A technique to study the mechanisms of pressure broadening of spectral holes

Kristjan Leiger[a] and Jaak Kikas[b]

[a] Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia; kristjan@fi.tartu.ee
[b] Institute of Materials Science, Department of Physics, University of Tartu, Tähe 4, 51010 Tartu, Estonia; jaakk@physic.ut.ee

Abstract. An experimental procedure to distinguish between the two possible mechanisms (dispersive and diffusive) of pressure broadening of spectral holes in nonisobaric experiments is proposed. The method makes use of nonlinear saturation properties of the hole burning process. The proposed four-step procedure consists of burning a hole, applying hydrostatic pressure to the system, additional burning at the hole minimum at this second pressure, and then applying more pressure. By model calculations it is demonstrated that, under certain conditions, the dispersive mechanism yields a double-minimum hole, while the diffusive mechanism does not. Experimental observability of such an effect is discussed.

1. INTRODUCTION

Pressure tuning of spectral holes [1–6] has been used in a number of works [1–13] in order to study local interactions and elastic properties of solids. When burning a hole into the inhomogeneously broadened band of probe molecules and then applying pressure, one observes both a hole shift and broadening. The pressure shift of the holes is explained by a change of the average interaction between the guest (probe) and the host molecules with compression of the sample. At the same time, the mechanisms of hole broadening are not always quite as clear. The fact that the broadening occurs signals that the subensemble of impurities selected by burning a hole is in a sense still not fully homogeneous.

In glasses the observed large broadening was ascribed to "heteropolar" interactions between host and guest molecules, i.e. to the interactions taking into account both long-range attractive and short-range repulsive terms [9]. This breaks the scaling between the matrix shift (shift from the vacuum frequency) and the pressure shift and yields, as a result, pressure broadening of spectral holes.

In crystals, where the long-range interactions with defects are the main sources of inhomogeneity, pressure broadening can be described [10] as arising from the diaelastic effect [14]. The diaelastic effect is an analogue of the diamagnetic effect, where an additional magnetic moment is induced in a molecule by an external magnetic field. Similarly, the inhomogeneous strain field created by point defects in a crystal is modified by applied external pressure. As shown in [10], a pressure-induced broadening of spectral holes in such a system takes place if the ensemble of defects is intrinsically inhomogeneous (e.g., includes point defects of different volume defects).

Whatever the exact physical mechanism, in all these cases the pressure broadening can formally be described by a statistical distribution of pressure coefficients over the impurities for every fixed transition energy within the inhomogeneously broadened band. Since it is the dispersion of the pressure coefficients that governs the hole broadening, we call such a mechanism of pressure broadening the dispersive mechanism.

Recently, a new mechanism of hole broadening with pressure [13] has been proposed to account for hole broadening in Shpol′skii systems [7,13]. In these systems there is a disproportion between an unexpectedly large pressure broadening of the holes and only a minor broadening of the inhomogeneous band as a whole. The proposed mechanism involves spatially (or otherwise) bistable (possibly multistable) vacancies within the host lattice that change their positions and are created or destroyed reversibly with pressure changes. This modifies the transition energies of impurity molecules and thus shifts the corresponding homogeneous lines. Within the frame of this mechanism it is not appropriate to speak of pressure coefficients of individual homogeneous lines. Instead, each of them undergoes quite a random (biased, maybe) spectral motion as the pressure changes. In other words, we are dealing with pressure-induced (reversible!) spectral diffusion. We therefore call this the diffusive mechanism of hole broadening.

In general, it may not be easy to establish which of the two mechanisms (diffusive or dispersive) is operative in a particular case: one observes some hole shift and broadening all the same. As follows from [13], one can also not rely on the irreversibility argument and consider pressure cycling experiments [6] in order to solve the problem: to a major extent the broadening in *n*-alkanes is reversible. In this paper, in Section II, we propose an experimental technique that can, in principle, solve the problem. In Section III we analyse the results of the corresponding numerical calculations and discuss some questions concerning the experimental observability of the effects.

2. MODEL

2.1. General

The inhomogeneous pressure effects, such as broadening of spectral holes in a pressure tuning experiment, are obviously brought about by the pressure-

induced spectral dynamics of the homogeneous lines of single probe molecules. Such a dynamics is generally to be considered a random process. However, the exact nature of this process is not revealed in a simple pressure tuning experiment that only allows a comparison of initial and final states of the process. An idea to obtain more information could be to label an intermediate state, e.g. by additional burning. With this in mind, we propose the following four-step experimental procedure (depicted graphically in Fig. 1):

(1) a spectral hole is burnt with an irradiation dose Q at a frequency v_0 within the inhomogeneously broadened band;

(2) an extra pressure Δp is applied to the system;

(3) the sample is irradiated again with the same dose Q at the spectral position $v_0 + \Delta v_0$, where Δv_0 is the shift of the hole minimum;

(4) the applied pressure is increased up to $2\Delta p$.

