Neutron Vibrational Spectroscopic Study of the Acetonitrile:Acetylene (1:2) Cocrystal Relevant to Titan, Saturn's Moon

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ABSTRACT: Saturn's moon Titan features a surface composed of various organic solids with pronounced compositional and structural diversity. On top of the icy core, the surface experiences temperature of ~93 K and pressure of ~1.45 atm. Under these conditions, most small organic molecules exist as solids and form Titanean minerals. Acetonitrile and acetylene are two of these molecules, which can form single-component molecular solids, but also a 1:2 binary cocrystal. Here we present a combined neutron vibrational spectroscopic study, neutron powder diffraction study, and theoretical modeling of the cocrystal and the corresponding single-phase solids. This combined study resulted in insightful spectra–structure–properties correlations for the cocrystal and the molecular solids. Furthermore, we observed quenching of the high-temperature form of acetonitrile in the presence of the cocrystal, which supports the possibility of the existence of metastable solids as minerals on Titan. The results presented in this study further the knowledge of the putative structure and composition of the surface of Titan, and, at the same time, contributes to better understanding of the fundamental thermodynamic properties of two of the smallest organic molecules in the Universe.

INTRODUCTION

Acetonitrile and acetylene are two of the smallest organic molecules and important commodity chemicals on Earth, with prominent industrial relevance as solvents and fuels. These molecules are also naturally found on other celestial bodies where they play different roles. While under Earth's ambient conditions, acetonitrile and acetylene are in liquid and gaseous states, respectively, on planetary environments featuring lower temperatures and/or higher pressures, these molecules exist in a solid state and form minerals.

Titan, Saturn's icy moon, is one such environment, with ambient conditions on the surface of ~93 K and ~1.45 bar. he recently concluded Cassini-Huygens mission (1997–2017) revealed that Titan possesses a dense and chemically active atmosphere composed mainly of dinitrogen and methane, ethane based lakes and seas on the poles, and sandy dunes on the equator.[1-5] Fuelled by radiation from the Sun and Saturn's magnetosphere, dinitrogen and methane react to produce various organic molecules,[3-4] including acetonitrile and acetylene, which are then carried by methane rainfall and vigorous storms[6] to the surface, where they dissolve in the lakes. A seasonal cycling of evaporation and precipitation of methane, a process notably like Earth's hydrological cycle, produces evaporite lakebeds and mineral deposits made of organic molecules.[7] This dynamic organic environment is believed to be conducive to life, which has been hypothesized to be methanogenic in nature.[8]

Expectedly, Titan remains in the center of the scientific interest, in 2019, NASA announced a New Frontiers mission to Titan.[9] The Dragonfly rotorcraft is planned to launch in 2026/27, and it is expected to arrive on Titan in 2034. During its 2.7-year baseline mission, the rotorcraft will explore various sites on Titan, searching for signatures of extinct, extant, or future life. Before to this imminent mission, laboratory studies directed towards predicting, modelling, and recreating the surface mineralogy of the moon can greatly further our understanding of the surface of Titan.

The target molecules of this study, acetonitrile and acetylene, have been detected in the upper atmosphere by Voyager 1,[6] and by the subsequent (and more comprehensive) Cassini-Huygens mission using the Cassini composite infrared spectrometer (CIRS),[10]gas chromatograph mass spectrometer (GCMS),[11] and ion and neutral mass spectrometer (INMS),[12] among others. These molecules are produced in the atmosphere and on the surface of Titan by various radical and ion facilitated reactions.[10-12] Carried by methane rainfall, they descent to the surface with high precipitation rates, together with many other organic molecules. Considering a scenario in which the precipitation of organic matter occurs for over 4 billion years (the age of Titan), the accumulated surface layer of organic crystals would reach up to several meters thickness.[4] This organic, solid-state layer is believed to feature a pronounced chemical and structural complexity and a unique mineralogical makeup.[4, 13]

