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Fourier Transform Infrared Matrix Isolation Study of Acetonitrile in Solid Argon

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The intramolecular fundamental vibrations of CH_3CN trapped in solid argon matrix have been reinvestigated by means of FT-IR spectroscopy in the spectral range of 4000-500 cm^{-1}. By employing a quantum detector, infrared spectra could be obtained at matrix to solute ratio of 10000, allowing the clarification of the peaks due to monomeric species more clearly. Temperature controlled diffusion was initiated to identify the dimeric and polymeric species in terms of difference spectra. The assignments of monomeric and dimeric species are found, in general, to agree with the earlier work performed at higher concentration ($Ar/CH_3CN=1500$) using a dispersive spectrometer. Nonetheless the difficulty of minute differences between the earlier infrared and Raman spectroscopic results could be resolved. Moreover, the previously unnotified peaks due to polymeric species have been identified.

Introduction

Acetonitrile is a Lewis base very useful for probing the acidic sites of various solid surfaces[1]. In our FT-IR spectroscopic study of acetonitrile adsorbed on silica supported nickel[2], a comprehensive information was needed on the details of molecular association. Although the dimer of acetonitrile is known to possess an anti-parallel centro-symmetric C_{2h} structure with the interaction centered on the CN dipoles[3], the structures of higher multimers are rather uncertain. A more thorough experimental and theoretical investigation seemed to be necessary to understand the molecular association of acetonitrile.

Matrix isolation is a technique for trapping isolated molecules of the species of interest in a large excess of an inert material by rapid condensation at a low temperature, so that the diluent forms a rigid matrix[4]. At a sufficiently low temperature, diffusion of the solute species is prevented and thus *e.g.*, molecular complexes may be stabilized for leisurely spectroscopic examination[5,6].

Freedman and Nixon[7] has investigated the infrared spectra of acetonitrile in solid argon matrices at 20 K. The maximum Ar/CH_3CN ratio they used was 1500. In order to achieve more accurate assignment of the vibrational spectra of aggregated acetonitrile, the matrix isolation study appeared to be performed for a much greater matrix/absorber ratio. In this respect, we have reinvestigated the infrared spectra of CH_3CN in solid argon matrix for $Ar/CH_3CN=10000$ and 715. Considering that earlier work was performed by using a rather insensitive dispersive spectrometer, we have attempted to obtain the high quality spectra by using a Fourier transform IR spectrometer. The intramolecular fundamental vibrations in the 4000-500 cm^{-1} range have been thoroughly analyzed and the assignments on monomer, dimer, and higher multimeric forms have been comparatively discussed with the earlier reports.

Experimental

Reagent grade acetonitrile was initially treated with a small piece of sodium metal to remove any water content, and then degassed by repeated trap-to-trap distillation at 77 K. Argon (99.99% purity) was transferred to a Pyrex bulb *via* a flexible stainless bellow immersed in liquid nitrogen. The purified CH_3CN and the matrix gas (Ar) were mixed in mole ratios varying from 1 : 715 to 1 : 10000 using a standard manometric technique. The gas mixtures were left overnight to attain equilibrium, and then sprayed through two deposition lines onto a cold KBr window held at 9 K. Deposition was performed for 4-5 hours, maintaining the deposition rate in the range of 7-9 mmol/h by using a fine metering valve.

A Janis Model 22 closed cycle helium cryocooler was used to cool the KBr substrate down to 9 K. To increase the temperature, a resistive heater was wrapped around the cryotip. Appropriate temperature was maintained by the Lake Shore DRC-80-M temperature controller. When needed, matrices were annealed at 33 or 45 K 10 min, and then cooled back to 9 K to record the IR spectra. The pressure of the cryostat, monitored with a Leybold Penningvac PM 310 gauge, was kept below 10^{-5} mbar.

Infrared spectra were recorded by using a vacuum-purged

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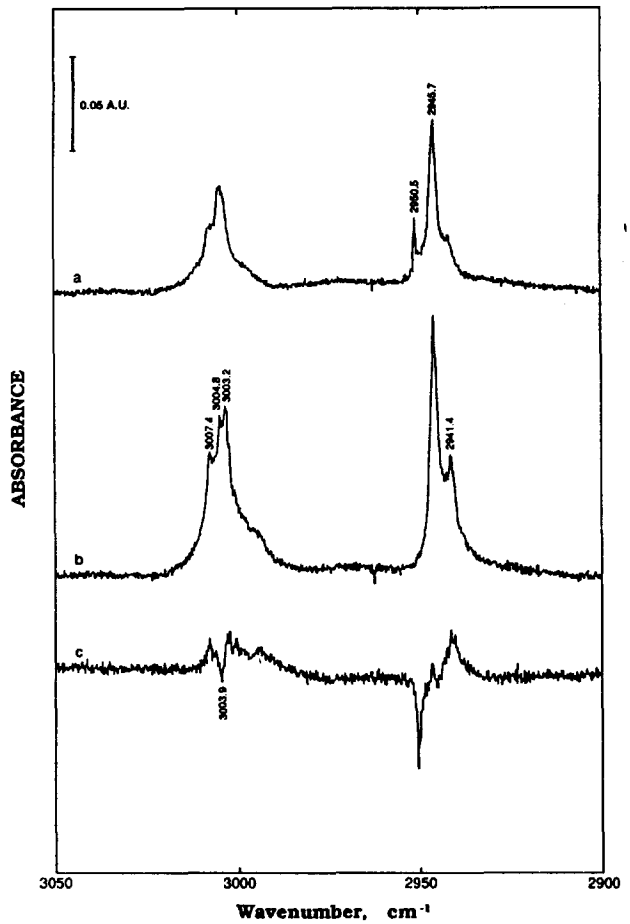

