

Enhanced Raman scattering mediated by long wave vector surface plasmon polaritons

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Surface-enhanced Raman scattering mediated by surface plasmon polaritons with wave vectors much larger than those of light is considered. The excitation of these polaritons and their efficient Raman scattering due to low group velocity and electric field localization at the surface is discussed for the case of two nearby surfaces. The Raman scattering depends not only on the intensity of the electric fields seen by the molecules but also on the surface plasmon density of states.

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Surface-enhanced Raman scattering (SERS) is currently employed as a useful analytical tool. Nevertheless, a well-established explanation of this effect is still lacking.¹⁻³ The different theories of SERS may be arranged into two types of quite different nature. The first one, known as electromagnetic theories, assumes that the Raman cross section of molecules is similar to that of isolated molecules and the Raman enhancement is caused by an amplification of the electromagnetic fields on the metallic surface where the molecules are located; i.e., the Raman enhancement is directly related to the amplification of the local electromagnetic field seen by the molecule. The hypothesis most generally admitted is that this amplification is due to surface plasmon excitations. The second type, known as theories of the chemical effect, assumes that the electronic interaction of the molecule with the metal surface leads to an increase of the Raman cross section similarly as in resonant Raman scattering.

In this paper I present a mechanism that may account for observed Raman enhancements. I will show that the Raman scattering cross section of molecules absorbed on a surface may be very large when Raman scattering is mediated by surface plasmon polaritons with large wave vectors and low group velocity. I will show that the scattering of these quasiparticles by phonons strongly depends on their group velocity and may be much more efficient than the usual Raman scattering by light. This mechanism is formally and conceptually very similar to the enhancement of the resonant Brillouin or Raman scattering through exciton polaritons in crystals in the excitonic spectral region, a phenomena well established today.^{4,5} In this paper I first discuss the Raman scattering mediated by surface plasmon polaritons and then I consider surface geometries which generate the peculiar surface polaritons giving rise to a very high Raman cross section.

Raman scattering mediated by surface plasmon polaritons may be described in a rather similar way as resonant Raman scattering by excitons⁴ using a factorization of the different steps. I will assume that the incoming photons scatter with the molecules in three steps schematically represented in Fig. 1, and summarized as follows:

(1) An impinging photon with energy $\hbar\omega_i$ excites a surface polariton with energy $\hbar\omega_i$ and wave vector k_i . The probability (or efficiency) of such conversion is T_i .

(2) The surface polariton ($\hbar\omega_i$, k_i) subsequently scatters with a molecule creating a phonon of energy $\hbar\Omega$ (for simplicity only the Stokes process is considered) and a surface plasmon

polariton of energy $\hbar\omega_s = \hbar\omega_i - \hbar\Omega$ and wave vector k_s . Note that k_i and k_s are wave vectors both on the surface and direction according to the momentum conservation.

(3) The surface plasmon polariton ($\hbar\omega_i - \hbar\Omega$, k_s) is converted back into a photon with an efficiency T_s and finally collected at the detector.

The probability for a polariton $|k_i\rangle$ to scatter into a polariton $|k_s\rangle$ by the interaction with a potential V with the molecule is given, to the first-order approximation, by the Fermi transition rate golden rule:

$$\left(\frac{dP^{\text{Pol}}}{dt}\right)_{k_i \rightarrow k_s} = \frac{2\pi}{\hbar} |\langle k_i | V | k_s \rangle|^2 \delta(\hbar\omega_i - \hbar\omega_s - \hbar\Omega).$$

The overall scattering probability accounts for all the possible final states k_s in the k plane. The differential element on the two-dimensional k surface is $ds = k_s d\alpha dk_s$ and the number of states between k and $k + dk$ is $k_s d\alpha dk_s / (2\pi)^2$. Integrating around all the possible directions in the plane and including $dk = d\omega / (d\omega/dk)$ we find that the overall scattering probability is

$$\frac{dP^{\text{Pol}}}{dt} = \frac{2\pi}{\hbar} |\langle k_i | V | k_s \rangle|^2 \rho(\omega),$$

where $\rho(\omega) = k_s / (2\pi\hbar v_{gs})$ is the surface polariton density of states and $v_{gs} = (d\omega_s/dk)$ the group velocity of the scattered surface polaritons. Without damping, v_{gs} corresponds to the energy velocity. $P^{\text{Pol}} = (dP^{\text{Pol}}/dt)\tau$, where τ is the lifetime of the excited polaritons that in the case of a long wave vector can be approximated by⁶

$$\tau = \frac{1}{2\epsilon''} \frac{d\epsilon'}{d\omega}. \quad (1)$$

An estimation with the dielectric constants⁷ gives for the damping for $\omega \sim \omega_s$, $\hbar/\tau \sim 0.1$ eV, in agreement with low energy loss experiments.⁸ The polariton lifetime is about 4×10^{-14} s.

