Temperature-Reversible Equilibria and Exchange among Trapping Sites for SOF₂ **Isolated in Noble Gas Matrices**

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High-resolution IR studies have been made for thionyl fluoride isolated in argon, krypton, and xenon matrices in order to probe matrix-molecule interactions and dynamics. Argon matrices show surprisingly complex site structure with at least five distinct monomer sites, whereas krypton and xenon matrices show two and three dominant trapping sites, respectively. The additional sites observed in argon are attributed to three-atom substitutional cages which are unstable in krypton and xenon matrices. The relative intensities of the various monomer sites in krypton and especially xenon change dramatically and reversibly with temperature, indicating that the inequivalent sites are in equilibrium. In addition, the frequency positions for the various sites merge and the lines broaden as temperature is raised to give single symmetric lines in the high-temperature limit. We attribute the collapse of the site structure at elevated temperatures to a facile exchange among inequivalent sites.

Introduction

High-resolution infrared spectra of molecules trapped in dilute inert gas matrices have provided new insights into guest-host dynamics and interactions.¹⁻⁶ Using FT IR methods with resolution of ca. 0.04 cm^{-1} we have shown that the rather broad bands observed for many matrix isolated molecules comprise a wealth of fine structure characteristic of multiple trapping sites.⁴⁻⁶ Simple host lattices such as the cubic inert gas solids can provide a remarkable number of unique environments for a diluent giving rise to distinctly different frequencies for a given fundamental mode of vibration and, at times, frequency splittings of degenerate modes. For example, SF_6 in argon shows evidence for at least seven distinct monomeric trapping sites.^{4,5} Most of these different trapping sites correspond to unique packing arrangements of the guest molecule and the surrounding host matrix atoms in substitutional trapping cages which are nominally the same.

In studying the temperature dependence of the absorption spectra of matrix isolated molecules, we^{5,6} have observed sharp bands (full width at half-maximum (fwhm) of less than 0.1 cm⁻¹) reversibly broaden and merge as temperature is raised, much like magnetic resonance spectra of systems undergoing chemical exchange. For SF_6 isolated in argon⁵ and xenon⁷ matrices, bands showing motional collapse at elevated temperatures can definitively be assigned to site symmetry split components of the triply degenerate asymmetric stretch, v_3 . The simplest picture is that molecules trapped in low-symmetry sites undergo exchange among equivalent sites (within the same cage) on the vibrational time scale. A more appropriate explanation is that increasingly rapid structural fluctuations result in phase exchange among environmentally split

components. It is often observed that other bands characteristic of different sites show line broadening suggestive of what Fischer and Lauberau⁸ refer to as direct vibrational dephasing involving the phonon bath. The dynamics which give rise to the temperature dependence of the absorption spectra can be linked to phonon-optic mode coupling which also controls vibrational energy transfer and relaxation.

The majority of our studies have focused on high-symmetry systems such as SF_6 , SeF_6 , SiF_4 , $Ni(CO)_4$, and CO where only one or two fundamentals can be probed in the mid-IR. In a recent study of CH_3F^9 the opportunity to probe all six fundamental vibrations provided information that could not be obtained from studying one or two modes alone. It is now clear that the temperature-reversible spectral changes are strongly mode dependent as is consistent with recent theories^{10,11} of vibrational dephasing.

The present study of SOF₂ in argon, krypton, and xenon matrices was undertaken to further clarify matrix-molecule interactions for an asymmetric molecule with a dipole moment. Four fundamental modes which are all nondegenerate can be probed in the mid-IR. Further, SOF_2 provides a system for which isotope effects can be studied. Earlier studies,⁵ particularly that of SF_6 in xenon,⁷ have shown remarkable isotope effects in the low-temperature spectra and their temperature-reversible changes. We will show that SOF_2 occupies multiple trapping sites in argon, krypton, and xenon with clear evidence for temperaturereversible changes in the equilibrium among trapping sites for the latter two inert gas host lattices. Temperaturedependence studies have also shown evidence for rapid exchange among inequivalent trapping sites for krypton and xenon matrices.