Figure 1. Infrared spectra of the CH stretching fundamentals of CH_3CN trapped in solid argon ($Ar/CH_3CN=715$) at 9 K. (a) After deposition, (b) after anneal at 45 K for 10 min, (c) difference (b-a).

Fourier transform infrared spectrometer (Bruker Model IFS 113v) at spectral resolution of 0.25 cm^{-1}. The 512 times scanned interferograms with a liquid nitrogen cooled MCT (Mercury Cadmium Telluride) detector were averaged for an individual spectrum. The single beam spectrum of the bare cold KBr window was taken as the reference spectrum. The rotational lines of gaseous CO and H_2O were used to calibrate the wavenumbers. The wavenumber accuracy read from the spectra is better than ± 0.1 cm^{-1}. To obtain a difference spectrum between two spectra obtained before and after annealing, A and B, we have adopted the method in which two parameters, α and β, are to be found to minimize the squared sum, $\Sigma_i(B_i-\alpha A_i+\beta)^2$. The optimum value of α was found to be close to 1. The difference spectrum thus obtained could be consistently interpreted with a physical significance reasonably.

Results and Discussion

Figure 1a shows the infrared spectrum of C-H stretching fundamentals of CH_3CN in solid argon matrices at 9 K for $Ar/CH_3CN=715$. At least three peaks can be identified in each region of the symmetric and asymmetric C-H stretching vibrations, namely at 2950.5, 2945.7 and 2941.4 cm^{-1} for the former region and at 3007.4, 3004.8 and 3003.2 cm^{-1} for the latter region. The spectral pattern hardly changed after annealing the matrix at 33 K and then cooling back to 9 K. However, noticeable changes occurred when the matrix had been annealed at 45 K. Figure 1b represents the IR spectrum recorded at 9 K after annealing at 45 K. The shoulder peak at 3003.2 cm^{-1} in Figure 1a was clearly resolved from the nearby peak at 3004.8 cm^{-1} and became the most intense band. On the other hand, the peaks at 2945.7 and 2941.4 cm^{-1} became more distinct while the peak at 2950.5 cm^{-1} in Figure 1a disappeared completely. This can be evidenced more clearly from the difference spectrum shown in Figure 1c. The negative peaks in Figure 1c correspond, in a relative sense, to the species lost by the annealing treatment whereas the positive peaks to those favorably produced at 45 K.

True isolation can be achieved only at a very high matrix/absorber (M/A) ratio, usually far greater than 1000. At low M/A ratios, molecular aggregates can be formed and trapped in addition to monomers[8]. The spectrum shown in Figure 1a is thus considered to arise from a composite mixture of monomer, dimer and higher multimers. Since monomers will diffuse on warming to form dimers and larger clusters, the negative peaks at 3004.8 and 2950.5 cm^{-1} in Figure 1c may then be assigned to the asymmetric and symmetric C-H stretching vibrations of monomeric CH_3CN. The present assignment looks in good accord with the earlier works. That is, the corresponding bands were reported to appear at 3004.0 and 2950.3 cm^{-1} by Freedman and Nixon[7] from the IR study and at 3005.6 and 2950.1 cm^{-1} by Givan and Loewenshuss[9] from the matrix isolated Raman study. It would be appropriate to mention that high quality spectrum in the C-H stretching region could not be obtained for Ar/CH_3CN greater than *ca.* 5000 owing to the very absorbing background. The higher the M/A ratio, the more gas mixture should be deposited to identify the peaks clearly. This enhances the background absorbance, more significant at higher frequency region. Accordingly, the relatively weak C-H stretching peaks become more difficult to be identified.

The 2945.7 and 2941.4 cm^{-1} peaks in Figure 1a which grow with annealing are attributed to symmetric C-H stretching mode of CH_3CN multimers. Since the latter peak becomes relatively more intensified than the former, the 2941.4 cm^{-1} peak is assigned to polymeric species while the 2945.7 cm^{-1} peak to dimeric form. Freedman and Nixon[7] assigned the peak at 2945.6 cm^{-1} to the dimeric species even though they could not identify the presence of polymeric forms. On the other hand, Givan and Loewenshuss[9] reported from the Raman spectroscopic study that the symmetric C-H stretching band due to polymeric species appeared at 2941.3 cm^{-1} along with a dimeric band at 2945.5 cm^{-1}.

