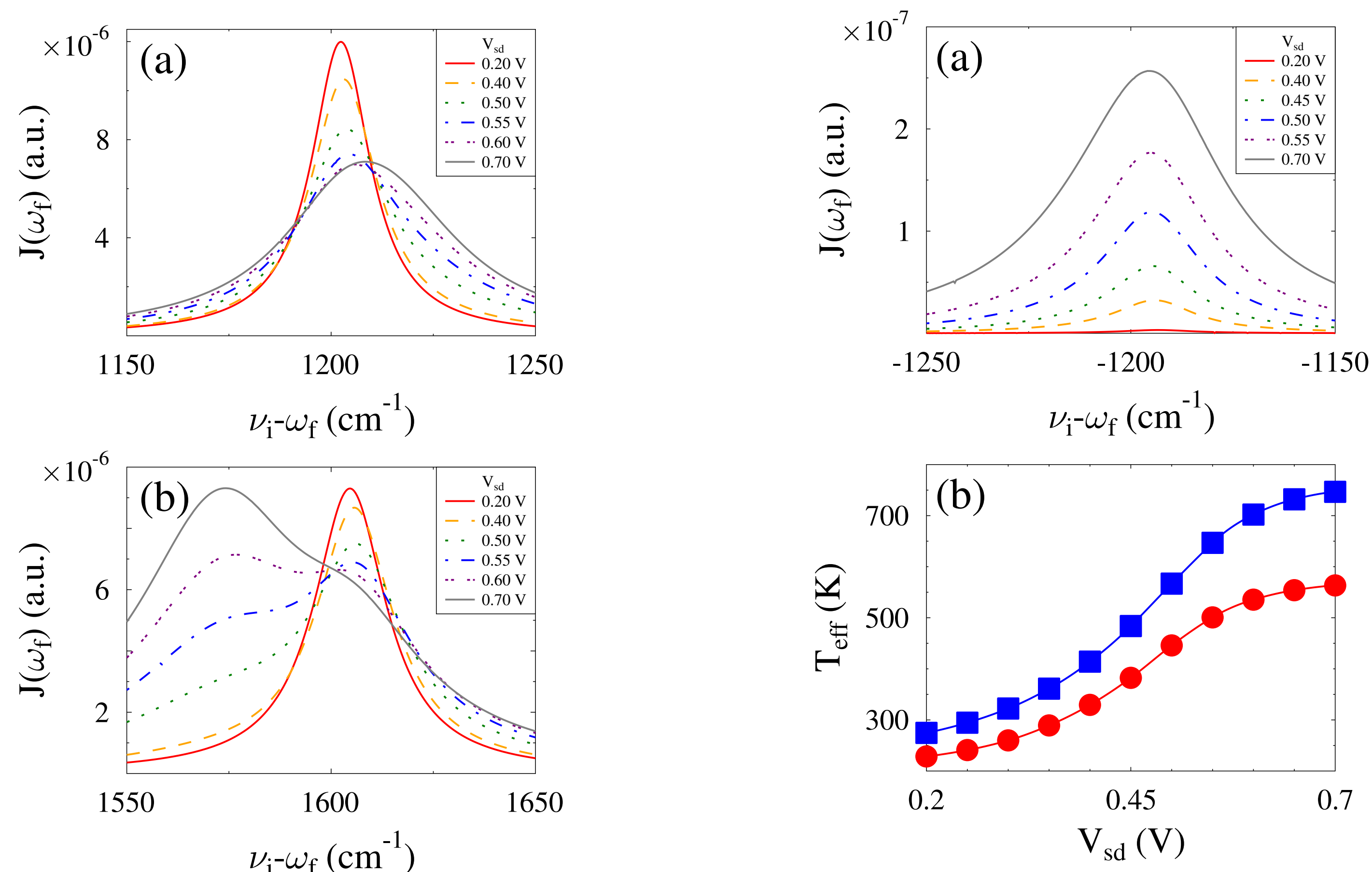
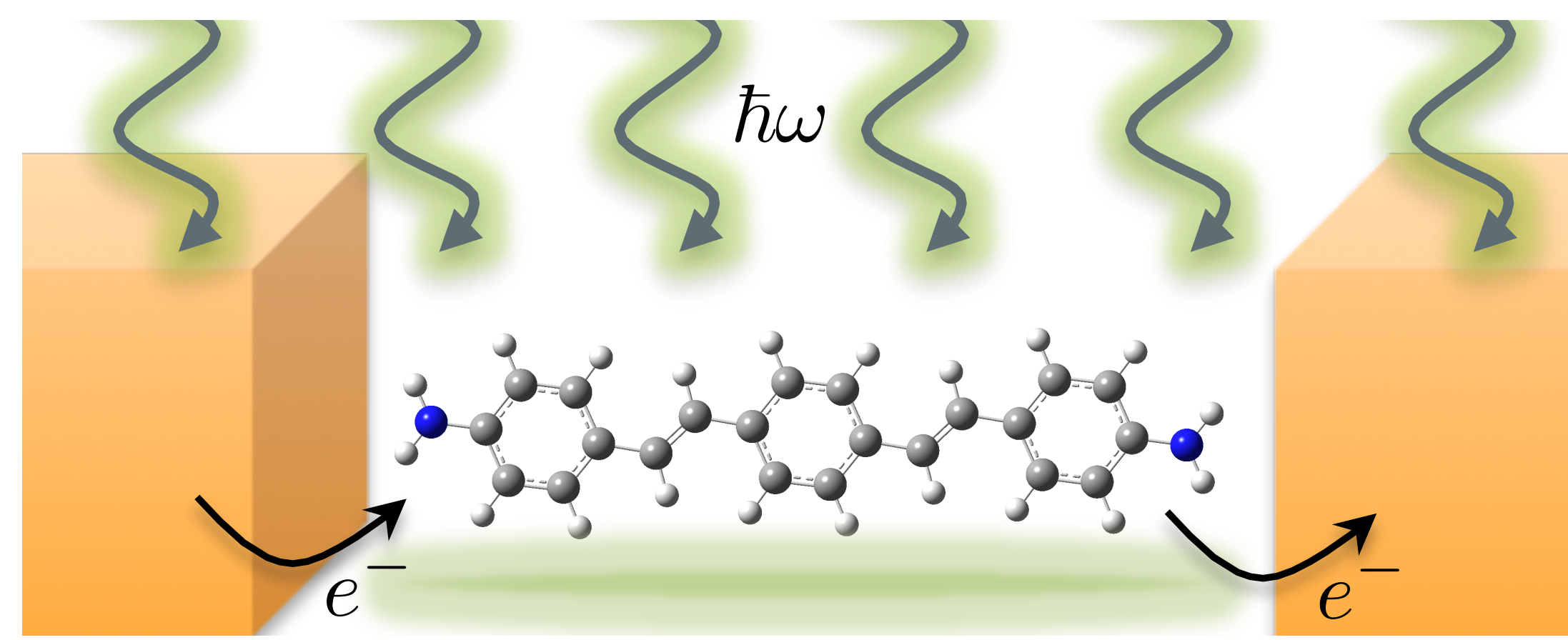


