

Novel Surface Vibrational Spectroscopy: Infrared-Infrared-Visible Sum-Frequency Generation

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A novel type of surface vibrational sum-frequency generation spectroscopy is presented that enables a highly specific measurement of the coupling of molecules on surfaces. With this doubly vibrationally resonant technique, two-dimensional vibrational spectroscopy of molecules on surfaces becomes possible. The technique is demonstrated for the C-O stretch vibration of CO on a ruthenium (001) surface. It allows for the determination of the intermolecular coupling strength of dipole-coupled CO molecules on the surface.

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Nonlinear spectroscopic techniques have been proven very powerful in revealing intermolecular interaction dynamics and homogeneous line shapes in the condensed phase. In particular, there has recently been great interest in infrared four-wave mixing (IR-FWM) spectroscopy [1–6], which is a third-order ($\chi^{(3)}$) nonlinear optical process. If both the incident IR fields are resonant with vibrational transitions in the sample [doubly resonant vibrationally enhanced (DOVE) IR-FWM [3,6]], this technique has been demonstrated to be an excellent probe of coupling of vibrational modes in liquids [6] and proteins [2].

We present here the first observation of a doubly vibrationally resonant DOVE-FWM signal from a surface, i.e., a resonant $\chi^{(3)}$ process leading to infrared-infrared-visible sum-frequency generation (IIV-SFG), which, in analogy to FWM from liquids, contains information on the coupling of vibrational modes at the surface. This demonstrates the possibility of extending multidimensional spectroscopy to surfaces, illustrated here for the C-O stretching vibration of carbon monoxide (CO) on a single crystal ruthenium (001) surface. The intermolecular coupling strength is determined from the IIV-SFG signal, which is demonstrated to be sensitive to the CO-CO distance.

The experiments were carried out in an ultrahigh vacuum chamber (base pressure 1×10^{-10} mbar) equipped with standard surface diagnostics. Our commercial laser system delivers 800 nm, 110 fs pulses of 4.5 mJ/pulse at 400 Hz, which are used to pump an OPG/OPA (optical

parametric generator/amplifier) providing tunable ($\lambda = 2\text{--}10 \mu\text{m}$, bandwidth $\sim 150 \text{ cm}^{-1}$) IR pulses with an energy of typically $10 \mu\text{J}$ and a duration of 150 fs. The portion of the 800 nm pulse which is not converted into IR in the OPG/OPA process is spectrally narrowed down to 4 cm^{-1} , and is used in the SFG experiments as the VIS-up-conversion pulse. Details can be found in Ref. [7]. Unless otherwise indicated, SFG spectra were recorded at 100 K.

The technique of SFG relies on the fact that the second-order nonlinear susceptibility $\chi^{(2)}$ is nonvanishing at centrosymmetric interfaces [8]. This enables the generation of an electric field E_{SFG} out of two incident fields E_{VIS} and E_{IR} , where energy $\hbar\omega$ and parallel momentum $k_{\parallel}$ must be conserved ($\omega_{\text{SFG}} = \omega_{\text{VIS}} + \omega_{\text{IR}}$ and $k_{\parallel}^{\text{SFG}} = k_{\parallel}^{\text{VIS}} + k_{\parallel}^{\text{IR}}$). For ω_{IR} within the IR bandwidth resonant with a vibrational transition, the signal is resonantly enhanced [9]. This is illustrated in the upper panel of Fig. 1, which depicts the resonant SFG spectrum from the well-ordered $(\sqrt{3} \times \sqrt{3})R30^\circ\text{-CO}$ [0.33 monolayer (ML) coverage] on Ru at 95 K, along with the nonresonant signal from the bare surface, which contains the entire infrared bandwidth. In these experiments the 690 nm SFG light (800 nm + 5 μm) is dispersed in a monochromator and detected by an intensified charge-coupled device (CCD) array. The resonant SFG signal can be well described by a Lorentzian line shape, with a linewidth of the C-O stretch resonance of 12 cm^{-1} . This is larger than that observed with reflectance infrared spectroscopy due to slight saturation of

