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Low-lying electronic excited states of dopamine

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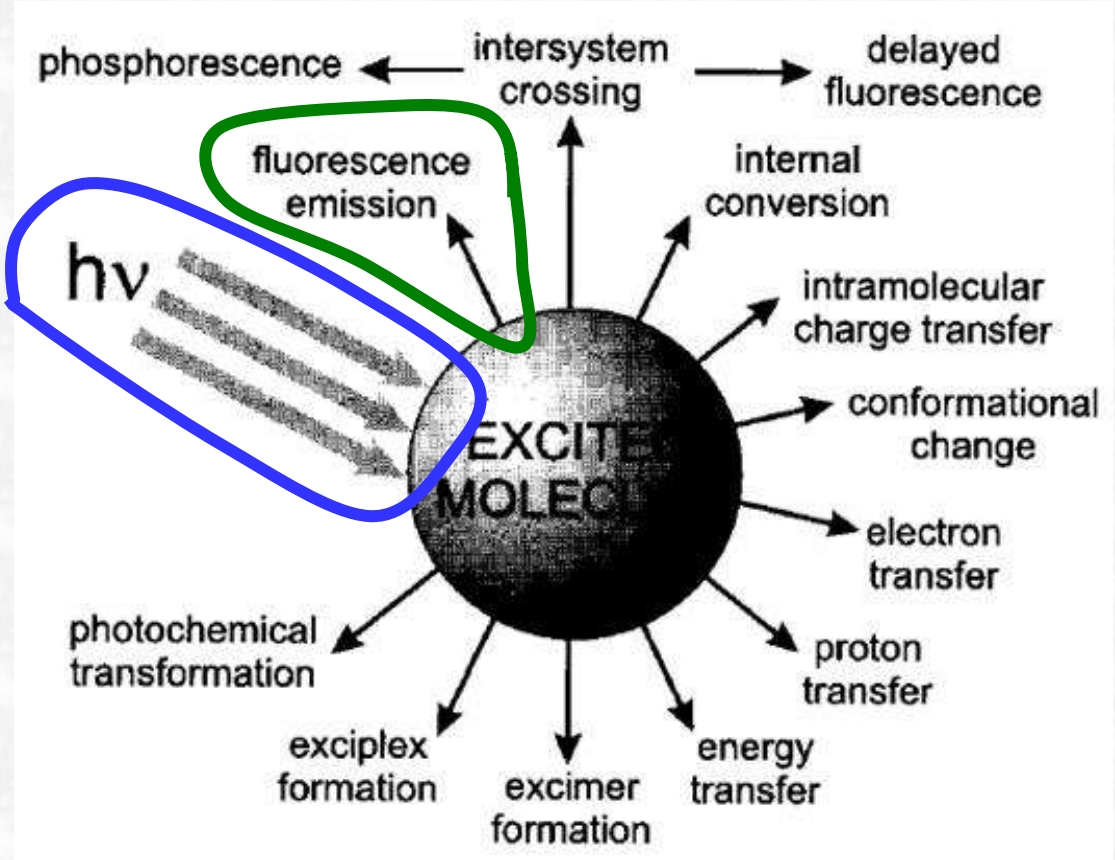
Outline

- General aspects of the theoretical photochemistry
- Theoretical and Experimental techniques
- Dopamine's low-lying excited states
- Dopamine's excited state deactivation
- Dopamine o-quinone's low-lying excited states

Photochemical processes in molecular systems:



Radiative and Non-Radiative Rates:

$$QY = \frac{\#\text{ of photons emitted}}{\#\text{ of photons absorbed}}$$

$$Q_F = \frac{k_r}{k_r + \sum k_{nr}}$$

Rate constants [s^{-1}]:

k_r = radiative (ex. fluorescence, phosphorescence)

k_{chem} = photochemistry

k_{dec} = decomposition

k_{ET} = energy transfer

k_{et} = electron transfer

k_{tict} = proton transfer

k_{tict} = twisted-intramolecular charge transfer

k_{ic} = internal conversion

k_{isc} = intersystem crossing

Radiative decay (Fluorescence):

$$\textbf{Excited state life-time} = \frac{\mathbf{1}}{\textbf{transition rate}} \; [\boldsymbol{S}]$$

Fluorescence → spontaneous transition from **(S_1, v_i)** to **(S_0, v_j)**

- vibrational effects could be important !!!