With this technique, as will be shown in the following, the dispersive mechanism should produce a characteristic double-minimum holeshape while with the diffusive mechanism the hole should retain a single minimum.

Let us view the situation analytically. The process of pressure tuning can be described by the joint distribution of the probe transition frequencies at the base (p_0) and final (p_1) pressures (the "pressure kernel") [15]. We denote these frequencies by ω_0 and ω_1, respectively, and the distribution by $\rho^{(2)}(\omega_0, p_0; \Delta\omega_1, \Delta p_1)$ where $\Delta\omega_1 = \omega_1 - \omega_0$, $\Delta p_1 = p_1 - p_0$. In essence, this distribution is the second-order density function (as denoted by the superscript index 2) characterizing the process of pressure-induced spectral dynamics of single-molecule homogeneous lines. The corresponding first-order density function $\rho^{(1)}(\omega_0, p_0) \equiv \rho_{ih}^{(1)}(\omega_0)$ represents the inhomogeneous distribution function at the base pressure.

The modification of the inhomogeneous distribution function $\rho_{ih}^{(1)}(\omega_0)$ upon burning a hole is, under a number of reasonable assumptions, described by multiplying it by an "exposure" function [16]

$$f_{hb}(\omega, v_0, Q) = \exp(-Q\kappa(v_0 - \omega)). \tag{1}$$
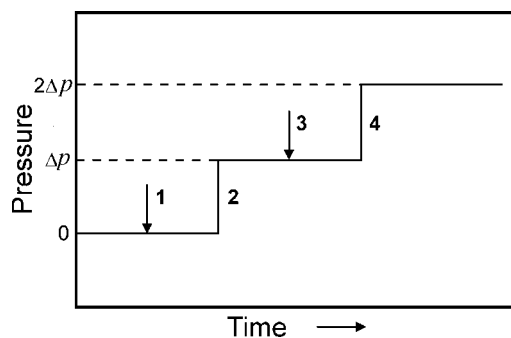
Fig. 1. The schematic of the proposed four-step process. Steps are denoted by numbers: 1 and 3 correspond to burning, 2 and 4 to applying the pressure. The pressure scale is relative to the base pressure, the timescale is arbitrary as long as we treat holes as time-independent once burnt.

Here $\kappa(\omega)$ is the (zero-peaked) homogeneous lineshape and Q is the irradiation dose of monochromatic burning light of frequency v_0 :

$$Q = I_0 t \eta \sigma, \tag{2}$$

where I_0 is the burning intensity, t the irradiation time, η the quantum yield of the burning process, and σ the peak absorption cross section. Likewise, the joint distribution $\rho^{(2)}(\omega_0, p_0; \Delta\omega_1, \Delta p_1)$ is multiplied by $f_{hb}(\omega_i, v_0, Q)$ during the hole burning with $i = 0$ or $i = 1$ for burning at initial or final pressure, respectively. So, given an initial distribution $\rho_0^{(2)}$, its evolution through the above-mentioned steps 1–3 is generally expressed as:

$$\begin{aligned}\rho_1^{(2)}(\omega_0, p_0; \Delta\omega_1, \Delta p) &= f_{hb}(\omega_0, v_0, Q) \rho_0^{(2)}(\omega_0, p_0; \Delta\omega_1, 0) \\ &= f_{hb}(\omega_0, v_0, Q) \rho_{ih}^{(1)}(\omega_0) \delta(\Delta\omega_1),\end{aligned} \tag{3}$$

$$\rho_2^{(2)}(\omega_0, p_0; \Delta\omega_1, \Delta p) = f_{hb}(\omega_0, v_0, Q) \rho_0^{(2)}(\omega_0, p_0; \Delta\omega_1, \Delta p), \tag{4}$$

$$\rho_3^{(2)}(\omega_0, p_0; \Delta\omega_1, \Delta p) = f_{hb}(\omega_0, v_0, Q) f_{hb}(\omega_1, v_0 + \Delta v_0, Q) \rho_0^{(2)}(\omega_0, p_0; \Delta\omega_1, \Delta p). \tag{5}$$

To obtain actual hole shapes, the second-order density function needs to be integrated over the initial frequency ω_0 and convoluted with the homogeneous spectrum $\kappa(\omega)$.

A proper description of step 4 generally requires the use of the third-order density function involving a second pressure change Δp_2 with the corresponding frequency change parameter $\Delta\omega_2 = \omega_2 - \omega_1$ (ω_2 now denotes the final frequency). From such a distribution $\rho^{(3)}(\omega_0, p_0; \Delta\omega_1, \Delta p_1; \Delta\omega_2, \Delta p_2)$ the second-order distribution for step 4 is obtainable by

$$\begin{aligned}\rho_4^{(2)}(\omega_0, p_0; \Delta\omega_1, \Delta p) &= f_{hb}(\omega_0, v_0 + \Delta v_0, Q) \\ &\times \int f_{hb}(\omega', v_0, Q) \rho_0^{(3)}(\omega', p_0; \omega_0 - \omega', \Delta p; \Delta\omega_1, \Delta p) \, d\omega'.\end{aligned} \tag{6}$$

It can be rather difficult to calculate the third-order density function from theoretical model situations. However, here the dispersive and diffusive mechanisms turn out to be the limiting cases in terms of pressure shifting autocorrelation of the homogeneous lines and hence the required order of the density function can be decreased.