In contrast with the case of symmetric mode, the asymmetric C-H stretching modes due to dimer and higher multimers are somewhat difficult to be assigned. Freedman and Nixon[7] assigned the 3004.0 cm^{-1} peak to encompass the monomeric and dimeric forms of CH_3CN. Similarly, Givan and Loewenshuss[9] rendered the peak at 3005.6 cm^{-1} to arise from both species. In the present work, we could observe, as mentioned earlier, at least three distinct peaks in the asymmetric C-H stretching region. From the difference spectrum, we attributed already the peak at 3004.8 cm^{-1} to the

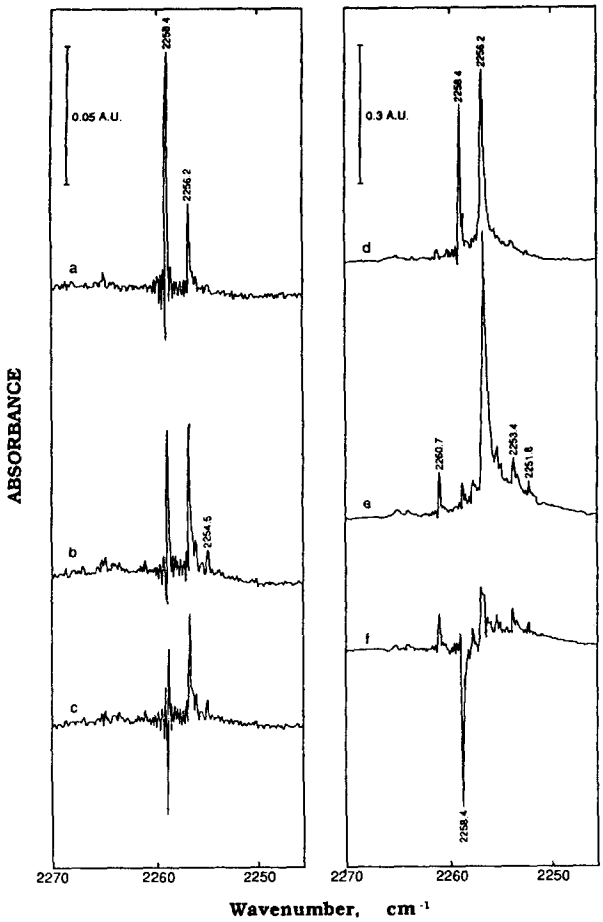

Figure 2. Infrared spectra of the CN stretching fundamentals of CH_3CN trapped in solid argon at 9 K. (a) After deposition with Ar/CH_3CN (M/A)=10000, (b) after annealing the matrix at 45 K for 10 min, (c) difference (b-a), (d) after deposition with M/A=715, (e) after annealing the matrix at 45 K, (f) difference (e-d).

monomeric CH_3CN. Its somewhat broad feature may occur from the removal of vibrational degeneracy caused by the inhomogeneous matrix environment. One may then assign the most intensified peak at 3003.2 cm^{-1}, after annealing, to trimer or higher multimers, and the somewhat less intensified 3007.4 cm^{-1} peak to dimeric species. On the contrary, one may accuse the two peaks at 3004.8 and 3007.4 cm^{-1} to arise wholly from monomeric species in different matrix environment. Namely, the 3007.4 cm^{-1} peak which gained intensity upon annealing might arise from monomeric species as likely that at 3004.8 cm^{-1} but in a substantially more homogeneous environment. The 3003.2 cm^{-1} peak can then be attributed to the dimeric species and its rather broader shoulder toward lower frequency side to the higher multimers. At present, it is not evident which interpretation would be more plausible. The latter interpretation seems, however, to be more preferably considered since the C-H stretching modes of acetonitrile are shifted to lower wavenumbers upon the formation of molecular clusters. For instance, the asymmetric C-H stretching vibrations of CH_3CN were observed at 3009.2 and 3002 cm^{-1}, respectively, for the gas phase[10] and the 3 mol % solution in CCl_4[11].

Figure 2a and 2b show the IR spectra of C-N stretching fundamental of CH_3CN in solid argon matrix at 9 K for Ar/CH_3CN=10000 before and after annealing at 45 K, respectively. Considering the M/A ratio, the peaks in Figure 2a may be attributed mainly to monomeric and possibly dimeric forms of CH_3CN. Since the two sharp peaks at 2258.4 and 2256.2 cm^{-1} exhibit different behavior upon annealing as can be evidenced from the difference spectrum in Figure 2c, the former band which becomes weakened after annealing may be rendered to monomeric CH_3CN, while the latter intensified to dimeric form. The present assignment is also in fair agreement with the earlier reports. Freedman and Nixon[7] assigned the peaks at 2258.4 and 2256.2 cm^{-1} in the Ar matrix to the CN stretching bands of monomer and dimer of CH_3CN, respectively. Givan and Loewenshuss[9] observed the corresponding bands at 2258.2 and 2256.0 cm^{-1} from the Raman spectroscopy.

