

VIBRATIONAL RELAXATION AND REORIENTATION PROCESSES OF CH₃F ISOLATED IN MIXED Kr/Xe MATRICES

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The relaxation of CH₃F isolated in mixed Kr/Xe matrices has been studied as a function of composition and temperature. For a specific composition reversible changes in relaxation rate are observed as a function of duration of irradiation. It is concluded that changes in rate result from a change in the molecule-cage environment.

Vibrational energy transfer studies of molecules isolated in inert-gas matrices are fairly recent [1-3]. Despite this, a variety of theories have been developed in an effort to understand vibrational relaxation processes in these media. As a result, a fairly uniform picture of relaxation dynamics has begun to emerge. It is, in general, agreed that for molecules with high-lying vibrational levels and small moments of inertia, relaxation via transfer of energy to the molecular rotations is important. A coupling to lattice phonons is invoked as an integral part of this process [1,4]. Studies of the temperature dependence of relaxation rates and the results of isotopic substitution experiments have been in accord with the predictions of these theories. However, the detailed nature of the coupling between the internal vibrations of the molecule and its rotations is not yet well understood.

For example, the dependence of relaxation rates on the nature of the inert-gas matrix is not well explained. The relaxation rate of HCl increases in different inert-gas matrices in the order Ar, Kr, Xe [5]. For CH₃F, the order is reversed and the deactivation rate in Ne is inbetween that of Ar and Kr [6]. Factors that may influence these variations are: the interaction potential between the molecule and cage atoms, the asymmetry of the cage and the translational motion of the molecular center of mass in the matrix cage.

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It is expected that the study of relaxation rates of a given molecule as a function of composition in mixed inert-gas matrices will shed light on the relative importance of the above factors affecting vibrational relaxation in a given system. Such studies have been reported for NH (A ³Π, *v* = 1) [7], OH (A ²Σ⁺, *v* = 1) [8], ¹⁶⁻¹⁸O₂ (C ¹Σ_u⁻, *v* = 2 and *v* = 1) [9] and CD₃F in mixed Ar/Kr matrices [10]. In this communication we report on our studies of CH₃F in mixed Kr/Xe matrices.

The overall observation with respect to the dependence of relaxation rate on the composition of the matrix are very similar to those previously reported in ref. [10]. However, in a particular concentration regime — 1 : 10 000 : 2 000 CH₃F : Xe : Kr, a reversible change in the measured relaxation rate is observed as a function of the duration of Q-switched laser excitation. After cessation of irradiation, the recovery of rates to their pre-excitation values occurs on the time-scale of minutes.

The experimental apparatus has been previously discussed [11]. Briefly, *v*₃ of CH₃F is excited by a low-power (1-2 mJ, fwhm = 0.5-1 μs) Q-switched CO₂ laser and emission is observed from 2*v*₃. 2*v*₃ is populated by V-V energy transfer from *v*₃ [11]. The matrix temperature is monitored by a thermocouple gauge and no bulk heating is observed in these experiments. The experiments were performed in dilute matrices, *M/R* = 12000, where *M* is the total amount of inert gas.

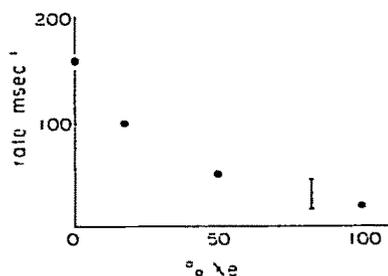


Fig. 1. Relaxation rate of $2\nu_3$ of CH_3F at 20 K in a 12 000 : 1, (Xe + Kr)/ CH_3F matrix as a function of mole% Xe. The vertical line shown at the 80% Xe composition spans the range of rates measured as a function of irradiation time.

The $2\nu_3$ relaxation has previously been reported for pure Kr and Xe matrices as a function of M/R ratio and temperature where it was shown that $2\nu_3$ relaxes at nearly twice the ν_3 relaxation rate due to the V-V mechanism which leads to its population [11]. In fig. 1 the dependence of the $2\nu_3$ relaxation on the composition of mixed inert-gas matrices is depicted. A linear dependence on composition would be expected based upon simple pairwise additive interaction considerations. If asymmetry of the cage dominated the relaxation process then the dependence of relaxation rate on composition would be expected to show a curve above the line joining the two end points. Thus, the observed dependence has to be explained as a sum of effects which include the change in cage size and variation of the overall molecule-cage interaction potential. It is conceivable that CH_3F could selectively crystallize in Xe enriched areas or cages but this appears to be an unlikely explanation for the observed effect.

