Optical properties of graphane in infrared range

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Abstract

The theory of optical effects in hydrogenated graphene (graphane) in the terahertz and infrared range is developed, including the analysis of complex conductivity, reflection coefficient for graphane on a substrate and dispersion of surface plasmon-polaritons. The calculations are based on quite simple analytical approximation of graphane band structure in the vicinity of Γ-point and on the modified model of quantum coherence relaxation. Comparison of the obtained theoretical results with corresponding experimental data can be used both for the determination of graphane characteristics (Fermi level, relaxation rate etc) and for the investigation of potential applications of this material in the design of new optical elements.

1. Introduction

In recent years, two-dimensional materials closely related to pure graphene [1], such as bilayer and multilayer graphene and graphane (hydrogenated graphene) [2–10], have become the subject of intense theoretical and experimental study. The main distinguishing features of these materials are associated with the formation of a finite bandgap instead of the zero gap (i.e., instead of the intersection of the valence and conduction bands at the Dirac point). In this work we study graphane, which has a unique property of controllable absorption and desorption of hydrogen atoms (for example, by annealing), including the complete return of the monolayer to the pure graphene state. With gradual hydrogenation, it is possible to obtain 2D materials with some specific parameters, for example, electrical or thermal conductivity. In this regard, graphane is considered as a promising material for the fabrication of hydrogen cells [11], the production of biosensors [12], transistors [13], and elements for spintronics [14].

The valence band of graphane consists of two subbands [15, 16] which can be attributed to ‘heavy’ and ‘light’ holes (see [17, 18]). In [16] these subbands near the Γ-point were considered and the averaged mass of charge carriers in the valence band was estimated, i.e. the effective mass of electron-hole excitons. Obviously, the average mass approximation is inapplicable for the calculation of conductivity at frequencies comparable to the characteristic frequency of intersubband transitions. Note that in this case, the electrodynamic properties of graphene should be very sensitive to the value of the Fermi energy, because it determines the frequency range of intersubband transitions allowed by the Pauli principle.

Another problem for correct description of graphane electromagnetic properties in this frequency range is a relatively short time of quantum coherence relaxation in graphene-based materials. Thus, in graphene it can be as small as several femtoseconds in some cases [19–21]. Under these conditions, the standard model for the relaxation of the density matrix off-diagonal terms, or so-called ’τ-approximation’ [22–24], leads to a number of fundamental incorrectness in determining the electrodynamic response in the terahertz and far-infrared ranges. First of all, the continuity equation is violated if the perturbations of current and electric charge are calculated independently. The correct expressions for the conductivity (or permittivity) of a fermion ensemble in a 2D crystal lattice in the case of finite dissipation are given in [25]. In particular, it was demonstrated in [25]
that the theoretical prediction for the graphene permittivity in the far-IR range significantly differs when passing from the standard to the modified relaxation operator.

A number of important nonlinear and quantum optical effects in graphene and topological insulators are closely interconnected with 2D plasmon-polariton modes [1, 26–31]. In specific geometries of interaction, surface plasmon resonance may enhance linear absorption of incident radiation and nonlinear susceptibilities by the orders of magnitude. Thus, key properties of the surface modes (like the dispersion relation and the propagation length) are important for understanding the complete picture of medium electrodynamics.

The main aim of the present paper is the theoretical study of graphene optical properties in the range of intersubband resonant frequencies. Comparison of the theoretically predicted and properly measured reflection, transmission and absorption coefficients in line with the dispersion of surface plasmons could directly verify the basic models of graphene band structure. For example, the experimental data on the propagation length of surface plasmons would make it possible to find the relaxation time of the intersubband and intrasubband quantum coherence in graphene in the terahertz and IR frequency ranges.

The paper is organized as follows. In chapter II the state functions of the system are calculated basing on the model Hamiltonian proposed in [16] (for the subbands of light and heavy holes near the Γ-point). In chapter III we generalize the theoretical results from [25] to the case of graphene and obtain the expressions for the permittivity in the frequency range where the influence of intersubband transitions is fundamentally important.

