Complete Reconstruction of the Vibrational Wavepacket of Electronically Excited Molecules from Resonant Coherent Anti-Stokes Raman-Scattering

David Avisar* and David J. Tannor
Department of Chemical Physics, Weizmann Institute of Science, Israel

Understanding the mechanisms of chemical reactions is a central goal of chemistry. Most photochemical reactions occur in excited electronic states and are governed by the excited potential energy surface. Except of very small molecules it is extremely challenging to know these potentials with any reasonable degree of accuracy.
In this work we show one can reconstruct the complete excited-state wavefunction (WF) of a reacting molecule [1,2]. Generally, WF reconstruction methods require a priori knowledge of the excited potential. The WF reconstruction methodology we propose uses no a priori information on any excited state, but only of the ground state.
We express the excited-state WF in the basis of the (assumed known) ground vibrational eigenstates. The superposition coefficients can then be extracted from CARS spectroscopy. The method applies to polyatomics, and to dissociative as well as bound excited potentials. Finally, we show that the unknown excited potential can be recovered from the excited WF.

*Current affiliation: Department of Chemistry, Bar-Ilan University, Israel.