Switching on H-Tunneling through Conformational Control

José P. L. Roque

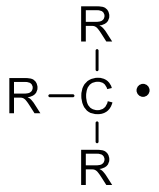
PRS Group Seminar

11 February 2022

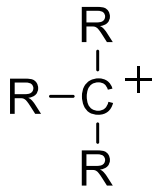
Coimbra - Portugal

Reactive Intermediates

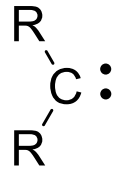
Radical



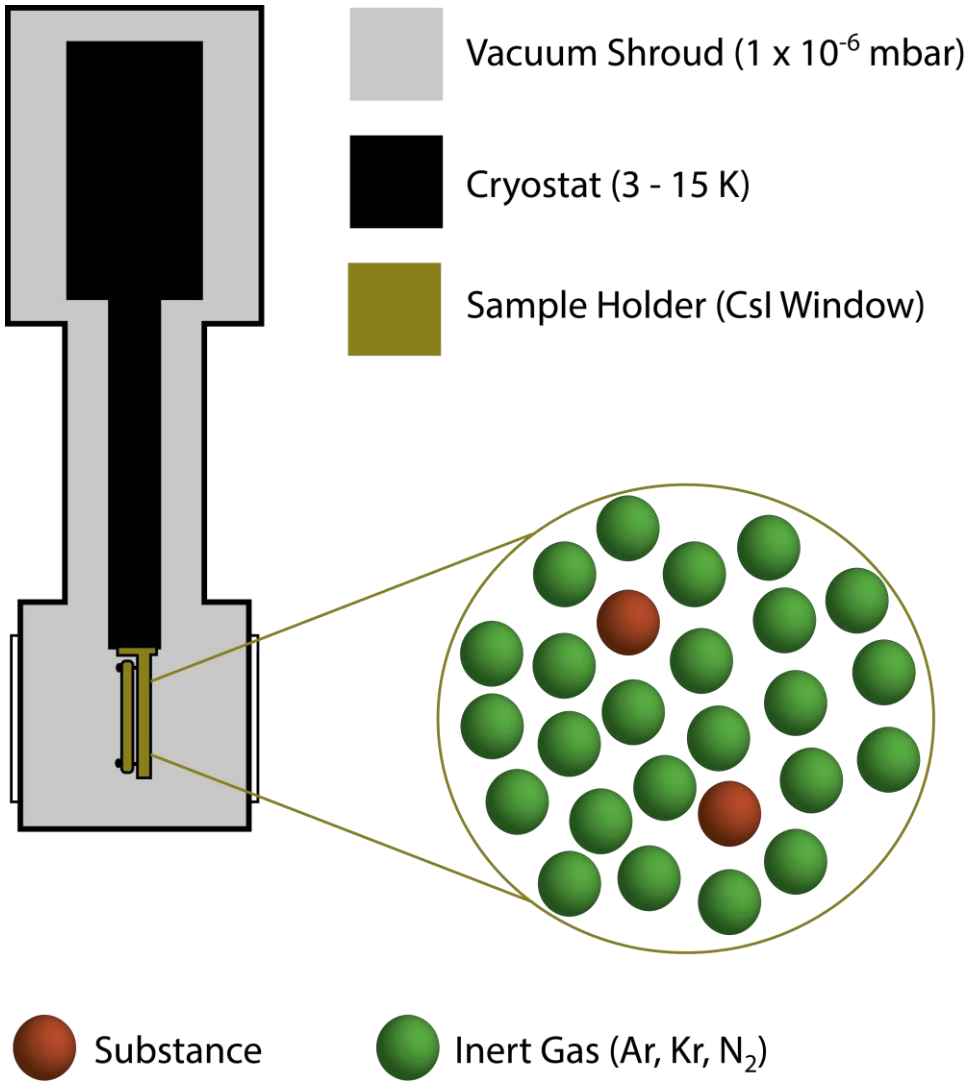
Carbocation



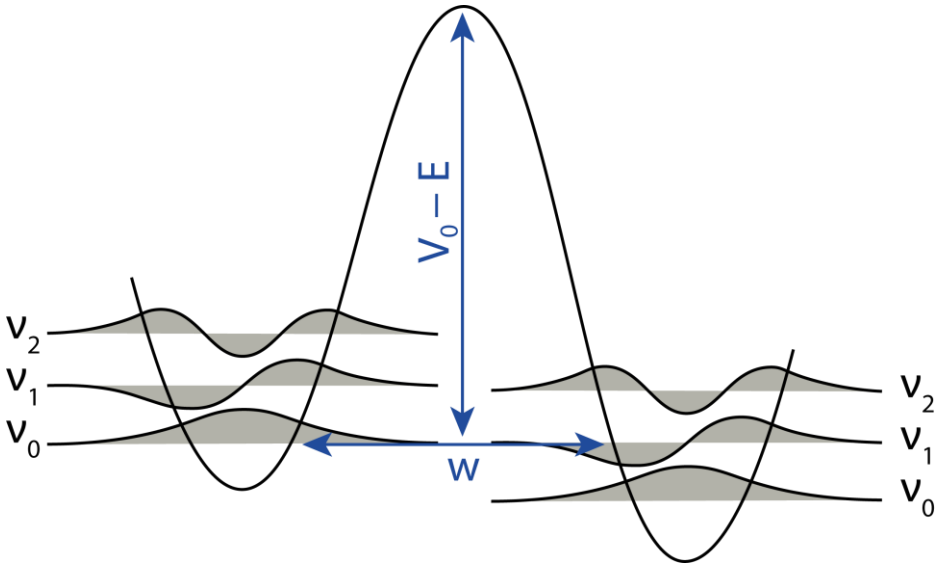
Carbene



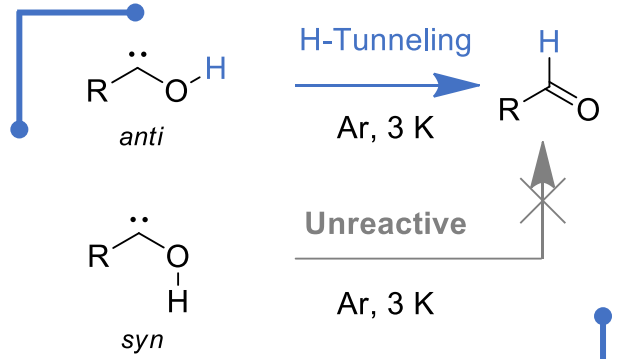
Nitrene



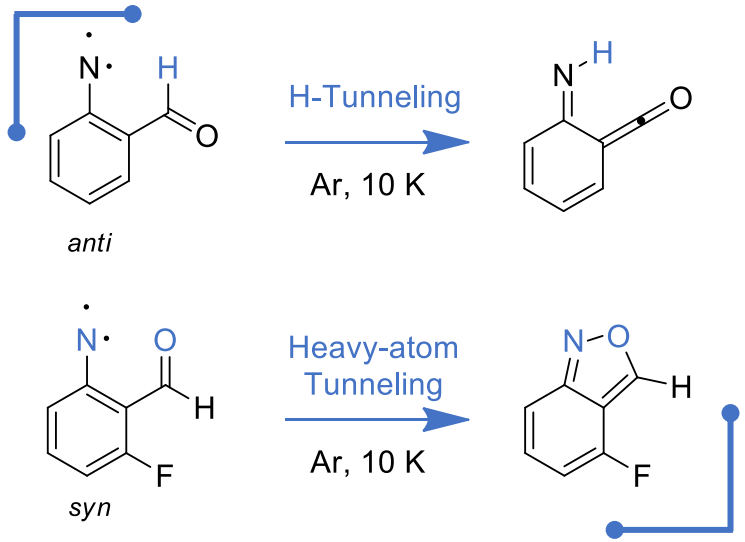
Quantum Tunneling



$$P(E) = \mathrm{e}\left(-\pi^2 w \sqrt{\frac{2m}{\mathrm{h}^2}(V_0 - E)}\right)$$

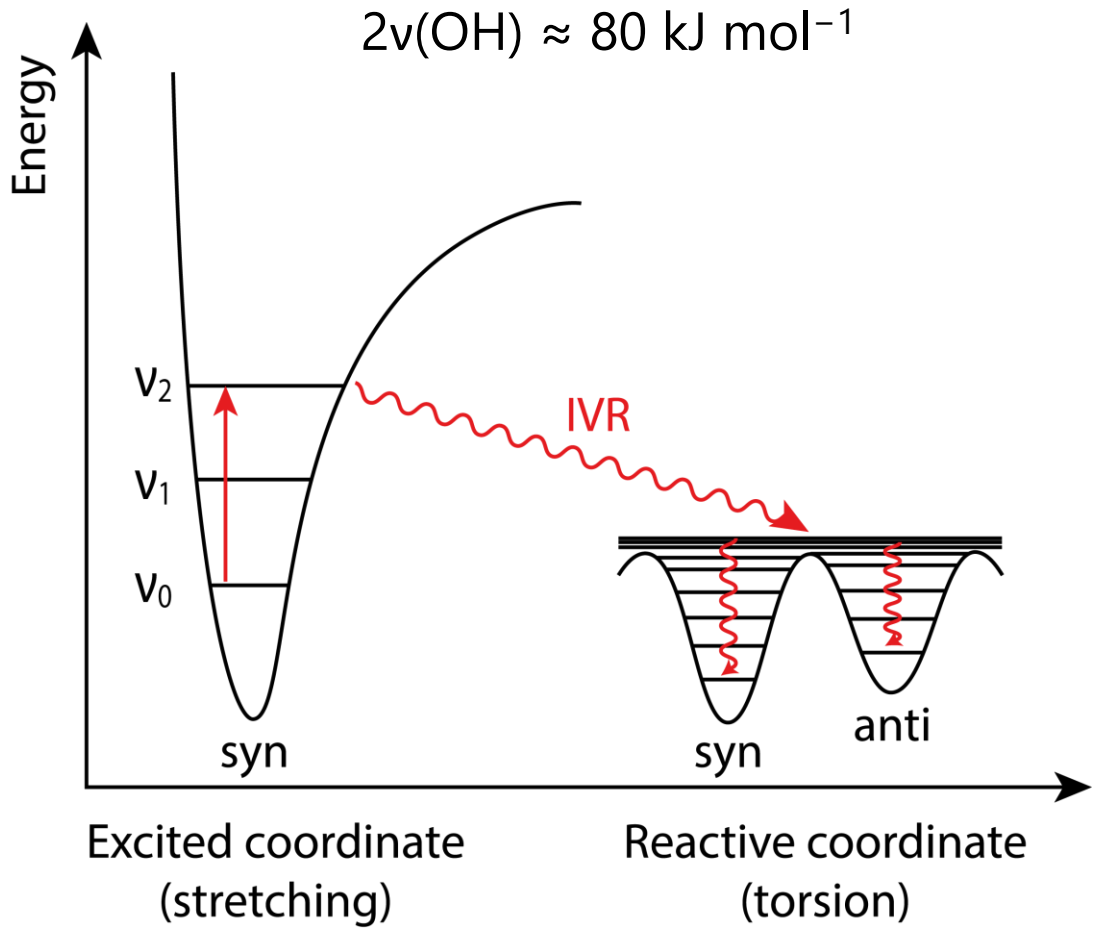


Nat. Chem. **2017**, *9*, 71–76.
Chem. Sci. **2019**, *10*, 802–808.

