Ephemeral Ice Clouds in the Upper Mesosphere of Venus

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Abstract

The conditions in Venus’ upper mesosphere at around 120 km have some similarities to the upper mesosphere of Earth and Mars where ice clouds form. Here we show, using published satellite products and numerical modelling, that the upper mesosphere of Venus is sufficiently cold that both H\textsubscript{2}O and CO\textsubscript{2} can condense to form particles. In fact, we show that there is likely to be a competition between the direct nucleation of particles from the gas phase (homogeneous nucleation) and the nucleation on meteoric smoke particles (MSPs, heterogeneous nucleation). Amorphous solid water particles (ASW) are likely to nucleate first, resulting in clouds of nano-scaled particles at around 120 km globally. The temperatures can then become sufficiently low that CO\textsubscript{2} particles can nucleate either on MSPs or on ASW particles (>30\% of the time poleward of 60\°). Since the main component of the atmosphere is CO\textsubscript{2} these particles will grow and sediment on a timescale of 10-20 minutes. Mie calculations show that these Venusian mesospheric clouds (VMCs) should be observable by contemporary satellite instruments, although their short lifetime means that the probability of detection is small. We suggest that VMCs are important for the redistribution of meteoric smoke and may serve as a cold-trap, removing some water vapour from the very upper mesosphere of Venus, through the growth and sedimentation of cloud particles, and possibly reducing the loss of water to space.
Ephemeral Ice Clouds in the Upper Mesosphere of Venus

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Key Points:

- The upper mesosphere of Venus is frequently supersaturated with respect to both amorphous solid water and crystalline carbon dioxide ice
- There is a persistent layer of nano-scale amorphous solid water particles encircling Venus
- Short-lived carbon dioxide ice clouds sporadically form in the upper mesosphere
Abstract

The conditions in Venus’ upper mesosphere at around 120 km have some similarities to the upper mesosphere of Earth and Mars where ice clouds form. Here we show, using published satellite products and numerical modelling, that the upper mesosphere of Venus is sufficiently cold that both H$_2$O and CO$_2$ can condense to form particles. In fact, we show that there is likely to be a competition between the direct nucleation of particles from the gas phase (homogeneous nucleation) and the nucleation on meteoric smoke particles (MSPs, heterogeneous nucleation). Amorphous solid water particles (ASW) are likely to nucleate first, resulting in clouds of nanometer-sized particles at around 120 km globally. The temperatures can then become sufficiently low that CO$_2$ particles can nucleate either on MSPs or on ASW particles (>30% of the time poleward of 60°). Since the main component of the atmosphere is CO$_2$ these particles will grow and sediment on a timescale of 10-20 minutes. Mie calculations show that these Venusian mesospheric clouds (VMCs) should be observable by contemporary satellite instruments, although their short lifetime means that the probability of detection is small. We suggest that VMCs are important for the redistribution of meteoric smoke and may serve as a cold-trap, removing some water vapour from the very upper mesosphere of Venus, through the growth and sedimentation of cloud particles, and possibly reducing the loss of water to space.

Plain Language Summary

Venus is renowned for extreme heat at the surface and clouds composed of sulphuric acid encircling the planet; however, there are regions of Venus’s atmosphere that are sufficiently cold to harbour ice clouds. In fact, the temperatures frequently fall to below 100 K at around 120 km altitude and under the right conditions we have shown that ice clouds composed of both water and carbon dioxide ices can form. We have used published data from satellites that orbit Venus to show that clouds composed of nanometer sized water ice particles may encircle the planet. The temperatures are so low in this part of Venus’ atmosphere that the ice in these water ice particles likely lacks any crystalline structure, that is, it has an amorphous (liquid-like) structure. Furthermore, when the temperature falls below about 90 K, we have shown that carbon dioxide ice crystals can form on top of water ice crystals. Since the atmosphere of Venus is mainly made of carbon dioxide, these carbon dioxide crystals grow and fall rapidly. If we were lucky enough to see one of these short-lived sporadic clouds it would look a bit like a mares’ tail cloud on Earth.

