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Vibrational Damping of Adsorbed Molecules: Methoxide on Cu(100)

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The lifetimes of the C-H and C-D stretch vibrational modes of methoxide adsorbed on Cu(100) have been measured by infrared spectroscopy. It is shown that the damping of these vibrational states is caused by excitation of electron-hole pairs in a region very close to the vibrating molecule. It is argued that the electron-hole pairs are excited because a resonance around the Fermi level fills and empties during the vibration.

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Detailed knowledge about the damping processes of vibrationally excited molecules on a metal surface is important for the understanding of the molecule-metal interaction. In addition, the damping rate may also contain information about the adsorbate-induced electronic structure as well as the rate of surface reactions. A chemical reaction might in fact be considered as a set of transitions among the different vibrational levels occurring along the reaction path. The rate at which the molecule makes these transitions is completely determined by the temperature and the frequencies and damping rates of the various vibrational states.

Investigations of the vibrational lifetimes of adsorbed molecules have to be done, in general, with infrared spectroscopy (IRS), which has at least one order of magnitude higher resolution than electron energy-loss spectroscopy (ELS). However, there exist only a very limited number of spectrometers with high enough sensitivity to study even adsorbed CO. Fortunately, the high sensitivity of our infrared spectrometer allows us to study the much weaker C-H stretch vibration without loss of resolution. In this Letter, we report on the IRS data (focusing especially on the linewidths) of methoxide (CH_3O) chemisorbed on a Cu(100) surface. The purpose of this study was to investigate the nature of the damping mechanism. In particular, the use of deuterated species reduces the vibration frequencies and amplitudes considerably, which will allow a critical test of theoretical calculations.

All experimental details were given in a recent letter.[1] The infrared spectrometer uses the so-called wavelength modulation technique giving a signal proportional to the second derivative of the absorptance. The intrinsic peak widths of such spectra are obtained in a rather detailed way described elsewhere.[2] The spectrometer resolution in the present work was about 4 cm^{-1}. The measured linewidths and vibration frequencies are given in Fig. 1 and Table I. A spectrum of the symmetric C-H stretch vibration is inserted in the figure. The values given in the table are taken for a coverage of 0.20, i.e., below the coverage where additional broadening due to nearest-neighbor molecular interaction sets in, and is therefore representative for the pure lifetime broadening. There is no sign of clustering, with the $c(2\times 2$ low-energy electron-diffraction pattern developing very close to the full-coverage exposure.[1] As seen in the table, the lifetime of the C-D vibration is almost twice as large as

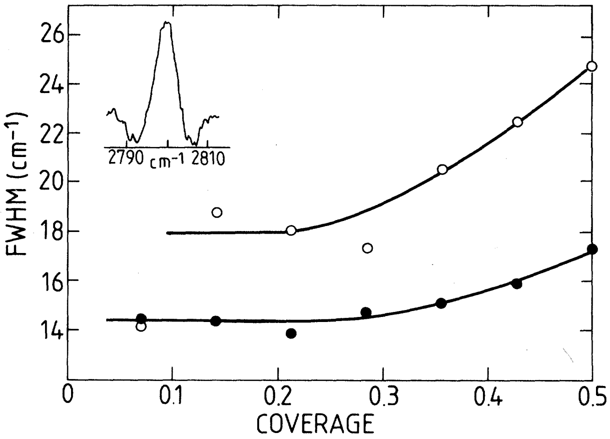

FIG. 1. The intrinsic linewidths (full width at half maximum) of symmetric (solid circles) and asymmetric (open circles) C-H stretch vibrational modes for different coverages of CH_3O on Cu(100). Inset is a spectrum for the symmetric mode at a coverage of 0.2.

TABLE I. The vibration frequencies and linewidths of the symmetric and asymmetric C-H (C-D) stretch vibrations of CH_3O (CD_3O) adsorbed at a coverage of 0.2 on Cu(100). The gas-phase data are taken from Ref. 3.