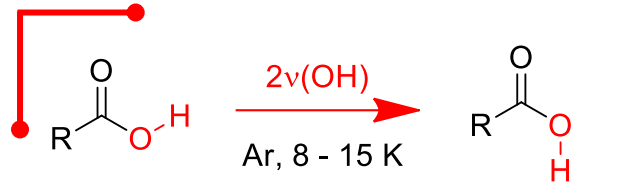


J. Am. Chem. Soc. **2016**, *138*, 15287–15290.
Angew. Chem. Int. Ed. **2020**, *59*, 17622–17627.

IR-Induced Chemistry



$\Delta H^{\ddagger} \approx 50$ kJ mol^{-1}

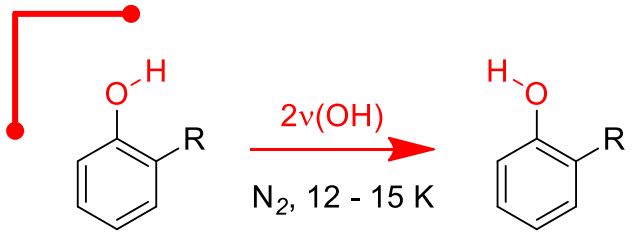


syn *anti*

R = H or CH_3

J. Am. Chem. Soc. **1997**, 119, 11715-11716.
J. Am. Chem. Soc. **2003**, 125, 16188-16189.

$\Delta H^{\ddagger} \approx 25$ kJ mol^{-1}

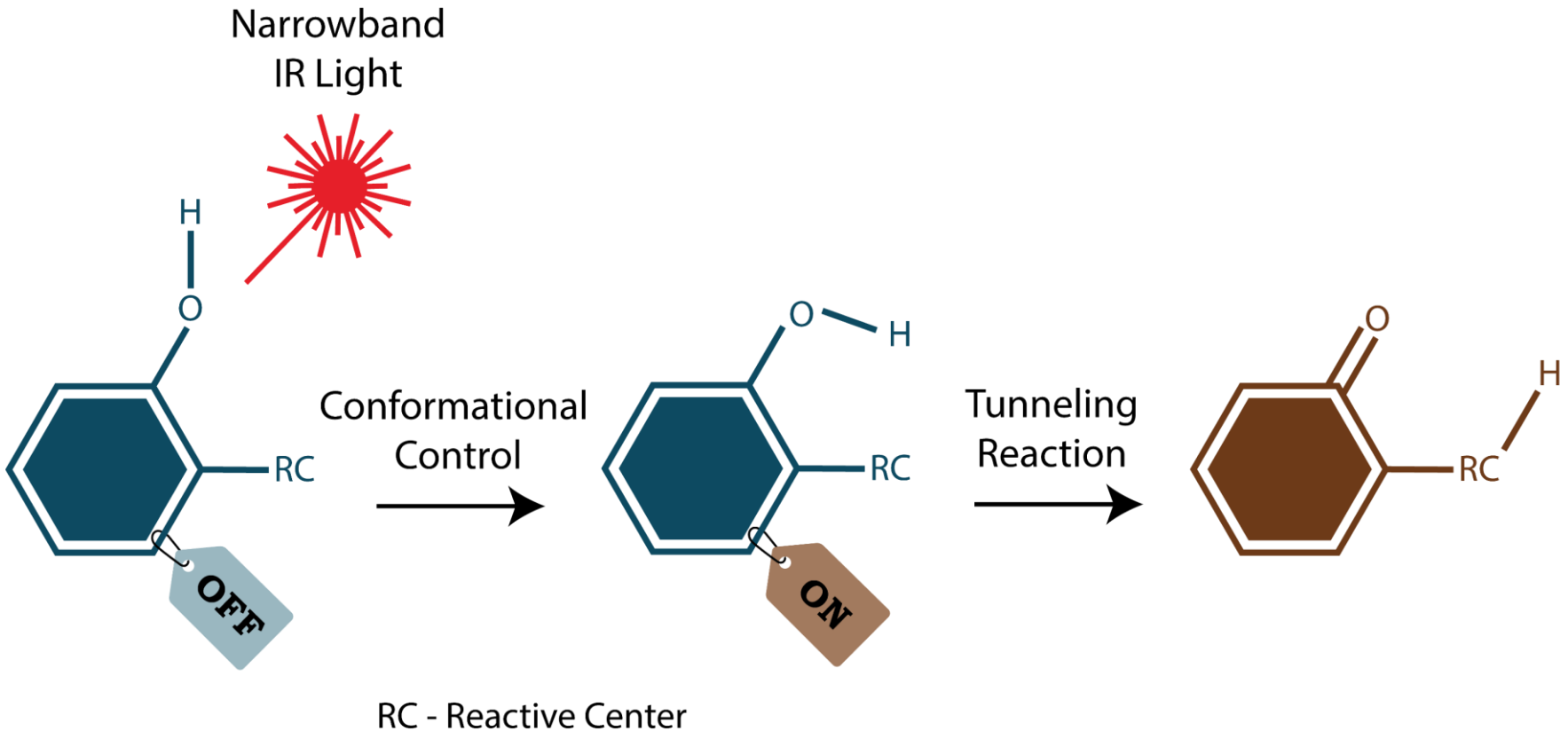


syn *anti*

R = CN or NC

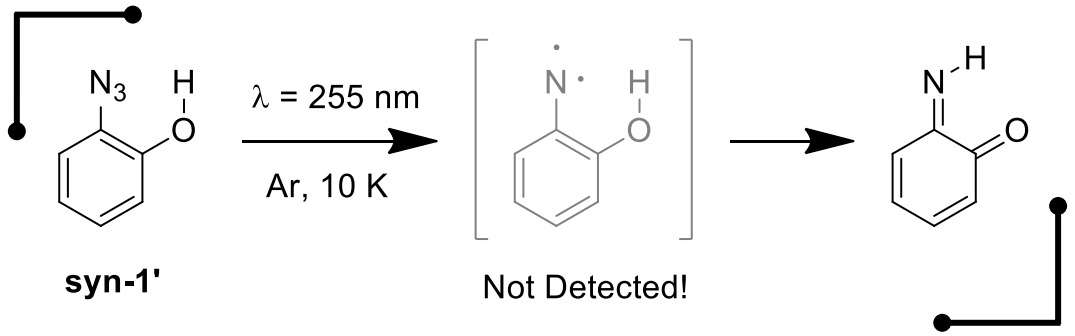
J. Phys. Chem. A. **2019**, 123, 4396−4405
Chem. Phys. Lett. **2020**, 747, 137069.

Proof of Concept



RC - Reactive Center

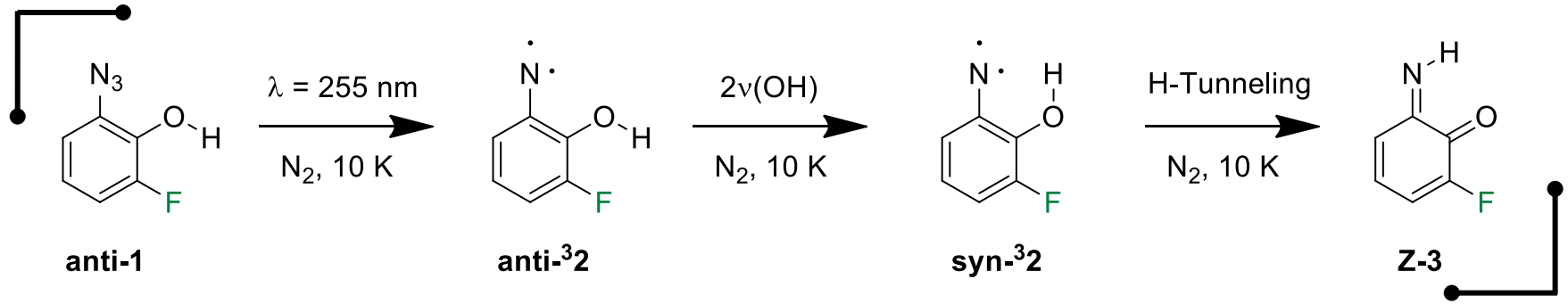
Concretization of Concept



syn-1'

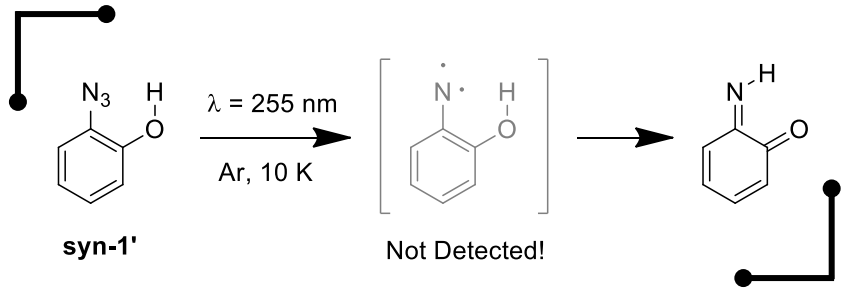
Not Detected!

Liebigs Ann. **1996**, 2029–2037.
Liebigs Ann. **1996**, 1971–1980.



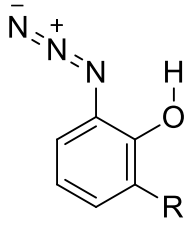
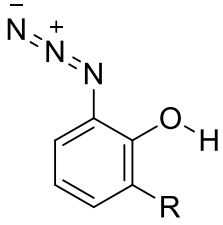
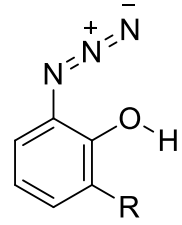
anti-1 **anti-^{3}2** **syn-^{3}2** **Z-3**

Concretization of Concept

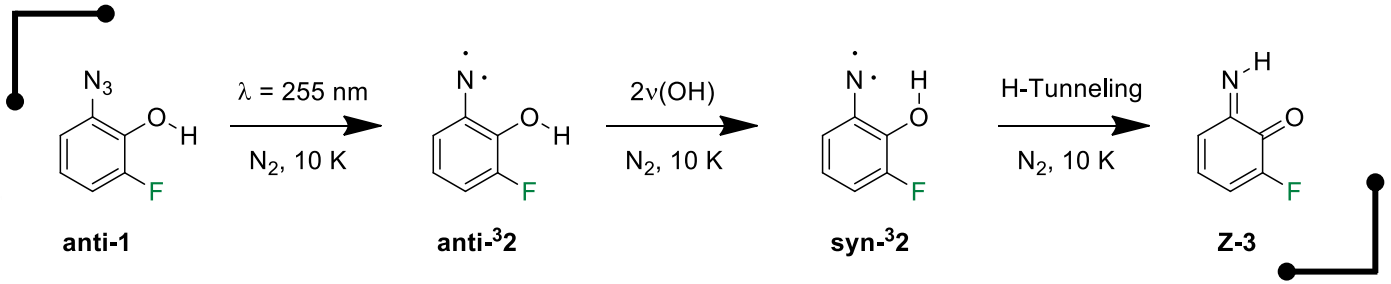


syn-1' Not Detected!