Such organic minerals, including acetonitrile and acetylene, can exist as single-phase molecular crystals, but also as cocrystals, solvates, hydrates, clathrates, and other forms. Both acetonitrile[14] and acetylene[15] have two polymorphs, a high- and low-temperature phases. The low temperature phases for these components are orthorhombic (α-phase) acetonitrile and (α-phase) orthorhombic acetylene, and their high temperature phases are monoclinic (β-phase) acetonitrile and cubic (β-phase) acetylene.[14-15] Additionally, both compounds form cocrystals with different co-components.[16] Recently, these cocrystals have attracted the interest of the research community as putative minerals on Titan. Some examples include the studies of acetylene and butane;[17] a ternary cocrystal of benzene, acetylene, and hydrogen cyanide;[18] acetylene and ammonia;[19-21] acetonitrile and benzene[22] and others. Acetonitrile and acetylene also form cocrystal stable at the conditions of Titan. This cocrystal has been studied with various experimental techniques: The crystal structure was solved by single crystal X-ray diffraction, described in the $Cmc2_1$ space group and with a 1:2 acetonitrile:acetylene stoichiometry.[21] The spectroscopic properties of the cocrystal have been studied by Raman spectroscopy revealing characteristic shifts of the vibrational bands as a function of cocrystallization.[23]

We have an on-going effort to expand the understanding of the vibrational structure of putative Titanean minerals using neutron vibrational spectroscopy (NVS). NVS is a far more comprehensive technique for examining the vibrational structure of materials, as compared to other symmetry-depended vibrational methods such as IR and Raman spectroscopy. Furthermore, NVS uses neutron particles as probes, which interact with the atomic nuclei of the material leading to particle–particle interactions, as opposed to the phonon–electron could interactions in optical measurements. These particle–particle interactions are particularly strong for H/D atoms, making the method extremely suitable for studies of hydrogen-rich materials, including hydrocarbons.[16] At the same time, particle–particle interactions can be more accurately modeled and explained by theoretical calculations, proving us an opportunity to accurately simulate, assign, and understand the spectra. Finally, NVS can also access vibrational modes in the low-frequency phonon range which is most relevant for studies of the extended structure of solids.[16]

Here we report a combined NVS and neutron diffraction study of the acetonitrile:acetylene (1:2) cocrystal. To confirm that the NVS data have been collected from the target solid, we have simultaneously collected and analyzed Time-of-Flight neutron powder diffraction (TOF-NPD) data. We have observed sharp and well-resolved vibrational modes from the cocrystal, which were modeled and assigned using density functional theory (DFT) methods. In our data, we have observed that the cocrystal concurrently exists in a phase mixture with solid acetonitrile. Surprisingly, acetonitrile does not adopt the thermodynamically stable orthorhombic form at low-temperature and rather forms the high-temperature monoclinic form by kinetic quenching. This prompted us to examine the low-frequency phonon modes of both forms of acetonitrile, revealing stark differences between both polymorphs. The combined spectroscopic, diffraction, and theoretical results provide relevant insights into the composition, structure, and properties of solid organic materials, expected to exist as minerals on Titan.

EXPERIMENTAL

Neutron Vibrational Spectroscopy. Data collection was performed on VISION (BL-16B) the neutron vibrational spectrometer at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory.[24] The cocrystal was synthesized *in situ* by condensing gaseous acetylene onto a solid acetonitrile crystal at 77 K. The vessel was then slowly cooled to 5 K over 3 hrs before data was collected. Measurements of NVS and TOF-NPD were collected in tandem at (5, 50, 75, 93, 125, 150, 175, and 235 K) with one-hour thermal equilibrations allowed between steps. Upon reaching 235 K, the samples were allowed to slowly cool back to 5 K under the same increments and NVS and TOF-NPD data were collected.

Time-of-Flight Neutron Powder Diffraction (TOF-NPD). Data collection was performed on VISION (BL-16B) the neutron vibrational spectrometer at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. NVS measurements and TOF-NPD patterns were collected in tandem. TOF-NPD data were analyzed using the GSAS-II software package.[26] The molecular components and cocrystal space groups and lattice parameters were taken from the literature and found to be *Aeam* for orthorhombic acetylene,[14] $Cmc2_1$ for β-acetonitrile,[15] and $Cmc2_1$ for the acetonitrile:acetylene cocrystal.[21] Precise lattice parameters, peak shapes, and background function were determined by Pawley refinement was performed on the TOF-NPD patterns to derive specific lattice parameters, background function, and peak shape parameters.[26]

