Substituent Effect on Tunneling in Heterodimers of Benzoic Acids

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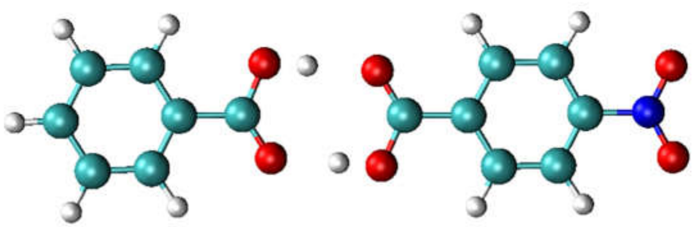
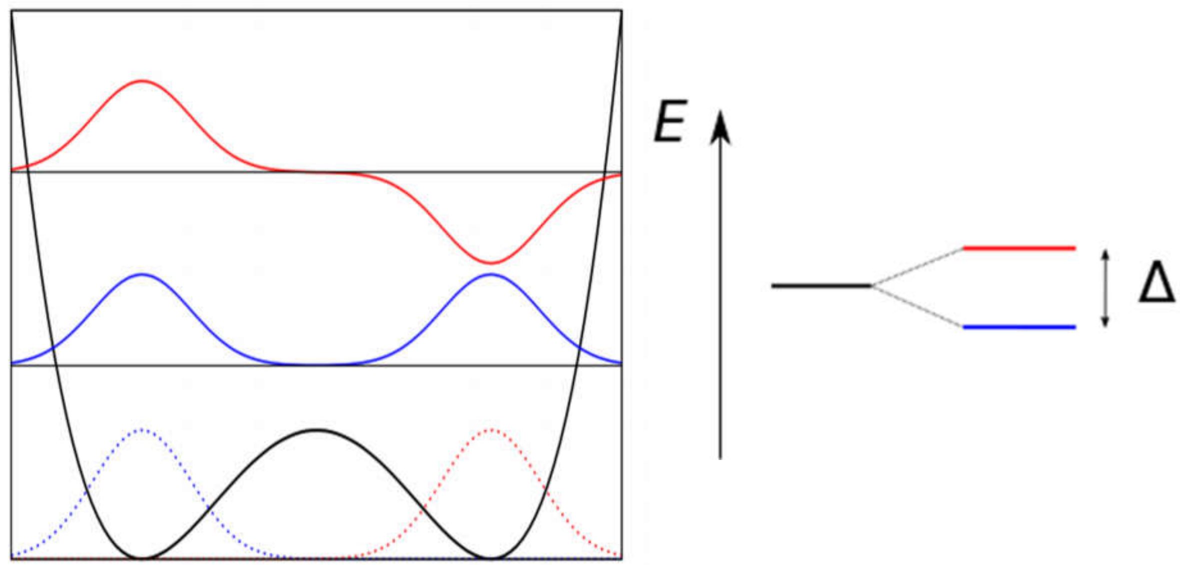
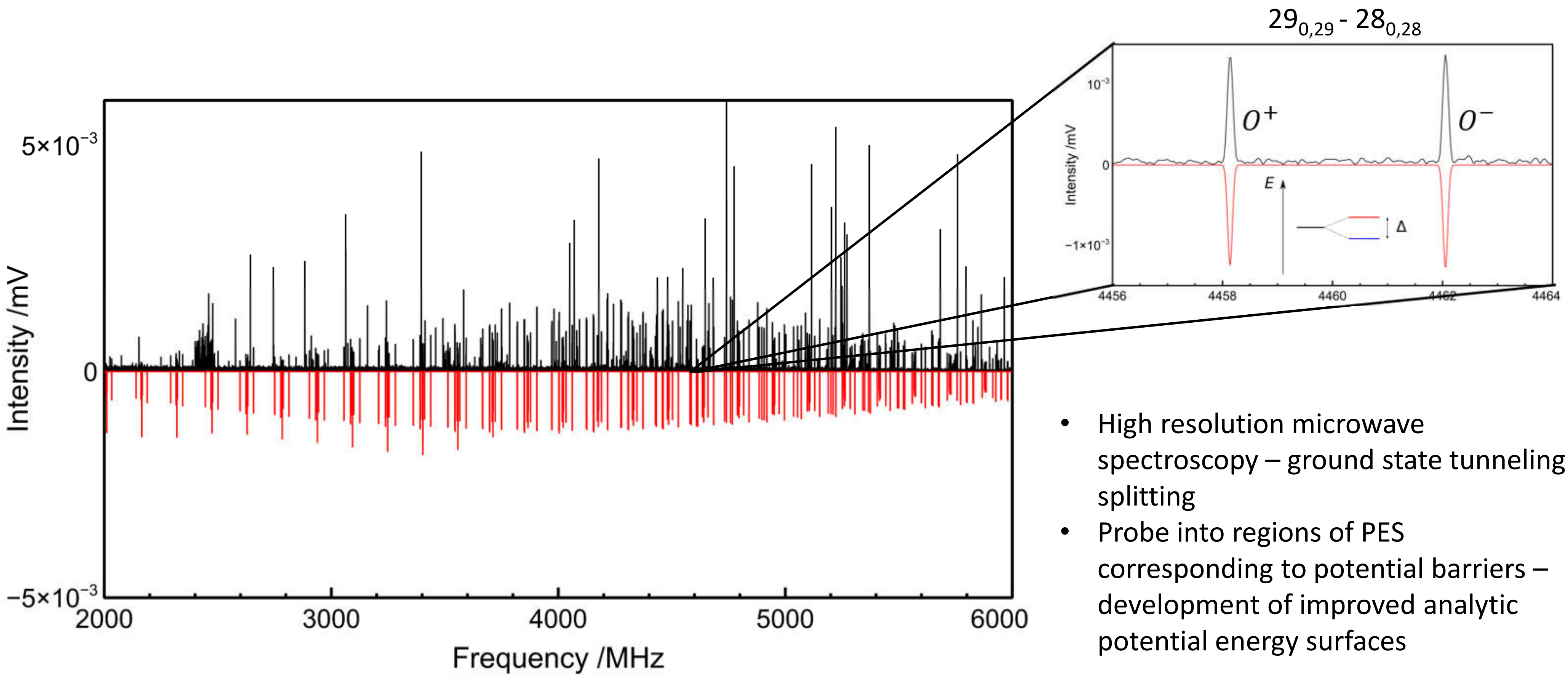
Tunneling Splitting

