Infrared Spectroscopic Study of Methane Ice, Pure and in Mixtures with Polar (H2O) and Nonpolar (N2) Molecules

Published as part of The Journal of Physical Chemistry virtual special issue “10 Years of the ACS PHYS Astrochemistry Subdivision”.

Shahnewaz M. Emtiaz, Francis Toriello, Jiao He, and Gianfranco Vidali*

ABSTRACT: Mid-infrared studies of fundamental modes of ices of pure CH₄ and its mixtures with polar (H₂O) and nonpolar (e.g., N₂) molecules are essential in order to learn the state of aggregation and thermal history of ices present in the interstellar medium and outer solar system bodies. Such data will be useful in the interpretation of observational data from the James Webb Space Telescope. Using an ultrahigh vacuum apparatus, we conducted reflection-absorption infrared spectroscopy measurements in the mid-IR range of pure methane ice and methane-containing ice mixtures of interest to interstellar and solar system ice chemistry, e.g., with H₂O and N₂ molecules. We found that nuclear spin conversion (NSC) in solid methane and its crystalline structures is affected—in different ways—by the presence of H₂O and N₂. Specifically, we found a relationship between the thickness and the solid-state ordering transformation in methane thin films. This new study of the NSC of pure CH₄ ice and of the CH₄:H₂O ice mixture at 7 K is carried out in relation to the segregation of H₂O using the ν₁ and ν₂ IR inactive modes of methane. The diffusion of N₂ and CH₄ in the CH₄:N₂ ice mixture with temperature cycling has been studied to obtain the relationship between IR features and the state of aggregation of the ice.

INTRODUCTION

Solid methane and its mixtures with other volatiles are present in ocean beds as clathrate hydrates,¹ in icy objects in the solar system,²,³ and in interstellar ices.⁴⁻⁷ In particular, methane ice has been detected in different solar system bodies either neat or mixed with other volatile molecules in different mixing ratios. Methane is found at the single digit percent level in interstellar ices⁴ but is abundant in outer solar system bodies, such as Titan, Triton, Pluto, and others. Its importance is related to the fact that is considered a key molecule in the development of prebiotic life.⁸,⁹

At cryogenic temperatures and low pressures, there are two recognized and well-documented solid phases.¹⁰ Phase I is the equilibrium phase at T > 20.4 K. It is a face-centered cubic (fcc) crystal with orientationally disordered CH₄ molecules. Phase II is stable below 20.4 K and consists of an fcc lattice with eight ferroorientational sublattices (orientationally ordered sublattices, six with dihedral symmetry D₁d and two sublattices of hindered rotators with octahedral symmetry O₈). Thus, in the primitive cell, the six CH₄ that are orientationally ordered are subject to both the crystalline and orientational fields, while at the location of the two virtually free rotators, the octupolar orientational field vanishes.¹¹ Recently, a metastable phase of solid methane at T < 7.0 K was discovered; it is a crystalline phase with orientational order between Phase II and Phase I.¹²

In the mid-IR, methane has two active vibrational modes, a C−H stretching at 3009 cm⁻¹ (3.32 μm, ν₁) and a deformation mode (ν₂) at 1302 cm⁻¹ (7.68 μm). In addition, methane solid goes through nuclear spin conversion (NSC) at cryogenic temperatures¹²⁻¹⁵ where the change in nuclear spin configuration influences the ro-vibrational spectrum. Molecular-level interaction between CH₄ and H₂O is accompanied by significant shifts in peak positions and spectral features in the near¹⁶ and mid-IR¹⁷ spectral regions. Specifically, the interaction of water with methane manifests itself in the detection of two additional modes, ν₁ and ν₂, which are inactive in pure solid methane.¹⁸,¹⁹