Computational Studies. Density Functional Theory (DFT) modeling was performed using the Vienna Ab initio Simulation Package (VASP).[27] The Projector Augmented Wave (PAW) method was used for these calculations [28-30] The energy cutoff was 800 eV for the plane-wave basis of the valence electrons. The total energy tolerance for was 10^{-8} eV for electronic energy minimization and was 10^{-7} eV for structure optimization. The maximum interatomic force after relaxation was below 0.002 eV/Å. The lattice parameters and atomic coordinates for the structures reported in the literature served as a starting point for this work. The optB86b-vdW functional[31] was used for dispersion corrections. The vibrational eigenfrequencies and modes were then calculated by solving the force constants and dynamical matrix using Phonopy.[32] The FT-calculated phonon results were converted to the simulated INS spectra using the OCLIMAX software package.[33]

RESULTS AND DISCUSSION

The acetonitrile:acetylene (1:2) cocrystal was prepared *in-situ* at VISION, the neutron vibrational spectrometer at the SNS at ORNL. Liquid acetonitrile and gaseous acetylene were quenched from room temperature to 5 K. To confirm the structure and composition of the resulting solid, TOF-NPD was collected in tandem with the NVS measurements. Figure 1 highlights the diffraction patterns collected at various temperatures. While fast cooling of the mixture resulted in measurable quantities of the acetonitrile:acetylene (1:2), heating of the sample has showed inconsistency of the composition, with varying amounts of the cocrystal and the corresponding single-phase components. We hypothesize that the culprit for this behavior is improper mixing due to the large disparity between the freezing point of acetylene (189 K) and the relatively high freezing

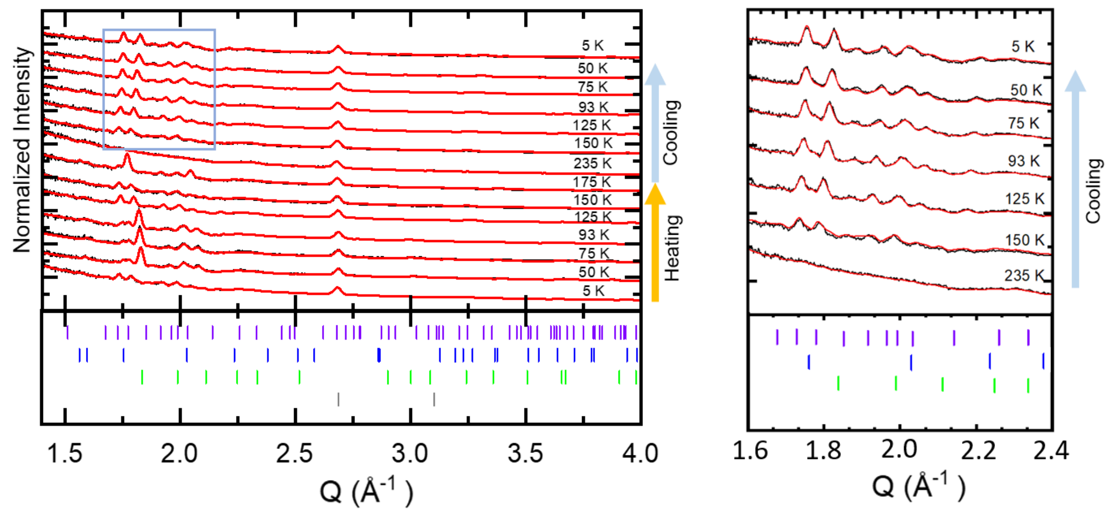

Figure 1. (Left) TOF-NPD patterns (black trace) and Pawley fits (red trace) for diffraction data collected at various temperatures. The direction of heating is from bottom to top. **(Right)** Q = 1.6-2.4 Å^{-1} range of Pawley fits for the region highlighted in blue. Tick marks refer to reflection from the cocrystal between acetonitrile and acetylene (purple), the reactants acetonitrile (blue), acetylene (green), as well as aluminum (grey).

point of acetonitrile (228 K). Improper mixing can result to partial conversion of the single phases to the cocrystal, and the content of such sample can move within the canister upon heating, exposing different parts of the sample in the path of the beam. Cyclic thermal treatment (heating/cooling) of such system can lead to better mixing and homogenization of the sample. In fact, heating to 235 K, and subsequently slowly cooling to 5 K, resulted in compositionally consistent sample.

