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**Cavity-coupled molecular vibrational spectra and dynamics**[1]
JEFFREY OWRUTSKY, ADAM DUNKELBERGER, JAMES LONG, KENAN FEARS, Chemistry Division, Naval Research Lab, WALTER DRESSICK, Center for Biomolecular Sciences and Engineering, Naval Research Lab, RYAN COMPTON, BRYAN SPANN, BLAKE SIMPKINS, Chemistry Division, Naval Research Lab — Coherent coupling between an optical transition and confined optical mode, when sufficiently strong, gives rise to new modes separated by the vacuum Rabi splitting. Such systems have been investigated for electronic-state transitions, for quantum wells and dots, however, only very recently have vibrational transitions been explored. Both static and dynamic results are described for vibrational bands strongly coupled to optical cavities. First, we experimentally and numerically describe coupling between a Fabry-Perot cavity and carbonyl stretch (˜1730 $cm^1$) in poly-methylmethacrylate as a function of several parameters of the system including absorber strength and concentration as well as cavity length. Similar studies are carried out for anions both in solution and exchanged into cationic polymers. Ultrafast pump-probe studies are performed on $W(CO)_6$ in solution which reveals changes to the transient spectra and modified relaxation rates. We believe these modified relaxation rates are a consequence of the energy separation between the vibration-cavity polariton modes and excited state transitions. Cavity-modified vibrational states and energy transfer may provide a new avenue for systematic control of molecular processes and chemistry.

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