Infrared Spectra, Optical Constants, and Temperature Dependences of Amorphous and Crystalline Benzene Ices Relevant to Titan

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Abstract

Benzene ice contributes to an emission feature detected by the Cassini Composite InfraRed Spectrometer (CIRS) near 682 cm\(^{-1}\) in Titan’s late southern fall polar stratosphere. It is also one of the dominant components of the CIRS-observed High-Altitude South Polar ice cloud observed in Titan’s mid stratosphere during late southern fall. Titan’s stratosphere exhibits significant seasonal changes with temperatures that spatially vary with seasons. A quantitative analysis of the chemical composition of infrared emission spectra of Titan’s stratospheric ice clouds relies on consistent and detailed laboratory transmittance spectra obtained at numerous temperatures. However, there is a substantial lack of experimental data on the spectroscopic and optical properties of benzene ice and its temperature dependence, especially at Titan-relevant stratospheric conditions. We have therefore analyzed in laboratory the spectral characteristics and evolution of benzene ice’s vibrational modes at deposition temperatures ranging from 15 to 130 K, from the far- to mid-IR spectral region (50–8000 cm\(^{-1}\)). We have determined the amorphous-to-crystalline phase transition of benzene ice and identified that a complete crystallization is achieved for deposition temperatures between 120 and 130 K. We have also measured the real and imaginary parts of the ice complex refractive index of benzene ice from 15 to 130 K. Our experimental results significantly extend the current state of knowledge on the deposition temperature dependence of benzene ice over a broad infrared spectral range, and provide useful new data for the analysis and interpretation of Titan-observed spectra.

Unified Astronomy Thesaurus concepts: Saturnian satellites (1427); Titan (2186); Ice formation (2092); Molecular spectroscopy (2095); Transmission spectroscopy (2133); Astrochemistry (75); Planetary atmospheres (1244); Laboratory astrophysics (2004); Far infrared astronomy (529); Near infrared astronomy (1093); Experimental techniques (2078)

1. Introduction

Benzene (C\(_6\)H\(_6\)), the simplest aromatic hydrocarbon, is a molecule that has raised great interest in the astrophysical community for almost four decades. This is mainly because C\(_6\)H\(_6\) is one of the main precursors of polycyclic aromatic hydrocarbons (PAHs) reported to be present in interstellar dust particles (Leger & Puget 1984; Allamandola et al. 1989; Tielens 2013 and references therein), carbonaceous chondrites (Perring & Ponomerupera 1971; Hayatsu et al. 1977; Hahn et al. 1988), and other astrophysical environments, such as carbon-rich, high-temperature environments (circumstellar and carbon-rich protoplanetary nebulae; Buss et al. 1993; Clemett et al. 1994). Benzene rings easily produce more complex, polycyclic structures by the one-ring build-up mechanism (Simoneit & Fettet 1996). In space, an analogous process to carbon soot formation occurring on Earth can be initiated through the completion of that first aromatic ring and may also lead to the synthesis of PAHs (Tielens & Charney 1997). Mechanisms involving the addition of hydrocarbons, such as acetylene onto aromatic rings as well as the attachment of other aromatic rings, or hydrocarbon pyrolysis, have been proposed to characterize the growth process of PAHs (Bittner & Howard 1981; Frenklach & Feigelson 1989; Wang & Frenklach 1997; Cherchneff 2011 and references therein).

PAH synthesis from shocked benzene has also been reported (Mimura 1995). PAHs are crucial materials involved in a variety of cosmochemical processes. For example, amino acids could be synthesized by aqueous alteration of precursor PAHs in carbonaceous chondrites (Shock & Schulte 1990). PAHs are also produced in laboratory-simulated planetary atmospheres of Titan and Jupiter (Sagan et al. 1993; Khare et al. 2002; Trainer et al. 2004), and results from these studies indicate that the formation of aromatic rings and polyaromatics may be, among other sources, a possible chemical pathway for the production of the atmospheric solid particles (Lebonnois et al. 2002; Wilson et al. 2003; Trainer et al. 2004). The formation and evolution of benzene in planetary environments or other solar system objects thus represents a fundamental primary stage of the PAH production and other subsequent relevant chemical and prebiotic processes (like soot formation). In this context, several works related to benzene have been devoted to better understand the physico-chemical processes of irradiated C\(_6\)H\(_6\) in its gaseous and solid phases, and the derived products, by acquiring high-resolution astronomical spectra, carrying out detailed laboratory studies or developing theoretical modeling (Allamandola et al. 1989 and references therein; Callahan et al. 2013; Materese et al. 2015; Mouzay et al. 2021). Laboratory astrophysical investigations have mostly focused on performing vibrational spectroscopy of ion, electron, or UV irradiated C\(_6\)H\(_6\) gas and C\(_6\)H\(_6\) ice. Such investigations aim to provide data on the spectral properties of the irradiated C\(_6\)H\(_6\) materials, compare them with spectra obtained from astronomical observations (e.g., observations of the interstellar medium),
or to study photoprocessed benzene ices to understand the fate of benzene ices in Titan’s stratosphere and help understanding the formation of aerosol analogs observed in Saturn’s moon’s stratosphere (Mouzay et al. 2021).

Our experimental study differs from such previous works. The main objective was to carry out a comprehensive experimental study on pristine benzene ice in order to accurately determine its chemical behavior and its infrared (IR) and optical properties at different deposition temperatures. The initial motivation behind our laboratory experiments was to constrain the role of benzene in the formation and chemical composition of Titan’s High-Altitude South Polar (HASP) ice cloud. The HASP ice cloud is a massive stratospheric ice cloud system, recently observed in far-IR limb spectra recorded by the Cassini Composite InfraRed Spectrometer (CIRS) in Titan’s late southern fall mid stratosphere (J−200 km altitude), at high southern polar latitudes (Anderson et al. 2018b).

During the Cassini mission, one of the highly unexpected findings was the detection of benzene gas in Titan’s upper atmosphere, as determined by in situ analyses by the Cassini Plasma Spectrometer (CAPS) and the Ion Neutral Mass Spectrometer (INMS) performed during Cassini’s first close flybys of Titan (Coates et al. 2007; Waite et al. 2007). During subsequent Titan flybys, C₆H₆ gas was also observed by Cassini CIRS in Titan’s stratosphere, at high northern and high southern latitudes (Coustenis et al. 2013, 2016, 2018). Atmospheric C₆H₆ gas, produced through the photodissociation of gaseous N₂–CH₄ in Titan’s upper atmosphere and successive ion-neutral reactions (Vuitton et al. 2008), enters altitude regions in Titan’s stratosphere where it can saturate and condense. Vinatier et al. (2018) reported the contribution of the ν₄ vibrational mode of benzene ice with other unidentified molecules during the observation of Titan’s south polar stratospheric cloud at mid-to-upper-stratospheric altitudes during southern fall, using CIRS nadir and limb observations in 2013 May and 2015 March, respectively. Anderson et al. (2018b) reported that later, in 2015 July during Titan’s late southern fall, C₆H₆ condenses at altitudes where the HASP cloud vertically resides (Figure 1), deeper in the stratosphere than the C₆H₆ ice cloud reported by Vinatier et al. (2018). The Anderson et al. (2018b) investigators experimentally demonstrated that C₆H₆ co-condensed with other organic ice components, likely contributes to the chemical composition of Titan’s HASP ice cloud. The temperatures in Titan’s mid-to-low stratosphere range from ~66 to 170 K (Schinder et al. 2011; Anderson et al. 2014; Teanby et al. 2019) and experience variations with altitude and season. Given that IR spectral features depend on the thermal excitation of the crystal’s vibrational modes, laboratory IR spectra of ices measured at various low and high temperatures, including the thermal conditions at different altitudes in Titan’s atmosphere, can considerably improve the accuracy of the interpretation of IR emission spectra obtained from remote sensing observations. Particularly, studying the deposition temperature dependences of benzene ice is necessary to constrain its spectral and optical properties, and ultimately its contribution to Titan’s cloudy stratosphere during winter seasons, because the temperature may alter the peak positions, widths, and shapes of the absorption bands of C₆H₆ ice.

