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## SELECTION OF HOMOGENEOUS LINEWIDTHS OF IMPURITY MOLECULES BY SATURATIVE SPECTRAL BURNING

(Presented by K. K. Rebane)

A theoretical analysis of the spectral hole burning kinetics is given for the case of statistically distributed homogeneous widths of the impurity no-phonon lines. This distribution can be «compressed» by applying a preburning with a monochromatic light of scanned frequency and of intensity saturating the triplet level in resonance. Such a preburning brings about a reduction of the probe hole widths, which can serve as a proof for the existence of homogeneous linewidth statistical variations.

### 1. Introduction

There is substantial evidence that in disordered impurity systems (particularly in molecular and polymeric glasses) not only the electronic transition energy but also other spectral parameters, such as Debye-Waller factors [1], fluorescence decay times [2], etc. are influenced by disorder and are subject to static variations characterized by respective statistical distributions. It has been proposed that statistical variations of the homogeneous linewidth can account for specific deviations of the shape of permanent spectral holes from the Lorentzian one [3, 4]. However, there exist alternative dynamic explanations, i.e. theories considering processes in a single impurity, yielding non-Lorentzian lineshapes without any statistical averaging over different impurities [5, 6]. The aim of this paper is to propose an experimental procedure to solve this ambiguity.

### 2. General

For purely dynamic models (i.e. models with identical lineshapes for all impurities) the hole burning kinetics in the absorption spectrum  $D(\nu)$  is governed by

$$D(\nu) = D(\nu, Q) = \int q^0(\omega, p) f_r(p) \kappa(\nu - \omega) \exp[-Q f_b(p) \kappa(\nu_0 - \omega)] d\omega dp. \quad (1)$$

Here  $Q$  is the dose of monochromatic burning light of the frequency  $\nu_0$  (the product of the burning intensity  $I$  and the time  $t$ ),  $\kappa(\nu - \omega)$  is the homogeneous absorption spectrum peaked at  $\omega$ , the peak frequencies being subject to statistical distribution. The multidimensional variable  $p$  accounts for all actual parameters (integral absorption cross-section  $\sigma$ , SHB quantum yield  $\eta$ , angular factors of impurity orientation, etc.) but the peak frequency  $\omega$ . The effect of  $p$  on burning and recording is accounted for by factors  $f_b$  and  $f_r$ , respectively;  $q^0(\omega, p)$  is the multidimensional joint distribution of all actual parameters before burning. (1) holds in convenient prepositions about weak excitation, small optical density and impurity concentrations, and the absence of back reaction [7]. For purely electronic holes in most actual cases  $q^0(\omega, p) \cong q^0(\nu_0, p) = \text{const}_\omega$

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within the actual frequency range. In the course of the SHB, this distribution is changed to

$$q(\omega, p) = q(\omega, p, Q) = q^0(\omega, p) \exp[-\bar{Q}(\omega, p)], \quad (2)$$

where

$$\bar{Q}(\omega, p) = Q f_b(p) \kappa(\nu_0 - \omega) \quad (3)$$

is the effective dimensionless burning dose for an impurity with the given values of  $\omega$  and  $p$ .

In principle, procedures can be developed to decide whether SHB kinetics is governed by (1). To outline just one without going into details:

(i) determine  $\kappa$  by deconvoluting the experimental hole shape at small burning times. Note the arising ambiguity about the sign of the frequency argument:  $\kappa$  can be determined up to the accuracy of mirror reflection.

(ii) determine the coefficients of the power expansion of  $D(\nu_0, Q)$  by  $Q$ .

(iii) using (i) and (ii) calculate  $D(\nu, Q)$  for different frequencies  $\nu$  and see whether they match experimental results.