Analysis of the TOF-NPD patterns collected at 5 K clearly shows the formation of the targeted acetonitrile:acetylene (1:2) cocrystal. The structure of the cocrystal has been previously solved and described in the $Cmc2_1$ space group.[21] We used the (0 2 1) and (3 1 0) reflections as indicators for the synthesis of

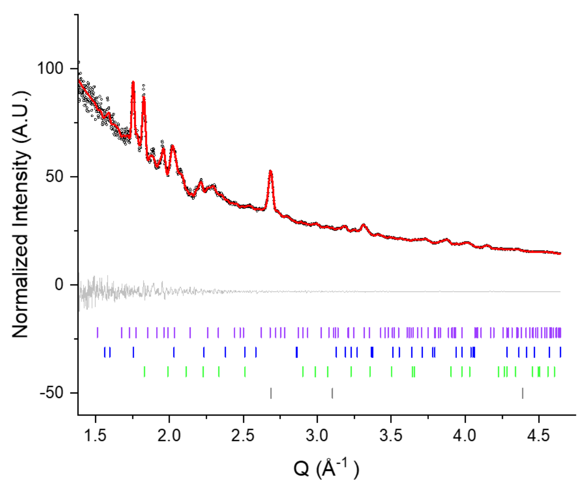

Figure 2. Pawley fit for the TOF-NPD measurements of acetylene-ammonia mixture slow cooled down to T = 5 K. Data shown as black triangles, fitted curve in red, and difference curve in dark grey. The Bragg reflections are presented as tick marks for the acetonitrile:acetylene (1:2) cocrystal in purple, monoclinic acetonitrile in blue, orthorhombic acetylene in green, and aluminum (from the sample holder) in grey. Fit statistics for this refinement was R_{wp} = 1.307%. GOF: 1.04. Symbols are larger than or commensurate with error which represent ±1σ.

the target cocrystal. Indeed, these reflections are clearly present in the patterns at 1.73 and 1.77 Å^{-1} respectively (Figure 1). Cooling/heating of this compositionally consistent sample showed the expected gradual shift of the scattered intensity as a function of temperature, consistent with the thermal expansion properties of each solid.

The cocrystal is expected to be the thermodynamically most stable phase for this mixture at low temperature and ambient pressure, however due to experimental limitations (including challenges with improper mixing of the reactants and finite time for reactivity/cocrystallization) the reactants are also present in the sample. Reflections form phase pure acetonitrile and acetylene were detected and are visible in the the full range of the TOF-NPD pattern and its respective Pawley fit at T = 5 K (Figure 2). We suspect that the interface between the acetonitrile solid and the acetylene condensate is where the majority of the cocrystal is localized. This is consistent with other literature reports for some of our previously reported cocrystals, as well as others in the literature.[16-22]

Acetonitrile[14] and acetylene[15] have two polymorphs, a high- and low-temperature phases. Interestingly, the crystallographic analysis of the pattern collected at 5 K (Figure 2) revealed that the sample is composed of the cocrystal, the low temperature form of acetylene, and, rather surprisingly, the high-temperature, β-phase of acetonitrile. It has been reported that rapid cooling of acetonitrile can result in a phase trapping of the high-temperature polymorph at low temperature.[34] Here we show that similar quenching can also occur depending on the phase composition. This observation further supports the hypothesis that metastable phases of organic materials can be viable mineral species on Titan. The putative presence of metastable minerals on this moon is yet another parallel with the mineralogy on Earth, where metastable minerals are often found in various locations and environments. For example, cristobalite (the quenched high-temperature form of silica, SiO_2) serves as an analogous case of a metastable mineral found in acidic volcanic rocks.