In chapter IV we give the expressions for the coefficients of electromagnetic radiation reflection and transmission through the graphene on a dielectric substrate and for the 2D plasmon dispersion. Finally, chapter V is devoted to the results of numerical calculations. The developed theory does not predict any nontrivial dependencies of the system properties on the dielectric permittivity of the substrate, so we limited ourselves to numerical calculations for the parameters of one of the most typical substrates—silicon carbide, SiC.

Notice that during the hydrogenation of a double-layer or multilayer graphene we can expect the appearance of two separated (but not touching) subbands in the valence band. In this regard, in appendix we analyze numerically a 2D system with the modified Hamiltonian, which contains the energy gap between two subbands as a parameter.

### 2. Model of graphene valence band

Let us consider a graphene monolayer lying in the plane \( xy \). In the paper [16] in the framework of the invariant method [32] the following model \( (\mathbf{k} \cdot \mathbf{p}) \)-Hamiltonian was proposed for the vicinity of Γ-point in the valence band:

\[
\hat{H}^{(c)}_k = -aI (k_x^2 + k_y^2) - b [\sigma_y (k_x^2 - k_y^2) + 2 \sigma_x k_x k_y],
\]  

(1)

and \( \hat{H}^{(s)}_k = \hbar^2 \frac{k_x^2 + k_y^2}{2m_0} \) for the conduction band. Here \( \mathbf{k} = x_o k_x + y_o k_y \), where \( \hbar \mathbf{k} \) is the electron quasimomentum (in the plane of the monolayer), \( x_o \) and \( y_o \) are unit vectors, \( a > b > 0 \), \( \sigma_{x,y} \) are standard Pauli matrices, \( I \) is the identity matrix, \( m_0 \) is the effective mass of charge carriers in the conduction band. The following dispersion law for the energies of heavy and light holes \( E_{\pm}(k^2) \) corresponds to the Hamiltonian (1) [16]:

\[
E_{\pm} = -(a \mp b) k^2,
\]  

(2)

where \( k = \sqrt{k_x^2 + k_y^2} \). Notice that two curves \( E_{\pm}(k^2) \) touch each other at the point \( k = 0 \).

In the conduction band, separated from the valence band by the energy gap \( W_{vc} \), we have a common dependence \( E = W_{vc} + \hbar^2 k^2/2m_0 \), thus, the described model gives one branch of the energy dispersion in the conduction band and two branches in the valence band, touching each other at the point \( k = 0 \) (see figure 1).

Considering the response of the graphene monolayer to the action of electromagnetic field at the frequency \( \omega \) when \( \hbar \omega \ll W_{vc} \) and \( \hbar^2 k^2/2m_0 \ll W_{vc} \), we can take into account only the charge carriers in the valence band. Here we use the Hamiltonian (1) corresponding to the band structure shown in figure 2, so that the state vector has the form \( \Psi = \begin{pmatrix} u_{\mathbf{k}} \\ u_{\mathbf{k}} \end{pmatrix} e^{-i\mathbf{k}\cdot\mathbf{r}} \). Using the Schrödinger equation

\[
(\hat{H}^{(c)}_k - i\mathbf{E}) \begin{pmatrix} u_{\mathbf{k}} \\ u_{\mathbf{k}} \end{pmatrix} = 0,
\]

we obtain the expression for the state vector in \( \mathbf{k} \)-representation:

\[
\begin{pmatrix} u_{\mathbf{k}} \\ u_{\mathbf{k}} \end{pmatrix}_{\left(\pm\right)} = \begin{pmatrix} \cos \theta_{\mathbf{k}} \\ \sin \theta_{\mathbf{k}} \end{pmatrix}, \quad \begin{pmatrix} u_{\mathbf{k}} \\ u_{\mathbf{k}} \end{pmatrix}_{\left(\mp\right)} = \begin{pmatrix} -\sin \theta_{\mathbf{k}} \\ \cos \theta_{\mathbf{k}} \end{pmatrix},
\]

