First-Principles Framework to Compute Sum-Frequency Generation Vibrational Spectra of Semiconductors and Insulators
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A first-principles framework to compute sum-frequency generation vibrational spectra of semiconductors and insulators

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We present a first-principles framework to compute sum-frequency generation (SFG) vibrational spectra of semiconductors and insulators. The method is based on density functional theory and the use of maximally localized Wannier functions to compute the response to electric fields, and it includes the effect of electric field gradients at interfaces. In addition, it includes quadrupolar contributions to SFG spectra, thus enabling the verification of the dipolar approximation, whose validity determines the surface specificity of SFG spectroscopy. We computed the SFG spectra of ice I$_h$ basal surfaces and identified which spectra components are affected by bulk contributions. Our results are in good agreement with experiments at low temperature.

The determination of the atomistic structure of surfaces and interfaces is a central problem in materials physics and in nanoscience [1, 2]. Among surface sensitive probes, non-linear optical spectroscopies such as sum-frequency generation (SFG) have been widely used for decades to study the structure and dynamics of surfaces and interfaces [3, 4]. However the interpretation of experimental data remains difficult and, in many instances, controversial [5]; in addition most theoretical models adopted to interpret experiments have been based on multiple approximations and on the use of empirical force fields [6, 7].

In an SFG experiment, an interface is illuminated by two beams, of frequency $\omega_1$ in the visible and $\omega_2$ in the infrared range, and the emitted sum-frequency (SF) light is detected, with a frequency $\omega_e = \omega_1 + \omega_2$. The total emitted intensity is proportional to the square of the complex effective second-order nonlinear (or SFG) susceptibility $\chi^{(2)}$ of the medium. Indeed, within the dipole approximation, the SFG signal of centrosymmetric bulk regions vanishes, and the intensity of the emitted SF light originates only from atoms or molecules present at the interface, where centrosymmetry is broken. We note that it is the absence of quadrupole and higher order contributions that ultimately determines the surface specificity of SFG spectroscopy. Experimentally, it is difficult to validate the dipole approximation, and to establish whether quadrupole contributions are negligible; only part of the quadrupolar effect may be identified experimentally, by comparing the intensities detected in transmission and reflectance optical geometries [8, 9]. Hence to understand and interpret SFG signals, a robust and predictive computational framework is required, inclusive of a quantitative estimate of quadrupole contributions.

The theoretical foundation of SFG vibrational spectroscopy dates back more than two decades [9–11]; nevertheless calculations of SFG intensities and comparisons between theory and experiments remain challenging problems: (i) The explicit inclusion of quadrupole contributions requires the calculation of both interfacial and bulk terms to obtain the total susceptibility (unlike dipole contributions, for which only interfacial terms are to be evaluated). In atomistic simulations using slab geometries to model interfaces, the consistent evaluation of bulk and interfacial terms is an extremely demanding task, from a computational standpoint. (ii) The evaluation of quadrupole contributions requires special care in the case of dipolar molecules, in order to avoid origin dependent results. (iii) The evaluation of SFG susceptibilities includes the calculation of local dielectric functions, necessary to properly evaluate the variation of the electric field at the interface; in many studies such variation was simply ignored.

Recently, Shiratori and Morita [12] proposed a computational framework for the evaluation of SFG spectra, using mixed quantum and molecular mechanics methods to compute dipole and quadrupole contributions from molecular non-linear polarizabilities. However their method was applied only to a non-polar molecular liquid [13], using empirical atomic potentials. Byrnes et al. [14] proposed a technique relying on cancellation between interface and bulk contributions, where the variation of the electric field at the interface was ignored. All investigations of SFG spectra reported so far used empirical potentials, expect that of Ref. [15] on liquid water. However the latter contained numerous approximations: quadrupole contributions and electric field variation at the surface were ignored; in addition, the authors used severe approximations in evaluating time correlation functions (TCF) [15] over short time scales ($\sim 3$ ps).

In this Letter, we propose a first principles theoretical framework to predict SFG spectra, which is based on density functional theory and includes both dipole, and surface and bulk quadrupole contributions. The latter were obtained with a technique yielding origin independent results. We computed SFG susceptibilities using Maximally Localized Wannier functions (MLWFs) [16, 17], within a general formulation valid for semiconductors and insulators, which includes the evaluation of local dielectric functions accounting for the variation of the electric field across the interface. We present an application of the method to the study of the SFG spectra of the ice
we will not show the frequency dependency ($\omega$; see Eq. S2 [25]); it is diagonal and its position and frequency dependent elements are defined in terms of local dielectric functions $\epsilon(\omega, z)$. The latter are of key importance to account for the variation of the electric field across the interface.

