

SPECTRAL HOLE BURNING IN THE INHOMOGENEOUS ν_3 ABSORPTION PROFILE IN CH_3F ISOLATED IN MIXED Ar:Kr MATRICES

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Using two diode lasers, homogeneous spectral holes are burned and recorded in the inhomogeneous ν_3 absorption profile of CH_3F isolated in mixed Ar:Kr matrices. The Lorentzian hole width, fwhm, is $(9.1 \pm 0.5) \times 10^{-3} \text{ cm}^{-1}$ at 5 K and narrows to $(5.6 \pm 1) \times 10^{-3} \text{ cm}^{-1}$ at 9.35 K. The hole refilling time at 5 K is ≈ 10 s. The hole width is ascribed to dephasing by localized librational modes, the refilling to thermal reorientation of the molecule in the trap site.

1. Introduction

Infrared-induced isomerization, dissociation and bimolecular reactions, with various degrees of mode specificity have been demonstrated in molecules isolated in cryogenic rare-gas matrices [1]. Rates of vibrational energy transfer and relaxation of both T_1 - and T_2 -type processes in these systems are the critical data required for developing a fundamental understanding of the observed chemistry. The relevant systems are polyatomics with large densities of states and hence expected to possess short vibrational lifetimes – too short to make IR time domain measurements practicable. These were the motivations for the pioneering studies of Dubs and Günthard, who resorted to the frequency domain measurements of non-photochemical hole burning to obtain relaxation times in matrix isolated 1,2-difluoroethane [2]. Spectral hole burning experiments yield homogeneous lineshapes in inhomogeneously broadened absorption profiles. The homogeneous linewidth is inversely related to the transition-dipole autocorrelation time of the probed states: a measure of the fastest dynamical process responsible in relaxing (T_1) or dephasing (T_2) a given degree of free-

dom. While the technique offers a means of measuring fast processes, and hence is particularly useful in the IR, the distinction between T_1 - and T_2 -type processes and in the latter case identification of the source of dephasing are not usually straightforward. The temperature dependence of lineshapes, following the elegant theoretical models that have been developed recently, is the standard means of diagnosis [3].

Matrix isolated CH_3F was chosen for study as a model due to its apparent simplicity and the existence of a great deal of information on both spectroscopy [4,5] and vibrational dynamics of this system [6]. The vibrational relaxation time, T_1 , of $\text{CH}_3\text{F}(\nu_3)$ has been measured in rare-gas matrices by several groups by time-resolved studies [6–9]. Indirect evidence for hole burning in the ν_3 absorption profile in mixed Kr:Xe matrices has previously been reported and ascribed to molecule-cage reorientation [10]. Thus unique interpretations of homogeneous profiles could be expected. In this Letter, we communicate the results of our first measurements.

2. Experimental

Matrices were prepared by pulsed deposition of the premixed gas sample $\text{CH}_3\text{F}:\text{Ar}:\text{Kr}$, 1:2900:4350 onto a substrate held at 17 K. A closed-cycle cryostat

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(Air Products Displex 202) fitted with a CsI substrate was used to obtain transmission spectra with an FTIR spectrometer. A liquid-helium transfer cryostat (Air Products Helitran) fitted with a polished copper substrate was used for the hole burning studies. Two temperature sensors were used: a gold:chromel thermocouple fixed at the cryotip and a calibrated diode sensor fixed directly on the copper substrate at opposite ends from the cryotip. For temperatures between 5 K and room temperature the two sensors were in agreement within the specified accuracy of the diode, ± 0.1 K. A temperature gradient across the substrate is observed for temperatures below 5 K. The results reported here pertain to the 5–10 K range. The thickness of the matrix, typically 10–30 μm , was calibrated by monitoring fringes from a reflect He:Ne laser [11].

Two lead salt diode lasers with independent temperature and current control were used for the hole burning studies: one in fixed frequency mode (burner), and one in scanning mode (scanner). The two beams were combined with a ZnSe beam splitter and focused with a single ZnSe lens on the copper substrate at 45° (spot size at substrate ≈ 200 μm). The reflected beams were collected with a AgBr lens and focused on a cooled Hg:Cd:Te detector. The laser scan was controlled by current modulation at a rate of 800 Hz. Non-linearities in the scan prevented the usefulness of higher rates. The detector output was amplified and digitized with a 100 MHz digitizer and averaged to improve S:N ratio. Both hole burning and refilling proceed on a timescale of ≈ 10 ns in these systems. Thus while the two lasers are of comparable power (≈ 0.2 mW), the contribution of the scanner beam to hole burning is negligible. Typically ≈ 10 spectra could be recorded during the growth or disappearance of the hole with 1000 averages per spectrum (1.5 s per scan and storage time). These were consistent with direct single-beam measurements. The latter were accomplished by monitoring the increase in transmission of the burner as a function of time, using lock-in detection.

