

Matrix-isolation FTIR study of azidoacetone and azidoacetonitrile

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Azidoacetonitrile ($\text{N}_3\text{CH}_2\text{CN}$) and azidoacetone ($\text{N}_3\text{CH}_2\text{COCH}_3$) were 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.

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Introduction

Organic azides are useful reagents in many fields [1–3]. Their strongly exothermic reactions make them useful as propellants [4]. Their ability to form highly reactive nitrene intermediates that are capable of inserting into otherwise stable chemical bonds makes them important synthetic reagents, with for instance a number of potential uses in semiconductor technology [5].

The compounds were studied both in solution and in solid phase, and the relative volatility of some of them, for example azidoacetonitrile ($\text{N}_3\text{CH}_2\text{CN}$, in this work abbreviated as AzN) and azidoacetone ($\text{N}_3\text{CH}_2\text{COCH}_3$, AzC), allows their studies in the gas phase [6]. The thermal decomposition of these two compounds was recently studied using ultraviolet pho-

toelectron spectroscopy (UVPES) and matrix-isolation spectroscopy in solid nitrogen, as part of a general project on decomposition of aliphatic azides [7,8]. Theoretical calculations have been also carried out for conformers of AzC [9].

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 computed vibrational frequencies and intensities.

Experimental

Sample preparation

Azidoacetonitrile was synthesized from chloroacetonitrile ClCH_2CN and sodium azide (NaN_3) as given in [10]. Azidoacetone was prepared from chloroacetone $\text{ClCH}_2\text{COCH}_3$ and NaN_3 , according to the procedure described in [7].

The pre-mixed organic azides vapors with matrix Ne, Ar and N_2 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 by silver and MgF_2) cooled to 6 K by a closed cycle helium cryostat, Leybold RGD 580. Argon and nitrogen samples were deposited by means of a pulsed valve at 12 K onto the KCl substrate mounted on the cryotip 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, $\text{N}_3\text{CH}_2\text{CN}$ and $\text{N}_3\text{CH}_2\text{COCH}_3$, in solid Ne, Ar, and N_2 were recorded with resolution of 0.06 cm^{-1} with 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 averaged. 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» suite of programs [11]. To check for errors due to the incomplete basis set, calculations using the larger B3LYP/6-311(3df,3pd) basis set were performed, which yielded no substantial changes from our previous results. Tables 1 and 2 summarize the results for the two most stable conformational minima, whose geometry is characterized by different values of the ϕ_{NNCC} dihedral angle. In the case of AzC the two local minima at 64° (gauche) and 180° (anti) are nearly

isoenergetic, 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.

Table 1

Calculated frequencies of vibrational modes of azidoacetonitrile conformers (method: B3LYP/6-31+G(d,p))

Anti: dihedral angle $\phi_{\text{NNCC}} = 180^\circ$		Gauche: dihedral angle $\phi_{\text{NNCC}} = 67^\circ$		Approximate assignment
frequency, cm^{-1}	intensity, km/mol	frequency, cm^{-1}	intensity, km/mol	
34.9	1.3	55.7	5.5	
145.2	9.2	193.1	7.7	
260.2	1.6	258.6	0.6	
358.6	0.6	351	0.1	C–C \equiv N bend
519.4	2.7	523	0.1	C–C \equiv N bend
544.9	6.9	556.3	8.7	NNN bend
628.1	5	687.3	15.7	NNN bend
945	20.7	884.4	13.4	C–C/C–N sym. str.
973.6	0.9	937.6	26	CH ₂ rock + C–C/C–N asym. str.
979	15.7	1006.2	9	CH ₂ rock + C–C/C–N asym. str.
1241.5	0.6	1253.9	1	CH ₂ twist
1332.6	145.2	1314.1	163.1	NNN sym. str.
1373.7	10.9	1372	10.9	CH ₂ wag.
1479.1	7.4	1476.5	8.4	CH ₂ bend
2255.1	517.8	2254.3	450.9	NNN asym. str.
2376.7	0.9	2358	0.6	C \equiv N
3021.4	15.4	3043.9	14.3	CH ₂ sym. str.
3062.3	4.3	3135.7	0.4	CH ₂ asym. str.

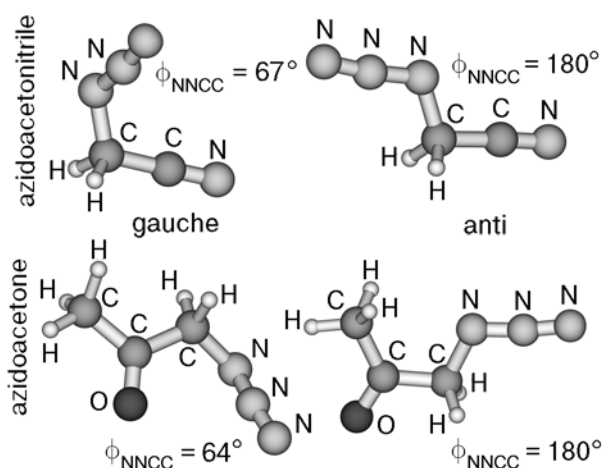


Fig. 1. Predicted structures of the gauche and anti conformers of azidoacetonitrile and azidoacetone.