- Systems with symmetry-related minima
- Vibrational wavefunctions are delocalized
- Degeneracy is broken
- Splitting pattern is a consequence of tunneling – extremely sensitive to shapes and heights of potential barriers





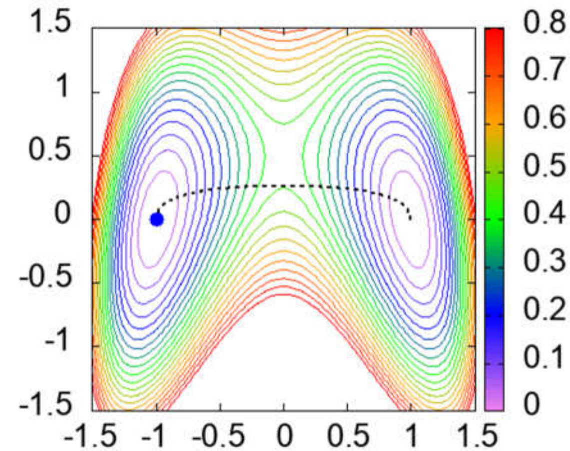
Tunneling Splitting



- High resolution microwave spectroscopy – ground state tunneling splitting
- Probe into regions of PES corresponding to potential barriers – development of improved analytic potential energy surfaces

Jacobi Field Instanton (JFI) theory

- Splitting pattern is given by eigenvalues of tunneling matrix
- Tunneling splitting can be computed using Herring formula
- Localized wavefunctions – obtained using WKB approximation



$$\Delta_{ij} = \frac{\int \left(\phi^{(i)} \frac{\partial}{\partial S} \phi^{(j)} \quad \phi^{(j)} \frac{\partial}{\partial S} \phi^{(i)}\right) \delta\big(f(\mathbf{x})\big) d\mathbf{x}}{\int \left|\phi^{(i)}\right|^2 d\mathbf{x}}$$

$$\phi^{(i/j)} = \mathrm{e}^{-\frac{1}{\ }\left(W_0^{(i/j)} + W_1^{(i/j)}\ \right)}$$

$$\frac{\partial W_0^{(i/j)}}{\partial x_\alpha} \frac{\partial W_0^{(i/j)}}{\partial x_\alpha} = 2V(\mathbf{x})$$

