

# Development and applications of first principles method for light-matter interactions beyond the dipole approximation

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Near field refers to a non-propagating light field. The interaction between the near-field and molecules can overcome the diffraction limit and can induce non-dipolar excitations, offering a unique platform for nanoscale spectroscopy and microscopy [1], as well as photochemistry [2]. Due to the localization of the near-field, theoretical framework beyond the dipole approximation is required. Thus, we have developed a first principles method based on the multipolar Hamiltonian, in which, the interaction is described by coupling the electric field and the molecular polarization field integrating over the space. The method has been used to study near-field electronic excitations [3] and vibrational excitations, i.e., the near-field IR combined with electrodynamics computations [4].

In this fiscal year, we have developed a method for near-field Raman [5]. The theoretical framework we established for near-field Raman is as follows. First, the multipolar Hamiltonian is implemented into a real-time time-dependent density functional code, namely, Octopus 9.2 [6] and calculate the near-field excited electron dynamics to obtain the induced dipole moment of a molecule in the time domain, which is later Fourier transformed into the frequency domain. The induced dipole moments are calculated  $6N$  times ( $N$  is the number of atom in a molecule) for distorted geometries where one of the  $x$ ,  $y$ , and  $z$  coordinates of an atom is shifted slightly in either the pos-

itive and negative direction to obtain a derivative of the induced dipole moment with respect to the atomic Cartesian coordinate, which is then transformed into the normal coordinate derivative using the transformation matrix obtained by a normal mode analysis, performed separately. Finally, the Raman spectrum is obtained from the square of the absolute value of the normal coordinate derivatives.

As a demonstration, on- and off-resonance near-field Raman of benzene is studied. We showed that the obtained Raman spectra are well understood by considering both the spatial structure of the near field and the molecular vibration in the off-resonance condition. For the on-resonance condition, the Raman spectra are governed by the transition moment, in addition to the selection rule of off-resonance Raman. Interestingly, on-resonance Raman can be activated even when the near field forbids the  $\pi-\pi^*$  transition at equilibrium geometry due to vibronic couplings originating from structural distortions.

**References** [1] R. B. Jaculbia, et al., *Nat. Nanotechnol.* 15, 105 (2020). [2] E. Kazuma et al., *Science*, 360, 521 (2018). [3] T. Iwasa and K. Nobusada, *Phys. Rev. A*, 80, 043409 (2009) and 82, 043411 (2010). [4] T. Iwasa, et al., *J. Chem. Phys.*, 144, 124116 (2016) and 152, 164103 (2020). [6] M. Takenaka, T. Taketsugu, T. Iwasa, *J. Chem. Phys.*, 154, 024104 (2021). [5] X. Andrade, et al., *Phys. Chem. Chem. Phys.* 17, 31371 (2015).