Mode	Frequency gas phase (cm^{-1})	Frequency adsorbed (cm^{-1})	Width FWHM (cm^{-1})
$C\text{-}H_{sym}$	2845	2795 ± 2	14 ± 1
$C\text{-}H_{asmy}$	2978	2870	18
$C\text{-}D_{sym}$	2080	2050	8
$C\text{-}D_{asym}$	2228	2171	10

that of the C-H vibration. We shall now show that this result is to be expected if the vibrational modes are damped as a result of excitation of electron-hole pairs.

The ELS data of Sexton[4] show that the methoxide is bonded with the oxygen atom towards the surface. Since a carbon atom is much heavier than a hydrogen atom, we can, as a first approximation, assume that there are three degenerate vibrational levels in which two hydrogen ions (i.e., protons) and the carbon ion are at rest while the third hydrogen ion exhibits oscillations around its equilibrium position, $\vec{R}_{eq}$, i.e., $\vec{R}(t) = \vec{R}_{eq} + \vec{e}Q(t)$, where $\vec{e}$ is a unit vector pointing from the carbon atom towards the oscillating proton. If the vibration is harmonic, then

$$Q \simeq (\hbar/2m^*\Omega)^{1/2}(b+b^\dagger) \equiv Q_0(b+b^\dagger), \tag{1}$$

where m^* is the reduced mass of the carbon-hydrogen system and Ω is the vibration frequency. Since Q_0 is small (≈ 0.07 Å), we can approximate the time-dependent Coulomb potential from the oscillating proton by keeping only the first two terms in a Taylor expansion in Q_0:

$$\frac{e}{|\vec{x}-\vec{R}(t)|} \simeq \frac{e}{|\vec{x}-\vec{R}_{eq}|} + Q(t)\vec{e}\cdot\frac{\partial}{\partial\vec{R}}\frac{e}{|\vec{x}-\vec{R}|}\Bigg|_{eq}$$

$$\equiv \frac{e}{|\vec{x}-\vec{R}_{eq}|} + \varphi(\vec{x},t).$$

To first order in Q_0, the total Coulomb potential is simply the sum of the potential from a proton at rest at $\vec{R} = \vec{R}_{eq}$ plus the potential φ from an oscillating point dipole with the dynamical dipole moment eQ_0, also located at $\vec{R} = \vec{R}_{eq}$.

The electric potential at a particular electron is not the "external" dipole potential φ, but φ screened by the other electrons, i.e., $\tilde{\varphi} = \hat{\epsilon}^{-1}\varphi$, where $\hat{\epsilon}$ is the dielectric operator (an integral operator) of the molecule-metal system. The screened dipole field $\tilde{\varphi}(\vec{x},t)$ can excite electron-hole pairs in the molecule-metal system. We want to calculate the transition rate for the process where the vibrationally excited molecule ($n = 1$) decays to its vibrational ground state ($n = 0$), while an electron is scattered from a continuum level α below the Fermi surface ($\epsilon_\alpha < \epsilon_F$) to a continuum level β above the Fermi surface ($\epsilon_\beta > \epsilon_F$). We denote the ground state of the conduction-electron liquid by $|0\rangle$ and the excited state by $|\alpha\beta\rangle$ (hole in α, electron in β). From the "golden rule" formula, the damping rate is obtained as

$$\frac{1}{\tau} = \frac{2\pi}{\hbar}\sum_{\alpha\beta}|\langle\alpha\beta, n=0|\int d^3x\,\hat{\rho}(\vec{x})\hat{\varphi}(\vec{x})|0, n=1\rangle|^2 n_\alpha(1-n_\beta)\delta(\epsilon_\beta-\epsilon_\alpha-\hbar\Omega)$$

$$\equiv \frac{2\pi}{\hbar}Q_0^2\sum_{\alpha\beta}|M_{\alpha\beta}|^2 n_\alpha(1-n_\beta)\delta(\epsilon_\beta-\epsilon_\alpha-\hbar\Omega),$$

