Antenna-enhancements of molecular vibrational responses in ultrafast infrared spectroscopy

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Abstract. We demonstrate surface-enhanced ultrafast vibrational spectroscopy employing periodic arrays of infrared-resonant gold nanoantennas. The antenna-enhancements of molecular vibrational responses are analytically formulated with a simple coupled-dipole model, and the linear/nonlinear local signal enhancements are evaluated to be $\sim 10^4$ and 10^7, respectively.

1 Introduction

Ultrafast infrared (IR) spectroscopy, including pump-probe and two-dimensional methods, is a powerful, label-free tool to resolve molecular conformational structures, structural dynamics, vibrational relaxations, etc. [1]. Despite their fascinating potential, however, their applications are somewhat limited because of insufficient detection sensitivity, which is due to small dipole moments of vibrational transitions. A promising approach for increasing the sensitivity is to amplify the interaction of molecular vibrations with IR ultrashort pulses by employing IR-resonant nanoantennas [2]. Recently, it has been demonstrated that nonlinear vibrational signals are amplified with colloidal gold nanoparticles [3] and randomly-arranged resonant nanoantennas [4]. However, further study is necessary to increase the sensitivity and to add new functionalities for wide use in materials science and life science.

In this contribution, we demonstrate surface-enhanced ultrafast vibrational spectroscopy by using periodically-arranged IR-resonant nanoantennas, which satisfy the condition near the collective resonance [5, 6]. In addition, we analytically formulate the antenna-enhancements of molecular vibrational responses with a simple coupled-dipole model (Fig. 1(a)), and evaluate the linear/nonlinear local signal enhancement factors by analyzing the experimental data with the analytic formulae.

2 Experimental methods and results

We perform linear/nonlinear spectroscopies for a $W(CO)_6$-dispersed 200-nm thick PMMA film, deposited on gold nanoantenna arrays. Each nanoantenna (100-nm wide, 30-nm high, and 1100-nm long) is arranged on a CaF_2 substrate at a period of 2.7 μm (1.6 μm) in the direction of its shorter axis (longer axis). Figure 1(b) shows the reflectance spectrum for the

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sample with nanoantennas (blue) and the absorption spectrum for the sample without nanoantennas (red). The broad resonance peak of the nanoantennas is modulated at the resonance frequencies of the two vibrational modes (T_{1u} CO stretching mode of $W(CO)_6$ at 1980 cm^{-1} and CO stretching mode of PMMA at 1737 cm^{-1}), with spectral features characteristic to Fano resonance. The nonlinear pump-probe spectroscopy is performed in reflection geometry, as shown in Fig. 1(c). The transient reflectance change spectra for T_{1u} mode of $W(CO)_6$ is clearly observed with a pump energy of as low as 10 nJ, as shown in Fig. 1(d), which is due to the substantially-enhanced near-fields of the nanoantenna arrays. The increased reflectance is attributed to the depletion of the v = 0 state and the stimulated emission from the v = 1 state, and the decreased reflectance is attributed to the induced absorption of the v = 1-2 transition. Here we note that the relaxation dynamics, shown in the inset of Fig. 1(d), does not change due to coupling to the nanoantenna.
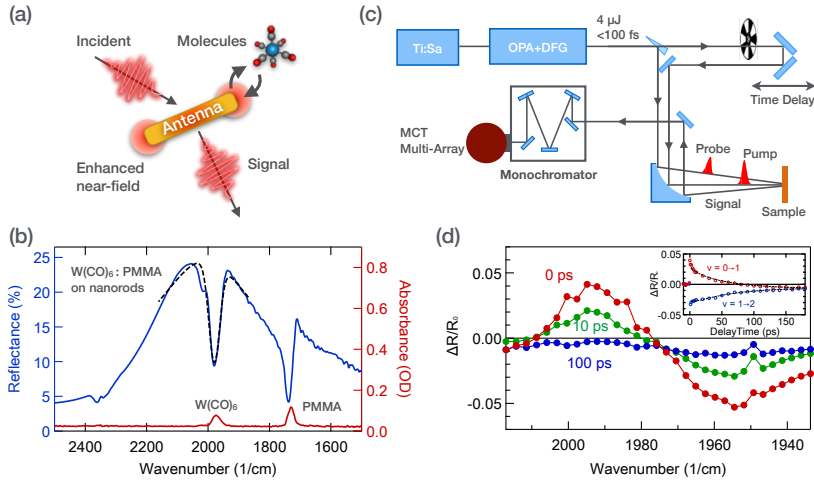

Fig. 1. (a) A schematic of the coupled antenna-molecule system. (b) The reflectance spectrum for the sample with nanoantennas (blue) and the absorption spectrum for the sample without nanoantennas (red). (c) A schematic of the reflection pump-probe system. (d) Transient reflectance change spectra for T_{1u} C=O stretching mode of $W(CO)_6$ interacting with nanoantennas. The inset shows the relaxation dynamics.

