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Transient-hole burning in the infrared spectrum of a polymer with intense picosecond pulses

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Transient spectral holes of 70-cm^{-1} width are observed in the OH stretching band (~3500 cm^{-1}) of hydrogen-bonded poly(vinyl butyral) films at room temperature. The lifetime of the holes is measured to be $T_1 = 5 \pm 2$ ps and interpreted as the population lifetime of the OH stretching vibration. Simultaneously inverse holes with a red shift of 210 ± 10 cm^{-1} and the same lifetime T_1 are observed and explained by excited-state absorption. The inhomogeneous broadening of the OH absorption band presents direct evidence for site-specific frequency shifts of the hydrogen bridges. Breaking of H bonds and establishment of a new thermal equilibrium is indicated with time constant $\tau = 15 \pm 5$ ps by blue-shifted induced absorption around the monomeric frequency position.

In the past spectral-hole burning was investigated for dye molecules in liquid solutions and solid matrices on vastly different time scales.[1-7] Long-lived photochemical holes of chromophores in polymer matrices at low temperatures gave valuable detailed information on the structural properties of the molecular surroundings.[2,3] More recently, persistent photochemical hole burning at low temperatures was extended to the infrared for smaller molecules in rare gas or glass matrices.[4,6] Related investigations at higher temperatures[5] are almost completely lacking, presumably because of the fast and complex dynamics of the doped dye molecules. An inherent problem of these studies is the question of to what extent the observed local inhomogeneity is an intrinsic property of the matrix or related to the solvent-solute interaction.

In comparison with the femtosecond dynamics of electronic transitions of dye molecules at room temperature,[8] the vibrational dynamics even of large systems (e.g., polymers) can be considerably slower.[9] As a consequence, spectral-hole burning experiments should be feasible on the picosecond time scale, if the vibrational transition of interest is inhomogeneously broadened. Investigation of this kind can provide information on intrinsic spectral properties of the sample, since a molecular subgroup may serve as spectroscopic probe and doping with solute molecules need not be necessary.

In this Rapid Communication the first observation of transient hole burning in the infrared spectrum of a polymer at ambient temperature is reported. A terpolymer of poly(vinyl butyral), poly(vinyl alcohol), and poly(vinyl acetate) groups is investigated. Our results demonstrate the inhomogeneous broadening of the absorption band at 3500 cm^{-1} that originates from the OH stretching mode of the polymer and is connected with hydrogen bonding to neighboring molecular subgroups. The ultrashort lifetime of the investigated spectral features necessitating picosecond time resolution should be contrasted to the persistent infrared holes observed recently at low temperature for doped rare-gas matrices,[4] inorganic glass,[6] and in hydrogen-bonded polymers.[7]

Our experimental technique is a double-resonance spectroscopy with intense tunable picosecond pulses. Details of the measuring system have been described recently.[10] In short, a first strong ir excitation pulse (energy ~100 μJ, duration 10 ± 2 ps, bandwidth 20 ± 2 cm^{-1} at 3500 cm^{-1}) is resonantly tuned to the OH absorption band and focused into the sample. A second time-delayed weak probing pulse (energy < 1 μJ, the other parameter as for the pump) with adjustable frequency serves to measure the sample transmission $T(\nu, t_D)$ as a function of delay time t_D and/or probe frequency ν (energy transmission T of the probe pulse). A peak intensity of 2×10^{10} W/cm^2 is estimated for the focal plane of the pump beam.

The samples are polymer films (thickness 20-60 μm) with high optical quality that are prepared as follows. Commercially available poly(vinyl butyral)[11] powder is dissolved in methylenbromide, the solution carefully spread over an aluminum foil and slowly dried under vacuum. This procedure is repeated until the desired sample thickness is reached. After detaching from the aluminum substrate, the polymer film is fixed between CaF$_2$ optical windows using poly(chlorotrifluoroethylene) oil as an index-matching fluid.

Figure 1(a) presents the chemical structure of the sample. Besides the dominant poly(vinyl butyral) groups (PVB, 77%) a smaller amount of poly(viny alcohol) (PVA, 20%) and also poly(vinyl acetate) (3%) groups are present.[11] Molecular weight is 36000 dalton. An infrared transmission spectrum of our PVB films (measured with a commercial ir spectrometer) is shown in Fig. 1(b). The strong absorption around 2900 cm^{-1} originates from the various CH groups of the sample. Around 3480 cm^{-1} a broad absorption band appears that is related to the OH stretching vibration of the PVA groups. The asymmetry of the band of approximately 170-cm^{-1} width suggests inhomogeneous broadening.

