Interaction of Acetonitrile with Alcohols at Cryogenic Temperatures

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Supporting Information



ABSTRACT: Temperature-dependent interaction of acetonitrile with methanol and ethanol, as codeposited and sequentially deposited films, was studied in the 10-130 K window, in ultra high vacuum. Films in the range of 50-100 monolayers were investigated using temperature-dependent reflection—absorption infrared spectroscopy (RAIRS), Cs⁺ ion scattering mass spectrometry, and temperature-programmed desorption (TPD). Acetonitrile interacts with methanol and ethanol through intermolecular hydrogen bonding. When a codeposited system was annealed, acetonitrile underwent a phase segregation at 110 K, and large changes in the infrared spectrum were observed. The OH stretching of methanol gave two peaks characteristic of the change to the α -phase of methanol, while ethanol gave three peaks at the same temperature. The surface composition of the systems probed by 40 eV Cs⁺ scattering showed that both the alcohols and the acetonitrile were of equal intensity below 110 K, while above 110 K the intensity of the latter went down substantially. We find that the presence of acetonitrile does not allow ethanol to undergo complete phase transition prior to desorption, while methanol could do so. This behavior is explained on the basis of the size, extent of hydrogen bonding, and phase transition temperature, of the two alcohols. Additional peaks in the hydroxyl region observed in alcohols in the 110–130 K window may be used as a signature of the presence of acetonitrile mixed with alcohol, especially ethanol, and hence this may be used in observational studies of such molecular environments.

1. INTRODUCTION

A systematic understanding of physical and chemical changes of molecular solids is a subject of intense study from several perspectives. It ranges from acquiring a fundamental knowledge on such systems to their relevance in space science.¹⁻³ In laboratory conditions, thin films of molecular solids having less ordered structure (also known as amorphous solids) are grown by vapor deposition at low temperature and pressure, which upon annealing to higher temperature undergo phase transition to their respective crystalline phases.⁴ Phase transition is one of the important physical changes that can drastically alter the face and fate of molecular solids. It can even initiate chemical reactions.^{5,6} Amorphous to crystalline phase transformation is a thermodynamically favorable process in such systems, with the exception of a few cases.⁷ Such irreversible phase transition to crystalline solids can affect the chemical processing of ices. Crystalline ices are less reactive as compared to their amorphous analogues.⁸ Once crystallized, the reactions of molecular solids can stop or may proceed through a different pathway. Phase transitions in interstellar ices occur through many channels. The main channel involves thermal activation, from the radiation produced by nearby stars or from new star forming regions. The other channels include surface reactions leading to thermal processes, exposure to UV and other high energy radiations, and ion or electron impact on ices, all of which can lead to an increase in temperature. Localized increase in temperature can also initiate a variety of chemical and physical changes in ices, besides other stimuli.

Methanol, besides water and carbon monoxide, is among the most abundantly identified molecules in various astrophysical

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regions and has been investigated extensively.⁹⁻¹⁴ It is detected in dense molecular clouds, star forming regions,¹⁵⁻²⁰ circumstellar and protostellar envelopes, as well as in comets.^{21,22} This molecule is plausibly formed upon hydrogenation of carbon monoxide-ice²³ and/or photon, electron, or high energy projectile collisions on methane and carbon monoxide-ice mixtures in ISM.²³⁻²⁶ Because of its simple structure and abundance, methanol is believed to be the precursor for a wide variety of complex molecular transformations in ISM. A recent investigation showed that electron irradiation on methanol ice, at conditions similar to ISM, produced a variety of products including glycerol.²⁷ Ethanol is also identified in gas and solid phases in ISM, but is less abundant than methanol.^{28,29} Ethanol can form in ISM through various pathways, such as redox reaction (hydrogenation followed by oxidation of acetylene),³⁰ photon irradiation (UV-induced reaction of ethane ice in the presence of CO_2^{31} and UV-induced reaction on methanol ice³²), etc. There are several reports on infrared spectroscopic investigations of methanol and ethanol in solid and liquid phases and their interaction with different molecules.^{10–12,33–36} Most of the interactions are based on their ability to form intermolecular hydrogen bonding.

Acetonitrile has been used to study molecular interactions, both in gaseous and in condensed phases.^{37–42} Distinct features of the nitrile functional group and its sensitivity as compared to other functional groups allowed several fundamental investigations, such as vibrational stark effects,⁴³ folding and unfolding of proteins,⁴⁴ hydrogen bonding,⁴⁵ etc. In ISM, acetonitrile is believed to act as a building block for the synthesis of amino acids.⁴⁶ It has been detected in diffused clouds of ISM, in comets, and in the atmosphere of Titan.^{47–50} Upon high energy electron irradiation on different aliphatic nitrile molecules, amino acids are detected in laboratory conditions.⁵¹

Probing the interaction of acetonitrile with methanol and ethanol has been a challenging topic for a long time.^{37,38,52-61} Most of the efforts are made in liquid phase as all three are widely used as solvents. Recently, we have reported the solid-phase interaction of acetonitrile with water at low temperatures.⁶ Acetonitrile and water vapors were codeposited at 40 K and were subsequently annealed to 130 K. RAIRS analysis of this mixture of molecular solids showed (i) hydrogen bonding interaction with two additional peaks in hydroxyl and nitrile stretching region; (ii) upon annealing above 110 K, acetonitrile started segregating and tended to form a pure layer within the water matrix; and (iii) it desorbed finally upon crystallization of the water film. Such an interaction was found to be absent when these molecules were sequentially deposited one over the other. Considering the outcome of this experiment and also due to profound interest in acetonitrile molecule and its interaction with other molecular entities present in ISM, we expanded our investigation to alcohol molecules. In the present work, we probed the interaction of alcohols (methanol and ethanol) with acetonitrile. The experimental procedure used was very similar to our earlier report, although the results obtained were quite different.

