First-principles theory of infrared vibrational spectroscopy in metals and semimetals: application to graphite

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Infrared (IR) spectroscopy is a well-established technique for analyzing the vibrational properties of crystalline solids. In insulating or semiconducting materials, not displaying electronic intraband transitions in the IR region of the electromagnetic spectrum, phonon features arise at energies much smaller than the band gap, and hence they can be clearly identified. On the other hand, the IR response in metals is dominated by the Drude peak – the signature of the free electron response – whose amplitude is proportional to the free carrier density \( \rho \), and therefore to the square of the plasma frequency \( \omega_p^2 \). The presence of a strong Drude peak generally precludes the detection of the vibrational features \[1\]. There are cases, however, in which this technique can also be useful in metallic materials, and even situations in which it is the only possible choice. To better understand these cases, it is useful to recall the quantum-mechanical description of the Fermi level \( \bar{\delta} \) and the average electronic velocity at the Fermi level \( \bar{v}_F \): \( \omega_p^2 \propto \bar{v}_F^2 D(\bar{E}_F) \). From this expression it is clear that, for example, systems with a pseudogap - like high-temperature superconducting cuprates \[2\] or transition metal dichalcogenides undergoing a charge-density wave transition \[3,5\] - displaying by definition a density of states which decreases significantly at the Fermi level, will have a small \( \omega_p \); this condition narrows the Drude peak, and makes the vibrational features sharp enough to be investigated (see e.g. Fig. 1 of Ref. \[6\], or Fig. 1 of Ref. \[7\]). Another significant example is given by systems under extremely high-pressure conditions. In metals under extremely high-pressure conditions, the IR reflectance absorption spectrum of metallic systems.

Ab initio calculations play a crucial role in the physical interpretation of experimental results. In this letter, by means of a time-dependent formulation of density functional perturbation theory (DFPT) \[14,15\], we introduce a new method to simulate from first-principles the IR reflectivity absorption spectrum of metallic systems.

The determination of the total (electronic + ionic) dielectric tensor \( \epsilon(\omega) \) gives a complete characterization of all the features appearing in IR spectra. Within a Huang’s-type approach \[16\] and \[18\], it is given by:

\[
\epsilon(\omega) = \epsilon^e(\omega) + 4\pi \sum_s \chi^I_s(\omega).
\]

where \( \epsilon^e(\omega) \) is the electronic dielectric tensor at fixed ions and \( \chi^I_s(\omega) \) represents the ionic contribution due to a phonon mode with index \( s \)

\[
\chi^I_s(\omega) = \frac{e^2}{\Omega} \frac{d_s(\omega_s) d_s^*(\omega_s)}{\omega_s^2 - (\omega + i\gamma_s/2)^2}.
\]

Here, \( \Omega \) is the unit cell volume, \( \omega_s \) and \( \gamma_s \) are the phonon frequency and inverse lifetime, respectively, and \( d_s(\omega_s) = \sum_{\kappa} Z_{\kappa}(\omega_s) \frac{q_{s\kappa}}{\sqrt{m_\kappa}} \) is the oscillator strength defined in terms of a frequency-dependent effective charge tensor \( Z(\omega_s) \), with \( m_\kappa \) the mass of the \( \kappa \)-th atom and \( e_{s,\kappa} \) the

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polarization vector of the s-th mode. Since phonon peaks are typically rather sharp, we can approximate \( \epsilon^e(\omega) \) by its value \( \epsilon^e_0(\omega_s) \) at each given phonon mode s.

