

# Time-dependent dipole coupling and line narrowing in adsorbate vibrational spectroscopy

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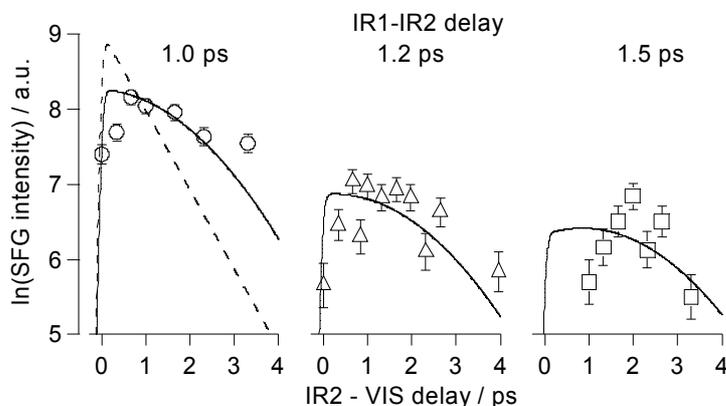
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**Abstract.** We use femtosecond infrared pump - sum frequency probe spectroscopy to measure all coherent and incoherent vibrational relaxation times for a molecule on a metal surface, CO/Ir(111), including midinfrared photon echoes from a metallic surface<sup>1</sup>. The echo peak shape changes as a function of delay time indicating a time-dependent inhomogeneity of the densely packed CO overlayer. We show that this is due to time-dependent dipole coupling induced line narrowing.

The vibrational linewidths of adsorbates with strong dynamic dipole moments are mainly determined by dipole-dipole coupling and do not fully reflect the inhomogeneity of the adsorbate layer. This well-known phenomenon in surface vibrational spectroscopy is due to intensity stealing as the high frequency oscillators in the distribution screen the external field at lower frequencies. Hence the infrared absorption is shifted towards higher frequencies with a tail at low frequencies. We show for the first time that time-resolved vibrational spectroscopy can determine the degree of line narrowing.

Our model system is the C–O stretch vibration in a strongly dipole-coupled CO layer on Ir(111) at 0.56 monolayer coverage. We obtain<sup>1</sup> a free induction decay time of  $T_2^{\text{inhom}}=1.9$  ps, a vibrational lifetime of  $T_1=2.4$  ps and vibrational echo peak shapes (see Fig. 1) which can be described by  $T_2^{\text{hom}}=4$  ps and an inhomogeneous contribution of  $\Delta\omega=3.0$   $\text{cm}^{-1}$ . This is identified as a lower limit to the inhomogeneity of the adsorbate layer, as a mixed CO isotope layer (which significantly reduces dipole coupling) has a much larger line width at the same coverage.

Careful analysis of the echo peak shapes shows that the measured inhomogeneity is not static, instead it increases with increasing IR1-IR2 delay (see Fig. 1). This is due to decreasing coherence in the collective CO overlayer vibration at longer delay times which reduces the intensity stealing. We incorporate the time-dependent dipole coupling by using a Green function formalism to solve the optical Bloch equations for the case of vibrational photon echoes<sup>2</sup>.



**Fig. 1.** Logarithmic plots of the CO/Ir(111) sum frequency infrared photon echo as a function of IR2-vis delay for IR1-IR2 delay times of 1.0 ps, 1.2 ps and 1.5 ps. The solid lines fit the echo decay with  $T_2 = 4$  ps and constant  $\Delta\omega=3.0$   $\text{cm}^{-1}$ . The dashed line is an example of a homogeneous decay of 1.9 ps.<sup>1</sup>

## References

- <sup>1</sup> Ian M. Lane, David A. King, Heike Arnolds, *J. Chem. Phys.* **126**, 024707 (2007).
- <sup>2</sup> Heike Arnolds, Ian M. Lane, unpublished.