2. EXPERIMENTAL SECTION

The present experiments were performed using a custom-built instrument. Instrument details are given elsewhere.⁶³ In brief, the instrument consisted of an ultrahigh vacuum chamber held at a base pressure of 5×10^{-10} mbar fitted with various probes to study molecular solids. There are provisions to do low energy ion scattering (LEIS), secondary ion mass spectrometry (SIMS)

induced by alkali ions, temperature-programmed desorption (TPD), and reflection-absorption infrared (RAIR) spectroscopy on vapor deposited molecular solids. A Ru(0001) single crystal, mounted on a copper holder and attached to a closed cycle helium cryostat with a capacity to lower the temperature up to 10 K, was used for sample deposition. The substrate can be heated using a resistive heater up to 1000 K range, controlled by a temperature controller (Lakeshore 336). The temperature was monitored using three sensors, a silicon diode sensor, a thermocouple sensor, and a platinum sensor with an accuracy of 0.001 K. All of the sensors give a temperature within ± 0.01 K. In the present study of the interaction of methanol and ethanol with acetonitrile, we have used mainly RAIRS to see the molecular interactions; Cs⁺ ion-based SIMS was used to probe the surface species upon heating and TPD to understand the desorption behavior of the ice films.

In RAIRS, the spectrum was recorded using a Bruker Fourier transform infrared spectrometer, Vertex 70 model, in combination with an external liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The IR beam was taken out of the infrared spectrometer and focused onto the substrate using gold plated mirrors. Reflected IR beam from the substrate was focused again using another silver-coated mirror to the external detector. The vacuum chamber was fitted with ZnSe flanges, which are transparent to the mid-IR beam. The chemicals were used as obtained or were further processed. Methanol (CH₃OH) (Fluka, LC-MS grade), ethanol (C_2H_5OH) (Rankem chemicals, fractionally distilled), acetonitrile (CH₃CN), and acetonirile- d_3 (CD₃CN) (both 99.95% from Sigma-Aldrich) were further purified by several freeze-pump-thaw cycles. The liquid samples were taken in glass to metal sealed adapter tubes and were connected to a sample line. Sample lines were pumped at 1 \times 10⁻³ mbar and were flushed several times with vapors of the desired molecule prior to deposition. Ethanol/methanol and acetonitrile were connected in two separate sample lines, and two different all-metal leak valves were used for vapor deposition into the chamber. The ruthenium substrate inside the chamber was precooled to 10 K, and the sample was backfilled inside the chamber. The pressure was monitored using a Bayard-Alpert (B–A) gauge (Pfeiffer Vacuum). We used sample coverages of 100 monolayers (ML). An exposure of 1×10^{-6} mbar for 1 s was taken as 1 monolayer.⁰⁴

Mixed solid films were prepared by codeposition and sequential deposition methods. In the codeposition method (prepared films are represented as Ru@CH₃CN:XOH, where X $= -CH_3$ or $-C_2H_5$), two leak values were used simultaneously to deliver vapors onto the target. Acetonitrile- h_3 (CH₃CN) [or acetonitrile- d_3 (CD₃CN)] vapor was leaked in using one leak valve, and methanol or ethanol vapors were deposited using the other leak valve, operated simultaneously. During deposition, pressure was maintained at 2×10^{-7} mbar for 10 min, which produced 100 MLs of film thickness, with approximately equal contribution from each source. This was confirmed through a residual gas analyzer, operated during deposition, to monitor the concentrations of both of the species (with respect to the intensities), which was maintained equal during deposition. Film thickness was further optimized and characterized by TPD profiles. During sequential deposition (notation used as Ru@ CH₃CN@XOH or Ru@XOH@CH₃CN, where $X = -CH_3$ or $-C_2H_5$; A@B implies that B is deposited over A), either acetonitrile or alcohol was deposited initially at $1\times 10^{-7}\,\rm mbar$ for 10 min. Subsequent layers were developed with a delay between to gain the base pressure (<5 \times 10⁻¹⁰ mbar). Because of the



Figure 1. Temperature-dependent RAIRS of pure and codeposited mixtures of acetonitrile and methanol. The OH stretching of pure methanol (a) and the CN stretching of pure acetonitrile (b) are compared to those of methanol (c) and acetonitrile (d), respectively, in the codeposited mixtures. Schematics within the figures show the composition of the system under study, along with cartoons of the molecules, illustrating the stretching motion. The peaks to be noted are highlighted with dashed lines. Full spectra of the codeposited mixture ice at different temperatures are given in Figure S1a. There is no feature due to CH₃CN in the region (c), and there is no feature of CH₃OH in the region (d). The spectra of the codeposited mixture (in c and d) at 10 K are fitted to Lorentzians, and the components are given as thin black lines. At temperatures above 110 K, the experimental spectrum itself shows distinct features, and in the in-between window, no new features are seen. The components and combined spectra are given in Figure S6.

higher coverage used (\geq 50 MLs), the ice systems studied here are substrate independent, and the properties are likely to be dependent only the molecular environment.

All depositions were carried out at 10 K, and the ice layers were heated slowly at the rate of 2 K/min to run the temperaturedependent RAIRS measurements. The low heating rate ensured less sample loss due to heating. Upon reaching a particular temperature, a delay of 3 min was given before collection of spectra. The spectra were collected in the mid-IR region with 2 cm^{-1} resolution. Each spectrum was an average of 512 scans to get better signal-to-noise ratio.

Besides spectroscopy, ice layers were also probed using Cs⁺ scattering mass spectrometry. This was studied with different ices composed of CD₃CN and alcohols (methanol or ethanol) either codeposited or sequentially deposited. The ice samples were prepared in the same way as mentioned above. Cs⁺ was generated from a low energy ion gun (Kimball Physics Inc.) at 40 eV kinetic energy, which was subjected to collide on the as-prepared solid ice sample. The scattered ions were analyzed by a quadrupole mass analyzer (Extrel CMS) kept at 45° with the surface normal. Low energy Cs⁺ scattering is a surface specific technique, which probes a few layers (1-10 MLs) of the surface.^{65,66} The scattered ions consist of Cs⁺ and the products arising from two other processes, such as reactive ion scattering (RIS) and low energy sputtering (LES). RIS is a peculiar property of the alkali and other ions (here Cs⁺). The low energy collision of Cs⁺ converts the neutral adsorbate species (X) to gas phase ions (CsX^+) by

association reaction. Some of the pre-existing ionic species could also be ejected out due to the ion impact, and the process is called LES. We used the RIS signal intensities, corresponding to $Cs(CH_3OH)^+$ (m/z 165), $Cs(C_2H_5OH)^+$ (m/z 179), and $Cs(CD_3CN)^+$ (m/z 177), to identify and understand the molecules appearing on the surfaces upon heating. Because the signal intensities are directly proportional to the surface population of the appropriate molecule on the ice surfaces, they can give insights into the surface dynamics upon heating. The surface was heated at 2 K/min, and Cs⁺ scattering was done at various temperatures. TPD measurements were done using a quadrupole mass analyzer (Extrel CMS) at a ramp rate of 10 K/ min on various samples.

