

# CO Stretch Vibration Lives Long on Au(111)

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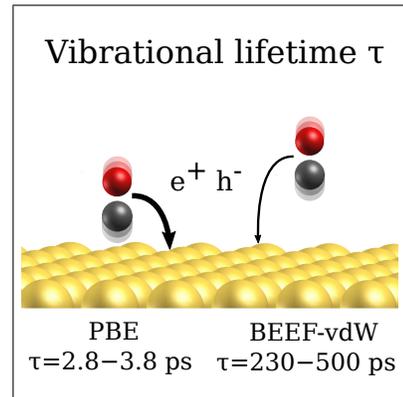
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## Abstract

Measured lifetimes of the CO internal stretch mode on various metal surfaces routinely lie in the picosecond regime. These short vibrational lifetimes, which are actually reproduced by current first-principles nonadiabatic calculations, are attributed to the rapid vibrational energy loss that is caused by the facile excitation of electron-hole pairs in metals. However, this explanation was recently questioned by the huge discrepancy that exists for CO on Au(111) between the experimental vibrational lifetime that is larger than 100 ps and the previous theoretical predictions of 4.8 and 1.6 ps. Here, we show that the state-of-the-art nonadiabatic theory does reproduce the long CO lifetime measured in Au(111) provided the molecule-surface interaction is properly described. Importantly, our new results confirm that the current understanding of the adsorbates' vibrational relaxation at metal surfaces is indeed valid.

## Graphical TOC Entry



The short vibrational lifetimes  $\tau$  of the high frequency modes of adsorbates at metal surfaces constitute a paradigmatic manifestation of non-adiabatic effects. Infrared fluorescence measurements showed that for a monolayer of CO adsorbed on the NaCl surface, for which there exists an energy threshold of around 9 eV for electronic excitations, the lifetime of the internal stretch (IS) mode lies in the millisecond regime.<sup>1</sup> This observation is in sheer contrast with the measured vibrational lifetimes of adsorbates on metal surfaces. For instance, early infrared absorption spectroscopy measurements provided a value of around 1.2-1.4 ps for the IS vibrational lifetime of an ordered CO monolayer adsorbed on the Cu(100) surface.<sup>2,3</sup> For the same system later pump-probe laser spectroscopy measurements reported lifetimes of  $2 \pm 1$  ps.<sup>4</sup> Also using pump-probe laser spectroscopy the coverage dependence of  $\tau$  was measured for CO adsorbed on Pt(111), obtaining values of around 2 ps.<sup>5</sup> The sharp reduction of the adsorbate IS lifetime from milliseconds in insulators to a few picoseconds in metals was ascribed to the effective non-adiabatic electron-vibration coupling that the adsorbates experience at metal surfaces. This interpretation has been confirmed by several theoretical works, which accounting for the nonadiabatic relaxation of vibrationally excited molecules at metal surfaces with different degrees of sophistication obtain lifetime values of the same order of magnitude as the experimental ones.<sup>6-20</sup> Remarkably, the recent incorporation of the electron-mediated coupling between vibrational modes has been decisive to finally achieve a quantitative assessment of the experimental lifetimes.<sup>21</sup> This also includes a precise identification of the ultrafast transient vibrational dynamics stimulated with femtosecond laser pulses.<sup>22</sup> All in all, it could be concluded that the mechanisms ruling the vibrational relaxation of molecules on metal surfaces are now correctly identified and well understood.

However, the new experimental results obtained by Shirhatti *et al.*<sup>23</sup> have put into question our current understanding of the vibrational relaxation of adsorbates on metal surfaces. In their work, the authors reported on

the adsorption and subsequent desorption of vibrationally excited CO from Au(111). These results allowed the authors to estimate a vibrational lifetime of the CO IS mode of  $\tau > 100$  ps that largely exceeds the aforementioned typical vibrational lifetimes measured and calculated on other metal surfaces. In fact, the existing first-principles theoretical calculations for this system predicted values of  $\tau = 1.6$  ps<sup>11</sup> and  $\tau = 4.8$  ps.<sup>15</sup> Clearly, these new experiments constitute a serious challenge for the prevalent theoretical model and, consequently, the current understanding of the vibrational energy dissipation at metal surfaces. In this work, we show however that the state-of-the-art nonadiabatic theory is still valid and that it correctly predicts the reported long experimental lifetimes, provided the CO-Au interaction is properly modeled.

