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Ikki Morichika[a], Fumiya Kusa[b], Akinobu Takegami[b], Satoshi Ashihara[*a]

[a] Institute of Industrial Science, The University of Tokyo,
4-6-1, Komaba, Meguro-ku, Tokyo, 153-8505, Japan
[b] Department of Applied Physics, Tokyo Univ. of Agriculture and Technology,
2-24-16, Nakacho, Koganei, Tokyo, 184-8588, Japan

Abstract

Plasmonic enhancements of optical near-fields with metal nanostructures offer extensive potential for amplifying light-matter interactions. We analytically formulate the enhancement of linear and nonlinear optical responses of molecular vibrations through resonant nanoantennas, based on a coupled-dipole model. We apply the formulae to evaluation of signal enhancement factors in the antenna-enhanced vibrational spectroscopy.

Keywords: infrared spectroscopy, surface plasmons, Fano resonance

I Introduction

Plasmonic enhancements of optical near-fields with metal nanostructures offer extensive potential for enhancing light-matter interactions. One of the successful applications in the infrared (IR) range is surface-enhanced IR absorption spectroscopy (SEIRAS)[1-3].

IR spectroscopy directly accesses to vibrational fingerprints of molecular structures, and is useful for functional studies of bio-molecules. It has been revealed that nonlinear IR spectroscopy is a powerful technique to resolve conformational molecular structures, structural changes, vibrational energy transfer, etc.[4] Its applications are, however, somewhat limited because of relatively small vibrational transition dipole moments. Plasmonic near-field enhancements may solve this issue by amplifying nonlinear light-matter interactions.[5,6]

In this contribution, we analytically formulate the enhancement of optical response of molecular vibrations by resonant nanoantennas based on a coupled-dipole model[7] and evaluate the signal enhancement factor in the antenna-enhanced nonlinear vibrational spectroscopy.

II Optical response of antenna-molecule system

As shown in Fig.1, we consider two point dipoles of a nanoantenna (A) and a molecular vibration (V), which are characterized by the linear polarizability α_A and α_V, respectively, with $\alpha_A \gg \alpha_V$. The incident electric-field E_0 of frequency ω induces an electric dipole moment of the nanoantenna given by

$$p_A = \alpha_A E_0. \qquad (1)$$

Nanoantennas exhibit local-field enhancements owing to half-wave dipole antenna resonances and geometrical effects.[2,5] Through the near-field, this antenna dipole induces dipole moment of the molecular vibration as

$$p_{VA} = \alpha_V \cdot G(r_V, r_A) p_A = \alpha_A G \cdot \alpha_V E_0, \quad (2)$$

where r_A and r_V are positions of the nanoantenna and the molecule, respectively, and G is the Green function describing an electric field by a radiating unit dipole. Here $\alpha_A G$ is regarded as the field-enhancement factor.

Dipole moment of the nanoantenna, induced by the nonlinear response of molecular vibration, is derived as

$$p_{AVA} = (\alpha_A G)^2 \cdot \alpha_V E_0 \equiv \alpha_{A,eff}^L E_0, \qquad (3)$$

where the effective polarizability $\alpha_{A,eff}^L$ is provided. In this way, the nanoantenna amplifies the linear vibrational polarization by the factor $(\alpha_A G)^2$.

We extend the formulation to the case of nonlinear IR spectroscopy. In the IR pump-probe spectroscopy, the third-order nonlinear dipole moment of the nanoantenna, originating from nonlinear vibrational dipole, is formulated in the same manner as described above. At simultaneous resonances of the antenna and the molecular

vibration, effective nonlinear dipole moment of the nanoantenna is approximated as

$$p_{\mathrm{AVA}}^{(3)} = \left(\alpha_A G\right)^4 \cdot \alpha_{\mathrm{V}}^{(3)} E_0^3 \equiv \alpha_{\mathrm{A,eff}}^{\mathrm{NL}} E_0^3, \qquad (4)$$

where $\alpha_{\mathrm{V}}^{(3)}$ and $\alpha_{\mathrm{A,eff}}^{\mathrm{NL}}$ denote the nonlinear polarizability of molecular vibration and the effective nonlinear polarizability of the nanoantenna, respectively. Here we see that the nanoantennas amplifies the nonlinear vibrational polarization by the factor of $(\alpha_A G)^4$.
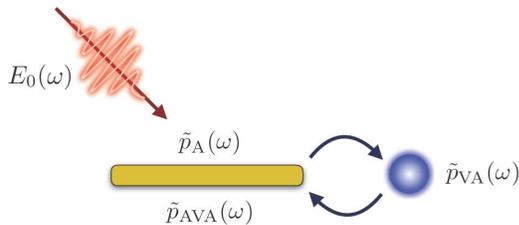
Figure 1. A schematic of the coupled-dipole model.