In what follows we view both mechanisms separately.

2.2. The dispersive mechanism

This mechanism corresponds to strong autocorrelation in the pressure-induced dynamics of the individual homogeneous lines. Since the frequency shift of the holes is always found to be linear with pressure and the same applies to the homogeneous spectra in the single-molecule pressure tuning experiments [17,18],

we may assume that each homogeneous line has a distinct pressure coefficient (frequency shift per unit pressure change) that is maintained throughout the process. In terms of the third-order density function this means that the parameters of the first pressure shift completely determine the parameters of the second shift and $\rho^{(3)}$ simplifies:

$$\rho^{(3)}(\omega_0, p_0; \Delta\omega_1, \Delta p_1; \Delta\omega_2, \Delta p_2) = \rho^{(2)}(\omega_0, p_0; \Delta\omega_1, \Delta p_1)\, \delta\left(\Delta\omega_2 - \Delta\omega_1 \frac{\Delta p_2}{\Delta p_1}\right).$$

(7)

With (6) the pressure kernel for step 4 of our four-step procedure now becomes:

$$
\begin{aligned}
&\rho^{(2)}_{4\,\mathrm{dsp}}(\omega_0, p_0; \Delta\omega_1, \Delta p) \\
&= f_{\mathrm{hb}}(\omega_0 - \Delta\omega_1, \nu_0, Q)\, f_{\mathrm{hb}}(\omega_0, \nu_0 + \Delta\nu_0, Q)\, \rho^{(2)}_0(\omega_0 - \Delta\omega_1, p_0; \Delta\omega_1, \Delta p).
\end{aligned}
$$

(8)

An important property for dispersive $\rho^{(2)}$, following from (7), is that

$$\rho^{(2)}(\omega_0, p_0; \Delta\omega_1, \Delta p_1) = |c| \cdot \rho^{(2)}(\omega_0, p_0; c\Delta\omega_1, c\Delta p_1)$$

(9)

for any c. This also means that

$$\rho^{(2)}(\omega_0, p_0; \Delta\omega_1, \Delta p_1) = \frac{1}{|\Delta p_1|} \cdot \rho^{(2)}\left(\omega_0, p_0; \frac{\Delta\omega_1}{\Delta p_1}\right),$$

(10)

i.e. $\rho^{(2)}$ is expressible as the joint distribution of the initial frequency and the pressure coefficient $\Delta\omega_1/\Delta p_1$.

Since the actual frequency range where hole burning and pressure broadening take place is mostly narrow as compared to the width of the whole inhomogeneous band, we can, for hole burning issues, approximately assume that the shape of the joint distribution does not depend on the initial frequency, i.e. $\rho^{(2)}$ can be expressed in the factorized form:

$$\rho^{(2)}(\omega_0, p_0; \Delta\omega_1, \Delta p_1) = \rho^{(1)}_{\mathrm{ih}}(\omega_0)\, \rho'^{(1)}(\Delta\omega_1, \Delta p_1),$$

(11)

where $\rho'^{(1)}$ accounts for the pressure-induced variations of frequencies. According to models [9,10], this is, rigorously speaking, not exact. Both hole shift and broadening can depend on the position within the inhomogeneously broadened band (the "colour effect" [5]). However, notable changes of these parameters only appear for frequency differences comparable with the width of the band.

The dispersive mechanism is considered to prevail largely in well-ordered systems such as crystals and to be applicable in some disordered systems, like glasses, too. Accepting the factorization (11), the part of the kernel accounting for the pressure-induced variations of frequencies in glassy and polymeric matrices is predicted to be approximately a Gaussian with a width linear in Δp [9]:

$$\rho_G^{\prime(1)}(\Delta\omega,\Delta p)=\frac{2\sqrt{\ln 2}}{\Gamma_p\Delta p\sqrt{\pi}}\exp\left(-\frac{4\ln 2\Delta\omega^2}{\Gamma_p{}^2\Delta p^2}\right). \tag{12}$$

In crystalline systems, as described earlier, we may view the diaelastic effect caused by the point defects as the source of spectral inhomogeneity. As shown in [10,11], the pressure kernel shape in the centre of the inhomogeneous band in that case is approximately given by an inverse fourth-order polynomial with even members. This shape is exactly obtained in one special case, namely when there are two subsets of defects with different elastic parameters; however, a different parameter distribution among the defects is shown not to alter the situation in the centre of the inhomogeneous band significantly. In the symmetrical case (the two defect subsets are equal) one obtains a squared Lorentzian:

$$\rho_D^{\prime(1)}(\Delta\omega,\Delta p)=\frac{4\sqrt{\sqrt{2}-1}}{\pi}\frac{(\Gamma_p\Delta p)^3}{((\Gamma_p\Delta p)^2+4(\sqrt{2}-1)\Delta\omega^2)^2}. \tag{13}$$

For the purposes of further calculations, both of the above distribution functions are normalized to unity and given in a representation that explicitly contains the full width at half maximum (FWHM) $\Gamma_p\Delta p$.