Method of characteristics → characteristic is instanton path

$$W_0^{(i/j)} = \int_0^S \sqrt{2V(S')}\, \mathrm{d}S' + \frac{1}{2} \Delta\mathbf{x}^\top \mathbf{A}^{(i/j)}(S) \Delta\mathbf{x}$$

$$\frac{\partial W_0^{(i/j)}}{\partial x_\alpha} \frac{\partial W_1^{(i/j)}}{\partial x_\alpha} \quad \frac{1}{2} \frac{\partial^2 W_0^{(i/j)}}{\partial x_\alpha \partial x_\alpha} + E = 0$$

Integration along characteristic →

$$W_1^{(i/j)} = \frac{1}{2} \int_0^S \frac{\mathrm{Tr}\left(\mathbf{A}^{(i/j)}(S) \quad \mathbf{A}_0^{(i/j)}\right)}{\sqrt{2V(S')}} \mathrm{d}S'$$

G. V. Mil'nikov, H. Nakamura, *J. Chem. Phys.* **115** (2001) 6881-6897.
M. Erakovic, C. L. Vaillant, MT Cvitas, *J. Chem. Phys.* **152** (2020) 084111.

Jacobi Field Instanton (JFI) theory

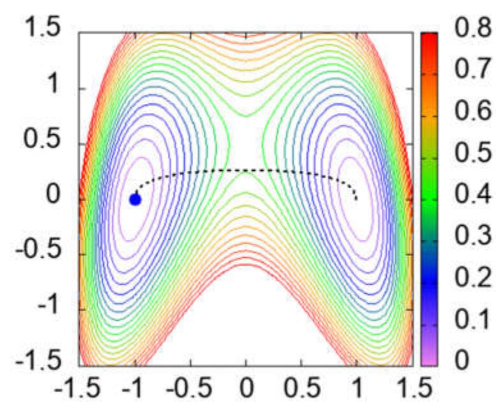
$$\Delta_{ij} = 2\sqrt{2V(0)}\sqrt{\frac{\det \mathbf{A}_0^{(i)}}{\pi \det' \frac{\mathbf{P}\left(\mathbf{A}^{(i)} + \mathbf{A}^{(j)}\right)\mathbf{P}}{2}}}\,\mathrm{e}^{-\int_0^{S_\mathrm{tot}}\sqrt{2V(S')}\mathrm{d}S' - \frac{1}{2}\int_0^{S_\mathrm{cp}}\frac{\mathrm{Tr}\left(\mathbf{A}^{(i)}-\mathbf{A}_0^{(i)}\right)}{\sqrt{2V(S')}}\mathrm{d}S' - \frac{1}{2}\int_0^{S_\mathrm{cp}}\frac{\mathrm{Tr}\left(\mathbf{A}^{(j)}-\mathbf{A}_0^{(j)}\right)}{\sqrt{2V(S')}}\mathrm{d}S'}$$

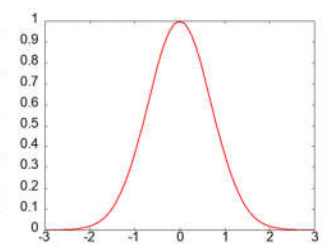
$$\sqrt{2V(S)}\frac{d}{dS}\mathbf{A}^{(i)} = \mathbf{H}^{(i)} \quad \left(\mathbf{A}^{(i)}\right)^2 \qquad \mathbf{A}^{(i)}(0) = \mathbf{H}_0^{\frac{1}{2}}$$

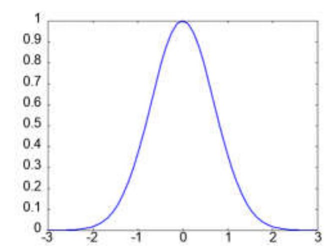
Eyring formula for rates, low temperatures - local quantities

$$k = A\mathrm{e}^{-\left(V_\mathrm{TS}+\frac{1}{2}\mathrm{Tr}\left(\mathbf{H}_\mathrm{TS}^{\frac{1}{2}}-\mathbf{H}_0^{\frac{1}{2}}\right)\right)/k_\mathrm{B}T}$$