3. RESULTS AND DISCUSSION

All of the experiments were started at identical conditions, and results of RAIRS analysis of ice mixtures made of alcohol (methanol or ethanol) and acetonitrile (codeposited) are shown first. Results and explanations from RAIRS data are further supported by RIS and TPD studies of the same mixtures, which are discussed later. The outcomes of these investigations were compared to those of the RAIRS investigations and similar other studies of sequentially deposited ice films of methanol/ethanol and acetonitrile. Ice is a generic term used for condensed molecular solids in astrochemistry literature. However, as the discussion in this Article is mostly on phase transition between amorphous and crystalline films, and the term "ice" generally refers to the crystalline phase of water, we have carefully avoided its use wherever it can cause confusion.

3.1. Interaction of Methanol with Acetonitrile. Initially, we performed temperature-dependent infrared spectroscopy of pure alcohols and pure acetonitrile, and later a similar experiment was performed on a codeposited mixture of acetonitrile and methanol to probe their interaction in the solid state. Pure methanol ice undergoes several structural transformations and possesses various phases at different temperatures. It has been well characterized in the condensed phase.^{10,11} Methanol vapor deposited below 90 K forms an amorphous phase, and upon annealing to 130 K, it undergoes a phase change to the crystalline α -phase.¹¹ This phase transition manifests as multiple changes in the IR spectrum and has resulted in a characteristic peak splitting of the spectrum in the hydroxyl stretching region. Although it undergoes another phase change to the β -phase above 165 K,¹⁰ it is not observed in UHV conditions. This is because pure methanol desorbs at 145 K under UHV conditions.¹³ In case of pure acetonitrile, our recent report,⁶² as discussed earlier, does not show any change until desorption (at 135 K), except a loss in intensity at 130 K. Yet later, in the current set of experiments, we observed an increase in intensity of the nitrile band $(-C \equiv N)$ stretching, 2251 cm⁻¹) at 110 K, which stays until pure acetonitrile desorbs at 135 K. This increase in intensity of the nitrile band is attributed to a phase transition. We have not observed this in our previous studies probably due to the high coverage used previously (500 monolayers).⁵¹

Methanol and acetonitrile were deposited together at 10 K, and the film was subsequently annealed to 130 K, while observing the changes in IR. The major interactions, expected and observed, were due to intermolecular hydrogen bonding between the -OH of methanol and $-C \equiv N$ of acetonitrile. We will discuss the major spectral changes observed in this region. Figure 1 shows the comparative RAIR spectra of pure methanol and acetonitrile (Figure 1a and b) along with codeposited acetonitrile and methanol ice mixture, in the -OH (Figure 1c) and $-C \equiv N$ stretching regions (Figure 1d) at different temperatures. We will limit our discussion to these regions as interesting changes are observed here. Please note that pure acetonitrile shows no features in regions a and c and pure methanol shows no features in regions b and d. The full spectra are given in Figure S1a. At 10 K, methanol and acetonitrile ice films are amorphous. When heated, bands do not show significant change until 110 K. However, distinctive changes were observed at 110 K, which continued until 135 K, and the features, upon desorption of the molecules, disappeared completely at 140 K.

In Figure 1, most of the features of pure and codeposited mixtures match in the regions a and c, except for a small hump at \sim 3410 cm⁻¹ (Figure 1c). To clearly understand the differences between the pure and the codeposited mixtures, the 10 K spectrum of codeposited ice mixture was fitted to Lorentzians. The component peak at 3410 cm⁻¹ is due to the fraction of molecules having intermolecular hydrogen bonding between methanol and acetonitrile. The other components at ~3300, 3250, and 3190 cm^{-1} have peak positions that, very similar to pure methanol, arise due to methanol having a hydrogen bond with itself.¹¹ Upon heating, this small hump (at 3410 cm⁻¹) disappeared, and the spectrum showed splitting at 110 K giving two new features, one at 3302 cm^{-1} and another at 3196 cm^{-1} respectively, in pure and mixed ices. This splitting is attributed to a phase transition from amorphous to α -phase¹¹ as mentioned before. In the codeposited mixture, however, even though this

splitting occurs at 110 K, the ratio of intensity of the two peaks (after splitting, Figure 1c) changes as compared to pure methanol (Figure 1a). The peak at 3196 cm⁻¹ shows relatively higher intensity in the codeposited mixture as compared to that of pure ice. Spectra in this region remained the same until 140 K (Figure S1a), before complete desorption of the ice mixture. As spectral components are obvious after splitting, we did not do peak fitting for all of the spectra.

Spectral analysis of −C≡N stretching at 10 K shows a band in the range of 2260-2244 cm⁻¹ for pure acetonitrile, but in the case of the codeposited film, a new feature appeared at 2263 cm⁻¹. This feature is assigned to intermolecular hydrogen bonding between acetonitrile and methanol molecules.³⁷ The 10 K spectrum of the ice mixture in the $-C \equiv N$ stretching region is fitted to Lorentzians, and the two components obtained are shown as thin black lines. They are centered at 2263 and 2252 cm⁻¹. A similar additional feature (at 2263 cm⁻¹) was observed in our previous report on the $-C \equiv N$ stretching region due to hydrogen bonding of acetonitrile with water.⁶² Upon heating until 80 K, the spectrum remained the same. Above 90 K, the feature at 2263 cm⁻¹ in the codeposited ice film showed a shift and decrease in intensity, and it disappeared completely beyond 105 K. This is due to the breaking of intermolecular hydrogen bonds leading to phase segregation. Similar behavior was observed in our previous study of water and acetonitrile codeposited mixture,⁶² but at a relatively higher temperature (above 120 K). At 110 K, the spectrum became narrow, due to more ordered structure of the ice layer (Figure 1d). The same behavior is found in the case of pure acetonitrile ice (Figure 1b, peak at 2251 cm^{-1}), and in both cases the spectrum remained the same until 130 K.

