PHOTOCHEMICAL AND PHOTOPHYSICAL HOLE BURNING IN
ELECTRONIC SPECTRA OF COMPLEX ORGANIC MOLECULES

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1. INTRODUCTION

The last 10-15 years were marked by a considerable progress in the understanding of the spectral band broadening nature in electron-vibrational spectra of complex organic compounds in solutions. It was established that in many cases, at sufficiently low temperatures, wide spectral bands (typical for solutions) are broadened mainly inhomogeneously and conceal a great number of narrow zero phonon lines (ZPL) ^{1,2}. It was also established that in case of the so-called quasi-line spectra of some organic impurity crystals the inhomogeneous line broadening proves to be decisive. By now methods have been developed which are capable of eliminating this inhomogeneous broadening and revealing the line structure in fluorescence, phosphorescence, and absorption spectra of complex molecules in arbitrary solvents by means of selective laser excitation (see, e.g. reviews ^{3,4} and references therein). These methods are often called "Site Selection Spectroscopy"*. In the emission spectra inhomogeneous broadening can be eliminated upon selective excitation of one type centres with an absorption line at laser

*) Upon monochromatic irradiation one excites selectively the molecules with identical energy of electron-vibration transition. Then, strictly speaking, it would be more correct to say "Energy Selection Spectroscopy".

frequency (sometimes this method is called "Fluorescence Line Narrowing Spectroscopy"). The second method enables to reveal a fine structure in absorption spectra. It is based upon selective photochemical or photophysical transformation of centres absorbing laser radiation. After transformations of such kind narrow stable holes can be observed in broad absorption bands at the electronic-vibrational transition frequencies of "burnt" molecules. At present this method is known as "Hole-Burning Spectroscopy". By now all the main peculiarities and characteristics of line spectra, obtained via selective methods, have been studied. The said methods opened up new possibilities for fine spectroscopic investigations of complex organic molecules and their interaction, and for many new practical applications.

The present review deals only with one of the above selective methods, i.e. the hole burning method.

2. PRINCIPLES OF THE METHOD

2.1. Essence of the Method

In order to eliminate inhomogeneous broadening in absorption spectra one must selectively effect the object so that it will be possible to separate a homogeneous component of the spectrum. In gaseous spectroscopy of atoms and simple molecules (sometimes even of solids) the saturation of absorption upon intensive monochromatic pumping is widely used. In our case we deal with effects of another type. Here the hole-burning is carried out by means of selective low-temperature photoreactions in a solid solution^{5,6} (see also reviews^{3,4,7-9} and references therein). If the photoreaction takes place, the absorption spectrum of the phototransformed molecules is shifted. The concentration of molecules absorbing at the "burning" frequency diminishes. This results in the emergence of a narrow hole in the inhomogeneously broadened absorption band. The

FIGURE 1 "Hole-burning" spectra (solid lines) at 4.2 K: (a) perylene in ethanol (burning time $t = 5$ min, $P = 5$ mW/cm²), the inset shows the hole in absorption band burnt at laser frequency; (b) porphin in polystyrene ($t = 1$ min, $P = 5$ mW/cm²). Dashed lines indicate the absorption spectra of the same samples.

life-time of such a hole is determined by the rate of the back reaction (if it is reversible) and turns out to be very long. At low temperature in the darkness these stable holes can conserve for dozens and hundreds of hours. As an example Figure 1a (top right) demonstrates one of the first results in stable-hole-burning.

2.2. Hole-Burning Spectra

It is clear, that the hole-burning with a monochromatic source results in the emergence of a hole in the density distribution function $n(\nu)$ of guest molecules along the purely electronic transition frequency. However, holes are to appear not only at the burning frequency but at all the vibronic transition frequencies of burnt molecules, as well. The difference of the sample absorption spectra before and after burning is called the "hole-burning spectrum"¹⁰. It is a fine-structure absorption spectrum of "burnt" molecules. Figure 1 exhibits two examples of the hole-burning spectra: for perylene in ethanol and for porphin in polystyrene. One can see that along with the 0-0 line (the hole at laser frequency) these spectra contain a great number of vibronic lines. The hole-burning spectrum, in particular, permits to identify the vibration frequencies of the molecule in the excited electronic state.

