PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Last changed: March 31, 2015

Activation of Weak IR Fundamentals of Two Species of Astrochemical Interest in the T_d Point Group – The Importance of Amorphous Ices

by

R. L. Hudson*, P. A. Gerakines, and M. J. Loeffler

Submitted to *Physical Chemistry Chemical Physics*

New measurements are reported on the weak ν_1 and ν_2 fundamentals of frozen CH_4, a solid of considerable astrochemical interest. Infrared spectra in the ν_1 and ν_2 regions are presented for three CH_4-ice phases at 10 - 30 K with new absorption coefficients and band strengths to quantify the results. In contrast to the situation with the two crystalline phases of CH_4, both ν_1 and ν_2 were seen clearly in methane's amorphous phase. To support our CH_4 work, we also present new results for NH_4SH, a component of Jupiter's atmosphere, showing that the ν_2 vibration of NH_4^+ undergoes a dramatic loss of intensity during an amorphous-to-crystalline phase transition, but is regenerated in equally-dramatic fashion by radiation-induced amorphization of the sample. Results are compared to work recently published in this journal and elsewhere.

Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA. E-mail: reggie.hudson@nasa.gov

1. Introduction

The identification and characterization of molecules in interstellar space and the Solar System is a continuing challenge for astrochemists. While most gas-phase interstellar identifications have been made with microwave spectroscopy, the infrared (IR) region has been that of choice for solid-phase molecules, collectively called ices. Laboratory work on molecular ices, both single-and multi-component, has been critical for progress in this field to the point that a large set of laboratory measurements now exists to support IR astronomy.

Of the twenty or so reported astronomical ice molecules and ions, some have been firmly established since their discovery, while others have had to wait for new supporting laboratory work, remain less certain, and are still under investigation. Among the former are H_2O, CO, and CO_2, while in the latter group are H_2CO and HCOOH. Of the interstellar ions in ices, OCN^- is the best established as it relies on an IR feature with little overlap with other IR peaks, but NH_4^+ and $HCOO^-$ also are candidates of interest. Many of these same species are important for Solar-System ice chemistry, such as CH_4, which has been identified on Pluto, and NH_4^+, which has been suggested as a surface component of Charon, Pluto's largest moon.[1]

In the present work it is precisely these two species, CH_4 and NH_4^+, that are of interest. A recent paper by Escribano *et al.*[2] in this journal noted that at 14 K the IR-forbidden ν_1 transition of methane was not observed in frozen CH_4, but that it was seen in amorphous H_2O + CH_4 (3:1) ice mixtures. However, in neither that paper nor two others from the same group was the phase of the CH_4 reference sample unambiguously demonstrated.[3,4] There are, however, several reasons to believe that the authors' comparison spectrum of pure CH_4-ice was not that of amorphous CH_4. First, the authors say that their spectra could be fit using the optical constants of Hudgins *et al.*[5] Those constants are for crystalline CH_4, although it may not have been so realized at the time of publication over 20 years ago. Second, the peak position given by Gálvez *et al.*[3] for the ν_4 band of pure CH_4, about 1301 cm^{-1}, matches that of both Chapados and Cabana[6] and Pearl *et al.*[7] for phase-II crystalline methane. Finally, close examination of Figure 4 of Gálvez *et al.* shows a hint of fine structure for the $\nu_2 + \nu_3$ (~4530 cm^{-1}) feature, a well-defined peak near 4315 cm^{-1} for the $\nu_3 + \nu_4$ combination band, and a small but distinct peak near 4284 cm^{-1}, all of which are characteristic of crystalline CH_4.[8]

These observations raise the question of whether the reported activation at 14 K of methane's IR-forbidden ν_1 feature in an amorphous H_2O + CH_4 ice mixture[2-4] is caused by H_2O molecules or arises simply from a disruption of phase-II methane's crystallinity. The most straightforward way to resolve this matter is through a careful inspection of the IR spectrum of amorphous CH_4, but we have been unable to find suitable comparison spectra in the literature. In this paper we provide such a spectrum of amorphous methane and use it to examine the intensity of the IR-inactive ν_1 fundamental band.

Recently we have completed a quantitative study of the IR spectra of three phases of CH_4 ices at 8 - 40 K with an emphasis on the intense ν_3 and ν_4 transitions.[9] We now build on that work and report positions and intensities of the two remaining fundamentals, ν_1 and ν_2, which are IR-forbidden in the isolated molecule. In addition, we characterize these forbidden features by measuring their absorption coefficients and band strengths to help quantify our observations. To support this new CH_4 work we also present new results for the isoelectronic ion NH_4^+ in NH_4SH, an ionic solid relevant to the atmospheres of Jupiter and other gas-giant planets. We show that the ν_2 vibration of NH_4^+ undergoes a dramatic loss of intensity during an amorphous-to-crystalline phase change, but that ν_2 is regenerated in equally-dramatic fashion by ion irradiation of crystalline NH_4SH.

2. Earlier Work

Scientific interest in observing the IR-forbidden fundamentals of methane reaches back to at least the 1940s. Earlier than that, Coblentz's classic work[10] hinted at an observation of IR-inactive ν_2 in CH_4 gas, but the first definitive detection was in 1949 by Burgess.[11] The latter reported a gas-phase CH_4 ν_2 feature at 1533.6 cm^{-1} and argued that it arose from a Coriolis interaction between the allowed ν_4 and forbidden ν_2 transitions. Only a few months later, Holden *et al.*[12] reported a similar ν_2 band in IR spectra of liquid and solid CH_4, and specifically mentioned a perturbation of methane's T_d symmetry by neighboring molecules as the cause. Savitsky and Hornig[13] later examined crystalline CH_4 films, but neither ν_1 nor ν_2 were seen, null results that were verified in similar IR experiments by Chapados and Cabana.[6]

The first thin-film study to report the forbidden ν_1 absorbance in crystalline CH_4-ice apparently was that of Khanna and Ngoh.[8] Their Table 1 gives 2905 cm^{-1} as the position of ν_1, but no spectrum was shown. Significantly, the authors chose to make their crystalline samples by depositing CH_4 at 10 K and annealing the resulting ices at 32 K "for at least 30 minutes", a point to which we will return. Later both Kaiser and Roessler[14] and Moore and Hudson[15] studied frozen CH_4, but the IR reflection method used in each case distorts band shapes and relative intensities.[16,17] Combined with the scales of the spectra published in those papers it is difficult to judge either the phase of the CH_4 ices or the presence of ν_1 and ν_2. Similar comments apply to subsequent work of Bennett *et al.*[18], who employed an incidence angle of 75° for their IR beam. Positions of forbidden features are indicated in their Figure 1, but they are too small to be seen without access to the original spectra. Their ice was described as "consistent with that of phase II methane … with some amorphous features". Amorphous mixtures of H_2O and CH_4 ices were reported by Moore and Hudson[19], and their spectra clearly showed the forbidden ν_1 and ν_2 bands, but they went unmentioned. Similar ice mixtures studied by Hodyss *et al.*[20] also showed methane's ν_1 feature.