2.3. The diffusive mechanism

As another limit, we may assume that the spectral movements of any given homogeneous line at the first and second pressure changes are completely uncorrelated. It is easy to see that this implies the total factorization of the third-order density function into three first-order ones whereas the components corresponding to the changes coincide:

$$\rho^{(3)}(\omega_0,p_0;\Delta\omega_1,\Delta p_1;\Delta\omega_2,\Delta p_2)=\rho_{\text{ih}}^{(1)}(\omega_0)\rho^{\prime(1)}(\Delta\omega_1,\Delta p_1)\rho^{\prime(1)}(\Delta\omega_2,\Delta p_2). \tag{14}$$

From here we get for the pressure kernel for step 4:

$$\begin{aligned}\rho_{4\,\text{dif}}^{(2)}(\omega_0,p_0;\Delta\omega_1,\Delta p)=&f_{\text{hb}}(\omega_0,\nu_0+\Delta\nu_0,Q)\,\rho^{\prime(1)}(\Delta\omega_1,\Delta p)\\&\times\int f_{\text{hb}}(\omega',\nu_0,Q)\,\rho_{\text{ih}}^{(1)}(\omega')\rho^{\prime(1)}(\omega_0-\omega',\Delta p)\,d\omega'.\end{aligned} \tag{15}$$

This situation describes the stochastic Markov process which requires that the second-order density function satisfy the Chapman–Kolmogorov equation. In our context it can be written as:

$$\rho^{\prime(1)}(\omega,\Delta p_1+\Delta p_2)=\rho^{\prime(1)}(\omega,\Delta p_1)\otimes\rho^{\prime(1)}(\omega,\Delta p_2), \tag{16}$$

where $\otimes$ means convolution by the frequency parameter ω. This requirement arises from the process additivity considerations and is formally obtained from the third-

order density function which, when integrated over ω_1, should yield the second-order density for the total pressure change $\Delta p_1 + \Delta p_2$. Known functions that can obey (16) are, for instance, the Gaussian and Lorentzian curves.

It is still largely a matter of discussion whether we can assume here a truly Markovian process and, if so, then whether we can count on its pressure reversibility. It is to be noted that for the temperature-driven (time-dependent) spectral diffusion, the Markovian limit is considered applicable in most models (see, e.g., [19]). On the other hand, these models often depend on an ensemble of two-level systems (or other type of perturbers) performing probabilistic configurational fluctuations which, if pressure-driven, would hardly be reversible. To account for the reversibility, one has to assume a deterministic pressure dependence of the perturbers' parameters. An example of such a parameter could be the position of a spatially bistable defect [13]. In this case, at least for relatively small pressures, the resulting process could be well close to Markovian, i.e. while the spectral trajectory of a homogeneous line is memoryless in the sense of its dependence on the previous values, the ensemble of the perturbers still holds the memory of the process course.

In real systems where the diffusive mechanism is present there are often probably dispersive components acting at the same time. This can be concluded from the single-molecule pressure tuning experiments in a Shpol'skii matrix hexadecane [17], where single-molecule spectra have all been found to shift linearly with pressure. In such matrices the diffusive mechanism has been suggested to be operative [13]. Note that this cannot be considered as any serious evidence against the diffusive mechanism as such, because of the low pressure level used (below 1 bar) and the small number of molecules considered. However, such a dispersive component can certainly establish some correlation in the spectral motion of the homogeneous lines. We still believe that our results remain qualitatively correct with respect to the prevailing pressure mechanism.

2.4. Calculations

In order to perform the calculations, a number of additional assumptions are required. By the same argument as used to justify the factorization (11), i.e. the relative narrowness of the frequency range under consideration as compared to the width of the whole inhomogeneous band, we may take in our calculations

$$\rho_{\text{ih}}^{(1)}(\omega) = \text{const.} \tag{17}$$

We will further assume that the homogeneous lineshape $\kappa(\omega)$ is a Lorentzian of width (FWHM) Γ_h and the burning position is at the origin, $v_0 = 0$.

Next we have to specify the function $\rho'^{(1)}(\Delta\omega, \Delta p)$. We choose it to be a single-maximum symmetric function of $\Delta\omega$, which is preferably peaked at zero. This enables us to discard the hole shift and set $\Delta v_0 = 0$.

