Time Domain Investigation on Vibrational Dephasing and Spectral Diffusion in CO-Doped Solid N_2

C. Crépin, M. Broquier, and H. Dubost
Laboratoire de Photophysique Moléculaire du CNRS, Université Paris-Sud, Bâtiment 210, 91405 Orsay Cedex, France

J. P. Galaup and J. L. Le Gouët
Laboratoire Aimé Cotton du CNRS, Université Paris-Sud, Bâtiment 505, 91405 Orsay Cedex, France

J. M. Ortéga
LURE, Université Paris-Sud, Bâtiment 209D, 91405 Orsay Cedex, France

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Infrared picosecond accumulated photon echo experiments have been performed for the first time, using the Orsay Free Electron Laser, on the $v = 0 \rightarrow v = 1$ transition of CO in solid nitrogen. The vibrational dephasing time is found to be exceptionally long ($T_2 \geq 120$ ns) at low temperature. The analysis of the observed spectral diffusion leads one to assume different energy transfer mechanisms depending on the CO concentration.

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In order to investigate molecular interactions in condensed phase, one commonly resorts to the analysis of electronic and/or vibrational transitions. Information is specifically derived from the transition linewidth. In addition to the contribution from the excited state lifetime it includes an homogeneous component, which arises from fast fluctuations in the oscillator-environment coupling, and an inhomogeneous contribution that comes from site disorder or slow fluctuations in the coupling between the oscillator and its surroundings. As a matter of fact, structural fluctuations occur over a broad range of time scales, and there is no strict separation between the time scales of the fast fluctuations, the experiment, and the slow fluctuations. As a consequence, what is regarded as the measured homogeneous linewidth critically depends on the temporal window covered by the experimental procedure. This effect is known as spectral diffusion. In conventional spectroscopy the explored temporal window ranges at most from microsecond to hours, so that faster processes contribute in an indistinct way to homogeneous broadening. Only coherent transient nonlinear spectroscopy gives access to a shorter time scale. The first infrared photon echo experiments have been carried out by the Fayer's group [1]. Recently, Hamm and co-workers [2] have applied a femtosecond three-pulse echo technique to study vibrational transitions. In the present paper, we report on the investigation of the vibrational dynamics of CO in solid N_2, in the picosecond and the nanosecond time scales, probed for the first time by accumulated three-pulse photon echoes.

Carbon monoxide in nitrogen matrices is a very nice model system: there is just one vibration to be tested in a well structured medium, the CO stretching in a crystallographic lattice. At low temperature (<34 K), the mass centers of nitrogen molecules form a fcc structure and molecular axes have well-defined directions, along the C_{3v} axis of the cubic cell [3]. CO has almost exactly the same size as N_2 and occupies only substitutional sites of the lattice. This simple geometry has already allowed and induced a lot of theoretical and experimental works on the fundamental vibrational mode of the carbon monoxide embedded in solid N_2. The population relaxation time T_1 is well known in the microsecond time scale [4]. The vibrational dephasing is dominated by interactions of the guest with its environment. As a consequence, the dephasing time T_2 is much smaller than T_1. However, T_2 has never been measured directly. In spectroscopy, one strives to reach the homogeneous bandwidth Γ_h, related to T_2 by $\Gamma_h = 1/\pi T_2$. The homogeneous line is hidden in the absorption spectra because of the inhomogeneous broadening. Dubost *et al.* have shown that the inhomogeneous bandwidth depends on the concentration, the broadening of the absorption line coming mainly from dipole-dipole interactions between the dispersed CO molecules [5]. In very diluted samples, the absorption width is then closer to the homogeneous one. Such measurements have been performed very recently [6]. The homogeneous bandwidth can also be reached in spectral measurements by hole-burning experiments. Transient antihole burning in the $1 \rightarrow 2$ transition has been performed [7], leading to homogeneous bandwidths increasing from 0.63×10^{-3} to $0.015\ \text{cm}^{-1}$ in the 9–18 K temperature range. As mentioned above, these values can involve spectral diffusion broadening. As a matter of fact, the spectral diffusion coming from energy transfer between the trapped molecules has been observed in these hole burning experiments [7] in the microsecond time scale.

