Ultrafast Surface Dynamics Studied with Femtosecond Sum Frequency Generation

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We present an investigation into femtosecond time-resolved vibrational sum frequency spectroscopy as a tool for studying ultrafast surface dynamics. It is demonstrated that the presence of experimentally observed new spectral features does not necessarily mean that a novel chemical species has appeared on the surface. In addition, we present a simple model for calculating the sum frequency intensity as a chemical reaction takes place on the surface via a transition state or reaction intermediate. These calculations show that a transition state can be observed and its lifetime can be determined.

Femtosecond spectroscopy has proven to be a powerful tool to study the dynamics of the interaction between molecules and metal surfaces, which is of fundamental importance in understanding chemical reactions and physical processes on surfaces.[1−9] These measurements generally employ a pump−probe scheme, in which the surface is excited by a femtosecond pump pulse and changes are probed with a time-delayed femtosecond laser pulse. Upon excitation with a femtosecond laser pulse, the energy is inserted into surface/substrate electronic degrees of freedom. The energy stored in these hot electrons can flow to the adsorbate via an electronic resonance or through coupling with the phonons.[8] Direct electronic excitation of the adsorbate[9] is a process of low probability and can often be neglected. Over the past decade several time-resolved studies have been carried out to investigate the dynamical surface−adsorbate interactions of, e.g., NO/Pd(111),[3] CO/Cu(100),[4,5,10,11] CO/Cu(111),[6] CO/Ni(111),[7] and Cs/Cu(111).[9] The aim of these experiments is to obtain information about reaction time scales and pathways, in particular, if present, on the transition state, since these are essential in the description and understanding of chemical reactions. As the transition state inherently has a short lifetime, a very good time resolution is required to observe it. Moreover, transition-state spectroscopy requires chemical specificity that allows one to probe the rearrangement of chemical bonds, such as vibrational spectroscopy. Recently, femtosecond time-resolved sum frequency generation (TR-SFG) was used for the first time[12] to probe the vibration of an adsorbate during desorption. This shows that TR-SFG should be an ideal candidate for observing transition states. To the best of our knowledge, transition states have not yet been observed on surfaces.

We present here a general investigation into TR-SFG as a probe of ultrafast surface processes, specifically surface reactions. It is demonstrated that there are important differences in the interpretation of vibrational spectra between TR-SFG and static vibrational spectroscopies such as reflection absorption infrared spectroscopy (RAIRS) and electron energy loss spectroscopy (EELS).[13] These effects are illustrated by calculating TR-SFG spectra for CO adsorbed on Ru(001) and comparing these with recent experimental data.[12] In addition, we have

investigated the effect on the SFG spectra of a simple chemical reaction taking place on the surface via a short-lived transition state and demonstrate that with this technique it is possible to observe transition states and determine their lifetimes.

Surface SFG spectroscopy is a second-order nonlinear process. By irradiating a surface with an infrared (IR) field, $E(\omega_{IR})$, and a visible field, $E(\omega_{VIS})$, a third field having the sum of the frequencies, $E(\omega_{SFG})$, can be generated. This process can be described by the second-order polarization, which is the source of the SFG field:[14]

$$P^{(2)} = \chi^{(2)}(\omega_{SFG} = \omega_{IR} + \omega_{VIS})E(\omega_{IR})E(\omega_{VIS}) \qquad (1)$$

where $\chi^{(2)}$ is the second-order nonlinear susceptibility, which describes the response of the surface−adsorbate system to the electromagnetic fields. Usually $\chi^{(2)}$ is written as the sum of a resonant and a nonresonant contribution: $\chi^{(2)} = \chi^{(2)}_{NR} + \chi^{(2)}_{R}$. As a surface vibrational tool SFG relies on tuning the IR field to a vibrational resonance of the adsorbate, leading to large values of $\chi^{(2)}_{R}$ and consequently a large SFG signal. The resonant susceptibility is usually modeled using a standard Lorentzian response function:

$$\chi^{(2)}_{R} = \frac{B}{((\omega - \omega_0) - i\Gamma)} \qquad (2)$$

where ω_0 is the resonance frequency, Γ the inverse of the total dephasing time (T_2), which determines the line width, and B a constant. This implies that the polarization decays exponentially as a response to the IR field with a typical time constant T_2. In a TR-SFG experiment the resonance frequency, line width, and intensity become time-dependent.

