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The atomic charge distribution in glasses obtained by terahertz spectroscopy

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Abstract

It is demonstrated that the width of the uncorrelated atomic charge distribution can be extracted from the frequency dependence of the coupling coefficient for far-infrared absorption measured experimentally by a time-domain terahertz spectroscopy technique. This value for As₂S₃ glass is found to be 0.12(*e*). A density functional theory-based tight-binding molecular dynamics model of As₂S₃ glass qualitatively supports these findings.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Disordered solids, such as glasses, are characterized by a lack of structural order, which leads to disorder in many physical quantities. For example, atomic charges in glasses fluctuate in space. The origin and properties of such fluctuations are of considerable interest in the field of disordered systems. One such intriguing question concerns the scale of charge fluctuations and possible charge ordering in glasses [1–5]. Another intriguing question is related to the possibility of obtaining information about the charge distribution from experiment. It has been recently discussed how terahertz absorption spectroscopy can be used for this purpose [6].

In this paper, we study the atomic charge distributions in glassy arsenic sulfide, As₂S₃, by means of first-principles tight-binding molecular dynamics simulations and compare the characteristics of these distributions with those obtained from experimentally available far-infrared (FIR) absorption coefficient measurements.

2. Theoretical background

First, we recall how the absorption coefficient in the FIR region is related to the atomic charge distribution [6]. The expression for the linear absorption coefficient of photons, $\alpha(\omega)$,

caused by the interaction with harmonic atomic vibrations in solids, is given by the following expression (see e.g. [1]):

$$\alpha(\omega) = \frac{2\pi^2 n}{c\sqrt{\varepsilon_\infty}} \left\langle \sum_\alpha \left| \sum_{i\beta} \frac{Z_{i,\alpha\beta}}{\sqrt{m_i}} e_{i\beta}(\omega) \right|^2 g(\omega) \right\rangle \quad (1)$$

where m_i and $Z_{i,\alpha\beta}$ are the mass and the dynamical charge tensor for atom i ($i = 1, \dots, N$, with N being the number of atoms in a solid of volume V ; α and β run over Cartesian coordinates), $e_{i\beta}(\omega)$ is the β -component of the vibrational eigenvector of frequency ω corresponding to atom i , ε_∞ stands for the high-frequency dielectric constant, $n = N/V$ is the atomic concentration and angular brackets denote configurational averaging. As follows from equation (1), the IR absorption coefficient is proportional to the self-averaging value of the vibrational density of states (VDOS),

$$g(\omega) = (3N)^{-1} \sum_j \delta(\omega - \omega_j), \quad (2)$$

where j runs over all the eigenfrequencies, i.e.,

$$\alpha(\omega) = \langle C(\omega) \rangle g(\omega). \quad (3)$$

The coefficient of proportionality, $\langle C(\omega) \rangle$, is called the coefficient of coupling between IR photons and atomic vibrations for linear light absorption. The VDOS behaves universally ($g(\omega) \propto \omega^2$ according to the Debye law) in the FIR regime and thus all interesting and possibly universal features can be attributed to the frequency dependence of the coupling coefficient.

The absorption coefficient given by equation (1) is temperature independent and some variations of $\alpha(\omega)$ with temperature found experimentally for microwave frequencies [7], $\omega/2\pi c \lesssim 1 \text{ cm}^{-1}$, which may possibly be attributed to excitations of two-level systems and/or to highly anharmonic atomic modes, are not considered here. The dynamical charge tensors are crucial for a correct description of the peak positions and their relative intensities in the bulk of the vibrational band (above the FIR region) [1, 8] but are not so significant in the FIR regime and thus a simpler (rigid-ion) model [9] can be used, so that

$$C(\omega) = C_0 \left| \sum_i \frac{q_i}{\sqrt{m_i}} \mathbf{e}_i(\omega) \right|^2, \quad (4)$$

with q_i being the fixed but spatially fluctuating atomic charges and

$$C_0 = 2\pi^2 n / c\sqrt{\varepsilon_\infty}. \quad (5)$$

In the well-studied case of ordered systems where the charges do not fluctuate, and the eigenmodes are phonons, the coupling coefficient is non-zero only for optic modes at the centre of the Brillouin zone. In disordered systems, structural disorder leads to charge transfer between atoms, i.e. to disorder in atomic charges q_i , and to intrinsic disorder in the components of the eigenvectors which lose their translational invariance. These two related sources of disorder, encoded in equation (4), are responsible for the peculiar behaviour of $C(\omega)$ in amorphous systems, which actually has a universal functional form in the FIR regime [6],

$$\langle C(\omega) \rangle \simeq A + B\omega^2, \quad (6)$$

where A and B are material-specific constants.