In order to attain the true dephasing time T_2, we have devised an accumulated stimulated photon echo experiment [8] with the Free Electron Laser at the Centre Laser Infrarouge d'Orsay (CLIO). This laser delivers bursts of three hundred 1 ps long pulses, evenly spaced by 32 ns intervals. The burst repetition rate is 25 Hz. The laser

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beam is split into two parts that are delayed from each other with an optical delay line tunable in the ±300 ps range [9]. They are focused on the sample with slightly angled wave vectors $\vec{k}_1$ and $\vec{k}_2$. The energy density per pulse is about 1 $\mathrm{mJ/cm^2}$. Pulse 2 arrives at a delay τ after pulse 1. A time-resolved degenerate four wave mixing (TR-DFWM) signal coming from the sample is detected in the $2\vec{k}_2$-$\vec{k}_1$ direction. The two-pulse trains form a succession of two-pulse sequences which create population gratings at different molecular frequencies ω. The grating lifetime is given by the recovery time $T_g = 26$ ms of the ground vibrational level [10]. The population gratings can then interact with all the pulses in the burst. Considering the population gratings created by one sequence of two pulses delayed by τ, the interaction with a third pulse, with wave vector $\vec{k}_2$, induces a third-order polarization of the sample that radiates the signal [11–13]. The third pulse is delayed with respect to the second pulse by fixed intervals θ of 32, 64, 96 ns, etc.... On the detector, there is an accumulation of all the possible three-pulse TR-DFWM signals involving different third pulses and different two-pulse sequences.

The sample is obtained by mixing CO and N_2, with concentration $c = \mathrm{CO}/\mathrm{N}_2 = 10^{-2}$ or 2×10^{-3}, and depositing the gas mixture on a cold window inside the cryostat. The laser spectral width of about 20 cm^{-1} exceeds the CO absorption bandwidth that ranges from 0.6 to 0.8 cm^{-1}. The corresponding fraction of excited molecules is thus only a few percent. Moreover, the vibrational relaxation of CO in solid N_2 is purely radiative. Therefore we do not expect local heating to be significant.

According to these experimental conditions, delta-function pulses are assumed. Then the polarization source term for the detected signal is given by [11]

$$P^{(3)}(\tau,t) \propto \int g(\omega)\gamma(\omega,\tau)\exp(i\omega t - t/T_2)\,d\omega\,, \quad (1)$$

where $\gamma(\omega,\tau)$ represents the population grating amplitude

$$\gamma(\omega,\tau) \propto \exp(-i\omega\tau - |\tau|/T_2) \quad (2)$$

and $g(\omega)$ is the inhomogeneous molecular distribution. The coherence relaxation description in terms of a T_2 time relies on the fact that, in our low temperature experiment, the picosecond observation time scale by far exceeds the correlation time of fast interaction fluctuations due to phonon perturbations. The polarization exists for $t > 0$, the origin of time being taken at the third pulse arrival.

The detected signal is then given by

$$S(\tau) = \int_0^\infty |P^{(3)}(\tau,t)|^2\,dt\,. \quad (3)$$

Depending on whether the homogeneous broadening is larger or smaller than the inhomogeneous one, $S(\tau)$ exhibits a symmetric or steplike shape, respectively. The evolution of $S(\tau)$ shows a characteristic exponential decay involving the dephasing time T_2. The observed signal is correctly described by Eq. (1) provided no spectral diffusion occurs during the θ time interval. In the case of spectral diffusion with characteristic time much shorter than θ, the third pulse cannot read the different gratings $\gamma(\omega,\tau)$. It has been shown [11] that $S(\tau)$ has then a symmetric shape and may be expressed as the modulus square of the Fourier transform (FT) of the absorption profile.

Experimental results at high temperature (20–25 K) are presented in Figs. 1b and 1d: the τ variation of the signal has a symmetric shape and decays in tens of picoseconds. This decay cannot be ascribed to homogeneous broadening, since T_2 is known to be at least in the hundred of picoseconds range, from absorption measurements. This is clearly a case of rapid spectral diffusion. The absorption spectra (Figs. 1a and 1c) can be fitted as a Voigt profile. The analytic expression of $S(\tau)$ obtained by FT contains characteristic times T_L and T_G, corresponding, respectively, to the Lorentzian and the Gaussian parts of the Voigt profile. These times have been extracted independently from the fits of absorption spectra and time-resolved signals and a very good agreement is obtained, as shown in Fig. 1.

At temperatures lower than 13 K, the τ variation of the signal exhibits a slowly varying component that becomes more and more intense upon further cooling. Results in the most concentrated sample are reported in Fig. 2. This slow component is certainly related to the dephasing time, and