Figure 1 shows TR-SFG spectra of CO adsorbed on Ru(001) in the $(\sqrt{3} \times \sqrt{3})$ structure (for experimental details, see ref 12). In these experiments the SFG spectra are taken at different delay times between the probe pair (consisting of a tunable femtosecond IR pulse and a spectrally narrow 800-nm pulse) and a femtosecond (800-nm) pump pulse. Due to energy flow from the metal to the adsorbate, the molecules become hot and desorption of a large fraction of the ad-layer takes place. As a consequence the spectra are strongly modified as a function of delay time consisting of changes in the resonance frequency,

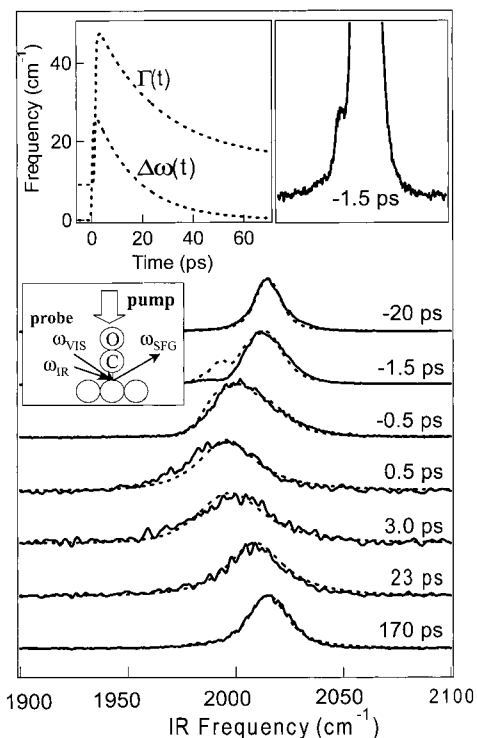* Corresponding author. Fax: +31-71-5274451. E-mail: roke@chem.leidenuniv.nl.

Figure 1. Normalized TR-SFG spectra of CO/Ru(001) (adopted from ref 12) (solid lines) at different delay times together with spectra (dotted lines) calculated with $\Gamma(t)$ and $\Delta\omega(t)$ depicted in the inset. Spatial averaging due to finite laser spot sizes has been taken into account. The calculated spectra reproduce important features such as the asymmetry (-0.5 ps) and side peak (slightly overestimated by the model, at -1.5 ps).

line width, and intensity and also the appearance of a side peak, most notably for -1.5-ps delay time (see inset).[15] The pump-induced spectral modifications were fully reproducible over an extended period of time, indicating no structural surface changes due to the excitation.

In the interpretation of static vibrational spectra, these observed spectral modifications would point toward structural or chemical changes on the surface, like new binding sites or tilted structures. To investigate if this is also the case for TR-SFG it is necessary to calculate these sum frequency spectra.

The SFG intensity can be calculated from the Fourier transform of the time-dependent polarization:[16]

$$I_{SFG}(\omega, \tau_d) \propto \left| \int dt \, e^{i\omega t} P_{IR}(t, \tau_d) E_{VIS}(t) \right|^2 \qquad (3)$$

where P_{IR} is the vibrational polarization set up by E_{IR} and τ_d is the pump–probe delay time. Evaluation of this expression requires knowledge of P_{IR}. P_{IR} can be found by numerically solving the Bloch equations, which describe the time-dependent evolution of the density matrix for a two level system[14,16] (with energy levels a and b and matrix elements ρ_{ba}, ρ_{ab}, ρ_{bb}, and ρ_{aa}):

$$\dot{u} = (\omega - (\omega_0 - \Delta\omega(t)))v - u\Gamma(t) \qquad (4)$$

$$\dot{v} = -(\omega - (\omega_0 - \Delta\omega(t)))u - v\Gamma(t) + \kappa E_{IR}w$$