Liebigs Ann. **1996**, 2029–2037.
Liebigs Ann. **1996**, 1971–1980.

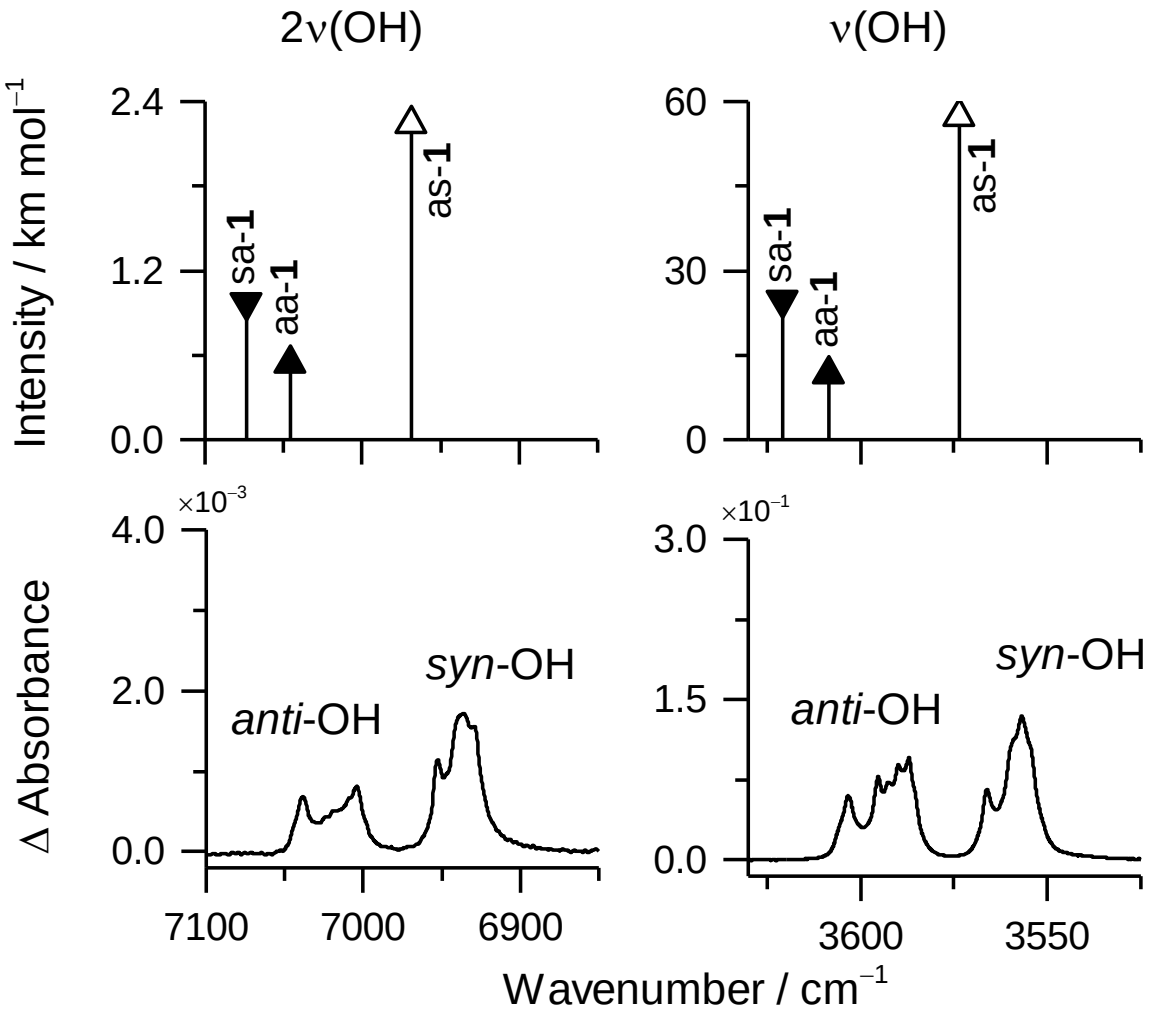
	syn-OH		*anti*-OH
Structures **1′**, **1** R = H, F			
Name	**as-1′** | **as-1**	**aa-1′** | **aa-1**	**sa-1′** | **sa-1**
ΔG_{298K} (CBS-QB3)	0.0 | 0.0	15.5 | 4.5	12.8 | 2.6
Pop_{298K}	99.2 | 66.1	0.2 | 10.7	0.6 | 23.1

Pop. (%); ΔG (kJ mol^{-1})

