Direct Time-Domain Observation of Ultrafast Dephasing in Adsorbate-Substrate Vibration under the Influence of a Hot Electron Bath: Cs Adatoms on Pt(111)

Kazuya Watanabe, Noriaki Takagi, and Yoshiyasu Matsumoto*

Department of Photoscience, The Graduate University for Advanced Studies (SOKENDAI), Hayama, Kanagawa, 240-0193, Japan
(Received 15 July 2003; published 3 February 2004)

The stretching vibration of Cs adsorbed on Pt(111) is excited coherently by resonant stimulated Raman excitation and its time evolution is probed by fs time-resolved second harmonic generation as a function of pump laser fluence I. As I increases, a fast dephasing component with the lifetime of $\tau = 0.7$ ps grows, being superimposed on a slow one with $\tau = 1.9$ ps. The fast component is a manifestation of pure dephasing caused by elastic and inelastic scattering of hot electrons at adsorbate.

The advent of femtosecond laser technology provides exciting opportunities to probe chemical reactions in real time and even to control their outcomes [1]. Laser pulses whose duration is sufficiently shorter than the vibrational period of a molecule make it possible to create coherent nuclear vibrational motion. Further interactions of a molecule with the radiation field of subsequent laser pulses can drive the molecule to a reaction pathway in a controlled fashion. In fact, tailored light pulses have been successfully used to control some chemical reactions in gas and liquid phases [2]. The major obstacle for this type of reaction control is various incoherent perturbations from the heat bath that molecules interact with. Therefore, it is vital to know how coherence is lost by incoherent perturbations and clarify the most effective cause for energy and phase relaxation to establish coherent control in the condensed phase.

Photochemistry at metal surfaces is of great interest fundamentally and practically. It is fascinating to control reactions at metal surfaces by a sophisticated use of the interaction of light with matter. However, this is a great challenge, since strong interactions of adsorbates with metals, the sea of electrons, are to lead a rapid loss of coherence. Thus, the first step toward the coherent control at metal surfaces is to understand the dephasing dynamics of coherently excited nuclear motion. Petek and co-workers [3] are the first who have succeeded in creating and probing a nuclear wave packet in an excited state of Cs adsorbed on Cu(111) by time-resolved two-photon photoemission spectroscopy. On the other hand, we have briefly reported the nuclear wave packet dynamics in the ground electronic state of submonolayer Cs adsorbed on Pt(111) by means of fs time-resolved second harmonic generation (TRSHG) [4]. These are a few exceptional studies directly observing the dynamics of coherently excited adsorbate motion with respect to metal surfaces.

When a metal surface is irradiated with an ultrashort light pulse, electrons in the metal are highly excited. Since the interactions of adsorbates with such highly excited electrons are inherently incoherent, hot electrons

will play a pivotal role in vibrational dephasing. Dephasing dynamics of vibrational motions under the influence of hot electrons have been investigated theoretically [5,6] and experimentally [7,8] in conjunction with desorption induced by multiple electronic transitions (DIMET) [9–14]. However, the dynamics of adsorbate-substrate vibrational motions most relevant to DIMET have been probed only *indirectly* by measuring transient shifts and broadenings of the spectral line of an intra-adsorbate vibrational mode [7,8].

In this Letter, we report the direct time-domain observations of nuclear wave packet dynamics in an adsorbate-substrate vibrational motion of Cs adsorbed on Pt(111), i.e., Cs-Pt stretching, under the influence of hot electrons in Pt substrate. We found that an ultrafast dephasing component grows as the laser fluence increases and that TRSHG traces deviate from a single exponential damped oscillating function observed at low fluence. We address possible roles of hot electrons in pure dephasing that is mostly responsible for the ultrafast dephasing component.