At this point in time it was not clear that the weak ν_1 and ν_2 peaks could be seen in the IR spectra of pure amorphous CH_4. In fact, it was not realized until later that this solid may not have been made in any of these experiments, and subsequent work did not fully clarify the situation. Figure 1 of de Barros *et al*.[21] indicates the position of ν_2 in a CH_4 spectrum, but not ν_1, somewhat opposite to the claim of Khanna and Ngoh.[8] The spectrum of de Barros *et al*. was described as "crystalline phase II structure with some amorphous features", but few additional details were provided. Mejía *et al*. later showed a CH_4 spectrum that indicated a position for the forbidden ν_2 band, but the arrow highlighting it actually is directed from a H_2O-ice feature near 1600 cm^{-1}, and the position listed in their Table 2 is incorrect for ν_2.[22] Their initial spectrum was described as being similar to those of others, but our own work suggests that it could have been for an amorphous sample, whereas most, or all, others published are for crystalline CH_4. The scale of their published spectra[20] makes it difficult to judge.

Concluding this long survey of earlier work are the recent papers of Escribano *et al*.[2], Gálvez *et al*.[3], and Herrero *et al*.[4] These unambiguously demonstrated that the ν_1 forbidden band of CH_4 was much stronger in their ice that contained frozen H_2O than in their pure-CH_4 ice, and it is this point that has helped to motivate the present paper.

3. Experimental Methods and Uncertainties

Most of the methods used in the work we present here are described in our earlier publications, such as Loeffler *et al*.[23] and Gerakines *et al*.[24], so only a summary is needed here. In short, we prepared ices by condensing gases from room temperature onto a pre-cooled KBr, aluminum, or gold-coated aluminum substrate (area $\approx$ 5 cm^2) mounted on the end of a cryostat's cold finger inside a stainless steel high-vacuum chamber (10^{-7} - 10^{-8} torr). To prepare amorphous methane we condensed gas-phase CH_4 onto a KBr substrate held near 10 K, with the condensation rate giving an increase in the sample's thickness of about 0.25 μm / hour as measured with laser interferometry at 670 nm. To prepare a phase-I crystalline sample of CH_4 we used a substrate temperature of 30 K and a condensation rate that gave a increase in ice thickness of about 1 μm / hour. Cooling such phase-I ices to 10 K produced phase-II crystalline CH_4.

Ammonium hydrosulfide (NH_4SH) was prepared by a method similar to that of Howett *et al.*[25] We simultaneously condensed gas-phase NH_3 and H_2S, in roughly a 1:1 ratio, from room temperature onto a metal substrate held at 50 K, and at a rate that caused the resulting ice to grow in thickness by about 1 μm / hour. The IR spectra of such ices showed features of NH_4SH, but it also showed evidence of unreacted NH_3 and H_2S. To remove any unreacted starting materials, the ice sample was warmed to 120 K over ~30 min. Recooling to 50 K gave amorphous NH_4SH with an IR spectrum showing no evidence of anything but NH_4^+ and SH^-. Subsequent warming of such amorphous samples to 160 K caused their crystallization. The spectrum of one such ice, after cooling to 50 K, is shown in our Results section.

The reagents (and suppliers) used in our work were CH_4 (Matheson Research Grade, 99.999%), $^{13}CH_4$ (Mound Laboratories, 99%), CD_4 (MSD Isotopes, 99.2%), NH_3, (Matheson, 99.99992%), and H_2S (Matheson, 99.5%). All reagents were used as received.

Our infrared spectra were recorded in two ways using two FTIR spectrometers. A Perkin Elmer Spectrum GX instrument was used for transmission measurements of ices on KBr substrates. A Bruker Vector spectrometer was used to record spectra of ices deposited on metal substrates, with the IR beam passing through the ice, reflecting off of the underlying substrate, and then passing back through the ice to the IR detector. In each type of measurement, the plane of the ice and substrate was essentially perpendicular to the direction of the IR beam. Ice spectra were recorded over 5000 - 500 cm^{-1} with 100 - 120 scans (accumulations) per spectrum. A resolution of 0.5 cm^{-1} was used for CH_4 studies and 2 cm^{-1} for others. Recent papers from our group, such as Moore *et al.*[26] provide additional experimental details.

The values of α' and A', apparent absorption coefficients and band strengths, that we report are equal to the slopes of graphs of 2.303 × (peak height) and 2.303 × (band area), respectively, for different ice thicknesses. We estimate that the error in our measurements of ice thicknesses is ±0.03 μm, which leads to uncertainties that are essentially negligible compared to those from sample reproducibility. For the latter, linear least-squares fits to the plots just mentioned had high correlation coefficients (e.g., above 0.999), which led to only small uncertainties in the slopes. See the table later in this paper for final values. The quantities used most often by practicing interstellar astrochemists are A', and these have a relative uncertainty on the order of 1% in our work.

The values of α and A, absolute absorption coefficients and band strengths, were determined from the derived imaginary part (k) of the optical constants. The values of k, and thus α and A, varied by only a few percent from sample to sample. The largest experimental source of uncertainty for α and A was from the noise in the IR spectrum used to determine k. The largest systematic uncertainties come from the n_{vis} used to derive k and from the value of ρ used to calculate A' and A. Again, final uncertainties are given for the values we report.

4. Results

We present IR spectral results on one molecule (CH_4) and one ion (NH_4^+) of astrochemical interest. Each has a tetrahedral geometry and hence T_d point-group symmetry when considered as an isolated species. A standard group-theoretical analysis for the isolated molecule or ion gives nine fundamental vibrations distributed among four different representations (symmetry species): $\Gamma_{\text{red}} = A_1 + E + 2F_2$. The IR-inactive fundamentals are $\nu_1(A_1)$, a totally symmetric vibration, and $\nu_2(E)$, a doubly-degenerate bending vibration. The IR-active modes are $\nu_3(F_2)$, a triply-degenerate stretching vibration, and $\nu_4(F_2)$, a triply-degenerate bending.

This analysis of the IR spectra of methane and ammonium is complicated by the fact that all of our work is with solids. For crystalline samples, the solid's structure imposes new symmetry conditions that result in an alteration of the selection rules for IR-allowed transitions of CH_4 and NH_4^+. Intermolecular motions (i.e., librations, translations) become important and indeed are crucial for a full spectral analysis. Further, on going from a crystalline phase to the disorder accompanying an amorphous solid (or a liquid) more reductions in symmetry are met with yet more expectations for IR transitions that would be forbidden in the case of an isolated molecule or ion. Viewed in this way, we expect *a priori* that CH_4 IR features that are weak or inactive in the gas phase could well gain intensity in methane's solid forms, with amorphous CH_4 being the most likely to show intensity enhancements.