Optical Response of Current Carrying Molecular Junctions

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The Stokes peak vs Raman shift for several source-drain biases V_{sd} . Shown are the results for molecular vibrational modes at (a) 1199 and (b) 1608 cm^{-1} .

Bias induced vibrational heating. (a) The anti-Stokes peak of molecular vibration at 1199 cm^{-1} . (b) Effective temperature vs applied bias for molecular vibrational modes at 1199 (red) and 1608 (blue) cm^{-1} .

Raman Spectroscopy

We developed a pseudo-particle formulation for Raman spectroscopy in molecular junctions. This framework allows us to describe an open non-equilibrium molecular system in the language of many-body states of the isolated molecule. The method treats all intra-molecular interactions exactly, while also keeping the information on hybridization between molecular states and those of the contacts, and on the nonequilibrium electronic population in the molecule. Parameters of the electronic and vibrational structure of the molecule were obtained from DFT and TDDFT quantum-chemical calculations and from experimental data. We believe that the developed method constitutes an important step towards full *ab-initio* calculations of optical response in molecular junctions.

Raman Signal:

$$J(\omega_f) = \sum_{\substack{g_i, g_f, x_1, x_2 \\ \bar{g}_i, \bar{g}_f, \bar{x}_1, \bar{x}_2}} \int \frac{d\omega_i}{2\pi} \iiint \frac{dE_i dE_f dE_x dE_{x'}}{-\zeta_{g_i}(2\pi)^4} \\ 2\pi\delta(\omega_i + E_i - \omega_f - E_f) \Pi_{g_i x_1, \bar{g}_i \bar{x}_1}^<(\omega_i) \Pi_{g_f x_2, \bar{g}_f \bar{x}_2}^>(\omega_f) \\ \times \frac{G_{\bar{g}_f g_f}^>(E_f) G_{\bar{x}_1 \bar{x}_2}^>(E_x) G_{x_2 x_1}^>(E_{x'}) G_{g_i \bar{g}_i}^<(E_i)}{[\omega_i - (E_{x'} - E_i) + i\eta][\omega_f - (E_x - E_f) - i\eta]}$$

Effective Temperature for mode v :

$$J(\nu_i + \omega_v) / J(\nu_i - \omega_v) \approx e^{-\hbar\omega_v / k_B T_{eff}}$$