2.3. Burning Mechanisms

After first publications^{5,6} hole-burning has been observed on many objects. At present it is widely employed to investigate homogeneous spectra characteristics of organic molecules in matrices⁷⁻⁹. In these procedures one deals with most various hole-burning mechanisms that can be divided into two types.

The first type is characterized by various photochemical reactions (photochemical hole-burning - PHB): photodissociation¹¹, proton phototransfer¹², electron phototransfer¹³, etc. Specific mechanism of PHB in case of metal-free porphyrins is widely known, in particular. It is connected with the transfer of two protons in the centre of the porphin ring^{14,15} (Figure 2a). Such modification in the proton pair position in the molecule fixed in a solid matrix results in its spectrum displacement by dozens or hundreds of wavenumbers. Figure 2b shows another example of the photoreaction observed in solid solutions of quinizarin¹². In this case, upon irradiation, there is a break (or formation) of a hydrogen

FIGURE 2 Some photoreactions in low temperature solutions: (a) proton tautomerization in free-base porphyrins; (b) intramolecular hydrogen-bond break (intermolecular hydrogen-bond formation) in quinizarin and some other molecules; (c) two-well potentials for ground and excited states of guest molecule.

bond. In both examples the reaction is reversible (i.e. upon further irradiation in the absorption band of the photoproduct the initial spectrum is restored).

Of considerable interest is the second type of hole-burning processes - the so-called nonphotochemical hole-burning (NPHB) first observed in^{1,2,5}. This term is used for photoprocesses which take place in low-temperature solutions of photostable (under ordinary conditions) molecules⁸. NPHB is apparently non-specific and can be observed in polar glassy solutions (e.g. in alcohol solutions) of many compounds and in some polymer matrices. As a rule, NPHB is not observed in non-polar crystalline matrices (e.g. in crystalline n-paraffins). By now this mechanism has not yet been established in full detail. One of the possible NPHB models (the so-called reorientation model¹⁶) suggests there be 2 (or more) minima at the potential curves of the guest molecule electronic states in a disordered matrix (Figure 2c)⁸. The displacement of the molecule after excitation into the other minimum results in

the frequency change of the purely electronic transition, and a hole emerges at burning frequency. From the qualitative viewpoint this model is in full accord with the NPHB one-quantum character and its universality. However, certain detailed investigations of the NPHB peculiarities on some objects show a picture that does not fit this model¹⁷. Possibly, the NPHB is not that universal and can have a different nature (in some cases positively photochemical) for various compounds.

2.4. Shape of Hole Profile

Let us analyse the shape of an optical band in the hole-burning spectrum in more detail. It is necessary to take into account that the spectral absorption band of the impurity centre is characterized not only by a zero phonon line (ZPL) but also by a broad phonon wing (PW), placed on the shortwave side from ZPL. The burning is realized not only via narrow ZPLs (i.e. "resonantly") but also via broad PWs (i.e. "nonresonantly"). This results in the additional wide distribution in hole-burning spectrum which is located both on the shortwave and on the longwave side from ZPL and determines the specific shape of the hole (Figure 1).

The shape of the inhomogeneously broadened absorption band is described by the convolution of the absorption band profile of a separate impurity centre - $\varepsilon(\nu - \nu_0)$ with the distribution function of the number of impurity centres along the 0-0 transition frequency - $n(\nu - \nu_1)$. It is clear that the band shape in the hole-burning spectrum - $\Delta\varepsilon(\nu)$ is determined then by the convolution $\varepsilon(\nu - \nu_0)$ with the distribution function difference $\Delta n(\nu_0 - \nu_1)$ before and after burning:

$$\Delta\varepsilon(\nu) = \int \varepsilon(\nu - \nu_0) \Delta n(\nu_0 - \nu_1, \nu_B) d\nu_0 \quad (1)$$

where ν_B is the burning frequency.

