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# Sum-Frequency Generation Vibrational Spectroscopy of an Extramolecular Chemical Bond

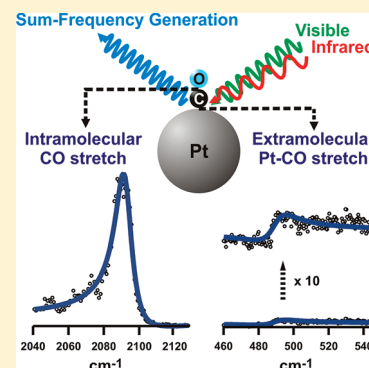
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**S** Supporting Information

**ABSTRACT:** Infrared–visible sum-frequency generation (SFG) vibrational spectroscopy is applied to evidence the extramolecular Pt–C chemical bond and deduce an experimental value of its Raman activity at the CO/Pt(110) interface. This measurement, performed on a flat metal surface, without surface roughening, does not involve any enhancement of the electromagnetic fields. We evidence that the experimental Raman polarizability of the extramolecular Pt–C stretching vibration mode is around 1.49 times smaller than that of the intramolecular CO stretching vibration mode. Furthermore, SFG data show that the infrared dynamic dipole moments differ in sign for the two vibrational modes, as suggested by density functional theory (DFT) calculations. The weak SFG intensity experimentally measured from the Pt–C chemical bond is accounted for by its low infrared activity. For surface chemistry, these results open the door to systematic investigation of extramolecular vibrational activity at the submonolayer level.

**SECTION:** Surfaces, Interfaces, Catalysis



Surfaces and interfaces host the molecular processes involved in heterogeneous chemistry, for example in interfacial electrochemistry, heterogeneous catalysis, and nanochemistry.<sup>1</sup> Vibrational spectroscopies are straightforward nondestructive analysis tools of in situ chemistry at interfaces. In the case of monolayers or less, they suffer from their low selectivity to discriminate between “bulk” and “surface-adsorbed” molecules, excepting polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS).<sup>2</sup> When applied to metals and other high refractive index materials, Raman spectroscopy additionally suffers from its usual geometry of investigation, relying much on information limited to components of the electric field parallel to the metal surface. While Raman data on flat metal surfaces have been recorded with specific high-yield molecules,<sup>3</sup> the most widespread way to extract such data is to perform surface-enhanced Raman spectroscopy (SERS) on a roughened or nanostructured surface. Local amplification of electromagnetic fields and specific charge-transfer effects lead to a strong enhancement of the Raman response, which becomes measurable. The case of flat surfaces, either single crystals or polycrystals, remains hard to address by traditional Raman methods, even if constant increase in their sensitivity has been evidenced by recent advances.<sup>4</sup>

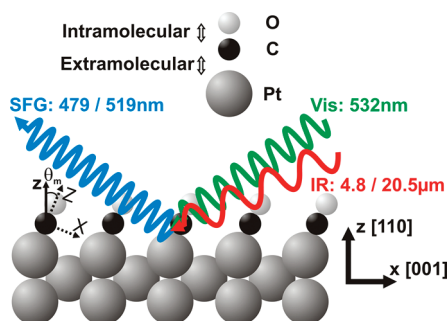
Nonlinear optics offers a solution to overcome this problem by infrared–visible sum-frequency generation (SFG) vibrational spectroscopy,<sup>5</sup> a specific probe of the surface and interface physical and chemical properties, with submonolayer sensitivity. Furthermore, the SFG cross section of a vibration is proportional to the product of its infrared (IR) and Raman activities. SFG spectroscopy has therefore established its reputation as a

sensitive probe of vibrational and electronic transitions at all kinds of interfaces, from the nanoscale to the biological scale, at static or dynamic equilibrium.<sup>6,7</sup> Here, we apply this method to a very challenging system, the far-infrared extramolecular metal–adsorbate vibration in a submonolayer of carbon monoxide (CO) deposited on a Pt(110) single crystal (Figure 1) in model (but close to realistic) conditions, that is, a nitrogen environment at ambient temperature. In other words, we perform SFG spectroscopy of the Pt–CO vibration in the first step (CO adsorption) of the heterogeneous catalysis mechanism. We show that it leads to an absolute determination of Raman cross sections of extramolecular and intramolecular bond vibrations on flat surfaces, which may in turn benefit the understanding of more complex interfaces (for example, nanostructured) and help validate quantum chemistry calculations.