To get a deeper understanding of the desorption behavior of the ice layers, we carried out TPD measurement of the codeposited equimolar mixture (Figure S2). Figure S2a shows the TPD spectrum collected at 10 K/min heating rate. This shows that desorption starts around 125 K for both acetonitrile and methanol, and maxima are observed at 136 and 139 K for acetonitrile and methanol, respectively. Pure methanol in UHV condition desorbs at 145 K, and in the case of pure acetonitrile, it is above 130 K. However, when they are mixed, the desorption temperature of the mixture shifts to a value that is an average of the desorption temperatures of the respective pure films. Such desorption behavior is expected because they are mixtures.^{12,13,67,68}

The C-H stretching band (3000-2910 cm⁻¹) (data not shown) has a contribution from both methanol and acetonitrile. To observe the effect of interaction in the C–H band region, we changed the composition of the ice mixture to CD₃CN and methanol. This ice layer was first probed using RAIRS, and results are shown in Figure S3. Spectra shown in Figure S3a-c are expanded views of the same plots, consisting of -O-H, -C-H, $-C \equiv N$, and -C - D stretching regions. The mixture of ices is compared to pure methanol and pure CD₃CN at various temperatures. The recorded features show a similar pattern as seen in Figure 1 with an additional peak at 2273 cm⁻¹, which disappears upon annealing to 110 K. This can be attributed to the breaking of intermolecular hydrogen bonding. The peak at 2251 cm^{-1} (Figure S3c) is the C–D stretching band of CD₃CN. The C-H stretching in Figure S3b has a contribution from methanol alone, as the mixture consists of CH₃OH and CD₃CN. The peaks at 2958 and 2987 cm⁻¹ are assigned to asymmetric -CH₃ stretching, and that at 2832 cm⁻¹ is from symmetric $-CH_3$ vibrations.¹¹ Upon comparing the 10 and 110 K spectra (in the



Figure 2. Temperature-dependent RAIRS of pure and codeposited mixtures of acetonitrile and ethanol. The OH stretching of pure ethanol (a) and CN stretching from pure acetonitrile (b) are compared to those of ethanol (c) and acetonitrile (d) in the codeposited mixtures. Schematics within the figures show the composition of the system under study, along with cartoons of the molecules, illustrating the stretching motions. The peaks to be noted are highlighted with dashed lines. The spectrum of the codeposited mixture at 10 K is fitted to Lorentzians, and the components are shown as thin black lines. The component and combined spectra are given in Supporting Information (S6). Full spectra of codeposited mixtures of ices at different temperatures are given in Supporting Information (S1b).

C–H region) of pure methanol and its codeposited mixture (with CD_3CN), we could not find any new peak suggesting new information on the nature of the molecular interaction. The spectrum at 10 K is broad and gets narrower at 110 K due to phase transition.

3.2. Interaction of Ethanol with Acetonitrile. Phase transition of amorphous solid ethanol starts above 125 K and gets completed between 130 and 135 K and it becomes crystalline. This crystalline phase remains until 145 K and gets desorbed later.³⁶ As in the previous case, we performed a temperaturedependent RAIRS measurement of pure ethanol followed by a codeposited mixture of acetonitrile and ethanol. Figure 2 shows the temperature-dependent investigation of the codeposited ethanol-acetonitrile ice mixture in the -O-H (Figure 2c) and $-C \equiv N$ stretching regions (Figure 2d), which are further compared to the spectra of pure ethanol and CH₃CN. The full range spectra of the codeposited mixture, recorded upon annealing, are presented in Figure S1b. Similar to the methanol-acetonitrile system, the spectra collected at 10 K showed no change in behavior until 100 K, but at 110 K, significant changes were observed in the spectra, which remained unchanged until the ice mixture underwent desorption. We also performed a TPD study of the codeposited mixture (Figure S2b). Here, unlike methanol, ethanol and acetonitrile molecules do not desorb close to each other. Acetonitrile starts desorbing above 130 K followed by ethanol (at 136 K). While acetonitrile completes the desorption at 136 K, ethanol was detected even above 145 K.

A broad band in the 3500–3050 cm^{-1} range (Figure 2a) appeared due to the amorphous nature of pure ethanol ice at 10 K. The spectral feature remains the same in pure ice and undergoes crystallization beyond 122 K. The spectrum presented at 135 K (blue line, Figure 2a) shows a sharp peak at 3251 cm^{-1} and a hump at 3179 cm⁻¹. The spectrum at 110 K (Figure 2a) is still amorphous in nature, which is evident from the broad band. Yet, in the ethanol-acetonitrile mixture, the scenario is totally different (Figure 2c). A broad spectrum is found until 100 K, but at 110 K, three peaks appeared at 3290, 3243, and 3179 cm^{-1} , which became more intense upon annealing to 130 K. Figure 2b and d shows a similar comparison in the $-C \equiv N$ stretching region of pure CH₃CN and the codeposited mixture. The spectrum at 10 K is broad in both cases with an additional hump at 2263 cm⁻¹ for the codeposited mixture. This arises from the fraction of molecules participating in intermolecular hydrogen bonding with ethanol. This hump reduced its intensity from 90 K and disappeared totally at 110 K. Again, at 110 K, the $-C \equiv N$ stretching feature is similar to that of pure CH₃CN. The spectrum at 10 K in the above region was fitted to Lorentzians. The $-C \equiv N$ stretching gave two components, as obtained in the methanol-acetonitrile mixture. In the OH stretching region at 10 K, we observed a small hump in the $3400-3500 \text{ cm}^{-1}$ range (Figure 2c), and the same is absent in pure ice. This peak is assigned to intermolecular hydrogen bonding between ethanol and acetonitrile. This spectrum in the -OH region gave four components upon fitting, which are shown with thin black lines.

To find more information on the nature of interaction, we modified the system, and acetonitrile was replaced by CD_3CN .



Figure 3. Temperature-dependent RAIR spectra of sequentially deposited alcohols (methanol and ethanol) with acetonitrile. Parts (a)–(c) show the stretching regions of hydroxyl, C–H, and nitrile regions, respectively, of films when methanol is deposited over of acetonitrile. The same regions are shown in the case of ice layers deposited in the reverse fashion in parts (d)–(f). Parts (g)–(i) indicate the same regions when ethanol was deposited on top of acetonitrile, while parts (j)–(l) are for a reverse system where ethanol was deposited before acetonitrile. Schematics are given within the figures for clarity along with the cartoons of molecules, illustrating the stretching motions, and the important peaks are highlighted with dashed lines.

The data are presented in Figure S3d-f. The O-H region showed features similar to those in Figure 2. The $-C \equiv N$ stretching frequency has a small hump at 2273 cm⁻¹ due to intermolecular hydrogen bonding. The peak at 2251 cm⁻¹ is due to C-D stretching of CD₃CN. The C-H stretching region (Figure S3e) in the ethanol-CD₃CN mixture has a broad band at 2971 cm⁻¹ due to asymmetric CH₃ stretching, and the other features at 2912 and 2877 cm⁻¹ are due to symmetric CH₃ and CH₂ stretching vibrations. These features get intensified when the film is annealed, but do not present any signature of molecular interaction. However, at 110 K, the feature at 2986 cm⁻¹ gets enhanced as compared to that of pure ice. This is attributed to an interaction of acetonitrile with ethanol.