This procedure, however, is quite complicated and does not yield measure for possible deviations from (1). In what follows, we take a different approach and start from the preposition about the existence of a statistical distribution of widths of Lorentzian no-phonon lines. Instead of (1) one obtains now

$$D(\nu, Q) = \int q^0(\omega, \Gamma, p) f_r(p) \kappa(\nu - \omega, \Gamma) \times \\ \times \exp[-Q f_b(p) \kappa(\nu_0 - \omega, \Gamma)] d\omega d\Gamma dp, \quad (4)$$

where

$$\kappa(\nu - \omega, \Gamma) = \pi^{-1} \Gamma / [\Gamma^2 + (\nu - \omega)^2] \quad (5)$$

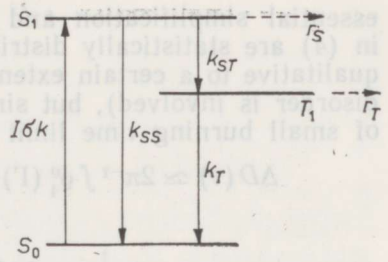
and the distribution of  $\Gamma$  is denoted explicitly.

Note that the burning efficiency essentially depends on both  $\omega$  and  $\Gamma$  and, as a result, monochromatic SHB creates a nontrivial (non-factorizable) joint distribution  $q(\omega, \Gamma, p)$  even in the case of initially factorized distribution ( $q^0(\omega, \Gamma, p) \cong q_1^0(\nu_0) q_2^0(\Gamma) q_3^0(p)$ ). In the latter case it is possible to develop procedures similar to the one discussed above to prove the self-consistency of (2), which mathematically, however, are even more complicated.

### 3. Saturative preburning

We propose here a method for changing  $\Gamma$ -distribution (its «compression» to small values of  $\Gamma$ ) which does not alter the independent nature of  $\Gamma$ - and  $\omega$ -distributions. Let us consider the burning process on scanning the frequency of monochromatic excitation at a constant rate  $\dot{\nu}_0$  in a spectral region broad compared with  $\Gamma_{\max}$ :  $\nu_1 \leq \nu_0 \leq \nu_2$ ,  $\nu_2 - \nu_1 \gg \Gamma_{\max}$ . Note that in the linear absorption regime such a procedure can affect the shape of  $\Gamma$ -distribution only if some other parameters determining the burning efficiency are distributed in a manner correlated with  $\Gamma$ . The physical reason for this is that the effective burning dose does not depend on  $\Gamma$ : lower absorption peak intensities at large values of  $\Gamma$  are exactly compensated by the increase of the over-line scanning time. The situation, however, is different when absorption is already saturated. The reason for this can be, for example, the population of an intermediate metastable level. Note that quite low intensities of light ( $\leq 1$  mW/cm<sup>2</sup>) are needed to

Fig. 1. Schematic of actual levels and transitions. Solid arrows — «fast» transitions resulting in the quasiequilibrium population of the three-level system; dashed arrows — «slow» photoburning.



saturate absorption in no-phonon lines of molecular impurities at LHE temperatures due to the population of metastable triplet levels [8, 9]. Let us suppose that the frequency scan is sufficiently slow to ensure the burning to take place at (quasi)equilibrium populations of excited levels.

This demand is satisfied when  $\nu_0 T \ll \Gamma_{\min}^{-1}$ , where  $T$  is the triplet state lifetime. In this case the excited state populations ( $n_S$  for  $S_1$  level and  $n_T$  for  $T_1$  level, see Fig. 1) are given by

$$n_S = I\sigma\kappa / [k_{SS} + k_{ST} + I\sigma\kappa(1 + k_{ST}/k_T)], \quad (6a)$$

$$n_T = I\sigma\kappa k_{ST} / k_T [k_{SS} + k_{ST} + I\sigma\kappa(1 + k_{ST}/k_T)], \quad (6b)$$

where  $I\sigma\kappa$ ,  $k_{SS}$ ,  $k_{ST}$ , and  $k_T (=T^{-1})$  are the rates of respective transitions (Fig. 1). Formulae (6) hold at the intensities at which the stimulated emission is weak as compared to the spontaneous one and do not account for  $T-T$  absorption. Introducing the burning rates  $r_S$  and  $r_T$  in  $S_1$  and  $T_1$  states, respectively, one obtains for the overall burning rate

$$R(\nu_0) = n_S r_S + n_T r_T = \alpha \beta \Gamma / [(\Gamma^2 + \beta \Gamma) + (\nu_0 - \omega)^2]^{-1}, \quad (7)$$

