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Ikki Morichika, Satoshi Ashihara, "Bond-breaking and adsorption of molecules at plasmonic hot-spots initiated by infrared vibrational excitation," Proc. SPIE 11522, Optical Manipulation and Structured Materials Conference 2020, 115221D (15 June 2020); doi: 10.1117/12.2573772

SPIE.

Event: SPIE Technologies and Applications of Structured Light, 2020, Yokohama, Japan

Bond-breaking and adsorption of molecules at plasmonic hot-spots initiated by infrared vibrational excitation

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Abstract

We demonstrate that metal-carbonyl compounds in liquid *n*-hexane are dissociated and adsorbed on gold surfaces upon vibrational excitation. We illuminate gold nanoantennas with temporally-shaped mid-infrared pulses to produce intense plasmonic near-fields. The produced near-fields induce vibrational ladder climbing and the resultant dissociation of metal-carbonyl compounds. A new band, cumulatively increase with irradiation, is attributed to the molecular species which are dissociated and adsorbed on gold surfaces. This demonstration proves that the plasmonic near-fields of mid-infrared pulses are useful for mode-selective reaction control at electronic ground states and for possible subsequent manipulation of molecules like trapping and alignment.

Keywords: pulse shaping, surface plasmon, vibrational ladder climbing, chemical reaction control

I Reaction control with infrared light

Mid-infrared (mid-IR) electromagnetic waves have a great potential not only for vibrational spectroscopy but also for mode-selective chemical reaction control [1,2]. Ultrashort laser pulses in the mid-IR range enable multi-quantum vibrational excitation or vibrational ladder climbing (VLC) [3,4], and therefore open a way to control molecular reactions at their electronic ground states. Molecular dissociation mediated by VLC has been achieved for gas-phase molecules [5], but similar attempts on liquid-phase molecules have been unsuccessful to date, because rapid vibrational relaxation disturb deposition of sufficient energy on a specific mode.

We may overcome this issue by introducing plasmonics, which takes advantage of coupling of light to metal electrons, enabling subwavelength localization, field enhancements, and enhanced light-matter interactions. Plasmonics in the mid-IR has recently been successfully applied to nonlinear vibrational spectroscopy [6,7] and strong-field nonlinear phenomena [8,9].

Here we employ temporal pulse shaping and plasmonic field enhancement of mid-IR pulses to boost VLC, and thereby realize bond-breaking of liquid-phase molecules for the first time (Fig.1) [10]. Interestingly, a new vibrational band emerges upon irradiation and we attribute the band to the dissociated species adsorbed on gold surfaces. In this way, we demonstrate that infrared

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vibrational excitation induces bond-breaking and subsequent adsorption on gold surfaces.

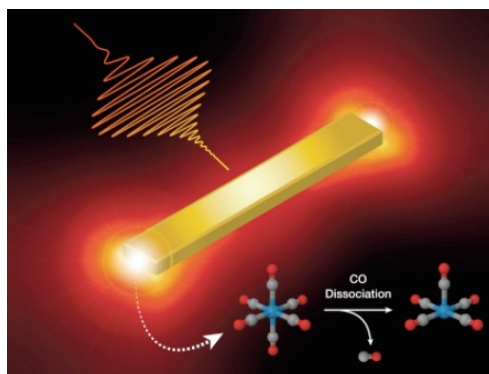


Figure 1. Schematic view of the plasmon-enhanced vibrational ladder climbing. The chirped mid-IR pulse, enhanced with plasmon excitation of the gold nanoantenna, excites the carbonyl stretch vibration of $W(CO)_6$ to induce CO-dissociation.

II Experimental methods

The sample is $W(CO)_6/n$ -hexane solution held between two CaF_2 windows. The target mode is the T_{1u} CO-stretching mode of $W(CO)_6$, which exhibits an absorption at a center frequency of 1983 cm^{-1} with a fwhm linewidth of 3 cm^{-1} (a black line in Fig.2). The gold nanoantenna arrays are patterned on one of the two CaF_2 windows. The reflectance spectrum of the nanoantenna arrays

immersed in $W(CO)_6/n$ -hexane solution is shown in Fig. 2. The broad peak of the antenna resonance is strongly modified at the resonance frequency of the T_{1u} mode because of the coupling between plasmon and the molecular vibration.

We perform mid-IR pump-probe experiments, where the enhanced near-field of the mid-IR pump pulse excites T_{1u} mode. The pump-induced reflectance changes are monitored by the probe pulse with controlled time-delay.