3. Results

The ν_3 absorption of CH_3F at 10 K is centered at 1035.9 cm^{-1} in Kr matrices, and at 1040.0 cm^{-1} in

Ar [4,5]. The ν_3 absorption in the mixed Ar:Kr host is shown in fig. 1a, where it can be seen that this inhomogeneous absorption spans the wavelength range of the pure hosts. The linewidth could not be appreciably altered by annealing cycles between 5 and 30 K. The lineshape is clearly inhomogeneously broadened. The guest CH_3F molecules are isolated in anisotropic cages composed of all statistically possible combinations of nearest neighbours; all Ar to all Kr. The choice of this mixture was strictly based on the fact that it provided an absorption line coincident with a range in which we possessed two well-behaved laser diodes.

The diode laser frequencies were calibrated by the gas phase absorption of CH_3F . The $^{\text{Q}}\text{P}(7)$ absorption, which is coincident with the matrix line is shown in fig. 2b. The calculated values of the different K components are also shown. The spectroscopic parameters are from laser Stark studies, and are accurate to four decimal places [1,2]. Reliable single-

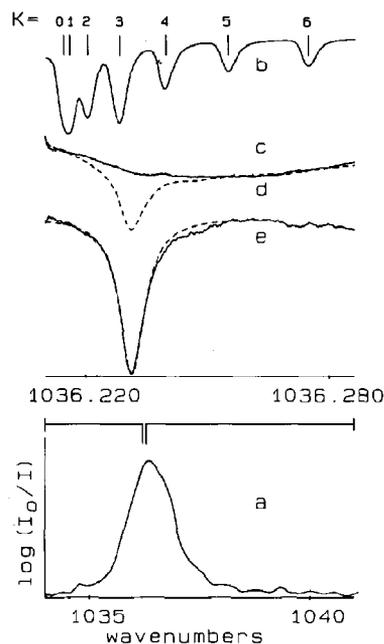


Fig. 1. The lowest trace, trace a, is an FTIR absorption spectrum of $\text{CH}_3\text{F}(\nu_3)$ in a mixed host matrix (1:2900:4350, CH_3F :Ar:Kr), recorded at 12 K. The upper traces are recorded with diode lasers: (b) the gas phase $^{\text{Q}}\text{P}(7)$ absorption of CH_3F used for calibration purposes, (c) background scan with burner off, (d) hole profile when burner is on, (e) ratio (d)/(c) and the fit to a Lorentzian of width (fwhm) 9.1×10^{-3} cm^{-1} .

frequency operation of both diodes was only limited to a narrow range $\approx 0.2 \text{ cm}^{-1}$ around the gas phase absorption. A typical scan with the burner off is shown in fig. 1c. The same range scanned with the burner laser on is shown in fig. 1d, and the ratio of the two scans is shown in fig. 1e. The hole profile seen in fig. 1e is well fit with a single Lorentzian as shown in the figure.

Holes could be burnt throughout the absorption profile at temperatures below 10 K. In all cases similar profiles were observed. The hole profiles as a function of temperature are illustrated in fig. 2a. The depth of the hole decreases as the temperature is increased such that above 10 K these sharp holes cannot be sustained. The observed widths of holes are plotted in fig. 2b as a function of temperature. The large error bars are due to the poor baselines that can