In this paper we adopt the terminology and notation of gas-phase studies for simplicity and designate the two weaker CH_4 fundamentals as ν_1 and ν_2, and refer to them as the IR-inactive or forbidden vibrations. We denote the two stronger transitions from methane fundamentals as ν_3 and ν_4, referring to them as IR-active or allowed. Strictly speaking, in amorphous methane ν_1 and ν_2 also are allowed transitions, albeit considerably weaker than ν_3 and ν_4 (*vide infra*). For details concerning the interpretation of solid-phase IR spectra see Halford[27], Hornig[28], Carter[29], Fateley *et al.*[30], and Ferraro.[31]

4.1 The ν_1 and ν_2 features in CH_4 ices

Our interest in interstellar and planetary ices recently led us to examine the IR spectra of the low-temperature, low-pressure (vacuum) phases of several hydrocarbons and nitriles in the near-, mid-, and far-IR regions. Infrared spectra recorded at multiple temperatures and ice thicknesses were used to determine the apparent IR absorption coefficients of the larger peaks of selected molecules and the apparent band strengths (integrated intensities) of the larger IR features. From our spectra we extracted the optical constants *n* and *k* from about 5000 to 400 cm^{-1} (Moore *et al.*[26]; Hudson *et al.*[32,33]), with results posted in electronic form on our group's web pages, one of the more-extensive such datasets now available.[34] Of interest for this paper is that we recently have completed such work for amorphous CH_4, reporting the first IR spectra and optical constants of this low-temperature solid.[9]

Figure 1 shows survey spectra of the three CH_4-ice phases of astrochemical interest. This figure shows at a glance the relative simplicity of the spectra, the relative intensities of the ν_3 and ν_4 features in each phase, and, again for each phase, the dominance of the strong ν_3 and ν_4 vibrations already mentioned. Figure 2 shows enlargements of the regions of solid methane's ν_1 and ν_2 vibrations. It is clear from this figure that these features are present in the spectrum of amorphous CH_4, but they are either very weak or absent from spectra of both phases of crystalline CH_4.

Table 1 lists the positions of the ν_1 and ν_2 vibrations of solid amorphous CH_4, along with the ν_3 and ν_4 positions. Measuring absolute intensities of weak features is difficult, and to date we have examined amorphous CH_4 in detail only at 10 K. Results are summarized in Table 1, which gives apparent absorption coefficients (α') and apparent band strengths (A') for the ν_1 and ν_2 bands based on a comparison with the intensity of the $\nu_2 + \nu_4$ overtone of methane at 2814 cm^{-1} (α' = 467 cm^{-1}, A' = 3.95 × 10^{-19} cm $molecule^{-1}$). A Kramers-Krönig analysis gave the absolute absorption coefficients (α) and absolute band strengths (A) listed, with all A' and A values calculated from a CH_4 density of 0.47 g cm^{-3} of Satorre *et al.*[35] Based on our recent measurements, the ν_1 and ν_2 IR features of amorphous CH_4 are about 0.6 and 0.2%, respectively, as intense as the ν_4 vibration.

To check our identifications of ν_1 and ν_2 in the spectrum of amorphous CH_4, experiments were carried out near 10 K with amorphous $^{13}CH_4$ and amorphous CD_4. In all cases, the ^{13}C isotopic shifts were 1 cm^{-1} or less, as expected for these symmetric stretching and bending vibrations. The deuterium isotopic shifts for ν_1 and ν_2 in amorphous CD_4 were about 811 and 440 cm^{-1}, respectively, roughly as expected from gas-phase work[36] and helping to confirm our assignments.

The influence of temperature on ν_1 and ν_2 was not investigated in detail, but we note that the peak positions and widths changed little as the amorphous CH_4 sample was warmed, whereas the intensities dropped by about 50% as the temperature was raised from 10 to 25 K. In general, the ν_1 and ν_2 bands were difficult to entirely remove by thermal annealing. For example, temperature cycling (warming then cooling) from about 10 K to progressively higher temperatures, up to about 30 K, reduced the ν_1 and ν_2 features by about 75%, whereas holding the temperature near 30 K overnight reduced them by about 80%, changes accompanied in each case by partial crystallization of the sample and a loss of methane due to sublimation.

Since H_2O molecules have been reported to enhance the intensity of the ν_1 vibration of methane in an amorphous 3:1 $H_2O + CH_4$ ice, we examined samples with two other concentrations to judge the extent of this effect. Figure 3 shows the IR spectrum of an amorphous $H_2O + CH_4$ ice with a 2:1 composition, taken from one of our earlier papers.[19] The inset shows an enlargement of the ν_1 region for this ice and also for a separate one having a 20:1 ratio ($H_2O : CH_4$). The ν_1 feature is seen clearly in both cases. We also reexamined archival data from our laboratory for other ices at 10 - 20 K, each being an amorphous X + CH_4 binary mixture with a molar ratio between about 2:1 and 1:2. The ice spectra found were with X = C_2H_2, NH_3, N_2, CO_2, and CO, and in all cases when methane was mixed with these molecules at these ratios the ν_1 band of CH_4 was observed. A few IR spectra of ices with even greater methane dilution were examined, such as $N_2:CH_4$ = 10:1, 50:1, and 100:1. In these particular cases, the ν_1 feature was seen to be very weak, even in ices with a thickness of about 10 µm, but whether the low intensity was simply due to the methane's small concentration or is related specifically to the N_2 molecule is unknown. A more-systematic investigation into such compositional effects on band intensities remains to be done. The point we emphasize is that the ν_1 and ν_2 peaks of CH_4 can be seen in many amorphous solids, not just those containing H_2O.

4.2 The ν_2 feature of NH_4^+ in NH_4SH

Observations of the forbidden ν_1 and ν_2 vibrations of CH_4 in the amorphous solid are interesting, but not entirely unexpected since both features already can be seen in spectra of the amorphous H_2O + CH_4 ice mixtures of Moore and Hudson's Figure 1.[19] Our conclusion is that a *lack of crystallinity* is the key to the apparent increase in intensity of such forbidden absorptions. As an independent test of this idea we turned to an isoelectronic species, NH_4^+, to see if it too would display one or more forbidden transitions in the IR spectrum of its amorphous phase.