Figure 1. Figure 1 from Anderson et al. (2018b). Titan’s pressure–temperature–altitude profile (black curve) at 79°S during late southern fall (2015 July) and vertical distributions for eight of Titan’s stratospheric organic vapors (color-coded curves). The intersection between temperature profile and the saturation vapor pressure curves provides the estimated altitude location for the condensation of each individual vapor. The saturation vapor pressure for benzene was taken from Fray & Schmitt (2009).

However, no such thorough study has been performed and reported for benzene ice related to Titan studies. The literature reports few works on the temperature effects on solid benzene (Mair & Hornig 1949; Hollenberg & Dows 1962; Ishii et al. 1996; Mouzay et al. 2021). However, the studies of Mair & Hornig (1949), Hollenberg & Dows (1962), and Ishii et al. (1996) focused on solid C₆H₆ at specific temperatures and did not span a wide range of temperatures that extend from the amorphous to crystalline phases. For example, Mair & Hornig (1949) recorded IR spectra of C₆H₆ ice obtained from the crystallization of the C₆H₆ liquid phase at 249, 218, and 103 K from 641 to 5000 cm⁻¹ (15.6–2 μm), and Hollenberg & Dows (1962) from condensed C₆H₆ gas at 85 K and annealed crystalline C₆H₆ ice at 155 K from 550 to 1600 cm⁻¹ (18.2–6.25 μm). Ishii et al. (1996) focused on Raman spectroscopy of C₆H₆ ice deposited from 17 to 78 K and the annealed ice from 17 to 98 K, while the work of Mouzay et al. (2021) reported annealed 16 K-C₆H₆ ice from 70 to 130 K and not C₆H₆ ice directly deposited at different temperatures, which is more appropriate to Titan’s ice cloud studies, as explained later in Section 2.

In this work, we have conducted a systematic and thorough study of benzene ice with the vapors directly deposited at several temperatures between 15 and 150 K. Deposition temperatures between 66 and 130 K are comparable to the condensation temperatures in Titan’s mid-to-low stratosphere. We decided to extend the spectral analysis to deposition temperatures lower than 66 K in order to fully understand the behavior of C₆H₆ ice with temperature changes, and to precisely identify the transition from its amorphous to crystalline phase in our laboratory sample. Direct vapor deposition studies (as opposed to annealing experiments) are almost nonexistent and are crucial to identify the chemical composition of Titan’s CIRS-observed stratospheric ice clouds.
2. Experimental Technique

Thin film transmission spectroscopy of amorphous and crystalline phases of pure benzene ice was conducted using the SPECTroscopy of Titan-Related ice AnaLogs (SPECTRAL) ice high-vacuum chamber (Anderson et al. 2018a; Nna-Mvondo et al. 2019), located at NASA Goddard Space Flight Center. The technique, used in our laboratory for the IR spectroscopy of ice analogs, consists of depositing the vapor of one or several molecules onto a cold diamond substrate maintained at low temperature (15–200 K) by a close-cycle helium cryostat. A thin ice film (≤10 μm) forms on the diamond substrate, and its spectral properties are monitored in real-time and in situ through a Fourier transform infrared (FTIR) spectrometer. A complete description of the SPECTRAL ice chamber, along with the standard experimental methodology for vapor deposition and data analyses utilized in the present work, is detailed in Anderson et al. (2018a).

C₆H₆ ice samples were prepared from pure benzene vapors that were obtained at saturation equilibrium from the purified liquid phase evaporated at room temperature (293 K). At room temperature, benzene has a saturation vapor pressure of 100 mbar. Benzene (Sigma-Aldrich, 99.99% HPLC grade) was purified from air contaminants (predominantly water and carbon dioxide) and other trace organic impurities, by freeze-pump-thaw cycling under vacuum using successive cold baths of ethanol (C₂H₅OH)/liquid nitrogen (LN₂) (157 K) and acetone (C₃H₆CO)/LN₂ (179 K). Afterwards, purified C₆H₆ was stored for further use in vacuo in an ultra-low-temperature freezer at −86°C (187 K).

The thin C₆H₆ ice films were obtained by slow deposition of pure benzene gas onto the diamond substrate inside the SPECTRAL chamber, under vacuum (10⁻⁸ mbar), at a flow rate of 0.66 ml minute⁻¹, at the desired low temperature, with an ice deposition rate of 0.56 μm minute⁻¹. The distance from the injection nozzles to the diamond substrate is ~1.3 cm. Warming and cooling rates of the diamond substrate on which the ice deposits were 4.8 K minute⁻¹ and 1.3 K minute⁻¹, respectively. The temperature was controlled with an accuracy of ±0.5 K from 2 to 305 K by a temperature controller connected to the cryocooler, a 36 Ω internal resistive Thermofoil heater, and two silicon diodes (accuracy ±0.5 K from 2 to 305 K). One of the diodes is located on the holder of the diamond substrate, which measures the temperature of the sample, and the other one is on the cold finger of the cryocooler (Anderson et al. 2018a). The thicknesses of the ice films at each deposition temperature (T₀) were determined by double laser interferometry (detailed in Anderson et al. 2018a, Section 4.3) and using the published n₀ value of 1.54 ± 0.02 at 632.8 nm for benzene ice formed after vapor deposition at 100 K determined by Romanescu et al. (2010). The calculated thickness for C₆H₆ ice films ranged between 3.6 and 4.1 μm, which corresponds to 26 and 30 μmol of benzene, respectively.

We decided to obtain the crystalline benzene ice from direct deposition of C₆H₆ vapor at low temperature rather than by annealing the sample, a technique commonly used to achieve the crystallization of an ice for most of the planetary ice laboratory studies found in the literature (e.g., Hollenberg & Dows 1962; Khanna et al. 1988; Kim & Kaiser 2009; Zhou et al. 2009; Mouzay et al. 2021). As we demonstrated with C₂H₅CN ice in a recent study by Nna-Mvondo et al. (2019), the annealing experimental method raises important concerns about the quality of the crystalline phase of the annealed ice. Indeed, in this previous work, we revealed spectral differences between the directly deposited crystalline ice and the annealed ice, indicating that the ice does not reach complete crystallization when annealed, and a portion of the amorphous structure is irreversibly retained in the final crystalline phase. The observed spectral variabilities also affect the optical constants of the ice being studied, i.e., the real (n) and imaginary (k) parts of the ice complex refractive index (or optical constants), which are needed for radiative transfer fits to observed spectra. Additionally, the annealing experimental approach, although appropriate to study ices formed in the interstellar medium, is not applicable for simulating ices formed in planetary atmospheres, such as Titan’s stratosphere. For example, for Titan, in order to reproduce ice cloud formation in the stratosphere, vapors must be directly deposited at warmer temperatures (e.g., 110 K), since most of Titan’s organic vapors condense as the vapors cool while descending throughout Titan’s stratosphere (as seen in Figure 1).