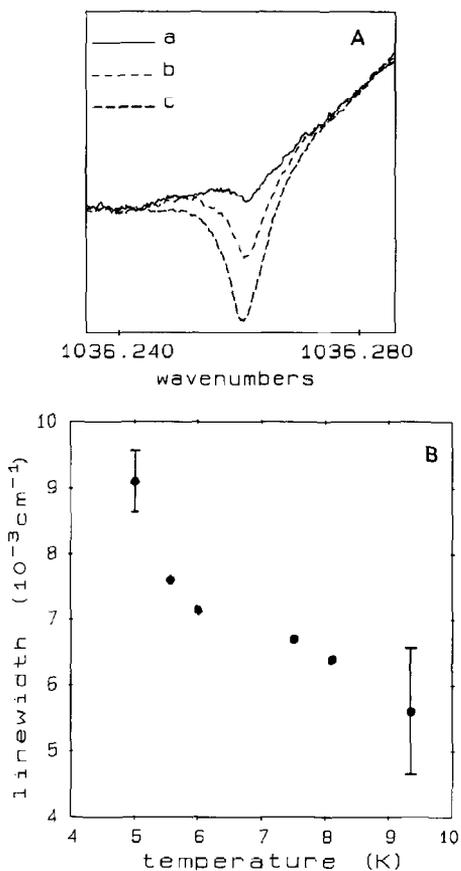


Fig. 2. (A) Hole profiles at three different temperatures (without ratioing of background): (a) 9.35 K, (b) 7.1 K, (c) 6.0 K. (B) Hole widths (fwhm) versus temperature.

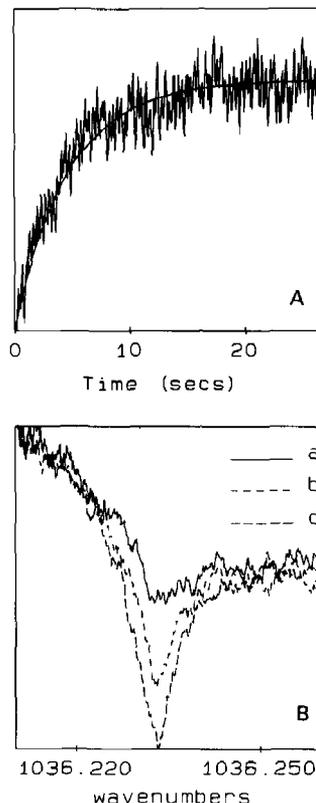


Fig. 3. (A) Transmission as a function of time. The hole burning is nearly exponential with a risetime of ≈ 10 s. (B) Disappearance of hole profiles. The spectra were recorded 8, 4 and 0 s after turning off the burner laser in (a), (b) and (c) respectively (recording time = 1.2 s).

be seen in fig. 2a. The time evolution of holes are summarized in figs. 3a and 3b. In fig. 3a the increase in transmission of the burner is shown as a function of time. The time evolution can be well fit with an exponential rise of 10 s. The disappearance of the hole upon blocking of the burner is shown in fig. 3b. The sequence is from a continuous series of scans, the scan time of each spectrum is 1.2 s.

4. Discussion

Since the observed hole profile is well approximated by a single Lorentzian, see fig. 1, the transition dipole autocorrelation can safely be related to a single-exponential decay:

$$\langle \nu_{0,3}(0) \nu_{0,3}(t) \rangle = A \exp(-|t|/\tau) \quad (1)$$

and the correlation time, τ , can be obtained from the Lorentzian linewidth as $\tau = 1/\pi c \Delta\nu$ (fwhm), where $\Delta\nu$ (fwhm) is the full width at half maximum of the Lorentzian in wavenumbers: $\tau = 3.7 \pm 0.3$ ns. The vibrational relaxation time T_1 of $\text{CH}_3\text{F}(\nu_3)$ is 3.0 ± 0.4 and 11.5 ± 1.3 μs in Ar and Kr matrices, respectively. In mixed rare-gas solids, decay times intermediate between those of the pure host values are observed [10]. A mild temperature dependence, commensurate with a one-phonon assisted decay, is observed for these relaxation times such that at temperatures below 10 K the lifetimes remain essentially constant. The correlation times obtained from the hole linewidths are three to four orders of magnitude shorter and therefore could not possibly be due to population relaxation from the excited state. The observed correlation times can then confidently be assigned to dephasing, a T_2 -type process.

A distinction can be made between two sources of dephasing: coupling of the molecular vibration to bulk phonons or to local phonons. In the 5–10 K range, based on the temperature dependence of the hole linewidth, the first possibility can be rejected. Coupling to bulk phonons should necessarily increase the linewidth, or shorten τ , as the temperature is increased with a very steep temperature dependence [3] ($\propto T^7$). From earlier studies of temperature dependence of linewidths, the effect of bulk phonons can be discerned to dominate above 10 K. As an example, in well annealed Kr matrices, the ν_3 absorption linewidth broadens from ≈ 0.1 to 1 cm^{-1} in the temperature range [5] of 10–45 K. Inhomogeneous contributions to the low-temperature linewidths cannot be eliminated in those FTIR studies; however, the high-temperature lineshapes are clearly homogeneously broadened. In the present hole burning studies, we can surmise that the depth of the hole is determined by the relative intensities of the zero-phonon line and the phonon sideband [13], hence the disappearance of the hole at 10 K is due to the dominance of bulk dephasing. The linewidth of the homogeneous hole is then to be ascribed to coupling to localized modes. The likely candidates are the librational degrees of freedom originating from the frustrated rotations of the trapped molecules. A dephasing time of $\approx 10^{-9}$ s is indeed long and implies a poor coupling between the molecular vibration and hindered rotations. Even longer dephasing times are

estimated for CO and NO in rare-gas and N_2 matrices [14].

