Matrix-isolation FTIR study of azidoacetone and azidoacetonitrile

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Azidoacetonitrile ($N_3 CH_2 CN$) and azidoacetone ($N_3 CH_2 COCH_3$) are studied by matrix-isolation FTIR spectroscopy in solid neon, argon, and nitrogen. The IR spectra calculated using the density-functional theoretical method are discussed in comparison with the experimental data. Significant broadening of the recorded azide bands indicate an awkward fit of these compounds into the solid environment. The strongest absorption is observed for both compounds in the regions of asymmetric and symmetric stretches of the $N_3$ azide group. Strong band splittings in the $N_3$ asymmetric stretch region can be most likely explained by very strong Fermi resonances with the CN stretch and combinations and overtones of the numerous lower-frequency vibrational modes. © 2003 American Institute of Physics. [DOI: 10.1063/1.1619361]

INTRODUCTION

Organic azides are useful reagents in many fields. Their strongly exothermic reactions make them useful as propellants. Their ability to form highly reactive nitrene intermediates that are capable of being inserted into otherwise stable chemical bonds makes them important synthetic reagents, with a number of potential uses in semiconductor technology, for instance.

The compounds were studied both in solution and in solid phase, and the relative volatility of some of them, for example, azidoacetonitrile ($N_3 CH_2 CN$, abbreviated in this paper as AzN) and azidoacetone ($N_3 CH_2 COCH_3$, AzC), allows their studies in the gas phase. The thermal decomposition of these two compounds was recently studied using ultraviolet photoelectron spectroscopy (UVPES) and matrix-isolation spectroscopy in solid nitrogen, as part of a general project on decomposition of aliphatic azides. Theoretical calculations have been also carried out for conformers of AzC.

One can often obtain more insight and additional information about the interaction of isolated compounds with the solid medium by examining and comparing the spectra in several matrices. In the present paper we report the infrared spectra in solid neon, argon, and nitrogen. We complement the experimental investigation by density-functional theoretical (DFT) computations of their properties and structures, and discuss their spectra with the help of the computed vibrational frequencies and intensities.

EXPERIMENTAL

Sample preparation

Azidoacetonitrile was synthesized from chloroacetonitrile $CICH_2 CN$ and sodium azide ($NaN_3$) as given in Ref. 10. Azidoacetone was prepared from chloroacetone $CICH_2 COCH_3$ and $NaN_3$, according to the procedure described in Ref. 7.

The pre-mixed organic azide vapors with Ne, Ar, and N$_2$ matrix gases were prepared at room temperature with an estimated concentration of 1:700 for all experiments. Neon samples were continuously deposited onto the copper substrate (coated with silver and MgF$_2$) cooled to 6 K by a Leybold RGD 580 closed-cycle helium cryostat. Argon and nitrogen samples were deposited by means of a pulsed valve at 12 K onto the KCl substrate mounted on the cryotop of an APD Cryogenics refrigerator. To improve the optical quality of the N$_2$ matrix, deposition was started from 60 K and then the substrate was gradually cooled down to 12 K in 10 min. In all experiments the deposition rate was kept in the range of 2.5–3 mmol/h for a deposition time of 2 hours.

Spectroscopy

The infrared spectra of both compounds, $N_3 CH_2 CN$ and $N_3 CH_2 COCH_3$, in solid Ne, Ar, and N$_2$ were recorded with a resolution of 0.06 cm$^{-1}$ on a Bruker IFS 120 HR Fourier-transform spectrometer equipped with a glowbar light source, liquid-nitrogen-cooled HgCdTe (MCT) detector, and a KBr beam splitter. Typically at least 500 scans were aver-
aged. The spectra were recorded immediately after deposition and then again after annealing of the samples, and after irradiation of the matrices with a tungsten lamp, a multi-line UV Ar$^+$ ion laser and the fourth harmonic of a Nd:YAG laser.

RESULTS AND DISCUSSION

Calculations

The optimized structures and vibrational frequencies of azidoacetonitrile and azidoacetone were calculated using the B3LYP/6-31+G(d,p) hybrid DFT technique as implemented in the Gaussian 98 program suite.$^{11}$ To check for errors due to the incomplete basis set, calculations using the larger B3LYP/6-31+G(3df,3pd) basis set were performed, which yielded no substantial changes from our previous results. Tables I and II summarize the results for the two most stable conformational minima, whose geometry is characterized by different values of the $\phi_{\text{NNCC}}$ dihedral angle. In the case of AzC the two local minima at 64° (gauche) and 180° (anti) are nearly isoenergetic, while in AzN the 67° gauche conformer is found to be considerably lower in energy than the 180° anti isomer. The tables list the computed, unscaled vibrational frequencies of both molecules. The geometries of AzN and AzC conformers are illustrated in Fig. 1.

Experimental results

The infrared absorption spectra of both compounds in solid neon, argon, and nitrogen were recorded in the range from 400 to 5000 cm$^{-1}$, with selected regions being shown in Figs. 2 and 3. A comprehensive listing of the bands observed in our experiments and their tentative interpretation, as well as the previous assignments by Klaeboe et al.$^6$ are collected in Table III.