Experiments were carried out by an ultrahigh vacuum chamber equipped with a cylindrical mirror analyzer for Auger electron spectroscopy (AES). A clean Pt(111) surface at 110 K was exposed to Cs atoms supplied from a well-degassed alkali dispenser (SAES getters). The Cs coverage θ was determined by AES and work function measurements. The method for TRSHG measurements has been described in detail elsewhere [4]. Briefly, near-infrared (800 nm) laser pulses with 150 fs duration from a Ti:sapphire regenerative amplifier (Spectra Physics, Spitfire, 1 kHz) were separated into two beams that were used as pump and probe pulses, respectively. The two beams with p polarization were focused with a good spatial overlap on the sample surface in the chamber, and p-polarized second harmonic (SH) signals of the probe pulses generated coaxially were detected by a photomultiplier. The pump-induced change in the SH signals, $\Delta I_{2\omega}(t) = I_{2\omega}(t) - I_{2\omega}^0(t)$, was recorded as a function of the pump-probe delay time t, where $I_{2\omega}(t)$ and $I_{2\omega}^0(t)$ are the SH intensities with and without irradiation of a pump

pulse, respectively. The sample temperature T_s was kept at 110 K during the measurement, unless noted specifically.

The coherent motion of Cs atoms modulates the electronic state at the surface and thereby the second order nonlinear susceptibility that is responsible for the SHG intensity [4]. Figure 1 shows a typical trace of $\Delta I_{2\omega}(t)$. After a sharp spike at $t \sim 0$, a clear oscillatory signal is observed up to $t = 5$ ps. The initial spike is due to the SH signal of a pump pulse scattered into the detector as a result of coherent coupling of pump and probe pulses. Thus, we concentrate hereafter on the traces in $t > 400$ fs. The oscillatory signal under the pump fluence of 1.7 mJ/cm^2 is fitted well with a single damped oscillator, $A_1 \cos(\omega_1 t + \phi_1) e^{-\Gamma_1 t}$, with a frequency of $\omega_1/2\pi = 2.29 \pm 0.01$ THz and a dephasing time of $1/\Gamma_1 = 1.9 \pm 0.1$ ps. Since this frequency is close to those of the Cs-substrate stretching vibrational modes on Cu(100) [15] and Ru(0001) [16], this oscillatory feature can be viewed as a manifestation of the vibrational wave packet motion of the Cs-Pt stretching mode.

TRSHG signals were strongly enhanced in the range of 0.24 ML $< \theta < 0.4$ ML (1 ML $= 1.5 \times 10^{15}$ cm^{-2}) with a maximum amplitude at $\theta = 0.26$ ML, where Cs adsorbates are known to form a $p(2 \times 2)$ structure [17]. At this coverage region, it is likely that the photon energy (1.5 eV) is in resonance with an interband transition between Cs-induced states [18]. Since the Cs-induced electronic excited state is quenched within a few tens of fs [3], the vibrational coherence in the electronic excited state does not contribute to the TRSHG signals considered here. Instead, the wave packet dynamics responsible for the signals are coherent Cs-Pt stretching vibrational motion on the ground potential energy surface created by resonantly enhanced impulsive Raman excitation.

As the fluence of the pump pulse I increases, a new feature emerges in TRSHG traces. Figure 2(a) shows the pump fluence dependence of TRSHG traces. The initial modulation amplitude rapidly increases with I and it

decays much faster. The TRSHG traces are no longer described by a single damped oscillating function, but they are well fitted to the following linear combination of two oscillating components,

$$\Delta I_{2\omega}(t) = \sum_{i=1,2} A_i \cos(\omega_i t + \phi_i) e^{-\Gamma_i t}. \qquad (1)$$

The obtained parameters are tabulated in Table I.