(3)

where \( \theta_{\mathbf{k}} \) is the angle between the x-axis and the vector \( \mathbf{k} \).
Let us find the matrix element of a dipole moment operator of direct transition between the states with the energies $E_{k^2} + 2$ and $E_{k^2} - 2$. Since the system is isotropic in the plane of the monolayer, it suffices to find the matrix element of the $x$ coordinate. In $k$-representation, we can use the following relation:

$$x_{(+|k(-k)|)} = \left( u_{k\bar{k}}^{(+)} \right) \left( \frac{i\partial}{\partial k} u_{k\bar{k}}^{(-)} \right),$$

whence it follows that

$$|x_{(+|k(-k)|)^2} = \frac{\sin^2 \theta_k}{k^2}. \quad (4)$$

Notice that the obtained expression for $|x_{(+|k(-k)|)^2}$ differs from the corresponding expression for the interband transitions in graphene near the Dirac point only by a numerical coefficient equal to 4 (see, for example, [25]).
3. Conductivity of graphane monolayer

To calculate the surface conductivity of a 2D dissipative system with a given band structure, we will use the results from [25]. In this paper a modified operator of density matrix relaxation was proposed, which does not violate the continuity equation for the current density and charge density perturbations in a dissipative system. Assuming that the characteristic electron wavenumber $\langle k \rangle \sim \frac{|E_F|}{\sqrt{a+b}}$ is very large compared to the inverse spatial scale of the electromagnetic field inhomogeneity $L^{-1}$, we can use the homogeneous field approximation. In this case, we obtain the following expressions for the surface conductivity from the formulas given in [25]:

$$\sigma(\omega) = \sigma_{\text{inter}}(\omega) + \sigma_{\text{intra}}(\omega)$$  \hspace{1cm} (5)

$$\sigma_{\text{intra}}(\omega) = \frac{e^2 g}{4\pi^2} \sum_{\alpha, \beta} \int_{\infty}^{\infty} \frac{|\eta \cdot r_{\alpha\beta}|^2}{(E_{\alpha\beta} - E_{\alpha\beta})^2 - \hbar^2 \omega^2 - 2i\hbar \omega \gamma_{\alpha\beta}} d\omega$$  \hspace{1cm} (6)

$$\sigma_{\text{inter}}(\omega) = \frac{e^2 g}{4\pi^2} \sum_{\alpha, \beta} \int_{\infty}^{\infty} \frac{|\eta \cdot r_{\alpha\beta}|^2}{(E_{\alpha\beta} - E_{\alpha\beta})^2 - \hbar^2 \omega^2 - 2i\hbar \omega \gamma_{\alpha\beta}} d\omega$$  \hspace{1cm} (7)

Here we separated the conductivity components due to intraband ($\sigma_{\text{intra}}$) and interband ($\sigma_{\text{inter}}$) transitions, respectively; also here $g$ is the degeneracy factor, $e$ is the elementary charge; $\alpha$ and $\beta$ are band indices, $E_{\alpha\beta}$ and $f_{\alpha\beta}$ are the energy and the occupation probability for the state $|\alpha\beta\rangle$ respectively, $r_{\alpha\beta} = \langle \alpha|\epsilon|\beta\rangle$ is the matrix element of a particle coordinate in the plane of the monolayer for `direct' transitions, and $\eta$ is the unit vector parallel to the electric field projection on the plane of graphane. The values $\gamma_{\alpha\beta} = \gamma_{\alpha\beta}^0$ and $\gamma_{\alpha\beta} = \gamma_{\alpha\beta}^0$ are the intraband and the interband relaxation constants for the quantum coherence, respectively. In order to avoid misunderstandings, we note that the value $\gamma_{\alpha\beta} = \gamma_{\alpha\beta}^0$ is defined as the inverse relaxation time of off-diagonal matrix elements $\rho_{\alpha\beta} = f_{\alpha\beta}$, which corresponds to the energy relaxation time. In the limit of zero dissipation, equations (5)–(7) exactly correspond to the standard Kubo formula (see the proof in [25]).

