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Infrared Transient Antihole Burning in the $1 \rightarrow 2$ Vibrational Transition of $^{12}\text{C}^{17}\text{O}$ in Solid N_2 : Evidence for Energy-Dependent Spectral Transfer

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The population hole burned within the inhomogeneously broadened ir fundamental absorption band of $^{12}\text{C}^{17}\text{O}$ in solid N_2 by a narrow-band pulsed laser is detected as an antihole in the transient absorption of a tunable cw probe beam whose frequency is swept through the $\nu = 1 \rightarrow \nu = 2$ resonance. The time development of the transient profile demonstrates that spectral diffusion is governed by an energy-dependent process, contrary to what has been observed in many disordered systems.

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The development of time-resolved hole-burning techniques has promoted the study of the time dependence of the spectral transfer of optical excitation in inhomogeneously broadened systems.¹⁻³ If an interaction mechanism exists which allows the excitation to be transferred from the initially excited centers to those whose frequencies lie outside the narrow band, then at later times the transient emission or absorption profile is altered and evolves towards the inhomogeneous equilibrium profile. Theories for the time development of the spectral transfer have been presented in a number of recent papers.⁴⁻⁹ Transfer processes involving inelastic phonon scattering to make up a small energy mismatch have been discussed by Holstein, Lyo, and Orbach.^{10,11} According to their dependence upon the difference between the initial and final states, these transfer processes can be divided into two categories: those which depend on ΔE and those which are independent of ΔE . The time evolution of the spectral profile has been calculated for both cases. When the transfer rate is independent of energy mismatch the full inhomogeneous profile appears undistorted. Simultaneously, the sharp line decays in intensity without any broadening. The equilibrium is reached at a rate which is independent of the energy position of the laser line. A quite different behavior is expected in the case of energy-

dependent spectral transfer. When excitation is achieved at the center of the inhomogeneous line, the sharp hole spreads out gradually. For the excitation in the wing, the transient profile shows a gradual spreading of the sharp line toward the inhomogeneous band center which gives rise to the gradual appearance of the equilibrium background.

All experimental studies that we are aware of indicate that to a first approximation the background always has the profile of the full inhomogeneous line. Energy transfer is thought to occur through either the one-phonon- or the two-phonon-assisted process in which phonon absorption and emission occur on different sites. These processes are independent of ΔE . We report in this Letter results which we believe represent the first experimental evidence for energy-dependent spectral transfer.

The principle of the experiment, which combines the methods of double resonance and saturation spectroscopy, is shown in Fig. 1. $^{12}\text{C}^{17}\text{O}$ molecules¹² are selectively excited to the $\nu = 1$ level within a narrow frequency band (< 20 MHz)¹³ centered at 2112.925 cm^{-1} , the sum frequency of the $P(8)$ and $P(10)$ lines of the 001-020 band of CO_2 . Simultaneous operation of these two lines in a Q-switched CO_2 laser allows sum generation of ~ 1 -W peak power, 200-nsec pulses in a

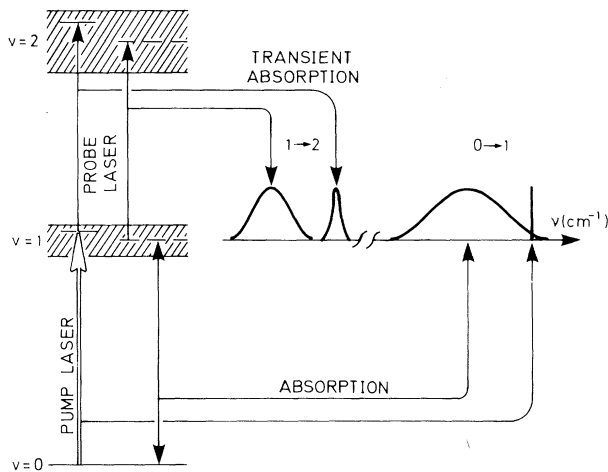


FIG. 1. Schematic diagram showing the inhomogeneously broadened vibrational levels, the ir transitions involved in the line-narrowing experiment, and the corresponding $0 \rightarrow 1$ absorption and $1 \rightarrow 2$ transient absorption spectra of CO in solid N_2 .

CdGeAs₂ crystal. The inhomogeneous $0 \rightarrow 1$ absorption band of $^{12}C^{17}O$ in solid N_2 is centered at 2112.879 cm^{-1} . The low-concentration line shape is rather Lorentzian with a full width at half maximum (FWHM) of 0.058 cm^{-1} .¹⁴ The laser is pumping on the high-frequency side with a detuning $\Delta\nu_L = 0.046 \text{ cm}^{-1}$. A tunable PbSSe diode laser from Laser Analytics is used as the cw probe beam. The frequency resolution of $\sim 20 \text{ MHz}$ is actually limited by temperature fluctuations.

