

Universal Features of Terahertz Absorption in Disordered Materials

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Using an analytical theory, experimental terahertz time-domain spectroscopy data, and numerical evidence, we demonstrate that the frequency dependence of the absorption coupling coefficient between far-infrared photons and atomic vibrations in disordered materials has the universal functional form, $C(\omega) = A + B\omega^2$, where the material-specific constants A and B are related to the distributions of fluctuating charges obeying global and local charge neutrality, respectively.

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Since their name indicates a lack of order, it is perhaps unexpected that all disordered materials, regardless of their chemical composition, often behave very similarly in response to external probes. Low-temperature anomalies in thermodynamical properties of amorphous solids are one example [1]. Related to these is the pileup of vibrational modes in excess of the Debye vibrational density of states (VDOS), $g(\omega) \propto \omega^2$, at typical frequencies $\sim 30 \text{ cm}^{-1}$, known as the boson peak (BP) (see, e.g., [2], and references therein). Interaction of photons with atomic vibrations in disordered materials is also expected to manifest universal behavior, especially in the far-infrared (FIR) frequency domain [3], $1\text{--}100 \text{ cm}^{-1}$, where the atomic vibrations are material independent and resemble distorted sound waves.

The simplest first-order perturbation process of photon interaction with atomic vibrations is FIR absorption characterized by a linear absorption coefficient, $\alpha(\omega) = C(\omega)g(\omega)$, which is measured by IR spectroscopy—one of the most valuable experimental techniques to assess the vibrational properties of amorphous materials [4,5]—and is found generally be $\alpha(\omega) \propto \omega^2$ in the FIR domain. The coefficient $C(\omega)$ quantifies the degree of coupling between IR photons and atomic vibrations. It depends on the vibrational eigenmodes and the distribution of atomic charges. The answer to the question about a possible universal frequency dependence of $C(\omega)$ for all or most disordered materials in the FIR range has so far been uncertain, because (i) $C(\omega)$ cannot be measured directly, and two independent experiments [for measuring $\alpha(\omega)$ and $g(\omega)$] are necessary, and (ii) there is no rigorous analytical theory for $\alpha(\omega)$ in disordered systems—previous theoretical models concentrated mainly on the origin of the BP modes [6] within a particular soft-potential model or on the role of charge disorder in simple lattice models without positional disorder [7].

In this Letter, we demonstrate that, for disordered materials in the FIR regime, $C(\omega)$ indeed exhibits a universal frequency dependence of the following form:

$$C(\omega) \simeq A + B\omega^2, \quad (1)$$

where A and B are material-dependent constants. This law is valid in the low-frequency part of the FIR domain, namely, for frequencies below the Ioffe-Regel crossover, $\omega \lesssim \omega_{\text{IR}}$, separating well propagating plane waves from strongly damped ones due to disorder-induced scattering [8]. In many materials, the Ioffe-Regel frequency is close to the BP [9]. We provide simple analytical arguments, confirmed by numerical analyses of molecular-dynamics (MD) models, and terahertz (THz) time-domain spectroscopy (TDS) measurements of $\alpha(\omega)$ for two glassy systems, SiO_2 and As_2S_3 , and use independently available experimental VDOS data for $g\text{-SiO}_2$ [10] and $g\text{-As}_2\text{S}_3$ [11,12] to extract $C(\omega)$.

Our analytical arguments are based on an analysis of the following general expression for the coefficient of absorption of FIR photons by harmonic atomic vibrations obtained within the rigid-ion model [13]:

$$C(\omega) \simeq C_0 \left| \sum_i \frac{q_i}{\sqrt{m_i}} \mathbf{e}_i(\omega) \right|^2, \quad (2)$$

where $C_0 = 2\pi^2 n / c\epsilon_\infty^{1/2}$, with m_i and q_i being the atomic masses and fixed atomic charges, $\mathbf{e}_i(\omega)$ the component of the eigenvector of frequency ω corresponding to atom i , ϵ_∞ stands for the high-frequency dielectric constant, and n is the atomic concentration. A more general model with the fixed charges replaced by charge tensors [4,14] should be used for higher frequencies in order to describe properly the absorption peak positions and their relative intensities across the IR vibrational band, but, in the FIR range, the rigid-ion model is adequate, as we have checked for our density functional theory-based tight-binding (DFTB) [15,16] MD model of $g\text{-As}_2\text{S}_3$ [17].