A rich literature of NH_4^+ spectroscopic studies, particularly on ammonium halides, has been produced over the past 65 years (e.g., Wagner and Hornig[37], Schumaker and Garland[38], Kearley *et al.*[39], Medvedev *et al.*[40]). However, it appears that the only pure ammonium salt of astrochemical significance is NH_4SH, ammonium hydrosulfide. This compound has been discussed for over 40 years as a likely component of and contributor to the colors of the clouds of Jupiter[41], with proposals concerning the reaction chemistry of NH_4SH reaching back even further.[42] In contrast, the experimental work on NH_4SH is extremely meager, which is why we recently have begun to study this compound.[43]

Ammonium hydrosulfide is unstable at room temperature, but can be formed and trapped by co-condensation of roughly stoichiometric ratios of NH_3 and H_2S gases. Figure 4(a) shows the IR spectrum of NH_4SH at 50 K. This spectrum agrees with the only one of amorphous NH_4SH in the literature[42] except that the literature spectrum shows, around 1050 cm^{-1}, evidence for unreacted NH_3. Ammonium-ion features dominate our spectrum near 3000 and 1450 cm^{-1}, with weaker bands in between, while the extremely weak absorption of HS^- can perhaps just be made out near 2590 cm^{-1}. Although both CH_4 and NH_4^+ have T_d symmetry as isolated species, their amorphous-phase spectra, Figures 1(c) and 4(a), show striking differences in line widths and overall complexity. We attribute these differences to the ion-ion interactions in NH_4SH being substantially stronger than the neutral-neutral intermolecular interactions among molecules in amorphous CH_4. As will be seen, the selection rule forbidding IR activity of ν_2 for NH_4^+ and CH_4 is broken for each species, but more dramatically in the former case than in the latter.

Figure 4(b) is the spectrum of crystalline NH_4SH, again at 50 K. In comparison to the amorphous sample's spectrum in 4(a), a considerable sharpening of the NH_4^+ bands near 3000 and 1450 cm^{-1}, and also of the HS^- feature, is readily seen. Figure 4(b) agrees with the only two spectra that have been published for crystalline NH_4SH.[44,45]

The crystalline sample of Figure 4 was made by warming an amorphous NH_4SH ice to about 160 K and then recooling to 50 K. A careful comparison of (a) and (b) in Figure 4 shows that there is one IR feature of NH_4SH that experienced a significant loss of intensity during the amorphous-to-crystalline phase change, namely the band near 1680 cm^{-1}. We assign this feature to the nominally-forbidden ν_2 vibration of NH_4^+.[37] A separate NH_4SH synthesis from $^{15}NH_3 + H_2S$ gave the ν_2 position of NH_4^+ as essentially the same as in Figure 4, a small ^{15}N isotopic shift which was as expected.[46] With NH_4SH there is little chance of observing the ν_1 vibration because of the large, broad complex of overlapping features at 3300 - 2600 cm^{-1}, a complication lacking in the case of CH_4.

4.3 Regeneration of forbidden transitions

If an amorphous solid is indeed the key to observing IR-forbidden features of CH_4 and NH_4^+ then it should be possible to enhance such IR bands by amorphizing a crystalline ice. From an astrochemical perspective, this is an important process and it is readily accomplished by radiation chemistry, an area in which we have long been active.[47] Ices in space are exposed to ionizing radiations such as cosmic rays, vacuum-UV photons, and magnetospheric electrons to the degree that significant exposure amorphizes crystalline solids at a rate that can increase with decreasing temperature.[48]

Figure 4(c) shows the result of the irradiation (0.8 MeV protons) of crystalline NH_4SH at 50 K to a dose of about 46.4 MGy (4640 Mrad). Comparison of (a) and (c) in Figure 4 shows that the irradiation amorphized the initially crystalline NH_4SH ice of (b), and that the ν_2 feature of NH_4^+ reappeared after the ice sample regained its amorphous character. Also indicated in (c) are two IR features of NH_3 formed by the radiation-induced decomposition of NH_4SH.

The corresponding experiment with crystalline phase-II CH_4 was attempted, but gave only a marginally positive result. With methane the forbidden ν_1 and ν_2 features are quite small, and so their increase with CH_4-ice amorphization is significantly offset by the rate of radiation-induced destruction of CH_4. Moreover, the radiolytic formation of hydrocarbon products obscures the 2900 cm^{-1} region of interest.[15]

5. Discussion

The work just presented clearly shows that the ν_1 and ν_2 features of CH_4 are enhanced in amorphous methane compared to crystalline CH_4. A similar conclusion applies to the ν_2 feature of NH_4^+. A lack of IR activity for ν_1 and ν_2 in the crystalline solids agrees with the correlation analyses of Bragin *et al.*[45] and Khanna and Ngoh[8] based on the space groups of NH_4SH and CH_4, respectively. In each case the ν_1 and ν_2 features were predicted to display little or no IR activity in the crystalline state, just as we have seen. (Note that E_1, E_y, and C_v should be replaced by F_1, E_g, and $C_{\infty v}$ in Table 2 of Bragin *et al.*[45])

We have not conducted a molecular-level examination to determine why the intensities of CH_4 and NH_4^+ IR features change on going to the amorphous phase. However, it seems reasonable that a symmetry reduction or solid-state perturbation is the cause, altering what is ostensibly the T_d symmetry and the associated IR selection rules for CH_4 and NH_4^+. We found that the addition of H_2O-ice *per se* to solid CH_4 was not required for the enhancement of the latter's weak ν_1 feature[2-4], but rather that the activation of ν_1 is more likely caused simply by H_2O molecules disrupting the lattice of crystalline CH_4. Supporting this is our observations that the intensity of methane's weak ν_1 band was enhanced over that seen in crystalline CH_4 when methane was present in binary amorphous, anhydrous mixtures containing C_2H_2, NH_3, N_2, CO_2, or CO.

We propose that our new results, particularly the spectra of Figure 2, help to resolve a 25-year old controversy involving the presence of the ν_1 band in IR spectra of crystalline CH_4. In 1990, Khanna and Ngoh[8] reported a weak ν_1 band near 2905 cm^{-1} in phase-II CH_4, but Calvani[49] saw no such feature despite having samples that were orders of magnitude thicker. The resolution of the disagreement appears to be that Khanna and Ngoh grew amorphous methane ices at 10 K and then annealed them "at 32 K for at least 30 min" to try and bring about crystallization, a method that we and others[13] have found difficult to successfully accomplish. In contrast, Calvani's samples were made by slowly cooling liquid CH_4 to its freezing point, a method much more likely to generate ices free of amorphous regions. The absence of methane's ν_1 band in the crystalline solid of Calvani agrees with our results in Figures 2(a) and 2(b), while residual amorphous material in the ices of Khanna and Ngoh would produce the weak ν_1 feature seen clearly in our Figure 2(c).