The spectra of C₆H₆ thin ice films were collected at deposition temperatures ranging from 15 to 150 K, in the far- to mid-IR spectral region (50–8000 cm⁻¹; 200–1.25 μm). For each resulting transmittance spectrum, 256 scans were averaged at a spectral resolution of 4 cm⁻¹. The motivation of our work was to use the experimental spectral data that we collected for studying and interpreting the stratospheric HASP ice cloud observed by CIRS in far-IR limb spectra. The spectral dependences of the majority of the CIRS-detected stratospheric ice clouds were determined from analyses of CIRS far-IR-targeted low-spectral-resolution limb scans acquiring many low-resolution spectra, as it was desirable in some circumstances, like during observations of strong gas emissions such as methane. Specifically, for the HASP ice cloud observations, the type of far-IR limb observation used was the far-IR aerosol scan (FIRLMAER), the second-closest observation to Titan, occurring at (15–25) 10⁷ km (45–75 minutes from closest approach), using a spectral resolution of 15 cm⁻¹ (the lowest spectral resolution of CIRS). For this reason, the resolution of 4 cm⁻¹ for the collection of our experimental spectra was very convenient and relevant for the objective of our experimental study.

In the mid-IR, the FTIR spectrometer’s gain and aperture size were initially optimized to reduce the intensity of the chemical vapor deposition (CVD) diamond’s strong absorption bands, which arise from the sample substrate and IR windows of the SPECTRAL high-vacuum chamber. This correction is necessary since CVD diamond strongly absorbs between 2300 and 2000 cm⁻¹. However, between the submillimeter and near-IR spectral regions, CVD diamond has excellent throughput, and using diamond transmission windows allows for automatic transitioning across the far- and mid-IR spectral regions while keeping the purge and experimental conditions intact. Thus, for each temperature, far- and mid-IR spectra can be recorded consecutively in the exact same experimental conditions. Prior to vapor deposition, background spectra were collected for each selected temperature. Ice absorption spectra were then recorded and automatically background corrected, i.e., the
studied the temporal variations of the C₆H₆ ice absorption bands, i.e., the time evolution of the C₆H₆ ice spectra after vapor deposition for each deposition temperature cited earlier. Contrary to our previous results on propionitrile ice (Nna-Mvondo et al. 2019), we did not observe any temporal variation of the C₆H₆ ice band positions, nor any variation in the band intensities and shapes for any of the C₆H₆ absorption bands at any given temperature, even 24 hr after deposition. Therefore, in this paper we only present the results for C₆H₆ ice spectra obtained at different deposition temperatures.

The absorption bands of C₆H₆ ice were assigned in the full far- to mid-IR spectral range studied in this work (50–8000 cm⁻¹, 200–1.25 μm), based on previous spectral studies of benzene in its liquid, gas, and solid phases (Mair & Hornig 1949; Miani et al. 2000; Bertie & Keefe 2004). Over the last few decades, experimental and theoretical investigations of the vibrational modes of benzene have become increasingly complete due to refined laboratory techniques and increased computational power. The vibrational modes of benzene have been extensively studied so that we were able to assign most of them in our experimental C₆H₆ ice IR spectra. All of the vibrational assignments observed in the C₆H₆ ice IR spectra that we recorded in our laboratory are listed in Table 1, for the amorphous and crystalline phases of benzene ice, deposited at 15 and 130 K, respectively. The vibrational mode assignments are numbered according to Herzberg’s notation (Herzberg 1945). We have considered with confidence spectral peaks in the IR spectra with signals rising above the 3σ noise level as C₆H₆ ice absorption bands. Spectral features with a low S/N (< 3) were disregarded. Apart from the assignment of the 2ν₁₄ first overtone mode at 5980 cm⁻¹ (at 15 K), it was not possible to assign all other spectral features above 4600 cm⁻¹ because, at these higher wavenumbers, anharmonic effects are so large that local-mode (LM) analysis is required (Bertie & Keefe 2004; Wyatt 1998). The LM analysis technique is usually developed to describe multiple-quantum (overtone) transitions where vibrational energy tends to become localized on a single bond. It differs from the normal-mode (NM) analysis of vibrations in polyatomic molecules that describes single-quantum transitions.

The benzene molecule belongs to the point group D₆h. It has a six-fold axis of symmetry (C₆) along a line through the center of the molecule and perpendicular to the plane of the paper, six vertical planes of symmetry (σᵥ) through C₆e at angles of 30° to one another, and one horizontal plane of symmetry (σᵥ) perpendicular to C₆. C₆H₆ has 12 different symmetry types (species) (A₁g, A₁u, A₂g, A₂u, B₁g, B₁u, B₂g, B₂u, E₁g, E₁u, E₂g, and E₂u) and 20 fundamental vibrations (see Table 1), which were all detected in the C₆H₆ ice spectra that we recorded from 15 to 130 K: ν₁(A₁g), ν₂(A₁g), ν₃(A₂g), ν₄(A₂u), ν₅(B₁u), ν₆(B₁g), ν₇(B₂g), ν₈(B₂u), ν₉(B₂u), ν₁₀(B₂u), ν₁₁(E₁g), ν₁₂(E₁u), ν₁₃(E₁u), ν₁₄(E₂g), ν₁₅(E₂g), ν₁₆(E₂g), ν₁₇(E₂g), ν₁₈(E₂g), ν₁₉(E₂u), and ν₂₀(E₂u).

In the next sections, we describe and analyze in detail the IR absorption spectra of benzene ice obtained in this study and their evolution with temperature; Section 3.1 details in the

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3. Experimental C₆H₆ Ice Spectra

Benzene ice was studied from the amorphous to the crystalline phase and we examined the variation of the C₆H₆ ice absorption bands, from the far- to mid-IR spectral region, at deposition temperatures ranging from 15 to 150 K. This study was performed in an effort to better understand the C₆H₆ ice phase transitions with the corresponding observed spectral changes, and to identify when the complete crystallization of benzene ice is achieved. Specifically, we have recorded absorbance spectra at the deposition temperatures of 15, 30, 32, 35, 45, 60, 90, 100, 110, 120, 125, 130, 135, 140, and 150 K (Figures 2–7). We have also

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4 The raw spectra were recorded with the software of the FTIR spectrometer sets for collecting data at 4 cm⁻¹ resolution; however, the default/standard configuration for normal work for a resolution of 4 cm⁻¹, with a zero-filling factor of two, sets the data spacing automatically at 2 cm⁻¹, i.e., the spectra are automatically oversampled by a factor of two in the standard configuration. The IR spectra displayed in figures are all shown in the default configuration as collected initially; i.e., with wavenumber spaced by 2 cm⁻¹ (oversampled by two).