In ordered systems, the eigenmodes are phonons and static atomic charges do not fluctuate and $C(\omega)$ is nonzero only for optic modes at the center of the Brillouin zone. In disordered systems, structural disorder leads to a static charge transfer between atoms, i.e., to static disorder in the q_i , and to intrinsic disorder in the components of the vibrational eigenmodes. These two related sources of dis-

order are encoded in Eq. (2) and are responsible for the peculiar behavior of $C(\omega)$ in amorphous systems. In order to demonstrate this, we use two known features about the structure of the vibrational eigenmodes in the FIR regime and about the distribution of atomic charges in glasses. First, the disordered eigenmodes in the low-frequency regime can be approximately expanded in plane waves (see Ref. [8] for more detail) characterized by a wave vector \mathbf{k} and unit polarization vector $\hat{\mathbf{p}}_{\mathbf{k}}$, i.e., $\mathbf{e}_i(\omega) \simeq \sum_{\mathbf{k}} \sqrt{m_i/\bar{m}} a_{\mathbf{k}}(\omega) \hat{\mathbf{p}}_{\mathbf{k}} e^{i\mathbf{k}(\omega) \cdot \mathbf{r}_i}$, with $\bar{m} = N^{-1} \sum_i m_i$ and \mathbf{r}_i being the position vector for atom i ($i = 1, \dots, N$). The distribution of coefficients $a_{\mathbf{k}}(\omega)$ for low frequencies (at least below ω_{IR}) has the shape of two relatively narrow peaks describing the disorder-induced hybridization between transverse and longitudinal acoustic phonons of the same frequency ω , with the peak positions scaling linearly with frequency [8,18]. Second, it has been found for an *ab initio* MD model of $g\text{-SiO}_2$ that the atomic-charge fluctuations preserve approximately local charge neutrality within SiO_4 tetrahedra [4]. Similarly, we have found local charge neutrality to be obeyed within AsS_3 pyramids in a DFTB MD model of $g\text{-As}_2\text{S}_3$ [17].

These two observations lead to Eq. (1). Assuming for simplicity that only a single plane wave with wave vector \mathbf{k} contributes to the disordered eigenmode [the presence of two peaks of finite widths in the distribution $a_{\mathbf{k}}(\omega)$ does not change qualitatively the results presented below, at least for $\omega \lesssim \omega_{\text{IR}}$], we can reduce the configurationally averaged Eq. (2) to the following form: $\langle C(\omega)\bar{m}/C_0 \rangle \simeq N^{-1} \langle |S|^2 \rangle$, where $S = \sum_i q_i e^{i\mathbf{k} \cdot \mathbf{r}_i}$. Further analysis is based on the following rather general properties of the random sum S : (i) if the values of q_i are not random, then the orientationally averaged S scales linearly with k for $k \rightarrow 0$ —the same holds for random but locally correlated values of q_i (see below); (ii) if the values of q_i are random and uncorrelated, then $S \rightarrow \text{const}$ for $k \rightarrow 0$. It is convenient to split the atomic charges into two components, $q_i = q_{1i} + q_{2i}$, with $q_{1i}(\{\mathbf{r}_i\})$ (depending on many atomic positions in a complicated fashion) representing uncorrelated charge components so that $\langle q_{1i} q_{1j} \rangle = \langle q_{1i} \rangle \langle q_{1j} \rangle = \sigma_1^2 \delta_{ij}$ and, e.g., $\langle q_{1i} e^{i\mathbf{k} \cdot \mathbf{r}_i} \rangle \simeq \langle q_{1i} \rangle \langle e^{i\mathbf{k} \cdot \mathbf{r}_i} \rangle = 0$. The random charges q_{2i} satisfy local charge neutrality and can be imagined as resulting from charge transfers between nearest-neighbor atoms, i.e., $q_{2i} = \sum_{j \neq i} \Delta q_{ji}$, where j runs over all nearest neighbors of atom i and $\Delta q_{ji} (= -\Delta q_{ij})$ is the charge transfer from originally neutral atoms j to i . In heteropolar crystals, the values of Δq_{ji} are finite and not random. In disordered systems, the values of Δq_{ji} are distributed around mean values which do not necessarily coincide with those for their crystalline counterparts (see, e.g., [4]). Such fluctuations in Δq_{ji} and deviations of the means are due to distortions in local structural units (e.g., the Si-O-Si bond angle in $g\text{-SiO}_2$) and the values of Δq_{ji} are highly correlated on this length scale. The random charges q_{1i} are not correlated with q_{2j} and thus