In addition to methane, nominally IR-inactive features have been reported in a variety of other amorphous solids, including several from our laboratory. Figure 5 in Moore and Hudson[19] clearly shows acetylene's forbidden C≡C stretch in amorphous $H_2O + C_2H_2$ ices. See also Figure 1 of Wu *et al*. for the same result.[50] Bernstein and Sandford[51] reported an IR intensity enhancement of the NN stretch of frozen N_2, an observation with roots in the older work of Smith *et al*.[52] Cairns and Pimentel recorded the IR-forbidden stretching vibration of O_2 and attributed the band's enhancement at the lowest temperature studied (~4 K) to the condensation of O_2 to give a solid that was at least partially amorphous.[53] The IR spectrum of pure amorphous C_2H_2 shows the forbidden ν_2 C≡C stretch near 1961 cm^{-1}, but it is not observed in crystalline acetylene.[32] And as a final example, in our recent study of IR spectra of ethylene ices, the IR-forbidden ν_1, ν_2, ν_3, and ν_6 features were observed in the amorphous solid's spectrum, but not in that of crystalline C_2H_4.[33]

With all of these observations in mind, our results agree with those of Gálvez *et al*.[3], subject to the identification of their CH_4 spectrum as that of a sample that is highly crystalline, perhaps 100%. With that interpretation, it is not surprising that methane's ν_1 feature was not observed by those authors in their CH_4 spectrum, but once the correct ice phase is identified then their results agree with ours and with expectations.

Turning to NH_4SH, there are far fewer published results with which to compare our work. Optical constants *n* and *k* were published by Howett *et al*.[25] and show a substantial reduction in the ν_2 band of NH_4^+ on going from amorphous to crystalline NH_4SH, in agreement with our spectra in Figure 4(a) and 4(b). Much earlier, Dows *et al*.[54] found that the ν_2 feature of NH_4^+ (1690 cm^{-1}) was present in amorphous NH_4N_3, but that it decreased substantially on crystallization of the sample at 150 - 160

K, again in agreement with our results in Figure 4. To our knowledge, the experiment represented by this same figure is the first to show the recovery of ammonium's ν_2 band by radiation-induced amorphization.

Finally, we consider the possible astrochemical value of our results. Perhaps their primary value is that they present a clear and consistent picture of the dependence of IR intensities on the phase of an icy solid, and particularly of the spectral intensity enhancements caused by an amorphous phase. However, Figure 1 and Table 1 show that the low intensities of the weak, but activated, transitions ν_1 and ν_2 of CH_4 make it doubtful that they will be used for astronomical observations in the foreseeable future. Nevertheless, since H_2O-ice is amorphous in many astronomical environments then studies of IR spectra of molecules and ions trapped in this non-crystalline solid can be of considerable value.

6. Conclusions

We have presented new observations of the IR-forbidden ν_1 and ν_2 features of CH_4 at ~10 K. We have shown that these bands are readily observed in amorphous CH_4, but only with difficulty, if at all, in crystalline methane. We also have reported several measures of the intrinsic IR-band intensities of ν_1 and ν_2 in amorphous CH_4. To support our work we have presented new measurements on the amorphous and crystalline phases of NH_4SH, showing that here too the forbidden feature is most readily seen in the amorphous solid. Finally, we have demonstrated that the presence of H_2O-ice is not necessary for enhancing the intensities of the ν_1 and ν_2 features of CH_4 at ~10 K, except perhaps to disrupt methane's crystalline structure.

Acknowledgements

NASA funding through the Outer Planets Research, Cassini Data Analysis, and Astrophysical Research and Analysis programs is acknowledged, as is partial support from the NASA Astrobiology Institute through the Goddard Center for Astrobiology. Chris Bennett, first author of Bennett *et al.*[16], is thanked for a copy of the original spectrum on which Figure 1 of that paper is based. The proton accelerator we used was maintained by Steve Brown, Tom Ward, and Eugene Gerashchenko, engineers in the NASA Goddard Radiation Effects Facility.

References

1 M. H. Moore, R. F. Ferrante, R. L. Hudson, and J. N. Stone, *Icarus*, 2007, **190**, 260.

2 R. Escribano, V. Timon, O. Gálvez, B. Maté, and V. J. Herrero, *PCCP*, 2014, **16**, 16694.

3 O. Gálvez, B. Maté, V. J. Herrero, and R. Escribano, *Astrophys. J.*, 2009, **703**, 2101.

4 V. J. Herrero, O. Gálvez, B. Maté, and R. Escribano, *PCCP*, 2010, **12**, 3164.

5 D. M. Hudgins, S. A. Sandford, L. J. Allamandola, and A. G. G. M. Tielens, *Astrophys. J. Supp. Ser.*, 1993, **86**, 713.

6 C. Chapados and A. Cabana, *Can. J. Chem.*, 1972, **50**, 3521.

7 J. Pearl, M. Ngoh, M. Ospina, and R. K. Khanna, *J. Geophys. Res.*, 1991, **96**, 17,477.

8 R. K. Khanna and M. Ngoh, *Spectrochim. Acta*, 1990, **46A**, 1057.

9 P. A. Gerakines and R. L. Hudson, *Astrophys. J.*, 2015, submitted.

10 W. W. Coblentz, *Investigations of Infra-red Spectra*, 1905, Carnegie Institution of Washington, Washington, DC, pp. 43 and 166.

11 J. S. Burgess, *Phys. Rev.*, 1949, **17**, 302.

12 R. B. Holden, W. J. Taylor, and H. L. Johnston, *J. Chem. Phys.*, 1949, **17**, 1356.

13 G. B. Savitsky and D. F. Hornig, *J. Chem. Phys.*, 1962, **36**, 2634.

14 R. I. Kaiser and K. Roessler, *Astrophys. J.*, 1998, **503**, 959.

15 M. H. Moore and R. L. Hudson, *Icarus*, 2003, **161**, 486.

16 S. Maeda and P. N. Schatz, *J. Chem. Phys.*, 1961, **35**, 1617.

17 J. Pacansky and C. D. England, *J. Chem. Phys.*, 1986, **90**, 4499.

18 C. J. Bennett, C. S. Jamieson, Y. Osamura, and R. I. Kaiser, *Astrophys. J.*, 2006. **653**, 792.

19 M. H. Moore and R. L. Hudson, *Icarus*, 1998, **135**, 518.

20 R. Hodyss, P. V. Johnson, J. V. Stern, J. D. Goguen, and I. Kanik, *Icarus*, 2009, **200**, 338.

21 A. L. F. de Barros, V. Bordalo, E. Seperuelo Duarte, E. F da Silveira, A. Domaracka, H. Rothard, and P. Boduch, *Astron. & Astrophys.*, 2011, **531**, A160.

22 C. F. Mejía, A. L. F. de Barros, V. Bordalo, E. F. da Silveira, P. Boduch, A. Domaracka, and H. Rothard, *Month. Not. Roy. Astron. Soc.*, 2013, **433,** 2368.

23 M. J. Loeffler, R. L. Hudson, M. H. Moore, and R. W. Carlson, *Icarus*, 2011, **215**, 270.

24 P. A. Gerakines, R. L. Hudson, M. H. Moore, and J-L. Bell, *Icarus*, 2012, **220**, 647.

25 C. J. A. Howett, R. W. Carlson, P. G. J. Irwin, and S. B. Calcutt, S. B., *J. Opt. Soc. Amer. B - Opt. Phys.*, 2007, **24**, 126.