Experimental Section

Infrared spectra were obtained at ca. 0.04-cm⁻¹ resolution by using a Nicolet series 7000 FT IR equipped with a liquid-N₂-cooled MCT detector. The matrices were deposited continuously at a rate of ca. 0.22 torr L/min from premixed gases onto a highly polished copper block atta-

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ched to a Displex closed cycled helium cryostat (Air Products). Transmission spectra were obtained by using Harrick reflectance optics to reflect the beam off the copper substrate. Temperature control was maintained by using a silicon diode and associated controller (Air Products). Unless otherwise stated, argon, krypton, and xenon matrices were annealed at 30, 40, and 60 K, respectively. Some experiments were performed by using a xenon overcoat¹² on krypton or argon matrices in order to stabilize the matrices for higher-temperature study or annealing. Typically, 10 torr L of xenon was deposited onto an existing matrix at 30 K and a rate of 0.22 torr L/min.

Recent experiments with SF_6 isolated in xenon matrices have shown that for certain trapping sites the SF_6 molecule is preferentially oriented depending on the deposition conditions.¹³ In order to ascertain whether or not SOF_2 preferentially orients, experiments have been carried out using a KCl substrate in a normal transmission arrangement. Xenon matrices with $Xe/SOF_2 = 1000$ were deposited at 35, 30, and 10 K. Spectra were obtained before and after 60 K annealing with the substrate oriented perpendicular to the plate and with the substrate rotated 45° about the vertical axis relative to the IR beam. While no orientational effects were found for matrices deposited at 35 or 30 K, there was evidence for preferred orientation in the case of the 10 K deposits (below).

Thionyl fluoride was synthesized in a stainless-steel vacuum line by the fluorination of SCl_2 and S_2Cl_2 to give SF_4 which was subsequently hydrolyzed to SOF_2 . In order to remove moisture from the vacuum line, we treated all surfaces with 50–80 torr of UF_6 at room temperature for several minutes followed by overnight evacuation of the system. Chlorine (liquid carbonic) was purified by condensing at -78 °C and pumping off volatile impurities. Uranium hexafluoride was supplied by the Oak Ridge National Laboratory and was purified by trap-to-trap distillation with a trace of HF, the only remaining impurity. The Los Alamos National Laboratory's ICONs program supplied the H_2 ¹⁸O. Sulfur was placed in a Monel reaction tube, evacuated, and then reacted (92 °C) with chlorine in a twofold excess to give 100% conversion to SCl₂. Excess chlorine was removed by cooling the vessel to -98 °C and evacuated. The resulting mixture (most likely SCl₂ and S₂Cl₂) was fluorinated at 92 °C by using an excess of UF_6 . The evolution of Cl_2 was followed by monitoring the pressure; after a maximum was reached, the vessel was cooled to -98 °C and the volatile species were transferred to another Monel tube where Cl₂ was removed by Hg. The SF₄ produced was analyzed for impurities by IR and mass spectrometry. Yields were in the range 69-78% based on sulfur with SOF_2 concentrations of 3.5-6%. SF₄ was condensed into a Kel-F tube containing excess H₂O and warmed to room temperature. After several hours, the tube was cooled to -98 °C and $SOF_2 + HF$ were transferred to another vessel containing NaF. The mixture was warmed to room temperature to allow HF adsorption by NaF and then cooled to -98 °C; the remaining SOF₂ was transferred to a Monel tube for storage. Yields were in the 60-70% range.

Results and Discussion

The vibrational spectrum of thionyl fluoride has been studied extensively,¹⁴⁻¹⁷ and a harmonic force field has been

refined by using the fundamental frequencies of the normal species and centrifugal distortion constants.¹⁸ Noftle et al.¹⁷ have recently reported isotopic shifts which are consistent with Lucas and Smith's GVFF.¹⁸ The molecule has C_s symmetry. Of the six singly degenerate fundamentals four are a' in symmetry (ν_1 , S-O stretch; ν_2 , S-F stretch; v_3 , F-S-O deformation; v_4 , F-S-F deformation) and two are of a" symmetry (ν_5 , S-F antisymmetric stretch and ν_6 torsion). It has been possible to probe four of the fundamentals $(v_1, v_2, v_3, and v_5)$ in the present study. The normal isotopic species shows a strong Fermi resonance between ν_1 and the combination mode $\nu_2 + \nu_3$ giving rise to two absorption bands of nearly equal intensity split by ca. 10 cm⁻¹ in the gas phase.¹⁵ We have employed the $S^{18}OF_2$ isotopic species, which does not exhibit the same coupling, to probe the dependence of Fermi resonance on the nature of the trapping site.