An example for our instantaneous infrared probe spectra is presented in Fig. 2; the absorption $-\ln T(\nu, t_D)$ is plotted versus the frequency position of the picosecond probe pulse. The open circles correspond to a measurement with blocked pump beam [hereafter denoted as $T_0(\nu)$] and indicate the sample transmission at thermal equilibrium. The solid circles represent the absorption $\ln T(\nu, t_D = 0)$ for probe pulses that propagate simultaneously with the pump pulse. Figure 2 clearly shows the spectral hole around the pump frequency of 3440 cm^{-1},

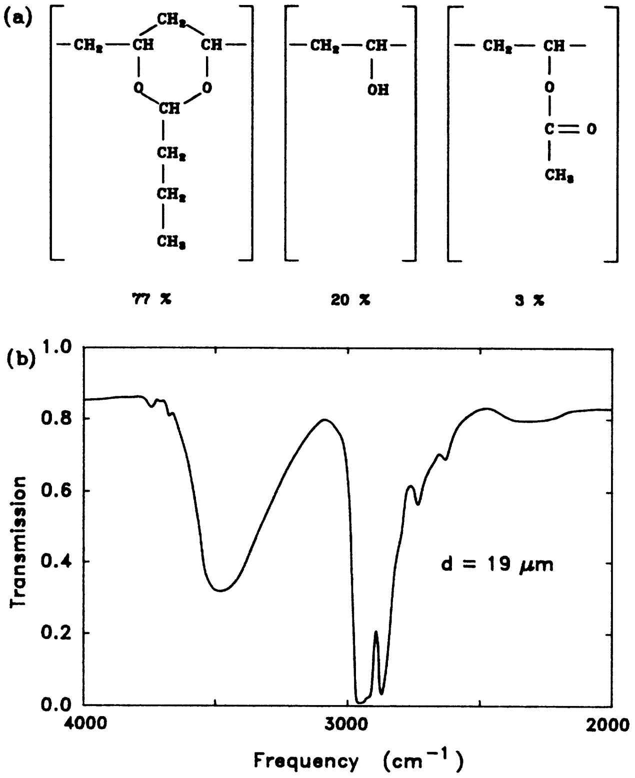

FIG. 1. (a) Structural units of the terpolymer poly(vinyl butyral) also containing poly(vinyl alcohol) and poly(vinyl acetate) groups; (b) conventional infrared spectrum of the polymer films (293 K).

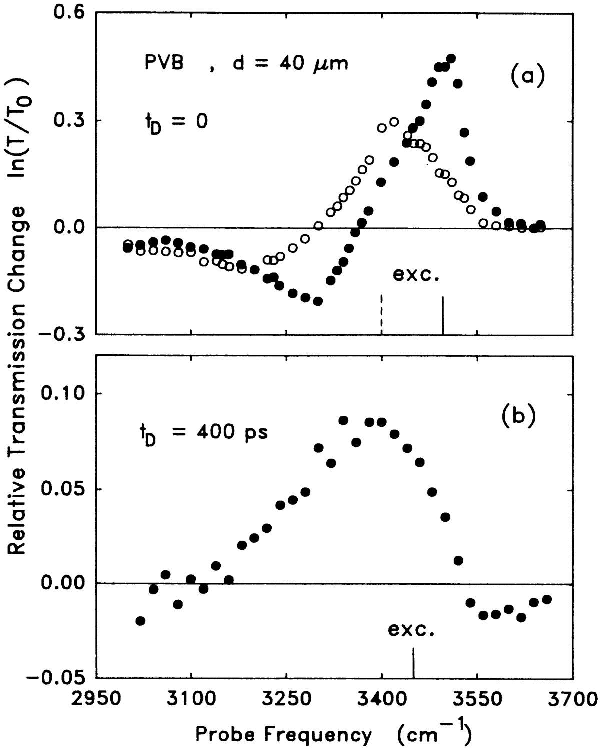

FIG. 3(a) Relative probe transmission change of the terpolymer PVB at 293 K for simultaneous excitation at 3500 cm^{-1} (solid circles) and 3400 cm^{-1} (open circles), respectively ($t_D=0$). The maxima and minima, respectively, denote the frequency positions of spectral holes and inverse spectral holes. (b) Same as (a) but 400 ps after excitation at 3450 cm^{-1}.

whereas ~70 cm^{-1} away only minor transmission changes are found. We mention here that a coherence peak artifact does not occur for $\nu=\nu_{pu}$ because of the independent generation of the pump and probe pulses.