26 M. H. Moore, R. F. Ferrante, W. J. Moore, and R. L. Hudson, *Astrophys. J. Supp. Ser.*, 2010, **191**, 96.

27 R. S. Halford, *J. Chem. Phys.*, 1946, **14**, 8.

28 D. Hornig, *J. Chem. Phys.*, 1948, **16**, 1063.

29 R. L. Carter, *J. Chem. Educ.*, 1971, **48**, 297.

30 W. G. Fateley, N. T. McDevitt, and F. F. Bentley, *Appl. Spectros.*, 1971, **25**, 155.

31 J. R. Ferraro, *Appl. Spectros.*, 1975, **29**, 354.

32 R. L. Hudson, R. F. Ferrante, and M. H. Moore, *Icarus*, 2014, **228**, 276.

33 R. L. Hudson, P. A. Gerakines, and M. H. Moore, *Icarus*, 2014, **243**, 148.

34 http://science.gsfc.nasa.gov/691/cosmicice/constants.html

35 M. Á. Satorre, M. Domingo, C. Millán, R. Luna, R. Vilaplana, and C. Santonja, *Planet. Space Sci.*, 2008, **56**, 1748.

36 T. Shimanouchi, *Tables of Molecular Vibrational Frequencies Consolidated*, Volume I**,** National Bureau of Standards, 1972.

37 E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, 1950, **18**, 296.

38 N. E. Schumaker and C. W. Garland, *J. Chem. Phys.*, 1970, **53**, 392.

39 G. J. Kearley, S. F. A. Kettle, and I. A. Oxton, *Spectrochim. Acta*, 1980, **36A**, 507.

40 S. A. Medvedev, M. I. Eremets, J. Evers, T. M. Klapötke, T. Palasyuk, and I. A. Trojan, *Chem. Phys.*, 2011, **386**, 41.

41 J. S. Lewis, *Icarus*, 1969, **10**, 365.

42 R. Wildt, *Astrophys. J.*, 1937, **86**, 321.

43 M. J. Loeffler and R. L. Hudson, *Icarus*, 2015, submitted.

44 J. R. Ferraro, G. Sill, and U. Fink, *Appl. Spec.*, 1980, **34**, 525.

45 J. Bragin, M. Diem, D. Guthals, and S. Chang, *J. Chem. Phys.*, 1977, **67**, 1247.

46 H. W. Morgan, P. A. Staats, and J. H. Goldstein, *J. Chem. Phys.*, 1957, **27**, 1212.

47 R. L. Hudson, M. H. Moore, and P. A. Gerakines, *J. Geophys. Res. - Planets*, 2001, **106**, 33275.

48 R. L. Hudson and M. H. Moore, *Rad. Phys. and Chem.*, 1995, **45**, 779.

49 P. Calvani, *Spectrochim. Acta*, 1991, **47A**, 1057.

50 C. Y. R. Wu, D. L. Judge, B. Cheng, W. Shih, T. Yih, and W. H. Ip, *Icarus*, 2002, **156**, 456.

51 M. P. Bernstein and S. A. Sandford, *Spectrochim. Acta*, 1999, **55A**, 2455.

52 A. L. Smith, W. E. Keller, H. L. Johnston, *Phys. Rev.*, 1950, **79**, 728.

53 B. R. Cairns and G. C. Pimentel, *J. Chem. Phys.*, 1965, **43**, 3432.

54 D. A. Dows, E. Whittle, and G. C. Pimentel, *J. Chem. Phys.*, 1955, **23**, 1475.

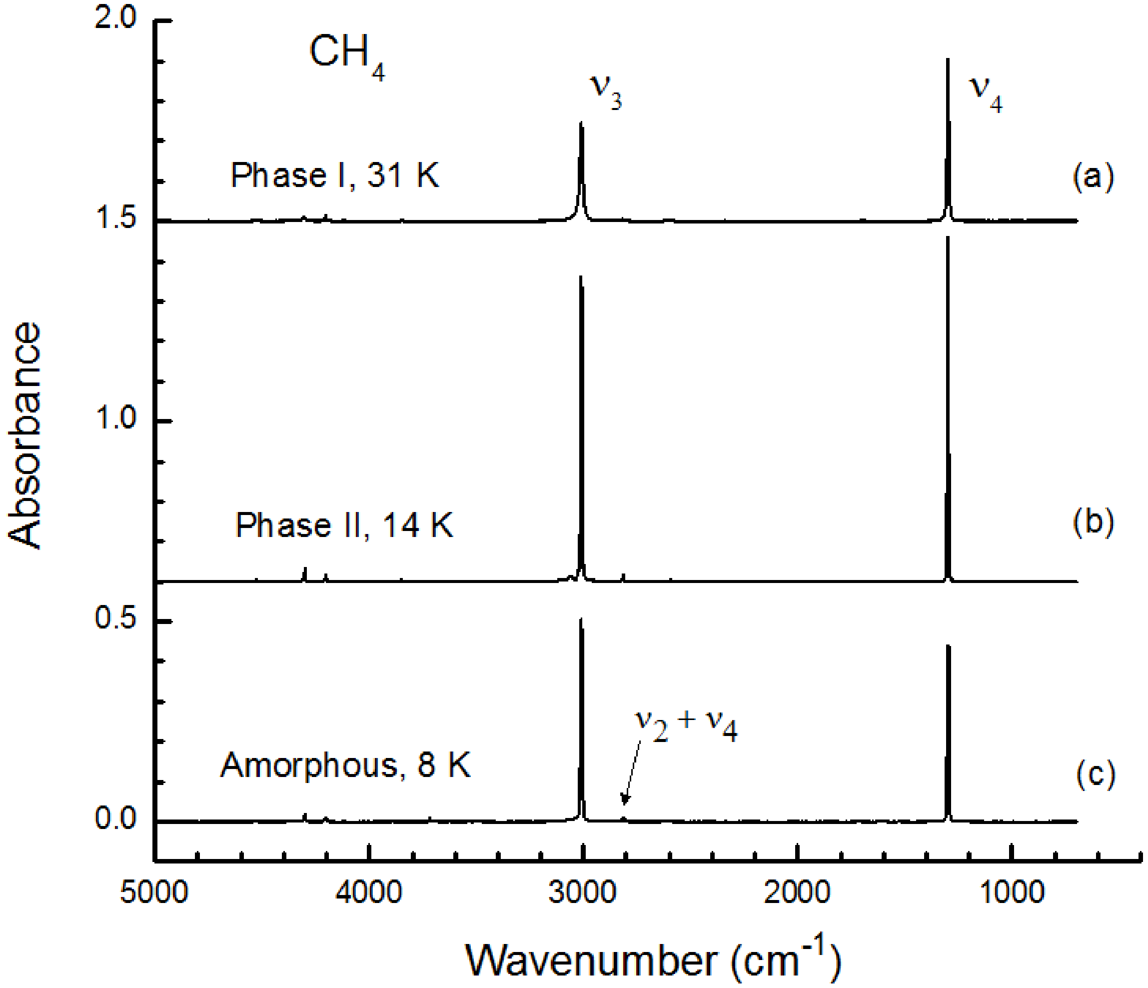

Fig. 1 Infrared spectra of the three phases of solid CH$_4$ studied, each sample having a thickness of ~0.52 µm. See Chapados and Cabana[6] for expansions of the ν_3 and ν_4 regions of crystalline CH$_4$, and Gerakines and Hudson[9] for the same for amorphous CH$_4$. Spectra are offset for clarity.