Considering an isotropic system in the plane of the layer, we can choose $\eta = \chi_0$ in equations (5)–(7) without loss of generality. Keeping in mind the presence of two subbands in the valence band, further we use the following notations in equations (5)–(7): $\alpha, \beta$ are denoted as ‘$\pm$’, $\gamma_{+,k\pm} = \gamma_{-,k\mp} \approx \gamma_{\text{inter}}$ and $\gamma_{+,k\pm} \approx \gamma_{-,k\mp} \approx \gamma_{\text{intra}}$. For a degenerate Fermi–Dirac distribution we obtain:

$$\sigma_{\text{intra}}(\omega) = \frac{i e^2 g}{4\pi \hbar^2 \omega} \sum_{\alpha} \int_{0}^{2\pi} \frac{d\theta}{\omega} k \frac{dE_{\alpha\beta}(k)}{dk}$$  \hspace{1cm} (8)

$$\sigma_{\text{inter}}(\omega) = -\frac{i e^2 g}{2\pi^2} \int_{\Delta E_{\text{max}}}^{\Delta E_{\text{min}}} \left( \int_{0}^{2\pi} |x_{+,k\mp}|^2 d\theta \right) \frac{dE}{d\epsilon} \frac{d\Delta E}{d\epsilon}$$  \hspace{1cm} (9)

where $\Delta E(k) = E_{+,k}\pm k - E_{-,k}\mp k$, $E_F$ is the Fermi level, the values $\Delta E_{\text{max}}, \Delta E_{\text{min}}$ are the points of intersection of the Fermi level with the curves $E_{\alpha\beta}(k)$ (see figure 2).

The expressions (8) and (9) lead to fairly general results for the case of power dependence $|E_{\pm}(k)| \propto k^{\alpha}$. First, for the intraband conductivity we obtain:

$$\sigma_{\text{intra}}(\omega) = \frac{i e^2 g}{4\pi \hbar^2 \omega} |E_F| \sum_{\pm} \frac{d\nu_{\pm}}{d\omega}$$  \hspace{1cm} (10)

Second, if $|\Delta E(k)| \propto k^\alpha$, then for the standard dependence of the coordinate matrix element on the quasimomentum

$$\int_{0}^{2\pi} |x_{+,k\pm}|^2 d\theta = Ak$$

\(^2\) For the interband component of the conductivity this approximation corresponds to the model of `direct' transitions.

\(^3\) Which follows, for example, from dimensional analysis.
we obtain

$$\sigma_{\text{int} \, \varepsilon} (\omega) = -\frac{e^2 g}{4 \pi^2 \hbar} \frac{A n^{-1}}{\sqrt{1 + 2 \gamma_{\text{int} \, \varepsilon} / \omega}} \ln \left( \frac{\Delta E_{\text{max}} - \hbar \omega / \sqrt{1 + 2 \gamma_{\text{int} \, \varepsilon} / \omega}}{\Delta E_{\text{max}} + \hbar \omega / \sqrt{1 + 2 \gamma_{\text{int} \, \varepsilon} / \omega}} \times \frac{\Delta E_{\text{min}} + \hbar \omega / \sqrt{1 + 2 \gamma_{\text{int} \, \varepsilon} / \omega}}{\Delta E_{\text{min}} - \hbar \omega / \sqrt{1 + 2 \gamma_{\text{int} \, \varepsilon} / \omega}} \right)$$

(11)

where \( A \) is an arbitrary constant. In particular, when \( \gamma_{\text{int}} / \omega \to 0 \) from equation (11) we get:

$$\text{Re} \, \sigma_{\text{int} \, \varepsilon} (\omega) = \frac{e^2 g A n^{-1}}{4 \pi \hbar} \left[ \Theta \left( \omega - \frac{\Delta E_{\text{min}}}{\hbar} \right) - \Theta \left( \omega - \frac{\Delta E_{\text{max}}}{\hbar} \right) \right].$$

(12)

where \( \Theta(x) \) is the Heaviside step function. Note that in a 2D quantum well with several parabolic subbands \((n = 2)\), the absorption dependence on frequency has the form of a set of plateaus similar to the one described by equation (12), which was observed experimentally in the paper [18].

