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Dephasing of highly vibrationally excited molecules at surfaces: CO/Ru(001)

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Abstract

The $\nu=0\rightarrow 1$ fundamental and the $\nu=1\rightarrow 2$ hot-band transitions of the C-O stretch vibration of CO chemisorbed on Ru(001) are investigated as a function of temperature using broadband-IR sum-frequency generation (SFG) spectroscopy. Although the linewidths are markedly different for the two transitions, we demonstrate that the temperature-dependent contribution to the linewidths from anharmonic coupling to the low-frequency frustrated translation mode (giving rise to pure dephasing) is identical for both transitions. This implies that the anharmonic coupling to the low-frequency mode is independent of the degree of vibrational excitation.

1. Introduction

Molecular vibrational up-pumping has been studied extensively using a variety of IR sources ranging from pulsed CO₂ lasers [1] to tunable femtosecond IR lasers [2-9]. One of the goals of these efforts is to perform bond-selective chemistry through selective vibrational excitation of a specific molecular mode. Indeed, the selective fission of a molecular bond by ultrashort infrared excitation has recently been demonstrated for the first time in the gas phase [10]. The extension of this approach to a wider range of systems depends on the dynamics of vibrational relaxation from highly vibrationally excited states, which is characterized by the energy lifetime (T_1) and the dephasing time (T_2). The dephasing time T_2 contains contributions from the energy lifetime T_1 and from pure (elastic) dephasing processes contained in T_2^* : $1/T_2 = 1/2T_1 + 1/T_2^*$. Finite T_2^* -times generally result from modulations of the transition frequency through interactions with low frequency modes that interact with the bath, or through direct interactions with bath modes. T_2 generally limits the degree of coherence that can be built up between two successive vibrational levels,

which subsequently determines the final amount of excited state population that can be transferred. Hence, the values of T_2 for a vibrational ladder system are essential in determining, for a given set of excitation parameters, the excited state population distribution. An equally important role is evident for the vibrational energy lifetime T_1 ; T_1 has to be sufficiently long for successive interactions with the driving infrared field to allow for efficient population transfer to higher-lying states.

Although in the gas phase these lifetimes may be long compared to typical durations of ultrashort infrared laser pulses [10], on surfaces [11], and more specifically on *metal* surfaces, complications arise as both lifetimes are on the order of ~ 1 ps or less [12,13]. In addition, the close proximity and preferential alignment of molecules on surfaces gives rise to strong intermolecular interactions, which may result in rapid vibrational energy delocalization within the adlayer [14-17]. Although, for surface vibrations, estimates of the energy (T_1) lifetime for highly excited states are readily available from straightforward theoretical considerations in conjunction with the lifetime of the fundamental transition [18], and the effects of intermolecular coupling are well understood [14-

[17], the situation is much less clear for pure dephasing processes of highly excited states that determine T_2^* for vibrations on surfaces.

In this contribution, we investigate the dephasing behavior of the second excited state of the C—O stretch vibration of CO adsorbed to the (001) face of a Ruthenium single crystal. This is a well-documented system, as previously infrared-reflection absorption spectroscopy (IRAS) has been used extensively to study the fundamental, the first overtone ($\nu=0\rightarrow2$ transition) and combination bands of CO/Ru(001) [18,19], as well the effect of intermolecular coupling on the vibrational dynamics[17]. However, as the $\nu=1\rightarrow2$ transition is not accessible with FT-IR spectroscopy, its dynamics has remained largely unexplored. We present strong evidence that the dephasing of the second excited state occurs by the same mechanism as the fundamental.

2. Experimental

The experiments were performed with a Ti:Sapphire laser system (800 nm, 110 fs, 400 Hz) combined with an ultra-high vacuum (UHV) chamber as described previously [20]. Part of the output is used to pump an optical parametric amplifier (OPA) with subsequent difference frequency mixing of the signal and idler to generate tunable mid-IR femto-second pulses (2-10 μm). The resulting broadband ($\sim 150\text{ cm}^{-1}$ FWHM, ~ 130 fs, 10 μJ) IR pulses are mixed on the surface with spectrally narrowed 800 nm pulses (bandwidth 5-8 cm^{-1} , 4 μJ) on a 300 μm diameter spot. The generated sum-frequency beam is focused into a spectrograph and dispersed across an intensified CCD camera [17,21,22]. The Ru(001) sample was mounted in a UHV chamber (base pressure 1×10^{-10} mbar) and could be cooled to 95 K.