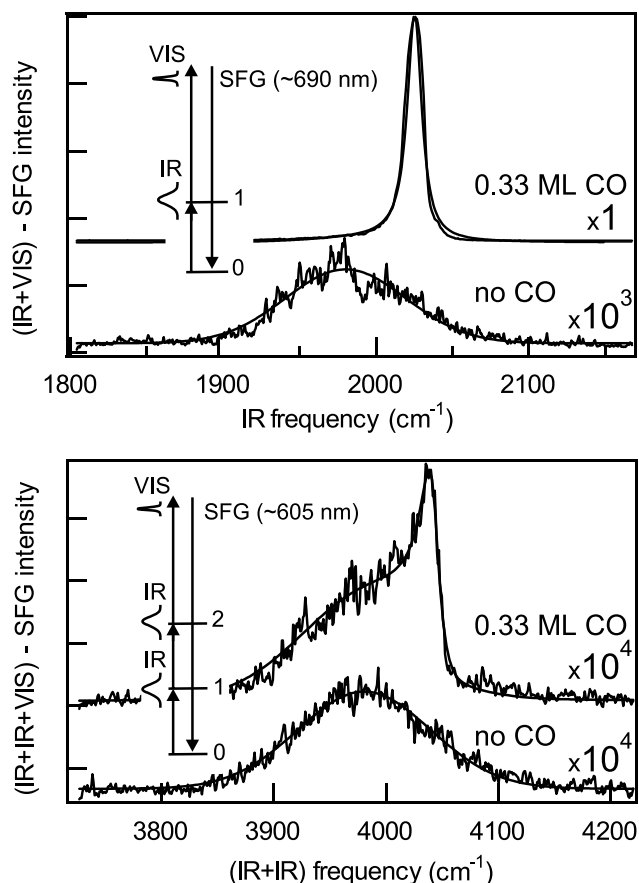


FIG. 1. Upper panel: IV-SFG spectrum of the C-O stretching vibration of 0.33 ML of CO on Ru ($\sqrt{3} \times \sqrt{3}$)-CO/Ru(001) (12.0 cm^{-1} FWHM) at 95 K and the nonresonant SFG signal from the bare surface. Lower panel: IIV-SFG spectrum from the ($\sqrt{3} \times \sqrt{3}$)-CO/Ru(001) surface, as well as from the bare surface. Scaling factors indicate the relative intensities of the signals. Lines through the data are fits described in the text.

the vibrational transition [10] and the limited spectral resolution ($\sim 5 \text{ cm}^{-1}$) [11] of our setup.

The lower panel of Fig. 1 depicts the higher-order $\chi^{(3)}$ IIV-SFG signal, both for the ($\sqrt{3} \times \sqrt{3}$)-CO/Ru(001) structure and the bare surface. This signal is centered around 605 nm ($\omega_{\text{IIV-SFG}} = \omega_{\text{VIS}} + \omega_{\text{IR}} + \omega_{\text{IR}}$) and comes off the surface at a slightly different angle than the IV-SFG, due to phase-matching considerations ($k_{\parallel}^{\text{IIV-SFG}} = k_{\parallel}^{\text{VIS}} + k_{\parallel}^{\text{IR}} + k_{\parallel}^{\text{IR}}$). In the incident infrared field, there was no IR intensity around 4000 cm^{-1} ($2.5 \mu\text{m}$), which could give rise to a IV-SFG signal at this frequency. Furthermore, the IIV-SFG signal intensity scales with I_{IR}^2 , and the position of the resonant peak was found to be independent of the IR center frequency.

The width of the nonresonant IIV-SFG is 1.4 ± 0.1 that of the nonresonant IV-SFG, in good agreement with the factor of $\sqrt{2}$ that one expects when the gaussian IR spectrum is convoluted with itself. Its relatively large intensity can be understood by noting that for the IIV-SFG there is a bulk $\chi^{(3)}$ contribution from the underlying metal [12]. The resonant IIV-SFG signal exhibits a narrow resonance

superimposed on a broad nonresonant background, which demonstrates that the signal is due to a doubly vibrationally resonant process; in a singly vibrationally resonant process (i.e., a combination of a singly resonant and a nonresonant process) a narrow peak cannot appear due to the large bandwidth of the IR pulse.

From Fig. 1 it is clear that the resonant IIV-SFG peaks at $\nu_{\text{IIV}} = 4040 \text{ cm}^{-1}$, at twice the frequency of the fundamental transition at $\nu_{\text{IV}} = 2020 \text{ cm}^{-1}$, and has approximately twice the width of the fundamental, $\Gamma_{\text{IIV}} = 2 \times \Gamma_{\text{IV}}$. ν_{IIV} and Γ_{IIV} are obtained from fits to the data described below and in [11]. One might expect to find the resonant IIV-SFG at the $\nu = 0$ to $\nu = 2$ transition, known from overtone spectroscopy [13] to be located at 3940 cm^{-1} at 100 K. The observation that $\nu_{\text{IIV}} = 2 \times \nu_{\text{IV}}$ could indicate that the IIV signal is due to two cascading *second-order* nonlinear optical processes [14], rather than a direct *third-order* process. However, the radiated IV-SFG field is much too weak to be able to create a cascaded IIV-SFG signal, even when one considers local field corrections [15]. Furthermore, the coverage dependence of the signal contradicts the cascading mechanism (see below). The observation that $\nu_{\text{IIV}} = 2 \times \nu_{\text{IV}}$ can be understood by noting the relatively strong dipolar interaction between CO molecules on the surface [10,16], apparently making an IIV transition at twice the fundamental frequency more likely than at the $\nu = 0 \rightarrow 2$ transition.