In further consideration of graphane electromagnetic properties in IR region, we use the expressions (10) and (11) to determine its conductivity. The valence band is set as two touching parabolas, which is presupposed by the Hamiltonian (1). Therefore, we use for the calculation:

a) of the intraband conductivity: \( \sum \pm n_\pm = 4 \);

b) of the interband conductivity\(^4\): \( A = \pi, n = 2, \Delta E_{\text{min}} = \frac{2b|E_b|}{a + b}, \Delta E_{\text{max}} = \frac{2b|E_b|}{a - b} \).

4. Optical properties of the monolayer

Let us consider a monolayer with surface conductivity \( \sigma (\omega) \) lying on a substrate with the permittivity \( \varepsilon \).

4.1. Transmission and reflection coefficients

Let a plane of electromagnetic wave be incident normally to the sample. Then the standard solution for the reflection \((r)\) and transmission \((t)\) coefficients for the complex amplitude of the electromagnetic field gives:

$$r = \frac{\sqrt{\varepsilon} - 1 + \frac{4\pi \sigma (\omega)}{c}}{\sqrt{\varepsilon} + 1 + \frac{4\pi \sigma (\omega)}{c}}, \quad t = \frac{2\sqrt{\varepsilon}}{\sqrt{\varepsilon} + 1 + \frac{4\pi \sigma (\omega)}{c}},$$

(13)

and for the power reflection and transmission coefficients we get \( R = |r|^2, T = \frac{1}{\sqrt{\varepsilon}} |t|^2 \).

4.2. 2D surface plasmon-polaritons in graphene

Now let us move to surface electromagnetic waves propagating in the plane of the monolayer (here we consider propagation along the \(x\)-axis, see figure 3).

Dispersion equation for surface plasmon-polaritons (SPP) for this configuration of the electromagnetic field is given in [26]:

$$\frac{4\pi i \sigma (\omega)}{\omega} + \frac{\varepsilon}{\sqrt{q^2 - \frac{\omega^2}{c^2}}} + \frac{1}{\sqrt{q^2 - \frac{\omega^2}{c^2}}} = 0,$$

(14)

where \( q \) is the wavenumber of the surface mode, the values \( \sqrt{q^2 - \frac{\omega^2}{c^2}} \) and \( \sqrt{q^2 - \frac{\omega^2}{c^2}} \) describe the inverse lengths of the electromagnetic field decay in the substrate and vacuum half-spaces, respectively. In the limit \( q^2 \gg \frac{\omega^2}{c^2} \), the equation (14) corresponds to the quasi-electrostatic approximation for the surface plasmon and so

$$\frac{4\pi i \sigma (\omega)}{\omega} q + \varepsilon + 1 = 0$$

(15)

\( ^4 \) For comparison, in the case of graphene \( A = \frac{\pi}{4}, n = 1 \) and \( \Delta E_{\text{max}} \to \infty \) in the vicinity of the Dirac point.
In the case of negligible interband conductivity and dissipation, from the latter expression it follows that 
\[ \omega \propto \sqrt{|E_F| \bar{q}}, \]
which coincides with the surface plasmon dispersion in graphene \[1\] and topological insulators \[26\].

5. Numerical calculations

5.1. Surface conductivity

In this section, the results of numerical calculations of the functions \(\text{Re}[\sigma(\omega)]\) and \(\text{Im}[\sigma(\omega)]\) for different relaxation rates \(\gamma\) and Fermi levels \(E_F\) are presented. All graphs are plotted in the range \(=10^{13} \ldots 10^{15}\text{rad/s}\), which corresponds to the range of 6.58 \ldots 658 meV in energy units.

Consider the frequency dependence of the surface conductivity of graphane in the case of different relaxation rates \(\gamma\). Here we choose a relatively large Fermi level (\(0.5\text{ eV}\)) to emphasize the key features of the conductivity related to the formation of the plateau mentioned in section 3 (see the frequency dependence of the real component of \(\sigma(\omega)\)). We chose the parameters of graphane to be of the same order as the corresponding parameters of graphene. For comparison, typical relaxation time in pure graphene is about \(10^{-13} \ldots 10^{-1}\text{s}\) \(\sim 10^{15}\text{s}^{-1}\) \[33\] and the Fermi level varies from 0.1 eV to 0.2 eV depending on external parameters \[34\]. For more detailed analysis, we give the graphs for the intersubband (figure 4) and intrasubband (figure 5) parts of the surface conductivity separately.