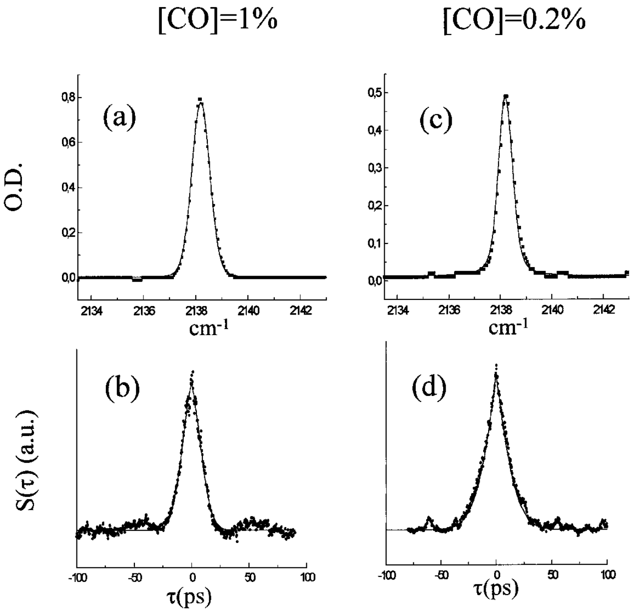

FIG. 1. (a),(c) Absorption spectra (squares) and their fits with a Voigt profile (lines); and (b),(d) time delay dependence of the TR-DFWM signal (dots) and its fit (lines) by the expression $S(\tau) = A\exp(-2\tau/T_L)\exp(-2\tau^2/T_G^2) + B$. $c = 10^{-2}$: (a) $T_L = 70$ ps, $T_G = 23$ ps; (b) $T_L = 64$ ps, $T_G = 20$ ps. $c = 2 \times 10^{-3}$: (c) $T_L = 42$ ps, $T_G = 34$ ps; (d) $T_L = 41$ ps, $T_G = 39$ ps.

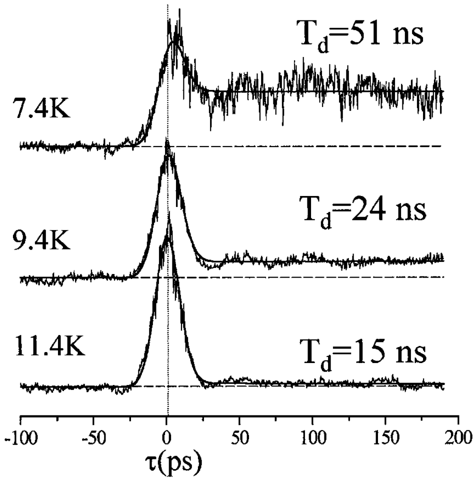

FIG. 2. Time delay dependence of the DFWM signal at different temperatures in the $c = 10^{-2}$ sample; experimental data with the fits from Eqs. (2)–(5) ($T_i = 17$ ps).

must have a τ dependence proportional to $\exp(-4\tau/T_2)$ with $\tau > 0$. There is no clear evolution in time in the short accessible range of a few hundred picoseconds given by the delay line (see Fig. 2). A lower boundary of 2 ns can thus be assigned to T_2, in good agreement with the spectral data [6,7]. At the lowest achievable temperature of 7 K, a signal is detected for any accessible delay τ, including hundreds of picoseconds before the origin $\tau = 0$ (see Fig. 3). The ratio of signal intensities immediately before and after the origin is identified with $\exp(-4\tau/T_2)$ where τ is set equal to the pulse sequence interval $\theta = 32$ ns. From the set of data recorded at 7 K, we infer a minimum value of $T_2 = 120$ ns. We conclude that the vibrational transition of CO in solid nitrogen has the narrowest homogeneous bandwidth ever observed in matrices.

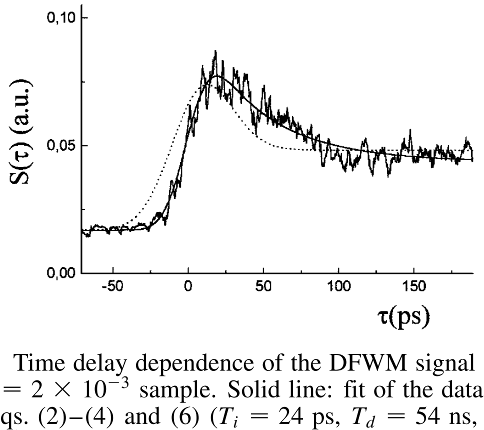

FIG. 3. Time delay dependence of the DFWM signal at 7.4 K in the $c = 2 \times 10^{-3}$ sample. Solid line: fit of the data according to Eqs. (2)–(4) and (6) ($T_i = 24$ ps, $T_d = 54$ ns, $\Delta\omega_d = 0.22$ cm^{-1}). Dotted line: best fit of the data according to Eqs. (2)–(5) ($T_i = 38$ ps, $T_d = 56$ ns) (the fitted T_i value is not in agreement with the absorption width).

