Vibrational lifetimes of cyanide and carbon monoxide on noble and transition metal surfaces

Mattias Forsblom and Mats Persson

Surface Science Research Centre and Department of Chemistry,

The University of Liverpool, L69 3BX, Liverpool, UK

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Abstract

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Adiabatic potential energy surfaces which define the forces on atoms and molecules involved in the formation and breaking of chemical bonds, assumes independently evolving nuclear and electronic degrees of freedom (the Born-Oppenheimer approximation). All dynamical simulations based on density functional theory (DFT) calculations are firmly based on this approximation (?). It has been thoroughly tested for gas phase reactions [1], and has lately been widely applied to chemical reactions on metal surfaces. However, for metallic systems the condition of independent nuclear and electronic motion can never be strictly met, because of the presence of a continuum of conduction electron states [2]. Recent experimental results have clearly demonstrated the significant role of electronic excitations in a wide variety of surface reactions [3–7]. Despite this fact, remarkably little progress has been made in developing theoretical methods that go beyond the Born-Oppenheimer approximation.

The first experimental evidence of electronic non-adiabaticity was provided by measurements of vibrational lifetimes of adsorbed molecules on metal surfaces (ref.?), which yielded lifetimes in the order of picoseconds for CO on different metal surfaces, in contrast to the millisecond lifetimes expected from a strictly vibrational coupling. The dramatic increase in vibrational damping was first accounted for in a model involving non-adiabatic coupling through an adsorbate-induced resonance near the Fermi level [8]. Recent advances in DFT calculations have enabled calculations of the magnitude of the electronic vibrational damping using a perturbative approach [9]. However, the number of such studies is still limited and there is currently no clear understanding of which electronic factors are important in determining the vibrational damping rate.

Most earlier theoretical studies of vibrational damping have been carried out for the internal stretch mode for the CO adsorbate (C-O mode), with very little having been done for other adsorbate species. Recent lifetime measurements [10, 11] on noble and transition metal surfaces have shown a striking difference in trends between the C-N and C-O modes. In this Letter, we use time-dependent DFT [9, 12] to address the question of which elements in the adsorbate-induced electronic structure are important in determining the electronic vibrational lifetime \( \tau \). We consider the internal stretch mode of CN and CO adsorbed on (111) surfaces of Ag, Cu, Au, and Pt, and are able to explain the difference in trends between the C-N and C-O modes in terms of details in the chemisorption bond and non-adiabatic electronic effects.
Total energy and structure calculations for the CN and CO adsorption were carried out using density functional theory (DFT). The calculations were based on a plane-wave basis set and a projected augmented wave method [13, 14] as implemented in VASP [15, 16]. Exchange-correlation energies were calculated using the Perdew-Wang form of the generalized gradient approximation [17]. CN and CO adsorption on the metal surfaces were modeled using a slab in a periodically repeated supercell [18]. The positions of the C and N (O) atoms and the metal atoms in the two outermost surface layers were geometrically relaxed until all forces in each direction were smaller than 0.03 eV/Å [19].

Vibrational energies and modes were obtained through a diagonalization of the dynamical matrix for the adsorbate. We constructed the dynamical matrix from calculated forces, obtained from the restoring forces due to finite displacements of the C and N (O) atoms in three mutually orthogonal directions, with a frozen substrate.

The vibrational damping rate $\gamma$ of the internal stretch mode of the adsorbed molecules by electron-hole pair excitations was calculated using the Fermi Golden-rule-like formula [9, 12]

$$
\gamma = \frac{2\pi\hbar}{M} \sum_{\nu,\nu'} |\langle \psi_{\nu'} | v' | \psi_{\nu} \rangle|^2 \delta(\epsilon_{\nu'} - \epsilon_{\nu}) \delta(\epsilon_F - \epsilon_{\nu}).
$$

(1)

Here $\psi_{\nu}$ are the Kohn-Sham states with energies $\epsilon_{\nu}$, $\epsilon_F$ is the Fermi energy, and $M$ is the reduced mass of the vibrational mode with coordinate $Q$. The electron-vibration coupling $v'$ is $v'(r) = (\partial v(Q)/\partial Q)|_{Q=0}(r)$, where $v(r;Q)$ is the effective Kohn-Sham potential. For details about applying Eq. (1) to a supercell with a slab geometry see Ref. 9.