The graphs of the total conductivity are shown in figure 6. It is seen from figures 4–6, that the intrasubband part of the surface conductivity is dominant in the far-IR range \(\omega = 10^{13} \ldots 10^{15}\text{rad/s}\), while in the range \(\omega = 10^{14} \ldots 10^{15}\text{rad/s}\) the intersubband part dominates and the plateau in the frequency interval from \(\frac{\Delta E_{\text{min}}}{\hbar}\) to \(\frac{\Delta E_{\text{max}}}{\hbar}\) appears (compare to figure 2). This plateau on the graph of \(\sigma_{\text{int}}\) is also predicted by the previously obtained formulas \(11\) and \(12\).

Now consider how the conductivity behavior changes with the change of the Fermi level (at \(\gamma = 10^{13}\text{s}^{-1}\)). As can be seen from figure 7, 8 and 9 with an increase of the absolute value of the Fermi level, the above-mentioned features of the intersubband absorption become more pronounced.

5.2. Transmission and reflection coefficients

Figure 10 shows the dependence of the reflection coefficient (in terms of total power of electromagnetic radiation, see expressions in section 4.A) on the Fermi level. Calculations were carried out for graphane on a silicon carbide (SiC) substrate with the permittivity \(\varepsilon = 9.7\) in IR range.

Figure 10 shows that the typical features of intersubband surface conductivity still manifest themselves as plateaus (they occur when calculating the coefficient \(R\) from the equations \(11\) and \(12\)), which become flatter when the relaxation rate increases. With the increase of the absolute value of a Fermi level, the plateau widens and shifts toward higher frequencies. That is why measuring of absorption profile makes it possible to determine independently a Fermi level in a graphane sample or, alternatively, to clarify the parameters of the band structure.
splitting if the Fermi level is already known from some other measurements. Figure 11 shows similar dependencies for the coefficient $W = 1 - R - T$, which characterizes the energy absorption in the graphane sample.

### 5.3. Dispersion of 2D plasmon-polaritons

In this section we consider graphane on a silicon carbide substrate ($\epsilon = 9.7$) and use the expressions obtained in section IV.B for numerical calculations. In figure 12 the frequency dependencies of real and imaginary parts of the surface plasmon-polariton wavenumber are shown for a constant Fermi level $E_F = -0.5$ eV and various relaxation rates.

The graphs for the quality factor $Q = \frac{\text{Re}(q)}{\text{Im}(q)}$ are plotted in figure 13. This value characterizes the distance of SPP propagation (in wavelengths) before damping. As a consequence, one can see a dip in dependence $Q(\omega)$ associated with the previously mentioned plateau of the interband conductivity (equations (11) and (12)). Also, there is a local maximum of $Q(\omega)$ at the frequency $3.5 \cdot 10^{14}$ rad/s, which is a left boundary of this plateau. The amplitude of this peak almost linearly decreases with the relaxation rate increasing.
Figures 14 and 15 show the characteristics of surface plasmon-polaritons at the constant relaxation rate $\gamma = 10^{13} \text{s}^{-1}$ and different Fermi levels.

As a Fermi level increases, the dip in dependence $Q(\omega)$ shifts toward shorter wavelengths and becomes wider (see figure 15). Outside this area the function $Q(\omega)$ can be approximated as $\frac{\text{Re}(q)}{\text{Im}(q)} \approx \frac{\omega}{2\gamma}$. This approximation is valid in the region where the intrasubband component of the complex conductivity dominates. Indeed, assuming the parameter $\epsilon$ in equation (15) to be real, we obtain:

$$q = i(1 + \epsilon) \frac{\omega}{4\pi\sigma}$$

$$q \propto \frac{i}{\sigma} \frac{\text{Re}(q)}{\text{Im}(q)} = \frac{\text{Im}(\sigma)}{\text{Re}(\sigma)} \approx \frac{\text{Im}(\sigma_{\text{intra}})}{\text{Re}(\sigma_{\text{intra}})}$$
Next, using equation (8), we get:

\[ \sigma_{\text{intra}}(\omega) = C \frac{i}{1 + \frac{i2\gamma}{\omega}} \]

where \( C = \frac{e^2g}{4\pi\hbar^2} \sum_{\pm} \left| k \frac{\partial E_{\pm}(k)}{\partial k} \right|_{E_k=E_F} \) is a real constant, \( \gamma_{\text{intra}} = \gamma \). Finally, as stated above, we obtain

\[ \frac{\text{Re}(q)}{\text{Im}(q)} \approx \frac{\omega}{2\gamma} \]
6. Summary