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Figure 2. Far-IR absorbance spectra of C$_6$H$_6$ ice obtained after deposition of the benzene vapors at temperatures from 15 to 130 K. Thicknesses of ice films at 15, 30, 32, 35, 45, 60, 90, 100, 110, 120, 125, and 130 K were 3.87, 3.82, 3.92, 3.70, 4.08, 3.70, 3.71, 3.59, 3.63, 3.42, 3.69, and 3.63 μm, respectively. The left panel shows the entire absorbance spectra from 340 to 635 cm$^{-1}$ (29.4–15.7 μm). The panels on the right depict specific spectral regions of C$_6$H$_6$ ring deformation modes, the ν$_{18}$ band (in the upper panel) and the ν$_{20}$ band (in the lower panel). Superimposed in the panels are the vibrational transitions, and the numbers are peak frequencies in cm$^{-1}$ for the observed ice absorption bands.

far-IR region from 50 to 640 cm$^{-1}$ (100–15.6 μm), and Section 3.2 describes in the mid-IR region from 640 to 8000 cm$^{-1}$ (15.6–1.25 μm).

3.1. Far-IR C$_6$H$_6$ Ice Spectra (50 to 640 cm$^{-1}$)

Figure 2 shows C$_6$H$_6$ ice far-IR spectra obtained in our laboratory for benzene vapors deposited at temperatures between 15 and 130 K. Even though we carried out experiments at higher temperatures (135, 140, and 150 K), we observed that at temperatures higher than 130 K, C$_6$H$_6$ ice sublimates under the experimental conditions of the SPECTRAL chamber, in which a vacuum pressure is constantly maintained at 10$^{-8}$ mbar during the vapor deposition, and the recording of the IR spectra. Thus, in this article we present the experimental results for $T_d \leq 130$ K.

The far-IR spectral region between 50 and 400 cm$^{-1}$ (100–25 μm) did not display any absorption bands of benzene ice defined as detectable (spectral features with an S/N > 3), for any of the deposition temperatures at which the spectra were collected. In this low-frequency range, several absorption bands between 55 and 130 cm$^{-1}$ have been previously assigned to vibrations characteristic of the crystal lattice. These torsional lattice vibrations, which correspond to out-of-plane and in-phase librations of all benzene molecules about the three crystal axes, are IR- and Raman-active. They have been previously observed in Raman spectra of solid benzene (Epstein & Steiner 1934; Bonadeo et al. 1972; Ishii et al. 1996), as well as in the far-IR spectra of crystalline C$_6$H$_6$ at 173 K (Chantry et al. 1967), 138 K (Harada & Shimanouchi 1967), 100 K (Harada & Shimanouchi 1971), and from 15 to 150 K (Satay et al. 1973; Satay & Ron 1976). We did not identify any of these absorption bands in our experimental far-IR spectra, even for thicker ice films (10 μm), since the signal in this low-energy far-IR spectral region has a low spectral resolution (due the intense noise produced by our FTIR spectrometer below 100 cm$^{-1}$). Thus, our experimental system and procedure did not allow us to distinguish them. Bertie & Keefe (2004) reported very weak bands at 264 and 301.6 cm$^{-1}$ for liquid benzene at 25°C. With our FTIR instrument and experimental protocol, we were able to detect absorption bands at this frequency range (with absorbance height as low as 0.002 absorbance unit for S/N > 3); for example, we detected the weak far-IR absorption bands of propionitrile between 100 and 390 cm$^{-1}$ (Anderson et al. 2018a; Nna-Mvondo et al. 2019). This was not the case for C$_6$H$_6$ ice. Very possibly, the bands of liquid C$_6$H$_6$ measured between 100 and 300 cm$^{-1}$ are very weak bands with intensity below the noise level of our spectra.

At frequencies higher than 400 cm$^{-1}$, two vibrational modes of C$_6$H$_6$ ice, the ν$_{20}$ and ν$_{18}$ ring deformation bands, were detected as shown in Figure 2 and listed in Table 1. For both vibrational modes, we observed spectral variations with the deposition temperature involving significant changes in absorption band position, intensity, and shape (Figure 2).

At 15 and 30 K, the ν$_{20}$ ring deformation mode peaks at 405 and 404 cm$^{-1}$, respectively, and appears as a broad band. From 32 K and higher, this band is split into an asymmetrical doublet. At 32 K, the ν$_{20}$ doublet-band branches at 405 and 419 cm$^{-1}$, with the first maximum at 405 cm$^{-1}$ more intense than the second maximum at 419 cm$^{-1}$. With increasing
deposition temperature, the ν20 doublet increases in intensity and in the splitting, and shifts slightly to lower energies (Figure 2). At 110 K, the doublet is symmetrical, with an equalization of the intensities of the doublet, but from 120 K and higher, the two maxima reverse in intensity with the second maximum more intense than the first one. At 130 K, the doublet is shifted by 1 cm⁻¹ and peaks at 404 and 418 cm⁻¹.

The ν18 ring deformation mode of C₆H₆ ice also undergoes significant spectral changes with the deposition temperature (Figure 2). The band appears as a doublet with a main maximum and an inflection at all deposition temperatures, but is poorly resolved compared to the ν20 absorption band, which appears with two distinct maxima. At 15 K, the main maximum peaks at about 608 cm⁻¹ and the inflection at about 615 cm⁻¹. With increasing deposition temperature, the maximum of the main band weakens and displaces toward higher frequencies. At 90 K, the maximum is relocated at 621 cm⁻¹, thus undergoing a shift of 13 cm⁻¹ to higher energies. No further shift of the maximum is observed at higher deposition temperatures, but its intensity at 621 cm⁻¹ increases with temperature.

3.2. Mid-IR C₆H₆ Ice Spectra (640 to 8000 cm⁻¹)

Figure 3 displays the mid-IR spectra of benzene ice that we have obtained for deposition temperatures ranging from 15 to 130 K.

Just like the liquid and gas phases, the mid-IR spectra of C₆H₆ ice (Figure 3) depict four C–H stretching modes (ν6, ν5, ν12, and ν15), four C–C stretching modes (ν2, ν9, ν13, ν16), four C–H symmetric (in-plane) bending modes (ν14, ν10, ν14, ν17), four C–H asymmetric (out-of-plane) bending modes (ν2, ν7, ν11, ν9), and one C–C symmetric bending mode (ν8), among the 30 molecular normal modes of vibration of benzene, which produce 20 different frequencies (see Table 1). Most of the fundamental vibrations of benzene ice are observed between 650 and 1600 cm⁻¹ (Figures 3–5). From 1600 to 6200 cm⁻¹, the C₆H₆ ice spectrum is dominated by weak combination bands, and only the four fundamental C–H stretching vibrational modes ν1, ν5, ν12, and ν15 are detected between 3000 and 3090 cm⁻¹ (Figures 3 and 4). In the spectral region 6200–8000 cm⁻¹ (1.61–1.25 μm), for ice film thicknesses ranging from 3.6 to 4.1 μm, benzene ice does not show any absorption bands (Figure 3).