Finally, in the global process, the scattering efficiency for a photon $\hbar\omega_i$ striking the surface in the Ω_i direction to generate a photon $\hbar\omega_s$ in the solid angle $d\Omega_s$ around Ω_s is

$$\frac{dP}{d\Omega_s} = T_i(\Omega_i) T_s(\Omega_s) \frac{k_s}{\hbar^2 v_{gs}} |\langle k_i | V | k_s \rangle|^2 \tau, \quad (2)$$

with τ given by Eq. (1). It is explicitly indicated that $T_i(\Omega_i)$ is the probability to excite a surface polariton by an incoming photon in the direction Ω_i and $T_s(\Omega_s)$ is the probability for

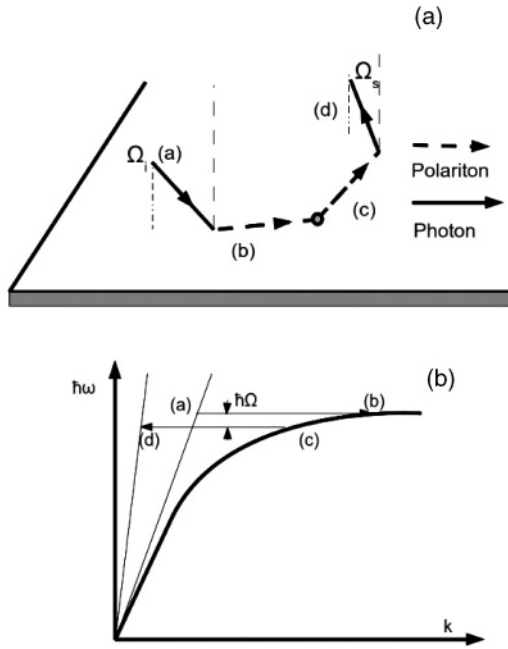


FIG. 1. Panel (a): Schematic representation of Raman scattering by surface polaritons: photon (a) impinging on the surface with an angle Ω_i generating a surface polariton with wave vector k_i (b) which scatters with a molecule into a polariton with wave vector k_s (c) that converts into a photon (d) leaving the surface at an angle Ω_s . Panel (b): Dispersion of surface plasmons and light. Polaritons are indicated in (b) and (c) and photons in (a) and (d).

a surface polariton to generate a photon in the direction Ω_s . Photons are collected in the solid angle $d\Omega_s$ around Ω_s . Insofar as the surface polariton propagation length is microscopic in our case, the outgoing photons are collected in the experiment at the same point as the impinging one. $T_i(\Omega_i)$ depends on the surface polariton density of states $\rho(\omega_i) = k_i/2\pi\hbar v_{gi}$ where $v_{gi} = (d\omega_i/dk)$ is the group velocity of the excited surface polaritons. We can admit that the probability that a photon converts into a polariton is proportional to the number of allowed polaritons, i.e., the polariton density of states, and thus $dP/d\Omega_s \sim 1/v_{gi}v_{gs}$. As the group velocity can be small this factor increases the Raman scattering. This is a first possible mechanism of Raman enhancement.