In this paper we have developed the theory of graphane electromagnetic response in the infrared and terahertz ranges, and found that this material is strongly absorptive and tunable with Fermi level change, which could be perspective for many applications. This theory is based on a simple analytical model of graphane band structure in the vicinity of Γ-point and on the modified model of quantum coherence relaxation. We should note that many resonant features of graphane conductivity are expected to be less sharp at room temperatures, especially in the far-IR region.

Comparison of the results of our calculations with the experimental data seems to be a reliable method for clarification of the used band structure model, proposed in recent literature; we hope that our paper will stimulate new experiments on the graphane properties in IR and terahertz range. Obtained theoretical results can be used to determine important parameters of charge carriers in graphane like the Fermi level and the relaxation rate. According to analytical and numerical estimations, this requires an experimental accuracy of the order of 0.1%–1% (see figures 10 and 11) in absorption or reflection measurements.
As for the further development of theory, machine learning methods seem to be very promising in the modelling of 2D materials and, in particular, graphane (see, for example, the paper [35] where the method of interatomic potentials trained over small supercells was proposed).

Figure 12. The real (a) and imaginary (b) parts of surface plasmon-polaritons wavenumbers at different relaxation rates $\gamma = 10^{13} \ldots 10^{14} \text{s}^{-1}$ and $E_f = -0.5 \text{eV}$.

Figure 13. Quality factor $Q(\omega) = \frac{\text{Re}(\omega)}{\text{Im}(\omega)}$ for surface plasmon-polaritons at different relaxation rates $\gamma = 10^{13} \ldots 10^{14} \text{s}^{-1}$ and $E_f = -0.5 \text{eV}$. 
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
Appendix A. A finite gap between subbands.

The dependences $E_{\pm}(k^2)$ given by the Hamiltonian (1) correspond to a tangency of the subbands at the point $k = 0$. We generalize the results obtained to the case of a finite gap. To describe this situation, we modify the Hamiltonian (1):

$$\hat{H}_k = -a\hat{I}(k_x^2 + k_y^2) - b[\sigma_z(k_x^2 - k_y^2) + 2\sigma_x k_x k_y + \hat{\sigma}_y H^2]$$  \hspace{1cm} (A.1)

where $H$ is the additional constant with the dimension of a wavenumber, $\hat{\sigma}_y$ is the $y$-Pauli matrix. The Hamiltonian equation (A.1) corresponds to two parabolic-like curves $E_{\pm}(k^2)$:

$$E_{\pm} = \mp ak^2 \pm b\sqrt{k^4 + H^4},$$  \hspace{1cm} (A.2)

Which are separated by the gap of width $W_{\text{min}} = 2bH^2$ (figure A.1).

In this case we get:

$$\begin{pmatrix} u_{1k} \\ u_{2k} \end{pmatrix} = \frac{1}{\sqrt{N_{\pm}}} \begin{pmatrix} 2k_x k_y - iH^2 \\ k_x^2 - k_y^2 + \sqrt{k^4 + H^4} \end{pmatrix},$$  \hspace{1cm} (A.3)

where $N_{\pm} = \frac{2\sqrt{k^4 + H^4}}{k^4 + H^4 + (k_x^2 - k_y^2)}$;

$$|x_{(+)k(-)k}|^2 = \frac{1}{k^4 + H^4} \times \frac{k_x^2 (k^4 + H^4) - k^2}{\sqrt{k^4 + H^4}} = \frac{2k_x^2 k_y^2}{\sqrt{k^4 + H^4}}\left(1 + \frac{k^2}{\sqrt{k^4 + H^4}}\right)^2,$$ \hspace{1cm} (A.4)

It can be proved that in the limit $k^2 \gg H^2$ the expressions equations (A.3) and (A.4) pass into the expressions equations (3) and (4) respectively. For $a \sim b$ the strong inequality $k^2 \gg H^2$ is equivalent to the physically transparent condition: $E_{(+)}(k^2) - E_{(-)}(k^2) \gg W_{\text{min}}$.

