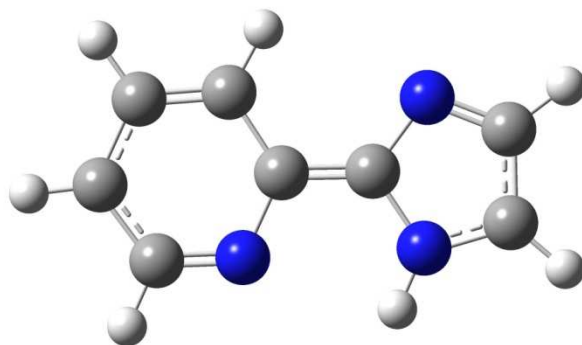**However, CASSCF identifies it as a S1 – T1 conical intersection point.**

```
S0: -850.23663
T1: -850.14903
T2: -850.10735
S1: -850.10706
```
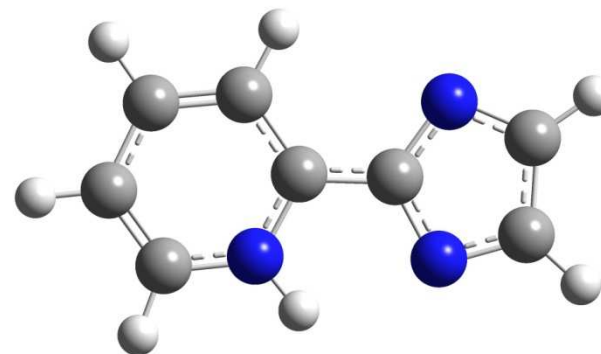
conical intersection

`CAS(10,10)/6-31G`

2-(7'-indolyl)-quinazolinone – CASSCF & MP2 CASSCF

S0 : -472.88972
T1 : 3.03 eV
S1 : 4.44 eV, f=0.34 absorption
opt S1 : 3.71 eV, f=0.13 emission
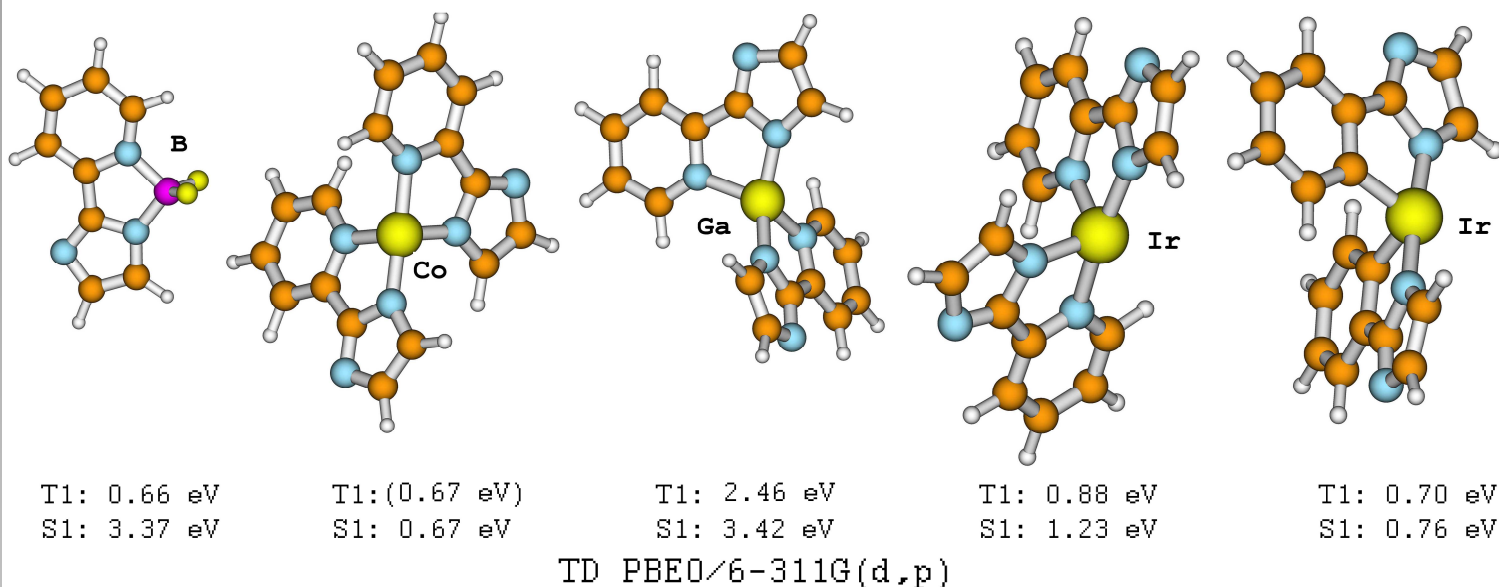   S1 : -472.87467