In order to see this, we use two facts known about the structure of the eigenmodes in the FIR regime and about the distribution of atomic charges. First, the disordered eigenmodes in the FIR regime resemble plane waves [10, 11] characterized by pseudo-wavevectors k and exhibiting pseudo-dispersion, $\omega_j(k) = c_j k$ (with c_j being the sound velocity for branch j),

and can be well approximated [6] by a plane wave characterized by wavevector \mathbf{k} and unit polarization vector $\hat{\mathbf{p}}_{\mathbf{k}}$,

$$\mathbf{e}_i(\omega) \simeq \sqrt{\frac{m_i}{N\bar{m}}} \hat{\mathbf{p}}_{\mathbf{k}} e^{i\mathbf{k}(\omega)\cdot\mathbf{r}_i}, \quad (7)$$

with $\bar{m} = N^{-1} \sum_i m_i$ and \mathbf{r}_i being the position vector of atom i .

The second useful fact concerns the distribution of charges in disordered systems. It has been found in simulations [1, 3–5] that the charges in the models of some amorphous materials preserve approximately charge neutrality within certain structural units. For example, the SiO_4 structural units in vitreous silica are approximately electro-neutral [1] meaning that the positive charge on an Si atom is approximately equal in magnitude to half of the sum of the charges on the four nearest oxygen atoms. The values of silicon and oxygen charges vary strongly between structural units, depending on local structural characteristics such as the Si–O–Si bond angle. Moreover, the electro-neutrality within the structural units is maintained only approximately (see below) and there is always a stochastic component in the charge distribution due to intermediate and long-range fluctuations in the structure. These observations allow the values of atomic charges to be split 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 and random charges q_{2i} satisfying local charge neutrality.

The values of $q_{1i}(\{\mathbf{r}_i\})$ depend on atomic coordinates $\{\mathbf{r}_i\}$ in a complicated fashion so we can approximately assume the absence of correlations between q_{1i} on different atoms, i.e.,

$$\langle q_{1i} q_{1j} \rangle \simeq \langle q_{1i} \rangle \langle q_{1j} \rangle \simeq \sigma_{1i}^2 \delta_{ij}, \quad (8)$$

where the variance σ_{1i}^2 can vary for different kinds of atoms, or the same atoms but e.g. abnormally coordinated. Similarly, we assume no correlations between q_{1i} and atomic position vectors, so that

$$\langle q_{1i} e^{i\mathbf{k}\cdot\mathbf{r}_j} \rangle \simeq \langle q_{1i} \rangle \langle e^{i\mathbf{k}\cdot\mathbf{r}_j} \rangle \simeq 0. \quad (9)$$

The random charges q_{2i} obeying local charge neutrality can be imagined as resulting from charge transfers between nearest neighbours, i.e. $q_{2i} = \sum_{j \neq i} \Delta q_{ji}$, where j runs through all the nearest neighbours of atom i and $\Delta q_{ji} (= -\Delta q_{ij})$ is the charge transfer from the originally neutral atom j to the originally neutral atom i . In heteropolar crystals, the values of Δq_{ji} are not random and finite. In disordered systems, the values of Δq_{ji} are distributed around mean value(s) which do not necessary coincide with those for crystalline counterparts (see e.g. [1]). Such fluctuations and deviations of means in Δq_{ji} are due to distortions in local structural units, e.g. in bond angles and bond lengths. We also assume that there are no correlations between randomly fluctuating charges q_{1i} and local charge transfers,

$$\langle q_{1i} q_{2j} \rangle \simeq \langle q_{1i} \rangle \langle q_{2j} \rangle \simeq 0. \quad (10)$$