Information from IR studies are generally extracted from transmission \( T(\omega) \) and reflectivity \( R(\omega) \) measurements. In the case of metals, \( T(\omega) \) can be obtained only for very thin materials, whereas \( R(\omega) \) can always be acquired. The standard formula of the reflectivity between the vacuum and the sample along one of the principal dielectric axes \( \alpha \) is 
\[
R_{s,\alpha}(\omega) = \frac{\sqrt{\epsilon_s(\omega)-1}}{\sqrt{\epsilon_s(\omega)+1}} \bigg|_{\text{abs}}, \tag{1}
\]
where \( \epsilon_s(\omega) \) is the diagonal element of the dielectric tensor. The general shape of the vibrational features in IR reflectivity spectra of metals can be deduced by a Taylor expansion of \( R_{s,\alpha}(\omega) \) around a given \( s \) phonon mode. In the limit \( |\epsilon^e_{s,\alpha}| \gg |\chi^1_{s,\alpha}(\omega)| \) the reflectivity reads [19]:
\[
R_{s,\alpha}(\omega) \sim R^e_{s,\alpha} \left[ 1 + 2 \text{Re} \left( \frac{4\pi\chi^1_{s,\alpha}(\omega)}{\sqrt{\epsilon^e_{s,\alpha}(\epsilon^e_{s,\alpha} - 1)}} \right) \right]. \tag{3}
\]
where \( R^e_{s,\alpha} \) is the purely electronic reflectivity. The vibrational contribution (second term in the square parenthesis) can be recast as a Fano profile
\[
\text{Re} \left( \frac{4\pi\chi^1_{s,\alpha}(\omega)}{\sqrt{\epsilon^e_{s,\alpha}(\epsilon^e_{s,\alpha} - 1)}} \right) = W_{s,\alpha} q^2_{s,\alpha} - 1 + 2q_{s,\alpha} \xi_s(\omega) (1 + q^2_{s,\alpha})(1 + q^2_s(\omega)). \tag{4}
\]
Here we defined the following quantities:
\[
W_{s,\alpha} = \frac{|D_{s,\alpha}|^2}{\gamma_s \omega_s}; \quad q_{s,\alpha} = -\frac{\text{Re} D_{s,\alpha}}{\text{Im} D_{s,\alpha}} \tag{5}
\]
\[
(D_{s,\alpha})^2 = i \frac{4\pi e^2}{\Omega} \frac{1}{\sqrt{\epsilon^e_{s,\alpha}(\epsilon^e_{s,\alpha} - 1)}} \tag{6}
\]
whereas \( \xi_s(\omega) = (\omega^2 - \omega_s^2)/\gamma_s \omega_s \), which, close to a phonon peak, can be approximated to \( \xi_s(\omega) \sim 2(\omega - \omega_s)/\gamma_s \). Eq. (4) is a Fano function in the variable \( \xi_s(\omega) \) which is completely determined by five parameters, namely \( R^e_{s,\alpha}, \omega_s, \gamma_s, W_{s,\alpha}, q_{s,\alpha} \). This implies that, in the case of metals, it cannot be used to obtain all the six parameters characterizing \( \epsilon(\omega) \), i.e. \( \text{Re} Z^e_s, \text{Im} Z^e_s \). Instead, the proper way to obtain both the real and the imaginary parts of \( Z^e_s \) is to fit the vibrational contribution of the real part of the optical conductivity; this can be done once the smooth electronic part has been previously subtracted, as was done e.g. in Ref. [22].