For 3 mol % solution of CH_3CN in CCl_4[11], the CN stretching vibration occurs at 2257.5 cm^{-1}. Hence, the frequency in the dilute solution state is greater than that of dimeric form in Ar matrix. This is in contrast with the case of CH stretching vibration. Assuming that dimeric CH_3CN is favorable in the 3 mol % solution, the present observation can be attributed simply due to the difference in the polarizabilities of CCl_4 and Ar. The nitrile group which is more polarizable than the methyl group will interact with CCl_4 more favorably than with Ar. On the contrary, one can alternatively assume that matrix shift is much the same as solvent shift. In fact, as Barnes suggested[12], several equations explaining solvent shifts could be applied to the vibrational shifts of solutes in matrices, since the only difference between solutions and matrices lies in the fact that in a matrix the solvent molecules surrounding the trapped species are fixed in position, forming a rigid cage, whereas in solution the solute occupies a flexible cavity. Acetonitrile was reported to exist in the form of clusters or aggregates even at the highest dilution state. Loewenschuss and Yellin[11] could deconvolute the CN stretching band into two Gaussian components centered at 2257.5 and 2250.0 cm^{-1} for an IR spectrum of 3 mol % CH_3CN in CCl_4. It is interestingly seen that the deconvoluted peak positions are very close to those of dimer and polymer assigned in the present matrix isolation work.

It can be seen from Figure 2b that a peak centered at 2254.5 cm^{-1} grows with annealing. The peak may be attributed to polymeric species. The shoulders in the lower frequency side of the 2256.2 cm^{-1} peak are also seen to grow concurrently. Although their origins are matters of conjecture, it is tempting to render them to multimeric species since various peaks ranging from 2260.7 to 2251.8 cm^{-1} are found to grow when the sample with the M/A ratio=715 is annealed at 45 K (see Figure 2d-2f). It is very intriguing to observe several peaks that can be attributable altogether to polymeric species. They may reflect the presence of clusters with different sizes in various heterogeneous matrix environments. In N_2 matrix, the CN stretching frequency of polymeric form of acetonitrile was reported to be greater than that of monomeric form[13]. Considering that the amount of matrix induced shift by N_2 should be comparable to that by Ar, the CN stretching mode is then very susceptible to the molecular cluster size. Since the CN stretching mode in the crystalline phase occurs at 2250.1 cm^{-1} at 9 K[14], it is very tempting to assign the 2251.8 cm^{-1} peak in Figure

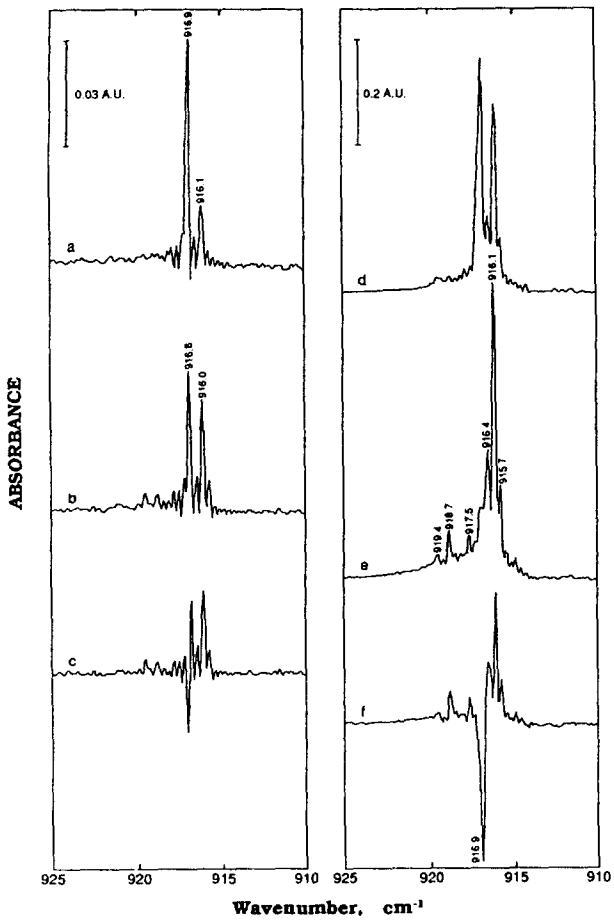

Figure 3. Infrared spectra of the CC stretching fundamentals of CH_3CN trapped in solid argon at 9 K. (a) After deposition with M/A=10000, (b) after anneal at 45 K, (c) difference (b-a), (d) after deposition with M/A=715, (e) after anneal at 45 K, (f) difference (e-d).

2e to a pseudo-crystalline phase produced by annealing at 45 K. In fact, it is noteworthy that under nearly the same experimental condition, earlier investigators could not identify the presence of any polymeric forms from the CN stretching region albeit they did from other spectral regions.