$$\dot{w} = -\frac{(w - w^{eq})}{T_1} - \kappa E_{IR}v$$

in which u and v are the real and imaginary parts of ρ_{ba}, w the population difference $\rho_{bb} - \rho_{aa}$, w^{eq} the population difference
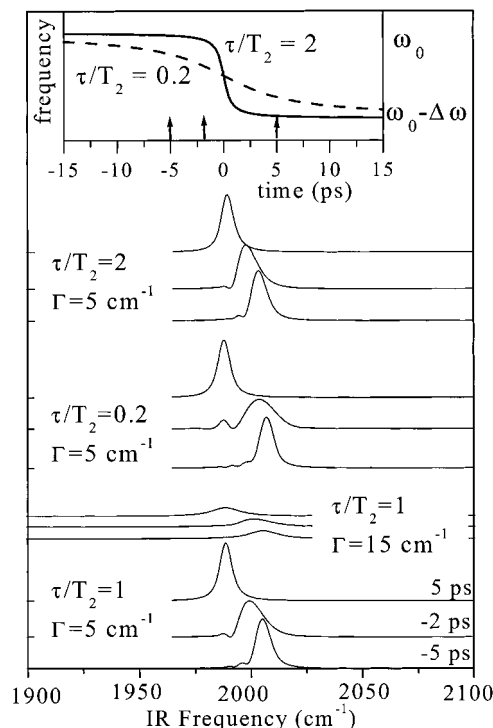

Figure 2. Calculated SFG spectra at different delay times (see the arrows in the inset) using the vibrational response function ($\Delta\omega(t)$) shown in the inset at different rates and dephasing times ($\Gamma = 1/T_2$). The rate of change is given with respect to the dephasing time. The resonance frequency ω_0 is chosen to be 2000 cm^{-1} and $\Delta\omega = 20$ cm^{-1}.

at thermal equilibrium, κ the atom-field coupling constant, T_1 the decay time from state b to a (assumed to be 3 ps), $\Delta\omega(t)$ the time-dependent response function of the resonance frequency, and $\Gamma(t)$ the time-dependent response of the line width of the CO stretch vibration (equivalent to the total dephasing time). The functional form of $\Gamma(t)$ and $\Delta\omega(t)$ can be obtained from the time-dependent adsorbate temperature in conjunction with anharmonic coupling theory.[12,17]

When the Bloch equations (eqs 4) are solved using $\Delta\omega(t)$ and $\Gamma(t)$ shown in Figure 1 the TR-SFG spectra can be reproduced (Figure 1), without assuming any chemical or structural change. The calculated spectra match the experimental data in the observed red shift, the line broadening, and the side peak. Apparently, these are not due to chemical or structural changes but rather to a strong transient perturbation of the vibration of the adsorbate. Hence there is no indication of an effect of desorption on these SFG spectra, in agreement with calculations presented below. Interpretation of TR-SFG spectra therefore has to be performed with some care.

To investigate spectral changes in more detail we have calculated the effect of a red shift ($\Delta\omega(t)$) of the vibrational frequency as a response to the pump pulse for the same experimental circumstances as for the spectra depicted in Figure 1. Figure 2 shows SFG spectra at several pump–probe delay times for frequency changes at different rates and dephasing times. The rate of change is expressed relative to T_2 and is depicted in the inset of Figure 2. At delay times as early as -5 ps the peaks are already distorted (also present in the data of Figure 1; note that here delay zero is defined at one-half the frequency change). This is due to the perturbed free induction decay (FID)[10] and is caused by interaction of the pump field with the remaining part of the polarization leading to changes in the measured SFG signal. When the delay time approaches zero, the effect of the pump pulse on the vibrational polarization

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field becomes increasingly large, which results in more pronounced sidebands appearing in the SFG spectra. These effects are largest at about -2-ps delay when the interaction time of the polarization with the pump-induced modifications is maximum. The spectral changes decrease when the interaction time becomes smaller, i.e., at larger delay times, or for a faster change of $\Delta\omega(t)$. A slow change of $\Delta\omega(t)$ increases the interaction time, accounting for the larger spectral changes for slower frequency modulation.

Figure 2 also shows that a shorter dephasing time (larger line width, $\Gamma = 15$ cm^{-1}) leads to broader peaks with less pronounced dynamical spectral features. This can also be explained in terms of interaction time: A shorter T_2 means that P_{IR} decays faster, reducing the interaction time and resulting in less pronounced spectral features.