Low group velocity ($v_g/c \ll 1$) has been measured for exciton polaritons⁹ and enhancement by several orders of magnitude of the Raman scattering of semiconductors due to this velocity factor are well documented in the literature.^{4,5} Enhancement of Raman scattering by slow group velocity in nonexcitonic media has already been evoked¹⁰ and experimentally observed¹¹ in photonic crystals for energies approaching the band edge. Stimulated Raman scattering enhanced by the same mechanism was predicted in optical guides.¹² These are some examples of the numerous slow light situations giving rise to interesting phenomena¹³ also observed in other kinds of waves such as ultrasound propagating on elastic plates.¹⁴

The second possible mechanism of Raman enhancement is the term $|\langle k_i | V | k_s \rangle|^2$ in Eq. (2). In the classical dipolar approximation, this term is proportional to the intensity of the incident and scattered fields seen by the molecule (electric fields at $z = 0$). According to Eq. (A5) of the Appendix, the

electric field intensity increases linearly with k approaching the frequency ω_{sp} for which $\epsilon \rightarrow -1$, $k \rightarrow \infty$, and $v_g \rightarrow 0$. In summary $dP/d\Omega_s \sim k_i k_s^2 / v_{gi} v_{gs}$ may become extremely large for photons with energies close to ω_{sp} . Nevertheless for real metals with flat surfaces, damping prevents having surface plasmons with $v_{gi}, v_{gs} \ll c$ and high fields at the surface.¹⁵ In Raman scattering mediated by surface plasmon polaritons excited by attenuated total reflection (ATR) as in Ref. 16, $v_{gi} \approx v_{gs} \approx c$ and the enhancement is due to the modest electromagnetic field amplification at the surface.

Today it is generally admitted that high electromagnetic fields in gaps or cavities of nanometric or sub-nanometric dimensions leads to SERS.^{17–20} In the case of metallic particles the electromagnetic enhancement increases upon reducing the distance between the particles.²¹ An extremely important point of our argumentation about Raman enhancement is that for more complex surfaces than a flat surface, long wave vector surface plasmon polaritons can be spontaneously generated simply by shining the sample with light.

It was recently theoretically demonstrated²² and experimentally observed²³ that rectangular grooves of nanometric dimension on otherwise flat surfaces may strongly absorb the impinging light by the excitation of standing surface plasmon polariton waves in the cavities. In such a case the conversion of photons to long wave vector surface plasmon polaritons is very efficient. The Le Perchec *et al.* results²² are extremely important in the present discussion because they demonstrate that light may generate electronic surface plasmon polaritons with high electric field and small magnetic fields. More recently it was demonstrated that this type of polariton exists for nanometric cavities of a variety of shapes.²⁴

Moreover, some other indications lead us to think that plasmons with extremely long wave vectors are excited when SERS occurs. Namely, the inelastic background assigned to a very rapid recombination of electron-hole pairs generated by the impinging light is necessarily created by quasiparticles with momentum on the order of k_F .

One feature of SERS is that the laser light is largely absorbed by the samples in spite of the fact that the metal itself must be very reflecting. Optical absorptions are observed, for instance in colloids, discontinuous films, or deposits on a cold substrate. Differential reflectivity measurements of Ag films deposited on a cold substrate have shown that the surface absorption follows the SERS excitation spectra.²⁵ These experiments show that many surface plasmons can be excited in rough surfaces but only those with the electric fields strongly localized at the surface contribute to SERS.

In a prophetic paper written almost one century ago about the anomalous optical absorption of Na condensed on cold substrates, R. W. Wood underlined,²⁶ “The spaces or cavities between the sodium crystals act as traps for radiation of definite frequencies.” It is well known today that these spaces or cavities have sub-nanometric dimensions.

The left panel of Fig. 2(a) schematically represents notches or grain boundaries of a metallic sample, and the right side the spaces between two closed particles such as coalesced colloids or grains of discontinuous films. Figure 2(b) shows two geometries to model such features. The electromagnetic fields for the geometries represented in this figure were extensively investigated.^{27–31} In both cases (closed and open