The expressions of the quadrupole contributions, $\chi_{\text{eff}}^{1Q}$ and $\chi_{\text{eff}}^{1Q}$, in terms of Fresnel coefficients and of the second-order nonlinear susceptibilities for quadrupole transitions ($\chi_2^{Q_1}$, $\chi_2^{Q_2}$ and $\chi_2^{Q_3}$), are given in Eqs. S3 and S6 [25]. Here we note that $\chi_{\text{eff}}^{1Q} = \chi_{\text{eff}}^{1Q} + \chi_{\text{eff}}^{1Q}$ [9, 12], where $\chi_{\text{eff}}^{1Q}$ is fully determined by bulk properties and can be computed using a bulk sample (with $x, y, z$ periodicity); $\chi_{\text{eff}}^{1Q}$ is instead computed using a slab geometry [25]. The $\chi_{\text{eff}}^{1Q}$ term [27] can be experimentally identified by comparing signals from transmission or reflectance optical geometries [9]. On the contrary the $\chi_{\text{eff}}^{1Q}$ term cannot be determined experimentally.

In sum, in our calculation the SFG susceptibility is decomposed as:

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{eff}}^{(2)} + \chi_{\text{eff}}^{(2)} + \chi_{\text{eff}}^{(2)} + \chi_{\text{eff}}^{(2)},$$

where the first two terms on the rhs are obtained by carrying out calculations in slab geometries and the last two terms are instead evaluated by bulk calculations with 3D periodicity. In order to obtain each contributions to $\chi_{\text{eff}}^{(2)}$ from first principles, we first computed $\epsilon(\omega, z)$ entering the definition of the Fresnel coefficients (Eq. S2 [25]) from the linear susceptibility $\chi_1^{(2)}(\omega)$:

$$\epsilon(\omega, z) = \epsilon_{\infty}(z) + 4\pi\chi_1^{(2)}(\omega, z),$$

where $\epsilon_{\infty}(z)$ is the local high-frequency dielectric constant used to approximate $\epsilon(\omega, z)$ and $\epsilon(\omega_1, z)$, since the frequency dispersion may be neglected in the visible range. Ignoring anharmonic effects, all the linear and nonlinear susceptibilities share the same form:

$$\chi_{\text{eff}}^{X}(\omega, z) = \sum_q \frac{\chi_{q}^{X}(\omega, z)}{\omega - \omega_q + i\Gamma_q},$$

where $X = L, D, Q_1, Q_2, Q_3$ and $\omega_q, \Gamma_q$ and $\chi_{q}^{X}(\omega, z)$ are the frequency, lifetime and amplitude of the $q$th vibrational normal mode. Hence the calculation of total SFG signals reduces to the calculation of $\chi_{q}^{X}(\omega, z)$, which may be obtained using normal mode analysis, and to the evaluation of dipole and quadrupole moments and their polarizabilities (see Ref. [25] for expressions of $\chi_{q}^{X}(\omega, z)$). We note that $\chi_{q}^{X}(\omega, z)$ coefficients may be recast into TCFs and computed using molecular dynamics for disordered or liquid systems [12].

The calculation of the quadrupole moment in $\chi_{q}^{X}(\omega, z)$ requires special care. The total quadrupole moment tensor $Q_{\text{eff}}^{q} = \frac{1}{2} \int \rho(r)r_{\text{eff}}^2 \text{d}r$ ($\rho(r)$ is the total charge density of the system) and the terms $\chi_2^{Q_1}$, $\chi_2^{Q_2}$ and $\chi_2^{Q_3}$ are well defined and origin independent only for a system with zero dipole and zero $\chi_2^{Q_3}$, respectively. Hence to
We emphasize that it is key to use properties from several formulations presented in the literature.

The use of MLWF allowed for a straightforward evaluation of the total charge density and the multipole moments of the system within PBC [16], which turned out to be key in the calculation of quadrupole contributions. We validated our method by computing $\chi_{\text{eff}}^{IQB}$ using two different origins in our supercell. We observed only minor differences, originating from small deviations from centrosymmetry of our relatively small (96 molecules) proton disordered ice samples (see Fig. S5 [25]). All of our calculations were implemented in the Qbox code [25, 33] and carried out using the PBE functional [34].