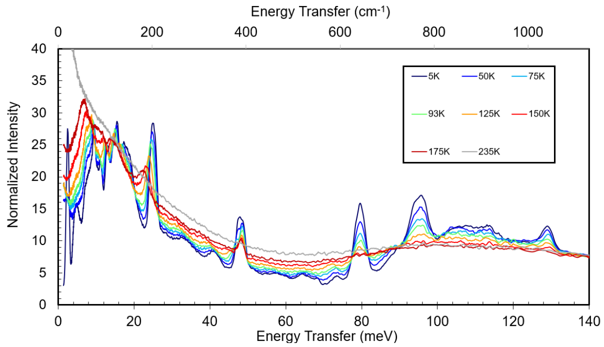

Figure 3. Variable Temperature NVS spectra overlay of the acetonitrile:acetylene (1:2) cocrystal mixture with peak assignments. The vibrational spectra were collected in tandem with diffraction patterns upon heating up from the crash-cooled sample at 5 K. Exact ranges for assigned peaks can be found in Table 1.

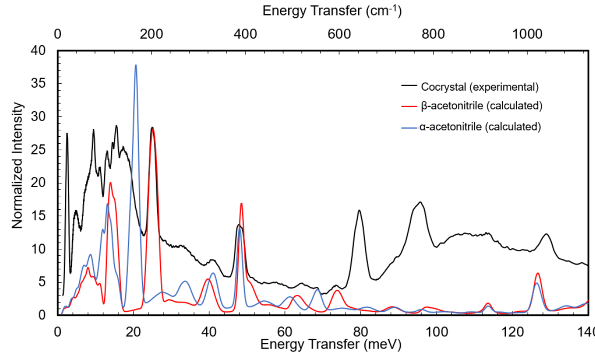

Figure 5. Overlay of NVS for the acetonitrile:acetylene (1:2) cocrystal collected at 5 K compared to the calculated NVS for the acetonitrile polymorphs.

The cocrystal was next studied with NVS. Spectra of the compositionally consistent sample were collected as a function of temperature (Figure 3), in tandem with the TOF-NPD patterns (Figure 1). The NVS signal typically exhibits strong thermal dependence, where peak intensity is inversely related to thermal motion. This is particularly prominent for organic molecular species devoid of strong intermolecular bonding within the crystal packing. Expectedly, the collected spectra show gradual sharpening of the peaks, with the best data set collected at 5 K. Figure 4 presents the NVS spectrum of the sample measured at 5 K, together with NVS of the pure component solids. The experimentally collected NVS spectra of acetylene[35] and β-acetonitrile[36] were taken from literature data. In agreement with the TOF-NPD data, the measured spectrum shows a mixture of three phases, the acetonitrile:acetylene (1:2) cocrystal, the high-temperature phase of acetonitrile, and the low-temperature phase of acetylene.

The NVS further confirmed the quenching of the high-temperature phase of acetonitrile. We have calculated the NVS spectra of both phases, shown in Figure 5. The CH_3 rotational libration I mode was found to be a defining feature for the two polymorphs. In the α-phase, this vibrational mode is expected to have a signal at 20 meV (161 cm^{-1}), whereas in the β-phase at 25 meV (202 cm^{-1}). The NVS spectrum of the cocrystal features a strong vibrational band at 25 meV (200 cm^{-1}) with no clear vibrational modes associated exclusively with the low-temperature α-acetonitrile phase. The theoretical calculations, and the TOF-NPD analysis, confirm that the excess acetonitrile contributing to the intensities in the experimental NVS originates from the kinetically trapped, high temperature β-acetonitrile polymorph.[34]

The NVS spectrum of the cocrystal was simulated (Figure 6) using DFT calculations performed on the published[21] $Cmc2_1$ crystal structure as a starting model. Generally, there is a good agreement between the computationally predicted spectra and the experiment. The overall profile of the predicted spectra matches well with the experimental spectrum, which enables us to confidently assign the peaks to the corresponding vibrational modes. Table 1 presents selected peak assignments.