MEP		MAP
Barrier height	⟶	Action
ZPE difference		$\mathbf{A}$ matrix traces

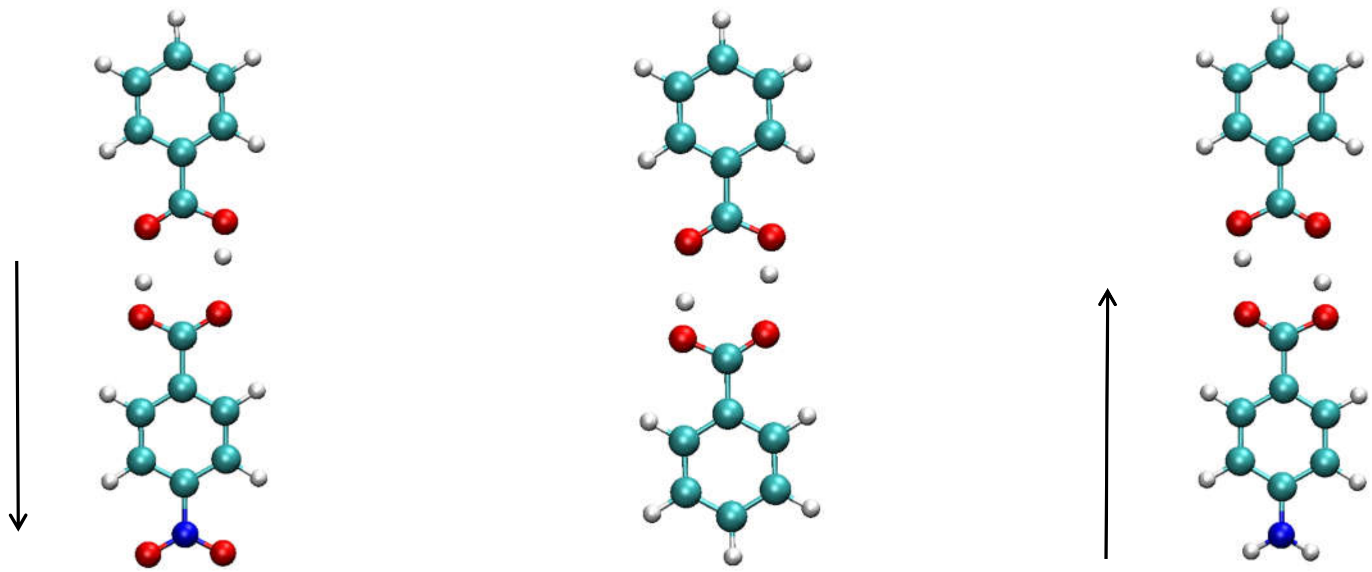






Benzoic Acid Dimers

- Substituent effect on tunneling splitting – probe into the differences in the barrier regions