The question arises if it is possible to observe short-time chemical changes induced by the pump pulse, i.e., whether it is possible to perform transition-state spectroscopy on surfaces with TR-SFG. To investigate this we consider a system in which substrate-mediated interaction of a pump pulse with an adsorbed overlayer leads to a chemical reaction that develops via a transition state:

$$A \xrightarrow{R(t)} A^\ddagger \rightarrow B \tag{5}$$

where $R(t)$ is the reaction rate that determines the number of molecules entering the transition state at time t. These three species can each be characterized by a resonance frequency (ω_0, $\omega_0 - \Delta\omega$, ω_1) for A, A‡, and B, respectively, and a total dephasing time (T_2 for A, A‡ and T$'_2$ for B). The transition state is further characterized by a short lifetime $\tau^\ddagger$. It is clear that $\Delta\omega$ contains information about the *structure* of the transition state and $\tau^\ddagger$ about its *dynamics*. For the three individual susceptibilities of the subensembles A (given by $\chi_A^{(2)}(t)$), A‡ ($\chi_{A^\ddagger}^{(2)}(t)$), and B ($\chi_B^{(2)}(t)$), we assume that the reaction to the IR field decays exponentially so that:

$$\chi_A^{(2)}(t) = e^{-t\Gamma_0} e^{i\omega_0 t} \tag{6}$$

$$\chi_{A^\ddagger}^{(2)}(t) = e^{-t\Gamma} e^{i(\omega_0 - \Delta\omega)t}$$

$$\chi_B^{(2)}(t) = e^{-t\Gamma_1} e^{i\omega_1 t}$$

where $\Gamma_0 = 1/T_2$, $\Gamma = 1/T_2 + 1/\tau^\ddagger$, and $\Gamma_1 = 1/T'_2$. Figure 3a illustrates the different species on the surface together with their susceptibility. Because the lifetime of the transition state is very short and the number of molecules residing in it is small compared to the total amount of molecules, the amount of molecules in state B can be approximated by the total number that has left A‡ at time $t - \tau^\ddagger$. The total susceptibility can now be given by the sum of three terms:

$$\chi^{(2)}(t) = [N_0 - \int_{-\infty}^t dt' R(t')]\chi_A^{(2)}(t - \tau_d) + $$

$$\int_{-\infty}^t dt' R(t')\chi_{A^\ddagger}^{(2)}(t' - \tau_d) + [\int_{-\infty}^{t-\tau^\ddagger} dt' R(t')]\chi_B^{(2)}(t - \tau_d) \tag{7}$$

where τ_d is the pump–probe delay and N_0 the total number of molecules. The first and third term consist of a product of an amplitude and a susceptibility, whereas in the second term the decay of the amplitude has been incorporated in the susceptibility. If $R(t)$ and the IR and visible fields are known, the SFG intensity can be obtained from eq 3.

For most surface reactions the reaction products desorb so that $\chi_B^{(2)} = 0$ as gas-phase molecules do not contribute to the
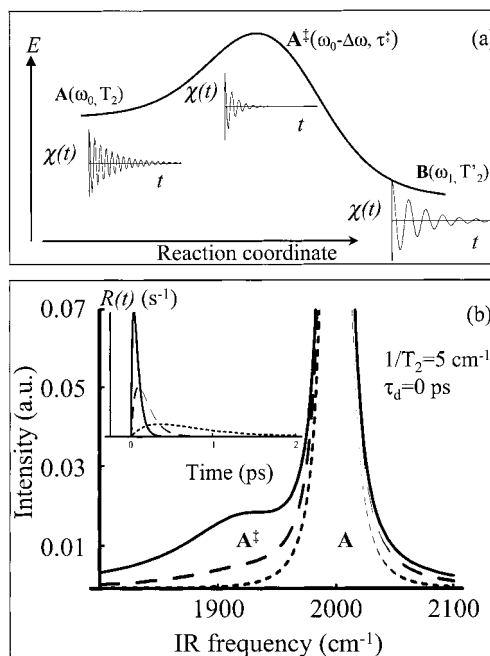

Figure 3. (a) Schematic representation of a reaction occurring via a transition state together with an illustration of the susceptibility. (b) Calculated SFG spectra for different desorption functions $R(t)$ (eq 8) shown in the inset having corresponding line types. The resonance frequency ω_0 is chosen to be 2000 cm^{-1} and $\Delta\omega = 80$ cm^{-1}. The maximum SFG signal is 1.