Methane has been detected in the interstellar medium (ISM)²⁰,²¹ at low concentrations in water-dominated ices;
when ejected in the gas phase it leads to a warm carbon-chain chemistry and the production of unsaturated hydrocarbons. In planetary systems, it is found in outer solar system bodies, in satellites of planets, and in water-rich comets. Near-IR features of methane ice on outer solar system bodies are blue-shifted, indicating that CH$_4$ is mixed with N$_2$, the other major component in those ices. The absence of combination modes (i.e., $\nu_1 + \nu_3$ and $\nu_2 + \nu_4$) involving IR inactive modes $\nu_1$ and $\nu_2$ in Triton’s spectrum has been used to infer that CH$_4$ molecules are isolated and dispersed in N$_2$:CH$_4$ ice. A study of the shift positions and broadening of mid-IR spectral features of CH$_4$ in CH$_4$:H$_2$O mixtures grown at 30 K is given in Gálvez et al. (2009). CH$_4$:H$_2$O mixtures in the 14–60 K range, and in particular the inactive $\nu_1$, are studied in Herrero et al. (2010). The possible origin of the activation of the $\nu_1$ mode of CH$_4$ in CH$_4$:H$_2$O mixtures is investigated by means of solid-state calculations in Etschbacher et al. (2014).

The goal of this work is to study the IR absorption features of pure methane ice and methane ice mixture with H$_2$O and N$_2$. We aim to quantify how the presence of these molecules in methane-rich ice produces changes in IR spectra. Furthermore, we want to see whether the state of aggregation can be discerned from IR features, as it was done for CO–CO$_2$ ice mixtures and CO$_2$ films on water ice. We proceeded as follows. We first measured the effect of deposition methods, thermal cycling, and deposition temperature on thin films of pure methane in ultrahigh vacuum (UHV) conditions. We then measured the spectral changes that methane ice experiences in the presence of H$_2$O and N$_2$. This allowed us to study the diffusion and segregation process in CH$_4$:H$_2$O and CH$_4$:N$_2$ ice mixtures.

### EXPERIMENTAL METHODS

Experiments were performed at Syracuse University in an UHV chamber in which the pressure can routinely reach 4.5 × 10$^{-10}$ Torr after a bake-out; see He et al. for details; here only the main features that are relevant to this study are summarized. Gases were deposited on a gold-coated copper disk mounted on a closed cycle cryocooler (ARS DE-204 4K). The temperature of the sample was monitored and manipulated by a calibrated silicon diode placed behind the sample and paired with a Lakeshore 336 temperature controller. A cartridge heater installed behind the sample can be used to heat the sample. By controlling the heating output of the cartridge heater, the temperature can be adjusted between 5 and 300 K with an accuracy of better than 50 mK.

Methane ices were grown on the sample disk by introducing methane through a stepper motor-controlled UHV variable leak valve. A LabVIEW program controlled the deposition rate and thickness. In all experiments, 100 monolayers (ML, defined as 10$^{15}$ molecules/cm$^2$) of ice were formed at a relatively high deposition rate of 100 ML/min. This deposition dose was calculated using the impingement rate; see the Appendix of He et al. for details. For the deposition of CH$_4$ and H$_2$O, two separate UHV variable leak valves were used. Distilled water underwent at least three freeze-pump–thaw cycles before being sent into the chamber. Premixed CH$_4$ and N$_2$ gas was deposited using a single leak valve for CH$_4$:N$_2$ mixture deposition except for one occasion: a molecular beamline was used to deposit 100 ML of CH$_4$ for the experiment presented in Figure 4. The deposition of methane via the beamline was much slower, by a factor 100, with respect to the gas-phase deposition.

In most of the experiments, methane was deposited at 10 K, unless otherwise mentioned. A Nicolet 6700 FTIR in the reflection absorption infrared spectroscopy (RAIRS) configuration with an incident angle of ~78° was used to obtain mid-IR spectra of the ice. Spectra were measured and averaged every 20 s at a resolution of 1 cm$^{-1}$. To measure the NSC, the IR spectra were continuously monitored at a fixed temperature for different lengths of time, depending on the features being measured. For example, the isothermal experiments in which the ice was brought and kept at 7 K from the deposition temperature of 30 K lasted approximately 12 h. In other experiments, the ice was deposited at 10 K, kept at this temperature for several minutes, and then heated at 3 K/min to the desired temperature and subsequently cooled to 10 K for temperature-cycling experiments. Table 1 provides a synopsis of experiments performed for this work.