The Pt/CO system is the archetype of molecular adsorption in surface science, with applications to catalysis and electrochemistry. On the one hand, the low energy of extramolecular Pt–C vibration facilitates its detection by low-energy electrons.<sup>8</sup> On the other hand, the need for in situ studies favors optical spectroscopies in non-UHV (ultrahigh vacuum) environments. The metal–carbon bond has been detected on Pt(111), Pt(110), rough Pt, and Pt-shell nanoparticles by infrared reflection absorption spectroscopy<sup>8,9</sup> (IRRAS), SERS,<sup>10,11</sup> IR emission,<sup>12</sup> and thermal emission spectroscopies.<sup>13</sup> For IRRAS processes, their low cross sections limit the experimental possibilities and

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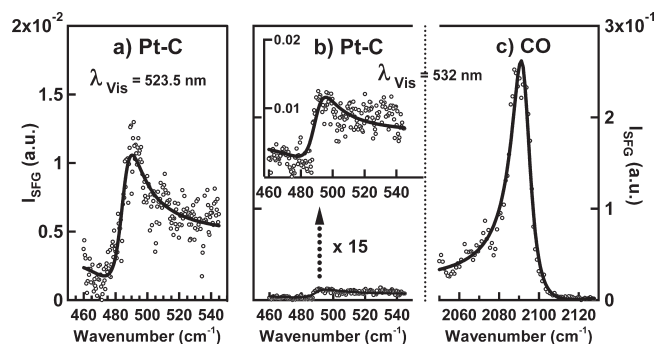
**Figure 1.** Sketch of the SFG process at CO/Pt(110)-(1 × 1) interface. The *z*-axis and *x*-axis are oriented along [110] and [001] directions of the Pt substrate, respectively. Incidence angles of the visible (green) and infrared (red) lasers are 55 and 65°, respectively. All beams travel in the (*xz*) plane. *Z* and *X* are parallel and perpendicular to the CO molecular axis, respectively.  $\theta_m$  is the tilt angle of the CO molecular axis with respect to the *z*-direction.

often require a synchrotron source.<sup>9</sup> The reported SERS efficiency offers more comfortable working conditions,<sup>11</sup> but the technique required until recently roughened surfaces rather than single crystals.<sup>4</sup> SFG spectroscopy overcomes such limitations and allows detection of the metal–adsorbate bond on various substrates beyond any electromagnetic amplification.

Attempts to detect extramolecular bonds by SFG were unsuccessfully performed a decade ago. They planned to benefit from the availability of the high-power tunable IR source of a free-electron laser (FEL)<sup>14</sup> to overcome the weak yields of IR tabletop optical parametric oscillators (OPO) to detect extramolecular vibrations at 500 cm<sup>−1</sup>. The lowest-energy intramolecular mode ever probed by SFG was the C–S stretch at 420 cm<sup>−1</sup>.<sup>15</sup> As for extramolecular vibrations, the Ag–S<sup>15</sup> and Pt–C<sup>16</sup> bonds, in thiophenol/Ag(111) and CO/Pt(111) systems respectively, could not be detected. The surface Pt–H or Si–H bonds (located at around 2000 cm<sup>−1</sup>) have been probed in the past,<sup>17</sup> but they should be regarded as the substrate outermost layer rather than extramolecular bonds.

Here, we report SFG spectra of the Pt–C extramolecular (Figure 2a and b) and CO intramolecular (Figure 2c) chemical bonds in nitrogen environment for 523.5 and 532 nm visible wavelengths, respectively. In order to relate our experimental data with the SFG literature on the subject, we will focus on Figure 2b and c (532 nm incident visible wavelength). We deduce the average peak positions ( $487 \pm 3$  cm<sup>−1</sup>;  $2093 \pm 1$  cm<sup>−1</sup>) and damping constants ( $7.6 \pm 1.5$  cm<sup>−1</sup>;  $5.3 \pm 0.5$  cm<sup>−1</sup>) of the extramolecular Pt–C and intramolecular CO stretching vibration modes.

These results are consistent with the literature investigating CO on Pt(110) substrates by IR (intra, extra),<sup>9,18</sup> HREELS (high-resolution electron energy loss spectroscopy, intra, extra),<sup>19</sup> and SFG (intra) spectroscopies.<sup>20,21</sup> Their positions refer to CO molecules adsorbed on the atop sites of the Pt atoms organized in the Pt(110)-(1 × 1) relaxed orientation at ambient temperature (Figure 1).<sup>22</sup> IRRAS experiments performed with a synchrotron source<sup>9</sup> locate indeed the vibrational mode at 480 cm<sup>−1</sup> at full coverage with a 8 cm<sup>−1</sup> resolution (and at least 10 cm<sup>−1</sup> lower for a (1 × 2) reconstruction). The IR laser beam of the CLIO FEL<sup>14</sup> used in our SFG experiment has a better spectral resolution. The slight frequency shift (2–3%) can be explained by the non-UHV environment (nitrogen atmosphere containing 1%



**Figure 2.** Experimental SFG spectra (O) of Pt–C (a) at 523.5 nm and Pt–C (b) and CO (c) stretches at a 532 nm visible wavelength with the same SFG intensity scale. Spectra show interference between the molecular and substrate responses. The inset in (b) displays a 15-fold magnified intensity scale, evidencing the derivative shape of the Pt–C vibration, inverted with respect to the CO one in (c). Lines are fits to the data (see Supporting Information).