Electron withdrawing

$\Delta = 1.34\ \mathrm{cm}^{-1}$

$\Delta = 1.50\ \mathrm{cm}^{-1}$

Electron donating

$\Delta = 1.99\ \mathrm{cm}^{-1}$

Potential Energy Barriers

$\Delta(H-NO_2)$=1.34 cm^{-1}

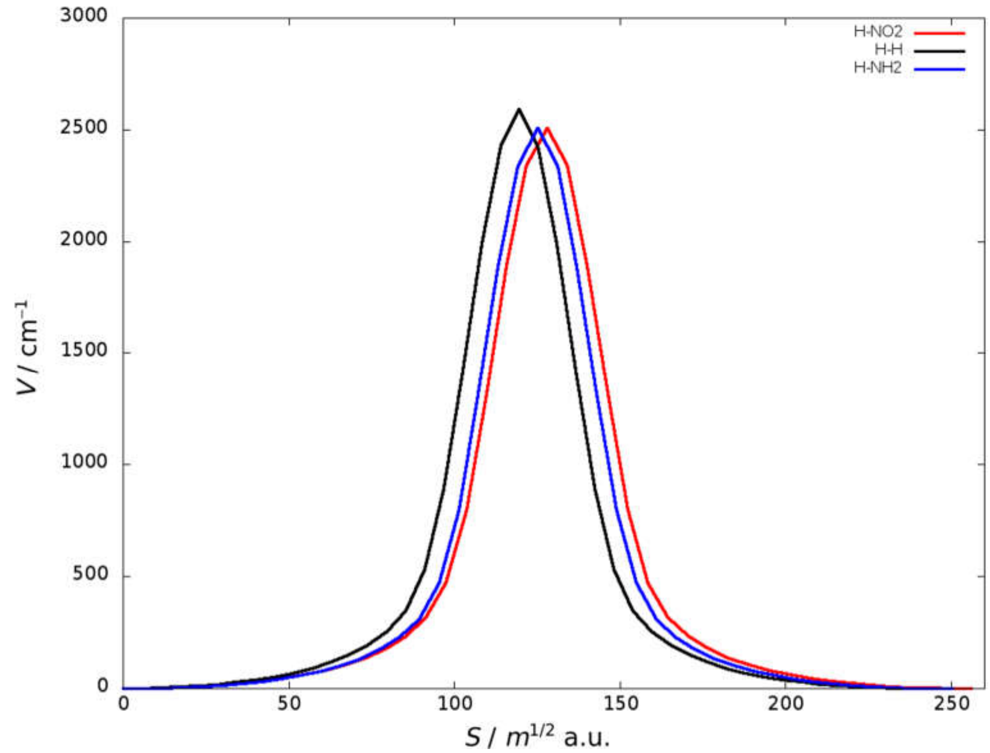
$\Delta(H-H)$=1.50 cm^{-1}

$\Delta(H-NH_2)$=1.99 cm^{-1}

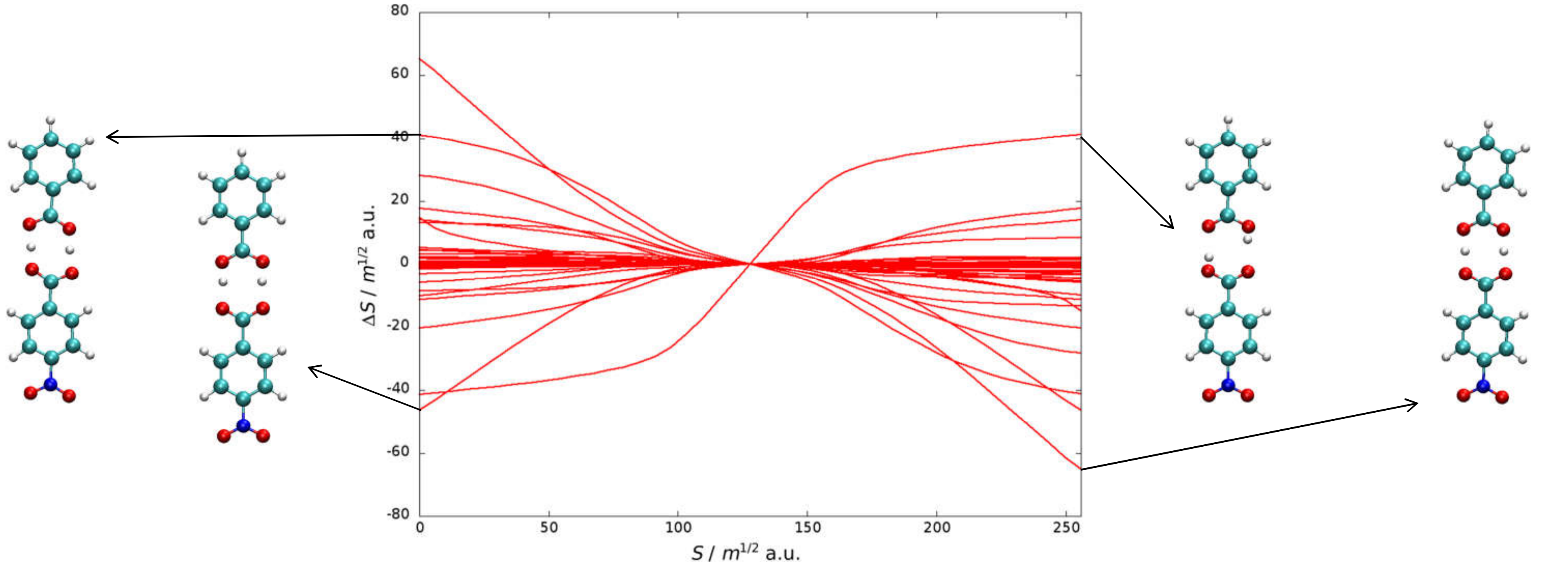
$S_{kink}(H-NO_2)$=11.737 a.u.