where

$$\alpha = (k_T r_S + k_{ST} r_T) / (k_T + k_{ST}),$$

$$\beta = (I\sigma / \pi k_T) (k_T + k_{ST}) / (k_{SS} + k_{ST}).$$

Note that for resonant impurities the triplet population is expressed as

$$n_T = [\beta / (\Gamma + \beta)] k_{ST} / (k_{ST} + k_T) \quad (8)$$

and for  $k_{ST} \gg k_T$

$$n_T = (\beta / \Gamma) / [1 + (\beta / \Gamma)]. \quad (9)$$

In the latter case, the dimensionless excitation intensity  $\beta / \Gamma$  can be expressed via the steady-state triplet population of resonant impurities

$$\beta / \Gamma = n_T / (1 - n_T). \quad (10)$$

The effective dimensionless burning dose for a certain impurity sufficiently removed from the starting and final points  $\nu_1$  and  $\nu_2$  of the broad scan is given by

$$\bar{Q} = \bar{Q}(\Gamma) = \nu_0^{-1} \int_{\nu_1}^{\nu_2} R(\nu_0) d\nu_0 = \pi \alpha \beta \nu_0^{-1} \Gamma^{1/2} / (\Gamma + \beta)^{1/2}. \quad (11)$$

For large values of  $\beta$   $\bar{Q} \approx \Gamma^{1/2}$ . Now the probability for a certain impurity to be burned out, given by  $\exp(-\bar{Q})$ , is essentially  $\Gamma$ -dependent. This results in a deformation of  $\Gamma$ -distribution: the impurities with large values of  $\Gamma$  are burned out relatively more efficiently. Nevertheless, the factorized nature of the initial distribution is not altered. «Probing» the preburnt spectral region by monochromatic burning (e.g. at frequency  $(\nu_1 + \nu_2)/2$ ) one expects a certain narrowing of the spectral hole, as compared with its width prior to the broad preburning. In what follows, we make an

essential simplification and suppose that no other parameters than  $\Gamma$  in (4) are statistically distributed. This makes our further consideration qualitative to a certain extent (surely in the case when the orientational disorder is involved), but simplifies essentially the calculations. In case of small burning time limit the shape of the probing hole is given by

$$\Delta D(\nu) \simeq 2\pi^{-1} \int \varrho_1^0(\Gamma) \exp[-\bar{Q}(\Gamma)] \Gamma / [4\Gamma^2 + (\nu - \nu_0)^2] d\Gamma. \quad (12)$$

#### 4. Model calculations

In Fig. 2b, the probe hole is depicted for different values of the preburning scanning rate  $\nu_0$  for a model  $\Gamma$ -distribution («box» — Fig. 2a):

$$\varrho(\Gamma) = \begin{cases} (\Gamma_2 - \Gamma_1)^{-1}, & \Gamma_1 \leq \Gamma \leq \Gamma_2 \\ 0, & \Gamma < \Gamma_1 \text{ or } \Gamma > \Gamma_2. \end{cases} \quad (13)$$

Note that an analytical expression exists for the hole shape at  $\bar{Q}=0$  (no preburning, curve 2 in Fig. 2b) [3, 4]:

$$\Delta D(\nu) \simeq \ln \frac{4\Gamma_2^2 + (\nu - \nu_0)^2}{4\Gamma_1^2 + (\nu - \nu_0)^2}. \quad (14)$$

The halfwidth (FWHM) of such a hole is given by a simple expression  $\delta = 4\sqrt{\Gamma_1\Gamma_2}$ , i. e. it is the geometrical mean of the limiting values  $4\Gamma_1$  and  $4\Gamma_2$ . With decreasing the scanning rate  $\nu_0$ , the number of burned-out

impurities is increased and the  $\Gamma$ -distribution is «compressed» to smaller values of  $\Gamma$ . This results in an effective narrowing of the probing hole. A similar effect is observable on increasing the preburning intensity (higher values of  $\beta$ , Fig. 3).