3 Analytical formulation and discussion

We consider a coupled-dipole model, where an antenna A and *N*-molecules (V_1, V_2, … ,V_N) are coupled through their near-fields, as illustrated in Fig. 1(a). Here the antenna A and each molecule V_j is characterized by a linear polarizability $\alpha_A(\omega)$ and $\alpha_V(\omega)$, respectively. If the antenna polarizability $\alpha_A(\omega)$ is much larger than the molecular polarizability $\alpha_V(\omega)$, coupled-dipole equations are given in a scalar form as

$$p_A = \alpha_A E_0 + \sum_{j=1}^{N} \alpha_A G(r_j)\, p_{V_j}, \tag{1}$$

$$p_{V_j} = \alpha_V G(r_j) p_A, \tag{2}$$

where r_j is the distance between the antenna and the j-th molecule, and *G* is a Green function, which defines the interaction between the antenna and each molecule. Equation (1) shows

that the antenna experiences an incident field $E_0(\omega)$ and the near-fields created by the molecules, and Eq. (2) shows that each molecule experiences the near-field created by the antenna. The self-consistent solutions are expressed as

$$p_A \equiv \alpha_{A,\text{eff}} E_0 = \frac{\alpha_A}{1 - \alpha_A \alpha_V N \bar{G}_{(2)}^2} E_0, \tag{3}$$

$$p_V = \sum_{j=1}^{N} p_{V_j} \equiv \alpha_{V,\text{eff}} E_0 = \frac{\alpha_A \alpha_V N \bar{G}_{(1)}}{1 - \alpha_A \alpha_V N \bar{G}_{(2)}^2} E_0, \tag{4}$$

where $\bar{G}_{(n)} \equiv \sqrt[n]{\frac{1}{N} \sum_{j=1}^{N} G^n(r_j)}$. Assuming $\alpha_A \alpha_V N \bar{G}_{(2)}^2 \ll 1$, the effective antenna polarizability is given by

$$\alpha_{A,\text{eff}} = \alpha_A + \alpha_V \left(\alpha_A \sqrt{N} \bar{G}_{(2)}\right)^2 E_0, \tag{5}$$

which indicates that vibrational polarization is amplified by a factor of $\left(\alpha_A \sqrt{N} \bar{G}_{(2)}\right)^2 \equiv F_L$. By considering the third-order nonlinear responses of the molecules, the total dipole moment of the antenna is expressed in the same manner as

$$p_A = \alpha_{A,\text{eff}} E_0 + \alpha_V^{(3)} \left(\alpha_A \sqrt[4]{N} \bar{G}_{(4)}\right)^4 E_0^3, \tag{6}$$

where $\alpha_V^{(3)}$ denotes the third-order nonlinear polarizability of each molecule. Here we see that the nonlinear polarization is amplified by a factor of $\left(\alpha_A \sqrt[4]{N} \bar{G}_{(4)}\right)^4 \equiv F_{NL}$. Equations (5, 6) describe that the signal enhancement factors of F_L and F_{NL} increase monotonically with each of the nanoantenna polarizability, the coupling strength, and the number of molecules coupled to the nanoantenna.

By analyzing the data shown in Fig. 1(b, d) using Eqs. (5, 6), we evaluate the signal enhancement factors to be $F_L \sim 10^4$ and $F_{NL} \sim 10^7$. From these numbers, the field enhancement factor is estimated to be $\sim 10^2$, which is in reasonable agreement with FDTD simulations.

4 Conclusions

We successfully demonstrate antenna-enhanced ultrafast vibrational spectroscopy using periodic arrays of IR-resonant nanoantennas. The linear and nonlinear local signal enhancement factors are estimated to be $\sim 10^4$ and $\sim 10^7$, respectively, using the analytic formulae based on the coupled-dipole model. The analytic formulae also indicate that the nanoantenna polarizability, the coupling strength, and the number of molecules should be increased for more linear/nonlinear signal enhancements.

References

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