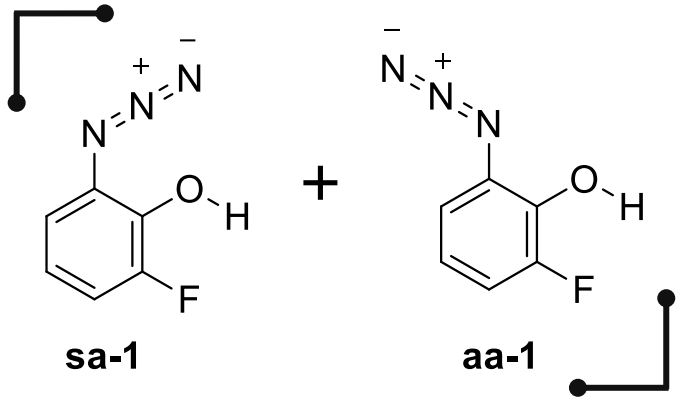


anti-1 **anti-^{3}2** **syn-^{3}2** **Z-3**

Characterization of PhenylAzide

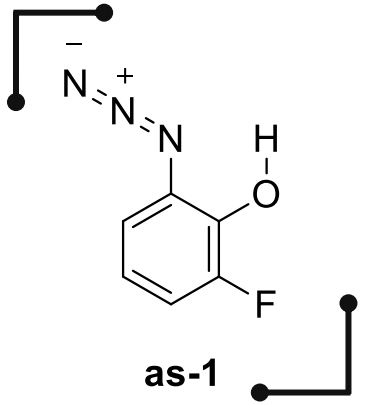


anti-OH



≈ 34%

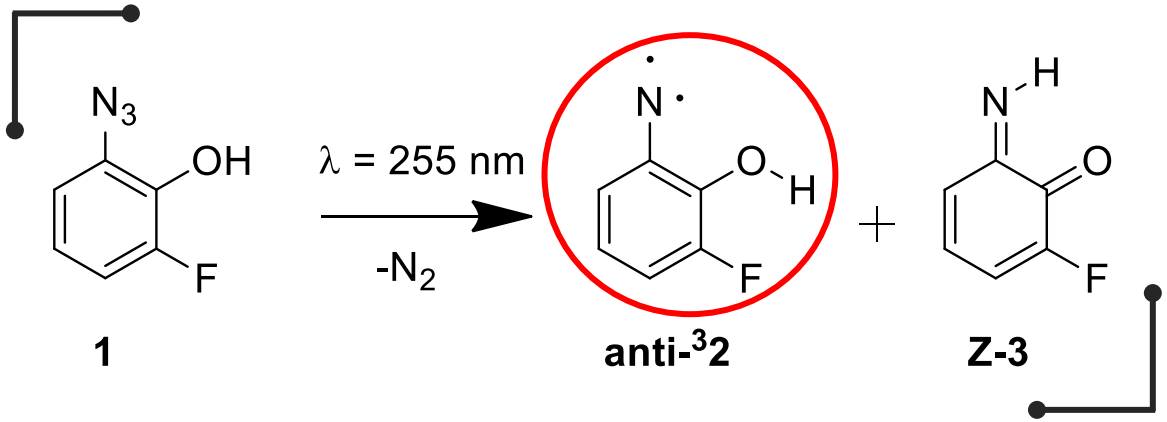
syn-OH



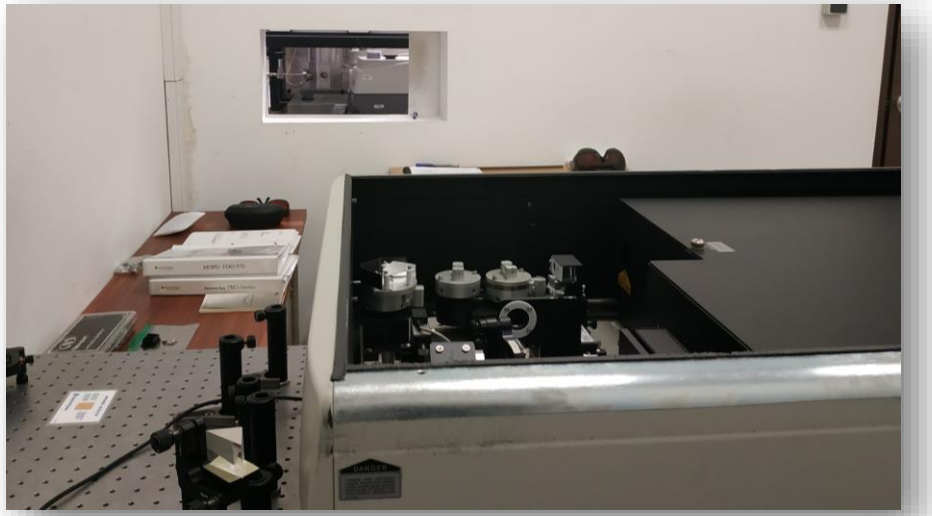
≈ 66%

J. Am. Chem. Soc. **2021**, 143, 8266–8271.

Photolysis of PhenylAzide

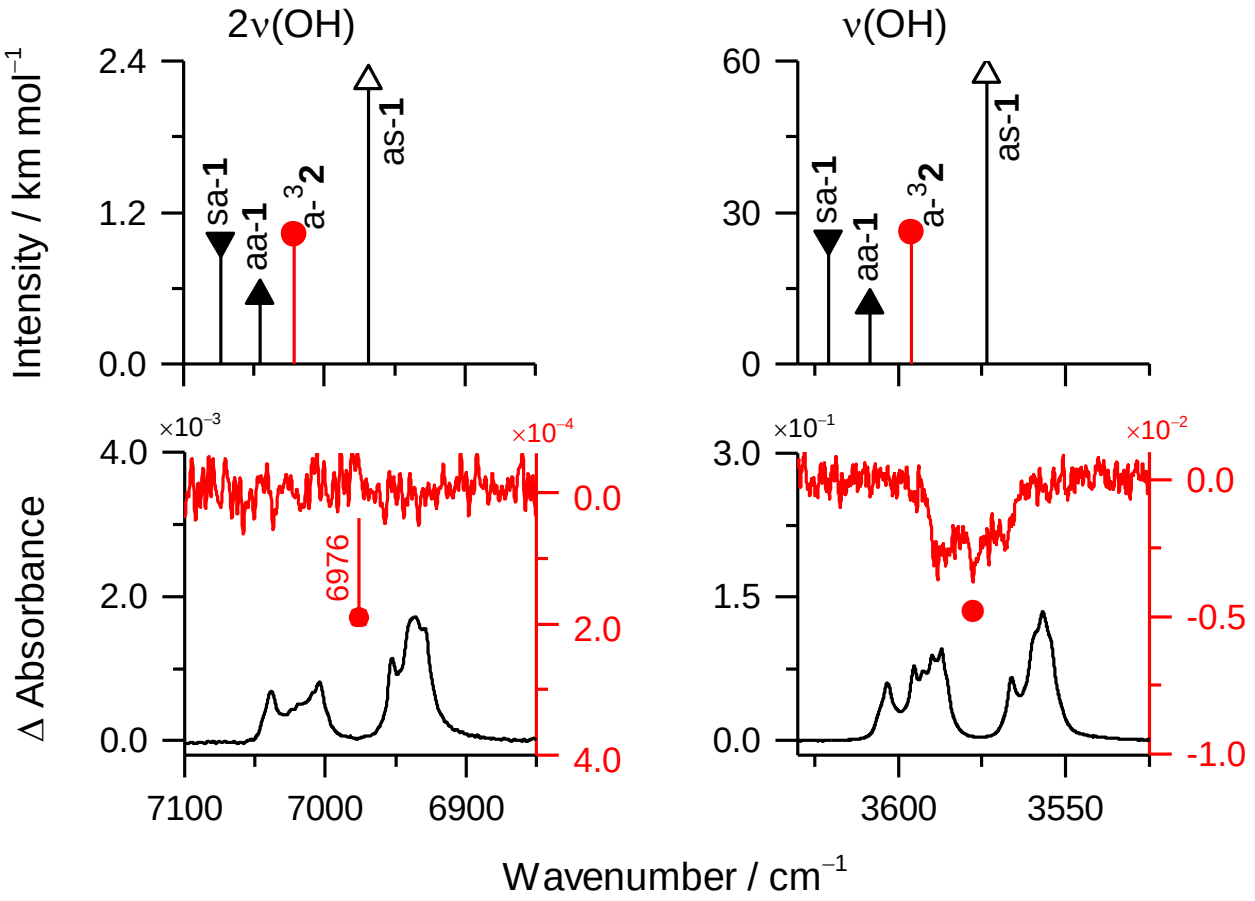


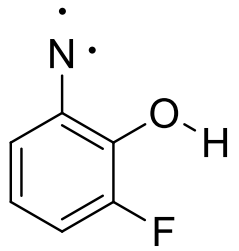
1 **anti-^{3}2** **Z-3**



J. Am. Chem. Soc. **2021**, 143, 8266–8271.

Characterization of Nitrene



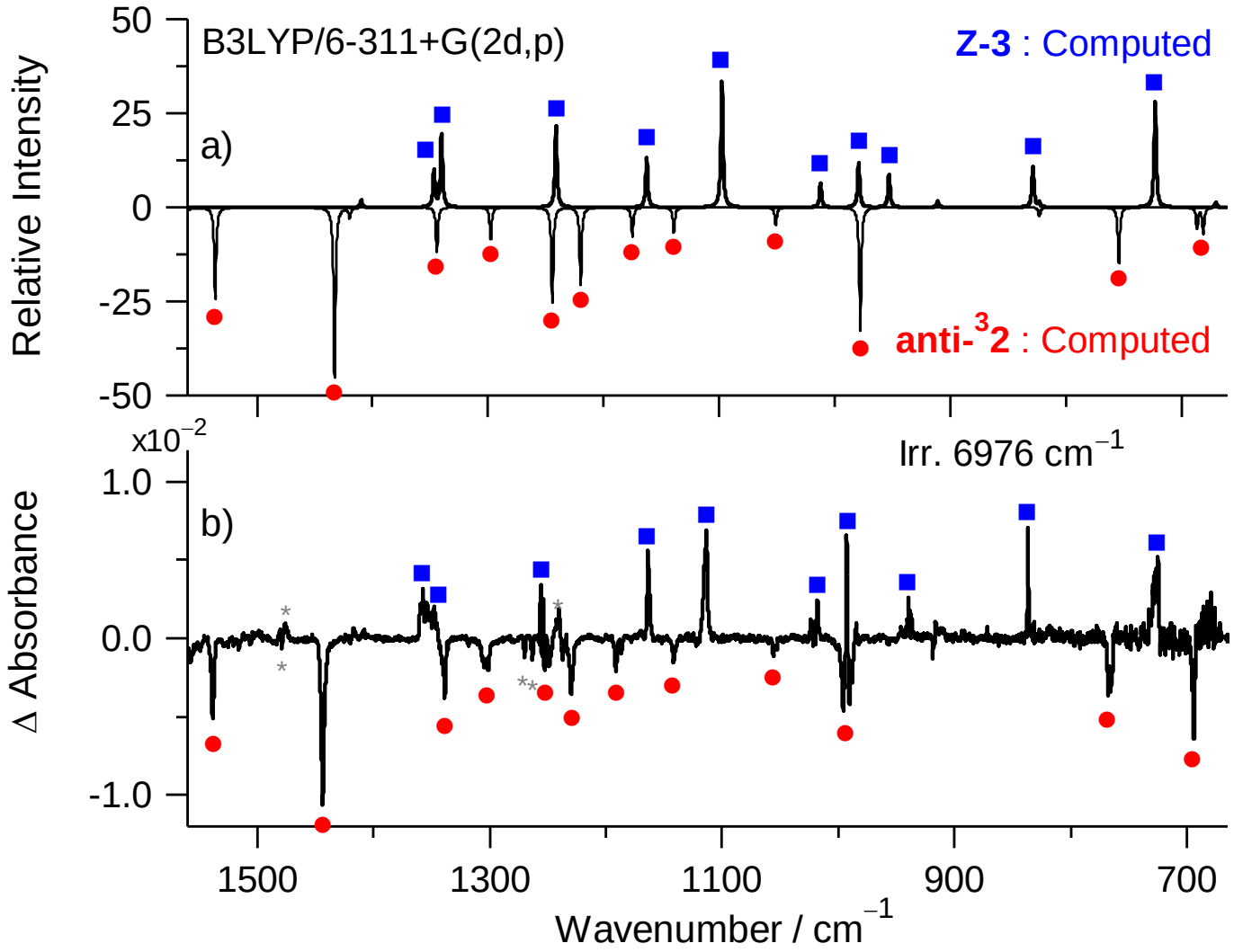


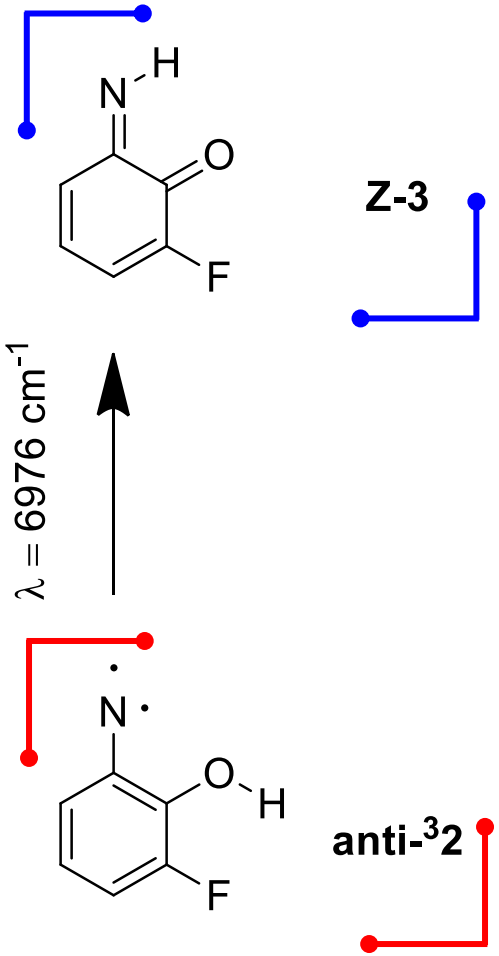
anti-³2