In expressions (equations (8) and (9)) for the conductivity components for the value $\Delta E \left| \frac{d\Delta E}{dk} \right|^{-1}$ there is the following compact ratio:

$$\Delta E \left| \frac{d\Delta E}{dk} \right|^{-1} = \frac{k^4 + H^4}{2k^3},$$ \hspace{1cm} (A.5)

In the case $|E| < bH^2 \Rightarrow W_{\text{min}}/2$ there is $\Delta E_{\text{min}} = 2bH^2 = W_{\text{min}}$ in equation (9). In the limit sufficiently large Fermi energy, when $\frac{|E|}{b} \gg H^2$ (i.e. $\Delta E_{\text{min}} \gg W_{\text{min}}$), both models (i.e. given by the Hamiltonians equations (1) and (A.1) respectively) lead to identical results.

Let’s consider how surface conductivity and a wavenumber of surface plasmon-polaritons change at different values of the parameter $H$. 

![Figure A.1. The model of valence with a gap, $H = 2.5 \cdot 10^7$ cm$^{-1}$.](image-url)
Calculations were carried out with the following parameters:

\[ 0, 0.5 \times 10^{13} \text{ cm}^{-1}, 1 \times 10^{17} \text{ cm}^{-1}, 1.6 \times 10^{17} \text{ cm}^{-1}, 2 \times 10^{17} \text{ cm}^{-1} \]

\[ \gamma = 5 \times 10^{13} \text{ s}^{-1}, E_F = -0.1 \text{ eV} \]

The figure A.2 shows numerical calculations of the real (a) and imaginary (b) parts of surface conductivity at various parameters \( \mathcal{K} \) and \( E_F \); box (c) is band structures at various parameters \( \mathcal{K} \).

Calculations were carried out with the following parameters: \( \mathcal{K}_1 = 0, \mathcal{K}_2 = 0.5 \times 10^7 \text{ cm}^{-1}, \mathcal{K}_3 = 1 \times 10^7 \text{ cm}^{-1}, \mathcal{K}_4 = 1.6 \times 10^7 \text{ cm}^{-1}, \mathcal{K}_5 = 2 \times 10^7 \text{ cm}^{-1}; \gamma = 5 \times 10^{13} \text{ s}^{-1}, E_F = -0.1 \text{ eV} \) (a Fermi level is calculated from the zero energy level corresponding to the arithmetic mean the extremes of the subbands).

The figure A.2 shows numerical calculations of the real (a) and imaginary (b) parts of surface conductivity; the box (c) shows band structures at various parameters \( \mathcal{K} \).

The numerical calculations demonstrate that the real part of surface conductivity dominates at frequencies \( 10^{13} - 10^{14} \text{ rad s}^{-1} \). And as the \( \omega \) increases, the imaginary component begins to prevail. The figure A.3 shows the real (a), imaginary (b) parts of the surface plasmon-polariton wavenumber and the quality factor (c) \( Q = \frac{\text{Re}(q)}{\text{Im}(q)} \).

The presence of the gap between the subbands significantly affects the surface plasmon-polaritons wavenumber. The figure A.3 shows that characteristic oscillations appear in the calculations of the real part. This happens than the parameter \( \mathcal{K} \) approaches the value, when there is an intersection of a Fermi level with only

\[ \text{If another zero energy level is selected, for example, it is the maximum of the upper subband, the replacement variable should be used} \]

\[ E_F \rightarrow E_F \text{ new} = E_F - |b| \mathcal{K}^2, \text{or it is necessary to shift the functions} \ E \text{ by the similar value (which will not match the Hamiltonian A1).} \]
one of the subbands. As the parameter $X$ increases further, these oscillations increase and shift to the shortwave region. The characteristic peak of the imaginary part shows similar behavior.

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