Previously we pointed out two possible kernel shapes for the dispersive mechanism, (12) and (13). We stress, however, that the results are not

qualitatively sensitive to the particular shape of distribution. It would therefore be illustrative here to use the same function for both mechanisms. This function should then satisfy both the conditions (10) and (16). Following these considerations, we use a Lorentzian with a width $\Gamma_p \Delta p$:

$$\rho'^{(1)}(\Delta\omega, \Delta p) = \frac{2}{\pi} \frac{\Gamma_p \Delta p}{(\Gamma_p \Delta p)^2 + 4\Delta\omega^2}. \tag{18}$$

In what follows, let us use dimensionless quantities for $Q, v, \omega,$ and Δp by the following scaling

$$\left.\begin{array}{l} Q \to Q/\kappa(0) \\ v,\ \omega \to \Gamma_h v,\ \Gamma_h\omega \\ \Delta p \to (\Gamma_h/\Gamma_p)\Delta p \end{array}\right\} . \tag{19}$$

We also take into account that the widths of the Lorentzians add up on convolution, and normalize the spectra to unity at $Q = 0$. We can then write down the hole spectra for all four steps as follows (see (3)–(5), (8), (15)):

$$I_1(v) = \frac{1}{\pi} \int \frac{1}{1 + (2v - \omega_1)^2} \exp\left(-Q\frac{1}{1 + \omega_1^2}\right) d\omega_1, \tag{20}$$

$$I_2(v, \Delta p) = \frac{1}{\pi} \int \frac{1 + \Delta p}{(1 + \Delta p)^2 + (2v - \omega_1)^2} \exp\left(-Q\frac{1}{1 + \omega_1^2}\right) d\omega_1, \tag{21}$$

$$\begin{aligned} I_3(v, \Delta p) = \frac{1}{\pi^2} \iint & \frac{1}{1 + (2v - \omega_1)^2} \frac{\Delta p}{\Delta p^2 + (\omega_1 - \omega_0)^2} \\ & \times \exp\left[-Q\left(\frac{1}{1 + \omega_0^2} + \frac{1}{1 + \omega_1^2}\right)\right] d\omega_0 d\omega_1, \end{aligned} \tag{22}$$

$$\begin{aligned} I_4^{\text{dif}}(v, \Delta p) = \frac{1}{\pi^2} \iint & \frac{1 + \Delta p}{(1 + \Delta p)^2 + (2v - \omega_1)^2} \frac{\Delta p}{\Delta p^2 + (\omega_1 - \omega_0)^2} \\ & \times \exp\left[-Q\left(\frac{1}{1 + \omega_0^2} + \frac{1}{1 + \omega_1^2}\right)\right] d\omega_0 d\omega_1, \end{aligned} \tag{23}$$

$$\begin{aligned} I_4^{\text{dsp}}(v, \Delta p) = \frac{1}{\pi^2} \iint & \frac{1}{1 + (2v - \omega_1)^2} \frac{\Delta p}{\Delta p^2 + (\omega_1 - \omega_0)^2} \\ & \times \exp\left[-Q\left(\frac{1}{1 + (2\omega_0 - \omega_1)^2} + \frac{1}{1 + \omega_0^2}\right)\right] d\omega_0 d\omega_1. \end{aligned} \tag{24}$$

3. RESULTS AND DISCUSSION

We first stress again the fact that all the spectra at steps 1–3 are identical for both mechanisms. This illustrates the above statement that from simple pressure-tuning hole spectra one cannot decide which mechanism is operative.

For step 4, however, the hole shapes for the both cases do not coincide. Moreover, for a certain parameter region (24) exhibits a double-minimum shape for the dispersive model. In Fig. 2 the situation is depicted for $Q = 5$ and $\Delta p = 20$.

Qualitatively, this double-minimum shape (Fig. 2d) can be explained as follows. The molecules that fill up the primary hole during the first application of pressure are those of medium "speed" whose initial position is far enough
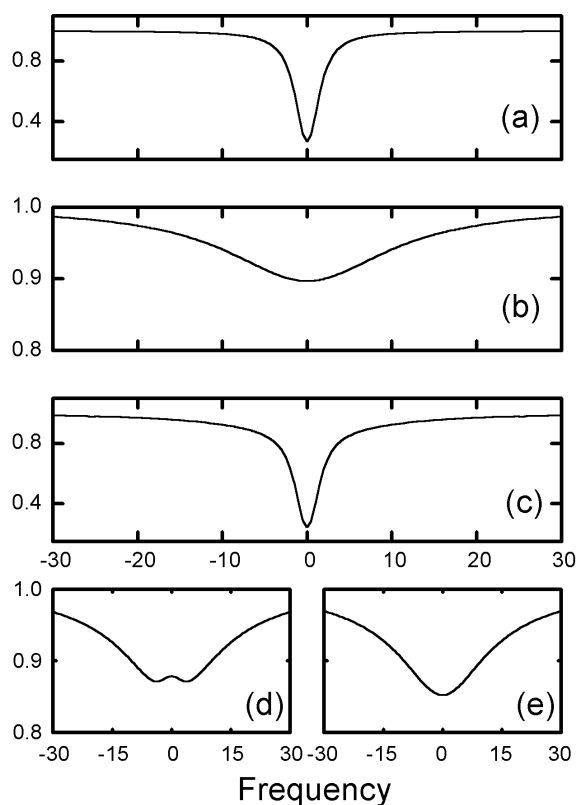
Fig. 2. The calculated hole shapes for the four-step procedure for $\Delta p = 20$ and $Q = 5$. The spectrum after the first burning (a), after the subsequent application of pressure (b), after the second burning (c), and after the second application of pressure for dispersive and diffusive mechanisms ((d) and (e), respectively) are depicted. For steps 1–3 the hole shapes for both types of pressure broadening mechanisms coincide. The frequency is in units of Γ_h, the intensity of the spectrum is normalized to its initial value. Note the different span of the intensity scale in (a), (c) and (b), (d), (e).