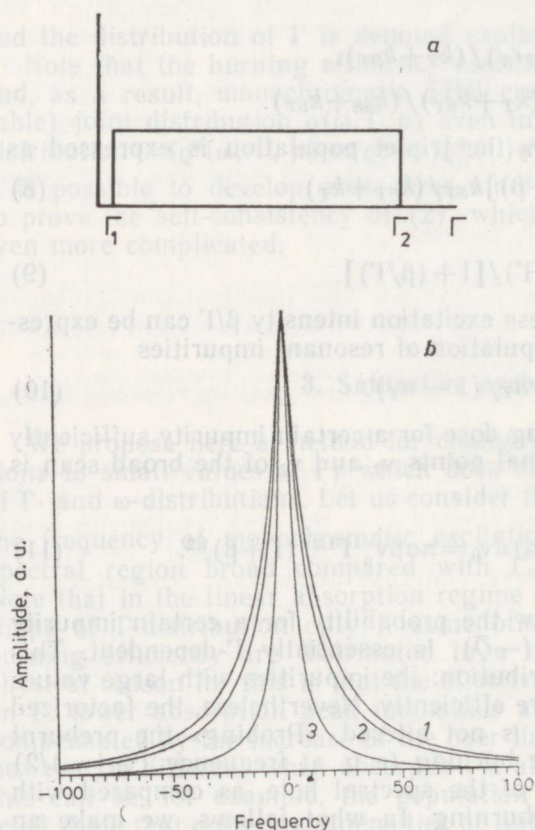


Fig. 2. Model distribution of homogeneous linewidths ( $a - \Gamma_2/\Gamma_1 = 20$ ) and the shapes of probe holes ( $b$ ) before (1) and after (2, 3) the saturative preburning at the scanning rates  $\nu_0/\pi\alpha = 1.0$  (2), 0.2 (3). The dimensionless intensity parameter  $\beta/\Gamma = 2.0$ . All holes are normalized to the same amplitude.

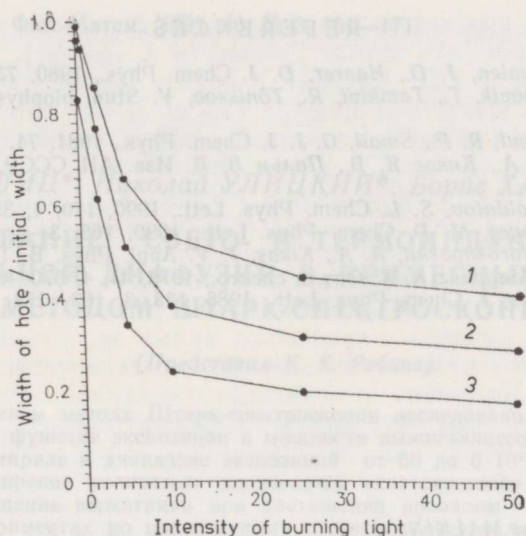


Fig. 3. Dependences of the probe hole width on the dimensionless intensity of the preburning  $\beta/\Gamma$  for different ratios of the limit widths  $\Gamma_2/\Gamma_1=10$  (1), 20 (2), 50 (3). The preburning scanning rate  $\dot{\nu}_0/\pi\alpha=1.0$ .

Naturally, as noted above, if other than  $\Gamma$  parameters are distributed in a manner correlated with  $\Gamma$  this can mask the above-discussed effect. Particularly, a negative (positive) correlation between  $\Gamma$  and  $r_S$  (or  $r_T$ ) yields a hole narrowing (broadening) already in the case of non-saturating preburning. To distinguish such a correlation-based effect from a saturational one, one has to compare results at different (saturating and non-saturating) preburning intensities. Note also that the use of monochromatic light for the preburning is essential. It can be easily seen that a broad-band excitation within the spectral region  $\nu_1 \dots \nu_2$  is equivalent to a very fast scan of the monochromatic light frequency ( $\nu_0 T \gg \gg \Gamma_{\max}$ ) and it results in the burning rates independent of  $\Gamma$  even at saturating intensities.

## 5. Conclusions

Summarizing, we have demonstrated that by using a frequency-scanned preburning with a monochromatic light saturating the triplet level, it is possible to select impurities by the values of their homogeneous linewidths, i. e. relatively more efficiently burn out impurities with large homogeneous linewidths. In the case of statistical distribution of the homogeneous linewidths this results in an effective narrowing of the probing hole and can be used for proving the existence of such distribution.