Generally speaking, the shape of $\Delta n(\nu_0 - \nu_1, \nu_B)$ depends on

the intensity and the time of laser burning, on the position and shape of the photoproduct absorption band, etc. If we neglect the overlapping of absorption bands of the initial substance and the photoproduct then at small burning irradiation intensity (and at one-quantum burning mechanism) the expression for Δn is relatively simple:

$$\Delta n(\nu_0 - \nu_1, \nu_B) = n(\nu_0 - \nu_1) [1 - \exp[-kA\varepsilon(\nu_B - \nu_0)]] \quad (2)$$

where $A = It$ is the exposition, and k is the constant. The latter depends upon the photoreaction mechanism and the kinetic parameters of the molecule. At small expositions instead of (2) one can write:

$$\Delta n(\nu_0 - \nu_1, \nu_B) \approx kA\varepsilon(\nu_B - \nu_0)n(\nu_0 - \nu_1) \quad (3)$$

When the distribution $n(\nu - \nu_1)$ is considerably wider than the homogeneous absorption band $\varepsilon(\nu - \nu_0)$, one can approximately present $n(\nu - \nu_1) = \text{const}$. In this case it follows from (2) that:

$$\Delta n(\nu_0 - \nu_1, \nu_B) \sim \varepsilon(\nu_B - \nu_0) \quad (4)$$

i.e. the distribution Δn repeats the shape $\varepsilon(\nu - \nu_B)$ reflected mirror-like with respect to ν_B . In this case (1) looks as follows:

$$\Delta \varepsilon(\nu) \sim \int \varepsilon(\nu - \nu_0) \varepsilon(\nu_B - \nu_0) d\nu_0 \quad (5)$$

The expression (5) is an autocorrelation function and thus, when it is valid, the band shape in the absorption spectrum must be symmetrical with respect to ν_B .

The band shape is schematically exhibited in Figure 3. The molecules burnt via ZPL (i.e. resonantly) form a narrow resonant hole (and a shortwave PW). The molecules burnt via PW (i.e. non-resonantly) yield a wide distribution, mainly on the longwave side and partly on the shortwave side from the narrow hole.

If we present the true absorption band as the summation of two terms: ZPL - $\varepsilon_1(\nu)$ and PW - $\varepsilon_2(\nu)$, then the expression (5) is

FIGURE 3 Formation of optical band in a hole-burning spectrum: (a) inhomogeneously broadened absorption band and homogeneous bands of resonantly (solid line) and nonresonantly (dashed lines) absorbing molecules; (b) impurity centres distribution function $n(\nu_0)$ before - (1) and after burning - (2). The hatched area represents a burnt part - $\Delta n(\nu_0)$. The narrow hole is formed by the resonantly burnt molecules, the wide longwave distribution - by the nonresonantly burnt molecules. (c) Optical band in the hole-burning spectrum. The figures 1-4 mark the contributions of different terms in (5).

the summation of four terms. The narrow hole $\Delta \epsilon_1(\nu)$ is determined by one of these terms:

$$\Delta \epsilon_1(\nu) \sim \int \epsilon_1(\nu - \nu_0) \epsilon_1(\nu_B - \nu_0) d\nu_0 \quad (6)$$

When ZPL has the Lorentzian shape (as usually happens), the narrow hole (6) has the Lorentzian shape, as well. Its width Γ_h is connected with homogeneous ZPL width as follows:

$$\Gamma_h = 2 \Gamma_{\text{ZPL}} \quad (7)$$

This relation is usually employed in the investigation of homogeneous ZPL width via hole-burning method.

With the exposition increase the shape $\Delta n(\nu)$ is not identified any more by (4) and is continuously varying with time. In this case we observe the change in both the shape of the narrow resonant hole and the shape and relative intensity of broad wings.

With burning time increase the narrow hole is broadened. In fact, those molecules are burnt very fast which have their ZPL maxima located very closely to the ν_B frequency. Due to the reduction in these centre concentration their burning rate is gradually slowed down in comparison with the centres the ZPL maxima of which are more displaced from ν_B (by the value of the Γ_{ZPL} order). To take into account the hole broadening related to the said, one usually extrapolates the measured width Γ_h to the limit $t \rightarrow 0$.