Thionyl fluoride, which is roughly the same size and shape as PF_3 ($R_{S-F} = 1.585$ Å, $R_{S-O} = 1.413$ Å, F-S-F =92.8°, see ref 18) can be approximated by a pyramid with base side length of ca. 5.0 Å and height of 4.2 Å when van der Waals distances are included. In contrast, three-atom substitutional sites in argon, krypton, or xenon have triangular shapes with bases of roughly 7.5, 8, and 8.6 Å, respectively, and heights of 3.76, 4, and 4.3 Å. It is likely that for each matrix, in particular krypton and xenon, a three-atom substitutional site is too large for SOF₂. In contrast, a two-atom substitutional site could accommodate SOF_2 with allowance for distortion of the host matrix atoms near the trapping site. The relative shapes and sizes of SOF_2 and a two-atom substitutional site are such that two of the three F-S-F, O-S-F angles will be bisected by host atoms. Examination of models suggests that there are several possible packing arrangements for SOF_2 in a three-atom substitutional cage and fewer in a two-atom substitutional environment. The only allowed point symmetries for either two- or three-atom cages are C_1 and C_s ; as a result, every discrete monomeric absorption band corresponds to a distinct trapping site.

Site Structure. The monomeric absorption bands in the v_1 , v_2 , and v_5 regions for an Ar/SOF₂ = 5000 matrix deposited at 9 K before and after annealing (30 K) are shown in Figure 1. The number of peaks observed as well as the relative intensities are quite sensitive to deposition conditions. The results show a surprisingly high number of trapping sites, each with different formation and degradation energetics. The peak patterns observed for ν_1 , ν_2 , and v_5 are surprisingly similar and, when combined with frequency shifts observed in temperature-dependence studies, suggest a one-to-one correlation of peaks in each mode with distinct trapping sites.

Spectral changes observed upon annealing or changing temperature or deposition conditions suggest that the several trapping sites of high, intermediate, and low frequency can be grouped into three subsets. The site represented by the single sharp peak with intermediate frequency in each mode region disappears irreversibly upon annealing at ca. 25 K. The remaining features change slightly, and the lower-energy sites appear to gain intensity, with annealing. For a given mode, the lower-energy peaks all increase in frequency as temperature is raised (see ν_5 in Figure 2) while the higher-energy doublet decreases in frequency.

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801.2

800.5

738.9

738.1

530.8

799.2

735.1

528.2

808

747

530

ν,

ν,

ν,

v,

V₃

TABLE I: Observed Absorption Frequencies in cm⁻¹ for SOF₂ in Rare Gas Matrices and in the Vapor State

795.7

795.3

733.2

732.7

?

797.8

796.9

735.4

734.5

530.1

797.7

797.0

735.2

734.5



Figure 1. Matrix of Ar/SOF₂ = 5000 before (upper curves) and after (lower curves) annealing at 30 K. Spectra of ν_5 (A), ν_2 (B), and ν_1 (C) regions at 10 K.

Argon matrices deposited at 18 K show several new features among the low-energy set at the expense of the intermediate-frequency peaks and to a lesser extent the high-frequency doublets. It is clear from several studies



793.3

792.8

730.4

729.7

528.7

Figure 2. Temperature dependence for $Ar/SOF_2 = 5000$; ν_5 of SOF_2 after 30 K annealing.

that the distribution of peaks and relative intensities are more sensitive to deposition temperature than annealing.

The situation for krypton and xenon matrices is simpler as both show evidence for doublets resembling those of the high-frequency set in argon. For xenon and krypton matrices annealing and changing the deposition temperature only affect the line shapes and distribution of the peaks and do not give rise to new absorptions. Two distinct sites are present in all temperatures for krypton whereas xenon shows evidence for three distinct sites (below).