3. Results and Discussion

Figure 1 depicts SFG spectra as a function of CO coverage at 400 K (left panel) together with the result of a fitting procedure used to extract the resonant CO response (right panel, see Refs. [17,23] for details regarding the fitting procedure). From the data, it is immediately apparent that a considerable fraction of the CO molecules is excited to the first excited $\nu=1$ state, so that SFG is radiated not only from the fundamental transition $\nu=0\rightarrow1$ at $\sim 1990\text{ cm}^{-1}$, but also from the $\nu=1\rightarrow2$ transition ('hot band') at $\sim 1960\text{ cm}^{-1}$: the infrared pulse is sufficiently powerful to excite the CO molecules and generate SFG from the excited state in a fourth-order non-linear optical process.

The right panel depicts the resonant contribution to the SFG signal derived from the data. These reveal that as much as 25% of the CO groups is vibrationally excited. From the figure it is evident that at 400 K (as observed also at 300K) the hot-band intensity varies significantly with coverage. In contrast, at 95 K, this is not the case [17]. A second surprising observation is that under equivalent excitation conditions, significantly more population that can be transferred into $\nu=1$ at higher temperatures ($n_{\text{exc}}=0.26$ at 400 K compared to $n_{\text{exc}}=0.22$ at 95 K) for low-coverages. A detailed analysis of the data indicates that these effects cannot be

caused by a temperature- or coverage-dependent cross section for the vibrational transition. Also, attempts to explain these observations by temperature-dependent dipole-dipole coupling (caused by the temperature-dependent linewidth) were unsuccessful. It should be noted, however, that the inability to account for these observations does not affect the conclusions regarding the linewidths here.

Figure 1. Left panel: experimental, normalized SFG spectra (gray) in the C—O stretching region for CO adsorbed on Ru(001) at different CO coverages indicated in the graph. The lower trace is the non-resonant signal from the Ru substrate, representing the spectrum of the incident IR pulse. The fundamental ($0\rightarrow1$) and hot-band ($1\rightarrow2$) transitions are clearly visible in the spectra. Black lines are fits to the data, consisting of a non-resonant contribution from the substrate and two resonant contributions from the CO. Right panel: extracted resonant contributions from the fits in the left panel.

The variation in the signal with coverage (e.g. the variation in the relative intensity of the fundamental and the hot band) is caused by dipole-dipole coupling between the CO molecules, which affects the spectra already at the very low coverages reported here. From these coverage dependent data, the linewidths and central frequencies can be obtained for isolated CO molecules, by extrapolating the resonance parameters to zero coverage. The result of this procedure for three temperatures, 95, 300 and 400 K is summarized in Table 1. The observed linewidths can be decomposed into contributions from the energy lifetime energy T_1 and the pure dephasing time T_2^* through:

$$\Gamma_{01} = \frac{2}{T_2^{*1-0}} + \frac{1}{T_1^{1-0}} \quad (1a)$$

$$\Gamma_{12} = \frac{2}{T_2^{*2-1}} + \frac{1}{T_1^{2-1}} + \frac{1}{T_1^{0-1}} \approx \frac{2}{T_2^{*2-1}} + \frac{3}{T_1^{0-1}} \quad (1b)$$

In these equations, T_1^{0-1} and T_1^{2-1} denote the energy lifetimes of the first and second excited states, and T_2^{*1-0} and T_2^{*2-1} the corresponding pure dephasing times. The contribution to the linewidth due to T_1 is temperature independent [12], and amounts to 2.5 cm^{-1} , from linear spectroscopy (by extrapolation of the linewidth to

Table 1: Linewidths (full width at half maximum G_{01} for the fundamental and G_{12} for the hot band), anharmonicity (difference between fundamental and hot band transition frequency $\nu_{01}-\nu_{12}$) and extracted contribution to the linewidths from pure dephasing processes. The reported linewidths (uncorrected for the 4 cm^{-1} broad system response function) and anharmonicities are obtained by extrapolating the coverage dependent data at three different temperatures to zero coverage. Pure dephasing times T_2^* are obtained by correcting the observed linewidths for the instrument response and the energy lifetime contributions. Values in parentheses behind G_{01} denote the values recorded with Reflection Absorption Infrared Spectroscopy, reproduced from Ref. [15].