where $n_\mu = 1$ if $\epsilon_\mu < \epsilon_F$ and $n_\mu = 0$ if $\epsilon_\mu > \epsilon_F$. If we introduce the density of states $\rho(\epsilon) = \sum_\mu \delta(\epsilon - \epsilon_\mu)$, then the above equation may be written

$$\frac{1}{\tau} = \frac{2\pi}{\hbar}Q_0^2\int_{\epsilon_F}^{\epsilon_F+\hbar\Omega} d\epsilon\,\rho(\epsilon)\rho(\epsilon-\hbar\Omega)\langle|M_{\alpha\beta}|^2\rangle$$

$$\simeq 2\pi Q_0^2\Omega\rho^2(\epsilon_F)\langle|M_{\alpha\beta}|^2\rangle. \tag{2}$$

Here the angular brackets imply a sum over all quantum numbers apart from the energy that are needed in order to completely specify the one-particle eigenstate. The last equality in Eq. (2) is valid if $\rho(\epsilon)$ and $\langle|M_{\alpha\beta}|^2\rangle$ vary slowly with energy over $\hbar\Omega \simeq 0.3$ eV.

According to Eqs. (1) and (2), $1/\tau \sim Q_0^2\Omega \sim 1/m^*$. Since $Q_0^2\Omega$ is the only term in the expression for the damping rate [Eq. (2)] which differs for CH_3O and CD_3O, we can now calculate the ratio $\tau(D)/\tau(H)$ between the C-D and C-H vibrational lifetimes: $\tau(D)/\tau(H) = m^*(D)/m^*(H) = \frac{13}{7} \simeq 1.86$, which agrees well with the experimental ratios $\tau(D)/\tau(H) = 1.8 \pm 0.1$ and 1.75 ± 0.1 for the asymmetric and symmetric stretch vibrations, respectively.

The screened potential $\tilde{\varphi}$ can be decomposed into a long-range dipole potential, $\tilde{\varphi}_{dipole}$, plus a local potential $\tilde{\varphi}_{local} = \tilde{\varphi} - \tilde{\varphi}_{dipole}$ which is nonzero only in the immediate vicinity (say, within a few angstroms) of the chemisorbed molecule. $\tilde{\varphi}_{\text{dipole}}$ can be written (outside the metal) as $\tilde{\varphi}_{\text{dipole}} = -2\mu\vec{n}\cdot\nabla(1/|\vec{x}|)$ where we have chosen $\vec{n}=0$ on the image plane just below the center of mass of the chemisorbed molecule and where $\vec{n}$ is a unit vector normal to the metal surface. The dynamical dipole moment μ can be obtained from the IRS spectra and for methoxide chemisorbed on Cu(100) we have estimated that $\mu \simeq 0.02ea_0$ $(=0.05\text{ D})$.

We now ask whether it is $\tilde{\varphi}_{\text{dipole}}$ or $\tilde{\varphi}_{\text{local}}$ which gives the largest contribution to the damping rate; i.e., do "frictional losses" associated with the long-range (however, localized to the metal surface) or short-range charge rearrangements give the main contribution? This question can be directly answered since we know the strength of the dipole field $\tilde{\varphi}_{\text{dipole}}$. We have shown previously[5] that the damping rate for a vibrating point dipole located a distance d above a metal surface is given by

$$1/\tau = \mu^2 F/4d^3\hbar, \tag{3}$$

where F depends on d, Ω, and the dielectric properties of the metal (F is defined in Ref. 5). For CH_3O chemisorbed on Cu(100), we estimate $d \simeq 1.5$ Å and with $\hbar\Omega = 0.36$ eV, it follows[4] that $F \simeq 10^{-2}$. Since $\mu \simeq 0.02ea_0$, we calculate from Eq. (3) $\tau \simeq 10^{-9}$ sec $(\simeq 10^{-3}\text{ cm}^{-1})$ which is about 10^{-4} times smaller than the observed damping rate.[6] Consequently, even if this calculation is based on a rather crude theory, we can safely conclude that the main contribution to the damping rate is derived from the local Coulomb potential $\tilde{\varphi}_{\text{local}}$.