CO molecules; see Supporting Information). From the Raman side, only SERS experiments, depending on the Pt surface roughness, have been performed ( $\sim 470$  cm<sup>−1</sup>),<sup>10</sup> precluding direct experimental comparison of IR and Raman data on the same single crystals.

The SFG prominent feature is the access to the IR and Raman activities of both vibrational modes on the same flat surface, which is not possible with other optical and electronic spectroscopic tools. We use hereafter a value of the IR activity ratio deduced from IR absorption data to estimate their Raman relative intensities. With  $(\text{Abs}_z^{\text{IR}})_{\text{int}} \propto (\partial\mu_z/\partial Q_{\text{vib}})^2$ ,  $(I_{\text{Stokes}}^{\text{Raman}})_{\text{int}} \propto (\omega_{\text{Stokes}})^3 (\partial\alpha_{zz}/\partial Q_{\text{vib}})^2 (\hbar/2\omega_{\text{vib}})$ ,  $(\mu_z^{\text{vib}})^2 = (\hbar/2\omega_{\text{vib}}) (\partial\mu_z/\partial Q_{\text{vib}})^2$ , and  $(\alpha_{zz}^{\text{vib}})^2 = (\hbar/2\omega_{\text{vib}}) (\partial\alpha_{zz}/\partial Q_{\text{vib}})^2$ , where  $Q_{\text{vib}}$ ,  $\mu$ , and  $\alpha$  are the vibrational normal mode coordinate, molecular dipole moment, and molecular polarizability, respectively, and *z* is the normal to the surface, we eventually calculate the  $\mu_z^{\text{Pt-C}}/\mu_z^{\text{CO}}$  IR dipole moment and  $\alpha_{zz}^{\text{Pt-C}}/\alpha_{zz}^{\text{CO}}$  Raman polarizability ratios given in Table 1. The complete derivation procedure, which takes account of laser spot sizes and time structures, Fresnel reflectivity, and hyperpolarizability tensor decomposition, will be detailed in a forthcoming publication.

No available IR absorption data enable a direct comparison of the IR cross sections of Pt–C over CO stretches on Pt(110). Values for relative IR intensities on a Pt(111) surface in the literature vary with the coverage and the reference.<sup>8,16,23</sup> We take an average value of  $2.76 \times 10^{-2}$  for the experimental Pt–C/CO IR absorption ratio,<sup>23</sup> compatible with a low coverage as in our experiment. Using this input value, we find  $\alpha_{zz}^{\text{Pt-C}}$  around 1.49 times smaller than  $\alpha_{zz}^{\text{CO}}$ , implying a factor of 0.63 for the relative experimental Pt–C/CO Raman scattering intensity in a typical configuration (excitation wavelength of 632.8 nm). This estimation is compatible with the experimental values measured on a rough Pt/CO system by SERS in an electrochemical environment, leading to experimental Pt–C/CO Raman intensity ratios between 0.60 and 2.80 (hence,  $\alpha_{zz}^{\text{Pt-C}}/\alpha_{zz}^{\text{CO}}$  between 0.66 and 1.42), depending on the electrochemical potential and surface preparation.<sup>10,11,24</sup> On the contrary, neither experimental method (i.e., SFG, SERS, or IR) fully matches the values of the dynamic infrared dipole moment and Raman polarizability ratios of the extramolecular and intramolecular vibrations calculated by density functional theory (DFT), probably because of its

**Table 1. Infrared and Raman Activity Ratios of Pt–C over CO Stretching Vibrational Modes from Optical Vibrational Spectroscopy (IR, Raman, SFG) and DFT Calculations<sup>a</sup>**

technique	infrared activity		Raman activity	
	$[(\text{Abs}_z^{\text{IR}})_{\text{int.}}^{\text{Pt-C}}]/[(\text{Abs}_z^{\text{IR}})_{\text{int.}}^{\text{CO}}]$	$\mu_z^{\text{Pt-C}}/\mu_z^{\text{CO}}$	$[(I_{\text{Stokes}}^{\text{Raman}})_{\text{int.}}^{\text{Pt-C}}]/[(I_{\text{Stokes}}^{\text{Raman}})_{\text{int.}}^{\text{CO}}]$	$\alpha_{zz}^{\text{Pt-C}}/\alpha_{zz}^{\text{CO}}$
IRRAS	$[2.76 \times 10^{-2} - 3.37 \times 10^{-2}]$	$[0.34 - 0.38]$		
SERS			$[0.60 - 2.80]$	$[0.66 - 1.42]$
SFG	$2.76 \times 10^{-2b}$	$0.34^b$	0.63	0.67
DFT	$1.87 \times 10^{-2}$	0.28	4.49	1.80