The weight of the slow component in $S(\tau)$ is related to the probability that no spectral diffusion occurs during the θ time. Then Eq. (1) must be replaced by

$$P^{(3)}(\tau, t) \propto \int g(\omega)\gamma(\omega, \tau) \times \int p(\omega' \mid \omega) \exp(i\omega' t - t/T_2)\, d\omega\, d\omega', \tag{4}$$

where $p(\omega' \mid \omega)$ represents the conditional probability distribution to find an energy transfer from ω to ω' at the time θ after pulse 2 arrival. Let the probability per unit time for a molecule to undergo a vibrational frequency jump be represented by $1/T_d$, where T_d is regarded as a macroscopic characteristic diffusion time. Let us assume that the elementary energy transfer rate depends only on the final energy after the transfer. Then the probability per unit time for a molecule to jump from ω to ω' is denoted as $g(\omega')/T_d$ [11], and one obtains

$$p(\omega' \mid \omega) = [1 - \exp(-\theta/T_d)]g(\omega') + \exp(-\theta/T_d)\delta(\omega - \omega'). \tag{5}$$

With a Gaussian distribution $g(\omega)$ defined by its Fourier transform, $|\mathrm{FT}[g(\omega)]| = \exp(-t^2/T_i^2)$, the experimental curves are fitted with three independent parameters T_d, T_2, and T_i. A very good agreement is obtained when the $\mathrm{CO/N_2}$ concentration is $c = 10^{-2}$, as shown in Fig. 2. The dephasing time cannot be determined in these fits. It must be arbitrarily fixed, but both T_d and T_i values are nearly independent of this value, when fixed to be larger than 2 ns. The same value $T_i = 17$ ps is determined at every temperature. It corresponds to an inhomogeneous broadening of 1 cm^{-1} (FWHM), in good agreement with the experimental absorption profiles. The fitted diffusion times are in the nanosecond range, decreasing from 56 ns at 7.2 K to 15 ns at 11.4 K.

In the case of $c = 2 \times 10^{-3}$ samples, low temperature signals are not so well described by the above model, especially around $\tau = 0$ (cf. Fig. 3). In hole-burning experiments [7], it has been proved that energy transfer processes were dependent on the involved energy shift. In order to take this behavior into account in a phenomenological way, we replace Eq. (5) by

$$p(\omega' \mid \omega) = [1 - \exp(-\theta/T_d)]f(\omega - \omega') + \exp(-\theta/T_d)\delta(\omega - \omega'), \tag{6}$$

where the f transfer function depends only on the energy shift. From usual considerations on resonant energy transfer (Förster type process) [7,14], $f(\omega - \omega')$ is assumed to be a Lorentz function centered at ω. The experimental curves are then well fitted with a $S(\tau)$ expression calculated from Eqs. (2)–(4) and (6) as shown in Fig. 3. These fits involve a fourth parameter, the FWHM $\Delta\omega_d$ of $f(\omega - \omega')$. It represents the average energy shift of the molecules during the θ time. Starting from 0.22 cm^{-1} at 7.4 K, $\Delta\omega_d$ increases with temperature, but Eq. (6) matches experimental data only if $\Delta\omega_d$ is much smaller than the inhomogeneous bandwidth. When the temperature is increased ($T > 9$ K), all the frequencies involved in the inhomogeneous distribution have significant probabilities to be reached by energy transfer during θ so that Eq. (5) leads to better fits. Anyway, the diffusion time is essentially determined by the relative weight of the signal for long τ times and is roughly the same whether Eq. (5) or (6) is applied. The fitted T_d values are surprisingly very similar to that obtained in the more concentrated sample: from 64 ns at 7.4 K to 17 ns at 12 K.

The T_d values derived here correspond to average diffusion times. If the spectral diffusion is assumed to be mainly governed by dipole-dipole energy transfer processes, a concentration dependence in c^{-2} is expected for T_d. Our tens of nanosecond evaluation of T_d at $c = 2 \times 10^{-3}$ concentration is consistent with hole-burning experiments at $c = 2 \times 10^{-5}$ where a T_d value of hundreds of microseconds is expected [7]. Obviously, such a dependence cannot be extended to the case of $c = 10^{-2}$. Besides, while the energy transfer rate depends on an energy shift for $c = 2 \times 10^{-3}$ as observed in hole-burning studies at very low concentrations, such a dependence is not observed in the more concentrated samples at any temperature.

In summary, accumulated three-pulse photon echoes have been applied for the first time to the investigation of vibrational dynamics in a ground electronic state. It shows that a lot of information is contained in the picosecond time range although the characteristic times of the system T_1 and T_2 lie in the microsecond and in the hundreds of nanoseconds range, respectively. The vibrational dephasing time of CO in solid nitrogen is evaluated from time-resolved experiments for the first time and is found to be exceptionally long. The analysis of the observed spectral diffusion suggests that different elementary vibrational energy transfer processes might dominate, depending on the guest concentration in the matrix.

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