We mention that there were no C₆H₆ ice absorption bands detected between 1940 and 2300 cm⁻¹ due to the intense absorption of the diamond, which is the optical material of the sample substrate and IR windows. Even when the parameters of the FTIR spectrometer were optimized to reduce the intensity of the diamond bands, the mid-IR region between 1940 and 2300 cm⁻¹ still showed intense absorption bands of the diamond. As a result, in the fringe-corrected mid-IR spectra shown in Figure 3, the diamond absorption bands were removed by averaging the absorbance values around 1860 and 1950 cm⁻¹ and maintaining this averaged value constant at all wavenumbers in between. Similarly, this approach was applied to the wavenumbers between 2000 and 2300 cm⁻¹.

As with the far-IR region, the mid-IR spectra of C₆H₆ ice revealed spectral variations with deposition temperature and significant changes in the position, intensity, and shape of the absorption bands, as displayed in Figures 4–7.
703 cm$^{-1}$ at 15 K undergoes a similar spectral evolution with temperature as with the $\nu_4$ vibrational band; although, the largest spectral shift occurs at lower temperatures between 35 and 60 K, and the band reaches a maximum intensity at 90 and 100 K. The intense $\nu_{13}$ C–C stretching mode of C$_6$H$_6$ ice at 1478 cm$^{-1}$ does not undergo significant spectral changes with temperature, but only a slight increase in band intensity and, at 90 and 100 K, a small shift of about 0.5 cm$^{-1}$ toward lower energies are observed. Additionally, a small shoulder around 1470 cm$^{-1}$ is growing with increasing temperature. One possible explanation for this shoulder is that at 4 cm$^{-1}$ spectral resolution, some of the vibrational bands are not fully resolved, and some side peaks may appear as a shoulder if positioned at less than the spectral resolution from the main band. The $\nu_{14}$ C–H in-plane bending mode is another intense absorption band of C$_6$H$_6$ ice. It peaks as a singlet band at 3033 cm$^{-1}$ at 15 K has a similar behavior as the $\nu_{14}$ band. It splits into two maxima as the temperature increases, which stabilize from 125 K and form an asymmetric doublet peaking at an intense maximum at 3031 cm$^{-1}$, and another one at 3037 cm$^{-1}$. Like for the $\nu_{13}$ band, a growing shoulder with increasing temperatures is observed at a higher energy around 3023 cm$^{-1}$. The main spectral changes for the $\nu_1$, $\nu_2$, and $\nu_{15}$ absorption bands are a shift to lower energies of 3 and 2 cm$^{-1}$, respectively, from 15 to 130 K and an increase in the band intensity. A small inflection starts to appear in the $\nu_1$ stretch band at 45 K but never achieves a resolved doublet with maxima. As for the $\nu_{12}$ vibrational mode, from 125 K, no more spectral changes are observed for the $\nu_1$, $\nu_2$, and $\nu_{15}$ stretch bands.

Figure 5 displays how the other 10 C$_6$H$_6$ ice fundamental vibrational modes ($\nu_2$, $\nu_3$, $\nu_6$, $\nu_7$, $\nu_9$, $\nu_{10}$, $\nu_{11}$, $\nu_{16}$, $\nu_{17}$, and $\nu_{19}$)
evolve with deposition temperature. These vibrations are much weaker in intensity than the fundamentals described above. The major result for this set of vibrational bands is the disappearance of several modes as the deposition temperature increases. This is the case for the $\nu_3$ and $\nu_{17}$ C–H symmetric bending modes, the $\nu_7$ and $\nu_{11}$ wagging vibrations, the $\nu_2$, and $\nu_{16}$ C–C stretching modes, whose bands peak at 1348, 1176, 991, 854, 999, and 1586 cm$^{-1}$ at 15 K, respectively. At temperatures higher than 15 K, these absorption bands decrease in intensity to disappear completely from 100 K. These specific vibrational modes are highly symmetric inactive modes in C$_6$H$_6$ gas. They are activated by the disorder of the asymmetric
environment of the amorphous phase, and then turn highly symmetric, again, in the ordered crystalline phase. Consequently, we identify this significant spectral change as an indication of the ongoing crystallization of the C₆H₆ ice phase.

The four other fundamental vibrations ν₆, ν₉, ν₁₀, and ν₁₉ display different spectral changes with the deposition temperature. The ν₆ C=C symmetric bending modes and the ν₉ C=C stretching bands, which peak at 1011 and 1311 cm⁻¹ at 15 K, respectively, increase in intensity as the temperature increases, and they reach a maximum intensity between 120–130 K. Between 15 and 130 K, the vibrational modes ν₆ and ν₉ shift to lower energies by 2 cm⁻¹ and to higher energies by 1 cm⁻¹, respectively. A small shoulder in the ν₉ appears from 90 to 130 K. The ν₁₀ C–H in-plane bending mode peaks at 1146 cm⁻¹ at 15 K and splits into two maxima from 45 K. At 130 K, the asymmetric doublet has maxima at 1143 and 1148 cm⁻¹.

The mid-IR spectra of C₆H₆ ice display a large number of binary to quaternary combination bands (Table 1). Several of the combination bands, for which a large number of combinations is possible, have no spectral assignment, especially for the spectral region between 4550 and 6200 cm⁻¹. Figure 6 shows the four most intense combination bands and their temperature dependences. The remaining combination bands observed in the C₆H₆ ice spectra are very weak in intensity. As for the absorption bands presented in Figure 6, all of the combination modes change markedly with the temperature. As the deposition temperature increases, several of them undergo splitting into two to four components with an increase in the band intensity and a frequency shift, as seen in Figure 6. While few of them experience a spectral shift to higher energies, like the three most intense combination bands at 1539 cm⁻¹, 1823 cm⁻¹, and 1966 cm⁻¹ at 15 K, the other combination modes displace to lower frequencies, as does the band at 4056 cm⁻¹ (Figure 6). At frequencies higher than 3620 cm⁻¹, all combination modes have a band shift toward lower energies.

In the very high-frequency region of the benzene ice spectra (frequencies higher than 5000 cm⁻¹), we observe the first overtone 2ν_C-H of the C–H stretching vibrations (Figure 7).

Figure 6. The most intense combination modes of C₆H₆ ice in the mid-IR region from absorbance spectra obtained after deposition of the benzene vapors at temperatures from 15 to 130 K. Ice film thickness ranges between 3.6 and 4.1 μm (all thickness values are listed in the caption of Figure 2).
temperatures from 15 to 130 K. Ice from absorbance spectra obtained after deposition of the benzene vapors at dependent spectral changes. Except for the absorbance spectra of benzene ice reveal several temperature-dependent behavior evidences the transition of C₆H₆ ice at a variety of temperatures in both the amorphous and crystalline phases. We observe that C₆H₆ ice has determined the glass transition temperature of benzene to be at 120 K (Dubochet et al. 1984) or at 130 K (Angell et al. 1978). And results from nuclear magnetic resonance absorption spectroscopy of solid C₆H₆ from 75 to 278 K have identified that the reorientation of C₆H₆ molecules about their six axes is initiated at about 90 K (Andrew & Eades 1953). In the present study, we assessed the crystalline temperature (i.e., the temperature at which crystallization is completely achieved) based on two criteria: (1) there are no observed changes (or almost no changes) in the strength and/or spectral dependence of the IR absorption bands after an increase in the deposition temperature, and (2) there is no noticeable sublimation of the ice film at the temperature held after vapor deposition. Based on these criteria and on our results of the temperature dependence of the far- and mid-IR spectra of benzene ice, we have identified that C₆H₆ ice has completed crystallization at the deposition temperature (Tₓ) determined as 120 K ≤ Tₓ ≤ 130 K. This result is compatible with the glass transition temperatures previously estimated. For this confined temperature range, the crystalline phase of benzene ice is unambiguously identified from the disordered amorphous and ordering transition phases.