The emergence of the rapidly decaying components is correlated with a transient heating of the electronic temperature of the substrate, T_e. Figure 2(b) shows the temporal variations of T_e and lattice temperature T_l as a function of I, obtained by numerical integrations of a pair of coupled diffusion equations [19,20]. Under irradiation with a fluence of $I = 13$ mJ/cm^2, T_e reaches more than 4000 K at $t \sim 100$ fs, while T_l rises more slowly and stays at an almost constant temperature of $\sim$2000 K after $t \sim 1.5$ ps. Although the surface suffered from substantial temperature jumps, the signal wave forms were almost identical throughout repeated measurements. Thus, we believe that fatal surface modifications due to Cs desorption or Pt substrate ablation did not occur even with the highest fluence in this study.
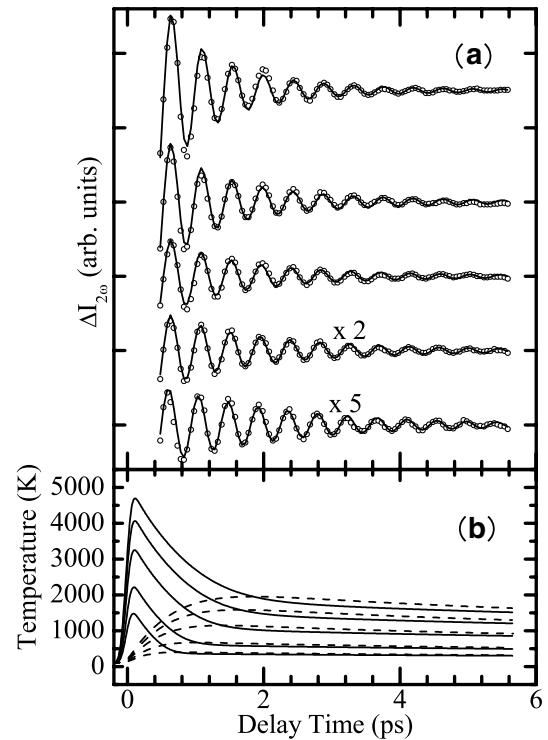
FIG. 2. (a) Pump fluence dependence of the TRSHG traces and (b) calculated electronic (solid curves) and lattice temperatures (dashed curves) at a Pt surface. $I = 1.7, 3.4, 6.7, 10,$ and 13 mJ/cm^2 from the bottom to the top traces for each panel. Solid curves in (a) are fitting results by Eq. (1). The calculations were performed with the laser pulse width of 150 fs and the thermodynamic parameters of Pt taken from Ref. [19].
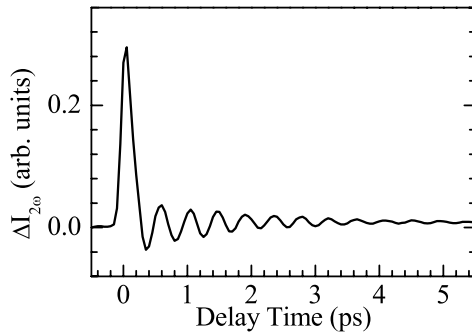

FIG. 1. A typical trace of TRSHG taken from Cs/Pt(111). The surface was covered with Cs of 0.27 ML and the temperature was kept constant at 110 K while irradiated with pump pulses of 3.4 mJ/cm^2.

TABLE I. Parameters obtained from fittings of the oscillatory traces in Fig. 2 by Eq. (1) with the fixed values of $\omega_1/2\pi = 2.29$ THz and $1/\Gamma_1 = 1.9$ ps.

Fluence (mJ/cm^2)	A_1	ϕ_1 (deg.)	A_2	$\omega_2/2\pi$ (THz)	ϕ_2 (deg.)	$1/\Gamma_2$ (ps)
13	1.8 ± 0.6	177 ± 21	15.7 ± 1.5	2.21 ± 0.02	208 ± 5	0.70 ± 0.07
10	1.5 ± 0.7	182 ± 29	8.7 ± 1.1	2.22 ± 0.02	214 ± 7	0.90 ± 0.12
6.7	2.1 ± 0.5	193 ± 15	4.0 ± 0.7	2.22 ± 0.02	198 ± 10	1.02 ± 0.16
3.4	1.9 ± 0.2	209 ± 8	0.7 ± 0.3	2.20 ± 0.03	177 ± 26	1.57 ± 0.48
1.7	1.0	221 ± 2	$\cdots$	$\cdots$	$\cdots$	$\cdots$

In general, the dephasing rate of an ensemble of coherently excited vibrational systems is governed by population decay and pure dephasing. At metal surfaces population decay is caused by electron-hole (*e-h*) pair excitation and direct coupling to substrate phonon. The rate of the population decay in both of the channels at a finite temperature is independent of temperature as long as a vibrational mode is treated as a harmonic oscillator [6]. However, the dephasing rate of the current system clearly depends on laser fluence and hence substrate temperature. Thus, pure dephasing likely contributes to the fast dephasing component. Note that the fast dephasing component dominates in $t < 1.5$ ps, where T_e is expected to be significantly high. This indicates that hot electrons play an important role in the appearance of the fast dephasing component in the high fluence range.