$\langle C(\omega)\bar{m}/C_0 \rangle = N^{-1} \langle |S_1|^2 + |S_2|^2 \rangle$, where S_n coincides with S in which q_i are replaced by q_{ni} . The first component, $N^{-1} \langle |S_1|^2 \rangle = N^{-1} \sum_{ij} \langle q_{1i} q_{1j} \rangle \langle e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} \rangle = \sigma_1^2$, is independent of k and thus of ω . The second component can be evaluated in the bond representation, in which $S_2 = 2i \sum_{(ij)} \Delta q_{ij} e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} \sin(\mathbf{k} \cdot \mathbf{r}_{ij}/2)$ with $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ and $\bar{\mathbf{r}}_{ij} = (\mathbf{r}_j + \mathbf{r}_i)/2$, and where the sum is taken over all the bonds (ij) in the system. In the FIR regime, $\mathbf{k} \cdot \mathbf{r}_{ij} \ll 1$, and hence $S_2 \simeq k \sum_{(ij)} \Delta q_{ij} e^{i\mathbf{k} \cdot \bar{\mathbf{r}}_{ij}} (i\hat{\mathbf{k}} \cdot \mathbf{r}_{ij}) \equiv k \tilde{S}_2$. Consequently, the contribution to the coupling coefficient from correlated charges preserving local charge neutrality is $N^{-1} \langle |S_2|^2 \rangle \simeq k^2 \langle |\tilde{S}_2|^2 \rangle \propto \omega^2$ (assuming linear dispersion), where the function $\langle |\tilde{S}_2|^2 \rangle = \text{const} + O(k^2)$ depends on precise structural details of the material but does not depend on k in the FIR range. Therefore, we have demonstrated that the frequency-independent part in Eq. (1) is due to uncorrelated charge fluctuations, while the quadratic frequency dependence results from correlated charge fluctuations satisfying local charge neutrality.

The range of validity of Eq. (1) is restricted at high frequencies by the requirement that the disordered modes should have acousticlike character with linear pseudodispersion. Generally speaking, for $\omega \gtrsim \omega_{\text{IR}}$, the disordered modes contain many plane waves with a wave-vector spread which is comparable with the mean value of k , and the dispersion law becomes modified, showing, e.g., the onset of second sound for the longitudinal branch in $g\text{-SiO}_2$ [8]. This means that the frequency dependence of $C(\omega)$ can be modified in a nonuniversal manner for $\omega \gtrsim \omega_{\text{IR}}$, as we actually found for $g\text{-SiO}_2$ and $g\text{-As}_2\text{S}_3$. Dynamical polarization effects can also become significant for $\omega \gtrsim \omega_{\text{IR}}$ [19]. Equation (1) is not restricted for low frequencies if possible low-frequency anharmonic effects are ignored [3].

In order further to support the form of the universal frequency dependence of the FIR coupling coefficient given by Eq. (1), we give the following evidence: (i) experimentally derived data for $C(\omega)$ in $g\text{-SiO}_2$ and $g\text{-As}_2\text{S}_3$, and numerical calculations of $C(\omega)$ for (ii) classical MD models of $g\text{-SiO}_2$ with fixed charges and for α -cristobalite (crystalline counterpart of $g\text{-SiO}_2$) with disordered charges and (iii) a DFTB MD model of $g\text{-As}_2\text{S}_3$ and of its crystalline counterpart, orpiment, with disordered Mulliken charges.