2ν(OH) = 6976 cm⁻¹

J. Am. Chem. Soc. **2021**, 143, 8266–8271.

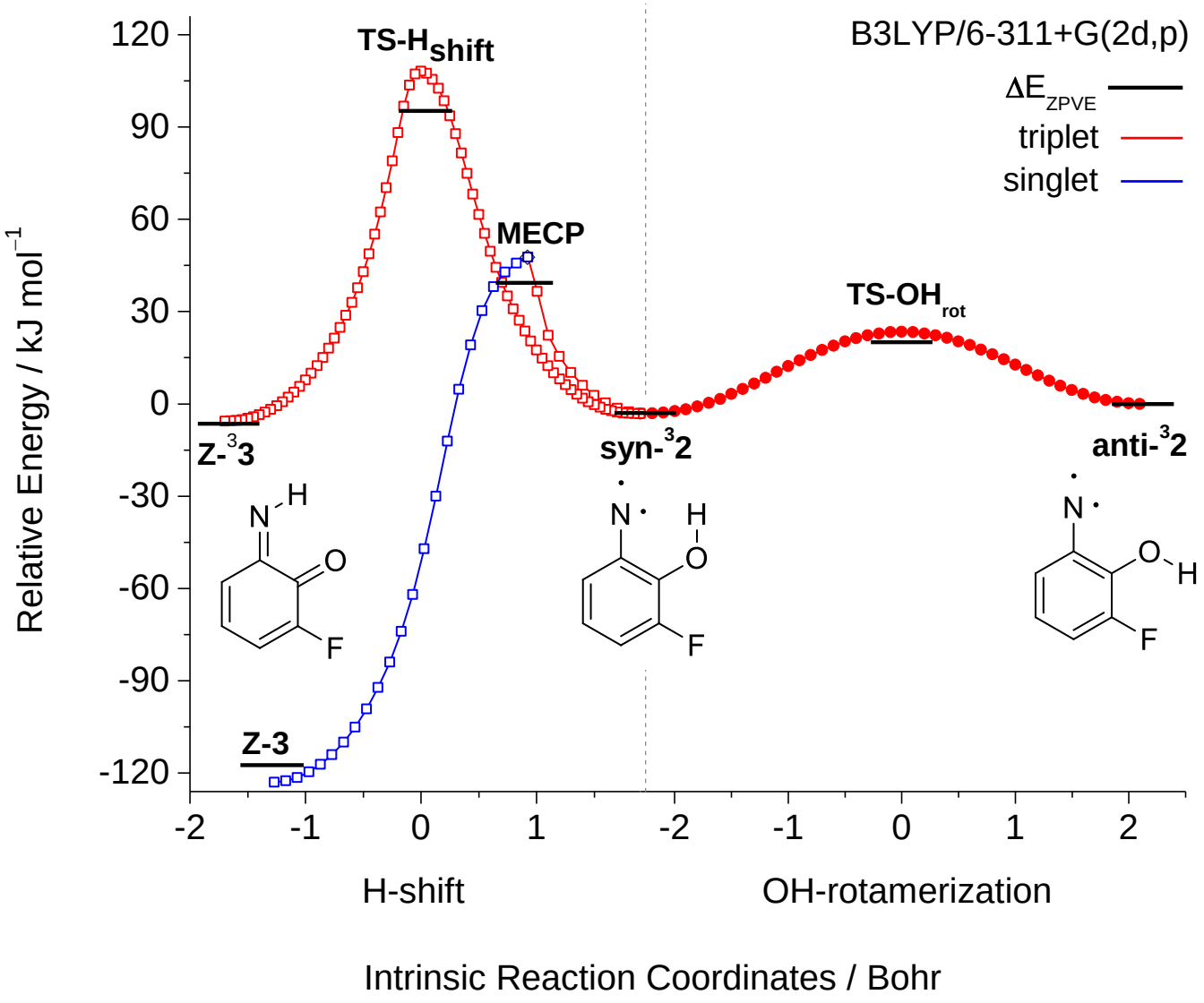
IR-Induced Reactivity





J. Am. Chem. Soc. **2021**, 143, 8266–8271.

Potential Energy Surface



Triplet Surface (WKB)

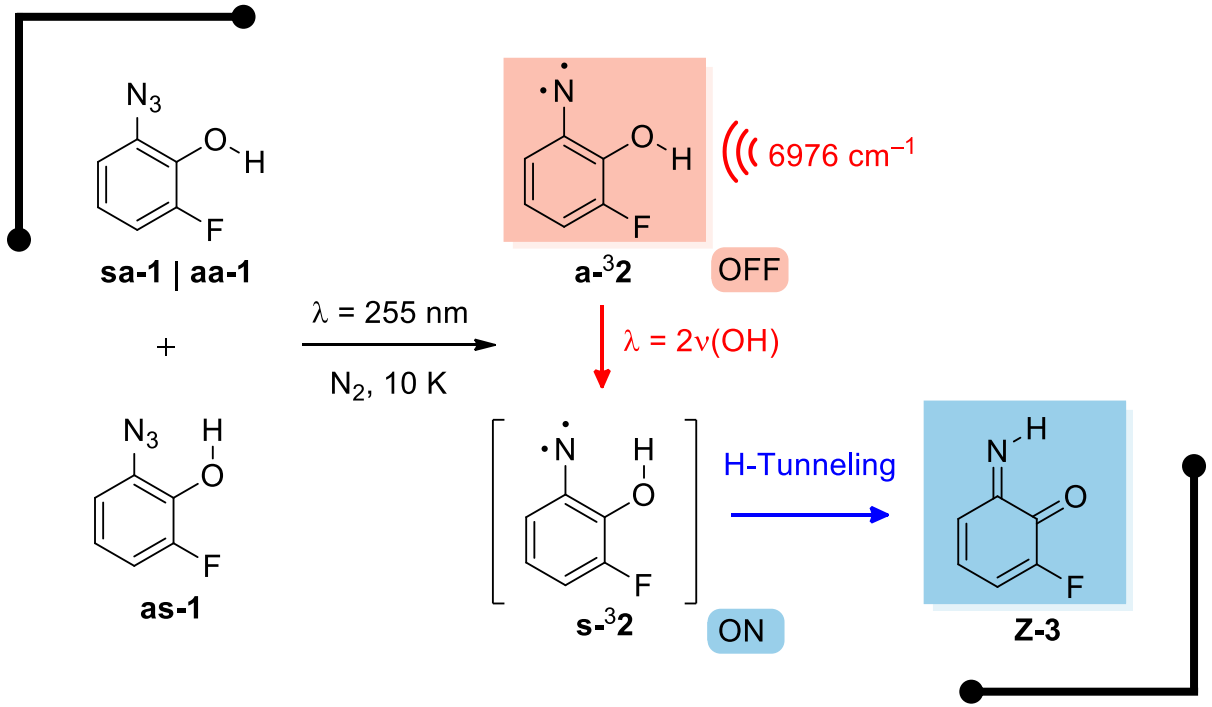
$t_{1/2} = 1.14 \times 10^{3}$ s

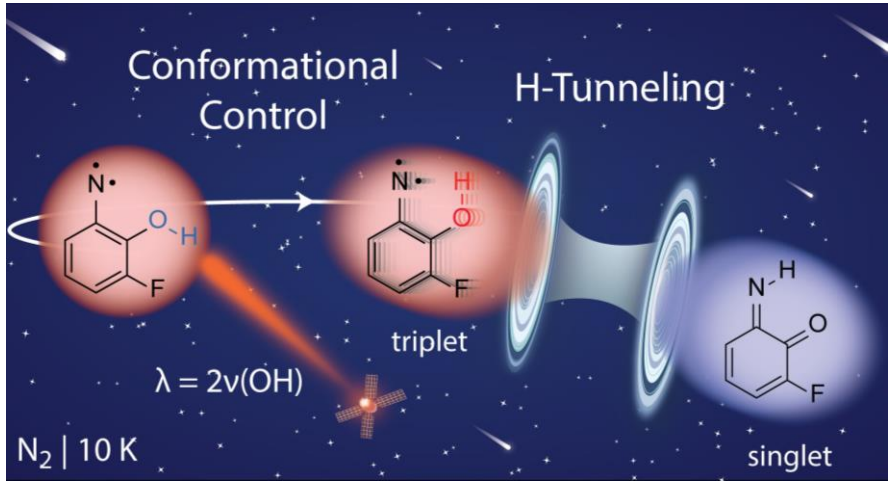
Crossing Surfaces (NA-TST)

$t_{1/2} = 2.6 \times 10^{-2}$ s

J. Am. Chem. Soc. **2021**, 143, 8266–8271.

Switching on H-Tunneling through Conformational Control

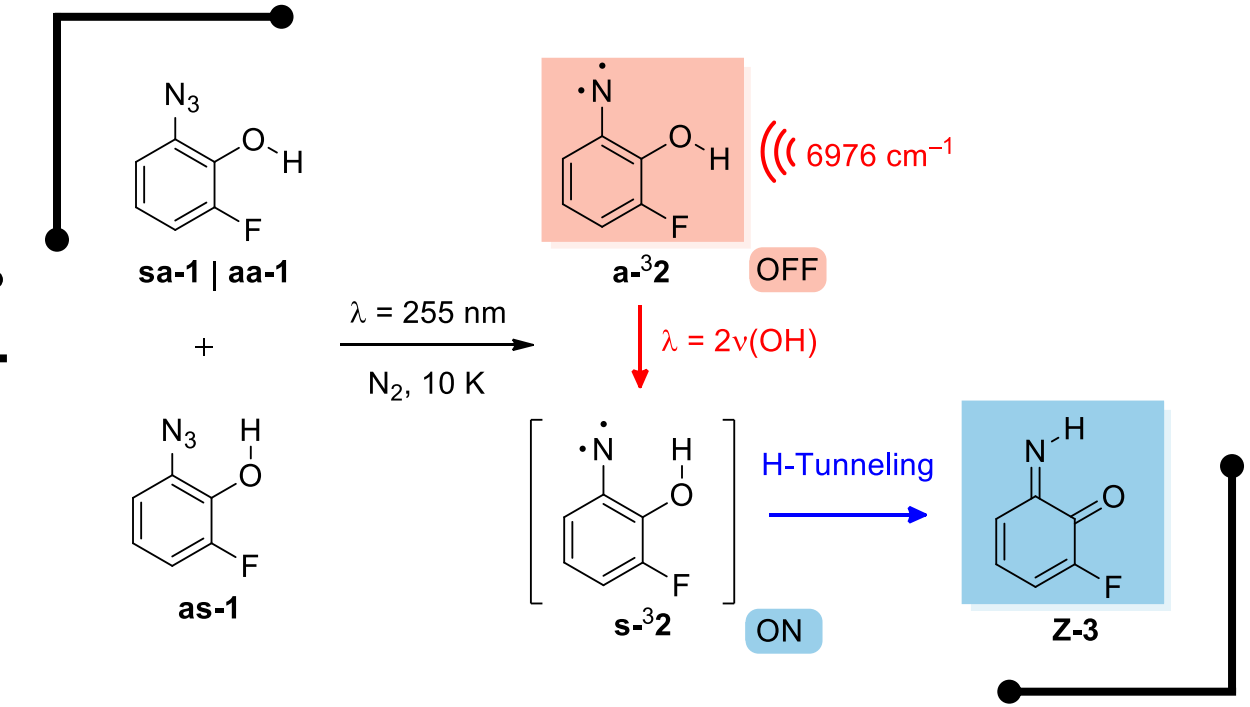




Featured in JACS Spotlights
J. Am. Chem. Soc. **2021**, 143, 8519−8520.

