

A More Stable Configuration of HArF in Solid Argon

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During the past decade a number of HRgY molecules (H = hydrogen; Rg = Ar, Kr, Xe; Y = an electronegative fragment) have been characterized experimentally in rare-gas solids and computationally by using ab initio methods.^{1,2} These species are formed from neutral fragments,³ and experiments support their intrinsic stability.⁴ These molecules constitute an important intermediate during UV photolysis of HY molecules in rare-gas hosts demonstrating the locality of the primary photolysis.⁵ One of the HRgY molecules, HXeI, has recently been observed in Xe clusters.⁶

A stable Ar-containing molecule, HArF, was identified in an Ar matrix.² The high-level ab initio calculations on HArF confirmed its intrinsic stability.^{7,8} An unclear experimental fact on HArF is its decrease upon annealing above 27 K,² which contradicts the calculated decomposition barrier of 0.33 eV.⁷ In this communication, we report an additional solid-state configuration of HArF with higher thermal stability.

The HF/Ar solid mixtures were studied in a closed-cycle helium cryostat (APD, DE 202A) at temperatures down to 7.5 K. The samples were deposited onto a cold CsI substrate by passing Ar gas (⁴⁰Ar from AGA and ³⁶Ar from ICON Services) over an HF-pyridine polymer (Fluka) at room temperature. Photolysis of HF was performed with a Kr continuum lamp (Ophos) emitting in the 127–160 nm spectral interval. Our HF/Ar matrixes are quite monomeric as indicated by the IR absorption bands at 3962.5 and 3953.8 cm⁻¹.⁹

HArF molecules are prepared in the following. First, HF is photodissociated, which stabilizes H and F atoms in solid Ar and leads to some formation of HArF. Next, the photolyzed sample is annealed, which mobilizes the atoms and leads to an increase in the HArF concentration below 20 K.² The formation of HArF molecules is demonstrated by strong absorption bands at 1965.7, 1969.4, 1972.3 ($\nu_{\text{H}-\text{Ar}}$), 686.9 ($\delta_{\text{H}-\text{Ar}-\text{F}}$), and 435.7 cm⁻¹ ($\nu_{\text{Ar}-\text{F}}$). The H–Ar stretching region is presented in Figure 1 (see the upper spectrum). The observed bands agree well with the calculated values and show proper shifts upon H and Ar isotopic substitutions. Surprisingly, annealing above 27 K destroys all bands listed above, which was tentatively explained by secondary reactions of mobile matrix species with HArF molecules.²

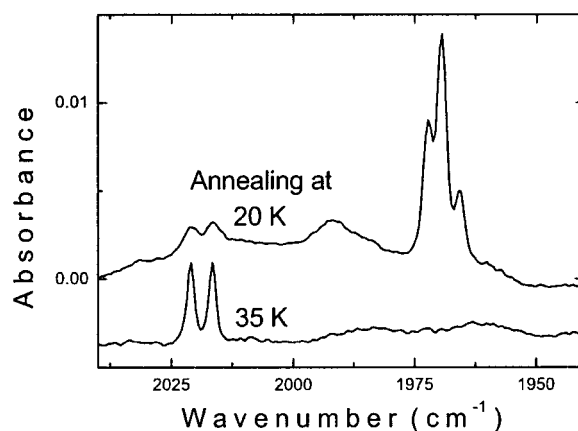


Figure 1. Formation of stable HArF in solid Ar. The HF/Ar matrix is deposited and photolyzed at 7.5 K and annealed at 20 and 35 K. Annealing above 27 K destroys unstable HArF (on the right) and forms stable HArF (on the left). The spectra are measured at 7.5 K.