### RESULTS AND ANALYSIS

We carried out two sets of experiments. In the first set, we studied the IR signatures of crystalline phases of methane under different conditions. For these experiments, pure methane ice of different thicknesses was deposited at either 6 or 10 K. Then methane ice was either kept at a specific temperature for an extended period of time or heated slowly at 3 K/min until the methane ice desorbed past 40 K. In the second set, methane ice mixed with either water or nitrogen was deposited at 10 K, and then the ice went through temperature cycling (heating and cooling) to study the state of the aggregation of the ice through changes in IR features during the process.

#### Dependence of Methane Crystalline Phases on Deposition Temperature

Experiments to characterize the Phase I–Phase II transition in methane ice are typically conducted in closed cells. In such experiments, the transition happens abruptly at 20.4 K. However, from an analysis of methane thin films deposited in the 7–30 K range, we observe that the transition from Phase II to Phase I occurs over a temperature range. Figure 1 shows the $\nu_4$ and $\nu_5$ modes of pure methane ice deposited at different temperatures. At 7 K the ice is in Phase II, which is a metastable phase without the presence of band splitting due to NSC. In pure methane ice, satellite peaks emerge near $\nu_4$ and $\nu_5$ due to IR-allowed transitions brought about by conversion of the nuclear spins of the hydrogen atoms in CH$_4$ ice. For methane deposited at 10 K, the ice is in crystalline Phase II with the fully emerged band splittings due to NSC, in agreement with the results.

#### Table 1. List of Performed Experiments

| no. | experiment summary | Figure |
|-----|-------------------|--------|
| 1   | 100 ML of CH$_4$ deposited at temperatures between 7 and 30 K | 1 |
| 2   | Slow heating of CH$_4$ ice between 2 and 100 ML and at temperature 10–45 K | 2 |
| 3   | Comparison of fast and slow deposited CH$_4$ ice to investigate temporal change at 6 K | 4 |
| 4   | Comparison of a CH$_4$:H$_2$O mixture with variable concentrations deposited at 10 K | 5 |
| 5   | Effect of temperature cycling on CH$_4$ IR modes for the CH$_4$:H$_2$O mixture | 6 |
| 6   | Comparison of a CH$_4$:N$_2$ mixture with variable concentrations deposited at 10 K | 7 |
| 7   | Effect of temperature cycling on CH$_4$ IR modes for the CH$_4$:N$_2$ mixture | 8 |
dependent on the deposition rate. The red shift in the peak position is more significant for 15 ML and thicker ice, while for 15 ML and thinner ice the transition temperature is a little less than 20.4 K, the value for bulk CH4 ice. These experiments suggest that methane ice experiences thin-film effects for coverage below 15 ML. For higher coverage (≥100 ML), the ice is independent of thin-film effects.

Dependence of NSC on the Deposition Rate of CH4. We know that at 6 K the methane thin film is in a metastable phase; at that temperature nuclear spin conversion does not take place over laboratory times. As we increase the temperature above 7 K, we observe an exponential increase in the relaxation rate up to 8.5 K. Depending on the deposition rate, we find different rates of NSC for methane ice. The left panel of Figure 4 shows 100 ML of methane ice deposited at 6 K and kept for 12 h. Methane ice was deposited by filling the chamber background with methane gas through a UHV leak valve at a rate of 100 ML/min. In this background-deposited methane ice, we do not see any emergence of band splitting of the ν3 mode, which is a sign of NSC in IR spectroscopy. On the other hand, the right panel of Figure 4 shows 100 ML of methane ice deposited with the molecular beamline; the ice was kept at 6 K for a similar amount of time as for the background deposition. In this case, we observe the emergence of band splitting upon the completion of deposition. It takes 100 min to finish the deposition through the beamline compared to 1 min using the UHV leak valve. Initially (see bottom two traces on the right), we see the emergence of the R(0) band (3010.9 cm−1) for the ν1 mode and the Q(1) band (1297.8 cm−1) for the ν4 mode. As we keep the ice at 6 K for 12 h, we see that the band splitting is more pronounced. In the ice prepared slowly, orientational ordering at lattice sites takes place; therefore, we see a significant rate of NSC even at 6 K. This fact further strengthens our argument that at 6 K we observe a metastable phase of methane which is a crystalline phase with an orientational ordering between Phase I and Phase II.