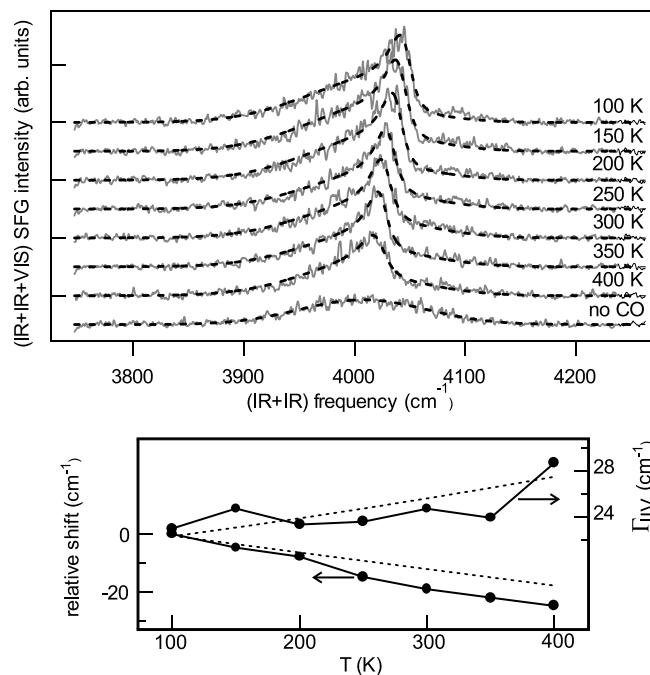


FIG. 2. Temperature dependence of the IIV-SFG spectrum for the ($\sqrt{3} \times \sqrt{3}$) structure. The results of the fits are summarized in the lower panel, representing the variation of width and center frequency with temperature. The dashed lines in this graph result from a model assuming temperature dependent anharmonic coupling of the fundamental of the C-O stretch vibration to the low-frequency frustrated translational mode [16], multiplied by a factor of 2.

The interpretation of the data in terms of coupled CO oscillators is corroborated by the temperature dependence of the IIV-SFG signal, depicted in Fig. 2. The lower panel depicts the temperature dependence of the width Γ_{IIV} and the shift of the center frequency ν_{IIV} of the resonant part of the IIV-SFG obtained from fits to the spectra in the upper panel. The lines through the data are the result of calculations of Γ_{01} and ν_{01} for the fundamental transition [16] that shifts and broadens due to anharmonic coupling to low-frequency modes [17]. The data can be described quite well setting $\Gamma_{\text{IIV}} = 2 \times \Gamma_{01}$ and $\nu_{\text{IIV}} = 2 \times \nu_{01}$ (and accounting for the experimental resolution and slight saturation effects). This supports the interpretation of the IIV-SFG data in terms of two $0 \rightarrow 1$ transitions, since for

the $0 \rightarrow 2$ transition, (i) the temperature dependence of the linewidth is 4 times stronger than for the $0 \rightarrow 1$ [13], increasing up to 40 cm^{-1} at 300 K whereas (ii) the shift of the resonance is only 5 cm^{-1} from 30 to 265 K.

It has recently been demonstrated theoretically [18] that the resonant part of $\chi^{(3)}$ that gives rise to the IIV-SFG signal can be expressed as $\chi_{\text{RES}}^{(3)} = \chi_{\text{AN}}^{(3)} + \chi_{\text{NL}}^{(3)}$, where $\chi_{\text{AN}}^{(3)}$ and $\chi_{\text{NL}}^{(3)}$ can be nonzero due to the anharmonicity of the vibration and higher-order (nonlinear) contributions from the expansion of dipole moment and polarizability operators, respectively [18]. A detailed analysis of the different contributions to $\chi^{(3)}$ that possibly contribute to the observed signal reveals that $\chi_{\text{RES}}^{(3)}$ giving rise to the IIV resonance is described by the $\chi_{\text{NL}}^{(3)}$ contribution:

$$\chi_{\text{RES}}^{(3)} = \sum_{jk} \frac{(\partial^2 \alpha_g / \partial Q_j \partial Q_k)_0 (\partial \mu_g / \partial Q_j)_0 (\partial \mu_g / \partial Q_k)_0 \langle 0, 0 | Q_j Q_k | 1, 1 \rangle \langle 1, 1 | Q_j | 0, 1 \rangle \langle 0, 1 | Q_k | 0, 0 \rangle}{(2\omega_{\text{IR}} - 2\omega_{01} + 2i\Gamma_{01})(\omega_{\text{IR}} - \omega_{01} + i\Gamma_{01})}, \quad (1)$$

where Q_i represents the vibrational coordinate of molecule i , α_g represents the collective polarizability of the sample in the electronic ground state, and μ_g the electronic ground state dipole moment associated with the CO molecules. The physical interpretation of this equation is that initially, one interaction with the IR field results in the vibrational excitation of the j th stretching mode from $\langle 0, 0 |$ to $\langle 1, 0 |$. Then, the second interaction vibrationally excites the k th CO molecule, from $\langle 1, 0 |$ to $\langle 1, 1 |$. Clearly, the energy of the $\langle 1, 1 |$ state is twice that of the fundamental transition. The final visible-field-matter interaction creates a third-order nonlinear polarization at frequency $2 \times \nu_{01} + \nu_{\text{VIS}}$, which radiates the observed IIV-SFG signal. This latter interaction with the visible field requires that the term $(\partial^2 \alpha_g / \partial Q_j \partial Q_k)$ is nonzero, which implies that the electronic polarizability should be affected by the vibrational coordinates of two different CO oscillators on the surface. Hence, the electronic states involved are delocalized over the two CO molecules and possibly also over the Ru metal surface. As can be seen in the lower panel of Fig. 1 and in Fig. 2, the IIV-SFG data are very well described by $I(\omega) \equiv |\chi_{\text{NR}}^{(3)} + \chi_{\text{RES}}^{(3)}|^2$, with $\chi_{\text{RES}}^{(3)}$ from Eq. (1) and $\chi_{\text{NR}}^{(3)}$ obtained from the IIV signal from the bare surface.

The intermolecular coupling giving rise to the resonant IIV signal is contained in the term $(\partial^2 \alpha_g / \partial Q_j \partial Q_k)$ appearing in Eq. (1). This is a measure for the intermolecular coupling strength, and for two CO molecules interacting with each other through a dipole-dipole-type coupling mechanism, it can be approximated in terms of single-molecule polarizabilities by [18]

$$(\partial^2 \alpha_g / \partial Q_j \partial Q_k)_0 \cong \frac{1}{4\pi \epsilon_0 r_{jk}^3} \times (\partial \alpha_j / \partial Q_j)_0 : \tilde{T}_{jk} : (\partial \alpha_k / \partial Q_k)_0, \quad (2)$$

where $\tilde{T}_{jk}$ represents the tensorial part of the dipole-dipole interaction tensor [18]. Thus, the IIV-SFG signal is dominated by neighboring CO molecules at short intermolecular

distances r and therefore contains information on this distance. The determination of the magnitude of the coupling strength $(\partial^2 \alpha_g / \partial Q_j \partial Q_k)$ and the intermolecular distance r from the signal requires knowledge of the magnitude of the terms $(\partial \mu / \partial Q)$ and $(\partial \alpha / \partial Q)$ appearing in Eqs. (1) and (2), respectively. It is a general problem in SFG spectroscopy that these prefactors are unknown.

Although unknown and hard to establish, it is possible to obtain the ratio of these prefactors for different coverages, and determine relative changes in the coupling strength. For N molecules on the surface, the infrared absorption intensity is proportional to $N(\partial \mu / \partial Q)^2$, the IV-SFG intensity to $N^2(\partial \mu / \partial Q)^2(\partial \alpha / \partial Q)^2$, and the IIV-SFG intensity is proportional to $N^2(\partial^2 \alpha / \partial Q_j \partial Q_k)^2(\partial \mu / \partial Q_j)^2(\partial \mu / \partial Q_k)^2$. Figure 3 depicts the IV-SFG and the IIV-SFG for two different coverages, at 0.33 ML and at the saturation coverage of 0.68 ML. The integrated IV-SFG signal decreases by a factor of 3.0 ± 0.2 going from 0.33 to 0.68 ML. The integrated resonant contributions to the IIV-SFG signals in contrast, are very similar, changing only by a factor of 0.97 ± 0.18 from 0.33 to 0.68 ML [note that for a cascading process the signal would decrease by a factor of $(3.0)^2$]. By comparison, the infrared absorption intensity decreases by a factor of 1.25 ± 0.05 due to dipole coupling effects [19]. This means that $(\partial \mu / \partial Q)_{0.33} / (\partial \mu / \partial Q)_{0.68} = 1.61 \pm 0.03$ and $(\partial \alpha / \partial Q)_{0.33} / (\partial \alpha / \partial Q)_{0.68} = 2.22 \pm 0.09$, where the subscript denotes the coverage. The coupling strength $(\partial^2 \alpha / \partial Q_j \partial Q_k)$ must therefore *increase* by a factor of 1.24 ± 0.08 going from 0.33 to 0.68 ML. This is due to the closer proximity of CO molecules at 0.68 ML.