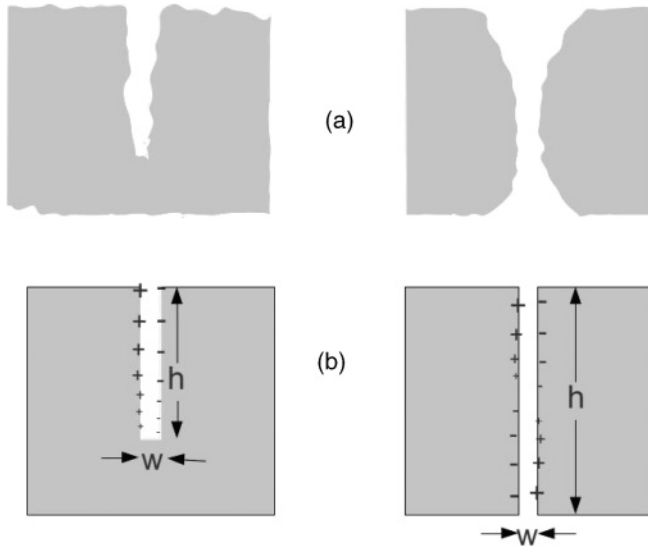


FIG. 2. (a) Representation of geometries with nanometric dimensions giving rise to SERS: a notch in a metal surface and an interstice between two closed particles. (b) Idealization of the geometries above with flat surfaces of length h separated by a distance w . In the figure the surface charges for standing wave resonances are qualitatively indicated.

cavities) resonances are generated by stationary waves built up by modes of two infinite metallic planes with antisymmetric charge distribution. Surface charges on the cavities for a first-order resonance are indicated in the figure. The electric field is nil at the bottom of the closed cavity and at the middle of the channel for the open cavities, similarly to sound intensity in pipe resonances. Actually, Rayleigh in a posthumous publication concerning acoustic resonances in a perforated wall³² wrote that sound may behave as light in cavities of alkali films studied by Wood.²⁶ To discuss polaritons in the geometries indicated in Fig. 2(b) I consider the well-known electromagnetic modes of two interacting metallic surfaces as indicated in the inset of Fig. 3.

The surface plasmon dispersion relations of two flat surfaces of identical metals (of dielectric constant $\epsilon \equiv \epsilon' + i\epsilon''$) separated by a distance w can be found in Ref. 33 and in the case relevant for us with $k \gg \omega/c$ are given by

$$\frac{\epsilon + 1}{\epsilon - 1} = \pm e^{-kw}, \quad (3)$$

where $k \equiv k' + ik''$ is the complex wave vector parallel to the surface. The “+” solution is the antisymmetric mode which exists for frequencies $< \omega_{sp}$ that is the only one I will consider. The real and imaginary parts of k normalized to w are shown in Fig. 3 for silver taking for ϵ values given in Ref. 7. It is important to underline that for a given frequency, k can be larger, the smaller the gap, while having a relatively small imaginary part. This is an important property and an essential difference with surface plasmons of a single surface. It can be shown that the fields at the surface are given by the same expression as that for a single surface, i.e., by Eq. (A5) (see Appendix) but with k given by Eq. (3). Very clearly the electric field becomes very high approaching ω_{sp} . For the case in which w is extremely small ($kw \ll 1$ with $k \gg \omega/c$) we have from

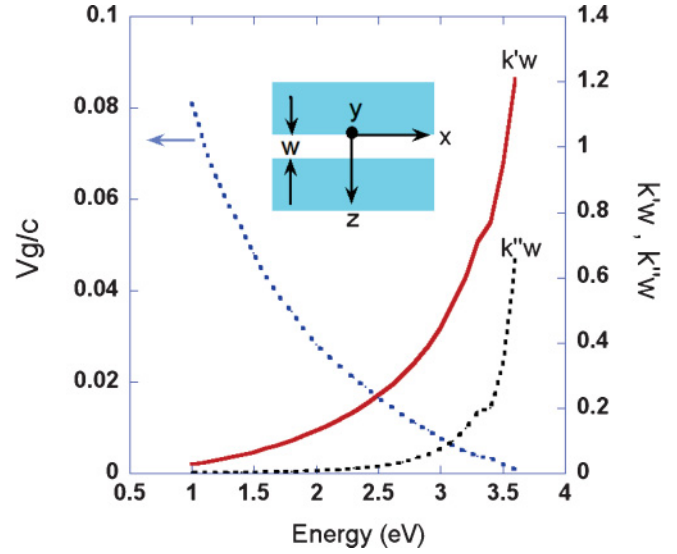


FIG. 3. (Color online) Group velocity v_g of surface plasmons of two silver surfaces separated by $w = 1$ nm and $k'w$ and $k''w$ for two closed surfaces with the approximation $k \gg \omega/c$.

Eq. (3) that $k \approx 2/w|\epsilon - 1|$. In this limit resonances of cavities in Fig. 3(b) occur for h much smaller than the wavelength of light.