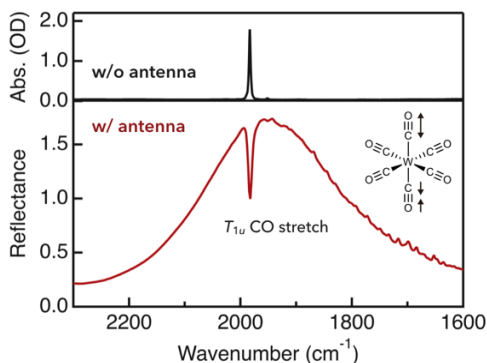


Figure 2. The measured reflectance spectrum for the nanoantenna arrays immersed in $W(CO)_6/n$ -hexane solution (red). The absorbance of the $W(CO)_6/n$ -hexane without nanoantennas are shown as a black line.

III Results and Discussions

The antenna-coupled molecular system exhibits a reflectance change that results from ground-state bleach ($v = 0 \rightarrow 1$) and stimulated emission ($v = 1 \rightarrow 0$), and excited-state absorptions ($v = 1 \rightarrow 2, 2 \rightarrow 3, 3 \rightarrow 4, 4 \rightarrow 5, 5 \rightarrow 6$, and $6 \rightarrow 7$). When pump pulses are down-chirped with the group delay dispersion of -24000 fs^2 , we observe vibrational excitation up to $v = 6$ [10], whose energy is close to the dissociation energy of one W-C bond.

Next we continuously the time-evolution of the reflectance change while irradiating the sample with the down-chirped pump pulse with a fluence of 0.2 mJ/cm^2 and a repetition rate of 1-kHz. Figure 3a shows the transient reflectance change at 1930 cm^{-1} measured at irradiation time of 0-60 min and Fig. 3b shows transient reflectance change spectrum for 60 min, subtracted by the one for 0 min. It is clearly observed that a new band at 1930 cm^{-1} grows cumulatively with the irradiation.

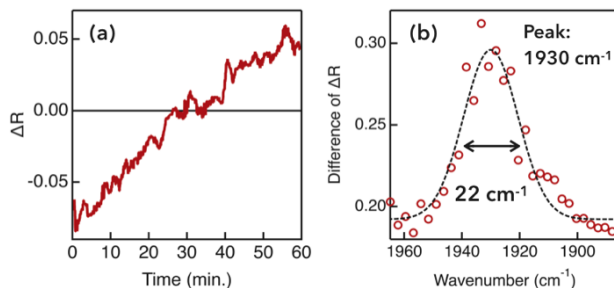


Figure 3. (a) Transient reflectance change at 1930 cm^{-1} measured for different irradiation time of 0-60 min. (b) Transient reflectance change for irradiation time of 60 min, subtracted by the one for 0 min. The dashed line represents Gaussian functions fitted to the data (markers).

The microscopic FT-IR measurement confirms that this new band exists only within the irradiation beam spot. This fact indicates that the new band originates from adsorbates, i.e., CO or $W(CO)_5$ adsorbed on gold surfaces.

According to the theoretical calculations based on the density functional theory, $W(CO)_5$ gets stabilized when adsorbed on gold surfaces and the fundamental transition frequency for A_1 mode of adsorbed $W(CO)_5$ is red-shifted by 45 cm^{-1} compared with that of the T_{1u} mode of $W(CO)_6$, as shown in Fig.4. This frequency shift agrees well with the value of 53 cm^{-1} observed in our experiments. Here, we assign the new band observed at 1930 cm^{-1} to the A_1 CO-stretching mode of $W(CO)_5$ adsorbed on the gold surface.

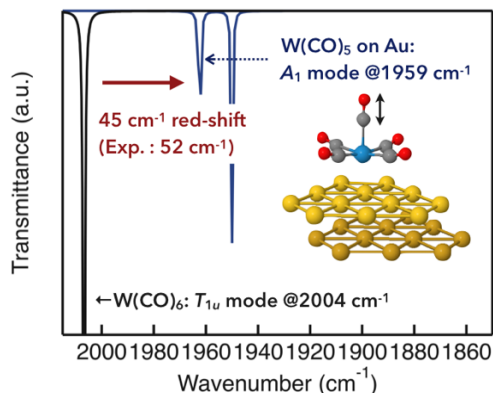


Figure 4. Transmittance of a $W(CO)_6$ molecule (black) and that of a $W(CO)_5$ molecule adsorbed on a gold surface (blue) obtained by density functional theory calculations.

IV Summary

Our experiments demonstrate that the plasmonic near-fields of mid-infrared pulses are useful for mode-selective reaction control at electronic ground states and for possible subsequent manipulation of molecules like trapping and alignment.

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