1 Introduction

The plausibility of ice clouds in Venus’ atmosphere has been discussed as early as the 1950s (Menzel & Whipple, 1954). Through differing analyses of infrared absorption seen at 3 μm from high altitude balloon measurements in the 1960s, both Bottema et al. (1965) and Pollack and Sagan (1968) suggested water ice clouds could explain the observed absorbances, although a rebuttal by Rea and O’Leary (1968) suggested this was possible only if the ice particles were submicron in size. Turco et al. (1983) expanded on these predictions, suggesting that water ice clouds may be present in two layers: one between 80 and 100 km, resulting from freezing of sulphuric acid haze droplets; and another layer at Venus’ mesopause (~120 km) consisting of water ice nanoparticles, possibly nucleated on meteoric dust particles.
Since the prediction of water ice clouds on Venus by Turco et al. (1983), our understanding of both the physics of ice cloud formation in planetary atmospheres and the structure and dynamics of the Venusesian atmosphere have increased greatly. A range of satellite observations of lower altitude (≤ 100 km) sulphuric acid haze layers have since been made (Titov et al., 2018), and recent observations by instruments onboard the Venus Express satellite have highlighted extreme temperature minima in Venus’ upper atmosphere (Mahieux et al., 2015).

Figure 1 illustrates an example of a typical cold temperature profile (green line) from the Solar Occultation in the InfraRed (SOIR) instrument onboard the Venus Express satellite (Orbit 669.1, taken at 81.6º latitude on the 19th February 2008 from Mahieux et al. (2015)). This profile includes the coldest region in Venus’ atmosphere, with temperatures below 100 K from 118 – 125 km, and a temperature minimum of 64 K at 121 km. The blue line in Figure 1 shows the saturation temperature for H₂O with respect to amorphous solid water (ASW), assuming a water vapour concentration of 1 ppmv (the expected range in the Venusesian upper atmosphere is 0.56 – 2.45 ppmv (Chamberlain et al., 2020)). This highlights that the atmosphere is sometimes significantly supersaturated with respect to ASW within the cold pocket. We show here the saturation (frost) point associated with ASW, rather than the stable crystalline hexagonal phase of ice I (ice Ih), because under these conditions in the upper atmosphere any ice formed should be amorphous (Mangan et al., 2021). The Turco et al. (1983) prediction of water ice clouds was based on an assumed water vapour concentration of 10 ppm at slightly lower altitudes than the example shown in Figure 1, but with a much higher temperature minimum of 110 K; this led to a many orders of magnitude smaller supersaturations than those shown in Figure 1. These atmospheric conditions for water ice evoke comparisons to Polar Mesospheric Clouds (PMCs) on Earth (Plane et al., 2015), and water ice clouds observed in the upper atmosphere of Mars (Stcherbinine et al., 2020). On Mars, upper mesospheric clouds are also thought to redistribute H₂O, although the process is not as effective as it might be if the growth of ice particles can quench the supersaturation (Fedorova et al., 2020); nevertheless ice cloud formation and sedimentation of ice crystals will limit the amount of water transported vertically.

Figure 1 also shows the saturation temperature for crystalline CO₂ ice (phase I), the phase that we expect cloud particles to be composed of under conditions in the upper mesosphere of Venus (Mangan et al., 2017b), even if nucleation occurs through a different phase. The primarily CO₂ atmosphere of Venus is sufficiently dense and the cold pocket sufficiently cold that the atmosphere is also supersaturated with respect to CO₂ ice around the temperature minimum at 121 km. These atmospheric conditions are again comparable to the Martian upper atmosphere, where gravity wave-induced cold pockets enable deposition of the primary atmospheric constituent, producing populations of micron-sized CO₂ ice particles (Listowski et al., 2014; Plane et al., 2018). At the time of Turco et al. (1983), CO₂ ice clouds were not considered as a possibility, given that the first confirmed observations of high-altitude CO₂ ice clouds on Mars were not made for another 20 years (Montmessin et al., 2006), and the temperature minima reported by Turco et al. (1983) were insufficient to produce supersaturated conditions with respect to CO₂ ice.