$S_{kink}(H-H) = 11.423$ a.u.

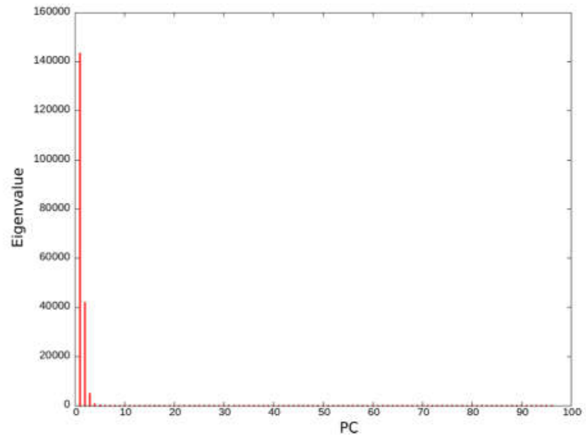
$S_{kink}(H-NH_2) = 11.343$ a.u.

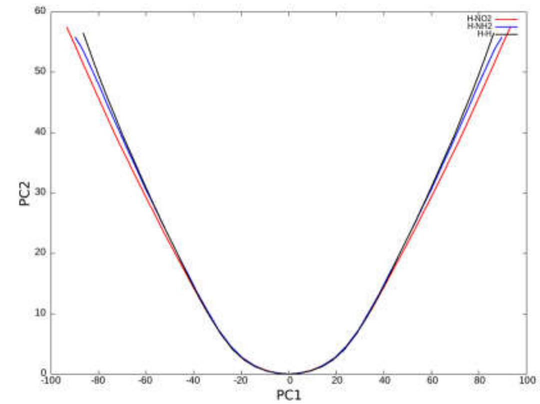


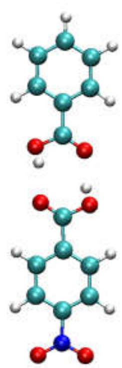
Trajectory Decomposition – Normal Modes



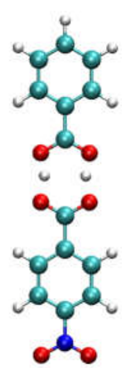
Trajectory Decomposition – Principal Components