In the spectral region with $\epsilon'' \ll \epsilon'$, and from Eq. (3), the group velocity is given, to a good approximation, by

$$\frac{1}{c} \frac{d\omega}{dk} \sim \frac{1}{2} w (\epsilon' - 1)(\epsilon' + 1) \left(\frac{d\epsilon'}{d\omega} \right)^{-1}.$$

The dielectric constant of Ag can be represented as the sum of two contributions: the s - p near free electrons, $\epsilon^f = 1 - \omega_p^2/\omega^2$, and the bounded d -band electron contribution, ϵ^b .³⁴ Neglecting the dispersion in the d -electron contribution, we have

$$\frac{1}{c} \frac{d\omega}{dk} \sim w \frac{\omega}{4c} (\epsilon' - 1)(\epsilon' + 1) \left(\frac{\omega_p^2}{\omega^2} \right)^{-1}. \quad (4)$$

Figure 3 shows $(d\omega/dk)/c$ for $w = 1$ nm computed with Eq. (4) and $\hbar\omega_p = 9$ eV.

In conclusion, for sufficiently small w polaritons with long wave vectors, high electric fields at the surface, and small group velocity exist in a rather large spectral region. More importantly, for these modes the real part of the wave vector can be large with a relatively small imaginary part provided that w is sufficiently small.

The factor $dP/d\Omega_s \sim k_i k_s^2 / v_{gi} v_{gs}$ can be very high for plasmons of the geometry indicated in the inset of Fig. 3. Around 3.5 eV this factor becomes very high but its accuracy may be questioned due the increasing damping and the validity of the local approximation. Nevertheless, an estimation of this factor at 2 eV, where the approximation is safer, shows that it is about 3×10^6 larger than that for Raman scattering mediated by surface plasmon polaritons of the same energy in an ATR experiment ($v_{gi} \approx v_{gs} \approx c$ and $k_i \approx ks \approx \omega/c$). An enhancement of 4×10^4 was determined for Raman scattering mediated by surface plasmons of a flat surface excited by photons of 2.4 eV in an ATR configuration.¹⁶ A realistic Raman

enhancement must be determined from the electric fields and velocities of polaritons for each specific geometry.

It is noteworthy to remark that first-order Raman scattering by surface plasmon polaritons may involve phonons with a noticeable momentum. This is not the case for Raman scattering with light. This is particularly true for polaritons with frequencies close to ω_{sp} for which momentum can be conserved in the scattering process even for phonons with large momentum. This may explain some intriguing differences concerning the Raman frequencies observed in SERS with respect to the molecules in solutions, sometimes attributed to molecular distortion by chemisorption. It is also important to point out that the hypothesis presented herein also applies to Brillouin scattering. Consequently Brillouin scattering enhancement of bulk and surface phonons should be observed in SERS, as well. This is probably the case, as evidenced by structures observed on the low-frequency region of the inelastic background. In particular, we observed, for silver deposited on cold substrates, features in the SERS background which correspond to the phonon density of states.³⁵ These structures can be understood as enhanced Brillouin scattering at metal surfaces.

All the features of SERS are consistent with the ideas presented herein. For instance the extremely large surface sensitivity of SERS,³⁶ unusual for an optical phenomenon, can be easily understood by the nature of the long wave vector surface polaritons. The presence of hot spots (or active sites) may also be understood as the few places on the surface where the photon polariton conversion occurs.

This paper shows that the Raman scattering depends not only on the intensity of the electric fields seen by the molecule but also on the surface plasmon density of states. Raman scattering mediated by surface polaritons is enhanced because (i) the density of states of these surface polaritons may be very large, and (ii) long wave vector surface polaritons have larger electric fields at the surface than photons of the same energy. Moreover the Raman selection rules are also different from those for the usual spontaneous Raman scattering. Plasmons or phonon polaritons on surfaces may propagate with a velocity much smaller than that of light and have a longer interaction time with molecules at the surface. For some surface spectroscopies (beyond SERS), it is important to consider that short wave length polaritons may interact with molecules more efficiently than photons do.