Figure 3a and 3b show the IR spectra in the C-C stretching fundamental region for $Ar/CH_3CN=10000$ at 9 K before and after annealing at 45 K, respectively. Figure 3c represents their difference spectrum. Since the M/A ratio is very high, the most prominent peak at 916.9 cm^{-1} in Figure 3a can be attributed to monomeric species and the next one at 916.1 cm^{-1} to dimeric species of CH_3CN. The difference spectrum shows the former peak to be weakened while the latter intensified upon annealing. It is seen, however, that the peak assigned to monomer is slightly shifted to lower wavenumber upon annealing. This causes the peak to be resolved into a doublet in the difference spectrum, one negative and the other positive at 916.8 cm^{-1}. Both peaks are supposed to arise from monomeric species in different matrix environment. Since the negative peak is more intense than the positive peak, substantial amount of monomers initially present are supposed to be converted to dimers or higher polymers by annealing. The peaks at 916.4 and 915.7 cm^{-1} which also grow with annealing are then rendered to polymeric species. This can be evidenced more clearly from the spectra obtained for $Ar/CH_3CN=715$ as shown in Figure 3d-3f. Since most of the monomers initially present are converted to dimers and polymers by annealing, doublet splitting is hardly observable in the difference spectrum. Several peaks attributable to polymeric species are seen in the difference spectrum, namely at 919.4, 918.7, 917.5, 916.4 and 915.7 cm^{-1}. The polymeric clusters appear to exist in different matrix environment with varying aggregate sizes. One may notice that the relative intensity of monomer to dimer peak in Figure 3d exhibits different behavior from that in Figure 1a or 2d. This can be understood, however, by referring that infrared peak intensities, which are directly related with the dipole moment derivatives with respect to normal coordinates, are generally much dependent on the kinds of vibrational modes.

The present assignment of the CC stretching modes for monomeric and dimeric species of CH_3CN is in good agreement with Freedman and Nixon[7]. They observed three peaks at 919.0, 916.9 and 916.1 cm^{-1} and attributed them to polymer, monomer, and dimer, respectively. It would be somewhat surprising to observe only one peak assignable to polymeric species. Considering that earlier study was performed by using dispersive instrument, weak bands will be hardly expected to be detectable. In this regard, high resolution FT-IR spectroscopy employed in the present work is certainly superior to low resolution dispersive method. It is noteworthy that the peak positions of the bands assigned to polymeric species are surprisingly close to those of crystalline phase. Pace and Noe[15] observed three peaks at 920.5, 919.0 and 915.4 cm^{-1} in the CC stretching region for the α crystalline phase of CH_3CN and one peak at 917.8 cm^{-1} for the β phase. Except for the band at 916.4 cm^{-1}, the CC stretching frequencies observed in the matrix isolated spectrum are in fact comparable to those in the crystalline phases. Hence, it appears that crystalline phases are produced in Ar matrix by a brief annealing treatment. Considering that the aggregate size of polymeric species in the matrix medium will be variously distributed and each species will exist in different environments, appearance of several polymeric peaks in the matrix medium can be understood.

It is interesting that the peak position of CC stretching band in neat liquid state is similar to that observed for 3 mol % solution in CCl_4. Deconvoluting the CC stretching band into two Gaussian component, the peak positions are located at 919.7 and 921.9 cm^{-1} for neat liquid and at 919.5 and 921.9 cm^{-1} for solution state[11]. Since the present matrix isolation study could resolve the CC stretching band into several peaks, the CC stretching band in the liquid state appears to be deconvoluted into more than two components. The broad envelope of the CC stretching band in the solution spectrum are certainly dominated by the polymeric species.

Figure 4a and 4b show the IR spectra in the symmetric CH_3 deformation region for $Ar/CH_3CN=10000$ at 9 K before and after annealing at 45 K, respectively. From the difference spectrum in Figure 4c, the two major peaks at 1376.0 and 1375.6 cm^{-1} are attributed to monomer and dimer, respectively. The present assignment is somewhat inconsistent with the earlier report. Freedman and Nixon[7] assigned the corres-