Density functional theory (DFT) calculations of the CO interaction with metals are known to be quite problematic. A prominent example is the inability of semilocal DFT to correctly predict the adsorption site of CO on some metal surfaces, the so-called ‘‘CO puzzle’’.<sup>24</sup> Without going into the details, we highlight two factors that are in many cases at the origin of the reported inaccuracies in the adsorption energies predicted by DFT: (i) PBE,<sup>25</sup> the most common exchange-correlation functional for solid state DFT calculations, tends to overbind CO on metals<sup>26</sup> and (ii) van der Waals (vdW) interactions are important in the CO-metal systems.<sup>27</sup> As shown here, these considerations are particularly crucial for CO/Au(111) because of the physisorption nature of the CO binding on this surface, which is experimentally proven by the small redshift in the CO IS mode frequency of 13-18.5 cm<sup>-1</sup>.<sup>23,28</sup> In this respect, we find that the BEEF-vdW exchange-correlation functional<sup>29</sup> provides an accurate description of the CO/Au(111) system. This functional is specifically designed for surface science. In particular, it aims to provide accurate adsorption energies of small molecules on metal surfaces. The accurate BEEF-vdW description of the CO interaction with various metal surfaces has been confirmed by benchmarking with experimentally determined adsorption energies<sup>30</sup>

and with more advanced random phase approximation calculations.<sup>31</sup>

In this work, the ground state adsorption properties and vibrational modes of CO on Au(111) are calculated with DFT using the BEEF-vdW<sup>29</sup> and PBE<sup>25</sup> exchange-correlation functionals, as implemented in the plane-wave based QUANTUM ESPRESSO package.<sup>32</sup> The system is modelled with a periodic supercell that consists of a  $2 \times 2$  surface unit cell and five Au-layers separated by 20 Å of vacuum. We used GBRV pseudopotentials<sup>33</sup> with a kinetic energy cutoff of 820 eV and a gaussian smearing of 0.27 eV for the electronic-state occupancies. The Brillouin zone is sampled with a  $(8 \times 8 \times 1)$  Monkhorst-Pack mesh.<sup>34</sup> The CO/Au(111) slab is relaxed keeping the two Au bottom layers fixed. Convergence is achieved when the energy differences and forces are smaller than 0.1 meV and 2 meV/Å, respectively. Next, the vibrational lifetimes of the CO vibrational modes due to electron-hole pair excitations are calculated within density functional perturbation theory,<sup>35</sup> i.e., by means of the following Fermi's golden rule expression for the nonadiabatic vibrational damping rate (i.e., inverse lifetime in atomic units)<sup>16</sup>

$$\begin{aligned} 1/\tau_\nu &= 2\pi \sum_{\alpha \neq \beta, \mathbf{k}} \left| g_\nu^{\alpha\beta}(\mathbf{k}) \right|^2 [f(\varepsilon_{\alpha\mathbf{k}}) - f(\varepsilon_{\beta\mathbf{k}})] \\ &\quad \times \mathcal{L}(\omega_\nu + \varepsilon_{\alpha\mathbf{k}} - \varepsilon_{\beta\mathbf{k}}), \end{aligned} \quad (1)$$

where  $\alpha$  and  $\beta$  are the electron band indices,  $\mathbf{k}$  is the electron momentum, while  $\varepsilon_{\alpha\mathbf{k}}$  and  $\varepsilon_{\beta\mathbf{k}}$  are the corresponding energies. The Fermi-Dirac electron distribution function is denoted with  $f(\varepsilon)$ . The vibrational modes are indexed with  $\nu$  and their frequencies are  $\omega_\nu$ . The electron-vibration coupling matrix is  $g_\nu^{\alpha\beta}(\mathbf{k})$ . Energy conservation of the vibrational excitation of electron-hole pairs is ensured by the Lorentzian function  $\mathcal{L}(x) = (\Gamma/\pi)/(x^2 + \Gamma^2)$ , where  $\Gamma$  is the broadening of the electronic states. Converged lifetimes are obtained with a dense  $72 \times 72 \times 1$   $\mathbf{k}$ -point mesh and physically-motivated electron state broadenings  $\Gamma = 50 - 150$  meV. For other calculation details see Ref. 16.