3.3. Sequential Deposition of Alcohols and Acetonitrile (CD₃CN) Mixtures. The investigation was continued on sequentially deposited molecules where a pure layer of alcohol (methanol or ethanol) was produced initially, which was covered by a CD₃CN film (Ru@XOH@CD₃CN). These ice layers were probed thoroughly using RAIRS at different temperatures. The film development sequence was changed to yield Ru@CD₃CN@ XOH, which was also studied. All of these data are shown in Figure 3. When CD₃CN was covered by alcohols, the $-C \equiv N$ stretching band (Figure 3c and i) changed its shape upon annealing (from a broad peak at 10 K to a sharp signal at 110 K with increased intensity). No additional shift or change was found in this band up to 130 K. When CD₃CN was on top, features were the same up to 110 K as mentioned above, but the IR intensities were lost at 130 K, which limited our studies.

The O–H stretching region (Figure 3a) in methanol in both cases showed a similar trend, but the peak intensity ratio after splitting was different. The C-H stretching region did not show any difference in both cases (Figure 3b). When CD₃CN was deposited under ethanol and annealed to 120 K, three peaks appeared in the O–H stretching region, but this change occurred at a higher temperature (>110 K) and with lesser intensity, as compared to the codeposited mixtures (see Figure S3). Upon reversing the sequence of the ice film, only two features appeared, and the ethanol layer behaved more or less like pure ethanol ice, which indicated that the intermolecular interaction with acetonitrile was less. Most of the features in the C-H stretching region of ethanol appeared similar in both of the sequentially deposited systems. However, a new feature in the CH₃ asymmetric stretching region at 2986 cm⁻¹ was observed in the Ru@CD₃CN@C₂H₅OH system, also at 130 K. This feature was previously assigned due to the intermolecular interaction of acetonitrile and ethanol (Figure S3e) in the codeposited mixture. This additional feature in the sequential deposition sytem indicates structural changes due to diffusional mixing in alcohols, in the presence of acetonitrile, and will be discussed later in the Discussion. Sequential deposition was tried for methanol(and ethanol)-CH3CN as well, and similar results were obtained (data not shown). Hence, we conclude that there is no significant isotope effect.

3.4. Cs⁺ Scattering Data. We performed low energy Cs⁺ ion scattering mass spectrometry on binary ice mixtures, mainly to probe the changes on the surface, during thermal annealing. Collision energy used for scattering was 40 eV throughout the



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Figure 4. Cs^+ scattering mass spectra collected from codeposited mixtures of methanol and acetonitrile (a), and ethanol and acetonitrile (b). Sequentially deposited ice layers of methanol with acetonitrile (c and e) and ethanol with acetonitrile (d and f) are also shown. Schematics showing the composition of the system under study are shown within the figures.

experiment. Cs^+ ion scattering is one of the best surface sensitive tools available and is very sensitive to a few top monolayers.⁶⁹

Low energy Cs^+ ion upon surface collision is capable of producing secondary ions. As described briefly in the Experimental Section, the scattered ions consist of Cs^+ , Cs^+ neutral adducts (reactive ion scattering (RIS), ions observed are $CsCH_3OH^+$, $CsC_2H_5OH^+$, and $CsCD_3CN^+$), as well as preformed ions (low energy sputtering, LES). The RIS mass spectra from different sample mixtures are shown in Figure 4. The ion intensity data of this plot are compared against different temperatures in Figure 5. Figure 4a and b shows the scattering data of codeposited mixtures of CD_3CN with methanol and

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Figure 5. Absolute ion intensities obtained from Cs^+ scattering mass spectra (data from Figure 4) are plotted against temperature. The data at 110 K are marked with a dashed line to note the change. Schematics showing the composition of the system are shown within the figures for clarity.

ethanol, respectively. Figure 4c–f shows results from sequentially deposited systems. When ethanol and methanol were codeposited with CD₃CN, we observed Cs(CD₃CN)⁺ (m/z 177), Cs(C₂H₅OH)⁺ (m/z 179), and Cs(CH₃OH)⁺ (m/z 165) with almost similar intensities at 10 K. Yet, this was not the case in the sequentially deposited film. When methanol or ethanol were on the top at 10 K (Figure 4c and d), it gave only m/z 165 and m/z 179 peaks, while m/z 167 due to Cs(CD₃CN)⁺ was

observed when CD_3CN was deposited on the top (Figure 4e and d) in both cases. As we annealed the sample, the ion intensities showed a significant change.

Upon looking closely into Figures 4 and 5, we found that two species (in two cases) maintain comparable intensities until 110 K for codeposited mixture samples, which are methanol + CD_3CN and ethanol + CD_3CN (Figure 5a,b). This suggests that they both stay on the surface with equal population. Yet at 110 K,

where we observed a change in the IR spectrum, $Cs(CD_3CN)^+$ (*m*/*z* 177) ion intensity went down until it disappeared totally at 130 K, while alcohol peak maintained the same intensity up to 130 K and above.

In the sequential deposition cases, when the sequence is Ru@CD₃CN@XOH where alcohol was on the top, only the alcohol peak was seen initially at 10 K. Yet from 30 K on, the $Cs(CD_3CN)^+$ (m/z 177) peak started emerging, indicating the presence of CD_3CN on the surface (Figure 4c,d). The presence of CD₃CN on the surface can be attributed to diffusional mixing of CD₃CN with alcohol. However, after 110 K, this peak at m/z177 disappeared. It can be said that above 110 K, the diffusional mixing of CD₃CN stops. In the other case of sequential deposition (Figure 4e,f) where CD_3CN was on top, we saw only the $Cs(CD_3CN)^+$ peak (m/z 177) until 110 K. At 110 K, intensities due to alcohols (both ethanol and methanol) started appearing and got intensified as the samples were annealed further. The signal at m/z 177 disappeared totally above 130 K. due to desorption of pure acetonitrile, and the bottom layer of alcohol stayed until 140 K and desorbed at their characteristic desorption temperatures.