$T\text{ (K)}$	$G_{01}\text{ (cm}^{-1}\text{)}$	$G_{12}\text{ (cm}^{-1}\text{)}$	$\nu_{01}-\nu_{12}\text{ (cm}^{-1}\text{)}$	$2/T_2^{*1-0}\text{ (cm}^{-1}\text{)}$	$2/T_2^{*2-1}\text{ (cm}^{-1}\text{)}$
95	8.5 (5)	14.5	27.2	2	3
300	17 (12)	24	26	10.5	12.5
400	20 (15)	28	27.5	13.5	16.5

zero temperature [15]) and time-domain experiments (which directly measure the lifetime on metal surfaces to be $\sim 2\text{ ps}$ [12,13]). In addition, it has been established that the energy lifetime of the second excited state is half of this, i.e. $T_1^{2-1} = 0.5 T_1^{0-1}$, which follows from wavefunction overlap considerations [18]. Thus we can calculate the pure dephasing contributions to the linewidth for both transitions, T_2^{*1-0} and T_2^{*2-1} , as shown in Table 1. The results are also shown in Fig. 2, together with the predictions from the anharmonic coupling model [15]. This anharmonic coupling model, that has been successfully applied to describe the dephasing of the fundamental transition [15], states that the high-frequency C—O stretch is coupled to the low-frequency parallel frustrated translation of the CO molecules. Thermal excitation of this low-frequency mode leads to a modulation of the C—O stretch transition frequency. In the theory, the CO molecules are described as forced harmonic oscillators, and a set of coupled equations of motion of forced harmonic oscillators is solved, after adding the variance of the low frequency mode $\langle Q^2 \rangle$ as a perturbation. The variance is calculated assuming a Markovian process for the thermal excitation and de-excitation of the frustrated translation.

Figure 2. Contribution to the linewidth from pure dephasing processes as extracted from the linewidths of the fundamental and hot-band transitions. The dashed line shows the prediction from anharmonic coupling theory, which is in reasonable agreement with experimental data for both transitions.

Within the accuracy of our experiment, the comparison between the model and the data suggests that the dephasing of the $\nu=1\rightarrow 2$ transition and fundamental follows the same mechanism of anharmonic coupling of the C—O stretch vibration to the frustrated translational mode. The small discrepancy between model and data at elevated temperatures may be traced back to the fact that, at higher temperatures, other low-frequency modes such as the frustrated rotational mode and the Ru—CO stretch vibration may be thermally excited and contribute to the dephasing, as argued previously [15].

The observation that the dephasing is more or less identical for the two transitions, contains information on the nature of the coupling between the C—O stretch high-frequency mode (normal coordinate q) and the low-frequency frustrated translation (normal coordinate Q). Following the theory of vibrational linewidths developed by Madden *et al.* [24] and Oxtoby *et al.* [25], the Hamiltonian of interaction between the C—O stretch vibration and the frustrated translation may be obtained by expanding this interaction in the C—O stretch vibrational coordinate, q :

$$H_{\text{int}} = Fq + Gq^2 \quad (2)$$

where F and G are implicit functions of the coordinate Q . The expressions for the linewidth of the fundamental (0-1) and hotband (1-2) can now be shown to be:

$$\Delta_{0-1} = 2a J_F(w)(1+3P_T)/(1+P_T) + a^2 J_G(0) \quad (3)$$

$$\Delta_{1-2} = 2a J_F(w)(3+5P_T)/(1+P_T) + a^2 J_G(0) \quad (4)$$

with $a = \hbar / m\omega$, $P_T = e^{-\hbar\omega/kT}$,

$$J_F(w) = 1/(1+P_T) \langle F^2 \rangle (1+w^2 t_F^2) \text{ and}$$

$J_G(w) = 1/(1+P_T) \langle G^2 \rangle$ where t_F and t_G are the respective correlation times of the correlation functions of F and G . The first terms in both equations corresponds to the contribution of population relaxation. It is apparent that in the appropriate limit of $\hbar\omega < kT$, the ratio of the lifetimes is 2, as argued above and used in the data analysis. The second term in both equations results from the contribution of pure dephasing processes, and is, indeed, equal for both transitions. This analysis shows that the identical dephasing observed for the two transitions in our measurements implies

that the interaction Hamiltonian is adequately described by terms up to and including the quadratic coupling term. Higher order terms are negligible. Note that this theory for vibrational linewidths is consistent with the theory for overtones and combination bands developed by Jakob and Persson [18]. The linewidth of the first overtone (0-2) is given by [23]:

$$\Delta_{0,2} = 2a J_F(w)(2 + 4P_T)/(1 + P_T) + 4a^2 J_G(0) \quad (5)$$

This shows that the pure dephasing contribution to the linewidth of the first overtone (second term in Eq. 5) is 4 times larger than the linewidth of the fundamental as was found previously both theoretically and experimentally by Jakob and Persson [18].

4. Conclusion

In summary, we have shown that at low CO coverages both the fundamental and the $v=1 \rightarrow 2$ hot-band transition follow the same dephasing mechanism, i.e., the anharmonic cou-

pling of the CO-stretch vibration to the low-frequency translational mode. The temperature-dependent behavior observed at higher CO coverages is in good agreement with previous IR results and predictions from the anharmonic coupling model, and demonstrate that the coupling is adequately described by a Hamiltonian containing linear and quadratic terms.

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