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APPENDIX: ELECTRIC FIELDS AND GROUP VELOCITY OF SURFACE PLASMONS

Let us consider a flat surface (in the x - y plane) between vacuum (medium 1) and a metal (medium 2) of dielectric constant ϵ with a surface plasmon of wave vector \mathbf{k} in the x

direction and the magnetic field in the y direction given by

$$\begin{aligned} (\mathbf{H}_1)_y &= H e^{ikx} e^{q_1 z} e^{-i\omega t}, \\ (\mathbf{H}_2)_y &= H e^{ikx} e^{-q_2 z} e^{-i\omega t}, \end{aligned} \quad (\text{A1})$$

with $q_1 = \sqrt{k^2 - (\omega/c)^2}$ and $q_2 = \sqrt{k^2 - (\omega/c)^2 \epsilon}$. The electric fields are given by the relation $\nabla \times \mathbf{H} = -i\omega\epsilon\mathbf{E}$:

$$\begin{aligned} (\mathbf{E}_1)_x &= -iH(q_1/\omega\epsilon_0) e^{ikx} e^{q_1 z} e^{-i\omega t}, \\ (\mathbf{E}_1)_z &= -H(k/\omega\epsilon_0) e^{ikx} e^{q_1 z} e^{-i\omega t}, \\ (\mathbf{E}_2)_x &= iH(q_2/\omega\epsilon_0) e^{ikx} e^{-q_2 z} e^{-i\omega t}, \\ (\mathbf{E}_2)_z &= -H(k/\omega\epsilon_0) e^{ikx} e^{-q_2 z} e^{-i\omega t}. \end{aligned} \quad (\text{A2})$$

The dispersion relation of this wave is obtained from the continuity of the components of the electric and magnetic fields parallel to the surface:

$$k = \frac{\omega}{c} \sqrt{\frac{\epsilon}{\epsilon + 1}}. \quad (\text{A3})$$

Without absorption the group velocity $v_g = d\omega/dk$ obtained from Eq. (A3) is given by

$$v_g/c = \frac{\sqrt{|\epsilon|}|\epsilon + 1|^{3/2}}{\epsilon(\epsilon + 1) + \frac{1}{2}\omega \frac{d\epsilon}{d\omega}}, \quad (\text{A4})$$

where c is the light velocity in vacuum. At the surface plasmons of frequency ω_{sp} , $\epsilon \rightarrow -1$, $k \rightarrow \infty$, and $v_g \rightarrow 0$.

Equations (A1) and (A2) show that for $k \gg (\omega/c)\sqrt{\epsilon}$ the electric field is much larger than the magnetic field and decay out of the surface over distances $\sim 1/k$.

The density of electromagnetic radiation for a nonmagnetic medium ($\mu = 1$) with a real dielectric constant is given³⁷ by

$$U = \frac{1}{4} \left(\epsilon_0 \frac{d(\omega\epsilon)}{d\omega} E^2 + \mu_0 H^2 \right),$$

where U is in mks units and E^2 and H^2 are the intensity of the electric and magnetic fields, respectively. The time-averaged energy density in medium 1 over a surface S is obtained by integrating in z from $-\infty$ to 0.

$$U_1 = \frac{S}{8q_1} (\epsilon_0 E^2 + \mu_0 H^2) = \frac{SE^2\epsilon_0}{4q_1} \frac{|\epsilon|}{|\epsilon - 1|},$$

where H^2 and $E^2 = H^2(q_1^2 + k^2)/\omega^2\epsilon_0^2$ are the intensities of the magnetic and the electric fields in the vacuum at the surface ($z = 0$). The corresponding energy density in medium 2 is

$$U_2 = \frac{SE^2\epsilon_0}{4|\epsilon|q_1} \left(\frac{1}{|\epsilon - 1|} + \frac{\omega}{2|\epsilon|} \frac{d\epsilon}{d\omega} \right),$$

and the overall density of the energy in both media,

$$U = \frac{SE^2\epsilon_0}{4|\epsilon|^2 q_1} \left(|\epsilon||\epsilon + 1| + \frac{\omega}{2} \frac{d\epsilon}{d\omega} \right).$$

For the case in which a photon of energy $\hbar\omega$ converts into a polariton with the energy distributed over a surface S , the electric field intensity of the polariton at the surface will be

$$E^2 \approx \frac{4\hbar\omega\epsilon^2 q_1}{S\epsilon_0} \left(|\epsilon||\epsilon + 1| + \frac{\omega}{2} \frac{d\epsilon}{d\omega} \right). \quad (\text{A5})$$

For long wave vectors [$k \gg (\omega/c)\sqrt{|\epsilon|}$], $E^2 \sim k$.

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