Experimental data for the FIR absorption coefficient of spectroil water-free $g\text{-SiO}_2$ and ultrapure $g\text{-As}_2\text{S}_3$ at room temperature have been obtained by THz TDS [20] in the frequency range 1–130 cm^{-1} using a TeraView TPI Spectra 1000 transmission spectrometer (experimental details will be given elsewhere). Experimental data for $\alpha(\omega)$ have been divided by the experimental VDOS obtained from inelastic neutron scattering [10,11] (see the insets of Fig. 1) and $C(\omega)$ thus obtained is shown in Fig. 1. Our data agree well with other experimental FIR data obtained by THz TDS or other techniques [20–24] and $C(\omega)$ can be well fitted by Eq. (1) in the fre-

quency range of its applicability (see the dashed lines in Fig. 1).

We have also calculated $C(\omega)$ for a classical MD model of $g\text{-SiO}_2$ [25] and a DFTB MD model of $g\text{-As}_2\text{S}_3$ [17] (see the dot-dashed lines in Fig. 1). The classical MD model of $g\text{-SiO}_2$ has fixed atomic charges $q_{\text{Si}} = 2.4$ and $q_{\text{O}} = -1.2$, and thus $C(\omega)$ should not contain the frequency-independent component, $\langle |S_1|^2 \rangle$, and should be proportional to ω^2 for $\omega/2\pi c \equiv \tilde{\omega} \lesssim \tilde{\omega}_{\text{IR}} \approx 35 \text{ cm}^{-1}$ solely due to positional disorder. This region, unfortunately, is not available in our MD model due to prominent finite-size effects below 50 cm^{-1} . However, in the range $50\text{--}300 \text{ cm}^{-1}$, we have found $C(\omega) \propto \omega^\beta$ with $\beta \approx 2$, which can be due to the existence of a peak-shaped spectral density and a linear pseudodispersion law in this frequency range [8]. The DFTB MD model of $g\text{-As}_2\text{S}_3$ incorporates both charge and positional types of disorder and thus can show the crossover from a quadratic frequency dependence to the plateau behavior with decreasing frequency (but this is also unavoidably masked by finite-size effects for $\tilde{\omega} \lesssim 20 \text{ cm}^{-1}$) as seen in Fig. 2(b). Between the BP frequency, $\tilde{\omega}_{\text{BP}} \approx 15 \text{ cm}^{-1}$ [12], and frequency 200 cm^{-1} we have found $C(\omega) \propto \omega^\beta$, with $\beta \approx 1.7$, which differs from that found for $g\text{-SiO}_2$ and might be due to nonlinear pseudodispersion in this frequency range in $g\text{-As}_2\text{S}_3$ and possible dynamic-polarization effects [19].

In order to unmask finite-size effects and reveal the role of charge fluctuations in the frequency dependence of $C(\omega)$, we argue that all the universal features of $C(\omega)$ can be seen in lattice models of corresponding crystalline counterparts incorporating correlated and uncorrelated charge disorder. Many properties of disordered systems