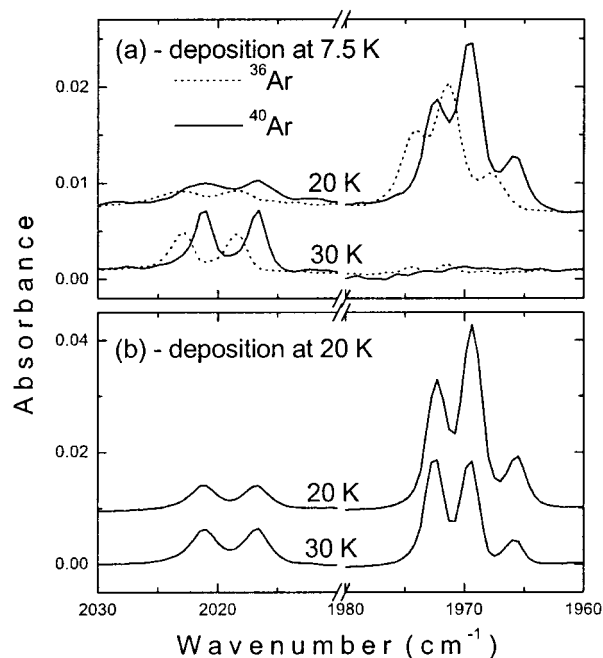


Figure 2. Two configurations of HArF in solid Ar. (a) ³⁶Ar/⁴⁰Ar isotopic substitution showing the same H–Ar stretching mode shift for both HArF configurations. The matrix is deposited at 7.5 K. (b) Effect of deposition at 20 K. Note the increasing thermal stability of unstable HArF (on the right). Annealing temperatures are shown in the plots. The spectra are measured at 7.5 K.

It was not noticed in the original paper on HArF² that the decrease of “unstable” HArF molecules is accompanied with an increase of other bands in the H–Ar stretching (2016.3 and 2020.8 cm⁻¹) and bending (693.5 and 697.0 cm⁻¹) regions. This central observation of the present work is illustrated by the lower spectrum in Figure 1. A sign of the novel bands is visible already after annealing at 20 K. We suggest that this novel set of bands belong to HArF in a different solid-state configuration. This additional configuration is thermally rather “stable” and the corresponding bands decrease only with evaporation of the sample. The H–Ar stretching doublet shifts to 1494.0 and 1496.9 cm⁻¹ upon deuteration, and to 2018.5 and 2023.1 cm⁻¹ upon ³⁶Ar/⁴⁰Ar substitution [see Figure 2a], i.e., in accord with the calculations and experiment on “unstable” HArF.² These observations prove that the doublet at ~2020 cm⁻¹ originates from the

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Table 1. Experimental Absorption Bands of Unstable and Stable Configurations of HArF Molecules

	ν (H–Ar) (cm ⁻¹)	δ (H–Ar–F) (cm ⁻¹)	ν (Ar–F) (cm ⁻¹)
unstable	1965.7, 1969.4, 1972.3 (1.3430)	686.9	435.7
stable	2016.3, 2020.8 (1.3498)	693.5, 697.0	
theory ^a	1912 (1.3495)	704	473

^a From ref 8. The H/D ratio for ν (H–Ar) is given in parentheses.

H–Ar covalent bond. Furthermore, the additional doublet at 693.5 and 697.0 cm⁻¹ agrees well with the HArF bending mode. Although we did not observe the Ar–F stretching absorption, it is not a surprise. Indeed, the nature of bonding in HRgY molecules dictates that the upshift of the H–Ar absorption should be accompanied with a downshift of the Ar–F absorption, and it escapes from the practical range of the spectrometer (>430 cm⁻¹). The two sets of bands show similar bleaching rate upon irradiation at various wavelengths in the UV spectral region (<350 nm), confirming that they belong to the same molecule.

Thus, it is safe to assign the bands found in the present work to a thermally stable configuration of HArF molecules. The bands of unstable and stable HArF are listed in Table 1 together with the ab initio results by Lundell et al.⁸ Two possible cases for the observed temperature dependence of HArF can be suggested: thermal relaxation of the solid host and diffusion-controlled secondary reactions. Our tentative model combines these two processes since their indications are seen in the experiments, and they are discussed in more detail below. In contrast, such processes as annealing-induced complexation of HArF with normal matrix impurities (water, nitrogen, etc.) find no experimental support.