III Analyses on signal enhancements

Gold nanoantenna arrays are fabricated on a CaF$_2$ substrate. Each nanoantenna is 100-nm wide, 30-nm high, and 1100-nm long. The nanoantennas are arranged at a period of 1.6 µm in longer-axis direction, and at a period of 2.7 µm in shorter-axis direction. Such antenna design results in resonance at around a wavelength of 5 µm with the FWHM width of ~400 cm^{-1}. Figure 2 shows the absorbance spectrum for a W(CO)$_6$-dispersed 200-nm thick PMMA film and the reflectance spectrum for the nanorod arrays covered with the sample film. The IR resonant features of the triply-degenerated T$_{1u}$ C=O stretching mode of W(CO)$_6$ and that of the C=O stretching mode of PMMA are observed at 1980 cm^{-1} and 1737 cm^{-1}, respectively.

Pump-probe reflection spectroscopy is performed by using IR femtosecond pulses. Figure 3 shows the transient reflectance-change spectra for T$_{1u}$ mode of W(CO)$_6$ measured with pump energy of as low as 10 nJ. The increased reflectance is attributed to the depletion of the v = 0 state and stimulated emission from v = 1 state, and the decreased reflectance is attributed to the induced absorption of the v = 1-2 transition. The transient reflectance change at 1 ps is fitted with two Gaussian bands, each of which corresponds to v = 0-1 and v = 1-2 transitions (anharmonicity of 19 cm^{-1}).
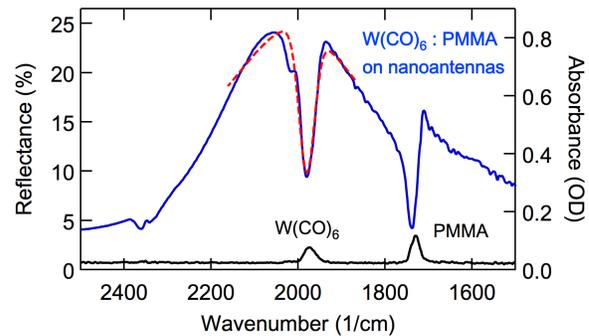
Figure 2. The reflectance spectrum for nanoantenna arrays covered with the sample film (blue line) and the absorbance spectrum for a W(CO)$_6$-dispersed 200-nm thick PMMA film (black line).
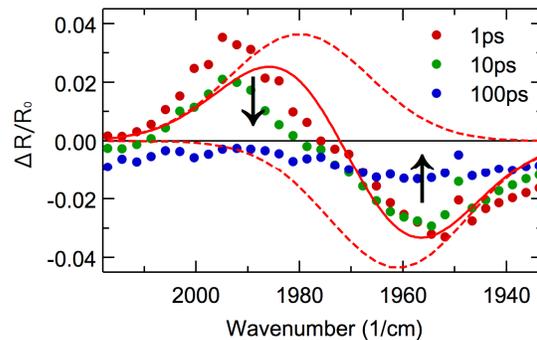
Figure 3. Transient reflectance-change spectra for T$_{1u}$ C=O stretching mode of W(CO)$_6$ wtih nanoantenna arrays. The red solid line represents a fitting curve composed of two Gaussian bands (red dashed line).

By applying Eqs.(3) and (4) to analyze the data shown in Fig.2 and 3, respectively, we extract the linear and nonlinear signal enhancement factors of 6×10^3 and 2×10^7, respectively. The corresponding field enhancement factor is estimated as ~70. Our proof-of-principle experiments, together with the theoretical analyses, demonstrate substantial enhancement of the optical responses of molecular vibrations by resonant nanoantennas.

IV Conclusions

We analytically formulate the enhancement of optical response of molecular vibrations by resonant nanoantennas based on a coupled-dipole model. We apply the formulas to evaluate the signal enhancement factor in

our antenna-enhanced linear/nonlinear vibrational spectroscopy. The local enhancement factor of the nonlinear signal is evaluated to be more than 10^7. The scheme is useful for the study on monolayer material, minute volumes of molecules, and marker vibrational modes with small transition moments.

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