sum frequency signal. Reaction rates typically lie in the subpicosecond region (for desorption, e.g., NO/Pd(111),[3] CO/Cu(100),[4,5,10] CO/Cu(111),[6] O$_2$/Pt(111)[18] and for oxidation of CO/Ru(001)[8]). The reaction rate can be approximated by the following expression:

$$R(t) = \frac{(a + b)N_0}{a^2} e^{-t/a}(1 - e^{-t/b})\theta(t) \tag{8}$$

where a and b determine the speed of the reaction, $\theta(t)$ is the Heavyside function, and $R(t)$ is normalized to the initial coverage N_0. All molecules are assumed to react due to (substrate-mediated) interaction with the pump pulse. When the femtosecond IR pulse is approximated by a δ-function in the time domain and the temporally long visible field by a cw field, the SFG intensity can be found analytically from eqs 3, 7, and 8, as opposed to solving eqs 4 numerically. As cross terms are negligible (they are smaller than $10^{-3}|\chi_{A^\ddagger}^{(2)}(\omega)|^2$) the sum frequency signal is given by:

$$I_{SFG}(\omega) \propto$$

$$\frac{(a + b)^2 N_0^2 e^{-2\Gamma_0 \tau_d}}{a^4 b^2 \Gamma_0^2((\omega - \omega_0)^2 + \Gamma_0^2)((\omega - \omega_0)^2 + (\Gamma')^2)((\omega - \omega_0)^2 + (\Gamma'')^2)} +$$

$$\frac{(a + b)^2 N_0^2 e^{-2\Gamma \tau_d}}{a^4 b^2 \omega^2((\omega - (\omega_0 - \Delta\omega))^2 + \Gamma^2)((\omega - (\omega_0 - \Delta\omega))^2 + (\Gamma + 1/a + 1/b)^2)}$$

$$\tag{9}$$

where $\Gamma' = \Gamma_0 + 1/a$ and $\Gamma'' = \Gamma_0 + 1/a + 1/b$. The first term in eq 9 represents the contribution to the spectrum of molecules still residing on the surface. This peak is centered at ω_0 and broadened by T_2, a, and b. The disappearance of molecules results in an additional broadening of this peak. The second term represents a peak centered at $\omega_0 - \Delta\omega$ whose width and intensity are dependent predominantly on $\tau^\ddagger$, a, and b.
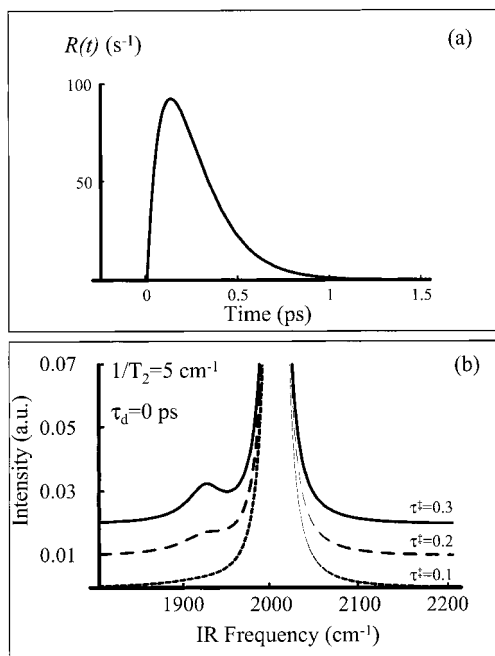
Figure 4. Calculated sum frequency spectra for desorbing molecules having different transition-state lifetimes and dephasing times ($\tau_d = 0$). The resonance frequency ω_0 is chosen to be 2000 cm^{-1} and $\Delta\omega = 80$ cm^{-1}, and all times are given in picoseconds. The maximum SFG signal is 1.

Figure 3b shows three calculated SFG spectra for different reaction rates (shown in the inset of Figure 3b) setting $\tau^{\ddagger} = 0.1$ ps and $\Gamma = 5$ cm^{-1}. This figure shows that, even for very short $\tau^{\ddagger}$, reacting molecules can contribute to the observed SFG signal and that it is possible to extract $\tau^{\ddagger}$ from the spectral intensity and line width. Fast reaction leads to a larger contribution from the molecules in the transition state to the SFG intensity. In all three reaction curves the molecules have left the surface after 3 ps. For the slowest reaction process the spectral changes are not very pronounced, demonstrating that reacting molecules only contribute significantly to the signal if the reaction occurs within several picoseconds, i.e., in an electron-mediated scenario. This explains why desorbing CO does not contribute to the SFG spectra shown in Figure 1: the desorption is phonon-mediated and takes ~20 ps.[8] Figure 4 shows the effect of different transition-state lifetimes on the SFG spectra. A longer lifetime is shown to lead to a bigger contribution of the desorbing molecules to the SFG spectra. Longer lived reaction intermediates should certainly be observable.