The temperature behavior of unstable HArF depends on the deposition temperature as seen in Figure 2. For deposition at elevated temperatures (~20 K), the absorption bands of unstable HArF do not decrease much even at 30 K. The annealing-induced modification of the site structure of unstable HArF is remarkable: the higher the frequency, the higher the thermal stability. The stable HArF configurations with its H–Ar frequency upshifted by ~50 cm⁻¹ follow this trend. It is plausible to accept that Ar host, stressed under deposition and photolysis, relaxes around 30 K, and HArF occupies a lower energy and more stable configuration. In fact, the H/D ratio of stable HArF is somewhat larger (see Table 1), which indicates a more harmonic potential well and agrees with its higher stability. The clear narrowing of the stable HArF doublet upon the higher temperature annealing (see Figure 1) supports relaxation of the environment. On the basis of these observations, we suggest transformation of unstable HArF to the stable configuration during local lattice relaxation upon annealing. The delayed decrease of unstable HArF observed for deposition at elevated temperatures might be due to initially more relaxed matrix morphology. It should be mentioned here that Feldman and Sukhov reported thermal modification of matrix sites for HXeH molecules.¹⁰ To test the hypothesis of matrix site modifications, we performed the following experiment. A photolyzed sample was annealed at 20 K producing a maximum of unstable HArF and then irradiated at 193 nm destroying HArF. After this treatment, the production of stable HArF under the higher temperature annealing (from 20 to 32 K) was about 3 times smaller than the corresponding value for the untreated samples, which supports conversion between the HArF configurations.

As judged by integrated IR band intensities, the annealing-induced increase of stable HArF is smaller than the corresponding decrease of unstable HArF indicating partial destruction of the species in secondary reactions. This process is illustrated by comparison of HArF with HOO¹¹ and FOO¹² radicals formed from impurity oxygen (see Figure 3). The increase of FOO and HOO

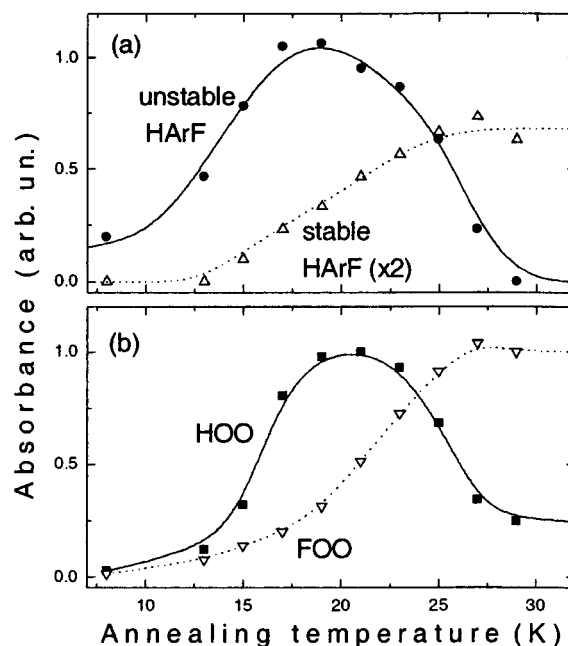


Figure 3. Integrated IR absorption intensities as a function of the annealing temperature: (a) unstable and stable HArF and (b) HOO and FOO radicals. The matrix is deposited at 7.5 K, and the spectra are measured at 7.5 K.

in annealing shows thermal mobility of H and F atoms in agreement with the literature data.^{13,14} HOO radicals are thermally stable at matrix temperatures but they decrease above 25 K, which offers a clear indication of the presence of secondary reactions that should also decrease the HArF concentration. The behavior of HOO shown in Figure 3b has never been observed when preparing other HRgY molecules.¹ We can speculate that the case of HArF is exceptional among the HRgY molecules due to high mobility of fluorine, and mobile F atoms are the most probable candidates for the reaction. For deposition at elevated temperatures (~20 K), the HOO concentration becomes rather stable above 25 K, which might be connected with the morphology-dependent atomic mobility suggested in the literature.¹⁵ However, unstable HArF finally disappears even for the matrixes deposited at ~20 K where HOO is rather stable. Thus, it is unlikely that the secondary reactions alone are responsible for the complete disappearance of unstable HArF, and its conversion to the stable configuration presumably occurs. At the moment, we stay in our model with the combinations of these two mechanisms although the proportion between them is unclear. More quantitative consideration is complicated by short-range separation of H + F pairs during photolysis.¹⁶

In conclusion, we detected a thermally stable solid-state configuration of HArF, an Ar-containing ground-state molecule, and this finding agrees with the calculated HArF energetics. Stable HArF is presumably a molecule in the thermally relaxed environment, it is visible in IR absorption spectra until the sample evaporates above 40 K, and it at least partially originates from unrelaxed (unstable) HArF reported in ref 2.

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Note Added after ASAP: There were errors in the absorption band data in the version posted ASAP August 2, 2001; the corrected version was posted August 10, 2001.

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