Ice Mixtures of CH4 and H2O with Different Ratios. Figure 5 shows IR data of ν4 and ν3 modes of pure methane and methane–water mixture with different mixing ratios. We observe a significant change in IR features and fwhm values for increasing amounts of water mixed with methane. For CH4:H2O (=95:5) we observe that the peak position is red-shifted by 0.8 and 0.7 cm−1 for ν4 and ν3, respectively. The fwhm becomes 14 and 7 cm−1 for the ν4 and ν3 modes, respectively, which is a significant increase from pure methane. The red shift in the peak position is more significant for the ν3 than for the ν4 mode. All the relevant values are listed in Table 2.

transition (from Phase II to Phase I), there is a change in the IR peak position and spectral features due to a change in the lattice field (for convenience’s sake, we call the phase transition an orientational phase transition irrespective if it goes from an orientational disordered to an orientationally ordered state or vice versa). We obtained the temperature range for the phase transition based on an analysis of the shifting of the peak position. The right panel of Figure 3 illustrates how the temperature range is determined, using the result of 15 ML as an example. Briefly, a Gaussian distribution is used to fit the ν4 peak, and the position is obtained for each spectrum during the warm-up. More details of the fitting scheme are described in Emia et al. The peak position is then plotted as a function of temperature and is shown in the right panel of Figure 3. We take the temperature at which the peak position is shifted by at least 0.25 cm−1/K as the starting point of the phase transition. The end point of the phase transition is more obvious from the plot. The temperature range for the phase transition for methane ices of different thicknesses is then shown in the left panel of Figure 3. At 5 ML coverage the transition temperature is 16.2 K (Figure 3). In this case, the disruption of neighboring lattice field sites is accelerated due to the thinness of the film. On the other hand, for 15 ML and thicker ice the transition temperature is a little less than 20.4 K, the value for bulk CH4 ice. These experiments suggest that methane ice experiences thin-film effects for coverage below 15 ML. For higher coverage (≥100 ML), the ice is independent of thin-film effects.

Dependence of NSC on the Deposition Rate of CH4. We know that at 6 K the methane thin film is in a metastable phase; at that temperature nuclear spin conversion does not take place over laboratory times. As we increase the temperature above 7 K, we observe an exponential increase in the relaxation rate up to 8.5 K. Depending on the deposition rate, we find different rates of NSC for methane ice. The left panel of Figure 4 shows 100 ML of methane ice deposited at 6 K and kept for 12 h. Methane ice was deposited by filling the chamber background with methane gas through a UHV leak valve at a rate of 100 ML/min. In this background-deposited methane ice, we do not see any emergence of band splitting of the ν3 mode, which is a sign of NSC in IR spectroscopy. On the other hand, the right panel of Figure 4 shows 100 ML of methane ice deposited with the molecular beamline; the ice was kept at 6 K for a similar amount of time as for the background deposition. In this case, we observe the emergence of band splitting upon the completion of deposition. It takes 100 min to finish the deposition through the beamline compared to 1 min using the UHV leak valve. Initially (see bottom two traces on the right), we see the emergence of the R(0) band (3010.9 cm−1) for the ν1 mode and the Q(1) band (1297.8 cm−1) for the ν4 mode. As we keep the ice at 6 K for 12 h, we see that the band splitting is more pronounced. In the ice prepared slowly, orientational ordering at lattice sites takes place; therefore, we see a significant rate of NSC even at 6 K. This fact further strengthens our argument that at 6 K we observe a metastable phase of methane which is a crystalline phase with an orientational ordering between Phase I and Phase II.