For the 10 000 : 2000 composition, the measured rate of relaxation varied as a function of length of time of laser irradiation. This dependence is depicted in fig. 2. The experimental points of fig. 2 were obtained by irradiating the matrix for ≈ 2 h, which was more than sufficient to guarantee constancy of observed rates on further irradiation, then blocking the laser for the length of time shown on the abscissa and measuring the relaxation rates. The measurement time was limited to ≤ 15 s. The observed variation of rate is completely reversible and reproducible in the same sample at different times and in different samples of the same composition. Finally, within the experimental

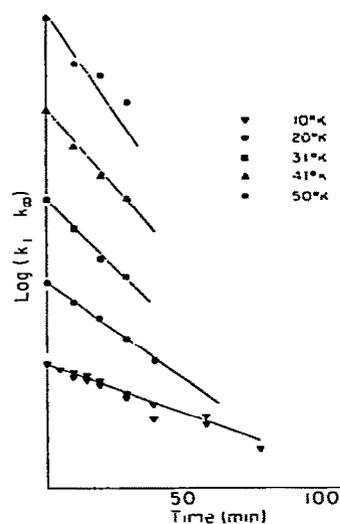


Fig. 2. The $2\nu_3$ relaxation rate is plotted at different temperatures as a function of dark time — the length of time the laser was blocked prior to the measurement. The ordinate is the log of the rate at time t minus the rate at infinite time (sufficiently long that the rate no longer changes). The ordinate is in arbitrary logarithmic units with the zero time origin of each temperature relaxation curve arbitrarily displaced from the curves of other temperatures. As indicated in the text, the sample was irradiated prior to the dark period for a sufficient time for the relaxation rate to reach its k_∞ value.

accuracy of the measurements, $\approx 5\%$, this effect was not observed in any of the other compositions.

The slow process leading to a change in observed rates on or following laser excitation cannot be attributed to either bulk heating or bulk diffusion. Bulk heating is eliminated based on the fact that no temperature rise is observed. Furthermore if bulk heating occurred, it would be expected to occur in all compositions. Bulk diffusion can be eliminated based on the fact that the process is reversible and can be repeated in a given sample with excellent reproducibility of measurement. The observations can be explained by a molecule-cage reorientation process. This model would imply that the observed slow change in the relaxation rate is associated with a reorientation of the molecule in its ground vibrational level or a reorientation of the matrix cage. It is conceivable that, as part of this process, rearrangement of the cage occurs by diffusion of atoms from neighboring lattice sites. In a

separate publication we were able to successfully interpret the experimental spectra of ν_3 of CH_3F in pure inert-gas matrices by an electrostatic model of a hindered symmetric top tumbler in an octahedral field [12]. The estimated barrier to tumbling, V^J , in Kr matrices was of the order of 80 cm^{-1} , or a well to hill height of $\frac{2}{3}V^J$ of the order of 130 cm^{-1} . In such a model, the molecule has access to the many wells of the potential by direct or phonon-assisted tunneling processes. In addition to the well to hill height, E_A tunneling rates are very sensitive to the symmetry of the potential [13]. Thus it may be possible to interpret the observed minute timescale process as tunneling in a strongly asymmetric multiwelled potential [13]. Whether the observed timescale of minutes can be justified on the basis of such a tunneling model, or is more characteristic of local diffusion and cage rearrangement processes, will be the subject of further investigation.

The different relative orientations of the ground-state molecule are associated with different relaxation rates of the excited-state molecule. A detailed kinetic model which will hopefully provide the actual relaxation rates of the excited states corresponding to different orientations of the ground-state molecule and which will lead to a determination of excited-state reorientation rates is under development and will be reported on in the future. Qualitative predictions of a simple kinetic model indicate that our observations are compatible with the aforementioned slow reorientation of a ground-state CH_3F molecule relative to its cage and a more rapid reorientation of excited-state CH_3F which occurs on the relaxation timescale. This latter implication would provide direct experimental verification of the role of rotations in the relaxation of CH_3F . The fact that the slow reorientation is not observed in compositions studied other than 10 000/2000 may well be due to the necessity of very specific molecule-cage interactions and/or conformations for reorientation to occur on the observation timescale. The above observations and conclusions are also compatible with a spectroscopic study of matrix-iso-

lated CH_3F where the spectrum can be well reproduced by the imposition of a high barrier to tumbling for CH_3F in the ground vibrational state [12].

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