As discussed below, the adsorption geometries of the CN and CO molecules can not be simply predicted from DFT calculations. Therefore we have restricted our geometry optimization to the experimentally suggested configuration of the adsorbed CN and CO molecules, corresponding to an atop site and a perpendicular orientation relative to the surface, with the C atom coordinated to the metal atom. A coverage of 1/4 was found to be sufficiently close to the low coverage limit of isolated molecules [20]. Table I gives our calculated vibrational energies $\hbar\Omega$ and lifetimes $\tau$ for the internal stretch mode for CN adsorbed on (111) surfaces of Ag, Cu, Au, and Pt. Our calculations for the C-O mode yielded $\tau = 1.5$ ps (Ag), 1.6 ps (Au), and $\tau = 1.8$ ps (Cu and Pt), and the vibrational energies $\hbar\Omega = 2056$ cm$^{-1}$ (Ag), 2040 cm$^{-1}$ (Cu), 2073 cm$^{-1}$ (Au), and 2078 cm$^{-1}$ (Pt). The results are well converged with respect to the choice of the surface Brillouin zone integration wave-vector mesh [21].
The current gradient approximations for the exchange-correlation functional in DFT have well known limitations in finding the minimum energy adsorption site for CO on metal surfaces [22]. For instance, DFT calculations predict that at low coverage CO prefers the hollow site to the experimentally determined atop adsorption site on Pt(111) [23]. Recent DFT calculations have also pointed out another limitation of these functionals for CN adsorption on metal surfaces. On Cu(111), CN was predicted to be most stable with its molecular axis perpendicular to the surface, in conflict with the experimentally determined parallel orientation, whereas the latter orientation was preferred using the local density approximation for the exchange-correlation functional [24]. However, the adsorption geometry of CN has been found from experiments to be sensitive to the electrochemical environment [25] and co-adsorption of oxygen [26].

Since the available experimental data for the lifetimes of the C-N mode [10, 11] were obtained from measurements on polycrystalline Ag and Au, Pt(111), and Cu(111) electrochemical interfaces, we have chosen the adsorption geometry suggested by experiments in electrochemical environments. Indirect information about the adsorption geometry was obtained from vibrational spectroscopy of the C-N mode. The unusually high vibrational energies $\hbar \Omega$ of about 2100 cm$^{-1}$ for this mode on the (111) surfaces of Ag, Au and Pt in an aqueous electrolyte, as shown in Table I, have been argued to be indications of atop adsorption sites. Also, the measured $\hbar \Omega = 2120$ cm$^{-1}$ and 2115 cm$^{-1}$ on the polycrystalline Ag and Au surfaces, respectively, are close to the corresponding measured values on (111) surfaces, suggesting a low-coordinated adsorption site such as the atop site. This conclusion about the adsorption geometry is supported by the favourable comparison of the calculated $\hbar \Omega$ for CN in the atop adsorption site with the measured $\hbar \Omega$, as shown in Table I, and the fact that $\hbar \Omega$ is very sensitive to the choice of adsorption site. For example, calculations for CN adsorbed in hollow sites on Cu(111) and Au(111) gave $\hbar \Omega = 2011$ cm$^{-1}$ and 1987 cm$^{-1}$, respectively. Furthermore, the calculated $\hbar \Omega = 1962$ cm$^{-1}$ for atop CN with a parallel adsorption geometry on Pt(111) [27] is also well below the $\hbar \Omega > 2100$ cm$^{-1}$ in Table I.

The experimentally observed trend from pumb-probe measurements [10, 11] of the lifetimes for the C-N mode on the Cu, Ag, Au, and Pt surfaces, $\tau(\text{Ag}) \gg \tau(\text{Cu}) \approx \tau(\text{Au}) \gg \tau(\text{Pt})$, is well reproduced by our calculations (cf. Table I). The C-O mode is found from experiments to be rapidly damped ($\tau \approx 2$ ps) and insensitive to the choice of metal and crystal orientation, and to the electrochemical environment [10, 11]. As previously mentioned,
our calculations yielded a lifetime for the C-O mode of about 2 ps for every metal surface considered here, in agreement with the measured lifetimes. Thus for the C-N mode there is a strong variation of $\tau$ with the metal surfaces whereas for the C-O mode the variation is weak.

This stark contrast between the trends for $\tau$ of the C-N and C-O modes raises the question of which electronic factors are important in determining $\tau$. Obviously, it is not simply the metal DOS at the Fermi level that determines the magnitude of $\tau$. Thus, one needs to analyze the electronic structure of the adsorbed molecules and how it influences $\tau$ to explain this difference in trends.

To begin with we have investigated the electronic structure and the chemisorption bond of the CN and CO molecules adsorbed on the metal (111) surfaces, by calculating projections of the DOS (PDOS) on molecular orbitals of the isolated molecules [28]. Since the behaviors of the PDOS for the CN and CO admolecules were found to be very similar on the noble metal surfaces, we show only the PDOS for CN and CO adsorbed on Ag(111) and Pt(111) in Figs. 1 and 2. The CN and CO molecules have the same configuration of molecular orbitals but they have different energies and electron occupations resulting in quite different interactions with the metal surfaces.