Analyzing the energy of vibrational modes in the cocrystal compared to single-component solids presents a valuable avenue for establishing spectra-structure-properties correlations. Figure 4 highlights the crystal structures of the phase-pure components, orthorhombic acetylene and monoclinic β-acetonitrile, and the crystal structure of the cocrystal.[15]

The molecules in the cocrystal show several colossal vibrational shifts compared to the individual components. Most notably, the rotational librational mode of the acetonitrile CH_3 group in the cocrystal shows a massive red shift compared to the same vibration in pure β-acetonitrile. In the molecular β-acetonitrile,

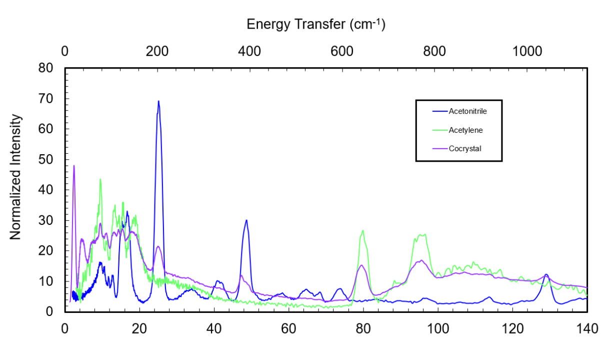

Figure 4. Overlay of NVS spectrum collected at 5 K (purple) and spectra of monoclinic acetonitrile (blue) and orthorhombic acetylene (green) taken from the ISIS INS database.[35-37]

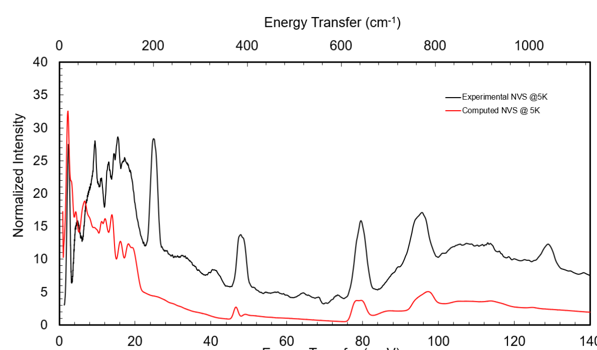

Figure 6. Experimentally observed NVS spectrum (black) of the acetonitrile:acetylene (1:2) cocrystal overlayed with computationally predicted NVS spectrum (red)

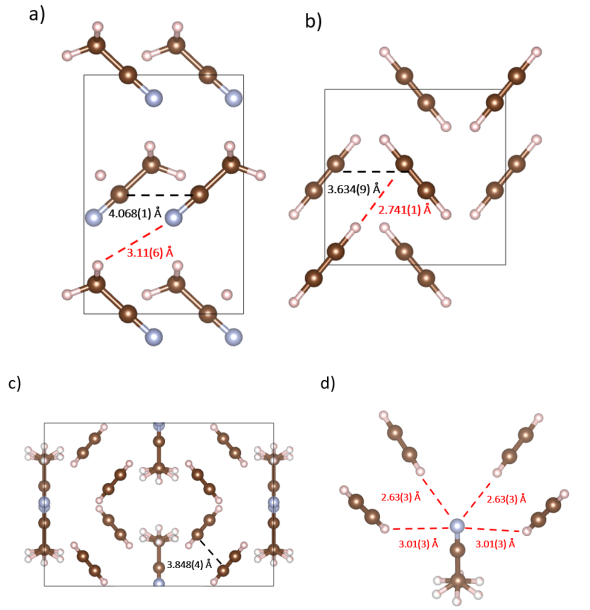

Figure 7. Crystal structures and selected bond distances of a) acetonitrile, *Cmc*2_1, b) acetylene, *Aeam*, c) acetonitirle:acetylene (1:2) cocrystal, *Cmc*2_1, d) close up of the acetylene to acetonitrile hydrogen bonding environment in the cocrystal (Color legend: blue = nitrogen, brown = carbon, off-white = hydrogen).

the energy transfer associated with exciting this mode was determined to be 25 meV (202 cm^{-1}), whereas in the cocrystal the energy transfer was 2.5 meV (20 cm^{-1}), resulting in a red shift of 22.5 meV (181 cm^{-1}).