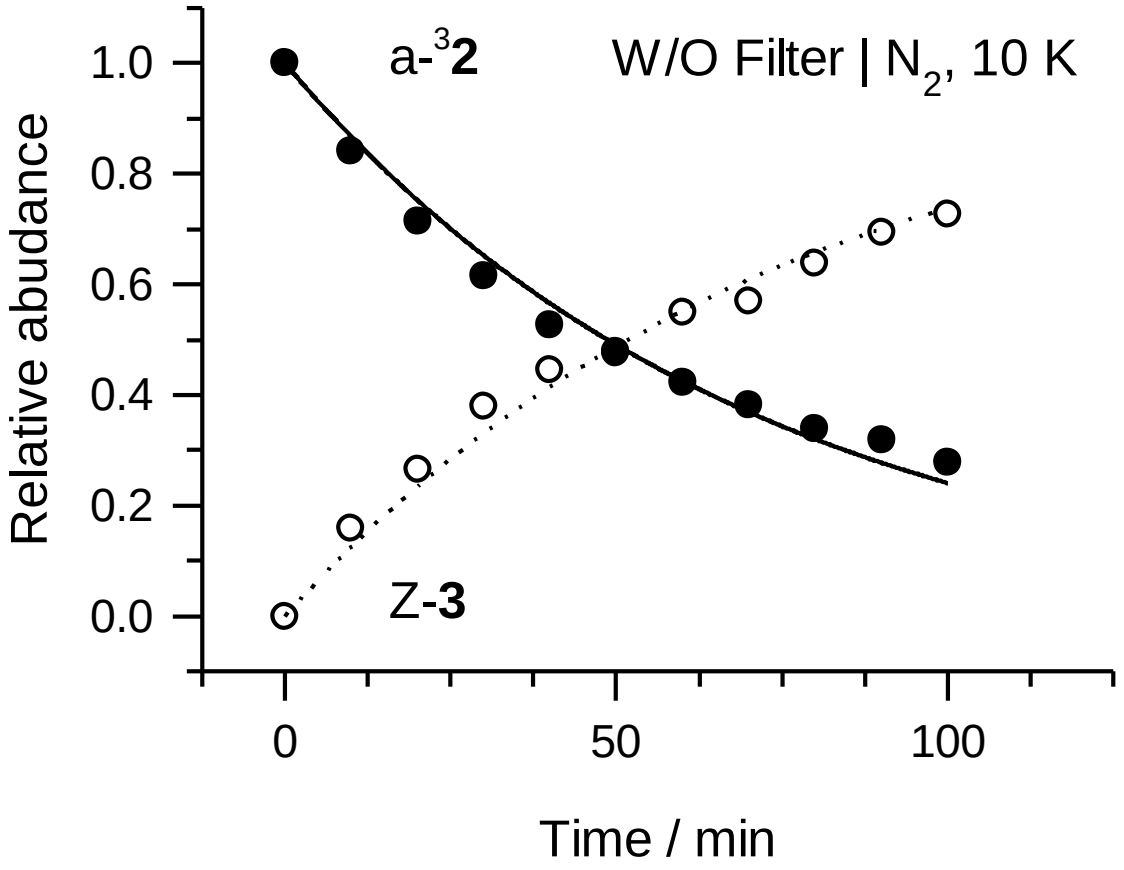
J. Am. Chem. Soc. **2021**, 143, 8266–8271.

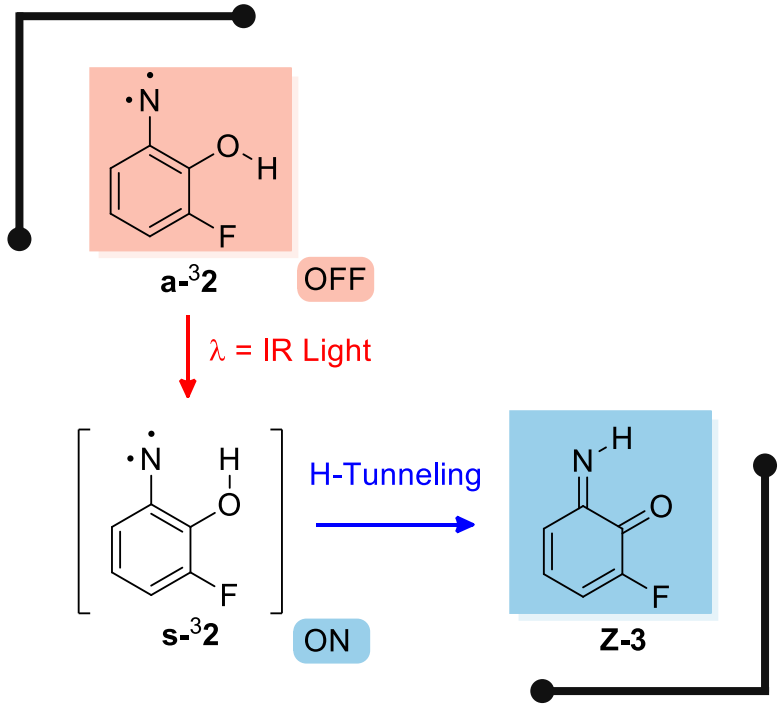
Questions to be Clarified



- Exposure to the Spectrometer Globar
- Stability of **a-^{3}2** in the Absence of Light
- Isotopic Labeling of the Hydroxyl Group

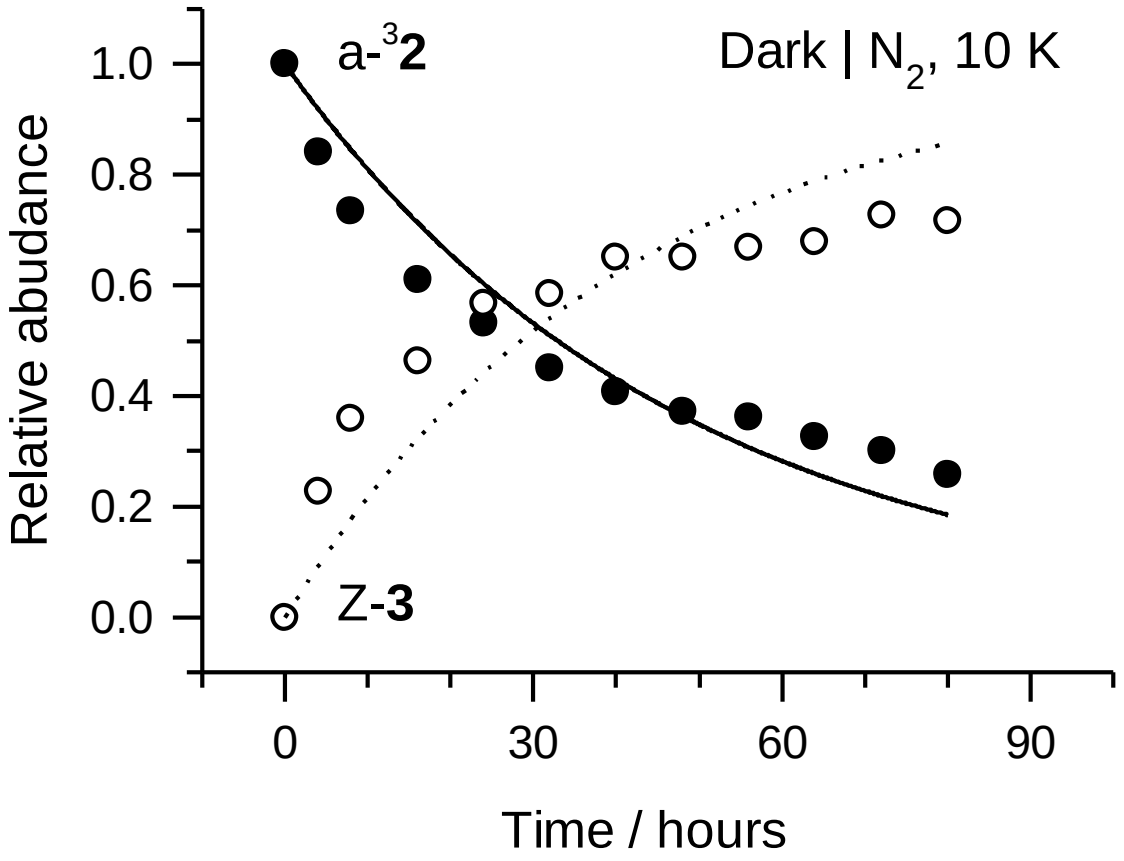
Exposure to the Spectrometer Globar

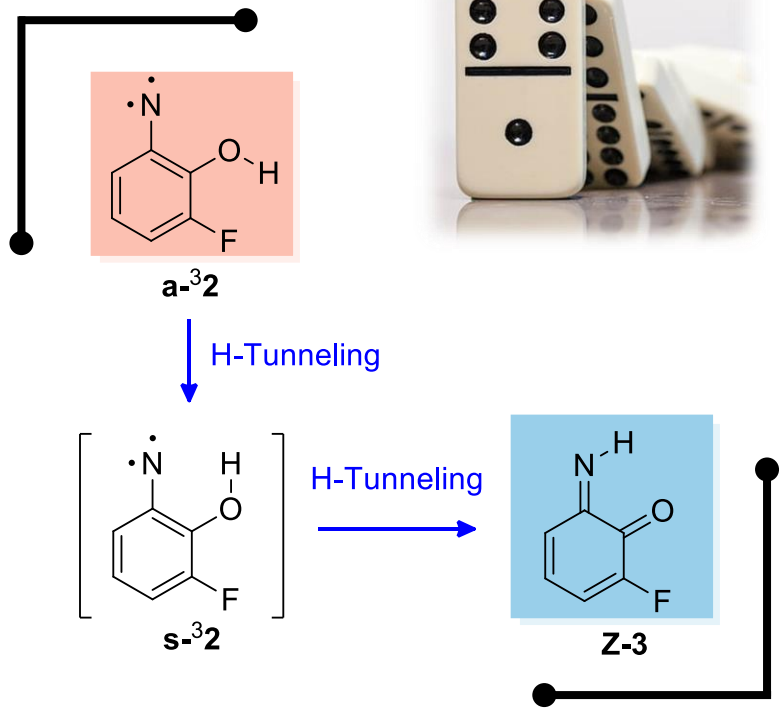




Unplublished Data.

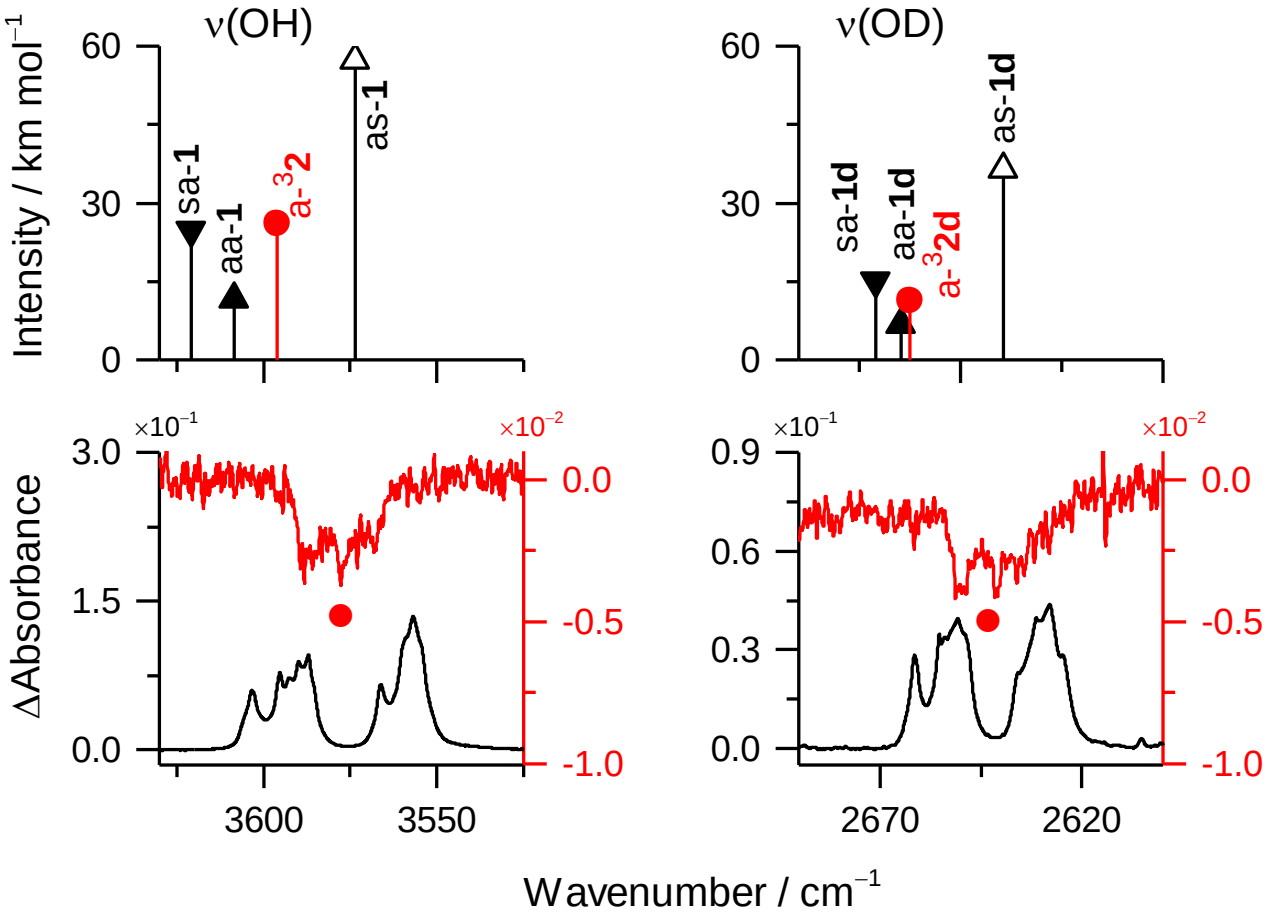
Stability of a-^{3}2 in the Absence of Light