Ice Mixtures of CH4 and H2O with Different Ratios. Figure 5 shows IR data of ν4 and ν3 modes of pure methane and methane–water mixture with different mixing ratios. We observe a significant change in IR features and fwhm values for increasing amounts of water mixed with methane. For CH4:H2O (=95:5) we observe that the peak position is red-shifted by 0.8 and 0.7 cm−1 for ν4 and ν3, respectively. The fwhm becomes 14 and 7 cm−1 for the ν4 and ν3 modes, respectively, which is a significant increase from pure methane. The red shift in the peak position is more significant for the ν3 than for the ν4 mode. All the relevant values are listed in Table 2.
In this section we investigate the CH$_4$:H$_2$O ice using the CH$_4$ IR inactive modes. Pure methane has two IR inactive modes: $\nu_1$ (2904.5 cm$^{-1}$) and $\nu_2$ (1540.0 cm$^{-1}$). When water is mixed with methane, there is no band splitting due to NSC in Phase II CH$_4$:H$_2$O mixtures at 10 K. However, the presence of water activates the IR inactive modes. Figure 6 shows IR spectra of CH$_4$:H$_2$O at two different stages of the same experiment. The dotted marked spectra represent CH$_4$:H$_2$O after the deposition at 10 K. The solid line shows the band after the ice is taken to 30 K and then cooled back to 10 K. Two intense bands are observed at 3500 cm$^{-1}$ (not shown) and at 1635 cm$^{-1}$, caused by O–H stretching and O–H–O scissors-bending, respectively. We observe significant changes in $\nu_4$ and $\nu_3$ modes before and after temperature cycling. Band splitting such as R(0) for $\nu_4$ and Q(1) for $\nu_3$ emerges after temperature cycling. Band strengths of $\nu_1$ and of O–H–O scissors-bending decrease by about 50% after the heating and cooling process. This change in IR features indicates that fewer CH$_4$ molecules are in contact with water molecules; therefore, a partial segregation of water in the CH$_4$:H$_2$O ice has taken place. This segregation process happens during orientational reordering of lattice field sites of methane molecules during temperature cycling.

Another piece of evidence of segregation is as follows. Nuclear spin conversion occurs in methane ice between 7 and 11 K. There is no NSC for CH$_4$:H$_2$O ice deposited at 10 K and kept at that temperature for 30 min. However, if the CH$_4$:H$_2$O ice is taken to 30 K and then rapidly cooled to 7 K and kept for 100 min, NSC splitting is observed, as in the case of pure methane ice. The fact that the CH$_4$:H$_2$O ice mixture when annealed at 30 K—goes through the NSC process similar to pure methane ice (while the mixture quenched to 7 K does not) indicates that water segregated and left patches of pure methane where NSC can take place. A similar segregation

Table 2. $\nu_4$ and $\nu_3$ Band Positions, Shifts, and fwhm of CH$_4$:H$_2$O with Different Mixing Ratios

| mixing ratio | peak position (cm$^{-1}$) | fwhm (cm$^{-1}$) | shift (cm$^{-1}$) |
|--------------|--------------------------|-----------------|------------------|
| $\nu_4$      |                          |                 |                  |
| 100:0        | 1304.8                   | 4.5             |                  |
| 95:5         | 1304.0                   | 14              | -0.8             |
| 90:10        | 1303.9                   | 14.5            | -0.9             |
| 80:20        | 1303.9                   | 15.5            | -0.9             |
| 20:80        | 1304.2                   | 21              | -0.6             |
| $\nu_3$      |                          |                 |                  |
| 100:0        | 3010.9                   | 7               |                  |
| 95:5         | 3010.2                   | 10.5            | -0.7             |
| 90:10        | 3010.0                   | 11.0            | -0.9             |
| 80:20        | 3009.9                   | 11.2            | -1.0             |
| 20:80        | 3008.1                   | 14.0            | -2.8             |
The process has been observed in CO:CO\textsubscript{2} = 9:1 ice mixtures when CO undergoes a phase transition from amorphous to crystalline. During the transition, CO\textsubscript{2} molecules form clusters. The segregation of H\textsubscript{2}O from the CH\textsubscript{4}:H\textsubscript{2}O mixture during NSC may be a process that is common on icy bodies in the solar system. All the relevant values of $\nu_3$ and $\nu_4$ vibrational modes peak position and band shift are listed in Table 3.