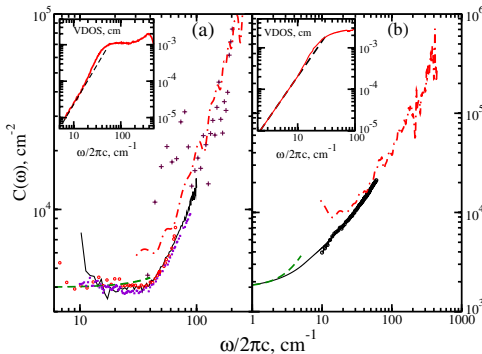


FIG. 1 (color online). Experimental TDS frequency dependence of the absorption coupling coefficient in the FIR range for (a) $g\text{-SiO}_2$ and (b) $g\text{-As}_2\text{S}_3$ (solid lines). Other experimental data from Ref. [20] (\circ), Ref. [24] (\times), Ref. [23] ($+$) in (a) and Ref. [22] (\circ) in (b) are shown for comparison. The dot-dashed lines represent the numerical data obtained from MD models. The dashed lines show the fits of the experimental data by Eq. (1) with $A = 4000 \text{ cm}^{-2}$, $B = 0.3 \text{ cm}^{-1}$ for $g\text{-SiO}_2$ and $A = 1780 \text{ cm}^{-2}$, $B = 75 \text{ cm}^{-1}$ for $g\text{-As}_2\text{S}_3$. The insets show the VDOS used to extract $C(\omega)$. The dashed line in the insets show the Debye VDOS, with the Debye temperature being 330 K for $g\text{-SiO}_2$ and 164 K for $g\text{-As}_2\text{S}_3$.

are rather similar to those of their crystalline counterparts (see, e.g., [8,26]). $C(\omega)$ shares such a similarity as well. In order to see this, it is convenient to split the expression for $C(\omega)$ into incoherent (self-atom) and coherent (correlated-atom) components, $C(\omega) = C^{\text{incoh}}(\omega) + C^{\text{coh}}(\omega)$, where, e.g., $C^{\text{incoh}}(\omega) = C_0 \sum_i (q_i^2/m_i) \mathbf{e}_i^2(\omega)$. These quantities, calculated both for MD models of amorphous solids and their crystalline counterparts, show striking similarities [cf. the solid and dashed lines in Figs. 2(a) and 2(b)], which suggests that the frequency dependence of $C(\omega)$ in amorphous systems can be mimicked by introducing correlated and uncorrelated charge disorder into crystalline systems (see also [7]). Indeed, we have found that uncorrelated disorder on its own, as expected, results in a frequency-independent coupling constant (see the thin solid lines in Fig. 3), the value of which depends on the variance of the distribution of q_{1i} , i.e. σ_1^2 . Correlated disorder on its own gives rise to the same frequency dependence (see the dashed lines in Fig. 3) of $C(\omega)$ found above the BP in the MD models (cf. the dashed and solid lines in Fig. 3). The slope of the curves does not depend on the variance, σ_2^2 , which influences only the intercept on the vertical axis. Incorporation of both types of disorder (see the dot-dashed lines in Fig. 3), with the plateau value coinciding with the parameter A found from the fit of Eq. (1) to experimental data, reveals rather well the frequency dependence of $C(\omega)$ found in the MD models above the BP (cf. the dot-dashed and solid lines in Fig. 3). Such a fit allows the widths of the distribution of uncorrelated charges, $\sigma_1 = \sqrt{A\bar{m}/C_0}$, to be estimated, $\sigma_{1,\text{SiO}_2} \approx 0.06e$ and $\sigma_{1,\text{As}_2\text{S}_3} \approx 0.12e$; these values are in accord with those expected from the relative ionicities of the two materials. Below 50 cm^{-1} (for $g\text{-SiO}_2$) and 20 cm^{-1} (for $g\text{-As}_2\text{S}_3$), the simulation data are not reliable due to finite-size effects. However, extrapolation to lower frequencies (larger sizes) is rather straightforward for lattice models with charge disorder. For example, in the case of $g\text{-SiO}_2$, the contribution from

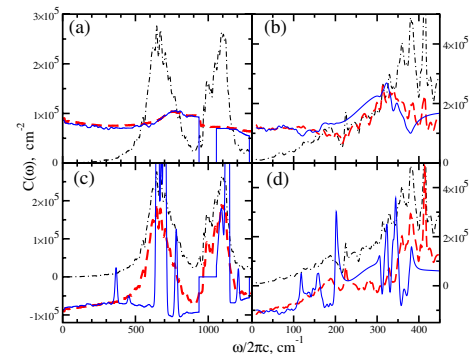


FIG. 2 (color online). (a),(b) Incoherent and (c),(d) coherent contributions to the coupling coefficients for MD models of $g\text{-SiO}_2$ and $\alpha\text{-cristobalite}$ (a),(c) and of $g\text{-As}_2\text{S}_3$ and orpiment (b),(d) to the total coupling coefficient (dot-dashed line). Solid lines represent crystalline models and dashed lines are for glassy ones.