<sup>a</sup>Quantities labeled “int.” are integrated over the infrared wavenumber.  $\text{Abs}^{\text{IR}}$  and  $I^{\text{Raman}}$  represent the infrared absorption and Raman scattering intensity (see text for definitions). <sup>b</sup>Values taken from ref 23.

limitations (Pt cluster size, available functionals, and basis sets) as well as the lack of information on the reduced masses of the vibrational modes.<sup>25</sup> Eventually, the weak SFG signal of the Pt–C stretch results from its weak IR activity but in no case from its Raman properties, similar to those of the CO stretch.

SFG data analysis gives access to a specific parameter, the relative signs of the amplitudes of both vibrational modes, provided that a resonant vibrational signal interferes with a nonresonant background from the substrate. The phase shift between adsorbate and substrate contributions accounts for the interference pattern (hence, the apparent width) in the vibrational fingerprint of the interface. In our case, this parameter converges to 0 during data fitting, which is consistent with the absence of interband contribution in the platinum response in the probed ranges.<sup>26</sup> With this result, the inverted derivative shapes of the spectra in Figure 2a and b with respect to that in Figure 2c imply opposite signs for the SFG oscillator strengths of Pt–C and CO vibrational modes to match these profiles. It means that SFG spectroscopy gives the additional information that either their IR or Raman contributions have dominant components of opposite signs along the *z*-direction normal to the surface. This result is in accordance with the cluster DFT calculations for this system,<sup>25</sup> suggesting that the polarizability keeps a constant sign whereas the dynamic dipole moment changes sign between both vibrations. SFG spectroscopy allows confirmation of such theoretical predictions, whereas IR absorption alone cannot.

Breaking the frontier of extramolecular bond spectroscopy by nonlinear optics offers promising prospects for in situ surface science and its applications such as electrochemistry and catalysis in the gas phase. The adsorbate–substrate bond, as the most directly involved in the adsorption process, is a first-choice vibrational signature when compared to the indirect information extracted from intramolecular modes. Literature also shows that Pt–C is more sensitive to adsorption sites and geometries than the CO stretch while being less disturbed by dipole–dipole coupling.<sup>11</sup> Furthermore, experimental measurements of absolute Raman activities, without an experimental enhancement factor (surface roughening, SERS effect), should serve as benchmarks for the consistency of theoretical predictions of vibrational activities on metal crystals and clusters by quantum chemistry (e.g., DFT, post-Hartree–Fock methods), helping at improving, in particular, the basis set accuracy for metals in vibrational applications at various levels of theory. The versatility of SFG optical spectroscopy will pave the way to applications related to harder problems, among which we point out the electrochemical environment on one side and the far-infrared studies of

metal–sulfur bonds, of great interest for the design of thin films, sensors, and transducers, on the other side. In addition, it opens the door to time-resolved studies of extramolecular bond monitoring at the picosecond scale.

## EXPERIMENTAL METHODS

In order to investigate the extramolecular low-energy range, a two-color SFG (2C-SFG) setup<sup>27</sup> is built around the CLIO FEL European facility.<sup>14</sup> A picosecond Nd:YVO<sub>4</sub> oscillator pumps two OPOs, tunable in the 1250–4000 cm<sup>−1</sup> IR and 420–700 nm visible spectral ranges, respectively. Constituting the key originality of the setup, the CLIO FEL may substitute within 1 min for the IR OPO and, as it is tunable from 50 to 1600 cm<sup>−1</sup>, allows performance of SFG spectroscopy over the whole IR spectral range on a single sample. As the strong CO and weak Pt–C SFG signals are both recorded on a single interface in the same conditions (sample environment, visible beam, and detection line), our experimental setup allows quantitative comparison of their SFG intensities. Finally, it makes it possible to check that no CO desorption was induced by the lasers as it might be a cause for the underestimation of the Pt–C signal.<sup>16</sup>

## ASSOCIATED CONTENT

**S Supporting Information.** Experimental procedures including SFG principles and the data fitting procedure and description of the SFG setup coupled to the FEL and CO/Pt(110) sample preparation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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