Very often matrix isolation yields excellent-quality spectra with sharp absorption bands, which exhibit little perturbation when compared with the gas phase. In fact, one way to judge the extent of the medium effect is to compare spectra using several different matrix materials, where negligible changes from matrix to matrix usually imply an also small medium shift from the gas phase to the matrix, and this was one of the reasons for performing our current study.

Unfortunately, in the present case, most of the observed spectral bands are relatively broad, and they also exhibit appreciable, matrix-dependent changes in terms of band width, band shape, and band intensity from matrix to matrix. Also somewhat surprisingly, the observed bands are broadest in solid neon, which usually yields the best-quality spectra. One

<table>
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<tr>
<th>TABLE I. Calculated frequencies of vibrational modes of azidoacetonitrile conformers (method: B3LYP/6-31+G(d,p)).</th>
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FIG. 1. Predicted structures of the gauche and anti conformers of azidoacetonitrile and azidoacetone.
usually gets excellent-quality sharp spectra when the guest fits well into the crystalline structure of the host. Thus linear compounds and cations of the type $X-(C_2)_n-Y$, or, for instance, fluorinated benzene cations, yield very sharp, unperturbed spectra. In fact, in both cases two spectrally shifted sites are observed, which were attributed to species isolated in relatively unperturbed closely packed crystalline fcc or hcp environment, respectively. The former, linear compounds replace a row in a plane of neon atoms, while the latter, benzenes, fit well into a site replacing seven atoms in a crystallographic plane. One interpretation of broad bands is an awkward fit of the relatively bulky, low-symmetry guest into the solid host, preventing formation of a well-developed local crystalline structure and resulting in poorly-defined sites, with a wide range of local geometries.

Also the theoretical computations are of less help than is often the case. Thus, as shown in Table I, by far the strongest band computed for AzN is the asymmetric stretching frequency of the N$_3$ group, predicted to lie in both conformers at about 2254 cm$^{-1}$ (unscaled) with the only other fundamental frequency in this region being the almost three-orders-of-magnitude weaker CN stretching frequency expected at 2358 cm$^{-1}$ (2377 cm$^{-1}$ in the anti compound). The experimental spectrum reveals at least seven bands, several of them quite strong, extending from 2085 to 2259 cm$^{-1}$ (Fig. 2b). Some of these bands exhibit asymmetric line shapes and additional splitting, and appreciable changes in their shapes, frequencies, and relative intensities from matrix to matrix. The corresponding N$_3$ symmetric stretch is computed to be the second strongest absorption band. It is predicted to be at 1333 and 1314 cm$^{-1}$ in the anti and gauche conformers, respectively, with the latter value scaled by a factor of 0.96 coming very close to the observed band appearing in all three matrices between 1260 and 1262 cm$^{-1}$ (Fig. 2a).

The three weak to moderately intense bands appearing in all three matrices in the relatively narrow regions around 1221–1225, 1343–1349, and 1438–1444 cm$^{-1}$ (Fig. 2a) are in all probability due to the motions of the CH$_2$ group—twist, wagging, and bending, respectively—in acceptable agreement with the predicted values of 1254, 1372, and 1476 cm$^{-1}$, unscaled (gauche, Table I). These modes are computed at similar frequencies and intensities in the gauche

FIG. 2. Infrared spectra of azidoacetonitrile in neon, nitrogen, and argon matrices (the “negative” lines in the CH$_2$ bend region originate from gas phase water subtraction).

FIG. 3. Infrared spectra of azidoacetone in neon, nitrogen, and argon matrices (the “negative” lines in the CO stretch region originate from subtraction of gas phase water). No spectral features have been observed in the interval 1800–2000 cm$^{-1}$.
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i) weak bands around 2500 cm⁻¹ and in the range of 2900–4500 cm⁻¹ as well as matrix-isolated water and regions of the CO₂ bands have been omitted; ii) frequencies grouped in braces show fine structure of the bands; m—medium, s—strong, vs—very strong; the others are weak or very weak; b—broad.

*Underlined frequencies for AzN/N₂ relate to a previous assignment."
and anti species and therefore do not provide a useful basis for distinguishing between the two.

Most useful for discriminating between the two conformers appears to be the 700–1100 cm\(^{-1}\) region. The three moderately intense bands observed in the experimental spectrum of AzN near 993–979, 928–931, and 873–878 cm\(^{-1}\), respectively (Fig. 2a), are in a distinctly better agreement with the comparably intense 1006, 938, and 884 cm\(^{-1}\) bands predicted for the gauche conformer than with the two strong and one very much weaker anti species bands, computed to be the asymmetric N\(_3\) vibration, computed to lie near 979, 974, and 945 cm\(^{-1}\).