Correlation of frequencies for the various matrices provides further evidence that the sites in krypton and xenon matrices are closely related to those giving rise to the high-frequency doublets in argon. Frequencies for the various monomer sites for ν_1 , ν_2 , ν_3 , and ν_5 are given in Table I. Examination of the table shows that the frequencies in set A for argon are roughly 3-5 cm⁻¹ higher for the stretching modes than those of krypton, which are a few cm^{-1} higher than those of xenon. Noting that all the observed frequencies in each matrix are lower than those of the gas phase¹⁵ (included in Table I), the systematic drop in frequencies for set A in proceeding from argon to xenon suggests similar packing arrangements. Note, however, that the frequencies of sets B and C in argon are the same as or lower than those of set A in krypton, indicating a very different packing arrangement. On the basis of their absence in krypton and xenon matrices and of their dependence on annealing and deposition conditions, sets B and C in argon are attributed to three-atom substitutional sites. The contention is that these sites become too unstable in the larger krypton or xenon lattices owing to larger differences in their size relative to SOF_{2} . The single, sharp intermediate feature (B) is attributed to a high pseudosymmetry arrangement of SOF_2 where the sulfur atom is located in the center of the three-atom substitution cage. Upon annealing, this site disappears irreversibly. The sites constituting set A in each matrix

793.3

793.0

730.4

729.9

528.7 528.6 we attribute to a two-atom substitutional cage.

The frequency spread for each of the stretching modes for the sites in argon matrices is quite large, showing that environmental perturbations of the internal modes for the trapped molecule are substantial. It is somewhat suprising that three-atom substitutional sites in argon have much lower stretching mode frequencies than two-atom sites. This difference is explicable in terms of weaker, repulsive van der Waals potentials for three-atom substitutional sites relative to two-atom sites. Strong, attractive potentials would be expected to shift the stretching mode frequencies to the low-energy side of the gas-phase values while repulsive potentials should have the opposite effect.¹⁹ Given the complexity of the number of sites in argon, it is clear that subtle changes in packing structure give rise to entirely different discrete absorption bands.

Studies of molecule orientational effects in xenon provide further information concerning site stability and structure. Matrices with $Xe/SOF_2 = 5000$ deposited at 10 K on a salt window show evidence for preferred orientation of molecules in one site; the intensity of one of the observed S-O stretch peaks is quite sensitive to rotation of the sample relative to the IR beam. Matrices deposited at 30 K show no evidence for preferred orientations of trapped molecules. Similar observations were obtained for SF_6 in xenon where it was argued that the preferred molecular orientation results from a surface effect.¹³ Essentially, the xenon crystals grow with a particular crystallographic plane, (111),²⁰ oriented parallel to the substrate surface. The arrangement of host lattice atoms in the growth plane fixes the orientation of trapping for the different molecules for certain sites. The existence of molecular orientation in xenon matrices and the observation that these effects diminish as the deposition temperature is raised, along with the striking change in site structure for set C in argon, all show that the types of sites present in a matrix and their structures are largely controlled by deposition conditions.

Temperature-Reversible Changes. One of the primary objectives of the present work was to investigate the possibility of rapid site-to-site exchange among inequivalent trapping sites. Earlier studies of degenerate modes for $\rm SF_6^5$ and $\rm SeF_6^6$ in inert gas matrices have shown that exchange among equivalent sites can occur on the vibrational time scale giving rise to motional averaging of sharp bands as temperature is raised. Our approach has been to follow spectral changes as a function of temperature for matrices which have been carefully annealed so as to remove any irreversible effects.

For argon matrices the frequency positions for sites in sets A and C (B cannot be followed as it is lost irreversibly upon annealing) change considerably as temperature is increased (results for ν_5 are shown in Figure 2). The centroids of frequency of the two sets merge relative to one another as temperature is raised, although spacings among peaks within a set do not change. There is also a hint of change in the relative intensities of the peaks constituting set A.

The most interesting changes are observed for krypton and xenon matrices where the relative intensities of the



Figure 3. Temperature dependence for ν_5 of SOF₂ in a krypton matrix, 1/5000.



Figure 4. Temperature dependence for ν_1 of SOF₂ in a krypton matrix, 1/5000.

peaks vary substantially with changing temperature. For xenon matrices the following discussions apply to those deposited at 35 K. Deposits at 30 K show the same fea-

⁽¹⁹⁾ See, for example, H. E. Hallam, Ed., "Vibrational Spectroscopy of Trapped Species", Wiley, New York, 1973.

⁽²⁰⁾ Low-energy electron diffraction studies of Xe adsorbed on a variety of metal surfaces have shown that the first monolayer adopts a hexagonal close packing structure (see, for example, P. I. Cohen, J. Unguris, and M. B. Webb, *Surf. Sci.*, 58, 429 (1976), and references therein). X-ray diffraction studies of a Xe matrix deposited on a CsI substrate have shown that the (111) crystallographic direction is oriented normal to the substrate surface (B. I. Swanson, L. H. Jones, and R. R. Ryan, J. Mol. Spectrosc., 45, 324 (1973).