Molecular Nanoplasmonics

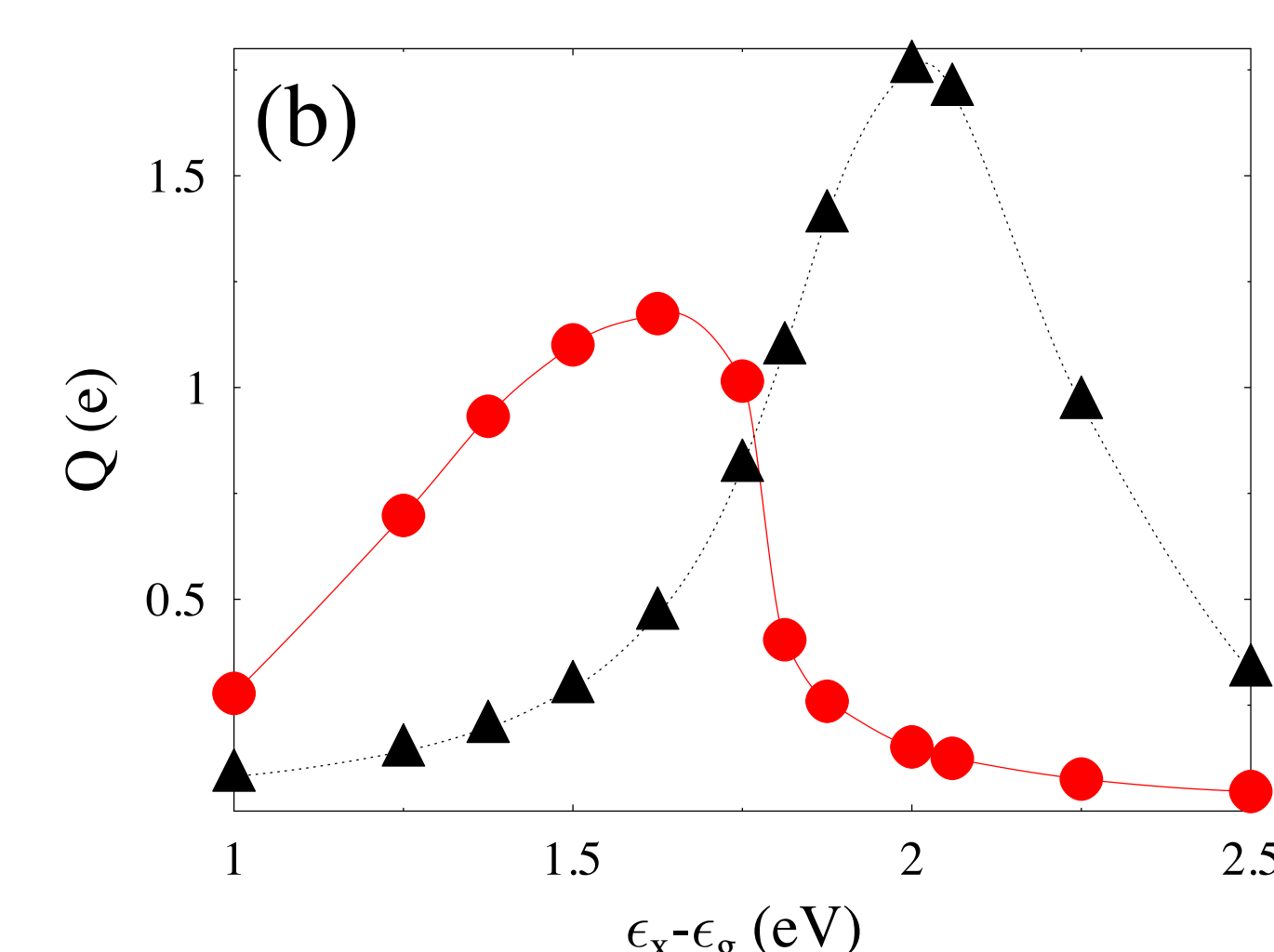
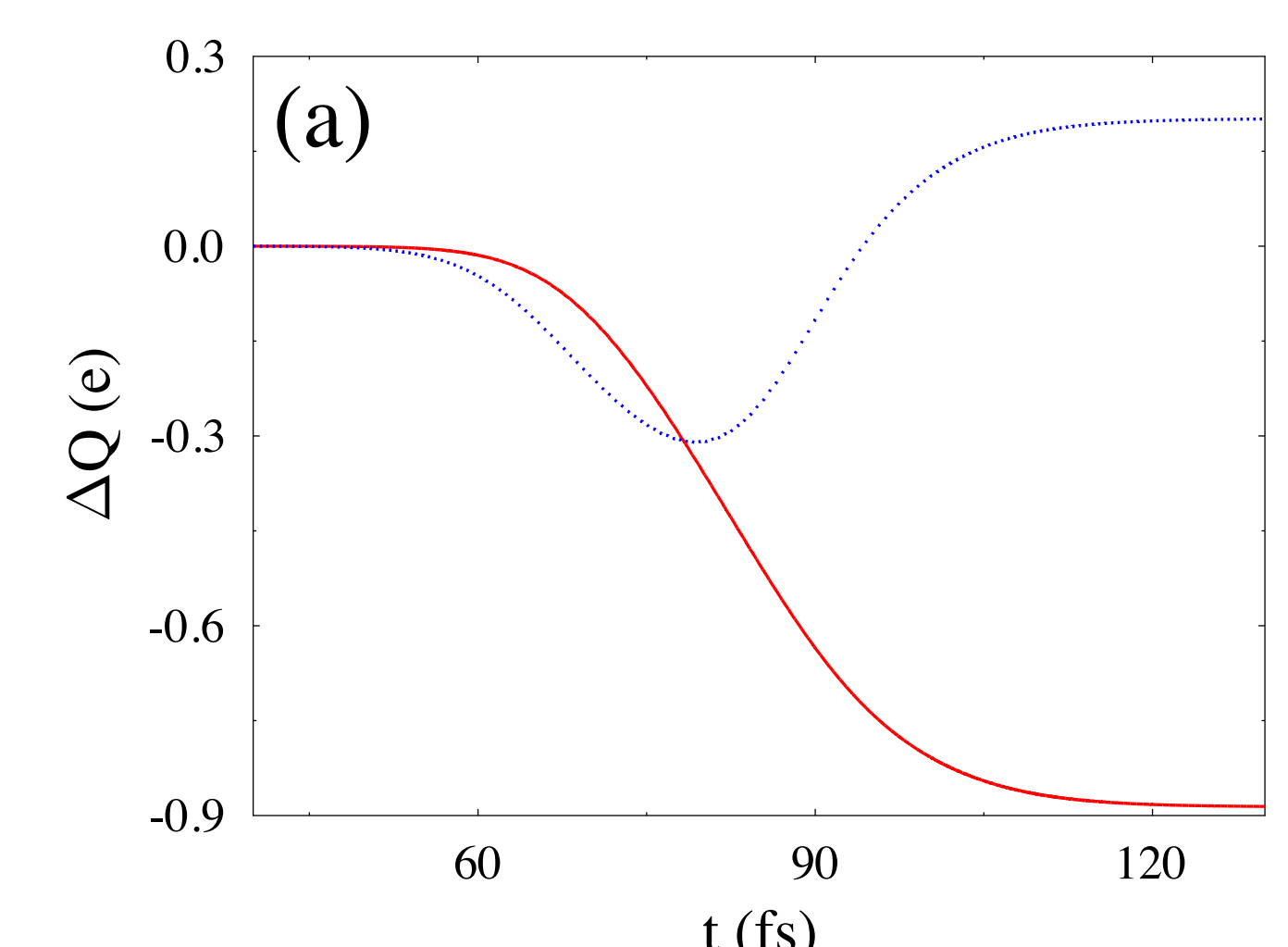
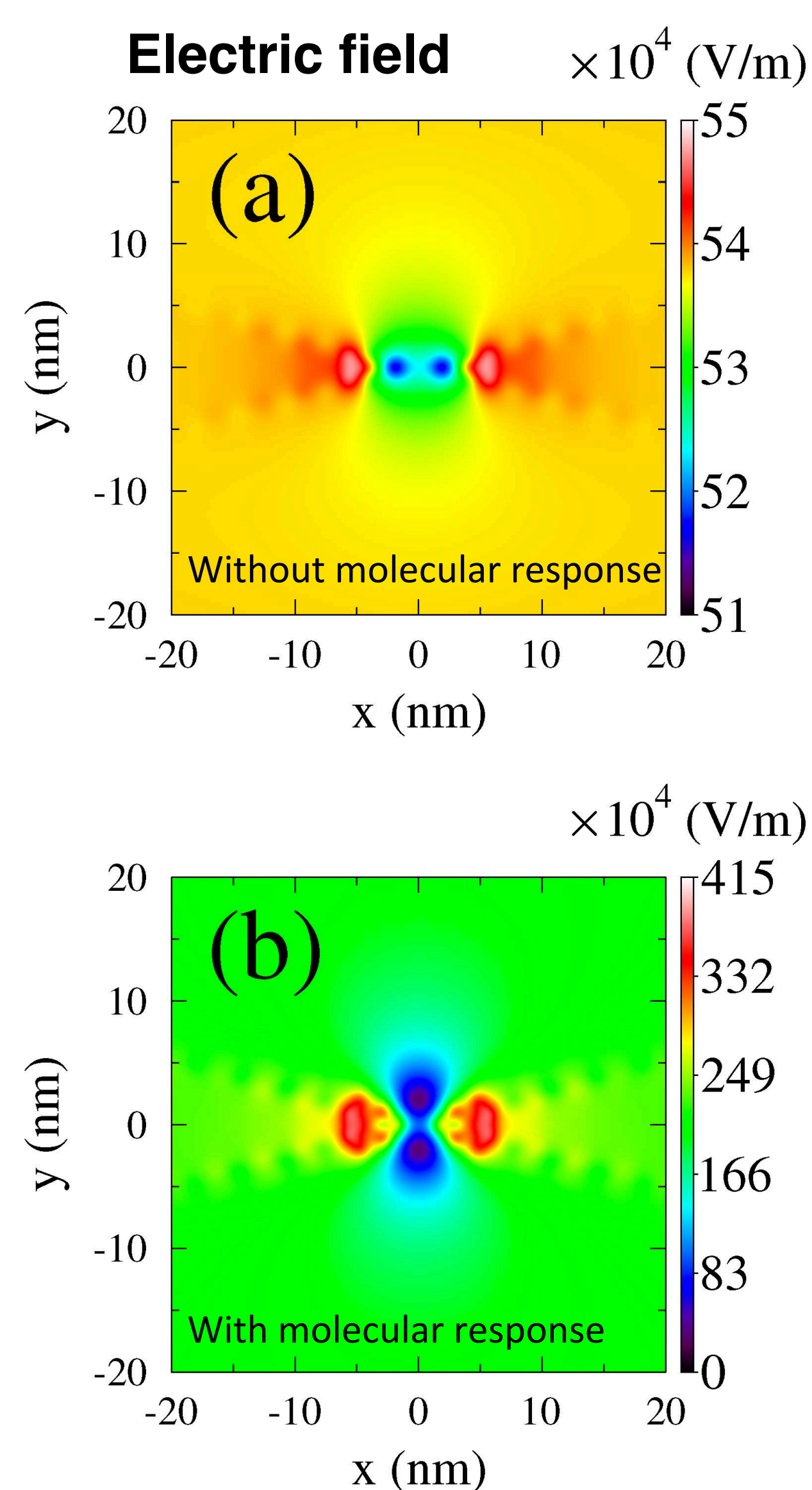
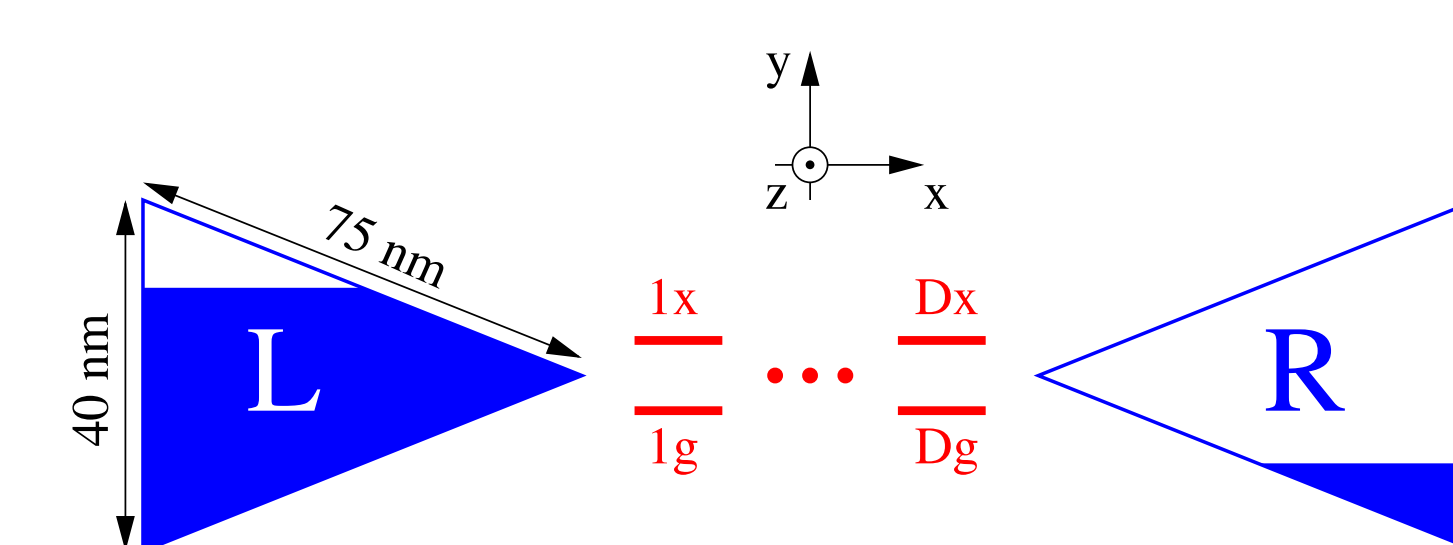
We consider a simple model of a molecular junction driven by external chirped laser pulses. The molecule is represented by a bridge of D two-level systems. The contacts geometry is taken in the form of a bow-tie antenna. The FDTD technique is used to calculate the local field in the junction resulting from SPP excitations in the contacts. Simultaneously we solve time-dependent nonequilibrium Green's function equations of motion to take into account the molecular contribution to the local field formation.