The CN molecule is a radical with a single electron in the $5\sigma$ orbital and forms a strong chemisorption bond with a metal surface. As shown in Fig. 1, the $5\sigma$ orbital hybridizes with the $4\sigma$ orbital and turns into a filled resonance structure below the Fermi level upon the interaction with the metal substrate states. The resulting adsorption state of CN is then essentially CN$^-$ which is isoelectronic with CO. The electrostatic repulsion associated with this electron donation shifts the centroids of the molecular resonances up to higher energies. In particular, the $2\pi^*$ resonance shifts to an energy far above the Fermi level. The main difference between the PDOS for the Ag and Pt surfaces is the behavior of the $5\sigma$ and $1\pi$ MOs. Figure 1 shows a broad resonance due to the $1\pi$ MO hybridizing with the high-lying Pt d-states. On Ag the $1\pi$ MO interacts weakly with the substrate, whereas the $5\sigma$ MO broadens appreciably when interacting with the metal states.

CO is a closed shell molecule with a large gap between the highest occupied molecular orbital $5\sigma$ and the lowest unoccupied molecular orbital $2\pi$ and forms weaker chemisorption bonds with the metal surfaces than the CN molecule. The interaction of the $2\pi^*$ orbital with the metal states results in a downward shift in energy and a broadening into a partially
occupied resonance. This backdonation of electrons to the $2\pi^*$ orbital from the metal and
the small donation of electrons from the $5\sigma$ orbital to the metal (not visible on the scale of
the vertical axis used in Fig. 2) is responsible for the formation of the chemisorption bond
according to the Blyholder model [29] and its later refinements [30]. On the Pt surface, the
formation of anti-bonding states of $5\sigma$ MO with the higher-lying d-band of Pt than on the
noble metal surfaces enhances the PDOS of the $5\sigma$ MO around $\epsilon_F$.

The adsorbate-induced electronic structure at $\epsilon_F$ influences the vibrational lifetime
through the behavior of the wave functions close to the molecule where the field from the vi-
brating ion-cores is strong [cf. Eq. (1)]. The calculated PDOS for the CO and CN molecules
exhibit characteristic and suggestive differences in this respect. Primarily, the $5\sigma$ and $1\pi$
MOs induce states close to $\epsilon_F$ for the CN admolecules with some characteristic differences
between the Ag and Pt surfaces, whereas for the CO admolecules the $2\pi$-induced resonance
states are much closer to $\epsilon_F$.

In order to quantify the influence of the adsorbate-induced electronic structure on the
vibrational lifetime, we have developed an approximation to Eq. (1) involving the PDOS on
the MOs of the isolated molecule. This approximation is based on the fact that the efficient
screening of the field from the vibrating ion-cores by the conduction electrons limits the
spatial range of the electron-vibration coupling $v'(r)$ to the vicinity of the molecule. An
expansion of $v'(r)$ in a truncated localized basis set $|\phi_n\rangle$, such as the MOs of the isolated
molecules, is then meaningful [31]:

$$v' \approx \sum_{n,m} |\phi_n\rangle v'_{nm} \langle \phi_m|.$$  \hspace{1cm} (2)

Inserting Eq. (2) in Eq. (1) gives the damping rate

$$\gamma_{\text{local}} = \frac{2\pi \hbar}{M} \sum_{n,m,k,l} \rho_{nm}(\epsilon_F) v'_{mk} \rho_{kl}(\epsilon_F) v'_{ln},$$  \hspace{1cm} (3)

where $\rho_{nm}(\epsilon)$ are the one-electron density matrix elements

$$\rho_{nm}(\epsilon) = \sum_\nu \langle \phi_n | \psi_\nu \rangle \langle \psi_\nu | \phi_m \rangle \delta(\epsilon - \epsilon_\nu).$$  \hspace{1cm} (4)

Note that the diagonal element $\rho_{nn}(\epsilon)$ is simply the PDOS on the orbital $n$. The specific
details of the vibrational mode and coupling enters only through $v'_{nm} = \langle \phi_n | v'| \phi_m \rangle$, which
is obtained from the first-order change of the first-order moment of $\rho_{nm}(\epsilon)$ with respect to


vibrational amplitude. In particular if the sum is dominated by the contribution from a single orbital \( n \), the result for the Persson-Persson mechanism for vibrational damping is recovered [8]:

\[
\gamma_{\text{local}} = \frac{2g\pi\hbar}{M} \rho_{nm}(\epsilon_F)^2(\nu_{mn}')^2,
\]

(5)

where \( g \) is the degeneracy of the orbital. In general, there may be contributions to \( \gamma_{\text{local}} \) from several orbitals in the sum.