In DFPT, both the \( \epsilon^e \) and \( Z^e_\alpha \) are defined as derivatives of the electronic polarization, the former with respect to the electric field \( \mathbf{E} \), the latter with respect to the ionic displacements \( \mathbf{u}_s \) [23]. The effective charge tensor can be decomposed in two contributions \( Z_\alpha = 1Z^e_\alpha + Z^e_\kappa \), the first (constant) term \( Z^e_\kappa \) is the (pseudo)charge of the nuclei, while the second electronic contribution \( Z^e_\alpha \) is due to the interaction between the electrons and the lattice; in the following we will focus on this last one. Within time-dependent DFPT [14, 15] and adopting the variational approach proposed in [24], the effective charge tensor can be expressed as:
\[
e^e Z^e_\alpha[n^E, n^u](\omega_s) = - \frac{2}{N_k} \sum_{k,\alpha,m,n} \left( f_{k,n} - f_{k,m} \right) \left( (E_{k,n} - E_{k,m})^2 - z_s^2 \right) \times \text{Im} \left( u_{k,m} \left( \xi_{\mathbf{k},\alpha} + V^E_{\text{Hxc}} \right) \left| u_{k,n} \right| \right) \times \text{Re} \left( \left| u_{k,m} \left( \xi_{\mathbf{k},\alpha} + V^E_{\text{Hxc}} \right) \left| u_{k,n} \right| \right) \tag{7}
\]
while the electronic dielectric tensor \( \epsilon^e(\omega_s) \) reads:
\[
e^e [n^E](\omega_s) = 1 + 4\pi \times \frac{2}{N_k \Omega} \sum_{\alpha, s, m,n} \frac{1}{(E_{k,n} - E_{k,m})^2 - z_s^2} \times \left( u_{k,m} \left( \xi_{\mathbf{k},\alpha} + V^E_{\text{Hxc}} \right) \left| u_{k,n} \right| \right) \tag{8}
\]
In these expressions, \( N_k \) is the number of points in the k-grid, \( \eta_k = \frac{1}{\hbar} \delta \mathbf{E}_{\text{Kohn-Sham}} \), where \( \mathbf{E}_{\text{Kohn-Sham}} = -i \hbar \mathbf{H} + \mathbf{H}_{\text{xc}} \mathbf{E} \) and \( \mathbf{H}_{\text{xc}} \) is the unperturbed Kohn-Sham (KS) Hamiltonian; \( E_{k,n} \) is the unperturbed KS eigenvalue and \( u_{k,n} \) is the periodic part of the corresponding KS eigenstate in the Bloch form. We denote with \( f_{k,n} \) the smearing function, while \( z_s = \hbar \omega_s + i\eta \), where \( \eta \) is a positive small real number with the dimension of an energy. The frequency-dependent charge density induced by \( \xi = \mathbf{E}, \mathbf{u}_s \), denoted as \( n^e = \frac{\partial \rho}{\partial \mathbf{k}} \) gives rise to a Hartree and exchange-correlation (Hxc) potential:
\[
V_{\text{Hxc}}[n^e](\mathbf{r}, \omega_s) = \int d^3 r K_{\text{Hxc}}(r, r') n^e(r', \omega_s), \tag{9}
\]
where \( K_{\text{Hxc}}(r, r') = \frac{\delta^2 E_{\text{Hxc}}[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \) is the Hxc kernel. Finally, the first-order perturbative expressions of the induced charge density with respect to the electric field and ionic displacements are:
\[
n^E(\omega_s) = \frac{2}{N_k} \sum_{\alpha, s, m,n} \left( f_{k,n} - f_{k,m} \right) \left( (E_{k,n} - E_{k,m})^2 - z_s^2 \right) u^*_k u_{k,n} \tag{10}
\]
and
\[
n^u(\omega_s) = \frac{2}{N_k} \sum_{\alpha, s, m,n} \left( f_{k,n} - f_{k,m} \right) \left( (E_{k,n} - E_{k,m})^2 - z_s^2 \right) u^*_k u_{k,n} \tag{11}
\]
and
\[
\int d^3 r d^3 r' n^E(\mathbf{r}, \omega_s) K_{\text{Hxc}}(r, r') n^E(\mathbf{r}', \omega_s).
\]
As discussed in [26], it is necessary to maintain the frequency dependence of all relevant quantities – namely, $n\xi$, $Z_n^e$ and $\epsilon^e$ – in order to have a stable and robust implementation of Eqs. (7, 8, 10) (as discussed in Ref. [24]), neglecting in all the self-consistent loops the imaginary part of the first order charge density:

$$Z_n^e(\omega_s) \approx \tilde{Z}_n^e(\omega_s) = Z_n^e \left[ \text{Re} n^F, \text{Re} n^u \right] (\omega_s)$$

$$\epsilon^e(\omega_s) \approx \tilde{\epsilon}^e(\omega_s) = \epsilon^e \left[ \text{Re} n^F \right] (\omega_s).$$

Regarding the practical implementation in the code, we used a dynamical extension of the linear response formalism described in Ref. [13], which is equivalent to the one of Ref. [21], employing a frequency-dependent Sternheimer equation with a similar scheme of Ref. [27]. Further details can be found in additional materials.