The time evolution of the transient spectral profile is obtained by sampling the signal at a preset delay after the excitation pulse with a gated integrator. The time dependence of the transient absorption intensity can also be monitored by setting the probe frequency at a fixed value within the $1 \rightarrow 2$ profile. The time resolution of the apparatus is limited to $\sim 10 \mu\text{sec}$ by the response time of the InSb detector.

In the temperature range $9\text{--}18 \text{ K}$ and at concentrations ranging from 6×10^{-4} to 5×10^{-6} a narrow antihole centered at 2087.021 cm^{-1} and a broader background on the low-frequency side are observed. The time-dependent behavior of the transient spectrum is shown in Fig. 2 for two different CO concentrations at $T = 12 \text{ K}$. As time evolves, the narrow antihole broadens and a

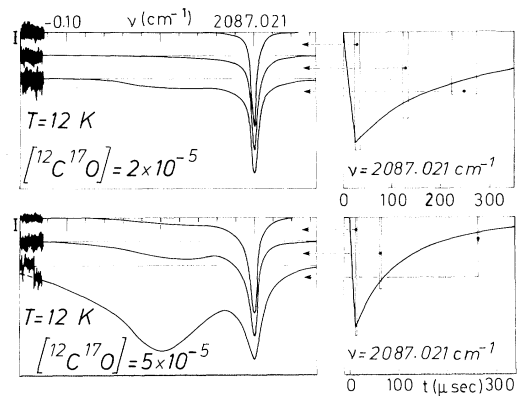


FIG. 2. Time-resolved sampling of the transient spectrum of $^{12}C^{17}O$ in solid N_2 . The delay and the width of the gate are shown on the right-hand side together with the time decay of the transient intensity at the center of the hole. At $[^{12}C^{17}O] = 5 \times 10^{-5}$ and the latest delay the background corresponds to the inhomogeneous line within the experimental accuracy.

background of increasing magnitude appears. However, this background has the shape, width, and maximum frequency of the full inhomogeneous profile only at the latest delay and provided the concentration is sufficiently high. At intermediate delays and/or lower concentrations a wing develops toward the inhomogeneous band center, increasing gradually both in magnitude and spread. At $T = 9 \text{ K}$ and $[CO] = 5 \times 10^{-6}$ only the sharp antihole with a FWHM of $1.5 \times 10^{-3} \text{ cm}^{-1}$ is observed. Furthermore, the width is found to be constant between 0 and $500 \mu\text{sec}$ delay after the excitation, which shows that the spectral diffusion is negligible in this case. The effect of tuning the probe frequency in small increments across the $1 \rightarrow 2$ absorption profile is illustrated in Fig. 3 where we show the time-resolved transient absorption intensity of several probe frequencies. These curves show the decay of the initially excited molecules and the buildup of the population across the inhomogeneous profile. Both the rise time and the decay time of the signal gradually increase from the center of the hole to the center of the inhomogeneous line.

The master equation describing the probability that site r_i with energy E_i is excited at time t is given by¹¹

$$dP(\vec{r}_i, E_i, t)/dt = \sum_j [W_{j \rightarrow i} P(\vec{r}_j, E_j, t) - W_{i \rightarrow j} P(\vec{r}_i, E_i, t)],$$

where $W_{j \rightarrow i}$ is the transfer rate from site \vec{r}_j, E_j to site \vec{r}_i, E_i . There is no simple method for solving this set of coupled equations in systems exhibiting simultaneous disorder in space and energy. Spec-

tral diffusion has been studied on the basis of a macroscopic transport equation first proposed by Motegi and Shionoya¹⁵:

$$dP(E, t)/dt = \int [g(E)W(E - E')P(E', t) - g(E')W(E - E')P(E, t)]dE',$$

where $P(E, t)$ represents the probability that molecules with energy E are excited at time t , $g(E)$ is the inhomogeneous line shape (or density of states), and $W(E - E')$ is the transfer rate from a site with energy E' to a site with energy E . This equation is an approximate description of the problem since the distance dependence of $W_{j \rightarrow i}$ is ignored. Numerical solutions have been obtained by Holstein, Lyo, and Orbach^{4,5} for the case of a transfer rate which falls off as the inverse square of the energy mismatch. The time development of the transient profile is very sensitive to the shape of the density of states. In particular a Lorentzian inhomogeneous line results in a broadening of the narrow hole at early times, followed by a gradual appearance of background whose peak is gradually shifted toward the inhomogeneous line center. Figure 5 of Ref. 5 resembles closely the time evolution of the transient profile shown in Fig. 2. This fact suggests that in the present system spectral transfer occurs via an energy-dependent process. The qualitative agreement between the experimental and calculated profiles indicates that the time evolution of the transient spectrum is mainly controlled by two key parameters: the energy dependence of the transfer rate and the density of states. However, quantitative agreement cannot be expected since the theory neglects the fluctuations in the transfer rate induced by the distribu-