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1. Friedrich, J., Swalen, J. D., Haarer, D. J. Chem. Phys., 1980, 73, 2, 705—711.
2. Avarmaa, R., Soovik, T., Tamkivi, R., Tõnissoo, V. Stud. biophys., 1977, 65, 3, 213—218.
3. Hayes, J. M., Stout, R. P., Small, G. J. J. Chem. Phys., 1981, 74, 8, 4266—4275.
4. Гороховский А. А., Кикас Я. В., Пальм В. В. Изв. АН СССР, сер. физ., 1982, 46, 5, 952—956.
5. Osadko, I. S., Soldatov, S. L. Chem. Phys. Lett., 1990, 170, 4, 353—358.
6. Pack, D. W., Fayer, M. D. Chem. Phys. Lett., 1990, 168, 3—4, 371—378.
7. Rebane, L. A., Gorokhovskii, A. A., Kikas, J. V. Appl. Phys. B, 1982, 29, 3, 235—250.
8. Авармаа Р. А., Мауринз К. Х. Опт. и спектр., 1976, 41, 4, 670—671.
9. Jaaniso, R., Kikas, J. Chem. Phys. Lett., 1986, 123, 3, 169—174.

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### LISANDIMOLEKULIDE SPEKTRIJONTE HOMOGEENSETE LAIUSTE SELEKTSIOON KÜLLASTAVAL SPEKTRAALSÄLKAMISEL

Teoreetiliselt on analüüsitud spektraalsälkamise kineetikat juhul, kui mittehomogeenselt on dispergeeritud lisandimolekulide foononvabade joonte homogeensed laiused  $\Gamma$ . Monokromaatse sälkamise kineetika (4) kirjeldamiseks tuleb sellisel juhul kasutusele võtta  $\Gamma$  ja üleminekusageduste  $\omega$  ühine jaotusfunktsioon, mis sälkava valguse lõplike dooside korral ei faktoriseeru. On näidatud, et  $\Gamma$  dispersiooni on võimalik vähendada antud üleminekusageduste vahemikus lisandimolekulide väljapõletamisega skaneeritava sagedusega monokromaatse valguse abil intensiivsusel, kus lisandimolekuli tripletseisund on resonantsis küllastunud. Mudelarvutuste varal on näidatud, et selline  $\Gamma$  dispersiooni vähenemine viib pärast küllastavat eelpõletamist põletatavate proovisätkude kitsenemisele. See võib olla kriteeriumiks, mis eristab ülalkäsitletud juhtu situatsioonist, kus proovisätku kuju erinevus Lorentzi omast on tingitud homogeense foononvaba joone Lorentzist erinevast kujust.

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### СЕЛЕКЦИЯ ОДНОРОДНЫХ ШИРИН ЛИНИЙ ПРИМЕСНЫХ МОЛЕКУЛ НАСЫЩАЮЩИМ СПЕКТРАЛЬНЫМ ФОТОВЫЖИГАНИЕМ

Теоретически проанализирована кинетика спектрального фотовыжигания при наличии дисперсии однородных ширин ( $\Gamma$ ) бесфононных линий примесных молекул. Для описания кинетики монохроматического выжигания (4) следует использовать функцию неоднородного распределения по  $\Gamma$  и частоте перехода  $\omega$ , которая при выжигании конечной дозой не факторизуется. Показано, что в некотором диапазоне частот перехода дисперсию по  $\Gamma$  можно уменьшить с помощью фотовыжигания сканируемым в данном диапазоне частот монохроматическим источником с интенсивностью, достаточной для резонансного насыщения триплетного состояния примесных молекул. На основании модельных расчетов показано, что уменьшение дисперсии по  $\Gamma$  приводит к сужению пробного провала, выжженного после предложенного выше насыщающего подготовительного выжигания. Наличие такого сужения может быть критерием для различения описанного в данной работе случая и случая, когда отличие формы пробного провала от лоренциана обусловлено не-лоренцевой формой однородной бесфононной линии.