### 3.4. Optical Constants of Amorphous and Crystalline C₆H₆ Ices

Figure 8 displays the real (n) and imaginary (k) parts of the ice complex refractive index of benzene ice in the far- and mid-IR from 50 to 8000 cm⁻¹ (200–1.25 μm). We calculated n and k from our laboratory spectra at each temperature from 15 to 130 K, and using n₀ value of 1.54 ± 0.02 determined by Romanescu et al. (2010). The complex indices of refraction of C₆H₆ ice can be used to determine absorption cross-sectional spectra, which can be compared with astronomical emission spectra. We are the first to report cryogenic measurements of n and k of C₆H₆ ice at a variety of temperatures in both the amorphous and crystalline phases. We observe that n and k vary with the temperature (Figures 8 and 9).

In Figure 9, we illustrate the spectral dependence of n and k for the most intense vibrational mode of C₆H₆ ice, the ν₁₄ C–H asymmetric bending mode, in the amorphous phase at 15 K (black curve) and in the crystalline phase at 130 K (red curve).
Table 1

| Amorphous (15 K) IR Frequencies (cm\(^{-1}\)) | Crystalline (130 K) IR Frequencies (cm\(^{-1}\)) | Band Assignment\(^b\) | References\(^c\) |
|-----------------------------------------------|-----------------------------------------------|----------------------|------------------|
| 405 \(\nu_{20}\) | 404 \(\nu_{20}\) | 418 \(\nu_{20}\) | \(\nu_{20}\) ring deform. | \(b, c\) |
| 608 \(\nu_{18}\) | 619 \(\nu_{18}\) | 611 \(\nu_{18}\) | 621 \(\nu_{18}\) | \(c\) |
| 703 \(s\) | 681 \(s\) | 706 \(m\) | \(785 \nu_{31}\) | \(b\) |
| 854 \(w\) | \(s\) | \(975 \nu_{986}\) | \(w\) | \(a, b, c\) |
| 991 \(w\) | \(s\) | \(1009 \nu_{31}\) | \(w\) | \(b, c\) |
| 1036 \(s\) | 1033 \(s\) | 1038 \(s\) | \(1109 \nu_{31}\) | \(a, b, c\) |
| 1146 \(w\) | \(1143 \nu_{31}\) | 1148 \(w\) | \(w\) | \(a, b, c\) |
| 2466 \(\nu_{12}\) | 2459 \(\nu_{12}\) | 268 \(\nu_{12}\) | 1277 \(\nu_{12}\) | \(a, b\) |
| 1311 \(w\) | 1312 \(w\) | \(s\) | \(s\) | \(a, b\) |
| 1348 \(w\) | \(s\) | \(1402 \nu_{12}\) | \(1413 \nu_{12}\) | \(a, b\) |
| 1478 \(w\) | 1478 \(w\) | \(s\) | \(s\) | \(a, b\) |
| 167 \(w\) | 1549 \(w\) | \(1561 w\) | \(w\) | \(a, b\) |
| 236 \(w\) | 235 \(w\) | \(s\) | \(s\) | \(a, b\) |
| 2383 \(w\) | 2381 \(w\) | \(s\) | \(s\) | \(a, b\) |
| 2466 \(\nu_{12}\) | 2459 \(\nu_{12}\) | 2490 \(\nu_{12}\) | \(\nu_{12}\) C-H bending | \(a, b, c\) |
| 2594 \(w\) | 2592 \(w\) | \(s\) | \(s\) | \(a, b\) |
| 2613 \(w\) | 2612 \(w\) | \(s\) | \(s\) | \(a, b\) |
| 2651 \(w\) | 2648 \(w\) | \(s\) | \(s\) | \(a, b\) |
| 2783 \(w\) | 2728 \(w\) | \(s\) | \(s\) | \(a, b\) |
| 2819 \(w\) | 2818 \(w\) | \(2831 w\) | \(w\) | \(b\) |
| 2849 \(w\) | \(s\) | \(2889 \nu_{18}\) | \(w\) | \(a, b\) |
| 2887 \(w\) | \(s\) | \(2907 \nu_{18}\) | \(w\) | \(a, b\) |
| 3447 \(w\) | 3457 \(w\) | \(s\) | \(s\) | \(a, b\) |
| 3610 \(w\) | \(s\) | \(s\) | \(s\) | \(a, b\) |
| 3639 \(w\) | \(s\) | \(3635 \nu_{31}\) | \(3641 \nu_{31}\) | \(a, b\) |
| 3659 \(w\) | \(s\) | \(3682 \nu_{31}\) | \(3691 \nu_{31}\) | \(b\) |
| 3684 \(w\) | \(s\) | \(3701 \nu_{31}\) | \(3705 \nu_{31}\) | \(b\) |
| 3934 \(w\) | \(s\) | \(3931 \nu_{31}\) | \(3933 \nu_{31}\) | \(b\) |
| 3955 \(w\) | \(s\) | \(3953 \nu_{31}\) | \(3955 \nu_{31}\) | \(b\) |
| 4021 \(w\) | \(s\) | \(4017 \nu_{31}\) | \(4023 \nu_{31}\) | \(b\) |
| 4056 \(m\) | \(s\) | \(4052 m\) | \(4056 m\) | \(b\) |
| 4079 \(w\) | \(s\) | \(4073 \nu_{31}\) | \(4080 \nu_{31}\) | \(b\) |
| 4174 \(w\) | \(s\) | \(4168 \nu_{31}\) | \(4174 \nu_{31}\) | \(b\) |
| 4193 \(w\) | \(s\) | \(4193 \nu_{31}\) | \(4193 \nu_{31}\) | \(b\) |
| 4258 \(w\) | \(s\) | \(4256 \nu_{31}\) | \(4256 \nu_{31}\) | \(b\) |
| 4348 \(w\) | \(s\) | \(4347 \nu_{31}\) | \(4347 \nu_{31}\) | \(b\) |
Table 1
(Continued)