Figure 5. Temperature dependence for ν_5 of SOF₂ in a xenon matrix, 1/5000.



Figure 6. Temperature dependence for ν_1 of SOF₂ in a xenon matrix, 1/5000. Peaks III, II, and I in order of increasing frequency.

tures, but the peaks are broader and have relative intensities different from those for a 35 K deposit even after annealing at 60 K. Figures 3–6 show the temperature dependence of ν_1 and ν_5 in krypton and xenon matrices. For each matrix the higher-frequency peak grows in intensity relative to the lower-frequency features. In Xenon the highest-frequency component is barely observed at 9 K and yet approaches 50% of the integrated intensity as temperature is raised to 50 K. Relative intensity changes



Figure 7. Plot of percent integrated intensity changes for peaks III, II, and I of S-O stretch (ν_1) for SOF₂ in a xenon matrix: (X) peak III; (\Box) peak II; (O) peak I; (Δ) sum of III + II.

in xenon matrices are further complicated by the very different behavior of ν_1 , ν_2 , and ν_5 . The ν_1 region clearly shows evidence for three distinct trapping sites; a wellresolved doublet is observed at 9 K with a new feature growing in on the high-frequency side as temperature is raised. In contrast, ν_5 shows a single sharp, slightly asymmetric peak at 9 K with a new feature again growing in as temperature is raised. There is some evidence for a third site in ν_2 where an asymmetric line is observed at 9 K. For each band the various peaks are observed to merge in frequency and broaden as temperature is raised.

The most likely origin of the observed relative intensity changes for SOF₂ in xenon matrices is a temperature-induced change in the site populations. Essentially the various sites are in equilibrium with small free energy differences so that the Boltzmann distribution is changed significantly as temperature is raised. The results are not entirely consistent with a simple equilibrium with stationary relative free energies among the sites. Both ν_1 and ν_5 for SOF₂ and S¹⁸OF₂ (this isotope was selected to obviate complications of Fermi coupling) have been curve resolved for several temperatures in a xenon matrix with Xe/SOF₂ = 5000.

From the curve resolution, percent areas for the three peaks of ν_1 have been obtained; with increasing frequency these are labeled III, II, and I, respectively. The accuracy is not great because of severe overlapping at the higher temperatures and apparent asymmetry of each peak. One could introduce further broad underlying peaks to achieve a better fit; however, we feel that this would not be justified as it is likely that the peaks are asymmetric as noted for other systems.⁷ The relative intensities for ν_1 of the normal isotope are plotted in Figure 7. Rather similar results are obtained for ν_1 of S¹⁸OF₂ though the scatter is somewhat greater as the two higher-frequency peaks are closer together than for the normal isotope. Though the limits of error are not known, the trend is the same for both isotopes and one cannot fit the observations without concluding that the middle peak, II, approaches very low intensity as temperature is raised, whereas peaks I and III approach equal intensities before they finally merge at high temperatures. Similar results are obtained for v_5 except that peaks from sites I and II are not resolved from each other. Thus, for both v_1 and v_5 the high-frequency component has essentially zero intensity at 9 K and yet increases to nearly



Figure 8. Plot of ln $[A_1/(A_{11} + A_{111})]$ vs. 1/T for ν_1 of SOF₂ in a xenon matrix.

50% of the total integrated intensity by ca. 50 K. The ν_2 mode shows similar behavior though the peaks are broader and poorly resolved. Inasmuch as there are three sites in xenon matrices, one would expect (neglecting differences in the degeneracies of the sites) the relative intensities to be equal in the high-temperature limit. However, we observe that one of the original sites in xenon (9 K) appears first to decrease and then increase again while the other component greatly diminishes in intensity as temperature is raised. Curve resolution of ν_1 and ν_5 for krypton matrices at various temperatures shows the highest-frequency component to start at ca. 9% and level off at ca. 25% of the total intensity at 25 K.

