CONTROLLING INTRAMOLECULAR H-BOND IN ONIUM IONS BY TUNING LONDON DISPERSION - PAULI REPULSION BALANCE

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London Dispersion is an essential element of structural stability and thus affects chemical reactivity and selectivity. However, estimating London forces is challenging due to the omnipresent solvent or crystal lattice effects that attenuate attractive interactions. Here, we report a spectroscopic study of the intramolecular H-bond in five series of onium ions with a systematic increase in Dispersion energy donors (DEDs). Remarkably, the intramolecular H-bond might be localized/delocalized, and therefore its spectroscopic signature is used as a readout reflecting overall steric effects in the system. Therefore, we can probe a delicate London Dispersion - Pauli Repulsion balance by analyzing 2D PESs, applying different energy decomposition schemes, and performing a comparative analysis of experimental data obtained in the gas phase without any external encumbrances, including messenger tags. [1,2] Finally, considering these findings, we can tune the barrier's height to achieve the desired reactivity for the intramolecular H-transfer reaction or, in other words, turn the hydrogen bond ON/OFF upon request.

[1] V. Gorbachev, A. Tsybizova, L. Miloglyadova, P. Chen, *J. Am. Chem. Soc.* **2022**, *144*, 20, 9007–9022
[2] A. Tsybizova, E. Paenurk, V. Gorbachev, P. Chen, *J. Phys. Chem. A* **2020**, *124*, 41, 8519–8528