Transition dipole moment:

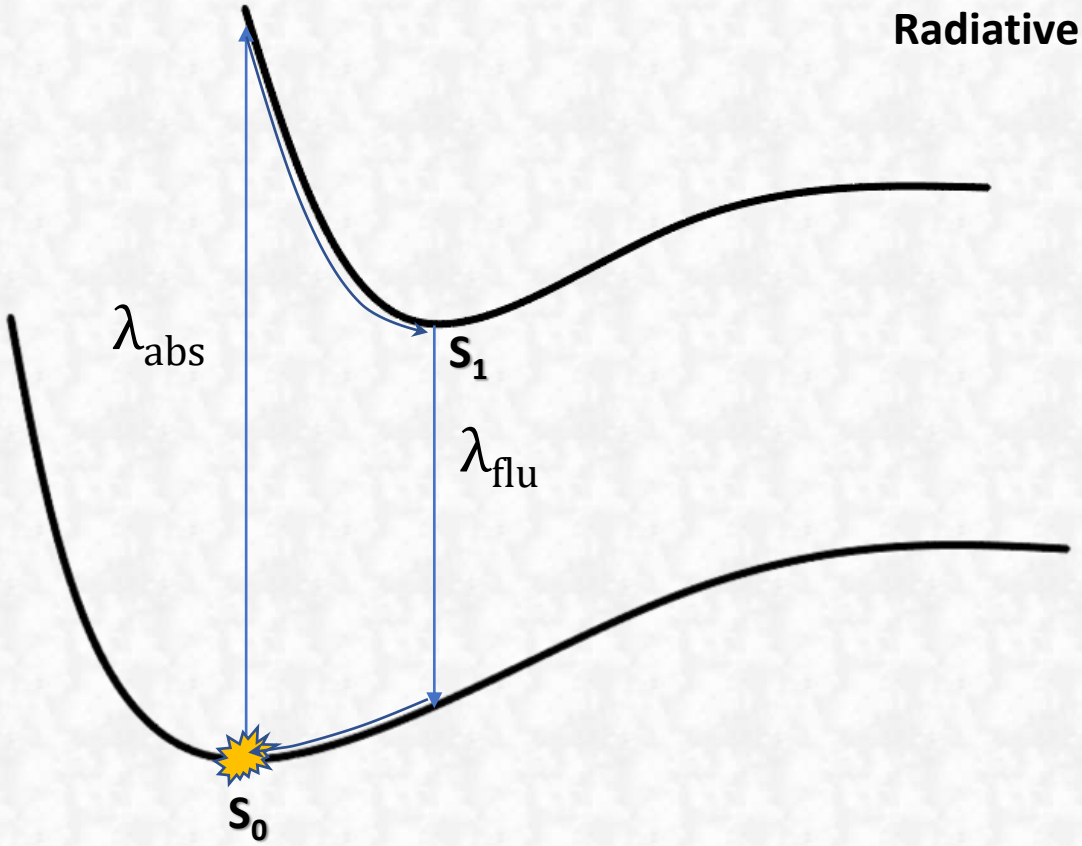
$$\vec{\mu}(\mathbf{Q}) = \vec{\mu}_0 + \sum_i \left.\frac{\partial \vec{\mu}}{\partial Q_i}\right|_{Q=0} + \cdots$$

Frank-Condon (FC) approx.

Herzberg-Teller (HT) approx.

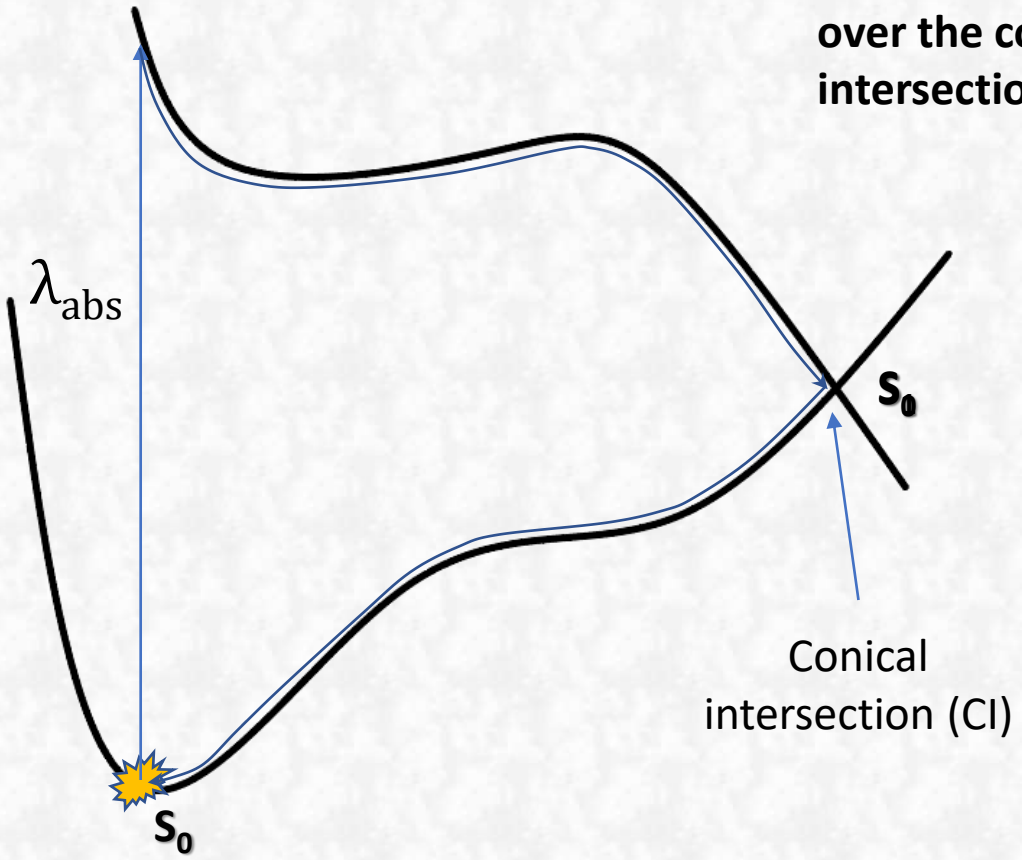
Q_i – vibrational normal mode displacements