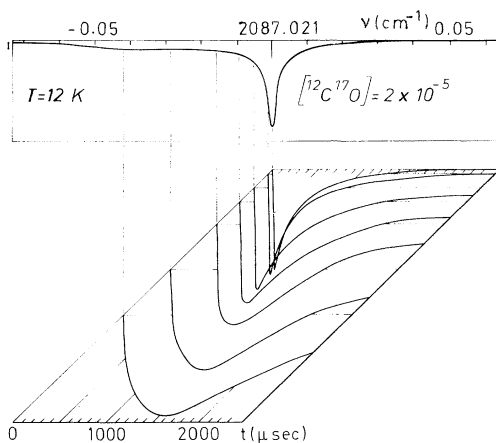


FIG. 3. Time dependence of the 1 \rightarrow 2 transient absorption intensity for several probe frequencies. The transient spectrum is integrated over 400 μ sec after the excitation pulse.

tion of the intermolecular separations.

A different approximate treatment consists in regarding the initially excited site as a donor and the rest of the molecules as acceptors.^{7,9} If energy transfer among acceptors is ignored, the time evolution of the transient profile results from single-step energy transfer from the donors to the acceptors. In the case of an energy-dependent transfer rate and for initial excitation in the wing, back transfer can be neglected, as discussed by Lyo.⁹ If we assume a Lorentzian transfer rate

$$W_{D \rightarrow A}(r_{DA}, \Delta E) = \frac{C_{DD}}{r_{DA}^6} \frac{\gamma^2}{\Delta E^2 + \gamma^2},$$

where, according to Förster's overlap integral formalism, γ is the homogeneous linewidth and C_{DD} the probability coefficient for resonant transfer; then the configurational average of the initially excited molecules is given by the following expression:

$$\ln\langle P_0(t) \rangle = - (Kt)^{1/2},$$

where

$$K^{1/2} = \frac{4}{3} \pi^{3/2} \rho \gamma C_{DD}^{1/2} \int dE g(E) (\Delta E^2 + \gamma^2)^{-1/2},$$

where ρ is the acceptor density. The experimental decay of the transient intensity at the center of the antihole indeed exhibits a nonexponential time dependence and the rate constant has the value $K_{\text{expt}} = 7.8 \times 10^3 \text{ sec}^{-1}$ for $[^{12}\text{C}^{17}\text{O}] = 2 \times 10^{-5}$ and $T = 12 \text{ K}$. Using in the above expression for K a Lorentzian density of states $g(E)$ with $\Delta\nu_{\text{inh}} = 0.058 \text{ cm}^{-1}$ and an homogeneous linewidth $\gamma = 3 \times 10^{-3} \text{ cm}^{-1}$ we find $C_{DD} = 7.3 \times 10^{16} \text{ \AA}^6 \text{ sec}^{-1}$. Such a value is very close to the probability coefficient $C_{DD} = 1.2 \times 10^{17}$ which is calculated directly from the molecular parameters.¹⁶ Temperature dependence of the transfer rate can be calculated in a similar way. From the temperature dependence of the antihole we find that the homogeneous linewidth can be expressed as $\gamma = 0.38 \exp(-57.6/T)$. Experimental and calculated values reported in Table I are in reasonable agreement. Unfortunately the experimentally accessible temperature range is quite limited.

The time development of the background intensity has been calculated by Huber and Ching.⁷ These authors have obtained the following expres-

TABLE I. Experimental and calculated temperature dependence of the decay rate of the transient absorption intensity at the center of the antihole for a CO concentration $[^{12}\text{C}^{17}\text{O}] = 5 \times 10^{-5}$.

T (K)	K_{expt} (sec^{-1})	K_{calc} (sec^{-1})
11	2×10^4	3.6×10^4
12	2.9×10^4	4.9×10^4
15	6.4×10^4	8.3×10^4

sion, valid only at short times and low concentration:

$$I(E, E_0, t) \propto g(E) (\Delta E^2 + \gamma^2)^{-1/2} t^{1/2}.$$

Applied to the present system, this expression leads to an intensity rise time which exhibits only a weak dependence upon ΔE . The strong ΔE dependence observed experimentally (Fig. 3) should be assessed to the Lorentzian character of the density of states which strongly favors transfer involving a small ΔE and multistep processes. The inadequacy of the pair approximation already suggested by full Monte Carlo calculations of Lyo⁹ for the case of wing excitation in a Gaussian density of states should be more pronounced for a Lorentzian inhomogeneous profile.

In conclusion, the time development of the spectral profile of the transient absorption demonstrates that in the CO/N₂ system the spectral diffusion is governed by a dipole-dipole, $1/\Delta E^2$ -dependent transfer process. This time development is strongly controlled by the Lorentzian character of the inhomogeneous profile, in agreement with theoretical predictions.

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