An independent estimate of the change in coupling strength can be made from Eq. (2) in combination with the average distance $r = 3.33 \text{ \AA}$ at 0.66 ML coverage and $r_{0.33} = 4.7 \text{ \AA}$ as determined from electron diffraction studies [20] (the factor $\tilde{T}_{jk}$ will not change from

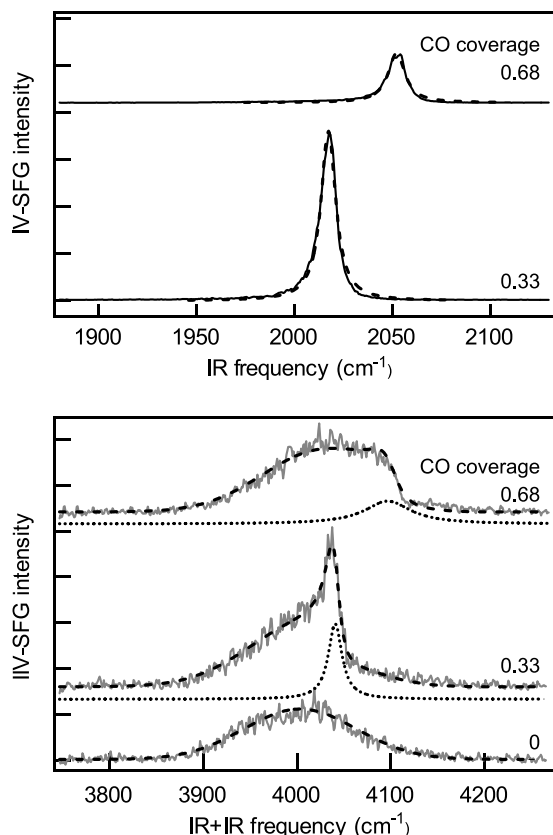


FIG. 3. Coverage dependence of the IV-SFG spectrum (upper panel) and the IIV-SFG spectrum (lower panel). At 0.33 ML CO molecules are in the well-ordered ($\sqrt{3} \times \sqrt{3}$) structure, whereas 0.68 ML is the saturation coverage. Dashed lines are fits and dotted lines in the lower panel represent the resonant contribution to the signal (multiplied by 2).

0.33 to 0.68 ML, since the relative orientation of CO molecules remains identical [20]). This results in a change in $(\partial^2 \alpha / \partial Q_j \partial Q_k)$ by a factor of 0.59 ± 0.03 going from 0.33 to 0.68 ML, significantly smaller than the 1.24 ± 0.08 obtained from the intensities. Electron diffraction, however, provides a measure of the average distance, whereas the IIV signal is very sensitive to the distribution of intermolecular distances, due to the r^3 dependence of the interaction: contributions to the IIV signal from pairs of CO molecules close to each other will be relatively large. The saturation coverage is not very well ordered due to a lattice mismatch between the CO lattice and the underlying Ru [20], and there will be a statistical distribution of intermolecular distances, to which the IIV signal is particularly sensitive. Calculating r with a coupling strength 1.24 ± 0.08 from Eq. (2) results in $r_{0.68} = 2.7 \pm 0.15$ Å, with $r_{0.33} = 4.7$ Å. Since the CO molecules are preferentially located on a-top positions [19], i.e., on top of Ru atoms, an appropriate comparison might be with the interatomic distance of Ru atoms on the Ru(001) surface of 2.71 Å, which corresponds well with the computed value. It should be noted however, that

a complete theoretical approach would have to include the image dipole of the CO molecules, the statistical distribution of intermolecular distances, and the number of neighboring molecules as well as interactions with next-nearest-neighbor molecules.

In conclusion, we have demonstrated a new type of surface vibrational spectroscopy that relies on a third-order nonlinear optical process. These experiments demonstrate the possibility of doing two-dimensional vibrational spectroscopy on surfaces. Such experiments can provide important and detailed information about the nature and the strength of intermolecular coupling of molecules at surfaces, which is essential for, for example, a full understanding of surface chemistry.

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