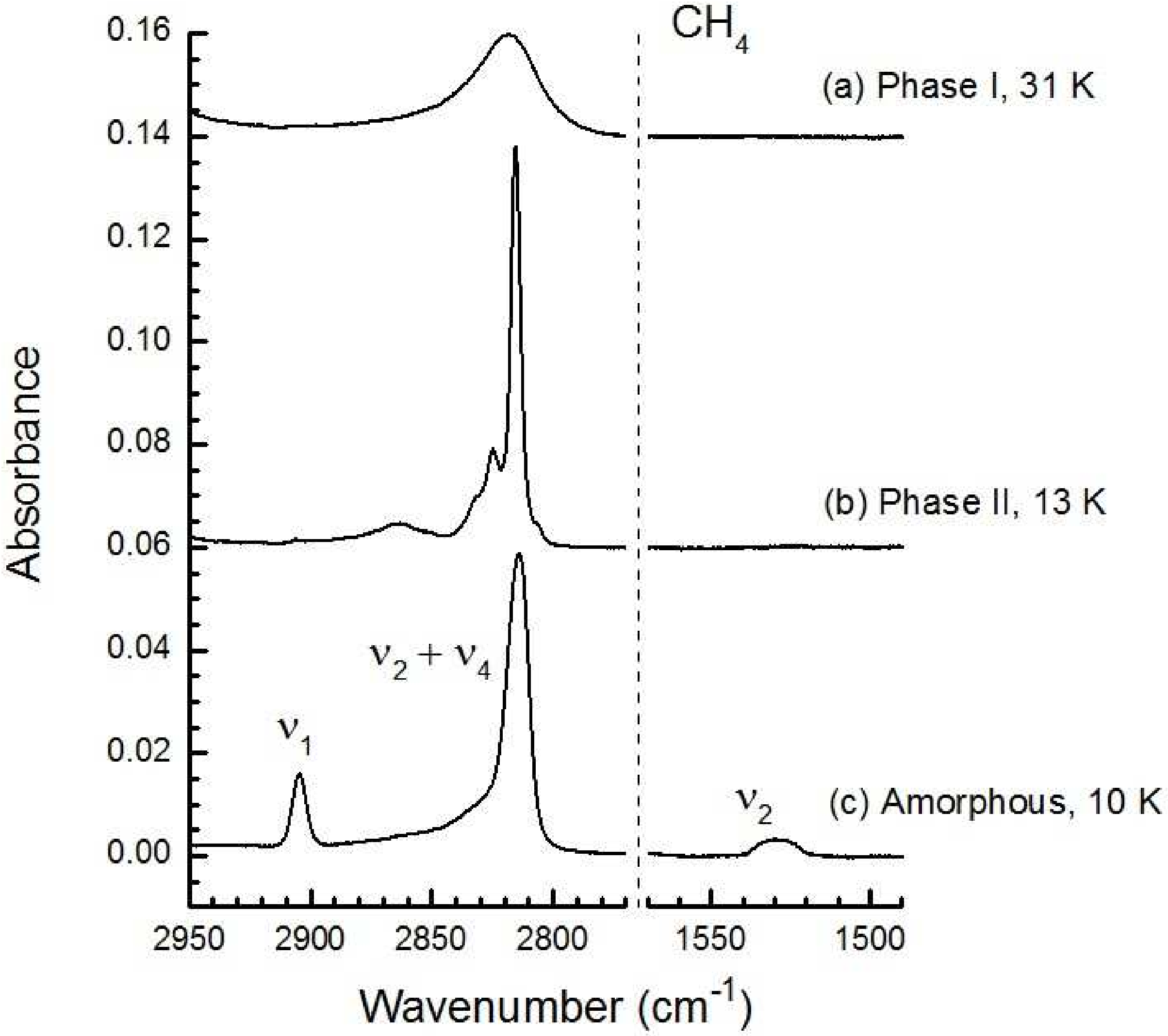

Fig. 2 Infrared spectra around the ν_1 band near 2904 cm^{-1} (left) and the ν_2 band near 1530 cm^{-1} (right) for the three phases of solid CH$_4$ studied. Spectra are shown for samples with a thickness of ~2.6 μm and are offset for clarity.

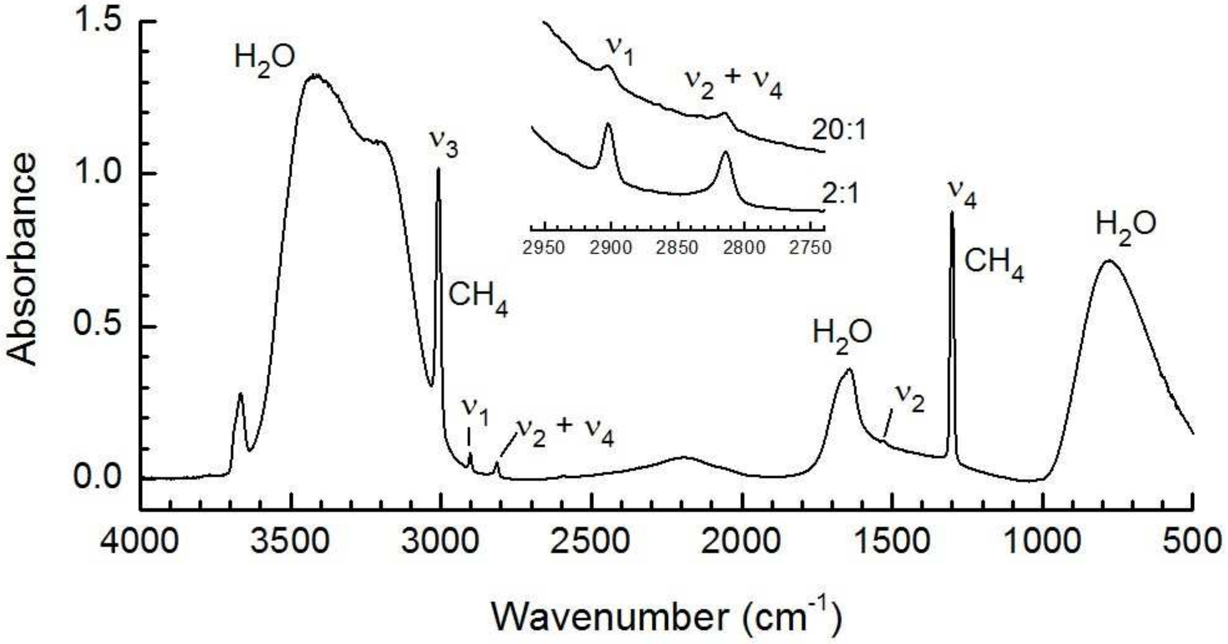

Fig. 3 Infrared spectra of amorphous H_2O + CH_4 (2:1) near 20 K showing the forbidden ν_1 and ν_2 bands taken in reflectance.[19] The inset shows the region around ν_1 for a more-dilute ice. The thicknesses for the (2:1) and (20:1) ices were about 4 μm.