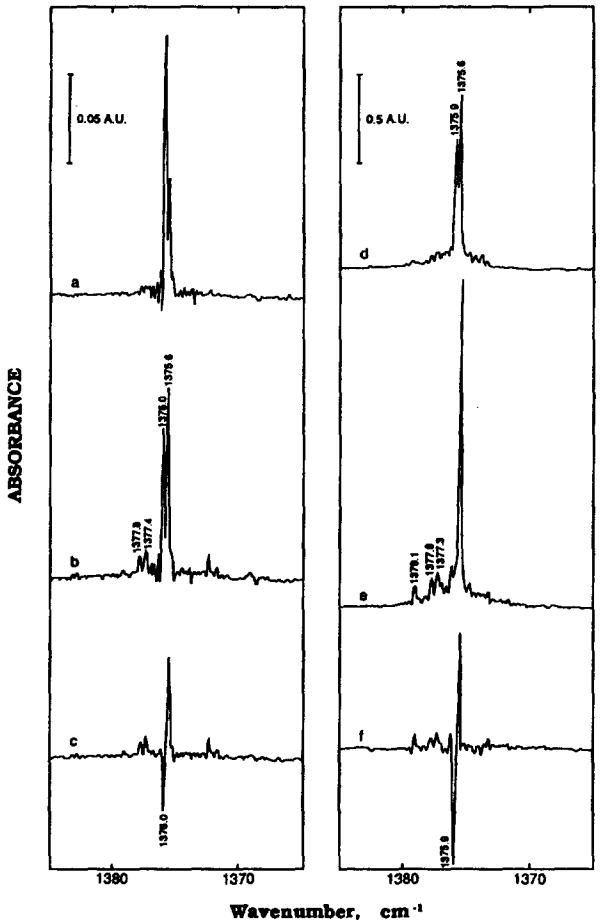

Figure 4. Infrared spectra of the symmetric CH_3 deformation fundamentals of CH_3CN trapped in solid argon at 9 K. (a) After deposition with M/A=10000, (b) after anneal at 45 K, (c) difference (b-a), (d) after deposition with M/A=715, (e) after anneal at 45 K, (f) difference (e-d).

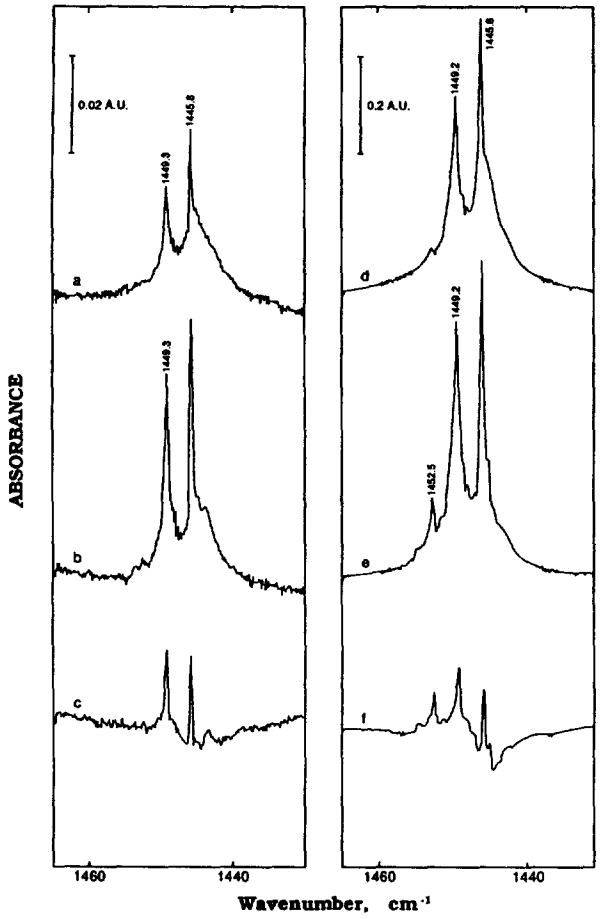

Figure 5. Infrared spectra of the asymmetric CH_3 deformation fundamentals of CH_3CN trapped in solid argon at 9 K. (a) After deposition with M/A=10000, (b) after anneal at 45 K, (c) difference (b-a), (d) after deposition with M/A=715, (e) after anneal at 45 K, (f) difference (e-d).

ponding band to appear at 1375.8 and 1377.6 cm^{-1}, respectively. Although we could observe several other peaks, namely at 1377.8, 1377.4 and 1376.3 cm^{-1}, their intensities were substantially weaker than those assigned to monomer and dimer. Since the M/A ratio was very great, those weak peaks seemed not due to monomeric and/or dimeric species. Even when the Ar/CH_3CN ratio was 715, the two peaks centered at 1375.9 and 1375.6 cm^{-1} were the most prominent (see Figure 4d-4f). The dimeric peak was observed to be more intense than the monomeric one even before annealing. The monomeric species became barely noticeable after annealing at 45 K. It can be noticed from Figure 4e that a weak peak appears at 1379.1 cm^{-1} after annealing. Its position is close to that of polymeric species assigned by Freedman and Nixon[7], 1379.6 cm^{-1}.

Although we have assigned the prominent peak at 1375.6 cm^{-1} in Figure 4 to the symmetric CH_3 deformation mode of dimeric species of CH_3CN, the peak may contain the polymeric contribution. So far, we could assign several distinct peaks due to polymeric species from other spectral regions. It is intriguing then why intense peak does not appear in the symmetric CH_3 deformation region even after annealing at 45 K for Ar/CH_3CN=715. Hence, it is strongly suspected that the 1375.6 cm^{-1} band might be attributed by a composite of dimer and certain crystalline polymeric aggregates.