As was first noted in¹⁸ there exists one more mechanism of hole broadening which is valid even at small burning time-intervals. This mechanism is due to the population of a metastable triplet state. High population of a triplet state, possible even at moderate intensities of burning radiation, results in the non-linear sample bleaching and in the hole broadening related to it. In this case the hole width depends upon laser intensity and is expressed as follows¹⁸:

$$\Gamma_h = \Gamma_{ZPL} (1 + \sqrt{1 + p}); \quad p = I \epsilon_{\max} \Phi_T / K_T \quad (8)$$

where I is the burning source intensity; $\epsilon_{\max}$ is the absorption coefficient in the ZPL maximum; K_T is the deactivation rate of the triplet state; Φ_T is the output of interconversion. At sufficiently low temperatures, when the ZPL width tends to the radiation limit ($\sim 10^{-3} - 10^{-4} \text{ cm}^{-1}$), $\epsilon_{\max}$ reaches the values of $10^{-10} - 10^{-11} \text{ cm}^2$. So the saturation can be achieved at the source intensities of the order of $10 - 100 \text{ } \mu\text{W/cm}^2$ ¹⁹.

With the exposition increase one can observe the deformation

of broad wings along with the narrow hole broadening. A longwave wing component, in this case, grows faster (due to a relative increase in the integral contribution of the non-resonantly burnt centres as compared to the resonant centres). As was shown in¹⁹ the saturation of a triplet state results in a similar increase in the longwave part of the wing at sufficient source intensity. This effect takes place even at the smallest exposures. It is worth noting that the wing asymmetry can be due to the band overlapping of the initial compound and the photoproduct, to peculiarities of the true shape of the $n(\nu - \nu'_1)$ function, etc. All these factors should be taken into consideration at the quantitative analysis of the hole-burning spectra.

3. METHOD APPLICATIONS

The hole-burning method opened up new possibilities for fine spectroscopic investigations of complex molecules in a condensed medium. These possibilities are: investigation of the vibrational structure of excited states; determination of homogeneous absorption spectra characteristics and of electronic and vibrational relaxation constants; studying of electric and magnetic field influence upon molecular spectra; determination of the photochemical reaction rates by the hole width; investigation of glass-like state peculiarities; etc. Here we shall briefly consider only some of them.

3.1. Measurement of Homogeneous ZPL Width and its Temperature Dependence

The homogeneous line width and its temperature dependence contain valuable information on the electron-phonon coupling in solid solutions. For the last 7-8 years a big number of investigations on the ZPL temperature broadening of organic molecules in crystalline and glassy matrices have been performed²⁰⁻²³ (see also reviews^{7,8}).

For a number of molecules, both in crystalline and in glassy matrices, a radiation limit of the width ($\Gamma \sim 10^{-3} \text{ cm}^{-1}$) was obtained. This occurred upon measuring the ZPL width in the low temperature range and upon extrapolation of results to a $T \rightarrow 0$ limit²¹⁻²³. However, in other cases of molecules in glassy matrices the evaluation of Γ at the $T \rightarrow 0$ yields appreciably greater values: $0.1 - 1 \text{ cm}^{-1}$ ^{8,9}. These values are 2 or 3 orders greater than the radiation width. The reasons for this are not quite clear. One of the possible reasons, briefly discussed in⁹, is the presence of relaxation processes in glasses developing even at extremely low temperatures. These processes chaotically shift the absorption lines of separate guest molecules and result in the so-called spectral diffusion. If typical-for-these-processes periods are less than the observation time, they will give an additional contribution to the ZPL width being measured. But the fact, whether these processes play an important role or not at low temperatures, does not have a reliable experimental proof.