4. DISCUSSION

Molecular interaction of alcohol and acetonitrile is strong in a codeposited mixture as compared to the sequentially deposited system. A portion of the molecules in the mixture interact through intermolecular hydrogen bonding with hydroxyl (alcohol) and -C≡N (acetonitrile) groups. This hydrogenbonding interaction in the -OH stretching region will be manifested as a blue shift from the alcohol ice phase (~3250 cm^{-1}) and a red shift from the alcohol gas phase (~3600 cm⁻¹) peak positions.^{61,70} Alcohols are more likely to form intermolecular hydrogen bonding with the same species. The hydrogen-bonding interaction energy for alcohol-alcohol in the case of methanol is -26.8 kJ/mol,⁷¹ and that of ethanol is -23.94kJ/mol.⁶⁰ Interaction energy for alcohol-acetonitrile is -25.1 and -18.84 kJ/mol for methanol and ethanol,⁶⁰ respectively. Hence, in the ice mixture at 10 K, the alcohol-alcohol interactions will be energetically more favored over alcoholacetonitrile interactions, even though the mixture we created in the gas phase is of 1:1 in ratio. The interaction energy of an acetonitrile dimer was calculated to be -20.81 kJ/mol.^{55,7} All of these reports used different levels of theory, and, therefore, interaction energies are not comparable. Nevertheless, the data suggest that these molecules can form clusters or aggregates with different combinations, some containing only alcohols and acetonitrile and others with both alcohols and acetonitrile, in various proportions. All of these interactions can be seen in the RAIR spectrum, as it probes the sample as a whole. In case of alcohol-acetonitrile ice mixture, the interaction between alcohol and acetonitrile was manifested as small humps at 10 K upon deposition. These peaks were absent in pure ice. Upon annealing beyond 100 K, the humps lost their intensity. In the case of water-acetonitrile codeposited mixture (in our previous report),⁶² we observed additional bands in the O-H stretching regions at 10 K due to intermolecular hydrogen bonding. These features also disappeared upon annealing, as acetonitrile underwent phase segregation. Here, the additional peak (in alcohols-acetonitrile) due to intermolecular interaction was just a small hump, unlike water acetonitrile mixture (where an additional band was seen), because the peak was more or less buried within the broad O-H band.

To clearly observe these small humps at 10 K, the mixture ice spectra were fitted to Lorentzians. The component peaks are given (as a thin black line) along with the 10 K spectra in Figures 1 and 2. The fitted peaks are centered around 3410, 3300, 3250, and 3190 cm^{-1} in the case of methanol-acetonitrile ice, in the O-H stretching region (Figure 1c and Figure S6a). Computed frequency shifts (-OH region) for isolated methanol clusters shows that a cluster size of n = 3-6 comes very near to the observed solid-state spectrum.^{71,73} The OH stretching frequencies vary from ~ 3500 cm⁻¹ for dimers to ~ 3200 cm⁻¹ for hexamers and other larger clusters. In an amorphous phase, all of the combinations (n = 3-6 and more) and structures (cyclic and chain like) are possible, resulting in a broad peak. Hence, the component peaks observed upon fitting at 3300, 3250, and 3190 cm⁻¹ are attributed to various such combinations of pure methanol. The component at 3410 cm^{-1} , which is shifted from the cluster peak position of the aggregate (in the solid phase), is attributed to methanol diluted with acetonitrile. In the case of ethanol-acetonitrile ice mixture, the fit gave four components centered around 3420, 3310, 3260, and 3180 cm⁻¹, respectively (Figure 2c and Figure S6c). These components are attributed similarly to the presence of aggregates embedded with acetonitrile (3420 cm⁻¹) to pure ethanol aggregates. The studies in liquid phase reported by Elangovan et al.⁶¹ showed that as the acetonitrile concentration increases in acetonitrile-ethanol mixtures, the O-H stretching gets more blue-shifted from pure ethanol.

Intermolecular hydrogen bonding between alcohol and acetonitrile is also manifested as a hump near the $-C \equiv N$ peak at 2263 cm⁻¹ in case of codeposited mixtures of methanol and ethanol with acetonitrile (Figures 1d and 2d). Corresponding features were also observed at 2273 cm⁻¹ in the case of CD₃CN-alcohol codeposited mixtures (Figure S3c). This hump is observed from 10 to 110 K. Disappearance of this feature at 110 K suggests that hydrogen bonds break at this temperature to allow phase segregation. We also observed that above 110 K, the $-C \equiv N$ stretching peak gets intensified or narrowed, which indicates that acetonitrile molecules get more oriented and ordered (Figures 1d and 2d) assisted by thermal energy.

In our previous work on water interaction with acetonitrile,⁶² we had reported phase segregation within the water matrix starting at 110 K, which was completed above 120 K. Here also, such a phase segregation takes place for acetonitrile, but at a lower temperature (110 K). This may be because the extent of molecular interaction of water–acetonitrile is much greater than that in the alcohol–acetonitrile system. Therefore, acetonitrile molecules can phase segregate within alcohol ice at a lower temperature.

Once acetonitrile molecules are phase segregated, they will try to stay inside as aggregates or crystallites along with similar aggregates or crystallites of alcohol. As the sample is annealed, acetonitrile molecules gain sufficient energy and try to desorb from the ice mixture. The extent of desorption depends on the other components present in the mixture. In the case of alcohols, the phase transition temperatures are around 110 K. It is known that as the molecules are nearing phase transition, their molecular motion increases.⁷⁴ This motion opens a path for acetonitrile to desorb upon annealing, and we see almost complete desorption of acetonitrile above 136 K in both acetonitrile—alcohol mixtures. This effect will be more for methanol due to stronger intermolecular interactions, leading to larger intermolecular motions in this system. In the case of ethanol, this effect is less, but still it desorbs before its regular desorption temperature



Figure 6. Infrared spectra of methanol (a and b) and ethanol (c and d) at 130 K in O–H and C–H stretching regions, with the spectra of pure alcohols and alcohols codeposited and sequentially deposited with acetonitrile compared. Schematics within the figures show the systems compared. Arrows in (a) are added to easily recognize the intensity ratios of peaks, and the dotted circles in (c) and (d) are to show the difference due to interaction with acetonitrile.