The configurationally averaged coupling coefficient can be recast in terms of correlated and uncorrelated charges in the following manner:

$$\tilde{C}(\omega) = \frac{\langle C(\omega) \rangle \sqrt{\bar{m}}}{C_0} = \left\langle N^{-1} \left| \sum_i q_{1i} e^{i\mathbf{k}\cdot\mathbf{R}_i} + \sum_i q_{2i} e^{i\mathbf{k}\cdot\mathbf{R}_i} \right|^2 \right\rangle \equiv \langle N^{-1} |S_1 + S_2|^2 \rangle, \quad (11)$$

where $S_n = \sum_i q_{ni} e^{i\mathbf{k}\cdot\mathbf{R}_i}$ ($n = 1, 2$). In the absence of correlations between q_{1i} and q_{2j} (see equation (10)) the above formula for $\tilde{C}(\omega)$ reduces to

$$\tilde{C}(\omega) = N^{-1} (\langle |S_1|^2 \rangle + \langle |S_2|^2 \rangle). \quad (12)$$

The first component in equation (12) can be further simplified as

$$N^{-1} \langle |S_1|^2 \rangle \simeq N^{-1} \sum_{ij} \langle q_{1i} q_{1j} \rangle \langle e^{i\mathbf{k}\cdot(\mathbf{r}_j - \mathbf{r}_i)} \rangle \simeq N^{-1} \sum_i \sigma_{1i}^2 = \bar{\sigma}_1^2, \quad (13)$$

where we used equations (8) and (9). In the case of a two-component system containing N_1 and N_2 atoms of different types, $\overline{\sigma}_1^2 = (N_1/N)\sigma_{11}^2 + (N_2/N)\sigma_{12}^2$. Therefore, the first contribution in the coupling coefficient is frequency independent and depends only on the variance of uncorrelated charge distributions.

The second component in the coupling coefficient, $N^{-1}\langle |S_2|^2 \rangle$, which is due to random and locally correlated charge fluctuations does not contain the frequency independent part and, in fact, is proportional to ω^2 . This can be demonstrated using the bond representation for S_2 ,

$$S_2 = \left\langle \sum_{(ij)} \Delta q_{ij} (e^{i\mathbf{k}\cdot\mathbf{r}_j} - e^{i\mathbf{k}\cdot\mathbf{r}_i}) \right\rangle = \left\langle \sum_{(ij)} \Delta q_{ij} e^{i\mathbf{k}\cdot\mathbf{r}_{(ij)}} (e^{i\mathbf{k}\cdot\mathbf{r}_{ij}/2} - e^{-i\mathbf{k}\cdot\mathbf{r}_{ij}/2}) \right\rangle, \quad (14)$$

with $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ and $\mathbf{r}_{(ij)} = (\mathbf{r}_j + \mathbf{r}_i)/2$, where the sum is taken over all the bonds (ij) in the system. In the absence of the plane wave ($\mathbf{k} = 0$), this sum equals zero, thus reflecting global charge neutrality of locally neutral units (the contribution from each bond is exactly zero due to the local charge neutrality). In the FIR regime, $\mathbf{k} \cdot \mathbf{r}_{ij} \ll 1$ and equation (14) can be recast as

$$S_2 \simeq k \sum_{(ij)} \Delta q_{ij} e^{i\mathbf{k}\cdot\mathbf{r}_{(ij)}} (i\hat{\mathbf{n}} \cdot \mathbf{r}_{ij}), \quad (15)$$

with $\mathbf{k} = k\hat{\mathbf{n}}$. Consequently, the contribution from the correlated charges to the coupling coefficient is

$$\langle |S_2|^2 \rangle \simeq k^2 \left\langle \sum_{(ij)(i'j')} \Delta q_{ij} \Delta q_{i'j'} e^{i\mathbf{k}\cdot(\mathbf{r}_{(ij)} - \mathbf{r}_{(i'j')})} (\mathbf{n} \cdot \mathbf{r}_{ij}) (\mathbf{n} \cdot \mathbf{r}_{i'j'}) \right\rangle, \quad (16)$$

so $\langle |S_2|^2 \rangle \propto k^2 \propto \omega^2$ implying linear dispersion in the FIR regime. The double sum in equation (16) depends on precise structural details of the material but does not depend on k in the FIR range (it is $\propto \text{Const} + O(k^2)$) and thus the dependence on ω^2 of the second contribution in the coupling coefficient is a general feature of the FIR absorption in disordered solids.

Therefore, we have demonstrated that uncorrelated atomic charges result in the frequency independent part of the coupling coefficient, while locally correlated charges, maintaining the charge neutrality within local structural units, give rise to the quadratic frequency dependence of the coupling coefficient.