In Fig. 1 we show the computed $\varepsilon_\infty(\omega)$ profile of a representative slab sample, showing good agreement with experiment. Our computed $\varepsilon_\infty \approx 1.8$ was also in good agreement with the experimental value ($\sim 1.7$). Note that the local dielectric constant $\varepsilon_{\infty,z}(z)$ of the dangling OH bonds of surface water molecules was estimated to be about 1.31 [23] from experiments; this value is defined in terms of the local field correction factors and hence it does not correspond to our definition of local dielectric constant.

The various contributions to the imaginary part of $\chi_{\text{eff}}^{(2)}$ in the OH stretching region are shown in Fig. S5, for two polarization combinations $ssp$ and $ppp$ [25]. The gradient of the Fresnel coefficients used in the calculation of $\chi_{\text{eff}}^{IQI}$ was estimated from the dielectric constant profile in Fig. 1 [25]. Because $\chi_{\text{eff}}^{IQI}$ is much smaller than $\chi_{\text{eff}}^{ID}$, the errors arising from its approximate, numerical evaluation are expected to be negligible. Interestingly, we found that in the $ppp$ spectra, $\chi_{\text{eff}}^{IQB}$ is the only significant quadrupole contribution, mostly influencing the peak at about $\sim 3150$ cm$^{-1}$. This finding is in agreement with previous speculations [19] that such peak includes significant quadrupole contributions. This high frequency peak has been previously assigned [19, 35] to a "bilayer-stitching mode", i.e. a stretching mode of the OH groups hydrogen bonded to water molecules in neighboring BLs, which are vibrating along the $z$ direction. These vibrations should indeed result in a large $zzz$ component of $\chi_{\text{eff}}^{IQB}$, which is an important contribution to $ppp$ spectra. Instead the contribution of $\chi_{\text{eff}}^{IQB}$ to $ssp$ spectra is less
SFG spectra arising from the first BL: in the \(ssp\) spectra (Fig. S4 [25]), the proton disordered surfaces show a feature about 100 cm\(^{-1}\) higher in frequency than proton ordered ones. However, when including three BLs and quadrupole contributions, the total spectra of proton ordered and disordered surfaces cannot be unambiguously distinguished. Our results are consistent with results reported by Ishiyama et al. [35], who found significant contributions originating from subsurface BLs. As shown in the top panels of Fig. 2, both experimental \(ssp\) spectra show a major peak at \(\sim 3100\) cm\(^{-1}\) and a shoulder at \(\sim 3200\) cm\(^{-1}\); however the spectrum measured at a lower temperature (100 K) and better surface conditions [21] show a weaker shoulder than the one taken at higher temperature (173 K) [23]. Overall our results appear to point to a proton ordered surface at low temperature, in agreement with the prediction of Ref. [24].

In summary, we developed a theoretical and computational method to compute SFG spectra from first principles. We consistently took into account the varying electric field across the interface and we included dipole and quadrupole contributions from both surface and bulk regions. We also provided a simple computational framework to avoid origin dependent terms in the calculation of quadrupole contributions. Finally, we computed the SFG spectra of the ice I\(_h\) basal surface and obtained good agreement with experiments. Our results highlight the importance of including electric field gradients and quadrupole contributions to properly describe the SFG spectra of the \(ppp\) polarization combinations. The first principles methodology developed here is general and applicable to ordered and disordered semiconductors and insulators.

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\[\chi_{\text{eff}}^{(2)}(\omega, z) \approx 1.\]


[25] See Supplemental Material at [URL will be inserted by publisher], which includes Refs [38–46], for the definition of Fresnel coefficients, derivation of quadrupole contributions, expressions for amplitudes $A_X$, polarization combinations, computational details and test results on slab sizes, origin dependency, anharmonic effects and effect of different incident angles.

[26] The position $z_b$ was chosen to be well beneath the surface so that the integral in Eq. 1 includes the entire interfacial area.

[27] In the calculation of $\chi_{\text{eff}}^B\Omega$, electric field phase factors are explicitly included, since the dimensions of a bulk sample are much larger than the light wavelength.