The asymmetric CH_3 deformation region of CH_3CN consists of two sharp peaks at 1449.3 and 1445.8 cm^{-1} which are superimposed on a broader background absorption. The former peak becomes somewhat intensified in a relative sense after annealing. But, as can be seen from Figure 5a-5c, their relative intensity change is insignificant on annealing at 45 K . This is in contrast with the observations made in other spectral regions. Hence, neither peaks seems to be related exclusively to the monomeric species. We assign both peaks to dimeric species since they appear distinctly even when the Ar/CH_3CN ratio is substantially higher such that polymeric species would be infavorable. When CH_3CN was moderately diluted (M/A=715), above two peaks were again dominantly observed at 1452.5 cm^{-1} began to grow after annealing at 45 K. We assign the peak due to polymeric species. The difference spectrum shown in Figure 5f exhibits further that the asymmetric CH_3 deformation band of monomeric CH_3CN seems to appear in the 1446.5~1444.4 cm^{-1} region with a rather broader bandwidth. Then, its band center will be very close to that of dimeric species at 1445.8 cm^{-1}. A little intensity decrease of the 1445.8 cm^{-1} peak

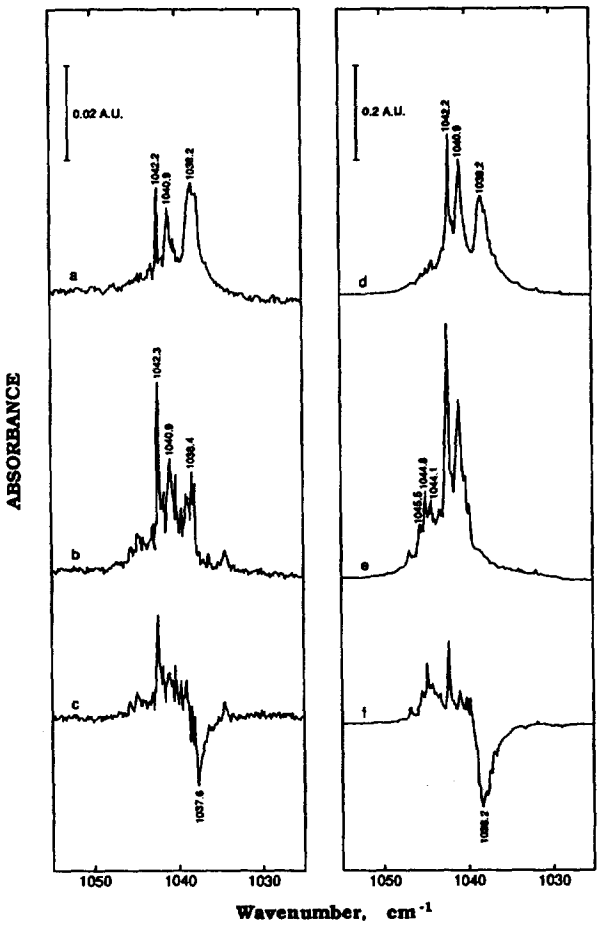

Figure 6. Infrared spectra of the CH_3 rocking fundamentals of CH_3CN trapped in solid argon at 9 K. (a) After deposition with M/A=10000, (b) after anneal at 45 K, (c) difference (b-a), (d) after deposition with M/A=715, (e) after anneal at 45 K, (f) difference (e-d).

upon annealing can be understood on this basis. It may be worth to point out that Freedman and Nixon[7] also attributed the two prominent peaks to dimer absorptions lying over a broader monomer band centered at about 1445 cm^{-1}. The broad feature of monomeric band as well as the appearance of two distinct dimeric bands are believed to be related with the removal of vibrational degeneracy of free molecule in the matrix medium.

Figure 6a and 6b show the IR spectra in the CH_3 rocking region for $Ar/CH_3CN=10000$ at 9 K before and after annealing at 45 K, respectively. On annealing a rather broader band at 1038.2 cm^{-1} in Figure 6a is splitted to multiplets along with intensity decrease in a relative sense. Appearance of several peaks even for $Ar/CH_3CN=10000$ is supposed to arise from the removal or vibrational degeneracy and the co-presence of monomeric and dimeric species. Considering the higher M/A ratio, the prominent peaks at 1042.2 and 1040.9 cm^{-1} in Figure 6b are rendered to dimeric species. On the other hand, monomeric bands are supposed to exist at about 1037.6 cm^{-1}. When the Ar/CH_3CN ratio was decreased to 715, the monomeric bands disappeared almost completely upon annealing at 45 K as can be seen from Figure 6e. From the presence of several shoulder peaks at the low

Table 1. Assignments of Fundamental Vibrations of CH_3CN Trapped in Solid Argon (cm^{-1})[a]