In Fig. 1 we show the results obtained for the

adsorption energies. The PBE functional predicts a deep adsorption well of around 200 meV that, in agreement with previous calculations,<sup>15</sup> corresponds to the CO adsorbed vertically atop Au and close to the surface with a C-Au distance of 2 Å. In contrast, BEEF-vdW predicts

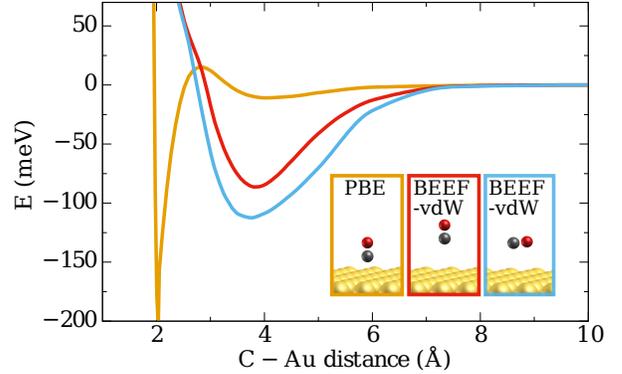


Figure 1: Adsorption energy as a function of the C-Au distance. The result obtained with the PBE functional for CO vertical to the surface is shown in orange. BEEF-vdW results for CO vertical and parallel to the surface are shown in red and blue, respectively. The position and orientation of the CO molecule in each adsorption well are shown in the corresponding colored rectangles.

a shallower well in which the CO molecule is further away from the surface with a C-Au distance of 4 Å. These features are those of a physisorption state. We have likewise explored different orientations of the CO molecule with respect to the Au surface. In the case of BEEF-vdW, we find that the lowest energy configuration corresponds to the molecule adsorbed roughly parallel to the surface. This result is consistent with the vdW character of the binding that is correctly captured by this functional. Nevertheless, note that the energy difference between the two configurations, parallel and normal to the surface, is rather small (of around 20 meV). The harmonic vibrational frequency of the IS mode calculated with BEEF-vdW is  $2190 \text{ cm}^{-1}$ . This is in better agreement with the experimental values of Refs. 23,28 ( $2124.5 \text{ cm}^{-1}$  and  $2130 \text{ cm}^{-1}$ , respectively) than the PBE value of  $2090 \text{ cm}^{-1}$  since the anharmonic correction softens the calculated values in around

$30 \text{ cm}^{-1}$ .<sup>36</sup> Finally, note that the BEEF-vdW functional used in this work underestimates the experimental binding energy of 180 meV obtained from temperature programmed desorption measurements.<sup>37</sup> However, as shown below, it describes correctly the long distance to the surface of the adsorption well and the vibrational frequency. These are the critical properties for a correct description of the IS vibrational lifetimes. In this regard, other functionals that fulfill these conditions are also expected to be a valid choice for this system.

