

Vibrational strong coupling in isotropic and smectic phase liquid crystals

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Strong coupling between molecular vibrations and confined electric fields promises new avenues for chemistry without traditional reagents. When a vibrational transition and a cavity mode are energetically resonant they form a vibrational polariton, a hybrid light-matter quasi-particle that can delocalize over a large number of molecules¹. Vibrational strong coupling is observed in the frequency domain as a mode splitting into upper $|P+\rangle$ and lower $|P-\rangle$ polaritons. Recent studies demonstrate reaction rate modification² and altered branching ratios under vibrational strong coupling³. Despite these exciting results, the mechanisms behind modified reactivity under strong coupling are not yet understood. We investigate the relation between coupling strength and molecular ordering using 4-n-octyl-cyanobiphenyl (8CB) liquid crystals in temperature-dependent ordered and unordered phases.

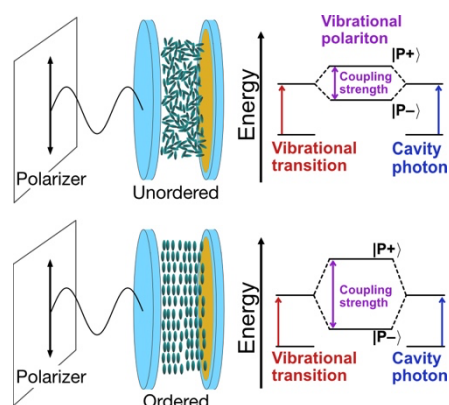


Fig 1. Influence of molecular alignment on the polariton formation. The coupling strength is enhanced when molecules are ordered and the incident light is polarized parallel to the molecular orientation. The coupling strength is less when liquid crystals are isotropic.

We can tune the coupling strength between the cavity mode and the $\text{C}\equiv\text{N}$ stretch mode of 8CB by: (1) heating or cooling the liquid crystals between isotropic and smectic A phases (Fig 1) or (2) adjusting the incident infrared light polarization when 8CB is in the smectic phase. A rubbed polyimide layer aligns the smectic phase molecules inside the cavity. In smectic A phase, light polarized parallel to the molecular orientation yields a ~44% larger coupling strength (48.8 cm^{-1}) compared to perpendicularly polarized light (27.3 cm^{-1}). The molecules become randomly oriented when heated to the isotropic phase, thus the splitting magnitude (37.0 cm^{-1}) is between the parallel and perpendicular splittings observed for the smectic phase. We also find that temperature does not affect the splitting within a given liquid crystal phase. These results show that adjusting the light polarization and temperature can tune the Rabi splitting parameter efficiently through the light-matter coupling between the cavity photon and collective $\text{C}\equiv\text{N}$ stretching motion.

- (1) Herrera, F.; Owrutsky, J. *J. Chem. Phys.* **2020**, 152 (10), 100902.
- (2) Thomas, A., *et al. Angew. Chem. Int. Ed.* **2016**, 55 (38), 11462–11466.
- (3) Thomas, A. *et al. Science* **2019**, 363 (6427), 615–619.