A convenient way to present the transmission changes generated by the excitation pulse is shown in Figs. 3(a) and 3(b). The relative transmission change $\ln[T(\nu,t_D=0)/T_0]$ is plotted versus probe frequency for two excitation frequencies, 3400 and 3500 cm^{-1} [open and solid circles, respectively; see Fig. 3(a)]. The measured dependence on pump frequency and also the larger spectral range as compared to Fig. 2 should be noticed. For the representation of Fig. 3, the spectral hole corresponds to the significant transmission increase, $\ln(T/T_0)>0$, around the excitation frequency. On the low-frequency side around 3200 cm^{-1} an absorption increase, $\ln(T/T_0)<0$, is found.

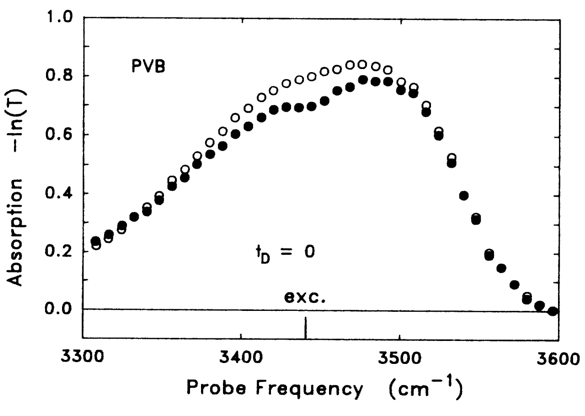

FIG. 2. Picosecond infrared probe spectrum of the terpolymer poly(vinyl butyral) for excitation at 3440 cm^{-1} (solid circles); the open circles represent the conventional ir spectrum (pump beam blocked); sample thickness $d=40$ μm (293 K).

Figure 3(b) shows the relative absorption changes 400 ps after the excitation at 3450 cm^{-1}. A much broader transmission increase with smaller amplitude is measured in comparison with Fig. 3(a), while the original hole and the induced absorption at the low-frequency side have disappeared. A new absorption increase occurs above 3550 cm^{-1}.

We have studied the dependence of the spectral holes on pump frequency. For short delay, $t_D \le 10$ ps, the maxima of the signal $\ln(T/T_0)$ occur at the excitation frequencies, the signal minima being downshifted by $\Delta\nu=210\pm10$ cm^{-1}. The long-time spectrum (≥ 100 ps), to the contrary, is independent on excitation frequency except minor amplitude changes due to varying absorption coefficients.

The picosecond dynamics of the spectral holes is deduced from time-resolved measurements. In Figs. 4(a)–4(c) the transmission changes are plotted versus delay time for three constant values of probe frequency; the pump pulse is tuned to 3480 cm^{-1}. The different ordinate