from the burning position so as not to get burnt out during the first exposition, however, close enough to reach the hole at the pressure change of Δp. Those are the molecules that suffer most from the second burning. After the second increase of pressure they fill in some area near the burning position. For some parameter values it may now occur that the hole in this area gets deeper than at the burning position due to the shortage of molecules expected to fill this region. Contrasted to the diffusive mechanism (Fig. 2e) this reflects the pressure coefficient memory of each particular molecule. Note that this result also demonstrates capabilities of spectral hole burning as a specific type of nonlinear spectroscopy. No double-minimum structure is observable in the linear expansion of (24) by Q, it only arises if the higher-order terms are taken into account.

A note should be made on determining the actual parameter values from experiment. Expanding (20) in series by Q and considering only the linear term, we get for the low dose values

$$I_1(0) \approx 1 - Q/2, \tag{25}$$

i.e., the dimensionless dose is directly related to the relative hole depth. To scale v back to the dimensional physical value one needs to know the homogeneous linewidth Γ_h. This can be determined from the low-dose holewidths, extrapolating them to the zero-dose limit $2\Gamma_h$. In order to scale Δp back to the real pressure one needs to know Γ_h and Γ_p. The latter is obtainable from the pressure broadening of spectral holes burnt in the linear regime (shallow holes). In other words, saying that $\Delta p = 20$ means using the pressure change which under linear conditions would broaden the hole by 10 widths, i.e. 11 times (keeping in mind that the low-dose holewidth is twice the homogeneous linewidth). Note that such a simple addition rule of hole and pressure kernel widths on convolution is not always exact (assuming a Lorentzian hole shape, it is exact only for the Lorentzian kernel), but it works fairly well e.g. for the dispersive kernels (12) and (13), especially when the hole and kernel widths are substantially different.

To analyse the magnitude of the hole-splitting effect, let us view the depth of the minimums with respect to the central maximum, i.e. the quantity $I_4^{\text{dsp}}(0) - I_4^{\text{dsp}}(v_{\text{min}})$, where $\pm v_{\text{min}}$ are the frequencies corresponding to the minima of the split hole. We will use here the pressure kernel shapes (12) and (13) in order to relate the results to specific systems.

It appears that for every given Δp there exists a dose Q for which this depth difference is maximal. However, for Δp less than about 7 the effect does not exist or is so small that it becomes hardly traceable. On the other hand, the maximal obtainable depth increases with Δp, though sublinearly. Simultaneously, the dose needed for the optimal depth increases rapidly with Δp. The position of the optimal minimums (spectral distance from the burning frequency) also shows a tendency of increasing with Δp. The situation is depicted in Fig. 3. A reasonable choice would be $\Delta p = 25\ldots30$, in which case the maximum depth of the side holes $I_4^{\text{dsp}}(0) - I_4^{\text{dsp}}(v_{\text{min}})$ would be of about $\frac{1}{100}$ from the maximum hole depth.

264
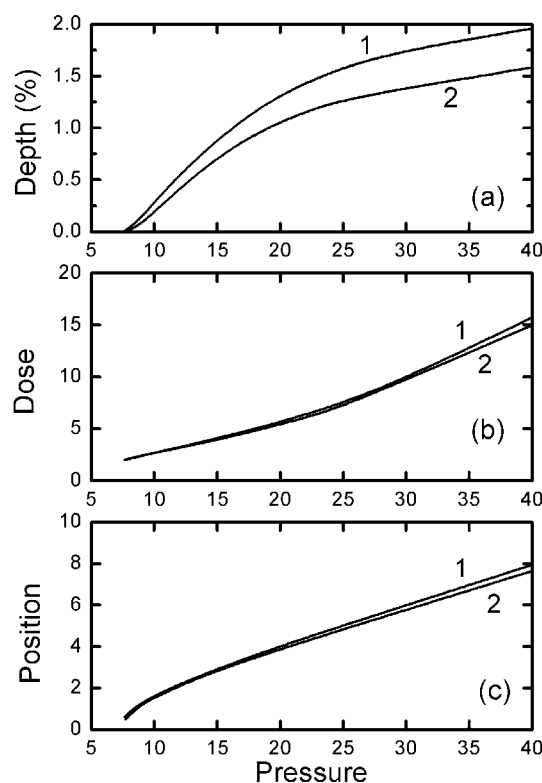
Fig. 3. The maximum relative depth of the side minima (Fig. 2d) (a), the optimized dimensionless dose Q to reach this value (b), and the minimum position (c) depending on the dimensionless pressure Δp. Numbers indicate the used pressure kernel type: 1, the Gaussian kernel (12); 2, the diaelastic kernel (13).