Figure 2 shows the results of the electron-vibration coupling calculated with BEEF-vdW for both the parallel and vertical adsorption configurations and with PBE for the vertical CO. The left y-axis shows the damping rate due to electron-hole pair excitations,  $1/\tau_\nu$ , for the different modes as a function of their frequency. The right y-axis corresponds to the vibrational spectral function defined as  $F(\omega) = \sum_\nu (1/\tau_\nu) \delta(\omega - \omega_\nu)$ , where the index  $\nu$  runs over all vibrational modes. The spectral function shows that the overall vibrational coupling between the vibrational modes and the electronic system is weaker in the real physisorption state described by the BEEF-vdW functional (parallel or vertical) than in the chemisorbed state described by PBE. The decrease in the overall coupling when using BEEF-vdW is due to the corresponding increase in the CO-surface distance. Another important difference between the BEEF-vdW and PBE results refers to the relative strength of the electron-vibration coupling for the different normal modes. In the BEEF-vdW physisorption state, the electron-vibration coupling is much weaker for the IS mode than for the frustrated rotation (FR) mode. However, in the PBE adsorption well, the IS and FR modes exhibit roughly the same coupling strengths. Finally, it is worth to mention that, as expected, the electron-vibration coupling strengths for the surface-related modes (for which the frequencies are approximately  $\omega < 150 \text{ cm}^{-1}$ ) are rather similar in the three studied cases.

The IS and FR vibrational lifetimes due to electron-hole pair excitations are presented in Table 1. Different physically motivated broad-

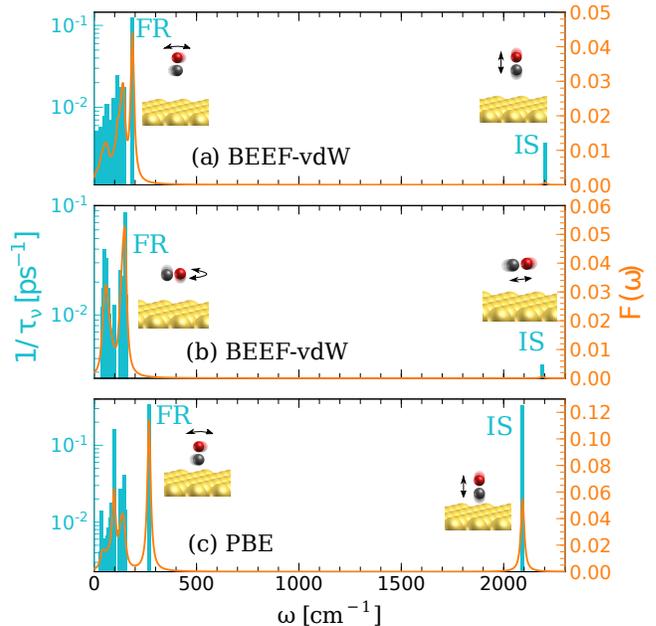


Figure 2: Damping rate  $1/\tau_\nu$  (left y-axis, blue bars) of CO and Au surface vibrational modes as a function of the mode frequency for (a) the vertical and (b) parallel adsorption wells obtained with BEEF-vdW, as well as for (c) the PBE vertical well. The vibrational spectral function  $F(\omega)$  that shows the degree of coupling with electron-hole pairs, is shown on the right y-axis (orange curves). The results for the CO internal stretch (IS) and frustrated rotation (FR) modes are labeled in order to emphasize their different coupling strengths to electron-hole pairs. Results obtained with an electronic state broadening  $\Gamma = 150 \text{ meV}$ .

enings of the electronic states have been used that vary between 50 and 150 meV. The range of electronic state broadenings determines the range of lifetimes obtained in each case, the longer lifetime corresponding to the smaller broadening and vice versa.<sup>16</sup> In the case of PBE, for which the CO-Au surface distance is small, we obtain a short lifetime of 2.8 – 3.8 ps that underestimates largely the experimental value  $\tau > 100 \text{ ps}$ .<sup>23</sup> In contrast, the BEEF-vdW functional, describing better the physisorption character of the CO-surface interaction, predicts a long vibrational lifetime of 230–500 ps and 270–330 ps for the vertical and parallel orientations, respectively. These large values are a consequence of the weak coupling to the electronic

**Table 1: Vibrational lifetimes of the internal stretch (IS) and frustrated rotation (FR) modes of CO adsorbed on Au(111) and Cu(100). Calculations performed with PBE and BEEF-vdW using electronic-state broadenings in the range  $\Gamma=50-150$  meV (in each case, the shortest lifetime corresponds to the largest  $\Gamma$  and vice versa). Distances between the C atom and the metal surface are shown as well.**