Using Eq. (3), we are able to quantitatively rationalize the different trends in damping rates for CN and CO adsorbed on (111) surfaces of Ag, Cu, Au, and Pt. As shown in Table II, the behavior and the magnitude of \( \gamma \) for the C-N and C-O modes are reproduced reasonably well by \( \gamma_{\text{local}} \) when using the localized basis sets of 5\( \sigma \) and 1\( \pi \) MOs and 5\( \sigma \), 2\( \pi \), and 6\( \sigma \) MOs for CN and CO, respectively. This makes it possible to analyze the calculated \( \gamma \) in terms of inter- and intra-orbital contributions to \( \gamma_{\text{local}} \).

From such an analysis we find that the larger damping rate for CN on Pt(111) compared to the (111) noble metal surfaces of Ag, Au, and Cu is due to a higher PDOS at \( \epsilon_F \) on the 1\( \pi \) MOs. For CN on Pt(111), we find that \( \gamma_{\text{local}} \) is totally dominated by the contribution in Eq. (5) for the two-fold degenerate 1\( \pi \) orbital. On the noble metal surfaces, this term decreases substantially due to the decrease in the PDOS on this orbital by a factor of about 3–4 and the corresponding contribution from 5\( \sigma \) orbital becomes comparable in magnitude, as shown in Table II. Note that the electron-vibration coupling matrix elements \( v_{5\sigma 5\sigma}' \) and \( v_{1\pi 1\pi}' \) are by comparison only weakly dependent on the metal and interorbital contributions are very small due to symmetry reasons.

The trend for the damping rate of the C-N mode on the noble metal surfaces is a combined effect of the variation of the electron-vibration coupling matrix elements and the PDOS. The larger value for \( \gamma \) on the Au(111) surface than on the (111) surfaces of Cu and Ag is primarily caused by an increase in the PDOS on the 5\( \sigma \) molecular orbital at \( \epsilon_F \).

The larger magnitudes of the damping rate for the C-O mode compared to the C-N mode, as shown in Table II, are due to large values of the PDOS originating from the 2\( \pi \)-induced resonance states close to \( \epsilon_F \). Hence \( \gamma_{\text{local}} \) for the C-O mode is dominated (except for Pt, cf. Table II) by the term in Eq. (5) for the two-fold degenerate 2\( \pi^* \) MO. There are also contributions to \( \gamma_{\text{local}} \) from (small) interorbital terms involving the 2\( \pi^* \) and 6\( \sigma^* \) MOs [cf. Eq. (3)]. However, the sum \( \gamma_{2\pi^*6\sigma^*} \) of such terms may be important, see Table II. (Show 6\( \sigma^* \) in PDOS plots?) For CO on Pt there is an additional contribution to \( \gamma_{\text{local}} \) from the
term in Eq. (5) for the 5σ MO. The weak variation of the damping rate for the C-O mode with respect to the metal surfaces is explained by an interplay between the PDOS and electron-vibration coupling terms which tend to smoothen out variations in γ.

Thus we find that the correlation between the measured τ and the position of the metal d-bands relative to the Fermi level as pointed out earlier [11] is not simply a causal relation. However, the behavior of the...

In conclusion, we have shown that...

[16] The plane waves were truncated at a kinetic energy of 500 eV and the surface Brillouin zone was sampled using a Γ-centered Monkhorst-Pack 8 × 8 wave vector mesh. A second-order Methfessel-Paxton smearing [32] with a width of 0.2 eV was used.
[18] The supercell consisted of a six layer slab of (111) atomic planes, each containing four metal atoms, and a vacuum region corresponding to seven atomic layers. The unrelaxed slab was constructed using the calculated equilibrium lattice parameter [22]. CN and CO admolecules
were positioned at a single side of the slab.

[19] The structural optimizations resulted in upright CN and CO molecules, with binding distances and C-metal distances in good agreement with earlier calculations for CO [22] and CN [33–35].

[20] The CN molecules with a surface coverage of 1/4 are weakly interacting. We performed a calculation for CN adsorbed at atop sites on Cu(111) with a coverage of 1/16, which gave very similar results in total energy, chemisorption parameters, and vibrational energies, compared to the calculation with a coverage of 1/4. CO adsorbate-adsorbate interactions have been found to be weak at coverages lower than about 1/3 [22].