Radiative relaxation:



Time scale: ≈ 100 ps – 100 ns

Nonradiative relaxation over the conical intersection points



Time scale ≈ 100 fs – 100 ps

Theoretical studies are based on:

1. Ground state geometry optimization (S_0)
2. Vibrational analysis of the ground state (S_0)
3. First excited state geometry optimization (S_1)
4. Vibrational analysis of the first excited electronic state (S_1)

ORCA QC package
ωB97X-D3 DFT XC-func.
ma-def2-TZVPP
Water as solvent

Transition rate:

Absorption ($S_0 \rightarrow S_1$), Fluorescence ($S_1 \rightarrow S_0$)

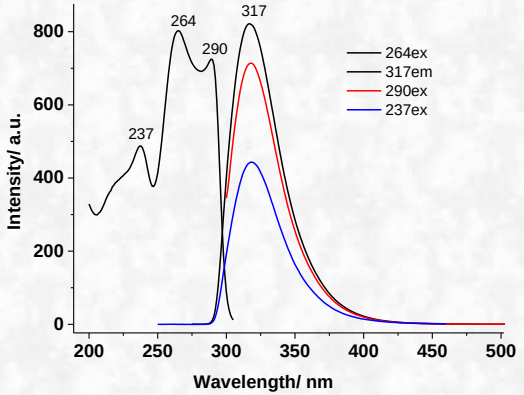
$$k(\omega)_{if} = \frac{4\omega^3 n^2}{3\hbar c^3} \left|\langle \Psi_{el-vib,i} | \hat{\mu} | \Psi_{el-vib,f} \rangle\right|^2 \delta\left(E_i - E_f \pm \hbar\omega\right)$$

where ħω is the photon energy (absorbed or emitted)

Experimental studies are based on:

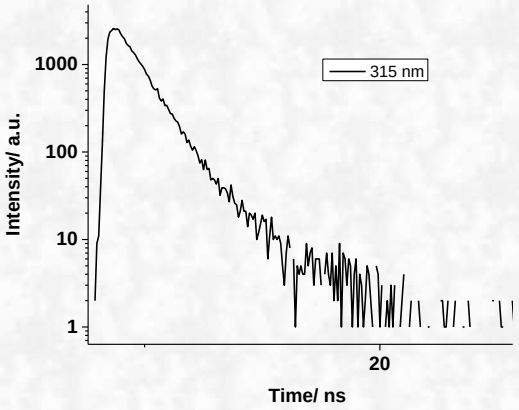
A. UV-Vis Spectroscopy measurements

Absorption and
Fluorescence spectra

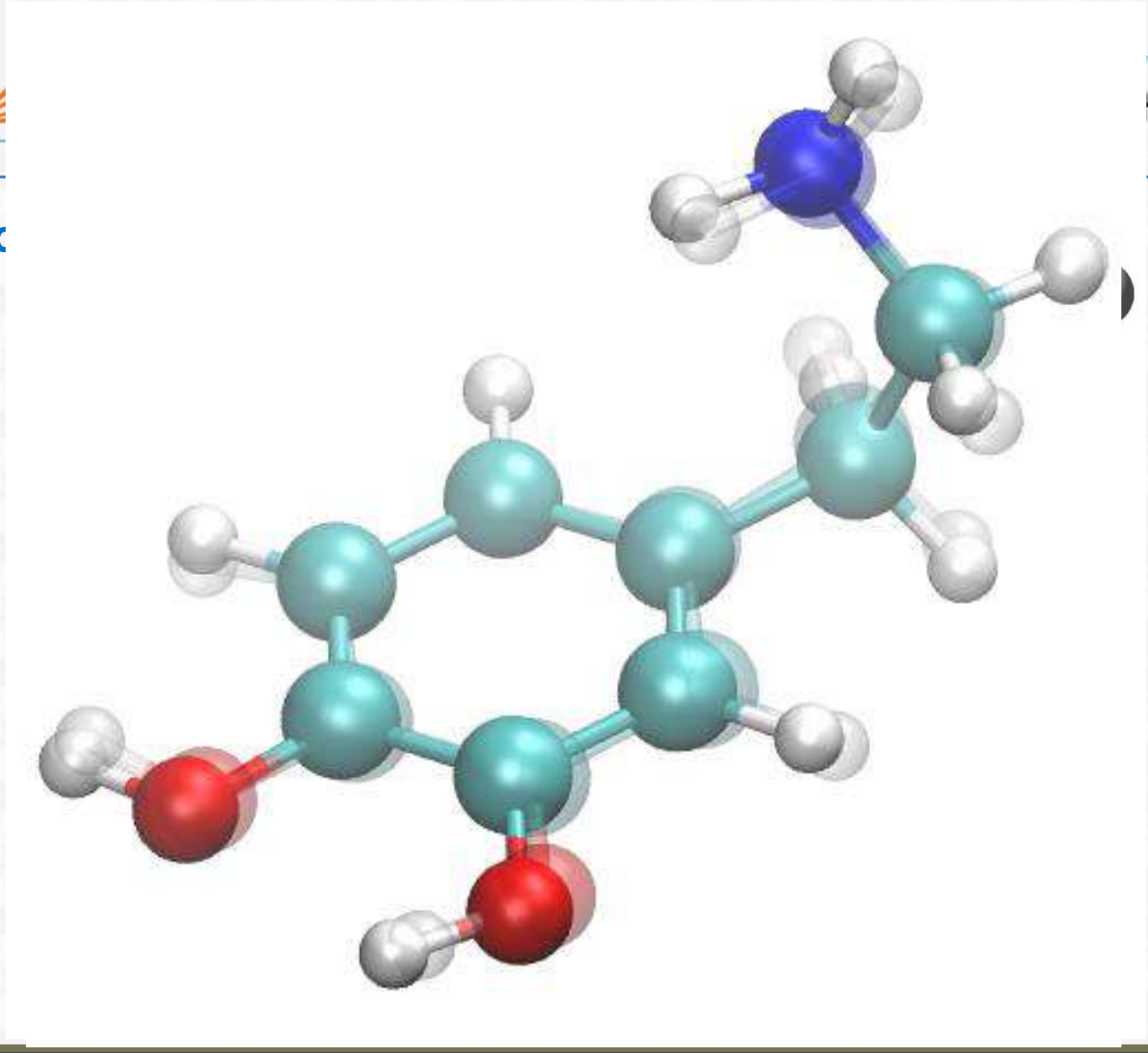


B. Time-Resolved Fluorescence
Spectroscopy measurements

Exited state life-time and
rate constants

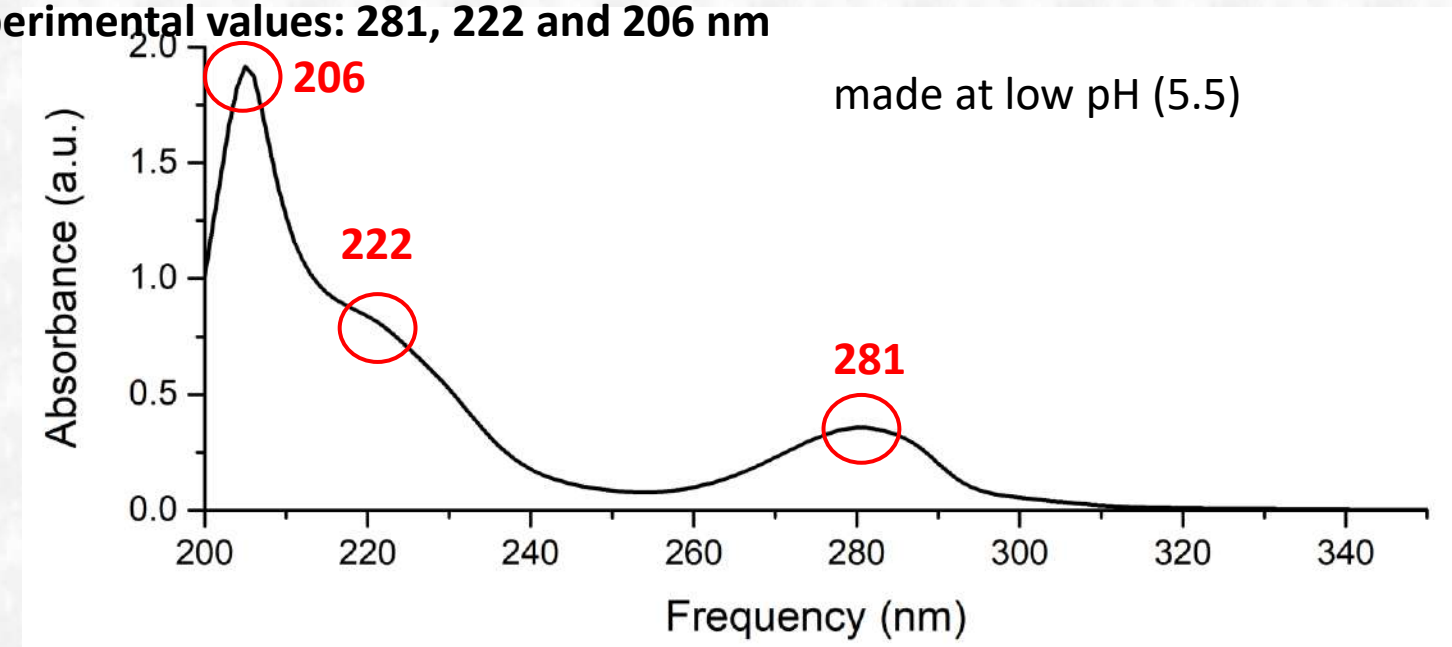


Do



UV Absorption spectra:

Experimental values: 281, 222 and 206 nm



UV Absorption spectra:

Experimental values: 281, 222 and 206 nm

Theoretical results:

ωB97X-D3/ma-def2-TZVPP/CPCM	**S_1: 240; S_2: 218 and S_3: 206 nm**
SCS-PBE-QIDH/ma-def2-TZVPP/CPCM	**S_1: 256; S_2: 224 and S_3: 208 nm**
STEOM-DLPNO-CCSD/ma-def2-TZVPP/CPCM	**S_1: 264; S_2: 226 and S_3: 204 nm**

Coupled-cluster (with singlet and doublet)

Fluorescence spectra:

0-0 energy difference: 318 nm

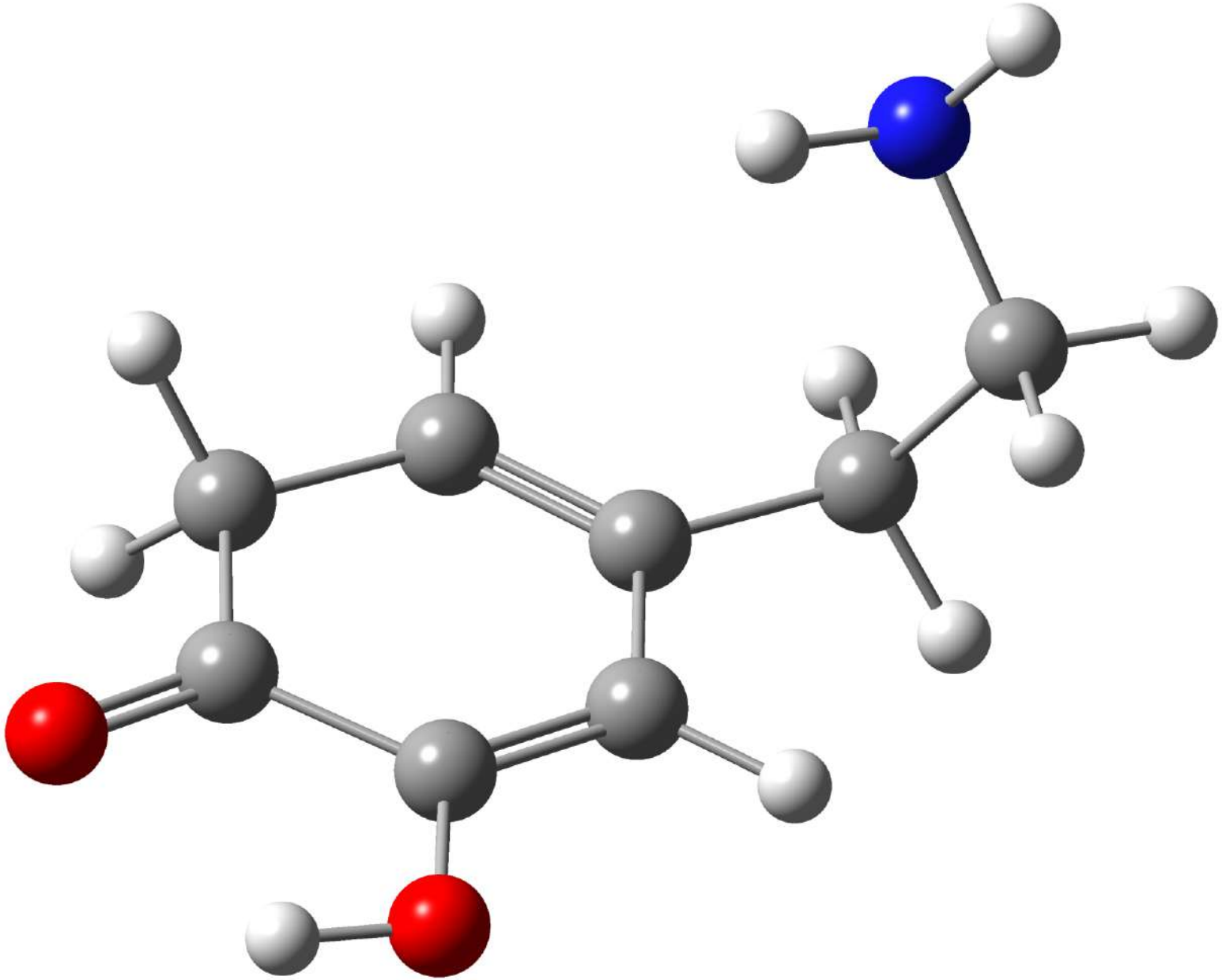
Experimental: 317 nm

The fluorescence life-time: 3.16 ns

Experimental: 0.95 ns

≈ 3 times faster