Ice Mixtures of CH\textsubscript{4} and N\textsubscript{2} with Different Ratios. N\textsubscript{2} is a nonpolar molecule, and the unit cell of N\textsubscript{2} has a lattice parameter of 5.64 \textangles, which is close to the value of the lattice parameter of fcc methane solid, 5.89 \textangles. Thus, it is a reasonable assumption that in the CH\textsubscript{4}:N\textsubscript{2} mixture, N\textsubscript{2} is in a substitutional site rather than in an interstitial site as the ices have similar lattice parameters and both have an fcc structure. Figure 7 shows the IR data of CH\textsubscript{4} $\nu_4$ and $\nu_3$ modes of CH\textsubscript{4}:N\textsubscript{2} with different mixing ratios. We observe that there is little change once we introduce a small amount of N\textsubscript{2} in the ice matrix. The CH\textsubscript{4} lattice symmetry is disrupted once the impurity level reaches 20%. At the CH\textsubscript{4}:N\textsubscript{2} = 80:20 ratio the satellite peaks of CH\textsubscript{4} $\nu_4$ and $\nu_3$ modes completely disappear which indicates that the N\textsubscript{2} molecules in the ice matrix cause enough disruption of the symmetry of the original CH\textsubscript{4} ice that the collective behavior giving rise to NSC is suppressed. We see a significant change in IR features and FWHM values in CH\textsubscript{4}:N\textsubscript{2} = 80:20. In this case, the peak position is red-shifted by 0.4 and 2.3 cm\textsuperscript{-1} for $\nu_4$ and $\nu_3$, respectively. The blue shift in the peak position is more significant in the $\nu_3$ mode than in the $\nu_4$ mode. All the relevant values are listed in Table 4.

Figure 8 shows IR spectra of solid methane in the $\nu_3$ and $\nu_4$ vibrational modes of the CH\textsubscript{4}:N\textsubscript{2} mixture for various concentrations. All the mixtures were deposited at 10 K.
orcid.org/orcid.org/10 K) on the IR CH$_4$:H$_2$O ice mixture induces the segregation of water and by thermal cycling. Our results show how thermal cycling of a important, as well the detection of IR features that are a including comets, the interaction of methane with water is thermal history of the mixture. In planetary environments, the formation of CH$_4$ aggregates likely requires fusion of CH$_4$ molecules, and we fusion of CH$_4$ ice structure changes.

Taken all together, these observations should help the interpretation of observations of CH$_4$ ice in interstellar and planetary environments, such as its thermal history and its degree of mixing with water and nitrogen molecules.

**SUMMARY**

The main findings of our measurements of mid-IR bands of pure methane ice and in mixtures with water and nitrogen are as follows:

- The orientational ordering transition (Phase II to Phase I) in methane ice films occurs over a range of temperature in contrast with measurements of bulk methane ice in closed cell experiments where the transition is abrupt.39
- Nuclear spin conversion at cryogenic temperatures depends on the deposition rate. NSC is virtually absent in a fast deposition from background gas (100 ML/min), but it shows up in a slow deposition of ice at 6 K (1 ML/min) from the beamline.
- A small (5%) amount of water present in the ice matrix causes changes in CH$_4$ IR bands. The peak position of the CH$_4$:H$_2$O matrix is red-shifted as we increase the amount of water in the mixture. Similarly, the fwhm of the CH$_4$:H$_2$O broadens with the increased percentage of water.
- The introduction of an amount of water greater than 5% during deposition at low temperatures (10 K) suppresses NSC, and forbidden CH$_4$ bands ($\nu_4$) appear. When the ice is taken to 30 K and then cooled back to 10 K, these forbidden bands get greatly reduced (50% for a CH$_4$:H$_2$O = 80:20 mixture), indicating that there are fewer CH$_4$ molecules in contact with H$_2$O molecules. This is an indication that water is partially segregated from CH$_4$.
- Compared to CH$_4$:H$_2$O mixtures, in CH$_4$:N$_2$ mixtures a much larger amount (20%) of N$_2$ is required to suppress NSC. Once the N$_2$ fraction is over 20%, there is a blue shift of peak positions of $\nu_3$ and $\nu_4$ modes. As the temperature is raised, the orientational symmetry of the CH$_4$ ice structure changes.