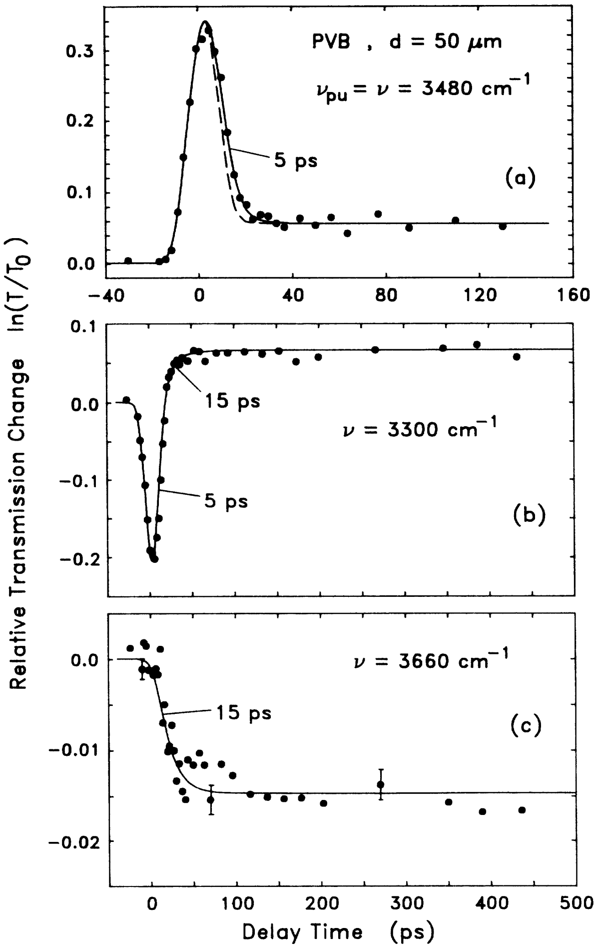

FIG. 4. Relative transmission change of the probe pulse vs delay time for terpolymer PVB excited at $\nu_{pu}=3480$ cm^{-1} (293 K); experimental points, calculated curves; (a) transient bleaching for $\nu=\nu_{pu}=3480$ cm^{-1} (spectral hole); a time constant of $T_1=5\pm2$ ps is measured; the dashed line represents the calculated signal transient for $T_1=1$ ps: (b) induced absorption for $\nu=3300$ cm^{-1} (inverse spectral hole): (c) induced absorption for $\nu=3660$ cm^{-1} (generation of monomeric OH subgroups with $\tau=15\pm5$ ps). The different ordinate and absicissa scales of (a)-(c) should be noted. The error bars in (a) and (b) are approximately equal to the size of the experimental points.

and abscissa scales of the figures should be noted. Figure 4(a) shows the result for $\nu=\nu_{pu}=3480$ cm^{-1}. One observes a rapid transmission increase according to the duration of the pump pulse followed by a fast decrease. For $t_D>50$ ps the transmission remains constant at an increased level. Only part of the data extending over 0.7 ns are shown in the figure. A careful analysis, with the use of a rate equation model (see calculated solid lines in Fig. 4), reveals that a finite time constant $T_1=5\pm2$ ps can be deduced from the signal decay. The dashed line in Fig. 4(a) is calculated for a time constant 1 ps and using available information on the shape and duration of the infrared pulses; the curve represents a measure of the instrumental time resolution and deviates notably from the experimental points.

When the probe pulse is tuned to 3280 cm^{-1} where strong induced absorption occurs [see Fig. 3(a), solid circles], the signal transient of Fig. 4(b) is measured. A fast absorption increase for short times is followed by a slightly slower return with the same time constant of 5 ps already noted in Fig. 4(a). For longer times one observes a decelerated transmission change consistent with a relaxation time of approximately 15 ps.

For probe pulses at ~3650 cm^{-1} the signal transient is depicted in Fig. 4(c). A transmission decrease is measured, which is notably slower than that of Fig. 4(a). The involved time constant amounts to $\tau=15\pm5$ ps. The induced absorption persists for long times (> 1 ns).

The conventional spectrum [see Fig. 1(b)] will be discussed first. It is interesting to compare the frequency of the absorption peak $\nu_{max}=3480$ cm^{-1} of the terpolymer PVB to PVA where $\nu_{max}\simeq3360$ cm^{-1}; one recognizes a difference of 120 cm^{-1} that may be explained as follows. In PVA with its higher number density of OH subgroups hydrogen-bonded chains of hydroxylic groups may build up; the situation for the OH absorption band should be similar to that of pure ethanol (~3350 cm^{-1}) with H-bonded oligomers.[12] For our terpolymer PVB the situation is different. For sterical reasons internal hydrogen bonds are most likely to be formed from the OH subgroups of the PVA groups to the oxygen atoms in the PVB rings; for such bonds an absorption frequency similar to that of ethanol dimers (~3500 cm^{-1}) may be expected in accordance with the spectroscopic findings.

An explanation of the observed spectral holes (see Figs. 2 and 3) is discussed next in terms of a local mode picture. A similar concept was discussed recently for polyalkenes.[9] The basic excitation process is the population of $v=1$ level of the local OH stretching vibrations. Assuming that the OH groups at various sites absorb at different frequencies only a subensemble is excited. It is well established in the literature that a frequency shift of the OH vibration is generated by a hydrogen bridge depending on bond angles.[13] A variation of these angles due to local disorder directly leads to a distribution of transition frequencies. In a polymer film at room temperature the structure is known to vary slowly (in contrast to a liquid) because of long orientational and diffusion time constants.[14] As a result, spectral diffusion of the OH transition frequency is of minor importance and a spectral hole centered at the pump frequency appears for suitable population changes. An excess population of (5-10)% is estimated from the band areas of Fig. 2.