Despite being higher on Venus, if H₂O and/or CO₂ ice clouds formed around this temperature minimum they would exist in a region with striking similarities to the mesospheric clouds observed on Mars, quite possibly with similar nucleating particles available. Hence, building on the predictions of water ice clouds by (Turco et al., 1983), we propose that ice clouds,
comprising both H$_2$O and CO$_2$ ice, may form in Venus’ upper atmosphere at around 120 km in altitude. In this paper, using the more extensive database of measurements for the Venus atmosphere that are now available, and applying our improved knowledge of high-altitude clouds on Earth and Mars, we examine the formation, growth and composition of H$_2$O and CO$_2$ ice clouds, and their detectability, in the upper atmosphere of Venus.

Figure 1. Atmosphere of Venus showing known and proposed cloud layers. General atmospheric profile (black) extracted from Palen et al. (2019). The temperature profile from orbit 669.1 (green) is taken from Mahieux et al. (2015). Saturation temperatures shown for H$_2$O with respect to amorphous solid water (blue) and CO$_2$ with respect to crystalline CO$_2$ (red). The water saturation ratios were calculated using the Nachbar et al. (2019) parameterisation for ASW in combination with the vapour pressure over hexagonal ice (Murphy & Koop, 2005). The frost point for crystalline CO$_2$ ice was calculated using saturation vapour pressure parameterisation from Azreg-Aïnou (2005). The altitude range over which meteoric ablation occurs is taken from Carrillo-Sánchez et al. (2020).

2. Nucleation of H$_2$O and CO$_2$ particles in Venus’ mesosphere

To evaluate the feasibility of nucleation of H$_2$O and CO$_2$ ice particles in Venus’ upper atmosphere we employ two theoretical approaches: Classical Nucleation Theory (CNT) and Kinetic Nucleation Theory (KNT). Atmospheres can exist in a metastable state where the partial pressure of some condensable component is greater than the equilibrium vapour pressure of a condensed phase (or phases) (Murray & Jensen, 2010). An atmosphere can persist in a supersaturated state because there is a free energy barrier to nucleation of a new phase related to the creation of a new interface. Nucleation can either occur spontaneously (homogeneous nucleation), or can occur at lower supersaturations on the surface of suitable particles. These ice-nucleating particles (INPs) stabilise the cluster of the condensed phase through favourable interactions with the surface. In cold clouds in Earth’s mesosphere (Murray & Jensen, 2010), there is thought to be a competition between homogeneous and heterogeneous nucleation, and the balance between the mechanisms results in clouds with very different hydrometeor size
distributions. Sometimes heterogeneous nucleation occurring at lower supersaturations than those required for homogeneous nucleation leads to the depletion of the supersaturation as the ice particles grow, thus preventing homogeneous nucleation from occurring. But, if the cooling rate is sufficiently rapid then homogeneous as well as heterogeneous nucleation can occur (Murray & Jensen, 2010).

In the upper mesosphere of Venus there are at least two condensable materials, CO$_2$ and H$_2$O. The stable form of both of these materials is crystalline under the conditions on Venus, but it is unlikely that the critical cluster is made up of the stable phase. In many nucleating systems the initial phase to nucleate is a metastable phase that has a smaller surface energy penalty than the stable phase (Mullin, 2001). The metastable phase may subsequently relax to the stable phase. In the case of water homogeneously nucleating from water vapour, measurements clearly show that it is the liquid phase that nucleates at temperatures to below 200 K, even though the liquid phase rapidly converts to crystalline ice under those conditions (Wölck et al., 2013). At below around 120 K, deposition of water on a surface results in amorphous solid water (ASW); hence, the nucleating phase was probably amorphous but at these low temperatures the kinetics of transformation to the stable phase were too slow for it to occur on the experimental time scale (mins-hours) (Duft et al., 2019; Mangan et al., 2021). Similarly, for CO$_2$ recent experiments and molecular dynamics studies show that the initial phase to nucleate is a liquid-like form of CO$_2$ between 75 and 92 K (Dingilian et al., 2020; Halonen et al., 2021).