3. Results

As follows from the previous section, the coupling coefficient for the FIR absorption has a universal frequency dependence (see equation (6)), containing a frequency independent part and a frequency dependent contribution ($\propto \omega^2$). The frequency dependence of the absorption coefficient, $\alpha(\omega)$, can be measured experimentally using THz time-domain spectroscopy [6, 12]. The VDOS can be also measured experimentally using, e.g., inelastic neutron scattering [13, 14]. Therefore, the frequency dependence of the coupling coefficient for the FIR absorption, $C(\omega) = \alpha(\omega)/g(\omega)$, can be found experimentally (see figure 1). Fitting experimental data with theory allows the values of constants A and B entering equation (6) to be estimated. We have done such a fitting to the experimental data for As_2S_3 glass (cf the solid and dashed lines in figure 1) and found the values of these constants to be $A = 1780 \text{ cm}^{-2}$ and $B = 75 \text{ cm}^{-1}$ [6].

The constant B depends on the structural characteristics of glass in a quite complicated fashion (see equation (16)) and cannot be used straightforwardly for extracting the charge

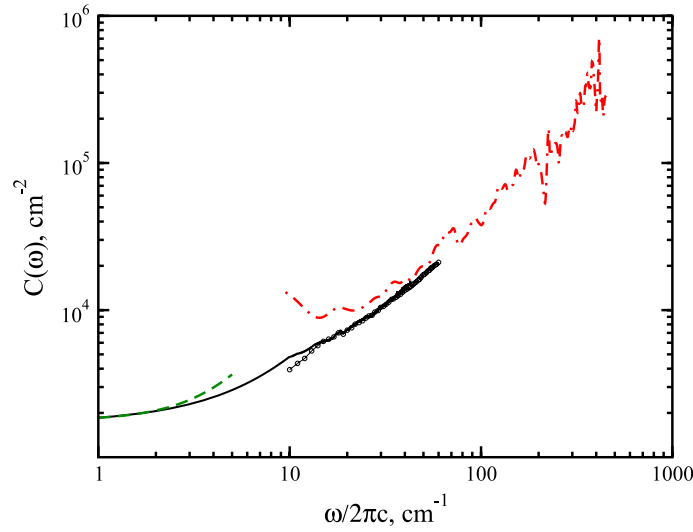


Figure 1. Experimental frequency dependence of the absorption coupling coefficient in the FIR range for As_2S_3 (solid line [6] and circles [18]). The dot-dashed lines represent the numerical data obtained from the DFTB molecular dynamics model. The dashed line shows the fit of the experimental data with equation (6) with $A = 1780 \text{ cm}^{-2}$ and $B = 75 \text{ cm}^{-1}$.

distributions. However, the constant A is directly related to the width of the uncorrelated charge distribution,

$$\bar{\sigma}_1^2 = \frac{A\bar{m}}{C_0}, \quad (17)$$

where the coefficient C_0 is given by equation (5). Using equation (17), we have estimated the value of $\bar{\sigma}_1 \simeq 0.12 e$ for As_2S_3 .

In order to verify and support the consistency of the model presented for the frequency dependence of the coupling constant, we have created a model of As_2S_3 glass using density functional theory-based tight-binding (DFTB) [15, 16] molecular dynamics simulations [17]. First, we checked the local charge neutrality within AsS_3 pyramids, these being typical structural units in As_2S_3 glass. The results presented in figure 2 clearly demonstrate correlations between the charge at the central As atom and surrounding S atoms. As expected, the local charge neutrality is not exact and the data points fluctuate around the bisector due to contributions from q_{li} .

Second, we calculated the Mulliken charge distributions for As and S atoms in our DFTB model of As_2S_3 glass (see figure 3). The charges are distributed approximately normally (see the dashed lines in figure 3) around the mean values $\bar{q}_{\text{As}} \simeq 0.56$ and $\bar{q}_{\text{S}} \simeq -0.36$ with the standard deviations $\sigma_{1\text{As}} \simeq 0.06$ and $\sigma_{1\text{S}} \simeq 0.05$. Therefore, the value of $\bar{\sigma}$ can be estimated as $\bar{\sigma}_1 = \sqrt{(2/5)\sigma_{1\text{As}}^2 + (3/5)\sigma_{1\text{S}}^2} \simeq 0.054$. This value is slightly less than that estimated from the fit of the experimental data for $C(\omega)$ with equation (6) (cf the solid and dashed lines in figure 1), i.e. $\bar{\sigma}_1 \simeq 0.12$. Several possible effects could account for such a discrepancy. The Mulliken charges are an artificial way of assigning charge values to particular atoms within the DFTB scheme—a different population analysis may give different absolute values of the charges and thus different widths of the charge distributions. Another possible reason for the discrepancy is due to the experimental uncertainty in measuring the absorption coefficient at

