Memory Effects on Infrared Adsorbate Spectra

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A vibrational bond between an adsorbed atom and a crystal can absorb photons from a weak (probe) laser field (frequency $\omega$). The line shape for this process is usually assumed to be a Lorentzian, which reflects that the kinetic coupling to the phonon reservoir is supposed to be a memoryless process. Due to the finite cutoff of the phonon dispersion relation (Debye frequency $\omega_D$), this is not an accurate approximation if the transition frequency $\omega$ between two levels of potential well is of the same order magnitude as $\omega_D$. A finite memory-time reservoir theory is applied to the evaluation of the line shape, and two distinct properties are found. First, it is shown that the modified Lorentzian is identically zero for $\omega > \omega_D$, and then a memory-induced line at $\omega : \omega + \omega_D$ is predicted. The physical origin of these features is explained in terms of energy-conserving diagrams.
MEMORY EFFECTS ON INFRARED ADSORBATE SPECTRA

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ABSTRACT

A vibrational bond between an adsorbed atom and a crystal can absorb photons from a weak (probe) laser field (frequency \(\omega\)). The line shape for this process is usually assumed to be a Lorentzian, which reflects that the kinetic coupling to the phonon reservoir is supposed to be a memoryless process. Due to the finite cutoff of the phonon dispersion relation (Debye frequency \(\omega_D\)), this is not an accurate approximation if the transition frequency \(\omega\) between two levels of potential well is of the same order of magnitude as \(\omega_D\). A finite memory-time reservoir theory is applied to the evaluation of the line shape, and two distinct properties were found. First, it is shown that the modified Lorentzian is identically zero for \(\omega > \omega_D\), and then a memory-induced line at \(\omega - \omega + \omega_D\) is predicted. The physical origin of these features is explained in terms of energy-conserving diagrams.

ABSORPTION PROFILE

An atom is confined to the surface of a harmonic crystal by the van der Waals force. The potential depends on the atom-surface distance. Thermal motion of the crystal atoms makes this distance a dynamical variable, and the coupling provides an energy-exchange mechanism. Phonons in the crystal can be absorbed by the adsorbate, and the bond can emit energy into the crystal by excitation of a phonon. This process gives rise to thermal relaxation of the adsorbate density operator \(\rho(t)\) to a steady state \(\rho\) (thermal equilibrium).

This system is irradiated by a low-intensity infrared laser, and the probability for the absorption of a photon as a function of its frequency \(\omega\) is indicated by \(I(\omega)\). With \(d\) the dipole moment of the bond, projected on the laser-polarization direction, \(L\) the Liouvillian of the atom in the potential well and a suppression of an overall factor, a general expression for the absorption profile reads

\[
I(\omega) = \text{Tr} \left( \frac{i\omega}{\omega - L + i\Gamma(\omega)} (d, \rho) - i\Gamma(\omega) \rho \right) .
\]

In a Markov approximation the relaxation operator \(\Gamma(\omega)\) becomes \(\omega\)-independent, and the second term in round brackets, \(\Gamma(\omega)\rho\), disappears. For potential wells which have resonance frequencies of the order of \(\omega_D\), a zero memory-time approximation, which leads to a Lorentzian line shape, cannot be justified.
MEMORY EFFECTS

Expression (1) for the profile pertains to any configuration of levels, any shape of the potential, and includes multiphonon transitions. In order to study the effect of a finite reservoir response time we consider the case where the potential supports only two bound states, separated by \( \omega_0 \). In Fig. 1 we have plotted the line shape for the situation \( \omega_0 \approx 3\omega_D \). The left peak comes from the term \([d, \rho]\) in Eq. (1), which would be a Lorentzian around \( \omega_0 \) in the Markov approximation. Due to the \( \omega \)-dependence of \( \Gamma(\omega) \) the line is cut off at \( \omega_D \), and only the low-frequency wing at \( \omega < \omega_D \) remains. The line at the right-hand side is situated at \( \omega = \omega_0 + \omega_D \), and it comes from the term proportional to \( T(\omega) \) in Eq. (1). Without a memory in the interaction, this line vanishes identically. We predict a memory-induced line at the sum frequency \( \omega_0 + \omega_D \).

In tracing back the mathematical origin of the operator \( T(\omega) \), it appears that this term enters as a consequence of the fact that the density operator of the entire system does not factorize into a product of the crystal density operator times the adsorbate density operator.

The physical origin of the two lines in Fig. 1 can be illustrated with the diagrams from Fig. 2. Process (a) is

![Figure 1. Typical absorption profile for a two-level system. Here, \( \hat{\omega} = \omega/\omega_D \) and the dotted line indicates the resonance frequency \( \omega_0 = 3\omega_D \).](attachment:figure1.png)
responsible for the line at \( \omega < \omega_0^D \), which would usually be a Lorentzian. Since there are no phonons with a frequency larger than \( \omega_0 \), however, photon absorptions with \( \omega > \omega_0^D \) do not occur. Consequently, the line vanishes for \( \omega > \omega_0^D \). Diagrams (b) and (c) explain the line around \( \omega - \omega_0 + \omega_0^D \), and it follows immediately that the line must disappear for \( \left| \omega_0 - \omega_0^D \right| > \omega_0^D \).

Figure 2. Transition diagrams which are responsible for the profile of Fig. 1. Double arrows indicate photons and single arrows are phonons.

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