Heterogeneous nucleation requires the presence of particles on which nucleation might occur. The most likely candidate for particles that might serve as ice-nucleating particles (INPs) for ice clouds on Venus are nm-sized Meteoric Smoke Particles (MSPs). MSPs form from the recondensation of metallic compounds (oxides, hydroxides and carbonates) formed from the ablation of metals such as Fe, Mg and Na from cosmic dust particles entering an oxidizing planetary atmosphere such as Venus (Plane et al., 2015). Current predictions for Venus by Carrillo-Sánchez et al. (2020) show that ablation should occur between 100 and 125 km, peaking around 115 km (Figure 1). This altitude range happens to coincide with the cold pocket (Figure 1). In the following sections we use CNT and KNT to test the likelihood of both homogeneous and heterogeneous nucleation of both CO$_2$ and H$_2$O particles in the upper mesosphere of Venus. Note that there are also significant concentrations of HCl in Venus’ upper mesosphere, approaching 1 ppm around 110 km and therefore ~ 1 – 10% of the H$_2$O mixing ratio (Mahieux et al., 2015). HCl may therefore play a role as a condensable vapour, though this is likely to be as a minor enhancement of that of H$_2$O.

2.1 Homogeneous nucleation of CO$_2$ and H$_2$O particles

Homogeneous nucleation directly from the vapour phase can occur under extreme conditions and it has been suggested that it may be important in the Earth’s mesosphere (Lübken et al., 2009; Murray & Jensen, 2010). Given the conditions in the upper mesosphere of Venus are extremely cold, it is worth considering if H$_2$O or CO$_2$ particles might nucleate homogeneously. We have used a Classical Nucleation Theory (CNT) formulation described by (Määttänen et al., 2005). The equations and the choice of parameterisations of physical quantities are set out in Appendix A. Key physical quantities have been updated to be consistent with the latest experimental and theoretical studies. This includes the use of a parameterisation of the vapour pressure of ASW from Nachbar et al. (2019), who showed that ASW is not simply the low temperature extension
of supercooled liquid water and is in fact a distinct phase of water. We also derived a self-
consistent interfacial energy for the liquid CO\textsubscript{2}–vapour interface, based on measurements of
homogeneous nucleation in a supersonic nozzle (Dingilian et al., 2020), and the ASW–vapour
interfacial energy from studies of water uptake onto trapped nano-scale meteoric smoke
analogues (Duft et al., 2019) (note that by self-consistent we mean that the interfacial energy is
derived using the CNT and physical constant chosen in this paper, and then these CNT models
are extrapolated to the conditions on Venus).

Nucleation rates (events per unit volume per unit time) for crystalline and amorphous/liquid-like
phases of H\textsubscript{2}O and CO\textsubscript{2} are shown in Figure 2a for an altitude of 121.6 km and a total pressure of
2.52 x 10\textsuperscript{-3} Pa (taken from the mean profiles derived from SOIR data in (Mahieux et al., 2015)).
We assumed a water mixing ratio of 1 ppm and the CO\textsubscript{2} mixing ratio was taken as unity (in
practice it is around 0.96). We also show, in Figure 2b, \(J_{\text{hom}}\) for one of the coldest temperature
profiles in the SOIR dataset, 691.1 from the 12\textsuperscript{th} March 2008 at 86.6° latitude from Mahieux et
al. (2015), where the temperature minimum was 63 K at 121.6 km.