The previously noted, complex structure in the region of the asymmetric N\(_3\) stretch, which is insensitive to the sample deposition rate and conditions and which does not change upon sample annealing or photolysis, is unlikely to be due to the presence of multiple conformers. The more than 150 cm\(^{-1}\) range of the observed bands is too large to be attributed to matrix sites and suggests that the appearance of the spectrum is due to an intrinsic property of AzN. The molecule has a low, \(C_1\), symmetry, and the most likely explanation for the observed multiple strong bands seems to lie in very strong Fermi resonances between the \(N_3\) asymmetric frequency, the CN stretching frequency, and combinations and overtones of the numerous lower-frequency vibrational modes expected in this region. It should be mentioned that a previous study\(^6\) has also suggested a similar complexity in this region even in the gas phase spectrum. A rather weak band observed in all three matrices around 2255–2259 cm\(^{-1}\), but absent from the spectra of azidoacetonitrile, to be discussed below, is undoubtedly due to the CN stretching vibration (Figs. 2b and 3b).

For the more complex azidoacetonitrile molecule, with its twelve atoms and thirty vibrational modes, more complex infrared spectra should be expected, making their interpretation correspondingly more difficult. As in AzN, by far the most intense infrared fundamental in AzC also is predicted to be the asymmetric N\(_3\) vibration, computed to lie in both conformers near 2255 cm\(^{-1}\) (unscaled). Here several structured bands are also found in this region, the appearance, width, and splitting of which changes substantially from matrix to matrix (Fig. 3b). In neon a dominant band appears at 2123.3 cm\(^{-1}\) with a much weaker shoulder at 2108 cm\(^{-1}\) and two much weaker ones at 2163 and 2222 cm\(^{-1}\). All these bands are relatively symmetric, and have widths in excess of 10 cm\(^{-1}\). In argon and nitrogen matrices there is not one dominant band, but a more complex structure, with the strong band appearing to have split into several components with differing widths and intensities, as can be seen in Fig. 3b.

Three other bands of the AzC gauche conformer are predicted to have appreciable intensities: the CO stretch at 1807, and bands at 1340 and 1182 cm\(^{-1}\), presumably the symmetric N\(_3\) stretch and a CH\(_2\) twist. These two latter modes are possibly strongly mixed, and they are computed to be somewhat shifted to 1349 and 1241 cm\(^{-1}\) in the higher-energy anti conformer. Experimentally, in all three matrices, two bands are found in the carbonyl region, at 1752.3 and 1744.9 cm\(^{-1}\) in neon, 1747 and 1721.5 cm\(^{-1}\) in argon, and 1748 and 1742 cm\(^{-1}\) in nitrogen (Fig. 3b). Besides significant changes in their frequencies from matrix to matrix, their relative intensities are also found to change, with the higher-frequency band being more intense in neon but the lowest, 1721.5 cm\(^{-1}\), band having the highest intensity in the argon matrix.

The assignment of the numerous lower-frequency modes, which, in view of the low molecular symmetry, are probably strongly mixed, becomes more difficult. Comparison with the AzN would seem to dictate assigning the rather strong band at 1282.8 cm\(^{-1}\) in solid neon to the N\(_3\) symmetric stretch, and the absorptions near 1222, 1363, and 1424 cm\(^{-1}\) to the twisting, wagging, and bending motions of the CH\(_2\) group (Fig. 3a).

We have already commented above that many of the spectral lines of the matrix-isolated molecules investigated here are unusually broad, and suggested that one explanation might be an awkward fit into the matrix site, preventing the formation of a well-developed crystalline structure of the host matrix in the neighborhood of the guest dopant. Another remarkable observation involves the significant shifts of individual bands from matrix to matrix, and in particular the large changes in the band widths and relative intensities. A possible interpretation of this may lie in the polar nature of the azide group. In general, matrices tend to stabilize strongly ionic or polar structures, and this stabilization will be a strong function of the polarizability of the host atoms or molecules.

Another conclusion is that in a series of annealing experiments and experiments on photolysis of the matrices at various wavelengths, no appreciable spectral changes were detected. No new bands appeared following irradiation of the matrices, nor were there substantial changes in the relative band intensities, and for a given matrix the relative intensities remained consistent from experiment to experiment. Overall, the observed spectra can be interpreted in terms of the azides being isolated in the lowest-energy, gauche conformation, and no clear evidence of the simultaneous presence of several conformers was found.

**SUMMARY**

The infrared spectra of organic azides, azidoacetonitrile (\(N_3CH_2CN\)) and azidoacetone (\(N_3CH_2COCH_3\)), isolated in low-temperature solids has been measured by means of Fourier-transform technique in the range from 400 to 5000 cm\(^{-1}\). A comparative study in neon, argon and nitrogen matrices has shown that most of the observed spectral bands are relatively broad, exhibiting appreciable changes in terms of band width, band shape, and band intensity from host to host. Significant broadening of the recorded azides bands indicate an awkward fit of the low-symmetry molecules into the solid host, resulting in a wide range of local environments. Based on DFT calculations of the IR spectra for optimized structures, the strongest absorption bands observed for both compounds were assigned to asymmetric and symmetric stretches of the N\(_3\) azide group. Strong Fermi resonances involving the N\(_3\) asymmetric stretch, CN stretch, and combinations and overtones of the numerous lower-frequency vibrational modes can most likely be interpreted as indicative of the strong band splittings occurring in the asymmetric stretch region of the N\(_3\) group.
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