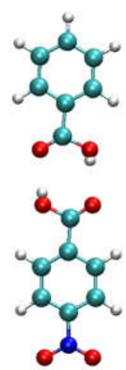




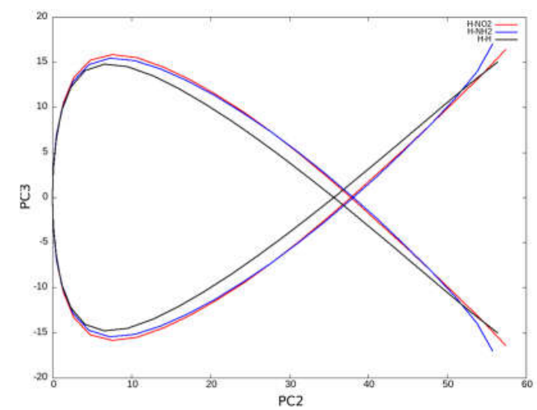
PC1



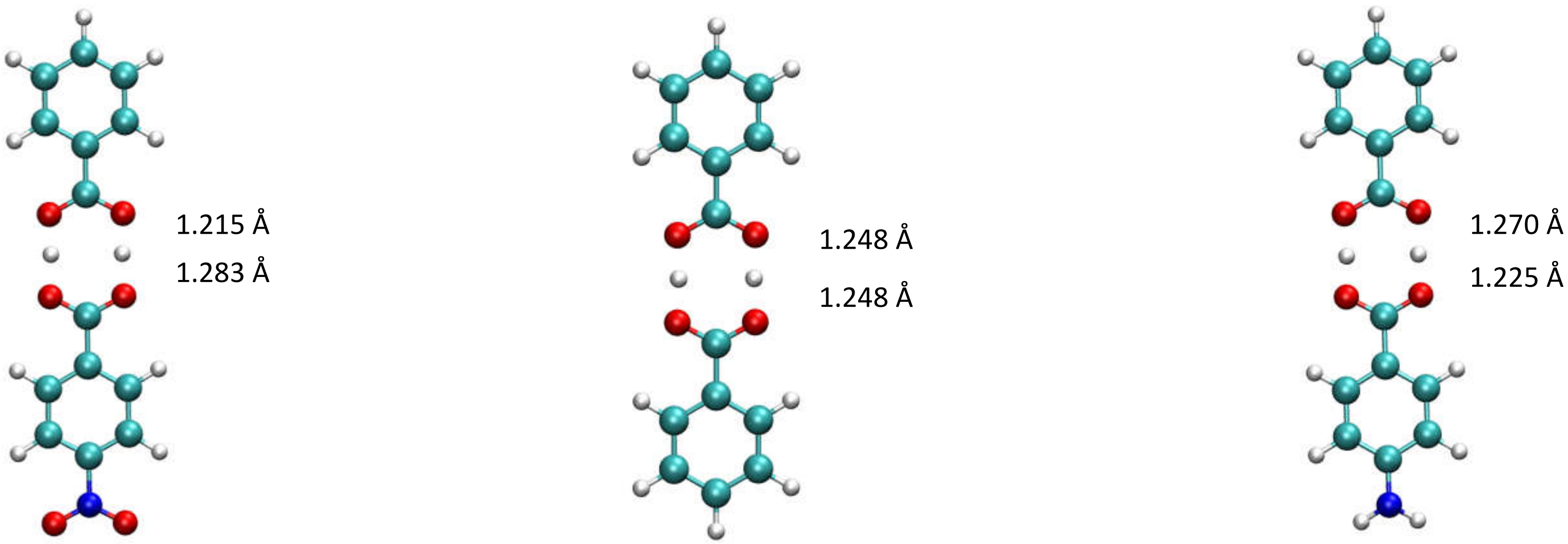
PC2



PC3



Trajectory Decomposition – Barrier Top

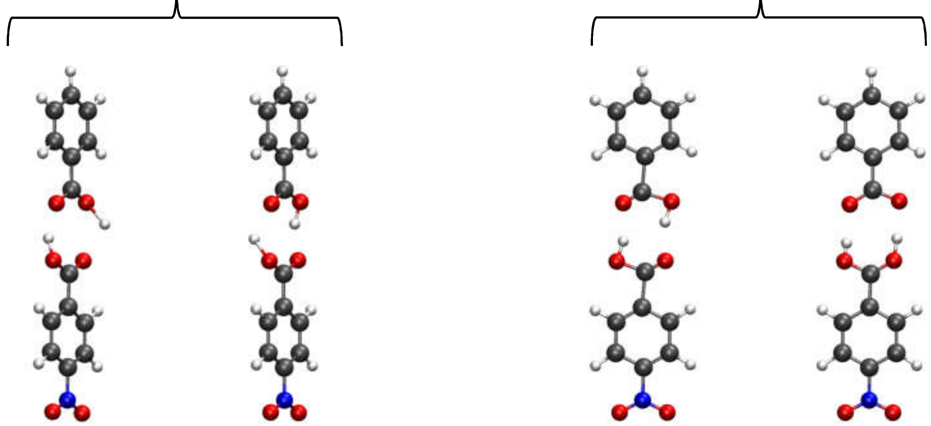


Vibrational Contributions

$$W_1 = \frac{1}{2}\int_0^{S_{\mathrm{cp}}} \frac{\mathrm{Tr}\left(\mathbf{A} \quad \mathbf{A}_0\right)}{\sqrt{2V(S')}}\mathrm{d}S' = \sum_i \frac{1}{2}\int_0^{S_{\mathrm{cp}}} \frac{A_{ii} \quad (A_0)_{ii}}{\sqrt{2V(S')}}\mathrm{d}S'$$