	Au(111)			Cu(100)		
	C-metal ( $\text{\AA}$ )	$\tau_{\text{IS}}$ (ps)	$\tau_{\text{FR}}$ (ps)	C-metal ( $\text{\AA}$ )	$\tau_{\text{IS}}$ (ps)	$\tau_{\text{FR}}$ (ps)
PBE vertical	2.0	2.8–3.8	2.5–4.2	1.9	3.0–4.6	2.1–3.2
BEEF-vdW vertical	4.0	230–500	6–17	1.9	3.8–4.9	1.7–2.6
BEEF-vdW parallel	3.7	270–330	66–68	-	-	-

system that the CO experiences at the usually large physisorption distances. Importantly, both the BEEF-vdW lifetime for the vertical and parallel orientations are in good agreement with the experimental observations.<sup>23</sup> This constitutes a signature of the robustness of our results. It is also worth to mention that the lifetime obtained with the BEEF-vdW functional for the FR mode is much shorter ( $\tau \sim 6 - 17$  ps in the vertical orientation and  $\tau \sim 66 - 68$  ps in the parallel one) than the lifetime of the IS mode. This is also consistent with the experimental observations indicating equilibration of the CO rotational degree of freedom with the surface.<sup>23</sup> Concerning the frustrated translation and the CO-Au modes it turns out that they are mixed with the Au surface modes (due to very similar frequencies) and the values of their lifetime vary between 120 and 600 ps (not shown). In addition, we would like to note that the calculated lifetimes, which correspond to a 0.25 CO coverage, might change when simulated for the zero coverage limit, for which the experimental lifetime estimation is made. Nevertheless, we do not expect qualitative nor significant quantitative variations.<sup>5,38,39</sup>

Finally, we also show in Table 1 the results obtained with BEEF-vdW and PBE for the prototypical chemisorption case of CO on Cu(100). The computational details of the vibrational lifetime calculations are the same as for CO/Au(111). The adsorption of CO on Cu(100) has become a paradigmatic system to analyze the electronically mediated vibrational deexcitation of adsorbates at metal surfaces. In

this respect, semilocal PBE and revPBE functionals<sup>40</sup> have been rather successful in describing the adsorption properties and measured vibrational lifetimes of this system.<sup>10,13–16,21</sup> Our results in Table 1 highlight that the BEEF-vdW functional can also describe this prototypical chemisorption system. First, the results of BEEF-vdW and PBE for the CO distance to the surface are identical. Moreover, the results obtained with BEEF-vdW for the IS mode frequency,  $2080 \text{ cm}^{-1}$ , and lifetime, 3.8–4.9 ps, are in very nice agreement with the ones we obtain with PBE here and with our previous revPBE calculations.<sup>16,21</sup> All these comparisons confirm the robustness of our approach, based on the BEEF-vdW functional, and the corresponding conclusions regarding the validity of current non-adiabatic vibrational relaxation theories.

In conclusion, we show that the existing theoretical tools can reproduce the long vibrational lifetimes measured by Shirhatti *et al.*<sup>23</sup> for the CO/Au(111) system, provided the molecule-surface interaction and the physisorbed character of the adsorption are adequately described. Importantly, our results confirm that our current understanding on the mechanisms behind the vibrational relaxation of adsorbates on metal surfaces, that had been recently put into question by the mentioned experiments, prevails.

**Acknowledgments.** I. L. was supported by the European Union through the European Regional Development Fund - the Competitiveness and Cohesion Operational Programme (KK.01.1.1.06) and the H2020 CSA Twin-

ning project No. 692194, RBI-T-WINNING. We acknowledge the Spanish Ministerio de Economía, Industria y Competitividad Grant No. FIS2016-76471-P. D.N. acknowledges financial support from the European Regional Development Fund for the “Center of Excellence for Advanced Materials and Sensing Devices” (Grant No. KK.01.1.1.01.0001). Computational resources were provided by the Donostia International Physics Center (DIPC) computing center.

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