London dispersion forces under Vibrational Strong Coupling

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Vibrational Strong Coupling (VSC) hybridizes molecular vibrations with the modes of an optical cavity, an interaction mediated by vacuum fluctuations. VSC has been shown to influence the rates and selectivity of chemical reactions.[1,2] However, a clear understanding of the mechanism at play remains elusive.

In order to expand the toolbox of analytical techniques that can be used to probe chemistry under VSC, we recently developed Fabry-Perot cavities compatible with Nuclear Magnetic Resonance (NMR) Spectroscopy.[3] Using these cavities, we showed by studying a conformational equilibrium of a molecular balance that London dispersion forces are altered by VSC. The NMR spectra also show no modification in chemical shifts, J-couplings, and spin-lattice relaxation time (T_1) indicating that VSC does not exert significant electron density redistribution. The behavior of both studied systems indicate that collective effects are present and that the effects of VSC are not to be found at the level of a single molecule.

During the talk I will also address important issues that may arise when measuring UV-vis absorption spectra in transmission mode which we believe will be instructive for the Strong Coupling community.[4]

References

1. Thomas, A.; Lethuillier-Karl, L.; Nagarajan, K.; Vergauwe, R. M.; George, J.; Chervy, T.; Shalabney, A.; Devaux, E.; Genet, C.; Moran, J.; Ebbesen, T. W. *Science*, **2019**, *363*, 615-619.
2. Ahn, W.; Triana, J. F.; Recabal, F.; Herrera, F.; Simpkins, B. S. *Science*, **2023**, *380*, 1165-1168.
3. Patrahau, B.*; Piejko, M.*; Mayer, R.; Antheaume, C.; Sangchai, T.; Ragazzon, G.; Jayachandran, A.; Devaux, E.; Genet, C.; Moran, J.; Ebbesen, T. W. *Angew. Chem. Int. Ed.*, **2024**, e202401368. (* - equal contribution)
4. Piejko, M.; Patrahau, B.; Joseph, K.; Muller, C.; Devaux, E.; Ebbesen, T. W.; Moran, J. *J. Am. Chem. Soc.*, **2023**, *145*, 13215-13222.

Maciej Piejko is a PhD student in the Complex Systems Chemistry Graduate School at the University of Strasbourg. He is working in the group of Prof. Joseph Moran where he studies chemical reactivity under Vibrational Strong Coupling. His other projects include mechanistic DFT calculations and supramolecular catalysis in hexafluoroisopropanol. In 2024 he was awarded the JSPS postdoctoral fellowship to conduct research in polaritonic chemistry at Hokkaido University in the group of Prof. Kei Murakoshi together with Prof. Tomohiro Fukushima.