Maxwell's Equations for Electric Field and current density:

$$\mu_0 \frac{\partial \vec{H}(\vec{r}, t)}{\partial t} = -\vec{\nabla} \times \vec{E}(\vec{r}, t) \\ \epsilon_0 \frac{\partial \vec{E}(\vec{r}, t)}{\partial t} = -\vec{\nabla} \times \vec{H}(\vec{r}, t) - \vec{J}(\vec{r}, t) \\ \vec{J}(\vec{r}, t) = \frac{\partial \vec{P}_m(t)}{\partial t} \delta(\vec{r} = \vec{r}_m)$$

NEGF for Polarization:

$$\vec{P}_m(t) = 2 \text{Im}[\vec{\mu}_{m_x, m_g} G_{m_g, m_x}^<(t, t)]$$



Charge pumped through the junction, Q . (a) Difference, $\Delta Q \equiv Q^{(sc)} - Q^{(no\ sc)}$, between results calculated with, $Q^{(sc)}$, and without, $Q^{(no\ sc)}$, molecular response vs. time for $\epsilon_x - \epsilon_g > \omega_0$ (solid line, red) and $\epsilon_x - \epsilon_g < \omega_0$ (dotted line, blue). (b) Total charge pumped during the pulse vs. molecular excitation energy calculated without (triangles, black) and with (circles, red) molecular response. ω_0 is the incoming field frequency, and $\epsilon_x - \epsilon_g$ is the molecular excitation energy.