Taken all together, these observations should help the interpretation of observations of CH$_4$ ice in interstellar and planetary environments, such as its thermal history and its degree of mixing with water and nitrogen molecules.

**AUTHOR INFORMATION**

**Corresponding Author**

Gianfranco Vidali – Physics Department, Syracuse University, Syracuse, New York 13244, United States; orcid.org/0000-0002-4588-1417; Phone: +1 315 443 3901; Email: gvidali@syr.edu

**Authors**

Shahnewaz M. Emtiaz – Physics Department, Syracuse University, Syracuse, New York 13244, United States; Present Address: ASML Silicon Valley, 125 Rio Robles, San Jose, California 95134, United States; orcid.org/0000-0002-5483-4663

Francis Toriello – Physics Department, Syracuse University, Syracuse, New York 13244, United States; Present Address: Atlantic Cape University, Mays Landing Campus S Building, Mays Landing, New Jersey 08330-2699, United States

Jiao He – Max Planck Institute for Astronomy, D-69117 Heidelberg, Germany

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpca.2c00287

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This research was supported by the NSF Astronomy and Astrophysics Research grant No. 1615897. J.H. acknowledges support from the European Research Council under the Horizon 2020 Framework Program via the ERC Advanced Grant Origins 83 24 28.

**REFERENCES**

(1) Ruppel, C. D.; Kessler, J. D. The interaction of climate change and methane hydrates. *Reviews of Geophysics* 2017, 55, 126–168.
(2) Telfer, M. W.; et al. Dunes on Pluto. *Science* 2018, 360, 992–997.
(3) Bockelée-Morvan, D.; Calmonte, U.; Charnley, S.; Duprat, J.; Engrand, C.; Gicquel, A.; Hässig, M.; Jehin, E.; Kawakita, H.; Marty,
B; et al. Cometary Isotopic Measurements. *Space Science Reviews* **2015**, *197*, 47–83.

(4) Boogert, A. C. A.; Gerardines, P. A.; Whitet, D. C. B. Observations of the icy universe. *Annual Review of Astronomy and Astrophysics* **2015**, *53*, 541–581.

(5) Boogert, A. C. A.; Schutte, W. A.; Helmich, F. P.; Tielens, A. G. G. M.; Wooden, D. H. Infrared observations and laboratory simulations of interstellar CH$_4$ and SO$_2$. *Astronomy & Astrophysics* **1997**, *317*, 929–941.

(6) Öberg, K. I.; Boogert, A. C. A.; Pontoppidan, K. M.; Blake, G. A.; Evans, N. J.; Lahuis, F.; van Dishoeck, E. F. The 2$d$2 Spitzer Spectroscopic Survey of Ices around Low-Mass Young Stellar Objects. *III. CH$_4$. * *Astrophysical Journal* **2008**, *678*, 1032–1041.

(7) Abplanalp, M. J.; Jones, B. M.; Kaiser, R. I. Untangling the methane chemistry in interstellar and solar system ices toward ionizing radiation: a combined infrared and reflectron time-of-flight analysis. *Physical Chemistry Chemical Physics (Incorporating Faraday Transactions)* **2018**, *20*, *5435–5468*.

(8) Markwick, A. J.; Miller, T. J.; Charnley, S. B. On the Abundance Gradients of Organic Molecules along the TMC-1 Ridge. *Astrophysical Journal* **2010**, *803*, 526–265.