In the course of investigations it turned out that the temperature dependence of $\Gamma(T)$ for molecules in crystalline and glassy matrices is appreciably different. While dealing with crystalline matrices, the temperature broadening appears to be either $\sim T^2$, or $\sim \exp(-E/kT)$. That falls in line with the theoretical assumptions on the interaction of an impurity centre with local or quasilocal vibrations. At the same time, when treating glassy matrices, in the majority of cases there was discovered a specific and universal enough dependence: $\Gamma(T) \sim T^{1.3 + 1.4}$. This dependence does not fit the ZPL broadening theory so well-developed earlier. In the works of recent years²⁴⁻²⁶ this unconventional temperature dependence is explained through the interaction of the impurity centre with the so-called two-level systems (see reviews^{8,9} and references therein). At first these two-level systems

(TLS) were introduced to explain the abnormal behaviour of specific heat, thermal conductivity, saturation effects in ultrasonic absorption, etc. at low and extremely low temperatures (see, e.g.²⁷). As different from phonons, such TLS are the Fermi systems. Therefore, if we take into account the impurity centre - TLS interaction we can obtain the following temperature dependence: $\Gamma(T) \sim T^n$ with the n values in the interval $1 \lesssim n \lesssim 2$ (see²⁶ and references therein). Thus, the use of TLS model enables to explain the ZPL broadening observed in molecular spectra in glasses. However, more direct proofs of the TLS influence upon the optical impurity characteristics are, apparently, needed to finally solve the problem. Physical concretization of this phenomenological model is also necessary.

3.2. Stark Effect

The possibilities to investigate the influence of external electric and magnetic fields (Stark and Zeeman effects) upon the spectra of complex molecules are essentially limited by a large width ($\Delta\nu \sim 10^2\text{--}10^3 \text{ cm}^{-1}$) of their spectral bands. Thus, for instance, the value of the absorption band shift under field influence is often two or three orders of magnitude less than their width. The situation is considerably improved if we follow the changes in the profiles of narrow holes under field influence. Owing to the small hole width ($\Delta\nu \sim 10^{-1}\text{--}10^{-2} \text{ cm}^{-1}$) the sensitivity of measurements increases by several orders.

Investigations of the Stark effect (which serve, in particular, to determine dipole moments and polarizabilities of molecules in excited electronic states) via hole-burning method were started in²⁸⁻³¹. In order to successfully interpret experimental data it was necessary to analyse the dependence of a hole profile upon the external field magnitude. Such theoretical analysis was performed for several simple cases in²⁹. It was supposed that under the

FIGURE 4 Dependence of the hole profile on external electric field (linear Stark effect). Parameters: $\gamma = \angle(\vec{\mu}, \vec{\mu}_{ga})$; $2\Delta\nu$ - homogeneous line width; $E_1 = hc\Delta\nu / (f_e |\Delta\vec{\mu}|) \cdot 299 \text{ ga}$;

external field influence ZPL absorption maxima of all molecules in solid solution undergo the displacements $\Delta\nu_0$:

$$\Delta\nu_0 = - (f_e \Delta\vec{\mu} \cdot \vec{E} + \frac{1}{2} f_e^2 \vec{E} \Delta\hat{\alpha} \vec{E}) / (hc) \quad (9)$$

where $\Delta\vec{\mu}$ and $\Delta\hat{\alpha}$ are changes of a static dipole moment vector and of tensor of molecular polarizability at electronic transition, and f_e is a local field factor. The first term in (9) corresponds to a linear Stark effect and the second - to a quadratic one. Using (9) and (5) it is possible to obtain an expression for the hole profile in the presence of the field (this is done with taking into account orientation factors and averaging over all possible orientations of molecules with respect to the field direction). The result depends on mutual orientation of the transition dipole moment $\vec{\mu}_{ga}$, $\Delta\vec{\mu}$ and polarizability tensor axes. Some results of numerical calculations for the dependence of the hole profile upon the applied field magnitude for the linear Stark effect are demonstrated in Figure 4. It is clearly seen, that the hole, upon the field influence broadens, but remains symmetrical with respect to the initial maximum position. Its shape depends upon the angle γ between $\vec{\mu}_{ga}$ and $\Delta\vec{\mu}$. According to the calculation, in case of the quadratic Stark effect the hole also broadens, but becomes asymmetrical and is shifted along the frequency scale²⁹

FIGURE 5 Change in the hole profile (linear Stark effect) with the voltage applied to 40 μm thick chlorin in polyvinylbutural film at $T = 2 \text{ K}$.³⁰

(see next section about the quadratic Zeeman effect).