[21] We carried out calculations of the CN Ag(111) system using 12 × 12 and 16 × 16 wave-vector meshes for the integration of the surface Brillouin zone. Compared to the calculation using a 8 × 8 wave-vector mesh, we obtained nearly identical results for the C-N binding distance, molecule-metal distance, and the vibrational energy of the internal stretch mode for the CN molecule. We observed variations in γ of only a few percent between the calculations.


[28] The valence molecular orbitals of the isolated CN molecule were calculated using spin-restricted DFT calculations.


<table>
<thead>
<tr>
<th>Surface</th>
<th>$\hbar \Omega$ (calc.)</th>
<th>$\hbar \Omega$ (exp.)</th>
<th>$\tau$ (calc.)</th>
<th>$\tau$ (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(111)</td>
<td>2160</td>
<td>2110$^a$</td>
<td>39</td>
<td>28–60$^b$</td>
</tr>
<tr>
<td>Cu(111)</td>
<td>2136</td>
<td>$^c$</td>
<td>22</td>
<td>18 ± 4$^d$</td>
</tr>
<tr>
<td>Au(111)</td>
<td>2176</td>
<td>2130$^e$</td>
<td>13</td>
<td>10–19$^b$</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>2142</td>
<td>2108$^f$</td>
<td>2.4</td>
<td>3–8$^b$</td>
</tr>
</tbody>
</table>

$^a$From Ref. 36.
$^b$From Ref. 10.
$^c$Not available.
$^d$From Ref. 11.
$^e$From Ref. 37.
$^f$From Ref. 27.

TABLE I: Calculated and experimental vibrational energies $\hbar \Omega$ (in cm$^{-1}$) and lifetimes $\tau$ (in ps) for the internal stretch mode of CN at atop sites on (111) surfaces of Ag, Cu, Au, and Pt.

FIG. 1: Calculated DOS projected on some of the molecular orbitals for CN adsorbed on (a) Ag(111) and (b) Pt(111), using the same C-N binding distances as for the adsorbed molecule. Both spin and orbital degeneracies have been included. The dotted vertical line denotes the position of the Fermi energy, and the dashed vertical lines are the positions of the free molecular orbitals. The color coding in (b) is the same as in (a).
<table>
<thead>
<tr>
<th>System</th>
<th>$\gamma$</th>
<th>$\gamma_{\text{local}}$</th>
<th>$\gamma_1\pi 1\pi$</th>
<th>$\gamma_5\sigma 5\sigma$</th>
<th>$\gamma_{2\pi^* 2\pi^*}$</th>
<th>$\gamma_{2\pi^* 6\sigma^*}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN/Ag(111)</td>
<td>0.026</td>
<td>0.032</td>
<td>0.014</td>
<td>0.020</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CN/Cu(111)</td>
<td>0.044</td>
<td>0.051</td>
<td>0.029</td>
<td>0.022</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CN/Au(111)</td>
<td>0.079</td>
<td>0.058</td>
<td>0.015</td>
<td>0.043</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CN/Pt(111)</td>
<td>0.41</td>
<td>0.20</td>
<td>0.19</td>
<td>0.0084</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CO/Ag(111)</td>
<td>0.65</td>
<td>1.52</td>
<td>0.00</td>
<td>0.00</td>
<td>2.02</td>
<td>-0.41</td>
</tr>
<tr>
<td>CO/Cu(111)</td>
<td>0.56</td>
<td>1.038</td>
<td>0.00</td>
<td>0.00</td>
<td>1.29</td>
<td>-0.28</td>
</tr>
<tr>
<td>CO/Au(111)</td>
<td>0.64</td>
<td>0.78</td>
<td>0.00</td>
<td>0.00</td>
<td>0.96</td>
<td>-0.18</td>
</tr>
<tr>
<td>CO/Pt(111)</td>
<td>0.57</td>
<td>0.19</td>
<td>0.00</td>
<td>0.079</td>
<td>0.11</td>
<td>-0.030</td>
</tr>
</tbody>
</table>

**TABLE II:** Vibrational damping rates for the internal stretch mode of CN and CO on the (111) surfaces of Ag, Cu, Au, and Pt. All rates are given in units of $10^{12}$ s$^{-1}$. The rates have been calculated using the full Kohn-Sham wave function as basis set ($\gamma$) and also using a truncated localized basis set formed from molecular orbitals of an isolated CN molecule ($\gamma_{\text{local}}$). Also, the sums of the individual contributions from intraorbital terms to $\gamma_{\text{local}}$ are given. (But rates cannot be negative - comment on this.)

**FIG. 2:** Same as for Fig. 1, but for CO.