We benchmark our approach by evaluating the reflectivity spectra of bulk graphite and analyzing the IR peaks $E_{1u}$ ($\omega_{E_{1u}} = 1587$ cm$^{-1}$) and $A_{2u}$ ($\omega_{A_{2u}} = 868$ cm$^{-1}$), which have been thoroughly investigated by IR spectroscopy measurements [21, 28, 36]. Lattice symmetry imposes for tensorial quantities to be diagonal, with the in-plane elements to be equal. In the following, we will denote as $T_{\parallel}$ ($T_{\perp}$) the components of a given tensor $T$ parallel (perpendicular) to the graphene sheets. $Ab$-initio calculations were performed using the PW and PHonon packages of QUANTUM-ESPRESSO [37], within which we implemented the theory described above [38, 39].

In Fig. 1 and Fig. 2 we compare our simulated reflectivity with the experimental data [40]. Importantly, we notice that the symmetry of the peaks depends on the phases of both $Z_n^e(\omega_s)$ and $\epsilon^e(\omega_s)$. In fact, from Eq. (6), $D_{s,\alpha} = |D_{s,\alpha}| e^{i \arg D_{s,\alpha}}$ where for $|e^{s,\alpha}| \gg 1$

$$\arg D_{s,\alpha} \approx \tilde{\xi} + \frac{3}{4} \arg D_{s,\alpha} - \frac{3}{4} \arg \epsilon^e_{s,\alpha}$$

and, from Eq. (5), $\tan (\arg D_{s,\alpha}) = -\frac{1}{q_{s,\alpha}}$. Using our computed values in Tables I and II for the $E_{1u}$ peak (Fig. 1) we find $q_{E_{1u},\parallel} \approx -52 (-19)$ at $T = 150 (300)$ K ($q \ll -1$ is the Lorentzian limit), which explains the symmetric shape of the resonance. Remarkably, the temperature dependence obtained from our calculations – mainly due to the temperature dependence of $\epsilon^e(\omega_s)$ – well reproduces the one reported in Ref. [32]. As for the $A_{2u}$ peak, we compare the calculated $R_{\perp}(\omega)$ with a fit proposed in Ref. [36] and realized taking into account several experiments. As shown in Fig. 2 also in this case our approach successfully reproduces the expected Fano asymmetric shape of the phonon peak, for which $q_{A_{2u},\parallel} \approx -1.3 (-1.4)$ at $T = 150 (300)$ K ($q = -1$ is the complete asymmetric case).

We report in Table I the oscillator strengths $d_{\perp}$ ($d_{\parallel}$) of Eq. (2) evaluated at $\omega_{E_{1u}}$ ($\omega_{A_{2u}}$) and properly rescaled by the square root of the carbon mass $m_C$ and a factor 2 stemming from the scalar product with the polarization vectors $\mathbf{e}_{\alpha,\parallel}$, and we compare them with available experimental estimates. In the case of graphite, they are equal to the average of the effective charges $Z_{\parallel} (Z_{\perp})$ of the four C atoms of the unit cell. More precisely, because of symmetry, the effective charges of the four C atoms are exactly equal in pairs, and have opposite sign. In addition, it is well-known that the components of the effective charge tensor obey the acoustic sum rule (ASR) $\sum Z_{\alpha} = 0$ [10]; noteworthy, we found that this rule in general is not respected in the dynamical case. For more information about ASR violation, i.e. the numerical values of the evaluated effective charges, see supplementary material.

We stress the fact that in older experiments the effective charge was supposed to be a real quantity and the imaginary part was completely neglected [21, 24, 50], an assumption that has been relaxed only recently [28]. Such neglect of the complex nature of the effective charges
may have led to inaccurate results because of a wrong fitting procedure of the experimental data. Within our approach, we find that indeed the imaginary part of $Z_\parallel$ is approximatively 1/3 of the real part, in good agreement with the experimental results reported in Ref. [28]. On the other hand, the out-of-plane component $Z_\perp$ has a negligible imaginary part, whereas the real one is found to be one order of magnitude smaller than $\text{Re} Z_\parallel$ (reflecting the dielectric-like properties of graphite in the transverse direction), with our calculations yielding a value in excellent agreement with the experimental estimates [21].

