Nonlinear optical and acoustic absorption in substances with weakly bound atoms

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The model of a system of anharmonic oscillators should be applied to substances with weakly bound atoms (e.g., *a*-Si:H at a high hydrogen concentration or ferroelectrics near the phase transition). Three effects should be expected in the absorption of electromagnetic or acoustic waves in such systems. The light and sound intensities required for observing these effects are estimated.

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The atomic vibration frequencies in several substances are quite low because of comparatively low binding forces. An example is the system *a*-Si:H at a hydrogen concentration which is not too low. Part of the hydrogen is weakly bound[1] and apparently not involved in blocking dangling bonds. Another example would be tunneling modes in amorphous semiconductors.

There is the possibility of an analogous sitution in certain large molecules (with van der Waals coupling) and in ferroelectrics (the soft mode). When a periodic external force of frequency ω is applied to a system of this type, we would naturally expect some significant anharmonic effects (the force could result from an electromagnetic or acoustic wave). We will talk primarily about the first of these examples. Because of the local nature of the vibrations of weakly bound hydrogen in that case, we can use a simple model of independent one-dimensional anharmonic oscillators. We denote by ω_0 the resonant frequency of an oscillator (for the time being we will ignore the unavoidable spread in the values of this frequency in a disordered system). We are interested in three effects: resonances at the frequencies $\overline{\omega} = \omega_0/2$ and $\overline{\omega} = 2\omega_0$ and discontinuities in the amplitude of the stimulated vibrations due to the S-shaped amplitude

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characteristic. In the latter case, there will be discontinuities in the absorption coefficient for the electromagnetic or acoustic wave.

The first of these effects occurs in principle at an arbitrary amplitude of the external force. The ratio of the amplitude of the corresponding stimulated vibrations at the resonance to the amplitude of the linear resonant vibrations in $8|\varkappa_1|F_0/9m\omega_0^4$ where F_0 is the amplitude of the external force, m is the reduced mass of the oscillator (in the case of the a-Si:H system, this mass is evidently the mass of the hydrogen atom, which is small in comparison with both the mass of the silicon atom and the masses of possible structural defects), and $\varkappa_1$ is the first anharmonic coefficient (the potential energy of the oscillator is $U = 0.5\, m\omega_0^2 x^2 + 1/3m\varkappa_1 x^3 + 1/4m\varkappa_2 x^4$; in order of magnitude we have $|\varkappa_1| \sim \omega_0^2/2r_0, |\varkappa_2| \sim \omega_0^2/6r_0^2$, where r_0 is the characteristic distance over which there is a significant change in the potential energy of the interaction between the entitites of which the oscillator is composed). The observation of a resonance at $\overline{\omega} = \omega_0/2$ would make it possible to determine the ratio $|\varkappa||/m$.

The other effects arise only if F_0 exceeds a certain threshold F_k. For the second and third effects we find, respectively, $F_k^{(2)} = 12\omega_0\mu r_0$, and $F_k^{(3)} = 8r_0 m(3\omega_0\mu^3)^{1/2}$, where μ is the linear absorption coefficient. Since resonance effects will be seen only if $\mu \ll \omega_0$, we conclude that $F_k^{(3)}$ is less than $F_k^{(2)}$, and we will consider only $F_k^{(3)}$ below. A weakly bound hydrogen atom may or may not have an effective charge ev $(0 \leqslant |y| \leqslant 1)$. Correspondingly, the force exerted on this atom by the electromagnetic wave is either $F = eyE \sin \omega t$ or $F = 0.5\sigma k E^2 \sin 2\omega t$, where ω and $k = \omega/c\sqrt{\epsilon}$ are the frequency and wave vector of the wave in a medium with a dielectric function $\epsilon(\omega)$, E is the electric field ampliutde in the wave, and σ is the polarizability of the system consisting of the hydrogen atom and a defect (for simplicity, we assume that the polarizability tensor is isotropic). In the second of these cases we would have $\overline{\omega} = 2\omega$.