In an earlier study of CH_3F in Kr matrices, the fate of rotational degrees of freedom upon trapping in the solid cage was considered along the lines of the Devonshire model [5]. It was established that the collapse of the rotational structure to yield a single line for the ν_3 absorption could be rationalized by assuming a barrier to rotation of the molecular axis of ≥ 130 cm^{-1} . While little could be learned about the CH_3 spinning motion, it is safe to assume that it too is somewhat hindered and could in principle couple to the ν_3 vibration which is a purely C–F stretching mode. The hole filling times can be well rationalized as ground-state reorientation of the molecular axis. If we assume a frequency, ν , of 10^{13} s^{-1} for collisions with this barrier, then a 10 s lifetime would imply a barrier height of $V^J = -kT \ln \tau/\nu \approx 100$ cm^{-1} , in agreement with the previous estimate of the barrier to rotation of the molecular axis [5]. Temperature dependence studies of refilling times could yield accurate Arrhenius parameters for this process. The presently available data do not allow a more accurate determination.

The observed temperature dependence of hole-widths in fig. 2b cannot be reconciled with standard models of dephasing by harmonic local modes – in all cases a broadening of the line as the temperature is increased is to be expected [3]. Given the limited data and their associated error bars, a reliable law for the observed temperature dependence in the present case cannot be extracted. However, the trend, namely that the linewidth broadens as the temperature is lowered, is believed not to be due to any experimental artifact. This behavior is reminiscent of motional narrowing. In the usual stochastic formulation of dephasing for a two-level system coupled to a bath, the linewidth of the transition, $1/T_2$, is related directly to the correlation time, τ_c , of the fluctuating energy [15,16]. Adopting the notation of ref. [16], the linewidth is given by

$$\frac{1}{T_2} = \frac{a^2 \langle \phi^2 \rangle}{\hbar^2} \tau_c, \quad (2)$$

in which a is the linear coupling constant to the random variable, $\phi(t)$. As long as the fluctuation correlation time is short, $\tau_c \ll T_2$, a homogeneous linewidth is to be expected and line narrowing ex-

pected as τ_c is shortened. We note that in the present mixed host solids, the guest molecules are isolated in locally anisotropic potentials. Thus even for a perfectly rigid case, the molecular frustrated rotations create a rapidly fluctuating field to be experienced by the molecule. It is therefore attractive to associate τ_c with the rotational period of the nearly free spinning motion of the methyl group; in which case a linewidth proportional to $T^{-1/2}$ would be expected. Within the indicated error bars, the experimental points of fig. 2b can be fitted with this law.

Finally it is worth noting that the linewidths measured in our experiments are very similar to that reported by Dubs and Günthard for difluoroethane in argon. This casts some doubt on their interpretation of the lifetime as that of T_1 decay. In the interpretation presented here, there would be little difference in the T_2 times of CH_3F and $\text{CH}_2\text{F}-\text{CH}_2\text{F}$. In both cases the C-F stretch is the excited vibration and the local modes of interest would be librations of similar groups in the trap site. If indeed T_2 was measured by Dubs and Günthard, the implication would be that the molecular vibrational relaxation is much longer.

5. Conclusions

Hole burning studies can be conveniently conducted with low-power diode lasers in matrix isolated molecules. Such experiments have a great promise in characterizing cage-molecule interactions.

The choice of matrix isolated CH_3F , a system in which vibrational relaxation processes are well understood, has allowed the direct interpretation of the homogeneous width of the hole as due to dephasing. The slow hole burning or refilling times of ≈ 10 s are ascribed to rotation of the molecular axis, while the nanosecond dephasing time to coupling to the localized librational degrees of freedom. The inverse temperature dependence is consistent with motional narrowing due to rotation of the guest molecule in the anisotropic traps. Systematic studies in neat and mixed matrices, and more extensive temperature- and power-dependent measurements in better characterized solids are planned to elucidate

the preliminary results and interpretations presented in this report.

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