Figure 5 exhibits the experimental data for the linear Stark effect on the hole burnt in the absorption band of chlorin in polyvinylbutyral. Comparing the experimental data for chlorin with the calculated ones it was possible to find $|\Delta\mu| = 0.2\text{--}0.4$ Debye.

Along with the spectral measurements of the hole shape depending upon the external field magnitude it is possible to make another type of the Stark hole experiments, i.e. to measure the so-called "field curves"^{29,32}. In the latter case we register the change in the optical density $\Delta D(E-E_B)$ (where E_B is a field at which the burning is performed) at a fixed frequency ν (e.g. $\nu = \nu_{\text{las}}$) as a function of the applied field E . A "field curve" $\Delta D(E-E_B)$ has the maximum at $E=E_B$, and its width is connected with the homogeneous absorption ZPL width of separate impurity centres. At known Stark molecular parameters the $\Delta D(E-E_B)$ measurements can serve as a relatively simple means for determining homogeneous ZPL width³². Such measurements are rather simple, do not need any spectrometer and can be performed by means of one laser with a fixed frequency.

The application of modulation technique seems to be also quite perspective for the investigations of the Stark effect on the holes³³. We only note that the Stark hole measurements turn out to be a subtle tool in studying impurity molecular crystals with line spectra, as well³⁴.

3.3. Zeeman Effect

Similar to the Stark spectroscopy the use of narrow spectral holes enable to appreciably increase the sensitivity of Zeeman experiments. In the last 5 years magnetic properties of singlet states of complex molecules have been investigated via this method.

As known, owing to low symmetry of complex molecules the latter, as a rule, do not conserve either the electronic moment or its projection on the molecular axis. Diamagnetism is a most characteristic manifestation of magnetic properties of complex molecules. In some cases, however, when the electronic levels of the corresponding symmetry are closely located we can come across the so-called Van-Fleck paramagnetism. The ZPL shift magnitude is proportional to H^2 and is expressed as follows:

$$\Delta \nu_o = - \frac{1}{2} \vec{H} \Delta \hat{\chi} \vec{H} \quad (10)$$

where $\Delta \hat{\chi}$ is the magnetic susceptibility change of the molecule at electronic transition ($\Delta \hat{\chi}$ is a summation of dia- and paramagnetic terms). The magnitudes of the effects expected are very small ($< 10^{-4} \text{ cm}^{-1}/\text{kG}^2$), and under ordinary conditions are not accessible for observation. The hole-burning method made it possible to perform direct spectroscopic measurements of such shifts. The exceptional narrowness of the holes burnt in the absorption bands of free base porphyrins ($\Delta \nu \sim 10^{-2}-10^{-3} \text{ cm}^{-1}$) was used to investigate induced paramagnetism in porphin and chlorin in the n-paraffin monocrystals^{35,36}. In this case, magnetic shifts $\leq 0.1 \text{ cm}^{-1}$ in the fields up to 86 kG were measured.

A much wider variety of objects to be investigated and the simplicity in sample preparation are provided by glassy solvents and polymers, and not by n-paraffin matrices. Two specific points should be born in mind while using such amorphous isotropic matrices. First, as was noted, the hole width for amorphous matrices is

FIGURE 6 a) Dependence of the hole profile on external magnetic field (quadratic Zeeman effect), calculated for the case, when the electronic transition dipole moment is perpendicular to z-axis of molecule and magnetic field direction coincides with incident and registered beam direction³⁷. b) Quadratic Zeeman effect on the hole in absorption band of chlorin in polystyrene film ($\lambda_{\text{burning}} = 6328 \text{ \AA}$, $P = 1 \text{ mW/cm}^2$, $t = 5 \text{ min}$): (1) - hole at $H = 0$; (2) - hole at $H = 400 \text{ kG}$. Experimental conditions are the same as in calculated case (a)³⁷.