The deactivation process may not be 100% radiative



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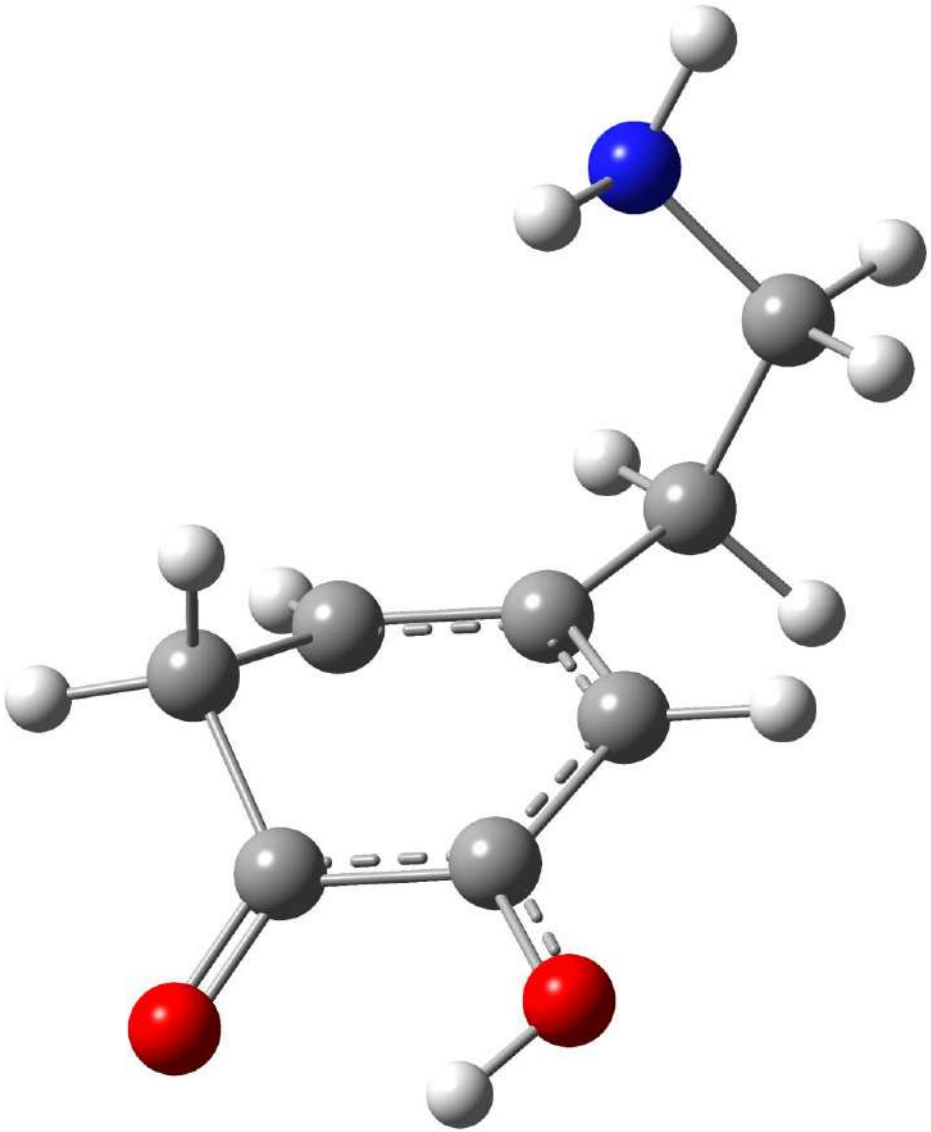
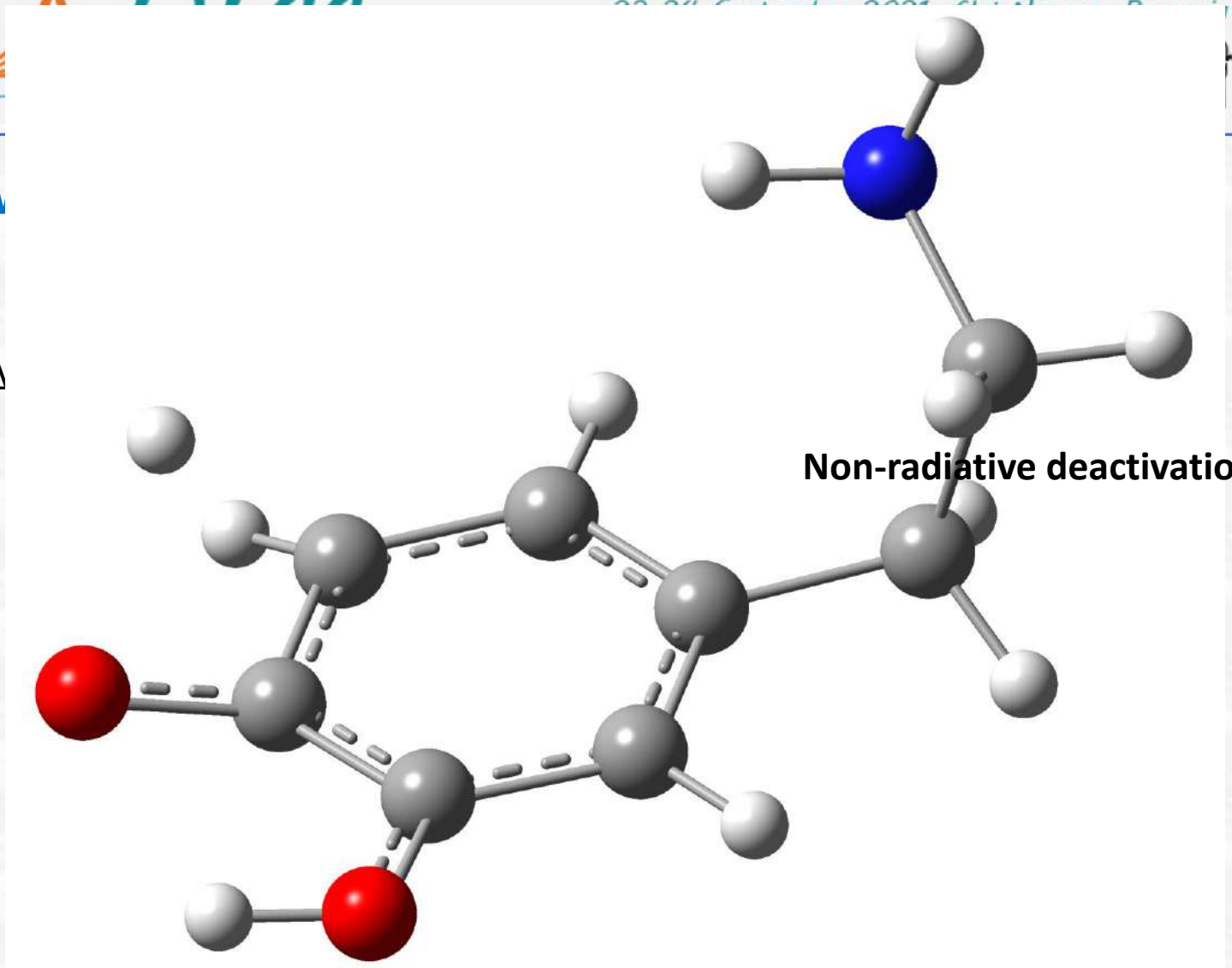
Enol ← ???:



to form

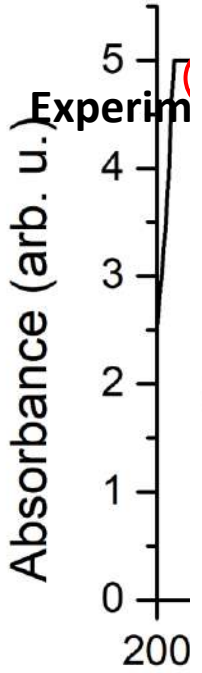
.0 kcal/mol

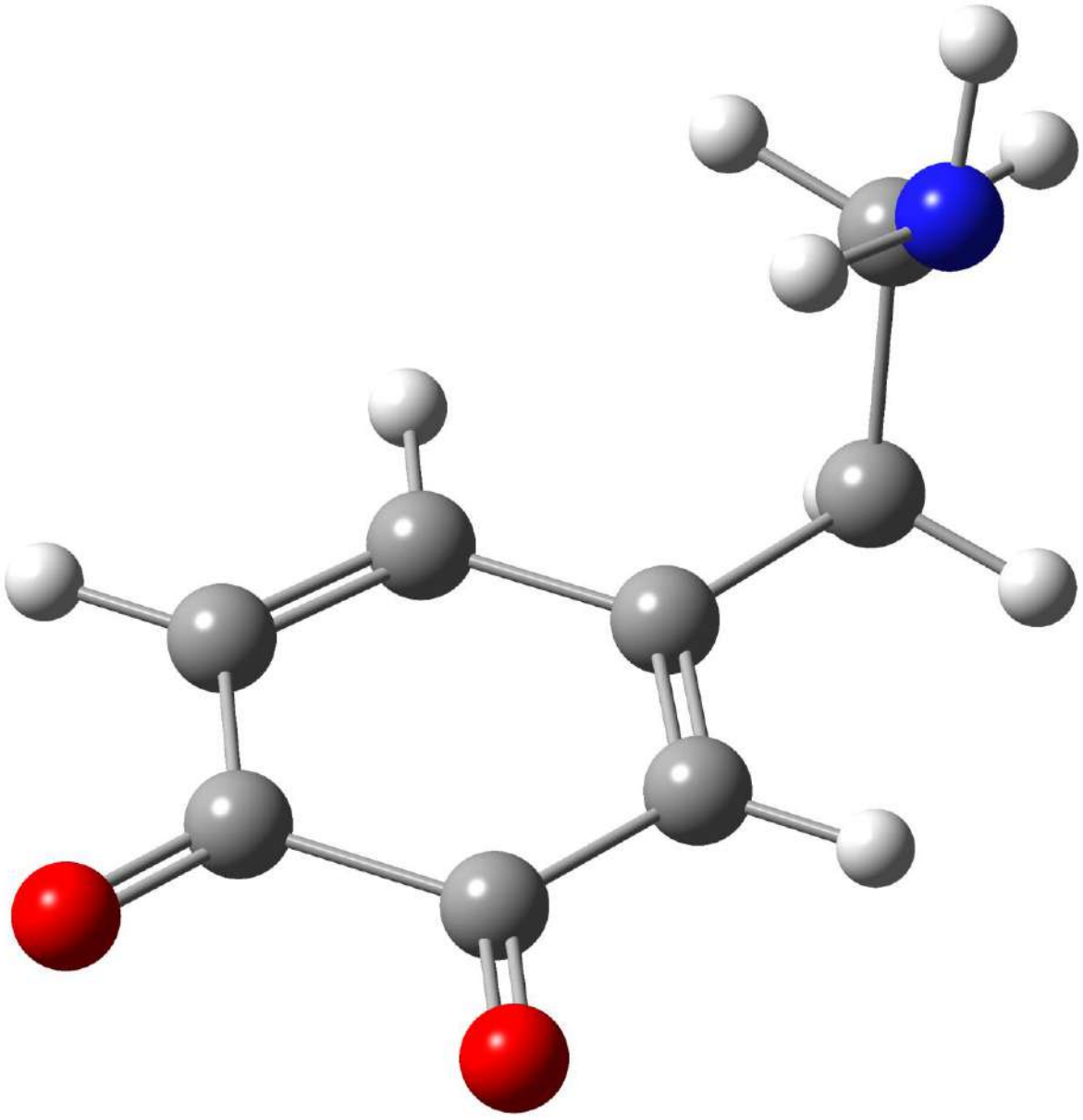
✓

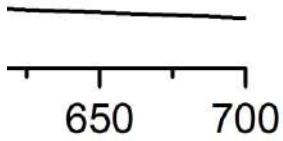

Non-radiative deactivation !!!

Experim

5.5) in
accase







UV Absorption spectra of dopamine o-quinone :

Experimental values: 470-475, 307, 291 and 210 nm

Theoretical results:

ωB97X-D3/ma-def2-TZVPP/CPCM	**S_1: 512; S_2: 366; S_3: 277 and S_4: 214 nm**
SCS-PBE-QIDH/ma-def2-TZVPP/CPCM	**S_1: 512; S_2: 367; S_3: 302 and S_4: 218 nm**
STEOM-DLPNO-CCSD/ma-def2-TZVPP /CPCM	**S_1: 581; S_2: 375; S_3: 248 and S_4: 213 nm**

Coupled-cluster (with singlet and doublet)

Fluorescence spectra:

0-0 energy difference: 543 nm

Experimental: ≈ 477 nm

The fluorescence life-time: 3.55 µs

Experimental: 4.89 ns

≈ 3 order of magnitude faster

The deactivation process might be strongly non-radiative !!!

Investigation of the deactivation mechanism is in progress.

Conclusions

- The photochemistry behaviour and the excitation deactivation mechanism of the dopamine were described in detail at DFT level of theory.
- The results for the vertical excitation energies, fluorescence band origin and excited state life-time of the dopamine match well with the experimental values.
- The dopamine's excited state deactivation mechanism shows strong radiative character.
- The dopamine o-quinone's excited state deactivation mechanism might shows strong non-radiative character (deactivation via internal conversion).

Thank you for your attention