Now considering the force exerted by an acoustic wave of frequency ω, we note that in a-Si:H the chemical bonds are partially heteropolar, because of the tightly bound hydrogen that blocks dangling bonds. For this reason, the vibrations of the matrix in the acoustic wave are acccompanied by a wave of an electric field, which is produced by dipoles with a dipole moment $\mathbf{d} = e^*\mathbf{Q}ka$, where $e^* = e\overline{y}$ is the effective charge of the tightly bound hydrogen, $k = \omega/s$, s is the sound velocity, a is the length of the Si--H bond, and $\mathbf{Q}$ is the displacement in the acoustic wave. Correspondingly, we find the same expressions for the force, except that we must set $E = d/r^3$ in them, where r is on the order of several interatomic distances. The quantities Q and E are conveniently expressed in terms of the energy flux density J in the acoustic and electromagnetic waves. From the expression for $F_k^{(3)}$ we find the following expressions for the critical energy flux densities in an electromagnetic wave ($J_{k,\mathrm{opt}}$) and an acoustic wave ($J_{k,\mathrm{ac}}$): (a) for charged atoms of weakly bound hydrogen,

$$J_{k,\,opt.}^{(1)} = 24c\epsilon^{1/2} r_0^2\, \omega\mu^3 m^2 (\pi e^2 y^2)^{-1}, \tag{1a}$$

$$J_{k,\,ac}^{(1)} = 96 s^3 \rho r^6 r_0^2 m^2 \omega_0 \mu^3 (e^4 y^2 \bar{y}^2 a^2)^{-1}; \tag{1b}$$

(b) for neutral atoms of weakly bound hydrogen,

$$J^{(2)}_{k,\,opt} = 2c^2 m r_0 (3\mu^3)^{1/2} (\pi\sigma\omega_0^{1/2})^{-1}, \tag{2a}$$

$$J^{(2)}_{k,ac} = 8s^4 \rho r^6 r_0 m (3\mu^3)^{1/2} (e^2 \bar{y}^2 a^2 \sigma \omega_0^{1/2})^{-1}. \tag{2b}$$

Here ρ is the mass density.

It is exceedingly difficult to generate any numerical estimates, since practically nothing is known about the state of weakly bound hydrogen in a-Si. The only clear point is that $\hbar\omega_0$ must be significantly lower than the binding energy of these atoms. This binding is probably a van der waals binding, we we can write $\hbar\omega_0 \lesssim 4\times 10^{-2}$ eV. Rough estimates using $s = 4\times 10^{-5}$ cm/s, $\rho = 2$ g/cm^3, $r_0 = r = 1.8\times 10^{-7}$ cm, $\epsilon = 12$, and $\mu = 0.1\ \omega_0$ lead to unrealistically large values in case (2a). In cases (1a), (1b), and (2b), we find, respectively, $J^{(1)}_{k,\mathrm{opt}} = 0.3\, y^{-2}(\omega_0 \cdot 10^{-10})^4$ W/cm^2, $J^{(2)}_{k,ac} = 7(y\bar{y})^{-2}(\omega_0 \cdot 10^{-10})^4$ W/cm^2, and $J^{(2)}_{k,ac} = 3y^{-2}(\omega_0 \cdot 10^{-10})^{3/2}\, 10^{-21}\sigma^{-1}$ W/cm^2. Here ω_0 is expressed in reciprocal seconds and σ in cubic centimeters.

In an actual material there would of course be an averaging over the distribution of resonant frequencies, damping coefficients, etc. Only the oscillators with the most suitable combination of properties will make any real contribution to the effect.

[1]M. Brodsky (editor), Amorphous Semiconductors (Russ. Transl. Mir, Moscow, 1982).
[2]L. D. Landau and E. M. Lifshitz, Mekanika, Fizmatgiz, Moscow, 1958 (Mechanics, Adison--Wesley, Reading, Mass., 1960).

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