appreciably larger than for crystalline ones. At helium temperatures this width is usually $0.1 - 1 \text{ cm}^{-1}$. Second, owing to the system isotropy it is necessary to average over all possible molecular orientations while theoretically analysing the experimental data. In case of the quadratic Zeeman effect in accordance with (10) the hole is broadened asymmetrically and is shifted (as in the quadratic Stark effect). In order to carry out reliable experimental observations of small magnetic shifts (even employing hole-burning) it is necessary, in such situation, to make use of strong fields produced in pulse set-ups. The first Zeeman effect measure-

ments on the holes in the strong pulse magnetic fields (up to 400 kG) were performed in³⁷. Figure 6a displays the calculated dependence of the hole profile upon a field magnitude. Experimental data for chlorin in a polymer film are shown in Figure 6b. These data yielded a magnetic susceptibility value for chlorin: $\chi = (2.6 \pm 0.3) \cdot 10^{-5} \text{ cm}^{-1}/\text{kG}^2$ (which practically coincides with the measurement data on monocrystals in stationary fields³⁵).

In conclusion, it is worth noting that the strong pulse magnetic field technique enables to investigate magnetic properties of high excited electronic states (S_2 and higher), transitions into which yield relatively broad ZPLs ($\Delta\nu \sim 1\text{-}10 \text{ cm}^{-1}$). Such measurements can assist in solving the problem of the contribution separation of dia- and paramagnetic parts to the measured χ value.

3.4. Vibrational Relaxation. Rates of Photochemical Reactions

Here we shall briefly point to one more type of information which can be obtained upon the hole width measurement. The homogeneous width and the temperature ZPL broadening have been already discussed. This temperature broadening is conditioned by a so-called pure dephasing time T_2^* . (In the considered cases the ZPL width tended to a natural limit determined by a life-time T_1 only at $T \rightarrow 0$.) However, even at $T \neq 0$ one can come across a situation when $T_1 \ll T_2^*$, and the ZPL width is determined by T_1 . Then, measuring the ZPL width via hole-burning technique, one can determine T_1 . Such situation is realised for vibronic transitions at low temperatures, for vibrational relaxation time in a condensed state lies within a picosecond range. The measurements of vibrational relaxation time via this technique were performed in^{38,39}.

The second case, when $T_1 < T_2^*$ is realised in some photoactive systems where photoreaction is the main excited state deactivation channel. Here the hole width yields information on the photoreaction rate. This method has been employed for determining the

FIGURE 7 Three dimensional (x-y-v) optical storage scheme.

rate of the proton phototransfer¹², and of the electron phototransfer¹³. The possibility to apply this method for investigation of biological systems and initial photosynthesis processes seems also exceptionally interesting.

3.5. Other Applications

It goes without saying that all possible domains for the hole-burning method application have not yet been studied to the end. It might happen that they lie beyond the scope of pure spectroscopy. Of practical interest are the works aiming at the increase in memory volume of optical storage devices (OSD). Diagram in Figure 7 shows the mechanism of such a device proposed in⁴¹. Using laser hole-burning a third - spectral - OSD coordinate should be added to the two spatial ones. The presence or absence of the hole at a given frequency will correspond to the information in binary code. The spectral coordinate capacity is determined by the ratio of the inhomogeneous absorption band width to the hole width. At

low temperatures this ratio can equal 10^3 - 10^4 . This means that owing to the spectral coordinate the OSD capacity can be increased by 3 or 4 orders. Now one has a right to say that it is quite possible to provide a large volume of the OSD memory. However, quite a number of problems should be solved for its technical realization. These, in particular, are: providing high material sensitivity, providing a necessary speed of response, protecting information from erasing upon reading-out, etc. The problem, whether these difficulties will be overcome and a technically advantageous device of such type will be constructed, rests with the future.

Still another interesting usage of the hole-burning method is its application in the so-called spatial-time holography⁴². Employing a frequency-selective medium for recording (i.e. employing a photoactive substance with a large inhomogeneous and a small homogeneous spectrum broadening) one can register not only a spatial, but also a time signal structure with a high time resolution. Whereas a time memory of usual media is determined by a life-time of the excited states, the hole-burning effect provides a media set with practically unlimited information storage time. These problems are considered in more detail in⁴³.

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