This colossal shift can be rationalized considering the differences in the local environment of the acetonitrile molecules in both crystal packings. In the β-acetonitrile phase, acetonitrile molecules form chains with hydrogen bonding interactions between the nitrogen of one acetonitrile atom and the adjacent H from the CH_3 groups on a neighboring molecular. The hydrogen bond is of moderate strength, as indicated by the C-H···N bond distance of 3.11(6) Å (Figure 7). In the acetonitrile:acetylene (1:2) cocrystal, acetonitrile molecules are surrounded by acetylene molecules, forming hydrogen bonding interactions between the acetylene C-H as bond donors and the nitrogen atoms of the acetonitrile as bond acceptors. There are two crystallographically distinct C-H···N interactions between acetonitrile and acetylene, one with a C-H···N distance of 2.63(3) Å and a slightly weaker interaction of 3.01(3) Å. Due to crystal symmetry, each acetonitrile molecule is surrounded by four acetylene molecules (Figure 7). At the same time, the methyl group does not engage in prominent hydrogen bonding, thus is free to rotate. Expectedly, crystallographic analysis of the cocrystal indicates towards disorder of the hydrogen atoms.

Furthermore, the related CH_3CH rocking libration shows a visible (yet comparably smaller) red shift, where in the molecular β-acetonitrile the energy of the vibration is 48 meV (387 cm^{-1}) and in the cocrystal it was found to be 44 meV (354 cm^{-1}). This red shift is likely caused by the same structural differences causing the red shift of the rotational librational mode.

In a recent study of the NVS characteristic of the acetylene:ammonia (1:1) cocrystal, we have identified a possible correlation between the plastic crystal (rotor phase) behavior of the cocrystal and the colossal shift of the NH_3 rotational libration mode in the cocrystal compared to phase-pure ammonia.[19] Based on the colossal red shift of 22.5 meV (181 cm^{-1}) observed in the acetonitrile:acetylene (1:2) cocrystal, we hypothesized that this solid may exhibit plastic crystal behavior. In fact, during the final stages of the preparation of this paper, molecular dynamics simulations were published,[38] further confirming the plastic nature of the cocrystal.

CONCLUSIONS

We have provided a detailed NVS study coupled and supported with TOF-NPD analysis of the acetonitrile:acetylene (1:2) cocrystal, a potential organic mineral relevant to the surface geology of Titan and other celestial bodies.

Our efforts to synthetize the cocrystal by co-condensation of liquid acetonitrile and acetylene resulted in mixed phase system, which composition heavily depended on the experimental conditions. The temperature-resolved TOF-NPD analyses further confirm the importance of thermal cycling in for the synthesis of organic cocrystals at cryogenic conditions. Regardless of our best efforts, the sample still contained solid phases of the reactants. Interestingly, we identified that the high-temperature form of acetonitrile is quantically quenched in the presence of acetylene. This composition-dependent quenching of molecular solids indicates towards the possibility of metastable minerals on Titan.

The temperature-resolved NVS showed pronounced influence of the thermal motion of the molecules on the observed spectral resolution. Well-resolved spectra were obtained at lower temperature and the analysis was done on the spectrum collected at 5 K. The cocrystal shows distinct spectral features, clearly visible in the experimentally obtained NVS spectrum. Detailed theoretical analysis enabled us to assign vibrational modes to the corresponding NVS peaks.

Analyzing the energy of vibrational modes in the cocrystal compared to single-component solids allowed us to draw spectra-structure-properties correlations. These correlations deepen our understanding of how the local crystalline environment influences vibrational energy levels. Most notably, we observed a massive red-shift of 22.5 meV (181 cm^{-1}) of the CH_3 rotational libration in the cocrystal. The observation of this vibration at much lower energy than pure acetonitrile is attributed to a less tightly packed environment surrounding the pendant methyl groups and the unique hydrogen bonding in the cocrystal structure. In the cocrystal, the methyl group is devoid of strong hydrogen bonding to neighboring acetonitrile molecules, facilitating molecular dynamics. Based on this colossal red shift, we hypothesize plastic phase behavior of the solid.

This study shows the intricate and complicated structure, composition, and properties of small organic molecules at cryogenic conditions. In light of their relevance as minerals on Titan and other celestial bodies, further theoretical and experimental studies are necessary to better understand their nature.

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ASSOCIATED CONTENT

Supporting Information

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