Mode	CH_3CN(gas) IR[b]	CH_3CN/Ar IR[c]	CH_3CN/Ar Raman[d]	CH_3CN/Ar IR[e]
Sym. CH str.	2953.9	2950.3(M)	2950.1(M)	2950.5(M)
(ν_1, A_1)		2945.6(D)	2945.5(D)	2945.7(D)
			2941.3(P)	2941.4(P)
Sym. CN str.	2266.5	2258.4(M)	2258.2(M)	2258.4(M)
(ν_2, A_1)		2256.2(D)	2256.0(D)	2256.2(D)
				2260.7(P)
				2253.4(P)
				2251.8(P)
Sym. CH_3 def.	1390.0	1375.8(M)	1376.0(M)	1375.9(M)
(ν_3, A_1)		1377.6(D)		1375.6(D)
		1379.6(P)		1379.1(P)
				1377.8(P)
				1377.4(P)
Sym. CC str.	919.9	916.9(M)	917.9(M)	916.9(M)
(ν_4, A_1)		916.1(D)		916.1(D)
		919.0(P)		919.4(P)
				918.7(P)
				917.5(P)
				916.4(P)
				915.7(P)
Asym. CH str.	3009.2	3004.0(M,D)	3005.6(M,D)	3004.8(M)
(ν_5, E)				3007.4(M)
				3003.2(D)
Asym. CH_3 def.	1448.0	1445.0(M)	1444.5(M)	1444.4~
(ν_6, E)				1446.5(M)
		1449.2(D)		1449.2(D)
		1445.7(D)		1445.8(D)
		1452.3(P)		1452.5(P)
CH_3 rock	1040.8	1037.9(M)		1038.4(M)
(ν_7, E)				1037.6(M)
		1042.2(D)		1042.2(D)
		1040.8(D)		1040.9(D)
		1044.2(P)		1044.8(P)

[a] M : monomer, D : dimer, P : polymer. [b] Ref. 10, [c] Ref. 7. [d] Ref. 9. [e] This work.

frequency side of the 1038.2 cm^{-1} peak in the difference spectrum (Figure 6f), it can be conjectured that monomeric species formed initially after deposition exist indeed under various heterogeneous environments. The weak peaks growing on annealing at 1045.5, 1044.8 and 1044.1 cm^{-1} in Figure 6e may be attributed in turn to the formation of polymeric clusters. The present assignment seems to be in accord with that of Freedman and Nixon[7]. They assigned the monomeric peak to appear at 1037.9 cm^{-1}, the dimeric peaks at 1040.8 and 1042.2 cm^{-1}, and the polymeric peak at 1044.2 cm^{-1}. Only four peaks were distinguished by them in the CH_3 rocking region. This indicates clearly that high resolution FT-IR spectroscopy provides in fact more fine vibrational struc-

tures than dispersive spectroscopy. The vibrational assignments made in this work are collectively summarized in Table 1.

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A Simple Synthesis of 3-Substituted 1-Amino-2-thioxo-4-imidazolidinones, Isolation of the Intermediates, N-Amino-N-ethoxycarbonylmethyl-N′-aralkyl-thioureas

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1-Aminothiohydantoin derivatives were prepared in good yields by the reaction of alkyl or arylisothiocyanates with ethyl hydrazinoacetate hydrochloride in presence of triethylamine. The intermediates, N-amino-N-ethoxycarbonylmethyl-N′-aralkylthioureas, which were formed during the reaction and could be transformed into the appropriate 1-aminothiohydantoins, were isolated and characterized.

Introduction

1-Aminothiohydantoin was synthesized first by Traube and Hoffa.[1] Uota[2] synthesized it by heating ethyl hydrazinoacetate·HCl and KCNS at 120℃ for 30 min. 1-Aminohydantoin was prepared by condensation of semicarbazones with ethyl monochloroacetate in presence of sodium alkoxide in dry ethanol by Jack.[3]

The 2-oxo analogues of title compounds, 1-aminohydantoin are important intermediates in the preparation of several hydantoin pharmaceuticals. Nitrofurantoin, the derivatives of 1-aminohydantoin is the most widely used urinary tract antibacterial agent.

In order to discover new useful therapeutic agents, 3-substituted 1-amino-2-thioxo-4-imidazolidinones are synthesized as intermediates of novel NSAIDS. The introduction of a heterocyclic ring in the amide side chain of 1, 2-benzothiazine-3-carboxamide derivatives increases antiinflammatory activity. We will describe a series of related compounds later.

Here we describe a simple synthesis of 3-substituted 1-aminothiohydantoin by reaction of Jacobsen.[4]

Result and Discussion

When ethyl hydrazinoacetate hydrochloride[5] **1** was added to a solution of an equimola of isothiocyanate and a twofold amount of triethylamine in dichloromethane, an intermediate was formed rapidly. The intermediate, N-amino-N-ethoxycarbonylmethyl-N′-aralkyl-thiourea **2** was isolated after about 2 hours and was subsequently transformed into 1-aminothiohydantoin **3** by reaction with triethylamine in dichloromethane for about 4 days. The cyclisation usually required a couple of days and in all cases was not over more than 4 days at room temperature as judged by T.L.C. (silica gel, ethyl acetate : dichloromethane, 1 : 3). This intermediates were reported first by Jacobsen,[4] N-amino-N-ethoxycarbonyl methyl-N′-phenylthiourea was isolated and characterized.

The cyclisation was not accelerated significantly by addition of more than twofold triethylamine. The cyclisation products were characterized by carbonyl absorptions in the