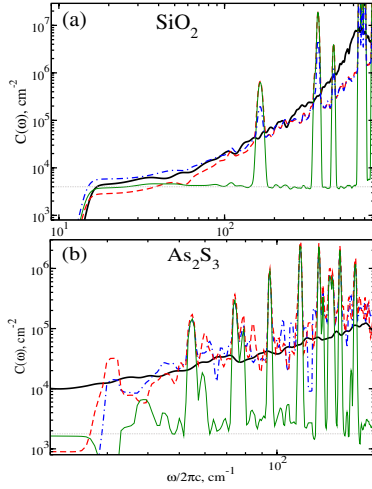


FIG. 3 (color online). Frequency dependence of $C(\omega)$ for MD models of α -cristobalite (a) and orpiment (b) with uncorrelated (thin solid lines), correlated (dot-dashed lines), and both types of charge disorder (dashed lines). The uncorrelated charges were drawn from normal distributions with standard deviations, $\sigma_{\text{Si}}/q_{\text{Si}} = \sigma_{\text{O}}/|q_{\text{O}}| = 0.04$ and $\sigma_{\text{As}}/q_{\text{As}} = \sigma_{\text{S}}/|q_{\text{S}}| = 0.06$, and zero means. The correlated charges were taken from a normal distribution with mean values and standard deviations of $\langle q_{2i,\text{Si}} \rangle = 2.4$, $\langle q_{2i,\text{O}} \rangle = -1.2$, $\langle q_{2i,\text{As}} \rangle = 0.56$, $\langle q_{2i,\text{S}} \rangle = -0.37$ and $\sigma_{2,\text{Si}}/\langle q_{2i,\text{Si}} \rangle = 0.6$, $\sigma_{2,\text{As}}/\langle q_{2i,\text{As}} \rangle = 0.6$. The random values of q_{2i} have been compensated by $-q_{2i}/Z$ placed on Z nearest neighbors in order to maintain local charge neutrality. The parameters of the distributions for uncorrelated charges were chosen to fit the experimental data for the plateau value [parameter A in Eq. (1)], and for correlated charges to fit the frequency dependence of $C(\omega)$ in the glassy MD models (solid lines).

correlated charge fluctuations [the dashed line in Fig. 3(a)] becomes insignificant below the BP in comparison with the dominant frequency-independent contribution from uncorrelated charge fluctuations [the thin solid line in Fig. 3(a) which should be extended to lower frequencies for larger models]. Therefore, the sum of correlated and uncorrelated charge fluctuations should result in a crossover to a plateau for frequencies below the BP, i.e., as in the experimentally observed behavior of $C(\omega)$ (see Fig. 1).

In conclusion, we have presented an explanation for the universal frequency dependence of the coupling coefficient for far-infrared photons with atomic vibrations. The coupling coefficient below the Ioffe-Regel crossover has two components. One is frequency independent and is due to uncorrelated static charge fluctuations caused by medium- and long-range structural irregularities. This results in the quadratic frequency dependence of the absorption coefficient frequently observed in disordered crystals and glasses. The other contribution depends quadratically on frequency and is caused by structural disorder on the short-range (interatomic) scale, leading to static correlated charge fluctuations obeying local charge neutrality within

structural units. For two glasses studied, $g\text{-SiO}_2$ and $g\text{-As}_2\text{S}_3$, we can conclude that, in $g\text{-SiO}_2$, uncorrelated charge fluctuations dominate through the whole frequency range below the Ioffe-Regel crossover (or boson peak) and result in a frequency-independent absorption coupling coefficient there. In contrast, in $g\text{-As}_2\text{S}_3$, uncorrelated charge fluctuations are less pronounced and correlated charge fluctuations preserving local charge neutrality become appreciable even below the BP and thus the absorption coupling coefficient exhibits an onset to an ω^2 dependence in this frequency range.

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