The unusual intensity changes in krypton and xenon matrices could have two origins. First, the degeneracy of the various sites may be different, thereby contributing unequal weighting factors to the population. The term degeneracy used here refers to more than one possible way to accommodate SOF_2 in its trapping cage with the same environmental symmetry and forces. For example, there are three equivalent ways to preserve the mirror plane symmetry for SOF_2 in a three-atom cage represented by the three vertical planes in the D_{3h} group. While differences in site degeneracy could help explain many of the unusual intensity changes observed here, it cannot explain the nonmonotonic intensity change observed for one site in xenon (viz., the S-O stretch). Another possibility here is that the relative free energies of the trapping sites change with temperature. While this may seem remote at first glance, it is noted that in the low-temperature region the external forces on trapping sites which are very nearly the same may be strongly influenced by the structure changes which occur with temperature.

We have attempted to estimate free energy differences for the three trapping sites for SOF₂ in xenon. At 9 K peaks III and II are nearly equal in intensity, indicating that their free energy difference is quite small. With increase in temperature above 25 K site II becomes quite unstable with respect to sites I and III. As seen in Figure 7, though III and II show rather erratic behavior, the decrease in the sum of intensities of III and II parallels the increase in I rather nicely. A plot of $\ln (A_{\rm I}/(A_{\rm II} + A_{\rm III}))$ vs. 1/T for normal SOF₂ gives a reasonable straight line (Figure 8) the slope of which yields a value of 32 cm⁻¹ for the free energy difference of the III, II sites relative to site I. For S¹⁸OF₂ we obtain a value of 27 cm⁻¹. A similar plot for the antisymmetric stretch, ν_5 , of normal SOF₂ yields a value of 29 cm⁻¹ for $\Delta F(\text{III}, \text{II} \rightarrow \text{I})$. The differences are certainly within the error of measurement and thus show consistency. Since the free energy differences among sites are small, it is likely that the activation barriers for inequivalent site exchange within a given trapping cage are also small. In principle, one could obtain direct information concerning the activation barrier from time-resolved studies of population change accompanying an incremental temperature change. Unfortunately, all that can be said at present is that the change in equilibrium among sites with changing temperature is complete within our observation time. However, the temperature dependence of the frequency positions and line shapes provides additional information concerning the activation barriers for site exchange.

The structure observed for ν_1 and ν_5 in either krypton or xenon matrices shows that the frequencies for different trapping sites merge with increasing temperature. For SOF₂ the frequencies do not begin to coalesce until 25 and 30 K for krypton and xenon, respectively, and the coalescence is not complete before line broadening obscures the frequencies. The results obtained here are similar to those obtained for the high-frequency doublet of ν_3 for SF₆ and SeF₆ in xenon⁷ where the coalescence is complete at ca. 55 K. As observed in earlier studies of SF₆^{5,7} and SeF₆,⁶ the line widths of the merging peaks increase as temperature is raised.

We believe that the frequency coalescence and line broadening are indicative of rapid site-to-site exchange on the vibrational time scale. In all previous examples of site exchange in matrices, the bands involved in the motional collapse were symmetry split components of degenerate vibrations and the exchange, therefore, occurred between symmetry equivalent sites. For SOF_2 the exchange involves inequivalent sites which, of necessity, have unique minimum free energies. Consequently, thermal changes in equilibria accompany the exchange phenomenon.

In previous studies⁵⁻⁷ of site exchange, we were able to obtain crude estimates of activation barriers by analyzing the temperature-dependent spectra using the Bloch formalism. A similar analysis here suffers from several problems: (1) Three sites are involved in the motional averaging. (2) The equilibrium changes alter the intensities in a manner which cannot, at present, be adequately modeled. (3) Possible changes in the relative free energies negate the applicability of the Arrhenius expression. At present the best estimate for the activation barrier which can be obtained from analysis of the data using only the frequency separations is roughly $30-40 \text{ cm}^{-1}$.

The exchange process observed here can be viewed as a problem in population exchange; an oscillation excited for one site environment is rapidly converted to the other site energy by a structural fluctuation. Theories developed by Oxtoby¹⁰ and Rice¹¹ for vibrational phase exchange involving two discrete fundamentals are pertinent to this problem as well. Accordingly, the activation barrier corresponds to the energy of a low-energy "dephasing" mode. In this case the only possible candidate for a dephasing mode is a low-energy-site local phonon mode. Temperature-dependence studies are now in progress in the far-IR to search for evidence of the dephasing modes.

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