As expected, homogeneous nucleation of crystalline H\textsubscript{2}O and CO\textsubscript{2} are very slow. In contrast, the
homogeneous nucleation of ASW and liquid-like CO\textsubscript{2} might perhaps contribute to cloud particle
populations. The nucleation rate for ASW is appreciable in this region, and is relatively
insensitive to temperature with values of around 10\textsuperscript{-2} cm\textsuperscript{-3} s\textsuperscript{-1} at 63 K, which would produce \(~1\)
cloud particle per cm\textsuperscript{3} in 100 s. While there are uncertainties in the physical constants that go
into the calculation of \(J_{\text{hom}}\), \(J_{\text{hom}}\) in this ‘plateau regime’ has a relatively weak temperature
dependence (Figure 2a) and is therefore insensitive to those uncertainties. Since the plateau
value of \(J_{\text{hom}}\) is defined by the rate of formation of ASW clusters, which in turn is related to the
H\textsubscript{2}O monomer concentration, this limit should be well defined and it is unlikely that the true \(J_{\text{hom}}\)
of ASW is many orders of magnitude larger (or smaller). The same cannot be said for \(J_{\text{hom}}\) for
liquid CO\textsubscript{2} at around 120 km in the atmosphere of Venus. \(J_{\text{hom}}\) for liquid CO\textsubscript{2} has a very strong
temperature dependence above \(~60\) K; hence, uncertainties in temperature and various physical
quantities can have a substantial effect on the nucleation rate. For example, while \(J_{\text{hom}}\) is
relatively small at 63 K, peaking at 10\textsuperscript{-5} cm\textsuperscript{-3} s\textsuperscript{-1} (Figure 2b), a shift of only 3 K to lower
temperatures would increase \(J_{\text{hom}}\) to \(~1\) cm\textsuperscript{-3} s\textsuperscript{-1}. This would produce 100 particles per cubic
centimetre in 100 s. Similarly, an interfacial energy only 15% smaller would also increase \(J_{\text{hom}}\)
by more than five orders of magnitude. On this basis one should certainly not rule out
homogeneous nucleation of liquid CO\textsubscript{2} particles, which would then rapidly convert to crystalline
CO\textsubscript{2} ice.

To summarise, the role of homogeneous nucleation in clouds at around 120 km in the
atmosphere of Venus, we can state that nucleation of crystalline particles cannot occur, whereas
homogeneous nucleation of ASW and liquid CO\textsubscript{2} is feasible. The resulting CO\textsubscript{2} particles would
likely rapidly crystallise, as was observed in experiments (Dingilian et al., 2020), whereas ASW
would likely persist in an amorphous state (Mangan et al., 2021). The nucleation of ASW would
proceed at a rate of up to 10\textsuperscript{-2} to 10\textsuperscript{-3} cm\textsuperscript{-3} s\textsuperscript{-1} in layers of \(~4\) km wide, depending on the shape of
the temperature profile, whereas nucleation of CO\textsubscript{2} might produce very high number
concentrations in very narrow layers at the locus of the temperature minimum, owing to the very
strong temperature dependence of \(J_{\text{hom}}\).
Figure 2. Homogeneous nucleation rates in the atmosphere of Venus. Panel a shows $J_{\text{hom}}$ for CO$_2$ and H$_2$O particles in both an amorphous/liquid and crystalline form for an altitude of 121.6 km where the pressure was 2.51x$10^{-3}$ Pa (from the average atmospheric profile for 80-90º latitude AM (AM refers to the morning terminator) in Mahieux et al. (2015)) and a mixing ratio of 1 ppm for H$_2$O and unity for CO$_2$. Panel b shows the corresponding $J_{\text{hom}}$ values corresponding to the temperature and pressure profiles derived for SOIR profile 691.1, from the 12th March 2008 at 86.6º latitude from Mahieux et al. (2015).

2.2 Heterogeneous nucleation of CO$_2$ and H$_2$O particles

For mesospheric water ice clouds on Earth and Mars, the primary ice-nucleating particles for both planets are thought to be MSPs (Hervig et al., 2021; Plane et al., 2018). In Venus’ atmosphere, metals such as Fe, Mg, Si and Na are modelled to ablate from dust particles of mostly cometary origin (within the altitude range shown in Figure 1 Carrillo-Sánchez et al. (2020). The metal atoms become oxidized and then polymerize into MSPs (Plane et al., 2018). To the best of our knowledge, no other particle sources are available above 100 km in Venus’ atmosphere. Hence, MSPs are a likely candidate for nucleation of both CO$_2$ and H$_2$O particles.

