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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 surfaces. 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 ω_1 in the visible and ω_2 in the infrared range, and the emitted sum-frequency (SF) light is detected, with a frequency $\omega_s = \omega_1 + \omega_2$. The total emitted intensity is proportional to the square of the complex effective second-order nonlinear (or SFG) susceptibility $\chi_{\text{eff}}^{(2)}$ 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 (~ 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

I_h basal surface and discuss the importance of considering the local dielectric constant and quadrupole contributions when interpreting experiments. [18–23]. To our knowledge our study represents the first comprehensive *ab initio* formulations of SFG spectra, as well as the first *ab initio* simulation of the SFG spectra of ice [18, 24].

An SFG process includes both infrared and Raman transitions (see Fig. S1 [25]): a system in its vibrational ground state first absorbs an infrared photon of frequency ω_2 and it is then further excited to a virtual state by absorbing a visible photon (ω_1). When the system decays, it emits a photon of frequency $\omega_s = \omega_1 + \omega_2$. The SFG susceptibility tensor $\chi_{\text{eff}}^{(2)}$ relates the effective induced polarization of the system $\mathbf{P}_{\text{eff}}^{(2)}(\omega_s)$ to the electric fields of the incident beams, $\mathbf{E}^0(\omega_1)$ and $\mathbf{E}^0(\omega_2)$: $P_{\text{eff},\nu}^{(2)}(\omega_s) = \chi_{\text{eff},\nu\mu\xi}^{(2)} E_{\mu}^0(\omega_1) E_{\xi}^0(\omega_2)$, where $\nu\mu\xi$ denote Cartesian coordinates. For a specific combination of incident angles and polarization directions of the beams, $\chi_{\text{eff}}^{(2)} = \mathbf{e}_s \cdot \chi_{\text{eff}}^{(2)} : \mathbf{e}_1 \mathbf{e}_2$, where $\mathbf{e}_s$, $\mathbf{e}_1$ and $\mathbf{e}_2$ are the polarization directions of the SF, visible and infrared lights, respectively. Experiments usually report $\chi_{\text{eff}}^{(2)}(\omega_2)$, and ω_s and ω_1 are kept constant. Hereafter for simplicity we will not show the frequency dependency (ω_2) of the susceptibilities.

SFG spectra are surface-specific probes if $\chi_{\text{eff}}^{(2)}$ is determined only by dipole transitions. If quadrupole transitions are included, then $\chi_{\text{eff}}^{(2)} \simeq \chi_{\text{eff}}^{\text{D}} + \chi_{\text{eff}}^{\text{Q}}$ where in this expression non-resonant background, magnetic multipole terms and higher electric multipole terms are neglected. The dipole contribution $\chi_{\text{eff}}^{\text{D}}$ describes the response to a constant electric field perturbation while $\chi_{\text{eff}}^{\text{Q}}$ includes the response to electric field gradients.

Using an approach similar to that of Ref. [12], we further decompose $\chi_{\text{eff}}^{\text{D}}$ and $\chi_{\text{eff}}^{\text{Q}}$ into interfacial (I) and bulk (B) terms: $\chi_{\text{eff}}^{\text{D}} = \chi_{\text{eff}}^{\text{ID}} + \chi_{\text{eff}}^{\text{BD}}$, and $\chi_{\text{eff}}^{\text{Q}} = \chi_{\text{eff}}^{\text{IQ}} + \chi_{\text{eff}}^{\text{BQ}}$. Note that $\chi_{\text{eff}}^{\text{BD}} = 0$ for an isotropic bulk system, e.g. bulk ice I_h . This decomposition is conceptually not necessary but of key importance in practice: calculations of both bulk and interface terms in one simulation would require using slab samples prohibitively large for any *ab initio* simulation.

The term $\chi_{\text{eff}}^{\text{ID}}$ is often considered the major contribution to $\chi_{\text{eff}}^{(2)}$ and has been the focus of most studies in the literature [6, 7]:

$$\chi_{\text{eff},\nu\mu\xi}^{\text{ID}} = \int_{z_b}^{\infty} dz L_{\nu\nu}(\omega_s, z) \chi_{\nu\mu\xi}^{\text{D}}(z) L_{\mu\mu}(\omega_1, z) L_{\xi\xi}(\omega_2, z), \quad (1)$$

where we assumed that the interfacial region is homogeneous in x and y directions and its thickness much smaller than the light wavelength [26]. $\chi^{\text{D}}(z)$ is the second-order nonlinear susceptibility for dipole transitions at position z (see below). $\mathbf{L}(\omega_g, z)$ is the Fresnel tensor as a function of the light at frequency ω_g ($g = s, 1, 2$) and position z (see Eq. S2 [25]); it is diagonal and its position and fre-