Inhibit tunneling – stiffer along the path

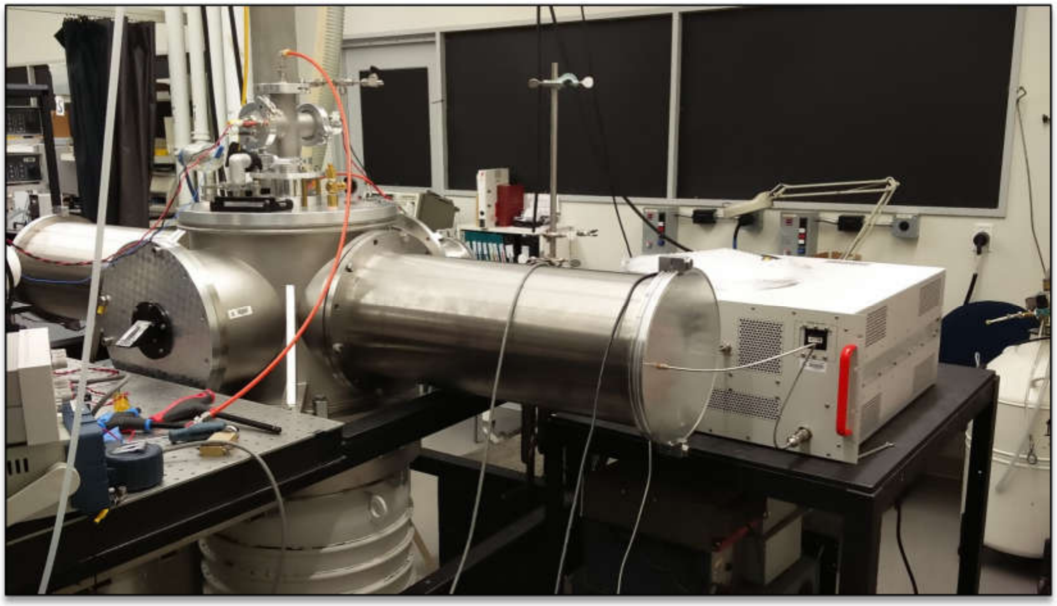
Promote tunneling – looser along the path

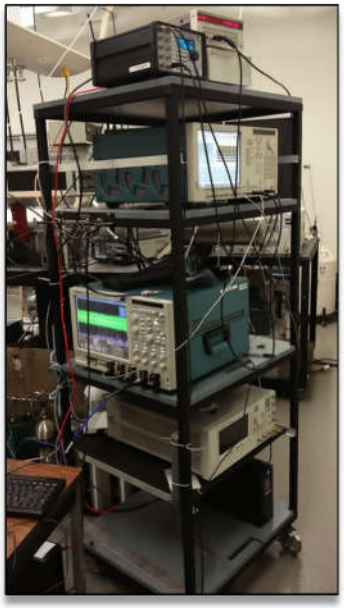


H-NO_2	0.571	0.502	–0.310	–2.186
H-H	0.486	0.522	–0.306	–1.953
H-NH_2	0.509	0.466	–0.277	–1.925

Experimental Data

- Chirped-pulse Fourier Transform Microwave Spectrometer





- Experimental value

$$\Delta(\mathrm{H-NO_2}) = 0.02829\ \mathrm{cm^{-1}}$$

- JFI M062X/6-311+G(2df,2p)

$$\Delta(\mathrm{H-NO_2}) = 1.34\ \mathrm{cm^{-1}}$$

- JFI barrier corrected DLPNO-CCSD(T)/cc-pVTZ

$$\Delta(\mathrm{H-NO_2}) = 0.00807\ \mathrm{cm^{-1}}$$

- More accurate level of theory for path optimization is needed (RICC2,…)

Conclusion

- JFI method can be used to decompose different contributions to tunneling splitting
- JFI is trajectory-based method – interpretation in terms of normal modes and principal components
- Vibrational contributions can be separated in a chosen diabatic basis
- Preliminary results indicate that electron withdrawing substituents decrease, while electron-donating substituents increase the tunneling splittings

Thank you for your attention!

Croatian Science Foundation

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