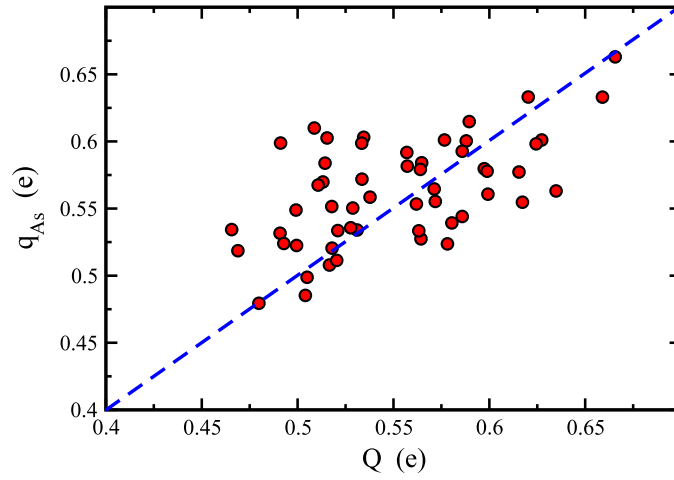


Figure 2. The charge of As atoms, q_{As} , in electron charge units versus neutralizing charge $Q = |\sum_{i \in n.n.} q_S|/2$ where the summation is taken over all three nearest neighbour sulfur atoms. The dashed line corresponds to the exact charge neutrality, $q_{As} = Q$, within the structural units.

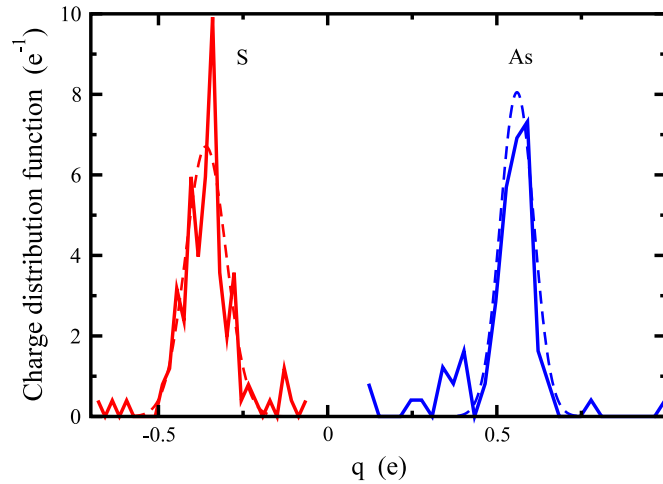


Figure 3. The atomic charge distributions for the DFTB model of As_2S_3 . The left curve is for S atoms while the right one is for As atoms. The dashed curves show the Gaussian fits for these distributions with the mean values $\bar{q}_{As} \approx 0.56$, $\bar{q}_S \approx -0.36$ and standard deviations $\sigma_{1As} \approx 0.06$ and $\sigma_{1S} \approx 0.05$.

very low frequencies, $\omega \lesssim 5 \text{ cm}^{-1}$, which is caused by the parasitic secondary reflections of THz pulses of light, which after the Fourier transform can contribute to this frequency range.

4. Conclusions

To conclude, it has been demonstrated that the frequency dependence of the coupling coefficient for far-infrared absorption can be used for extracting the characteristics of the atomic charge distribution in glasses. Namely, a fit of such an experimentally measured dependence with the

theoretically predicted law, $A + B\omega^2$, allows the constants A and B to be extracted. The value of A is proportional to the variance of the uncorrelated charge distribution, $\overline{\sigma}_1^2$. In the case of As_2S_3 glass, we have estimated this value to be $\overline{\sigma}_1 \simeq 0.12$. A similar estimate of $\overline{\sigma}_1 \simeq 0.054$ has been obtained from a first-principles molecular dynamics model of the same glass.

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