We find that the combined effect of the thermal lattice expansion and the increase of electronic temperature has no effect on $\text{Re} Z_\parallel$ and $Z_\perp$. Instead, $\text{Im} Z_\parallel$ does not depend appreciably on thermal expansion, but it increases with $T$, contrary to Ref. [28]. However, it is worth to mention that the parameter $\eta = \text{Im} z$, accounting for the damping of the electronic states, is also $T$-dependent. We have not studied such dependence; nevertheless in supplementary material we show that the variation of $\eta$ can markedly affects $\text{Im} Z_\parallel$.

As for the electronic dielectric tensor $\epsilon^e(\omega_s)$, in Table II we report $\epsilon_\parallel(\omega_s)$ evaluated at $\omega_{E_{1u}}$ ($\omega_{A_2u}$). We found that the components of the dielectric tensor depend only on the electronic temperature and not on the lattice thermal expansion. Finally, we note that also for $\epsilon^e(\omega_s)$, as well as for $Z_\parallel(\omega_s)$, the in-plane components are always larger than the out-of-plane ones, both for the real and the imaginary parts. This is a consequence of the mirror reflection symmetry with respect to the carbon planes, that is exact in monolayers like graphene, and only approximate in graphite, which forbids low-energy electronic excitations for perturbations perpendicular to the layered structure in the linear response regime.

In conclusion, we introduced an ab-initio scheme to describe the IR vibrational spectra of metallic crystalline solids in reflectivity measurements. We benchmarked our method by calculating the phonon signatures in the reflectivity spectra of graphite, finding good agreement between our results and available experimental data. We believe that our work will allow for a reliable first-principles description of reflectance spectra in metallic systems, in particular for those systems under extremely high-pressure conditions, as the new superconducting hydrides, where the IR vibrational spectroscopy represents one of the few possible tools of investigation.

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**TABLE I.** Comparison between ab-initio and experimental oscillator strength $d_u = \sqrt{\text{mC}} d_u/2$. The parallel component refers to the $E_{1u}$ mode, the perpendicular one to the $A_{2u}$ mode.

| Reference | $T$ (K) | $\text{Re} d_\parallel$ | $\text{Im} d_\parallel$ | $\text{Re} d_\perp$ | $\text{Im} d_\perp$ |
|-----------|---------|--------------------------|--------------------------|--------------------------|--------------------------|
| Ref. [21] | 21      | 0.41                     | 0.08                     |                          |                          |
| Ref. [29] | 30      | 0.30                     | 0.21                     |                          |                          |
| Ref. [30] | 150     | 0.29                     | 0.14                     |                          |                          |
| Ref. [30] | 300     | 0.31                     | 0.13                     |                          |                          |
| Present work | 150 | 0.27                     | 0.09                     | 0.07                     | 0.0001                   |
| Present work | 300 | 0.27                     | 0.10                     | 0.07                     | 0.0001                   |

**TABLE II.** Comparison between ab-initio and experimental dielectric tensor. For comparison, we also report the value of $\text{Re} \epsilon_\parallel$ at $\omega = 9679$ cm$^{-1}$ (taken from Ref. [35]) because, although it is not the characteristic frequency of the $A_{2u}$ mode, the dielectric tensor is not expected to vary appreciably from 686 to 9679 cm$^{-1}$ since there are no interband electronic transitions in such frequency range.

| Reference | $T$ (K) | $\text{Re} \epsilon_\parallel$ | $\text{Im} \epsilon_\parallel$ | $\text{Re} \epsilon_\perp$ | $\text{Im} \epsilon_\perp$ |
|-----------|---------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Ref. [31] | 21      | 8.8                          | 50                            | 8.8                          | 50                            |
| Ref. [33] | 21      | 0.73                         | 73                            | 0.73                         | 73                            |
| Ref. [34] | 21      | 5.3                          | 0.68                          | 0.33                         | 0.68                          |
| Ref. [35] | 20      | 3.3                          | 0.68                          | 0.33                         | 0.68                          |
| Ref. [30] | 20      | 4.2                          | 0.89                          | 0.33                         | 0.89                          |
| Present work | 150 | 6.1                          | 62                            | 3.9                          | 0.79                          |
| Present work | 300 | 7.9                          | 69                            | 3.4                          | 0.71                          |

$a$ as reported by Ref. [35]

$b$ values corresponding to a fit realized taking into account many experimental data.