Table 2

Calculated frequencies of vibrational modes of azido-acetone conformers (method: B3LYP/6-31+G(d,p))

Anti: dihedral angle $\phi_{\text{NNCC}} = 180^\circ$		Gauche: dihedral angle $\phi_{\text{NNCC}} = 64^\circ$		Approximate assignment
frequency, cm^{-1}	intensity, km/mol	frequency, cm^{-1}	intensity, km/mol	
35.4	15.3	61.1	1.9	
46.9	1.3	81	2.5	
137.8	3.8	98.6	0.3	CH ₃ torsion + ?
140.9	0	216.5	4.5	CH ₃ torsion + ?
262	10.5	274	4.9	
449	1.1	381.1	5.2	
473.8	0.8	461.3	2.5	
499	18.4	556	6	NNN bend + ?
556.1	8.1	573.4	20.9	NNN bend + ?
644.2	11.7	694.3	8.2	
799.9	2.3	794.6	2.2	
839.1	0.5	858.6	17.1	
969.6	19.5	949	23.5	
1012.3	2.1	994.7	4.5	
1069.5	0.5	1077.9	1.6	
1232.5	2.2	1181.8	95.9	CH ₂ twist + ?
1240.6	132.4	1251	2.9	CH ₂ twist + ?
1342.8	5.8	1340.3	105.4	NNN sym. str. + CH ₂ wag.
1348.9	147.5	1368.1	32.1	NNN sym. str. + CH ₂ wag.
1394.6	45.2	1393.5	32	CH ₃ umbrella mode
1454.5	8.3	1463.4	2.3	CH ₂ bend + CH ₃ umbrella
1461.4	52.3	1469.6	22.5	CH ₂ bend + CH ₃ umbrella
1468.3	12.8	1482.5	10.7	CH ₃ str. + torsion
1794.3	207.7	1807.4	109.7	CO str. + ?
2255.3	604.8	2255.9	522.3	NNN asym. str.
3024.1	21.8	2990.8	31.9	CH ₂ sym. str.
3050.2	0.3	3041.7	3.4	CH ₃ sym. str.
3069.8	7.5	3104.6	8	CH ₂ asym. str. + ?
3110.9	3.3	3112.3	7.8	CH ₂ str + CH ₃ str.
3167.2	10	3161.2	5	CH ₃ asym. str.

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 Klæboe et al. [6] are collected in Table 3*.

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 also a small medium shift from

gas phase to 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 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 [12–14]. 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 1, by far the strongest band computed for AzN is the asymmetric stretching frequency of the N₃ 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. 2,b). 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 N₃ symmetric stretch is computed to be the second strongest absorption band. It is predicted to be in the anti and gauche conformers to be at 1333 and 1314 cm^{-1} , 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 1260–1262 cm^{-1} (Fig. 2,a).

* Footnotes for Table 3: i) weak bands around 2500 cm^{-1} and in the range of 2900–4500 cm^{-1} as well as matrix isolated water and CO₂ bands regions 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 previous assignment [6].

Experimental data for azidoacetonitrile and azidoacetone isolated in Ne, N₂ and Ar solids*

