

Femtosecond Free Induction Decay of Metal Surface Adsorbate Vibrations

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Recently there has been intense interest in the vibrational dynamics of molecular adsorbates on simple surfaces [1]. In this contribution we present free induction decay (FID) measurements of the vibrational dephasing of CO adsorbed on Cu(111). To our knowledge this represents the first measurement of a FID signal from an adsorbate on a metal, and the fastest coherent transient IR measurement performed on surface adsorbates thus far. The experiments described are the first in a series of ultrafast surface dynamical studies that are underway in our laboratory.

In the experiment we coherently excited molecular CO with an infrared pulse, and then probed the temporal evolution of this coherence by surface induced upconversion using a time-delayed visible probe pulse. The FID measurements were performed using a Nd:YLF regenerative amplifier based laser apparatus. The system can provide 380 fsec, 5 nJ, $\sim 5 \mu\text{m}$, IR pulses at a 1 kHz repetition rate by difference frequency generation in LiIO_3 . Upconversion of the vibrational coherence was accomplished with 270 fsec, 10 μJ , visible pulses that were also mixed with 527 nm pulses to generate the IR.

The sample consisted of approximately 1/3 monolayer of CO adsorbed on the atop sites of Cu(111) in ultrahigh vacuum (1×10^{-10} torr) at 93 K. The Cu(111) was prepared by standard UHV procedures and then dosed with 0.45 L of CO. A spectrum of the dosed CO surface was taken by IR-visible sum frequency generation after narrowing the frequency spectrum of the IR pulses. The data yielded a central frequency of 2074 cm^{-1} and a FWHM of $4.2(\pm 0.6) \text{ cm}^{-1}$ in agreement with reference [2]. The data also enabled us to determine the relative amplitudes and phase of the non-resonant and resonant metal-adsorbate second-order susceptibilities.

The time domain measurement, along with the IR-visible cross-correlation, is shown in Fig. 1. Interestingly we found that the temporal profile of the infrared ($E_{\text{ir}}(t)$) and visible ($E_{\text{vis}}(t)$) input electric fields could significantly influence the shape of the curve in Fig. 1, and therefore conclusions concerning the total dephasing time. In essence, the resonant and non-resonant contributions of the upconverted field interfere. To account for the interference it is convenient to consider the macroscopic polarization giving rise to the sum frequency signal in the Born-Oppenheimer approximation [3]. In that case the response is given in terms of the macroscopic observables of the surface-adsorbate system. For field envelopes $\mathcal{E}_v^{(j)}(t)$ and $\mathcal{E}_{\text{ir}}^{(j)}(t)$ corresponding to polarization j , the complex macroscopic dipole $P_i(t, \tau)$ oscillating at the sum frequency ($\omega_v + \omega_{\text{ir}}$) is given by:

$$P_i(t, \tau) e^{-i(\omega_{\text{ir}} + \omega_v)t} = \langle \beta_{ijk} \rangle \{ \mathcal{E}_v^{(j)}(t - \tau) \mathcal{E}_{\text{ir}}^{(k)}(t) + \mathcal{E}_{\text{ir}}^{(j)}(t) \mathcal{E}_v^{(k)}(t - \tau) \} + i \mathcal{E}_v^{(j)}(t - \tau) \int_{-\infty}^t dt' \mathcal{E}_{\text{ir}}^{(k)}(t') \{ [\alpha_{ij}, \mu_k(t' - t)] \} e^{i\omega_{\text{ir}}(t' - t)} \quad (1)$$

Here μ_k , α_{ij} and β_{ijk} are the dipole, polarizability and hyperpolarizability operators respectively, and τ the time delay between the visible and the IR pulses. The first term corresponds to the instantaneous (electronic) response from the surface-adsorbate hyperpolarizability. The second term is the polarization resulting from the visible field coupling with the polarizability induced by the infrared field driving the nuclear vibrational motions. If there is no angular motion the nuclear term may be written as:

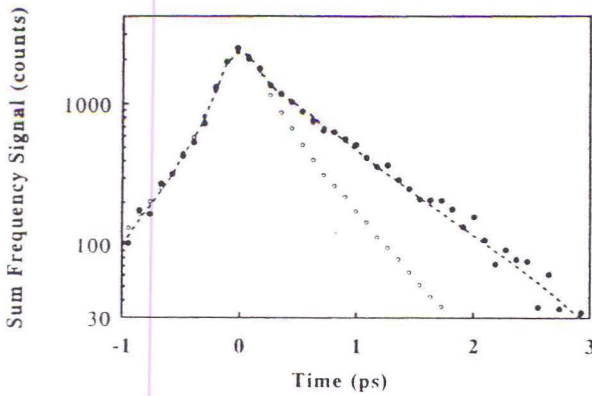


Fig. 1: Measured FID signal (solid circles); IR-visible pulse cross-correlation (open circles); dashed line is our best fit to the data using Eq. 3.

$$-i \left(\frac{d\alpha_{ij}}{dq} \right)_0 \left(\frac{d\mu_k}{dq} \right)_0 \mathcal{E}_v^{(j)}(t - \tau) \int_{-\infty}^t dt' \mathcal{E}_{ir}^{(k)}(t') \langle qq(t' - t) \rangle e^{i\omega_{ir}(t' - t)} \quad (2)$$

and is seen to depend on the polarizability and dipole derivatives of the surface adsorbate system and the convolution of the correlation function of the nuclear displacements, $q(t)$, with the IR field. For a homogeneous system the correlation, or coherence, of the nuclear displacements decays exponentially with a the characteristic decay of T_2 . The signal observed for a time delay τ is the time integral of the square of the sum frequency polarization magnitude, $S(\tau) = \int_{-\infty}^{\infty} dt |P(t, \tau)|^2$. To fit our data we used an equation of the form:

$$S(\tau) = \int_{-\infty}^{\infty} dt I_{vis}(t - \tau) |A \mathcal{E}_{ir}(t) + BG(t)|^2, \quad (3)$$

Here $G(t) = \int_{-\infty}^t dt' \mathcal{E}_{ir}(t') e^{-(t-t')/T_2}$, and the coefficients A and B are functions of β_{ijk} , $\left(\frac{d\alpha_{ij}}{dq} \right)_0$, $\left(\frac{d\mu_k}{dq} \right)_0$ and the IR pulse time-bandwidth product. Using this analysis of the decay and modeling the pulses with gaussian shapes, yields a CO vibrational dephasing time $T_2 = 2 \pm .3$ psec which is in good agreement with our frequency domain results.

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