(which is ~150 K). This phenomenon was observed in the TPD profiles of codeposited mixtures also (Figure S2). The TPD profiles of codeposited ice mixtures are complicated due to the interactions and incomplete phase segregation of alcohol and acetonitrile molecules. Pure acetonitrile has a peak maximum at 130 K. For pure methanol and ethanol, the desorption maximum is around 145–150 K. In the mixture, we have alcohol peaks starting from 130 to 160 K, but the desorption maxima were shifted, which is due to the molecules still interacting with acetonitrile and also due to incomplete phase segregation. In the case of water, where the desorption temperature is 160 K, the phase segregation of acetonitrile is almost complete, and it desorbs only at the onset of crystallization of water, as a molecular volcano, at 145 K.^{62,74}

Physical phenomena observed in sequentially deposited mixtures are mainly due to diffusional mixing. Because of weak intermolecular interaction (between acetonitrile–acetonitrile molecules), they diffuse through alcohols upon annealing, and a fraction of those molecules are observed on the surface starting from 30 to 110 K (in the Ru@CD₃CN@C₂H₅OH system). The other fraction of acetonitrile gets trapped inside the alcohol ice.

Alcohols likely form porous solids when they are vapor deposited at 10 K similar to water. Acetonitrile molecules use these pores to diffuse to the surface. During this diffusional process, acetonitrile may also make intermolecular hydrogen bonding with alcohols and may get trapped inside the pores as mentioned above. Diffusional mixing of molecules at temperatures as low as 30 K (in Ru@CD3CN@XOH) is unexpected. However, we may note that the peak intensity (and concentration) of acetonitrile is poor. We believe that the diffusion may be facilitated by the thermal fluctuation during deposition of a second layer over the first, making the interface mixed. This effect leading to diffusion and appearance of the under-layer at the surface is more likely when alcohol is deposited over acetonitrile and not in the reverse due to extensive hydrogen bonding in alcohols. The temperature change due to condensation could have been quantified using the heat of condensation and heat capacities of the condensed solids. Unfortunately, the above data, for the systems of interest, are not available in the literature. Assuming the values for water ice and solid benzene (as models of hydrogen-bonded and nonhydrogen-bonded systems, respectively) at 270 K, the ΔT for the deposition of 50 MLs of water over solid benzene is 4 times larger than the reverse. Similar diffusion and trapping of molecules inside water pores are reported recently.75 Beyond 110 K, the intensity of acetonitrile on the surface shows substantial reduction. This can be due to the following reasons: first, above 110 K, acetonitrile molecules acquire sufficient energy as they approach the desorption temperature, but the molecules avoid forming intermolecular hydrogen bond with alcohols, and instead they phase segregate. Because of this, a proportional reduction occurs on the surface. Second, if CH₃CN molecules are on the surface, they possess sufficient energy to desorb before attaching itself with Cs⁺ upon collision. Third, when alcohols undergo phase transition beyond 110 K, they form an ordered structure within themselves, preventing the acetonitrile from existing on the surface. These three effects combined together reduce the acetonitrile peak intensity (in the Cs⁺ scattering experiment) for the sequentially deposited mixtures above 110 K. The movement of acetonitrile through alcohol, especially ethanol, makes it act like the codeposited mixture at 110 K, giving three peaks in the -OH region (in IR spectra).

The case is different when acetonitrile is at the top (Ru@ C₂H₅OH@CD₃CN system). Here, acetonitrile related mass peaks alone are visible, and no alcohol peaks are observed from 10 to 110 K, which indicates that alcohol is not diffusing through acetonitrile. This is expected as alcohol forms an intermolecular hydrogen-bonded network within itself easily at 10 K and the network is strong, which stops individual alcohol molecules from diffusing through the acetonitrile layers to reach the surface. Above 110 K, the acetonitrile ice layer gets more ordered due to the phase transition. At this temperature, alcohol molecules in the underlying layer possess sufficient energy to reorient themselves, because it is near the phase transition temperature. This, in turn, can break some of the hydrogen bonds, and diffusion of a few individual alcohol molecules takes place, making them appear on the surface. When acetonitrile is deposited above the alcohol films, the intermolecular interaction between acetonitrile and alcohols is less as compared to the reverse case (where alcohols are deposited on acetonitrile layer). In other words, when alcohols are deposited first followed by acetonitrile vapor (during sequential deposition process), the mixture behaves similar to a pure acetonitrile-alcohol ice system, which does not happen when the order of deposition is reversed. Upon depositing alcohols on the top of acetonitrile, molecular diffusion of acetonitrile molecules through the alcohol ice layer triggers molecular mixing. IR measurements (Figure 6) support this, as explained below.

The spectral features recorded at 130 K (when phase transition is complete) for methanol and ethanol for codeposited and sequentially deposited mixtures with CD₃CN are shown in Figure 6. They are compared to the crystalline peaks of pure methanol and ethanol. Comparing the spectral features of O-H stretching of methanol at 130 K for different ices gives us the evidence to support and conclude our arguments. The ratios of the two peaks of α -phase of methanol at 130 K for these different ices have different intensities. Quantitatively, the peak 1 (3300 cm^{-1}) to peak 2 (3197 cm^{-1}) ratio is 3:1 in pure ice, while it is 2:1 in the case of codeposited mixtures (Figure 6a). In case of sequentially deposited mixtures, when methanol is at the top $(Ru@CD_3CN@CH_3OH)$, the ratio of peak 1 to 2 is more similar to the codeposited one. While it is at the bottom (Ru@ $CH_3OH@CD_3CN$), these peak ratios are very similar to the pure ones (Figure 6a). This change in the case of the former (Ru@ CD₃CN@CH₃OH) system to behave like the codeposited

system is due to the diffusional mixing of acetonitrile through methanol layers as evident from our Cs⁺ scattering data (Figure 5b). In the latter case (Ru@CH₃OH@CD₃CN), this mixing is poor, and hence the O–H stretching region is more like pure methanol ice. In the C–H stretching region (Figure 6b), we could not find any additional peak or change in the four cases, except in relative intensities.

The results agree very well with our arguments in the case of the ethanol–acetonitrile system too. Both the codeposited and the sequentially deposited mixtures with ethanol on top (Ru@ $CD_3CN@C_2H_5OH$) revealed three features in the O–H stretching regions at 130 K (Figure 6c). The reason for the latter to behave similar to the codeposited one is the diffusional mixing of acetonitrile when it is under ethanol, as discussed before. When ethanol is under acetonitrile (Ru@C_2H_5OH@ CD_3CN), diffusional mixing is not so evident, and it acts like pure ice giving two features in the O–H stretching region in the IR spectrum.