Azidoacetonitrile					Azidoacetone				
Ne	N ₂	Ar	assignment		Ne	N ₂	Ar	assignment	
			prev. (N ₂) #						
561.8 563.3	560.0 [#] ~561.3	560.1	NNN bop		-573.7 -643.3	-573.9 -641.1	~575	NNN bend	
689.1 691.5	~684 ~691	686.1 698.1	NNN bend	NNN bend	-695.5	-700.2			
878.2 m	872.8 873.6 874.1] m	873.1 m	C-C/C-N bend	C-C/C-N sym. str.	852.2		882.3		
-925.5 -929.2 931.0 931.8] s	927.6 929.7] s	928.4 931.2] s	CH ₂ rock	CH ₂ rock + C-C/C-N asym. str.	931.0 -939 m,b	927.6 -939	932.4 ~935.1		
943.7 944.6					959.7 -961.0 m,b	943.8 -956.6 b			
990.0 992.6 993.9 962.2 997.0] m	-989.4 -993 994.7 996.8]	982.8 b 993.0 m		CH ₂ rock + C-C/C-N asym. str.	-980 b				
~1123 1149.1					1050.8 1061.0 1149.1 1168.4 s		1091.7 1161.3 ~1163] _{sh}		
-1206 1218.9 1220.0 1221.1 1222.1 1223.1 1224.9] s	1218.5 1223.4 1225.5 1228.7] m	1225.3 s		CH ₂ twist	-1208] b -1210] b 1222.3 s 1235.4	-1201 -1223.3 1225.4] 1234.0] m -1236.0] m	~1195.9 1216.4 s	CH ₂ twist	
1248.6 1254.0 ~1256.3 ~1258.9 1260.7 1262.7 ~1266.8 ~1270.7 ~1272.2] vs	1256.6 1258.6 1260.8 ~1266.7 ~1272.3] vs	~1252.5 1254.7] m ~1258.9 1262.2] vs 1263.5]	CH ₂ wag.	NNN sym. str.	-1249 b 1264] m 1267.8] m 1282.8 s	1260.8 1266.7 1271.8 1280.9] m 1285.7]	1283.3 ~1289 b	NNN sym. str.	
1330.3 1332.6 1334.5]	~1331.6	1332.5	N=N str.		1316.5 1317.8 1318.9 1319.9] m ~1339.5 b	~1315.0 ~1318			
1343.4 1343.8 1345.5]	1349.2 vs	1349.2 vs		CH ₂ wag.	1349.2 s 1363.4] s 1364.4] 1365.6]	1349.2 s 1359.2] m 1360.0] 1361.3]	1353.9 s 1354.8 1356.2 1357.6 1358.1 1361.4 vs 1362.6 1363.1] m 1363.2] m	CH ₂ wag.	
1365.5		1361.4							
1437.4 b 1443.9 1449.7]	~1440 1440.5 1441.0]	1438.7 1442.7 1442.8	CH ₂ bend	CH ₂ bend	1421.9 1423.9] s 1432.9 m,b	~1422 b	1406.7 1429.3	CH ₂ bend	
					~1729 ~1744.9] s 1752.3 s 1788.5	~1732.4 m 1742.0 1748.0	1721.5 s ~1747 m,b	CO str.?	
2087.5] s ~2092.2]	2085.8] s 2088.3] s	2085.9] s 2087.8] s 2103.8 s				-2087			
2113.4 2115.6 2116.9 2117.7] vs	2113.9] vs 2117.7] 2124.8] 2127.6]	2112.0 vs	N=N str.	Bands due to anharmonic resonance involving mainly NNN asym. str.	~2108 s 2123.3 vs	2107.9] s 2109.7] s 2113.9] ~2117] vs 2120.0] vs 2127.8 vs	~2095.1 2102.1 s 2112.1 s 2115.6] s 2116.8] s	Bands due to anharmonic resonance involving mainly NNN asym. str.	
2141.0	2137.5 s	2135.9] s ~2140.3]							
2152.3] vs 2154.6]	2151.4] s 2153.6] s	2153.5 s				2163 b	2151.4] 2153.6]		
2189.7 m	2185.8 m 2191.4	2187.9 m							
2216.9 2218.0 2222.6] m	2218.8] m 2221.4]	2218.8				~2222 m,b	~2219.0] m,b 2224.9]	2211.3 2222.9	
~2253.6 2258.9]	~2254.7 b	2256.5	C≡N str.	C≡N str.					

multiple conformers. The more than 150 cm^{-1} range of the observed bands is way too large to be attributed to matrix sites, and suggests 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 of 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 also a previous study [6] suggested a similar complexity in this region even in the gas phase spectrum. A rather weak band observed in all three matrices around $2255\text{--}2259\text{ cm}^{-1}$, but absent from the spectra of azidoacetone to be discussed below is undoubtedly due to the CN stretching vibration (Figs. 2,*b* and 3,*b*).

For the more complex azidoacetone molecule, with its twelve atoms and thirty vibrational modes, more complex infrared spectra should be expected, making their interpretation correspondingly more difficult. Similar to AzN, also in the AzC by far the most intense infrared fundamental is predicted to be the asymmetric N_3 vibration, computed to lie in both conformers near 2255 cm^{-1} (unscaled). Also here several structured bands are found in this region, whose appearance, width and splitting changes substantially from matrix to matrix (Fig. 3,*b*). 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. 3,*b*.

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. 3,*b*). Besides significant changes in their frequencies from matrix to matrix, also their relative intensities are 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 are probably in view of the low molecu-

lar symmetry strongly mixed, becomes more difficult. Comparison with the AzN would seem to dictate assigning in solid neon the rather strong band at 1282.8 cm^{-1} 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. 3,*a*).

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 photolysis of the matrices at various wavelengths, no appreciable spectral changes were detected. No new bands appeared following irradiation of the matrices, there were also no substantial changes in 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 the DFT calculations of 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 N_3 asymmetric stretch, CN stretch and combinations and overtones of the numerous lower frequency vibrational modes can be most likely an interpretation of the strong band splittings occurring in the asymmetric stretch region of the N_3 group.

Acknowledgments

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