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

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

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{eff}}^{\text{ID}} + \chi_{\text{eff}}^{\text{IQI}} + \chi_{\text{eff}}^{\text{IQB}} + \chi_{\text{eff}}^{\text{BQ}}, \quad (2)$$

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 $\chi^{\text{L}}(\omega)$:

$$\epsilon(\omega, z) = \epsilon_{\infty}(z) + 4\pi\chi^{\text{L}}(\omega, z), \quad (3)$$

where $\epsilon_{\infty}(z)$ is the local high-frequency dielectric constant used to approximate $\epsilon(\omega_s, z)$ 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:

$$\chi^{\text{X}}(\omega, z) = \sum_q \frac{\mathbf{A}_q^{\text{X}}(z)}{\omega - \omega_q + i\Gamma_q}, \quad (4)$$

where $\text{X} = \text{L}, \text{D}, \text{Q}_1, \text{Q}_2, \text{Q}_s$ and ω_q , Γ_q and $\mathbf{A}_q^{\text{X}}(z)$ 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 $\mathbf{A}_q^{\text{X}}(z)$, 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 $\mathbf{A}_q^{\text{X}}(z)$). We note that $\mathbf{A}_q^{\text{X}}(z)$ coefficients may be recast into TCFs and computed using molecular dynamics for disordered or liquid systems [12].

The calculation of the quadrupole moment in $\mathbf{A}_q^{\text{X}}(z)$ requires special care. The total quadrupole moment tensor $Q_{\nu\mu} = \frac{1}{2} \int \rho(\mathbf{r}) r_{\nu} r_{\mu} d\mathbf{r}$ ($\rho(\mathbf{r})$ is the total charge density of the system) and the terms χ^{Q_1} , χ^{Q_2} and χ^{Q_s} are well defined and origin independent only for a system with zero dipole and zero χ^{D} , respectively. Hence to

FIG. 1. Computed local, frequency-dependent dielectric constant, $\epsilon_z(\omega)$, averaged over different bilayers (BL), compared with experimental measurement (blue line) for bulk ice I_h [28]. The black and red lines represent averages over the first BL and the second and third BLs, respectively.

properly compute quadrupole contributions from isotropic bulk regions, we used the total charge density of the supercell; we avoided summations over quadrupole contributions associated to single polar molecular units, at variance from several formulations presented in the literature [12, 14]. We emphasize that it is key to use properties of the entire system, such as the total charge density, to evaluate χ^{Q_1} , χ^{Q_2} and χ^{Q_s} , thus insuring that, as long as the entire sample under consideration is centrosymmetric ($\chi^D = 0$), the results are origin independent.

In principle, the exact same formulation as adopted here for ice could be applied to disordered systems consisting of polar molecules, such as liquid water. Indeed in an isotropic liquid $\chi^D = 0$ and hence χ^{Q_1} , χ^{Q_2} and χ^{Q_s} are guaranteed to be origin independent when a fixed origin in the lab coordinates is used, instead of a moving one such as the center of mass of the molecules. However for a liquid, the second-order nonlinear susceptibilities need to be defined in terms of TCFs; obtaining $\chi_{\nu\mu\xi}^D \propto \int \langle M_\xi(t) \Pi_{\nu\mu}(t + \Delta t) \rangle dt \exp(i\omega_2 \Delta t) \simeq 0$ (and hence recovering the origin independence of χ^{Q_1} , χ^{Q_2} and χ^{Q_s}) requires simulations of the order of nanoseconds, which are not yet affordable from first principles.