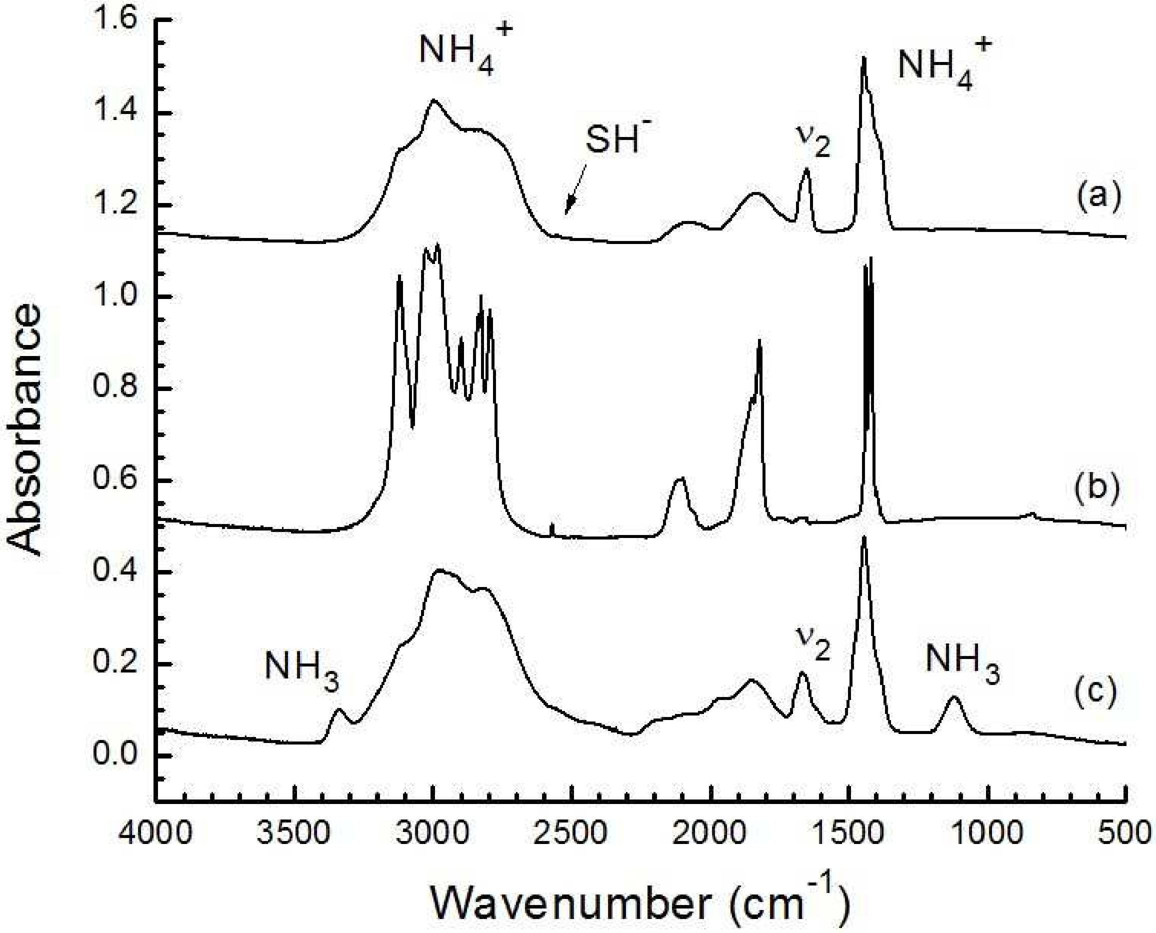

Fig. 4 Spectra of NH_4SH at 50 K - (a) amorphous NH_4SH, (b) crystalline NH_4SH, and (c) crystalline NH_4SH after irradiation to a dose of about 46.4 MGy (4640 Mrad). The peaks in (c) near 3350 and 1100 cm^{-1} are assigned to NH_3, a radiation product of NH_4SH. The thickness of the ice samples was about 1.2 μm. Spectra are offset for clarity. Note the disappearance and then the reappearance of the ν_2 feature on going from (a) to (b) to (c).

Table 1

IR Fundamentals of Amorphous CH_4 at 10 K [a]

Property	ν_1	ν_2	ν_3	ν_4
$\tilde{\nu}$ / cm^{-1}	2904	1530	3010	1297
λ / μm	3.444	6.536	3.322	7.710
FWHM / cm^{-1}	6	14	8	8
α' / cm^{-1}	116 ± 2	26.7 ± 0.5	21860 ± 230	16980 ± 990
α / cm^{-1}	115 ± 4	28.4 ± 4	23790 ± 4	18470 ± 4
A' / cm $molecule^{-1}$	$5.43 \pm 0.04 \times 10^{-20}$	$2.29 \pm 0.02 \times 10^{-20}$	$1.40 \pm 0.01 \times 10^{-17}$	$9.71 \pm 0.12 \times 10^{-18}$
A / cm $molecule^{-1}$	$3.94 \pm 0.54 \times 10^{-20}$	$2.09 \pm 0.63 \times 10^{-20}$	$1.42 \pm 0.01 \times 10^{-17}$	$1.01 \pm 0.01 \times 10^{-17}$
Integration range / cm^{-1}	2916 - 2892	1542 - 1514	3160 - 2930	1345 - 1255

[a] FWHM = full width at half maximum; α' and A' denote apparent absorption coefficient and apparent band strength taken directly from a set of IR spectra using a Beer's law type plot; α and A denote absolute absorption coefficient and absolute band strength calculated from optical constant k using $\alpha = 4 \pi \tilde{\nu} k$; A' and A were found by integration of α' and α, respectively, over the band of interest; a reference value of n(670 nm) = 1.28 for CH_4 at 10 K was used throughout to calculate optical constants[35]; entries for ν_3 and ν_4 are from the data of Gerakines and Hudson.[9]