Keeping this in mind, let us consider the prospects for observation of the discussed effects in real systems. A very convenient way to create tunable pressures is to use helium gas as a pressure transmitting medium [5,7]. On the other hand, this confines the maximal obtainable pressure to about 140 bar at 4.2 K, because of the helium solidification. This means, with (21), that a ratio $\Gamma_P/\Gamma_h \approx 0.3$ bar^{-1} is needed to reach a 1%-effect in a crystalline system (we need to raise the pressure up to $2\Delta p$). For chlorin-doped bensophenone in the crystalline phase [8], this ratio is 0.045–0.24 bar^{-1}, depending on the site. This limits the maximum observable effect to 0.8%. This is quite a small value, yet within the reach of careful experiments. A recent study [12] on crystalline durene doped with dimethyl-s-tetrazine yields a similar value of Γ_P/Γ_h, 0.15–0.24 bar^{-1}, depending on the position within the inhomogeneous band. To enhance inhomogeneity, a small amount (about 2 mol%) of hexachlorobenzene was added to some of the samples, which raised the value to a somewhat higher degree, 0.25–0.36 bar^{-1}. This shows that samples with higher defect concentration, expected to exhibit higher absolute values of pressure broadening [10], are favoured

for observing the hole-splitting effect. As to the observation of the diffusive mechanism, the above-discussed Shpol′skii systems [7,13] seem to provide a good opportunity, since values of Γ_P/Γ_h as high as 1.1 bar^{-1} for chlorin-doped n-octane [7] and more than 10 bar^{-1} in dimethyl-s-tetrazine doped n-hexane [13] should favour an observation of the hole splitting or, vice versa, to prove its absence and thus verify the proposed diffusive mechanism.

Glasses constitute quite an intriguing class of materials for the proposed experiments. In glasses the values of Γ_h at 4.2 K are much higher than the corresponding values in crystals with the excited state lifetimes of dopants about or more than 1 ns. High absolute values of pressure broadening, however, yield ratios Γ_P/Γ_h not much different from the molecular crystals, e.g., 0.2 bar^{-1} for chlorin-doped benzophenone in the glassy phase [8]. On the other hand, as can be read from Fig. 3, the dimensionless pressure needed to obtain the same depth of the side minima is lower for the Gaussian kernel (only about $\Delta p = 15 \ldots 20$ for 1%).

The question whether or not the pressure broadening in glasses can be fully attributed to dispersive-type mechanisms [9], is not clear. Within the context of this problem we refer to a recent paper by Alexander [20] on elastic properties of amorphous solids. The author argues that internal buckling in such materials is an inherent ingredient of their structural stability. If so, essential nonlinearities (discontinuities) in the pressure dependence of the molecular probe frequencies may be expected, i.e. the diffusive mechanism may be operative. Experiments like the one described in this paper could cast some light on this problem, too. Potentialities of single-molecule pressure tuning [17,18] to face the same question should also be mentioned. Universal nonphotochemical hole burning processes in glasses [21], however, may obscure this approach.

Following the proposed lines of thinking, it may well be possible to devise experimental techniques yielding more prominent effects. It has already attracted our attention that a simple modification of the scheme, namely burning at base and high pressures and then returning to the intermediate pressure, could considerably enhance the maximum reachable relative depth of the side minima. Calculations regarding this effect are on the way.

4. CONCLUDING REMARKS

We have demonstrated capabilities of spectral hole burning as a specific type of nonlinear high-resolution spectroscopy to distinguish between two different mechanisms of pressure-induced broadening of spectral holes. The experiments proposed could give further insight into the local elastic-plastic properties of crystalline and glassy solids. Though our main interest was to address the problem of pressure broadening of spectral holes, a similar approach may be, with appropriate modifications, applicable to other broadening mechanisms as well, e.g., broadening caused by electrical or magnetic fields in single crystals with orientationally ordered dopants or even by temperature.

ACKNOWLEDGEMENTS

REFERENCES

1. Sesselmann, Th., Richter, W. and Haarer, D. Correlation between pressure-induced optical shifts and compressibilities of polymers with dye molecules. *Europhys. Lett.*, 1986, **2**, 947–952.

2. Sesselmann, Th., Richter, W. Haarer, D. and Morawitz H. Spectroscopic studies of impurity-host interactions in dye-doped polymers: hydrostatic-pressure effects versus temperature effects. *Phys. Rev. B*, 1987, **36**, 7601–7611.

3. Sesselmann, Th., Richter, W. and Haarer, D. Hole-burning experiments in doped polymers under uniaxial and hydrostatic pressure. *J. Lumin.*, 1987, **36**, 263–271.