We applied the formulation described above to compute the SFG spectra of ice I_h basal surfaces. In order to compute $\chi_{\text{eff}}^{\text{ID}}$ and $\chi_{\text{eff}}^{\text{IQI}}$ we considered 8 different slab models, each with 6 bilayers (BLs) and in total 144 water molecules. We sampled 8 proton disordered and 8 proton ordered surfaces (each slab had 2 surfaces). For proton ordered surfaces, we considered the Fletcher’s striped phase, which was predicted to be one of the most stable phases of ice I_h basal surfaces [24]. We computed the bulk contributions $\chi_{\text{eff}}^{\text{BQ}}$ and $\chi_{\text{eff}}^{\text{IQB}}$ for four proton disordered ice I_h samples using super cells with 96 water molecules and 3D periodicity, after carefully checking the chosen cell size yielded converged spectra [25]. The

optical geometries, i.e. incident angles, used for the calculation of Fresnel coefficients were taken from Ref. [23]. We computed dipole and quadrupole moments and their corresponding polarizabilities entering the definition of $\mathbf{A}_q^X(z)$ (Eq. S7 [25]), within formulations based on MLWFs. In particular, we adopted the expression of the dipole moment proposed in [29] and the expression of polarizabilities that we recently derived for the calculations of Raman spectra, within density functional perturbation theory [30]. We computed quadrupole moments using MLWFs and the formulation proposed in Ref. [31]; finally, we evaluated quadrupole polarizabilities by finite differences (finite displacements of the applied electric field) using an electric enthalpy functional [32].

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 $\chi_{\text{eff}}^{\text{IQB}}$ 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 $\epsilon_z(\omega)$ profile of a representative slab sample, showing good agreement with experiment. Our computed $\epsilon_\infty \sim 1.8$ was also in good agreement with the experimental value (~ 1.7). Note that the local dielectric constant $\epsilon_{\infty,z}(z)$ 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 $\chi_{\text{eff}}^{\text{IQI}}$ was estimated from the dielectric constant profile in Fig. 1 [25]. Because $\chi_{\text{eff}}^{\text{IQI}}$ is much smaller than $\chi_{\text{eff}}^{\text{ID}}$, the errors arising from its approximate, numerical evaluation are expected to be negligible. Interestingly, we found that in the *ppp* spectra, $\chi_{\text{eff}}^{\text{IQB}}$ is the only significant quadrupole contribution, mostly influencing the peak at about $\sim 3150 \text{ cm}^{-1}$. 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 $\chi_{\text{eff}}^{\text{IQB}}$, which is an important contribution to *ppp* spectra. Instead the contribution of $\chi_{\text{eff}}^{\text{IQB}}$ to *ssp* spectra is less

FIG. 2. SFG intensities for *ssp* (left panels) and *ppp* (right panels) polarization combinations for ice I_h basal surfaces. We report measured (at 173 K, Ref. [23], and at 100 K, Ref. [21]; top panels) and computed results (as averages over 8 samples, for proton disordered surface models in the middle panels, and proton ordered surface models in the bottom panels). The spectra were computed by including the interfacial dipole (ID) contribution originating from the top three surface bilayers (see text). The black and violet curves show only the ID contribution, with the violet one obtained by setting $\epsilon(\omega, z) = 1$. The total spectra $|\chi_{\text{eff}}^{(2)}|^2$ including the ID contribution as well as IQI, IQB and BQ contributions are shown by the red curve. The computed spectra were red-shifted by 100 cm^{-1} to align them with experiments at 3100 cm^{-1} . The discrepancy in peak positions is ascribed to the neglect of quantum effects [36] and the use of the PBE functional [37]. Anharmonic effects were not found to be significant for this system (see Fig. S3 [25]).

intense since it has only *yyz* components.

In Fig. 2, we present the computed SFG intensities $|\chi_{\text{eff}}^{(2)}|^2$ averaged over several surface models and compared with experiments. The difference in the measurements [21, 23] likely originates from different temperatures and surface cleanliness [25]. The dipole contribution to SFG intensities was considered converged when including three BLs, with the first two BLs ($\simeq 7 \text{ \AA}$) yielding most of the total contribution [25]. Similar to our results for $\text{Im}\chi_{\text{eff}}^{(2)}$ spectra, we found that quadrupole contributions are only significant in the *ppp* spectra. We also found that it is important to properly include the frequency dependent dielectric constant (shown in Fig. 1) in computing the *ppp* spectra, as it is seen by comparing calculations with $\epsilon(\omega, z)$ set to 1 with those including the proper $\epsilon(\omega, z)$. As shown in Eq. S11 [25], $\chi_{\text{eff},ssp}^{(2)}$ and $\chi_{\text{eff},ppp}^{(2)}$ have different dependencies on $\epsilon(\omega)$ and the former is largely unaffected when setting $\epsilon(\omega) = 1$.

Our results show that the proton ordered and disordered surfaces do exhibit different contributions to the

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 $\sim 3100 \text{ cm}^{-1}$ and a shoulder at $\sim 3200 \text{ cm}^{-1}$; 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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