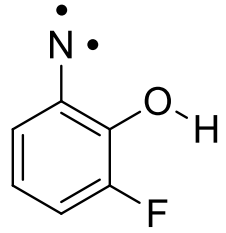




Unplublished Data.

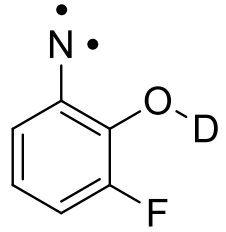
Isotopic Labeling of the Hydroxyl Group





a-^{3}2

ν(OH) = 3575 cm^{-1}

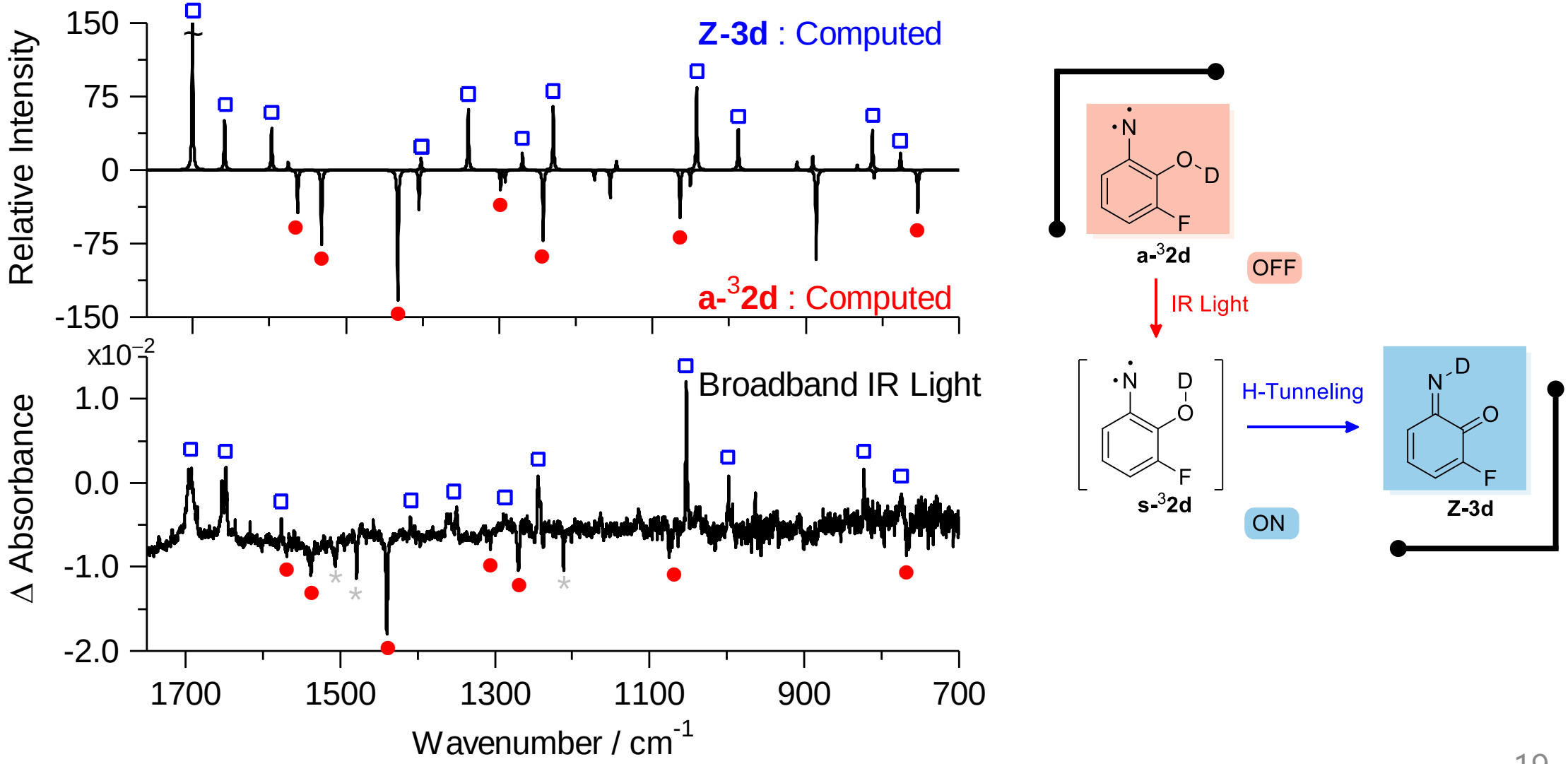


a-^{3}2d

ν(OD) = 2640 cm^{-1}

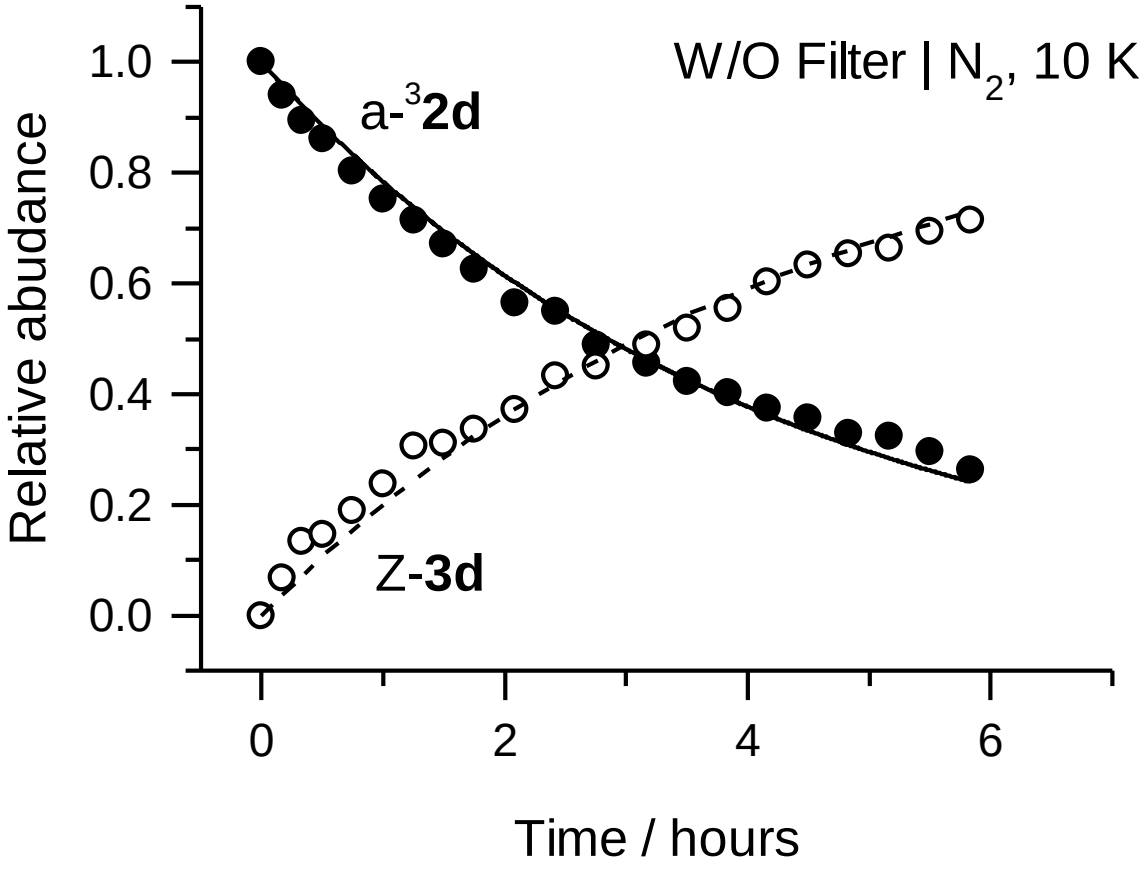
Unplublished Data.

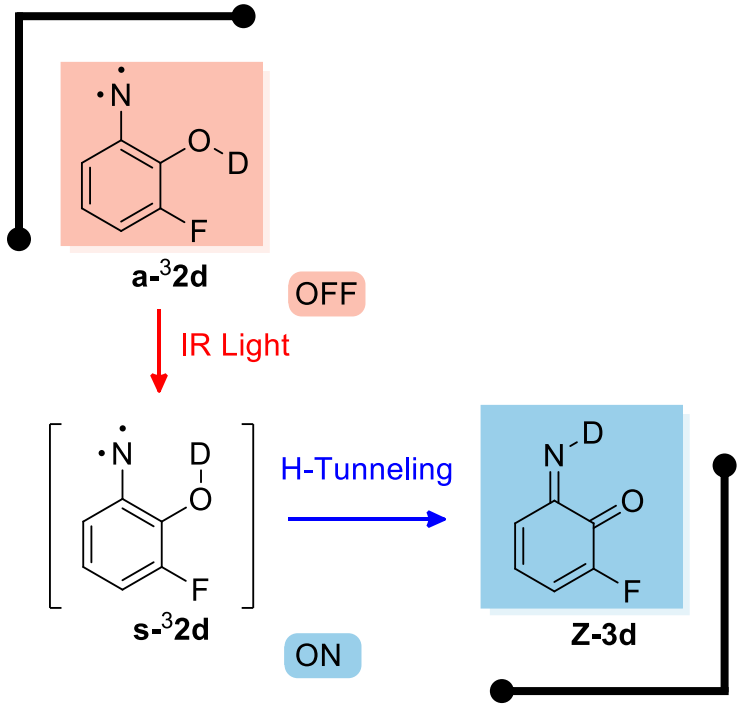
Deuterated Sampled Exposed to Spectrometer Globar



Unplublished Data.