| Amorphous (15 K) IR Frequencies (cm$^{-1}$)$^a$ | Crystalline (130 K) IR Frequencies (cm$^{-1}$)$^a$ | Band Assignment$^b$ | References$^c$ |
|-----------------------------------------------|-----------------------------------------------|--------------------|--------------|
| 4375 $vw$ | 4361 $vw$ 4372 $vw$$^d$ 4377 $vw$$^d$ | $\nu_9 + \nu_{35}$, $\nu_3 + \nu_{12}$ | a, b |
| 4411 $vw$ | 4409 $vw$ | $\nu_3 + (\nu_2 + \nu_{13} + \nu_{16})$ | b |
| 4429 $vw$ | 4423 $vw$$^d$ 4428 $vw$$^d$ | $\nu_3 + (\nu_{13} + \nu_{16})$ | b |
| S/N $< 3^c$ | 4481 $vw$ | Not assigned | |
| 4541 $vw$ | 4520 $vw$$^d$ 4529 $vw$$^d$ 4541 $vw$$^d$ | $\nu_{13} + \nu_{15}$ | b |
| 4581 $vw$ | 4580 $vw$ | $\nu_1 + \nu_{13}$ | b |
| 4602 $vw$ | 4602 $vw$$^d$ 4609 $vw$$^d$ | Not assigned | |
| 4619 $vw$ | 4618 $vw$ | Not assigned | |
| 4641 $vw$ | 4640 $vw$ | Not assigned | |
| 4667 $vw$ | 4663 $vw$$^d$ 4673 $vw$$^d$ | Not assigned | |
| 4686 $vw$ | 4684 $vw$ | Not assigned | |
| 5326 $vw$ | 5345 $vw$ | Not assigned | |
| S/N $< 3^c$ | 5513 $vw$ | Not assigned | |
| S/N $< 3^c$ | 5530 $vw$ | Not assigned | |
| S/N $< 3^c$ | 5542 $vw$ | Not assigned | |
| S/N $< 3^c$ | 5605 $vw$ | Not assigned | |
| 5637 $vw$ | 5636 $vw$ | Not assigned | |
| 5689 $vw$ | 5680 $vw$$^d$ 5687 $vw$$^d$ 5692 $vw$$^d$ 5707 $vw$$^d$ | Not assigned | |
| 5773 $vw$ | 5768 $vw$$^d$ 5777 $vw$$^d$ | Not assigned | |
| S/N $< 3^c$ | 5858 $vw$$^d$ 5864 $vw$$^d$ | Not assigned | |
| S/N $< 3^c$ | 5877 $vw$ | Not assigned | |
| 5910 $vw$ | 5909 $vw$ | Not assigned | |
| S/N $< 3^c$ | 5926 $vw$ | Not assigned | |
| S/N $< 3^c$ | 5947 $vw$ | Not assigned | |
| S/N $< 3^c$ | 5961 $vw$ | Not assigned | |
| 5980 $vw$ | 5976 $vw$$^d$ 5989 $vw$$^d$ 5997 $vw$$^d$ 6019 $vw$$^d$ | $2\nu_{\text{CH}}$ 1$^{st}$ overtone (C–H stretch) | b |
| 6066 $vw$ | 6047 $vw$$^d$ 6061 $vw$$^d$ 6074 $vw$$^d$ | Not assigned | |
| 6140 $vw$ | 6135 $vw$ | Not assigned | |
| 6178 $vw$ | 6171 $vw$$^d$ 6184 $vw$$^d$ | Not assigned | |

Notes.

$^a$ Intensities of band: $vw$ very strong, $s$ strong, $m$ medium, $w$ weak, $vw$ very weak, $vvw$ very very weak.

$^b$ The fundamental vibrations are numbered following Herzberg (1945).

$^c$ The band assignments are based on crystalline ice spectral data published in (a) Mair & Hornig (1949) and on liquid and gas phase data reported in (b) Bértie & Keefe (2004) and (c) Miani et al. (2000), respectively. Bértie & Keefe (2004) uses Herzberg notation, while Mair & Hornig (1949) and Miani et al. (2000) follow the notation of Wilson (1934) and Wilson et al. (1955).

$^d$ Multiple frequencies that appear for the same vibrational assignment designate a band that is split into two, three, or four.

$^e$ Features for which frequencies are not indicated are below three times the noise level (S/N $< 3$) and therefore are not considered with sufficient confidence as absorption bands of C$_6$H$_6$ ice.

$^f$ — Non-observed frequencies.

4. Implications for Titan Studies

As indicated in Section 1, Vinatier et al. (2018) have recently identified benzene ice mixed with other unidentified compounds in Titan’s stratosphere by analyzing Cassini CIRS nadir and limb mid-IR spectra. From limb observations acquired in 2015 March, they detected an ice cloud emission feature peaking at 682 cm$^{-1}$ at altitudes between 168 and 278 km, and identified solid benzene as the best chemical match of this emission feature. For their study, they used the experimental spectrum of crystalline C$_6$H$_6$ ice deposited at 130 K by Schmitt et al. (2015). Specifically, they analyzed the C$_6$H$_6$ $\nu_4$ C–H out-of-plane bending mode detected in the IR spectrum of Schmitt et al. (2015), to fit the 682 cm$^{-1}$ emission feature, and they determined the spectral dependences of the extinction, absorption, and scattering cross sections per unit particle volume of pure C$_6$H$_6$ ice. In the Schmitt et al. (2015) experiment, a 1.65 $\mu$m thin film of C$_6$H$_6$ ice, produced by vapor deposition of C$_6$H$_6$ vapors at 130 K, was analyzed in the mid-IR region from 400 to 4200 cm$^{-1}$ (25–2.38 $\mu$m). In their mid-IR spectra, the $\nu_4$ C–H out-of-plane bending mode appeared as an asymmetric doublet band with the two maxima at 679 and 681 cm$^{-1}$ and a width of $\sim$6.5 cm$^{-1}$. Vinatier et al. (2018) indicated that in the Schmitt et al. (2015) experimental C$_6$H$_6$ spectra, the most intense bands of C$_6$H$_6$ ice were very weakly sensitive with temperature, with an observed spectral shift $\sim$0.5 cm$^{-1}$ between 60 and 130 K. We, however, were unable to corroborate this result since we did not find any published work from Schmitt et al. (2015) reporting a study on the spectral and temperature dependence of C$_6$H$_6$ ice. From personal communication, we have been acquainted that Schmitt and colleagues carried out this experimental study by condensing C$_6$H$_6$ at 130 K and then cooling to temperatures down to 60 K. Our results displayed in Figure 10 differ slightly from data obtained by Schmitt et al. (2015). In our mid-IR spectra, the $\nu_4$ vibrational mode at 130 K appears as a singlet band that is less intense than the doublet observed by Schmitt et al. (2015). In our studies, this band peaks at 681 cm$^{-1}$ and has a width of $\sim$7.5 cm$^{-1}$ (Figure 10). Mouzay et al. (2021) reported in their C$_6$H$_6$ crystalline ice spectra at 130 K also a single band for the $\nu_4$ C–H out-of-plane bending mode, but
peak at 679 cm$^{-1}$. For condensation temperatures from 60 to 130 K, we observe a band displacement of 2 cm$^{-1}$ to higher energies and also that the $\nu_4$ vibrational mode is temperature dependent (Figure 4). As pointed out in Section 3.2, we observe that as the condensation temperature increases, the $\nu_4$ band becomes sharper with an increase in band intensity and shifts to higher energies.

Mouzay et al. (2021) showed that the $\nu_4$ vibrational mode is shifted to higher frequencies from 16 to 130 K by 5 cm$^{-1}$, but, contrarily to our results, its shape looks almost identical. And after depositing the vapor of C$_6$H$_6$ onto a gold-plated substrate at 130 K, keeping at 130 K for a few hours and finally cooling down to 70 K, no significant frequency shift in the $\nu_4$ band is observed with temperature. The band intensity varies very slightly from 70 to 130 K.

