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

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

II Experimental methods
The sample is W(CO)$_6$/n-hexane solution held between two CaF$_2$ windows. The target mode is the $T_{\text{uv}}$ 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 T₁u 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 T₁u mode. The pump-induced reflectance changes are monitored by the probe pulse with controlled time-delay.

![Figure 2](image)

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 (ν = 0→1) and stimulated emission (ν = 1→0), and excited-state absorptions (ν = 1→2, 2→3, 3→4, 4→5, 5→6, and 6→7). When pump pulses are down-chirped with the group delay dispersion of -24000 fs², we observe vibrational excitation up to ν = 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/cm² 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](image)

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 A₁ mode of adsorbed W(CO)₅ is red-shifted by 45 cm⁻¹ compared with that of the T₁u 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 A₁ CO-stretching mode of W(CO)₅ adsorbed on the gold surface.

![Figure 4](image)

Figure 4. Transmittance of a W(CO)₅ molecule (black) and that of a W(CO)₆ 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.

References