Deuterated Sampled Exposed to Spectrometer Globar





Unplublished Data.

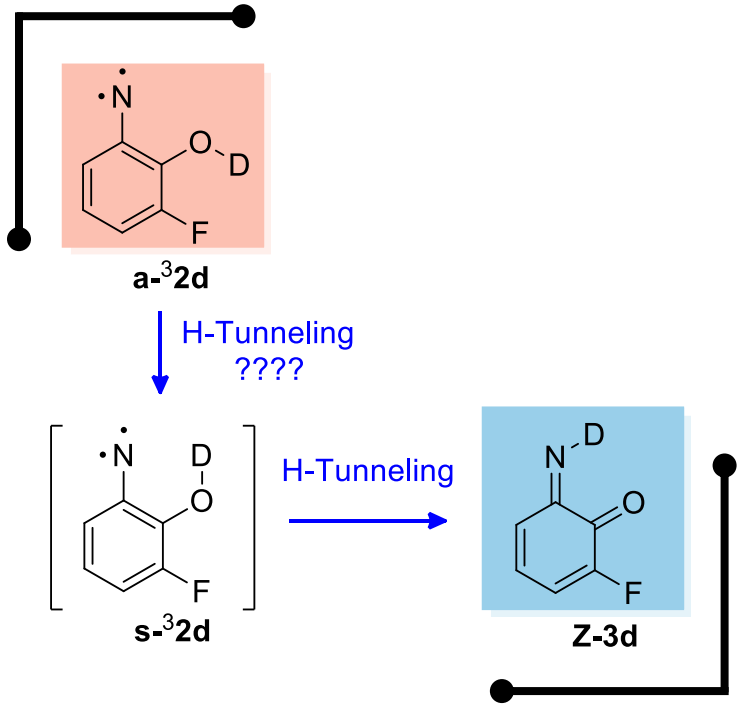
Is Tunneling Inducing the OD Rotamerization?

Data collected is not unambiguous

Requires additional clarification

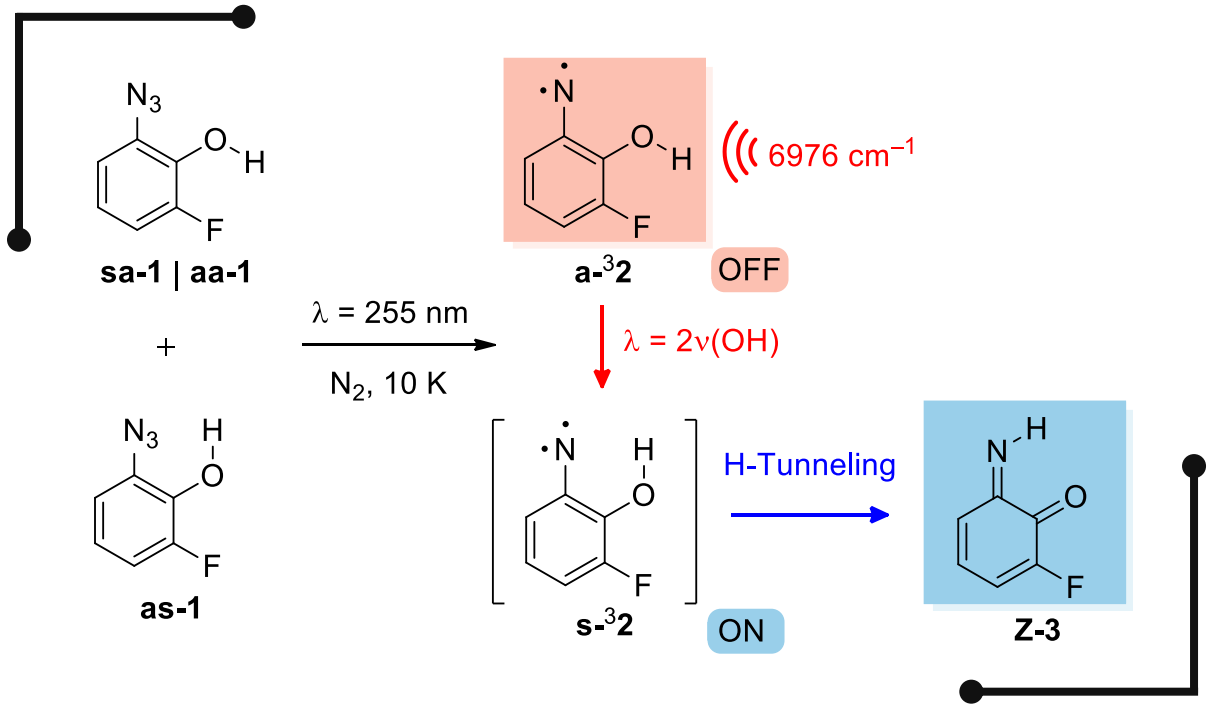
WKB predicts no D-Tunneling

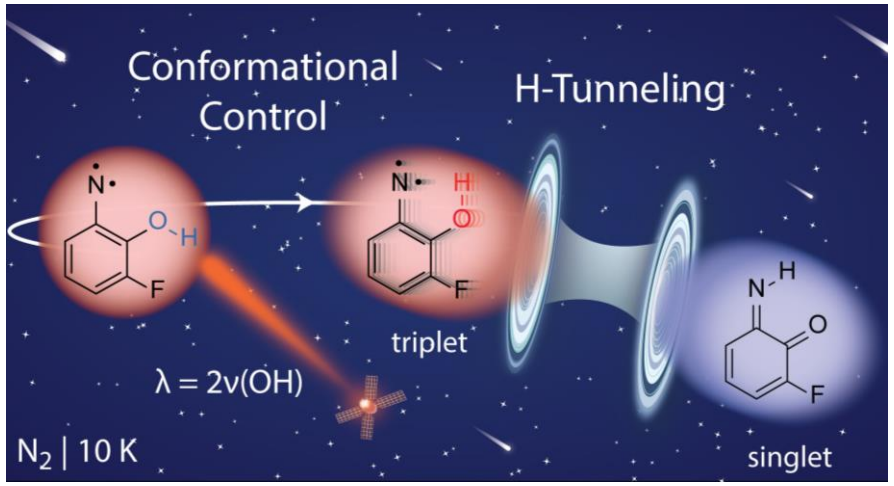
SCT is being computed



Unplublished Data.

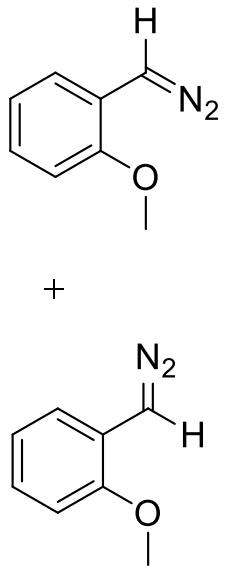
When IR Induced Chemistry meets Quantum Tunneling





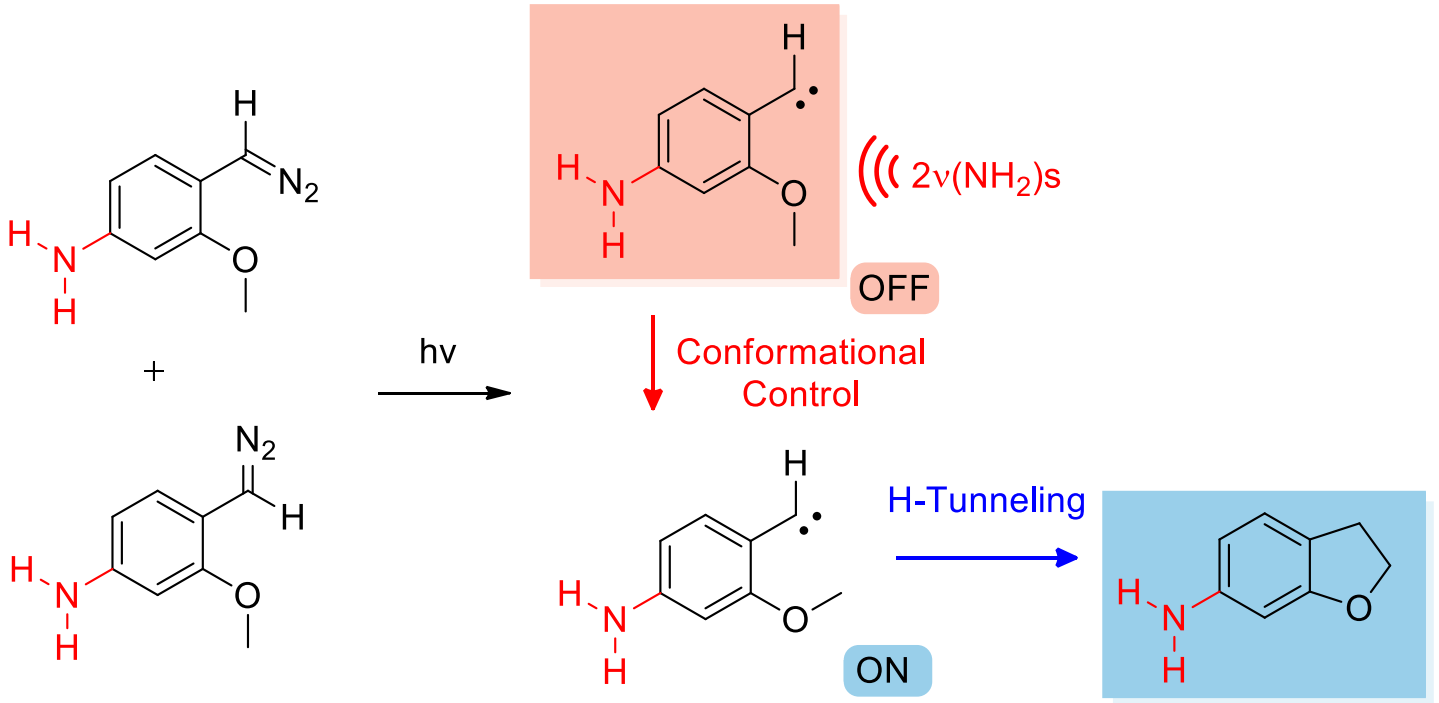
J. Am. Chem. Soc. **2021**, 143, 8266–8271.

When IR Induced Chemistry meets Quantum Tunneling



Plausible Working Hypothesis for Future Devolpments.

When IR Induced Chemistry meets Quantum Tunneling



Introduction of Remote Molecular Antennas

Generalized Strategy to Activate Tunneling via Conformational Control

Plausible Working Hypothesis for Future Devolpments.

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Thank You!!

For the Warm Welcoming

For your Attention