There are two ways for hot electrons to give rise to pure dephasing: elastic and inelastic scattering at adsorbate. First, even if hot electrons are scattered elastically, the phase of vibrational wave packet motion is interrupted and shifted. This random perturbation causes pure dephasing. Morawitz [21] predicted that the rate of dephasing due to e-h pair scattering increases with T_e^3. In the current system, the dephasing rate of the fast component increases from 0.64 to 1.43 ps^{-1} as I increases from 3.4 to 13 mJ/cm^2. From the calculation results in Fig. 2(b), it is clear that the rate is almost proportional to the maximum of T_e attained with the fluence utilized. Thus, the rate does not depend so steeply on T_e as the theory predicted.

Second, the inelastic scattering of hot electrons excites the lateral modes of Cs. Multiple inelastic scattering results in populating higher vibrational states as in the case of DIMET. We expect that the lateral modes on Pt(111) have similar low frequencies as those on Cu(001) reported in the range of 0–5 meV (0–1.2 THz) [22]. Anharmonic couplings between the stretching mode and the highly excited low frequency lateral vibrational modes introduce frequency modulations of the Cs-Pt stretching mode, leading to pure dephasing [23]. Although T_l increases at much slower rates than those of T_e, the increase in T_l within an excitation pulse is rather substantial. If energy transfer were effective from bulk phonons to the lateral modes, these modes would be also excited by hot bulk phonons. However, the calculations

based on the elastic continuum model [24] suggest that the damping rate of the lateral modes is slow, i.e., $1/30$ ps^{-1}, indicating the energy transfer from bulk phonons would be ineffective within the time scale of a few picoseconds. Consequently, the inelastic scattering of hot electrons is likely responsible for the excitation of lateral modes, which leads to the pure dephasing.

At the coverages the current study employed unoccupied Cs-induced states relevant to the scattering of hot electrons would be metallic quantum well states in the Cs adlayer as in the case of Na on Cu(111) [25]. Hot electrons whose energy matches to those of unoccupied quantum well states are resonantly scattered. As I increases, resonant scattering of hot electrons becomes more frequent. The number of hot electrons resonant with the unoccupied states will increase nonlinearly with I. Thus, in both cases of elastic and inelastic scattering, the extent of pure dephasing contribution in TRSHG traces will show nonlinear dependence on I. In fact, Fig. 3 shows that the amplitude of the fast component increases as $I^{2.2}$. This is consistent with the hot electron mechanism.

Pure dephasing due to the anharmonic coupling with lateral modes is evident in the initial temperature dependence of TRSHG traces. When the sample temperature T_s is increased from 110 to 400 K while the laser fluence was kept constant at $I = 3.4$ mJ/cm^2, the dephasing rate increases monotonously with T_s [26] and becomes about twice as large as that at $T_s = 110$ K. Since the vibrational
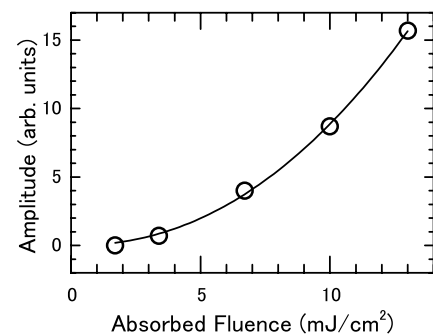

FIG. 3. A variation of the amplitude A_2 as a function of I. A solid curve is a fitting result showing that A_2 increases with I nonlinearly as $I^{2.2}$.
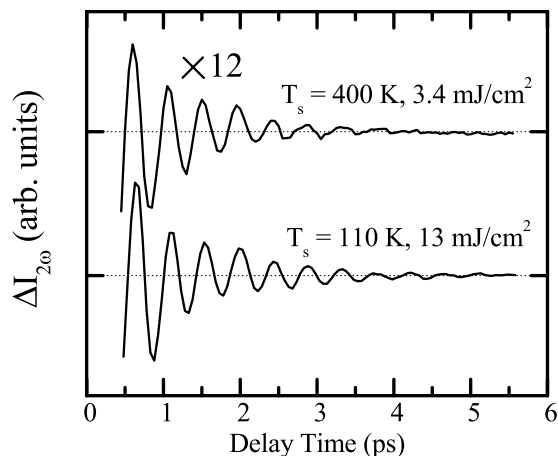
FIG. 4. Comparison of TRSHG traces in two different conditions. The upper trace: the initial surface temperature $T_s = 400$ K, fluence $I = 3.4$ mJ/cm^2, the lower trace: $T_s = 110$ K and $I = 13$ mJ/cm^2.