In these calculations the parameters determining the transition-state susceptibility (Γ and $\Delta\omega$) were taken to be constants. This means that no response due to coupling of the vibration with phonons or low frequency vibrations were considered and that the reaction does not proceed through a continuum of states (as one would expect for, e.g., a barrierless desorption process). Both effects can be incorporated into the theory by making $\Delta\omega$ and Γ time-dependent. As a reaction that might be suited for obtaining information on the transition state as described in this

Letter we suggest the oxidation of CO on Ru(001). This is a very rapid electron-mediated reaction[12] which occurs via a transition state.[19]

In summary, we have shown that changes in the TR-SFG spectra do not necessarily point to chemical or structural changes on the surface and can be reproduced with calculations. We have also calculated SFG spectra for a pump pulse inducing a simple reaction occurring via a transition state. For the reaction of an adsorbed overlayer we found that if the reaction is fast in response to the pump pulse, i.e., within several picoseconds, measurable changes in the SFG spectra can be observed. Thus, it should be possible to determine transition states and lifetimes from SFG measurements.

References and Notes

(1) Cavanagh, R. R.; King, D. S.; Stephenson, J. C. *J. Phys. Chem.* **1993**, *97*, 786−798.
(2) Dai, H. L.; Ho, W. *Laser spectroscopy and photochemistry on metal surfaces, Part II*; World Sceintific: Singapore, 1995.
(3) Prybyla, J. A.; Tom, H. W. K.; Aumiller, G. D. *Phys. Rev. Lett.* **1992**, *68*, 503−507.
(4) Morin, M. J.; Levinos, N. J.; Harris, A. L. *J. Chem. Phys.* **1992**, *96*, 3950−3956.
(5) Struck, L. M.; Richter, L. J.; Buntin, S. A.; Cavanagh, R. C.; Stephenson, J. C. *Phys. Rev. Lett.* **1996**, *77*, 4576−4579.
(6) Owrutski, J. C.; Culver, J. P.; Li, M.; Kim, Y. R.; Sarisky, M. J.; Yeganeh, M. S.; Yodh, A. G.; Hochstrasser, R. M. *J. Chem. Phys.* **1992**, *97*, 4421−4427.
(7) Bandara, A.; Kubota, A.; Onda, K.; Wada, A.; Kano, S. S.; Domen, K.; Hirose, C. *Surf. Sci.* **1999**, *427-428*, 331−336.
(8) Bonn, M.; Funk, S.; Hess, C.; Denzler, D. N.; Stampfl, C.; Scheffler, M.; Wolf, M.; Ertl, G. *Science* **1999**, *285*, 1042−1045.
(9) Petek, H.; Weida, M. J.; Nagano, H.; Ogawa, S. *Science* **2000**, *288*, 1402−1404.
(10) Germer, T. A.; Stephenson, J. C.; Heilweil, E. J.; Cavenagh, R. R. *J. Chem. Phys.* **1994**, *101*, 1704−1716.
(11) Springer, C.; Head-Gordon, M. *Chem. Phys.* **1996**, *205*, 73−89.
(12) Bonn, M.; Hess, C.; Funk, S.; Miners, J. H.; Persson, B. N. J.; Wolf, M.; Ertl, G. *Phys. Rev. Lett.* **2000**, *84*, 4653−4656.
(13) Dumas, P.; Weldon, M. K.; Chabal, Y. J.; Williams, G. P. *Surf. Rev.* **1999**, *6*, 225−255.
(14) Boyd, R. W. *Nonlinear optics*; Academic Press: New York, 1992.
(15) It should be noted that the time resolution in these experiments is determined by the duration of the femtosecond IR and excitation pulse, rather than by the decay of the IR polarization (typically ~1 ps). The SFG spectrum is fully determined by the time-dependent polarization (eq 3). Therefore, although the polarization is upconverted by a quasi-continuous wave (cw) pulse and spectrally dispersed, the SFG spectra contain all the information on the ultrafast perturbation of the adsorbate, and this information can be obtained by simulating the data, as demonstrated here.
(16) Shen, Y. R. *The principles of nonlinear optics*; Wiley: New York, 1984.
(17) Jakob, P.; Persson, B. N. J. *Phys. Rev. B* **1997**, *56*, 10644−10650.
(18) Busch, D. G.; Gao, S.; Pelak, R. A.; Booth, M.; Ho, W. *Phys. Rev. Lett.* **1995**, *75*, 673−676.
(19) Zhang, C. J.; Hu, P.; Alavi, A. *J. Chem. Phys.* **2000**, *212*, 10564−10570.