In the ethanol-acetonitrile codeposited system, we performed a few control experiments by reducing the acetonitrile ratio (Figures S4 and S5). We found that upon reducing the ratio to 1:20 (acetonitrile:ethanol), the response of the system was similar to that of pure ethanol ice, and as the ratio was increased, the system showed a characteristic spectrum with three peaks in the O-H stretching region (Figure S5a). These results suggest that the crystallization process is highly modified or prevented in ethanol due to the presence of acetonitrile. In the case of the methanol-acetonitrile system, because the phase changes of methanol and acetonitrile occur very near to 110 K, there appears a competition between phase segregation and phase transition. At 110 K, methanol undergoes a phase segregation and phase transition forming discontinuous layers of α -phase (as crystallites) along with acetonitrile crystallites. This mixture desorbs together between 130 and 140 K (Figure S2a), which is a lower desorption temperature as compared to pure methanol and a higher desorption temperature as compared to pure acetonitrile. This change in desorption curve suggests that there is still an interaction between these molecules (after phase transition) and it needs higher energy for acetonitrile to come out. Desorption of acetonitrile molecule triggers desorption of methanol at a relatively lower temperature than usual in frozen methanol, which is above 145 K.

However, the scenario in the case of ethanol is different. Its phase transition starts above 125 K, and complete crystallization takes place near 135 K in the pure film. In a codeposited mixture of ethanol with acetonitrile, acetonitrile tends to undergo a phase segregation between 90 and 110 K (Figure 2d). This phase segregation leads to partial collapse of the intermolecular hydrogen-bonding network between acetonitrile and ethanol, which in turn favors greater molecular interactions between the same molecules. Because of the larger size of the ethanol molecule (as compared to acetonitrile and methanol), its diffusional motion is hindered, and it does not segregate to form an extended chain, as compared to acetonitrile. This makes acetonitrile form crystallites or aggregates inside ethanol ice. The lack of restricted motion of ethanol leads to various orientations, finally giving three O–H stretching features at 110 K.

The third new feature at 3290 cm^{-1} is higher in intensity as compared to the other two features and is at a higher frequency (Figure 2c). Also, this feature appears when the concentration of acetonitrile increases, as observed from our control experiment (Figure S4). Hence, we propose that this feature arises from the alcohol molecules that still interact with acetonitrile. Above 110

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K, the acetonitrile molecules tend to phase segregate. This phase segregation may not be complete, and a few molecules of acetonitrile will be trapped and get crystallized within ethanol ice. These layers embedded with acetonitrile and ethanol reorient as temperature is increased from 110 to 130 K, giving higher intensity for the peak at 3290 cm⁻¹ at 130 K. The phase segregated acetonitrile crystallites or aggregates tend to desorb near 130 K, not allowing ethanol molecules to further assemble together and trap acetonitrile. Molecular motions of this trapped acetonitrile make ethanol molecule desorb early (145 K) in the acetonitrile—ethanol mixture (Figure S2b).

5. SUMMARY AND CONCLUSIONS

In the present work, we studied the temperature-dependent interaction of acetonitrile with methanol and ethanol separately, at low temperatures starting from 10 K. We produced codeposited mixtures and sequentially deposited mixtures. It was investigated using temperature-dependent (i) RAIRS, (ii) Cs⁺ scattering mass spectrometry, and (iii) TPD in the 10–130 K range, and the results of the studies were compared. Cs⁺ scattering data mainly looked at the ratio of the surface population of molecules at various temperatures, while RAIRS data probed the bulk ice composition. The combination of these two techniques gave an insight into the interaction between these two molecules. RAIRS study of the codeposited solid sample at 10 K revealed that the interactions of acetonitrile with methanol and ethanol are through intermolecular hydrogen bonding. A characteristic hump observed at 2263 cm⁻¹ in the case of CH₃CN $(2273 \text{ cm}^{-1} \text{ in the case of } CD_3CN)$ with both methanol and ethanol is the proof of the above hydrogen-bonding interaction. An additional hump observed in the O-H stretching regions of the mixture ices gave peaks at 3410 cm^{-1} in the case of methanol and at 3420 cm⁻¹ in the case of ethanol, assigned to the above intermolecular hydrogen-bonding interactions. However, they were less resolved and were buried in the broad OH stretching regions. When the system was annealed, acetonitrile underwent phase segregation at 110 K, and we observed breaking of this intermolecular hydrogen bonding and large changes in the entire IR spectrum were seen in codeposited ice mixtures. The OH stretching at 110 K in methanol produced two peaks, characteristic of the change to the α -phase, while ethanol gave three peaks at 110 K in the mixture. This observation of ethanol is attributed to the partial crystallization of acetonitrile molecules, which are trapped within ethanol and still continue to interact above 110 K in the acetonitrile-ethanol mixture.

The surface composition with respect to temperature probed by 40 eV Cs^+ scattering showed that both alcohols and acetonitrile were of equal intensity below 110 K, while above 110 K the intensity of acetonitrile went down substantially. In sequentially deposited mixtures, Cs^+ scattering revealed the diffusional mixing of acetonitrile leading to a better interaction when they were under the alcohol layers. This diffusional mixing led the sequentially deposited mixture to behave similar to the codeposited mixture when acetonitrile was under the alcohol film. When it was above alcohol, it behaved more like the corresponding pure ices.

Overall, we conclude that the presence of acetonitrile does not allow ethanol to undergo a complete phase transition, but instead the system forms irregular crystals of acetonitrile, trapped within ethanol at 110 K, and this mixture desorbs at a characteristic temperature above 140 K. Yet in the case of the methanol acetonitrile mixture, both of the molecules phase segregate to a better extent, forming crystallites that desorb together. This behavioral difference is explained on the basis of the difference in size, extent of hydrogen bonding, and phase transition temperature of the two different alcohols. Moreover, we suggest that the additional peaks in the hydroxyl region, observed in alcohols at 110-130 K, can be used as a signature of the presence of acetonitrile mixed with alcohol, especially ethanol, and hence can be used in observational studies of such molecular environment. Although the abundance of these molecules in ISM is less likely to have a one to one interaction as implied here, these molecules have been discovered with higher concentrations in comets and atmospheres of Titan, and such interactions are possible there.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b11483.

Temperature-dependent RAIR spectra of codeposited methanol–acetonitrile, ethanol acetonitrile ices, both for CH_3CN and for CD_3CN , TPD profiles of codeposited alcohol–acetonitrile mixtures, and a control experiment where acetonitrile concentration was varied in mixed ethanol ice (PDF)

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Notes

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