(9) Kobayashi, K.; Geppert, W. D.; Carrasco, N.; Holm, N. G.; Mousis, O.; Palumbo, M. E.; Waite, J. H.; Watanabe, N.; Zirys, L. M. Laboratory Studies of Methane and Its Relationship to Prebiotic Chemistry. *Astrobiology* **2017**, *17*, 786–812.

(10) Yamamoto, T.; Kataoka, T.; Okada, K. Theory of phase transitions in solid methanes. X. Centering around Phase II in solid CH$_3$J. *Chem. Phys. Phys. 1987*, *66*, 2701–2730.

(11) Chapados, C.; Cabana, A. Infrared spectra and structures of solid CH$_4$ and CD$_4$ in phases I and II. *Can. J. Chem. 1972*, *50*, 3521–3533.

(12) Emtilia, S.; Torrelli, F.; He, J.; Vidal, G. Infrared Spectroscopic Study of Solid Methane: Nuclear Spin Conversion of Stable and Metastable Phases. *J. Phys. Chem. A* **2020**, *124*, 552–559.

(13) Chapovsky, P. L.; Hermans, L. J. F. Nuclear Spin Conversion in Polyatomic Molecules. *Ann. Rev. Phys. Chem. 1999*, *50*, 315–345.

(14) Sugimoto, T.; Yamakawa, K.; Arakawa, I. Infrared spectroscopic investigation of nuclear spin conversion in solid CH$_3$I. *J. Chem. Phys. 2015*, *143*, 224305.

(15) Persson, C. M.; Olofsson, A. O. H.; Le Gal, R.; Wiström, E. S.; Hassel, G. E.; Herbst, E.; Olberg, M.; Faure, A.; Hily-Blant, P.; Black, J. H.; et al. Ortho-para ratio of NH$_2$. Herschel-HIFI observations of ortho- and para-NH$_3$, rotational transitions towards W31C, W49N, WS1, and G34.3 + 0.1. *Astronomy & Astrophysics* **2016**, *586*, A128.

(16) Bernstein, M. P.; Cruikshank, D. P. Infrared spectra of H$_2$O-CH$_4$ ice mixtures. *Icarus 2006*, *181*, 302–308.

(17) Hudgins, D. M.; Sandford, S. A.; Allamandola, L. J.; Tielens, A. G. G. M. Mid- and Far-Infrared Spectroscopy of Ices: Optical Constants and Integarted Absorbanes. *Astrophysical Journal Supplement 1993*, *86*, 713.

(18) Hudson, R. L.; Gerardines, P. A.; Loeffer, M. J. Activation of weak IR fundamentals of two species of astrochemical interest in the Tdpoint group - the importance of amorphous ices. *Physical Chemistry Chemical Physics (Incorporating Faraday Transactions)* **2015**, *17*, 12545–12552.

(19) Hudgins, R.; Johnson, P. V.; Stern, J. V.; Gougen, J. D.; Kanik, I. Photochemistry of methane water ices. *Icarus 2009*, *200*, 338–342.

(20) Boogert, A. C. A.; Schutte, W. A.; Tielens, A. G. G. M.; Whittet, D. C. B.; Helmich, F. P.; Ehrenfreund, P.; Wesselius, P. R.; de Graauw, T.; Prusti, T. Solid methane toward deeply embedded protostars. *Astronomy & Astrophysics 1996*, *315*, L377–L380.

(21) Boogert, A. C. A.; Blake, G. A.; Öberg, K. Methane Abundance Variations toward the Massive Protostar NGC 7538 IRS 9. *Astrophysical Journal* **2004**, *615*, 344–353.

(22) Cordiner, M. A.; Charnley, S. B.; Wiström, E. S.; Smith, R. G. Organic Chemistry of Low-mass Star-forming Cores. 1. 7 mm Spectroscopy of Chamaeleon MMS1. *Astrophysical Journal 2012*, *744*, 131.