We now proceed one step further and ask what kind of local charge rearrangements are important for the damping. We know that it is only electrons within $\epsilon_F - \hbar\Omega \leq \epsilon \leq \epsilon_F$ which can give rise to energy-loss processes [although electrons with $\epsilon < \epsilon_F - \hbar\Omega$ are not unimportant as they will give a contribution to the screening of the "bare" Coulomb potential $\varphi(x)$]. From this, we can draw the following important conclusion: A *necessary* condition for the excitation of any real electron-hole pairs by φ_{local} is that the density of states of the molecule-metal system, *projected* on the region where $\tilde{\varphi}_{\text{local}}$ is nonzero, is nonvanishing somewhere in the energy interval $\epsilon_F - \hbar\Omega < \epsilon < \epsilon_F$. We now apply this conclusion to methoxide chemisorbed on Cu(100).

In the simplest description of the chemisorption bond between the carbon atom and a hydrogen atom in CH_3, one forms molecular orbitals (MO's) by linear combination of suitably chosen (to give large overlap) atomic orbitals centered at the carbon and hydrogen atoms. In the present case, from a $2sp^3$-hybridized orbital on the carbon atom and the $1s$ orbital on the hydrogen atom one gets a bonding orbital σ and an antibonding orbital σ^*. When the methoxide is chemisorbed on a metal surface, the originally sharp free molecular energy levels turn into resonances. The energy of the bonding orbital σ is far below the Fermi level and gives no direct contribution to the damping rate. The antibonding level σ^* in the free molecule is pulled down in energy as a result of "image" and hybridization effects. Furthermore, it will be broadened if the final (i.e., shifted) level is located within an energy band of the metal. We assume that the σ^* resonance is located in the vicinity of the Fermi energy and is partly filled. Now, if a C-H bond is stretched, the center of the σ^* resonance will move downwards in energy (since it is derived from an antibonding level). Consequently, as the Fermi level remains fixed electrons must flow from the metal to the σ^* orbital. Therefore, when the C-H vibration is excited, there will be a periodic fluctuation of charge between the metal and the σ^* orbital. Associated with the charge rearrangements will be a damping of the vibrational motion. Formally, the damping rate is given by Eq. (2) but this equation can be simplified in the present case. If the σ^* resonance is the only molecular-derived resonance with a weight at the Fermi energy and if this resonance has a Lorentzian shape, then it can be shown[7] that Eq. (2) reduces to

$$1/\tau \simeq \pi(\delta n_{\sigma^*})^2\Omega, \tag{4}$$

where δn_{σ^*} is the fluctuation of charge in the σ^* orbital during the vibration. Using this equation with $\hbar\Omega = 0.36$ eV and $\tau = 3\times 10^{-13}$ sec one obtains $\delta n_{\sigma^*} \simeq 0.04$ for the asymmetric C-H vibrational mode of CH_3O.

To summarize, we have shown that the damping of the C-H stretch vibrations of chemisorbed methoxide is caused by electron-hole pair excitations. Furthermore, we argue that in many cases the damping rate of vibrational modes is a measure of the tendency for filling the (antibonding) affinity level (e.g., $2\sigma^*$ of H_2 and CH_3O, and $2\pi^*$ for CO) as the relevant bond length is increased. But filling an antibonding molecular orbital reduces the strength of intramolecular bonds. Thus one should expect to find a correlation between the damping rate and the activation energy for dissociation as suggested by Demuth, Ibach, and Lewald.[8] We will discuss this interesting question in a forthcoming paper.

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