4. Zollfrank, J., Friedrich, J., Fidy, J. and Vanderkooi, M. Photochemical holes under pressure: compressibility and volume fluctuations of a protein. *J. Chem. Phys.*, 1991, **94**, 8600–8603.

5. Gradl, G., Zollfrank, J., Breinl, W. and Friedrich, J. Color effects in pressure-tuned hole-burned spectra. *J. Chem. Phys.*, 1991, **94**, 7619–7624.

6. Gradl, G., Feis, A. and Friedrich, J. Pressure tuning of spectral holes in organic crystalline materials: irreversible effects. *J. Chem. Phys.*, 1992, **97**, 5403–5409.

7. Ellervee, A., Kikas, J., Laisaar, A., Shcherbakov, V. and Suisalu, A. Hydrostatic pressure effects on spectral hole burning in a Shpol′skii system. *J. Opt. Soc. Am. B*, 1992, **9**, 972–977.

8. Schellenberg, P., Friedrich, J. and Kikas, J. Spectral hole burning in polymorphic systems: single site pressure phenomena and glassy behavior. *J. Chem. Phys.*, 1994, **100**, 5501–5507.

9. Laird, B. B. and Skinner, J. L. Microscopic theory of reversible pressure broadening in hole-burning spectra of impurities in glasses. *J. Chem. Phys.*, 1989, **90**, 3274–3281.

10. Kikas, J. and Leiger, K. Diaelastic pressure-induced effects on spectral holes in crystals. *J. Chem. Phys.*, 1996, **104**, 5384–5390.

11. Leiger, K. *Pressure Effects in Inhomogeneous Spectra of Doped Solids.* Ph.D. Thesis. Tartu, 2002.

12. Leiger, K., Kikas, J. and Suisalu, A. Diaelastic pressure-induced broadening of spectral holes in molecular crystals. *J. Lumin.*, 2002, **98**, 171–176.

13. Friebel, J., Friedrich, J., Suisalu, A., Kikas, J., Kuznetsov, An., Laisaar, A. and Leiger, K. Pressure-induced dynamics in solid *n*-alkanes as probed by optical spectroscopy. *J. Chem. Phys.*, 1998, **108**, 1830–1835.

14. Teodosiu, C. *Elastic Models of Crystal Defects.* Editura Academiei, Bucuresti; Springer-Verlag, Berlin, 1982.

15. Kikas, J. and Rätsep, M. Correlation of transition frequencies in impurity spectra of inhomogeneous solids. *Phys. Stat. Sol. (b)*, 1982, **112**, 409–415.

16. Rebane, L. A., Gorokhovskii, A. A. and Kikas, J. V. Low-temperature spectroscopy of organic molecules in solids by photochemical hole burning. *Appl. Phys. B*, 1982, **29**, 235–250.

17. Iwamoto, T., Kurita, A. and Kushida, T. Pressure effects on single-molecule spectra of terrylene in hexadecane. *Chem. Phys. Lett.*, 1998, **284**, 147–152.

18. Croci, M., Muschenborn, H. J., Guttler, F., Renn, A. and Wild, U. P. Single molecule spectroscopy: pressure effect on pentacene in *p*-terphenyl. *Chem. Phys. Lett.*, 1993, **212**, 71–77.

19. Reilly, P. D. and Skinner, J. L. Spectroscopy of a chromophore coupled to a lattice of dynamic two-level systems. II. Spectral diffusion kernel. *J. Chem. Phys.*, 1994, **101**, 965–973.

20. Alexander, S. Amorphous solids: their structure, lattice dynamics and elasticity. *Phys. Rep.*, 1998, **296**, 65–236.
21. Hayes, J. M. and Small, G. J. Non-photochemical hole burning and impurity site relaxation processes in organic glasses. *Chem. Phys.*, 1978, **27**, 151–157.

Eksperimenditehnika spektraalsälkude rõhulise laienemise mehhanismide uurimiseks

Kristjan Leiger ja Jaak Kikas

Artiklis on välja pakutud põhimõtteline eksperimentaalne protseduur, eristamaks mittehomogeenselt laienenud lisandispektritesse põletatud sälkude rõhulise laienemise mehhanisme. Protseduur põhineb küllastuslikul sälkamisspektroskoopial ja tema idee on märgistada mitteisobaarilises rõhktüürimiseksperimendis vahepealne rõhuline seisund lisapõletamisega. Kui üksikutel homogeensetel joontel on spektraalses liikumises rõhu suhtes tugev korrelatsioon (nt fikseeritud rõhukoefitsient, nn dispersiivne mehhanism), siis peaks protseduuri tulemusel sobivate süsteemi- ja eksperimendiparameetrite korral olema jälgitav sälgu lõhenemine. Nõrga korrelatsiooni piirjuhul (nn difusiivne mehhanism) sellist nähtust ei esine. On esitatud ka parameetrite optimeerimise tulemusi ja arutletud efekti vaadeldavuse üle reaalsetes süsteemides.