S0 : -472.86410 (ΔE ~ 15 kcal/mol)
T1 :
S1 : 2.08 eV, f=0.04 absorption
opt S1 : 1.90 eV, f=0.03 emission
    S1 : -472.84352 (DE > 18 kcal/mol)

(TD) pbe1pbe/6-311G(d,p)

Both planar aromatic and "quinoid" forms are minima on the S0 DFT-potential energy surface. At the CAS SCF(10,10)/6-31G* surface, the quinoid form is again a S1 – T2 conical intersection.

2-(2'imidazolyl)-pyridine – CASSCF & MP2 CASSCF

T1: 0.66 eV
S1: 3.37 eV

T1: (0.67 eV)
S1: 0.67 eV

T1: 2.46 eV
S1: 3.42 eV

T1: 0.88 eV
S1: 1.23 eV

T1: 0.70 eV
S1: 0.76 eV

TD PBE0/6-311G(d,p)

Lamansky, et al. *J. Am. Chem. Soc.,* **2001***, 123, 4304-4312*
Holmes, et al. *Chem. Commun.,* **2005***, 4708–4710*
Chang, et al. *Angew. Chem. Int. Ed.* **2008**, *47, 4542 –4545*
Shi, et al. *J. Phys. Chem. A* **2010,** *114,* 6559–6564, etc... etc...

TTA – IUPAC definition: two triplet excited species may produce (upon collision) an excited singlet species, and a ground state singlet one. This may often result in delayed luminescence – photon upconversion.

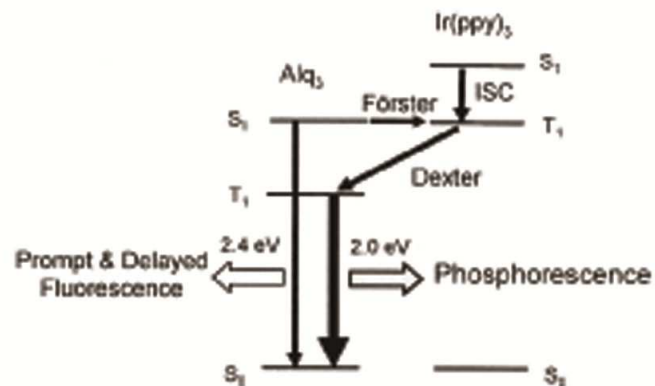# Avoiding 3D-intersystem crossings...

FIG. 3. Schematic energy level alignment of singlet-excited state (S_1), triplet-excited states (T_1), and singlet-ground states (S_0) in Alq$_3$ and Ir(ppy)$_3$, and the energy-transfer and light-emission processes.

Figure 1. Energetic scheme of a TTA supported up-conversion process

I. Tanaka, S. Tokito, *J. Appl. Phys.* 2005, *97*, 113532

S. Balushev, et al., *Nano Lett.* 2005, 5, 2482

Photon upconversion energy diagrams

- **Acknowledgments**:

- Project CTQ2009-07120, Ministerio de Educacion y Ciencia, España

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