A necessary consequence of this physical picture is a corresponding peak (inverse hole) of comparable magnitude in the excited-state absorption spectrum, since the distributions of fundamental and higher-order frequencies are correlated and shifted by vibrational anharmonicity. It is emphasized that these inverse spectral holes have been experimentally observed around 3300 cm^{-1} (see Fig. 3). A quantitative piece of information supplied by the measurements is the anharmonic frequency shift $\Delta\nu=210\pm10$ cm^{-1} for the $v=1\rightarrow v=2$ transition with respect to the fundamental absorption band. A comparison with conventional spectral data is not possible; the deduction of the anharmonicity from conventional spectral data (e.g., comparison of the $0\rightarrow1$ and $0\rightarrow2$ OH absorption bands) is made difficult because of the necessary large sample thickness (~1 cm) and perturbing additional effects on the band contours (combination bands, Fermi resonance, etc.).

The linewidth of the spectral hole [Fig. 3(a)] at 293 K is approximately 70 cm^{-1}. It is much narrower than the conventional absorption band of Fig. 1(b). Preliminary data reveal a significant temperature dependence of the hole width in agreement with theoretical models for the spectral bandwidth of hydrogen-bonded systems.

The spectral changes for long delay times [Fig. 3(b)] may be explained by a temperature rise of the sample, when the vibrational excess energy deposited in the OH stretching mode has equilibrated with corresponding rearrangement of H bonds. The comparison with conventional transmission spectra at different temperatures shows that a temperature rise by a few tens of degrees is sufficient to explain the observed spectral changes. In fact, partial breaking of H bridges and production of monomeric OH groups is indicated by the measured absorption increase above 3600 cm^{-1} [Figs. 3(b) and 4(c)].[15]

Finally, we discuss the time evolution of the OH vibration as indicated by the data of Fig. 4. The arguments given above show that the time constant of $T_1 = 5 \pm 2$ ps deduced from the transmission changes at 3480 and 3280 cm^{-1} [Figs. 4(a) and 4(b)] represents the vibrational population lifetime of the stretching mode of H-bonded OH subgroups in the terpolymer PVB. T_1 also denotes the lifetime of the spectral hole. The time constant $\tau = 15$ ps, on the other hand, inferred from Figs. 4(b) and 4(c) accounts for the breaking of hydrogen bonds after infrared excitation; a new thermal equilibrium is reached with the dissociation time $\tau = 15$ ps, without evidence for vibrational predissociation (and partial geminate recombination) as observed for ethanol in liquid solution.[15] The different behavior may be explained by a faster thermalization rate of the polymer.

It is interesting to compare the result on T_1 with other findings. The value is remarkably shorter than for monomeric OH groups in liquids and solids, where 70–200 ps have been reported;[16] it may be surmized that hydrogen bonding plays an important role for population relaxation of the OH vibration. For ethanol oligomers in liquid solution a lifetime of 5 ps was measured that was mostly due to predissociation of H bridges.[15]

Very recently, persistent infrared spectral holes were measured in three polymeric alcohols in the temperature range of several 10 K.[7] The absorption band of the OH stretching mode of substituted polystyrenes and poly(vinyl alcohol) was investigated using very small excitation intensities (~10 $\mathrm{mW/cm}^2$) and long exposure times (1–10 min) to generate the spectral holes. A narrow linewidth of ~6 cm^{-1} and a lifetime of the order of 1 h were observed with significant temperature dependence. The spectral effects are interpreted in terms of inhomogeneous broadening due to H bonds, similar to the ultrashort spectral holes studied here. The following points are emphasized for our experiments: (i) Population changes of the OH vibration dominantly contribute to the transient spectral holes; (ii) red-shifted inverse holes are measured that are readily explained by excited-state absorption; the corresponding finding was not made in persistent hole burning; (iii) rearrangement of H bonds leading to blue-shifted antiholes[7] at low temperature is also observed in our room-temperature investigation.

In summary we point out that we have observed for the first time transient spectral holes in the vibrational spectrum of condensed matter at room temperature. The short population lifetime (5 ± 2 ps) of the OH stretching vibration in the investigated terpolymer requires picosecond time resolution. The experimental data also indicate breaking of hydrogen bonds after infrared excitation with a time constant of 15 ± 5 ps to a new thermal equilibrium position. The corresponding inverse spectral holes due to excited-state absorption are also measured, which allow us to determine the anharmonic frequency shift of 210 ± 10 cm^{-1}. Further experiments are under way to establish the properties of the spectral holes in more detail.

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