The discrepancies in temperature dependences between our spectral results, those of B. Schmitt et al. (unpublished work), and those of Mouzay et al. (2021) certainly result in the fact that we have studied IR spectra of C$_6$H$_6$ condensed (or deposited) at different temperatures, whereas Schmitt et al. (2015) and Mouzay et al. (2021) compared the spectra of a sample condensed at 130 K and then cooled it down to 60 K, or 70 K, respectively. While we have compared how the temperature affects the state of crystallization as a function of deposition temperature, Schmitt et al. (2015) and Mouzay et al. (2021) studied the reversible temperature effects upon cooling-warming their crystallized C$_6$H$_6$ ice at temperatures below its condensation temperature.

The difference in the shape of the band between our experimental study and the work of Schmitt et al. (2015) in which C$_6$H$_6$ is condensed at 130 K is certainly the result of the distinct spectral resolution of the data used in both experiments: 4 cm$^{-1}$ in our work, while 1 cm$^{-1}$ in Schmitt et al. (2015). The bands may not be fully resolved at 4 cm$^{-1}$ resolution and can induce spectral shape changes such as wider and weaker bands and even some spectral shifts of the order of up to 1 cm$^{-1}$ if the band is asymmetric or if there exists a weaker side band or a shoulder at a separation less than the spectral resolution. This can explain that our experimental spectra display only a single band at 681 cm$^{-1}$ and maybe only part of the shift. It can also explain the width and intensity difference of the narrow 706 cm$^{-1}$ band in Schmitt et al. (2015) and our wider less intense $\nu_8$ ring deformation mode. However, it is difficult to fully explain the shift of the $\nu_4$ C–H out-of-plane bending mode at 681 cm$^{-1}$ and its strong difference in intensity between our work and Schmitt et al. (2015). Both states of crystallization may not be exactly the same. In our experiments, we used diamond as the substrate material while Schmitt et al. (2015) used cesium iodide (CsI), which may also play a role in the crystallization. We note that, except for using a different substrate material, we have no explanation for the spectral differences observed between the results of Mouzay et al. (2021; single band of $\nu_4$ at 679 cm$^{-1}$) and those of Schmitt et al. (2015; $\nu_4$ asymmetric doublet band at 679 and 681 cm$^{-1}$), even if using a similar laboratory technique and the same spectral resolution of 1 cm$^{-1}$ to obtain crystalline C$_6$H$_6$ ices and look at their temperature spectral dependence.

Compared to the Vinatier et al. (2018) C$_6$H$_6$ ice cloud emission feature at 682 cm$^{-1}$, our data at 130 K gives a peak frequency of the $\nu_4$ band of crystalline C$_6$H$_6$ ice 1 cm$^{-1}$ lower in energy.

Schmitt et al. (2015) have also provided the real and imaginary parts of the ice complex refractive index of benzene ice at 130 K from 400 to 4200 cm$^{-1}$ available in the SSHADE database. Complex refractive indices, which are temperature dependent (as we show in Figures 8 and 9), are crucial to determine the abundances of condensed species observed in...
planetary atmospheres. Moreover, for low-temperature environments, such as Titan’s atmosphere and surface, where thermal energy is at a minimum, it is essential to obtain experimental optical data in the far-IR spectral region that has high thermal emission below 400 cm$^{-1}$, where CIRS has measured in detail during the 13 yr Cassini mission, and for which optical constants of organic ices observed in Titan’s stratosphere are still lacking. In our work, we have generated a wide database of optical constants of benzene ice from 50 cm$^{-1}$ up to 8000 cm$^{-1}$ in order to provide critically missing experimental spectroscopic and optical data for C$_6$H$_6$ ice needed to continue interpreting Cassini-observed spectra of Titan’s atmosphere.

Regarding the CIRS-observed HASP ice cloud detected by Anderson et al. (2018b) in Titan’s late southern fall stratosphere at high southern latitudes, its emission feature peaks near 200 cm$^{-1}$ (see Figure 19 in Anderson et al. 2018b). The vertical extent of the HASP ice cloud is observed at stratospheric altitudes where pure C$_6$H$_6$, pure hydrogen cyanide (HCN), and pure cyanoacetylene (HC$_3$N) are expected to condense and form stratospheric ice clouds (see Figure 1). In Titan’s atmosphere, most of the organic vapors will condense to form ice shells on aerosol solid particles as the vapors cool while descending throughout Titan’s stratosphere. The C$_6$H$_6$ ice spectra that we have obtained in this study did not display any detectable absorption bands between 50 and 400 cm$^{-1}$ (100–25 μm), for any of the deposition temperatures studied (15–130 K). With our FTIR instrument and experimental protocol, we are able to detect absorption bands at this wavenumber range with an absorbance height as low as 0.002 absorbance unit (for S/N $> 3$). For example, we...
detected the weak far-IR absorption bands of propionitrile between 100 and 390 cm$^{-1}$ (see Anderson et al. 2018b; Nna-Mvondo et al. 2019). This was not the case for C$_6$H$_6$ ice. The HASP ice cloud has a very intense and broad far-IR spectral feature centered at 200 cm$^{-1}$ (Anderson et al. 2018b). Compared with those previous measurements of other molecules absorbing in this frequency range integrated with other observed ice cloud bands that we carried out with the same setup and method (Anderson et al. 2018a, 2018b; Nna-Mvondo et al. 2019), we should be able to detect such an intense and wide band around 200 cm$^{-1}$ if it was present for C$_6$H$_6$ ice. Additionally, other published far-IR spectral studies of solid benzene (Chantry et al. 1967; Harada & Shimanouchi 1971; Sataty et al. 1973; Sataty & Ron 1976) did not detect any absorption band around 200 cm$^{-1}$. So we agree that we can rule out C$_6$H$_6$ ice as the only absorber of the HASP ice cloud spectral feature.

Therefore, our results definitely rule out pure C$_6$H$_6$ ice as the spectral match of the HASP cloud emission feature. However, as reported in Anderson et al. (2018b), the HASP ice cloud could be formed by a co-condensation scenario, in which Titan’s organic vapors, including benzene, enter altitude regions in the stratosphere where the HASP cloud is observed and where they can simultaneously saturate to form a mixed (or co-condensed) ice cloud. In addition to the HASP ice cloud, ice cloud formation processes in Titan’s stratosphere via vapor co-condensation have already been reported for the formation of the northern winter 160 cm$^{-1}$ ice cloud observed in Titan’s northern winter lower stratosphere (Anderson & Samuelson 2011; Anderson et al. 2018a). This 160 cm$^{-1}$ ice cloud was experimentally determined to contain (at a minimum) co-condensed HCN and HC$_3$N.

5. Conclusion

To the best of our knowledge, our work is the first publication of far- and mid-IR absorbance spectra of benzene ice conducted over a large range of deposition temperatures. We have provided the associated optical constants for each of the studied temperatures from 15 to 130 K. These spectra and optical constants generated from cold to warmer temperatures provide valuable data for research related to Titan’s stratosphere but also to Titan’s surface. Indeed, solid benzene has been tentatively identified on Titan’s surface (Niemann et al. 2005; Clark et al. 2010). Our low-temperature data of C$_6$H$_6$ ices (<80 K) are also useful for the investigation of other cold astronomical environments where benzene has been observed, such as in the atmospheres of Jupiter (Kim et al. 1985) and Saturn (Bézard et al. 2001), and in the protoplanetary nebula CRL 618 (Cernicharo et al. 2001).

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