frequencies of the lateral modes are very small, the highly excited stated of the modes are populated at $T_s = 400$ K prior to the arrival of a pump pulse. These excited states will couple to the stretching mode via potential anharmonicity. In Fig. 4, the TRSHG trace taken under $T_s = 400$ K and $I = 3.4$ mJ/cm^2 is plotted in comparison. The remarkable resemblance between the TRSHG traces depicted in Fig. 4 indicates that very effective excitation of the lateral modes by inelastic scatterings of hot electrons takes place when the high laser fluence is utilized.

In summary, we performed the first observation of the nuclear wave packet motion of Cs adsorbates on Pt(111) under the influence of hot electrons in the Pt substrate. An ultrafast dephasing component appears as the pump fluence increases. Hot electrons play a major role in pure dephasing that mostly contributes to the ultrafast dephasing. Elastic scattering of hot electrons induces a phase shift of the vibrational motion. Inelastic scattering of hot electrons excites the lateral modes of adsorbate that couple with the stretching mode via potential anharmonicity. Both scattering processes cause pure dephasing.

*Electronic address: matsumoto@soken.ac.jp
Also at Institute for Molecular Science, Okazaki 444-8585, Japan.

[1] J. C. Polanyi and A. H. Zewail, Acc. Chem. Res. **28**, 119 (1995).
[2] A. Assion et al., Science **282**, 919 (1998).
[3] H. Petek et al., Science **288**, 1402 (2000).
[4] K. Watanabe, N. Takagi, and Y. Matsumoto, Chem. Phys. Lett. **366**, 606 (2002).
[5] J. Tully and M. Gomes, J. Vac. Sci. Technol. A **11**, 1914 (1993).
[6] B. N. J. Persson and J. W. Gadzuk, Surf. Sci. Lett. **410**, L779 (1998).
[7] T. A. Germer et al., Phys. Rev. Lett. **71**, 3327 (1993).
[8] J. Culver et al., Surf. Sci. **368**, 9 (1996).
[9] J. A. Prybyla et al., Phys. Rev. Lett. **64**, 1537 (1990).
[10] F. Budde et al., Phys. Rev. Lett. **66**, 3024 (1991).
[11] J. A. Misewich, T. F. Heinz, and D. M. Newns, Phys. Rev. Lett. **68**, 3737 (1992).
[12] F. J. Kao et al., Phys. Rev. Lett. **71**, 2094 (1993).
[13] J. A. Misewich, T. F. Heinz, P. Weigand, and A. Kalamarides, *Laser Spectroscopy and Photochemistry on Metal Surfaces* (World Scientific, Singapore, 1995), Chap. 19.
[14] L. M. Struck et al., Phys. Rev. Lett. **77**, 4576 (1996).
[15] G. Witte and J. P. Toennies, Phys. Rev. B **62**, R7771 (2000).
[16] P. He and K. Jacobi, Phys. Rev. B **53**, 3658 (1996).
[17] T. Kondo, H. Kozakai, T. Sasaki, and S. Yamamoto, J. Vac. Sci. Technol. A **19**, 2866 (2001).
[18] N. Fischer et al., Surf. Sci. **314**, 89 (1994).
[19] T. A. Germer et al., J. Chem. Phys. **98**, 9986 (1993).
[20] D. Burgess, Jr., P. C. Stair, and E. Weitz, J. Vac. Sci. Technol. A **4**, 1362 (1986).
[21] H. Morawitz, Phys. Rev. Lett. **58**, 2778 (1987).
[22] G. Witte and J. P. Toennies, Phys. Rev. B **62**, R7771 (2000).
[23] B. N. J. Persson and R. Ryberg, Phys. Rev. B **32**, 3586 (1985).
[24] B. N. J. Persson et al., Phys. Rev. B **59**, 11 777 (1999).
[25] G. Hoffmann, J. Kliewer, and R. Berndt, Phys. Rev. Lett. **87**, 176 803 (2001).
[26] K. Watanabe, N. Takagi, and Y. Matsumoto (to be published).