The CNT formulation we adopt here has been used previously to evaluate nucleation of CO$_2$ and H$_2$O in Mars’ upper atmosphere (Listowski et al., 2014; Listowski et al., 2013; Määttänen et al., 2005; Määttänen et al., 2007; Mangan et al., 2017b; Nachbar et al., 2016), but here we have updated the physical constants (see Appendix A). For CO$_2$ we use CNT to model the nucleation of crystalline ice on iron oxide or silica MSPs, and also on water ice. In addition, we use the KNT approach to study nucleation of CO$_2$ on metal carbonates, which are a more likely composition of MSPs in the CO$_2$ atmosphere of Venus (Plane et al., 2018). Since the KNT approach is somewhat different to CNT, we introduce it separately in section 2.4. Note that in
Venus’ atmosphere these metallic carbonates and oxides may be partially converted to metal chlorides by the large concentrations of HCl present (Mahieux et al., 2015). However, electronic structure theory calculations of the kind described in Section 2.4 show that polar metal chlorides would be even more effective nuclei for CO$_2$ and H$_2$O, if they form. Figure 3a shows the probability of nucleation in one second as a function of temperature for the four potential nucleation pathways based on CNT. Three of these pathways involve MSPs (0.4 nm radius): nucleation of ice I$_h$ is defined by the experiments of (Saunders et al., 2010) who quantified ice nucleation on MSP analogues in a cloud chamber at temperatures down to 180 K, reporting $m = 0.985$ at 190 K ($\theta = 10^\circ$); nucleation of ASW on MSPs is defined by the experiments of (Duft et al., 2019) who studied absorption and particle growth kinetics between 128 and 147 K, showing ASW was indeed the phase to nucleate under these conditions and surface adsorption of water resulting in an $m$ of $\sim$1; and nucleation of CO$_2$ on MSPs composed of iron oxides or silica was defined by (Nachbar et al., 2016) between 64 and 73 K, reporting $m = 0.78 \pm 0.02$. In addition we illustrate the nucleation of CO$_2$ on H$_2$O ice particles of 1 nm and 5 nm radius, where nucleation was defined experimentally by (Glandorf et al., 2002) between 130 and 140 K, finding $m = 0.95$. Details of each of these CNT formulations are given in Appendix A.

Inspection of the nucleation probabilities in Figure 3a shows that the nucleation of ASW on 0.4 nm MSPs is most favourable, with nucleation probability increasing from an infinitely small value to unity on decreasing the temperature by only a few degrees. This occurs at a saturation ratio with respect to ASW of $\sim$250, and larger MSPs would be expected to nucleate at even lower supersaturations. A nucleation probability of unity means that 100% of 0.4 nm MSP particles would activate to form ASW particles, hence consuming all MSPs before CO$_2$ or ice I$_h$ might nucleate on them. If the MSP particle concentrations were 100 cm$^{-3}$, then a cloud of 100 ASW particles would nucleate and grow. These particles would only grow to a few nanometers given the availability of H$_2$O in the rarefied upper atmosphere of Venus. If the atmosphere were to become sufficiently cold, the curves in Figure 3a suggest that CO$_2$ might then nucleate on these small ASW particles. CO$_2$ is much more abundant than H$_2$O, and these particles would then grow rapidly (this is explored in more detail in Section 3 below).

We examine heterogeneous nucleation corresponding to a specific SOIR profile (691.1) in Figure 3b. The probability of nucleation in one second is shown for the nucleation of ASW on MSP and for CO$_2$ on ice. We do not show the probability of nucleation of ice I$_h$ or CO$_2$ on MSP because according to these calculations all the MSP would be activated to form ASW particles before the saturation was great enough for these other pathways to become active. It can be seen in Figure 3b that a broad layer of nanoscale ASW particles will form between 118 km and 125 km. The ASW saturation point is around 120 K at 122 km, hence these ASW particles will persist until the temperature goes above this threshold or when they slowly sediment out of the layer. SOIR profile 691.1 is a particularly cold profile and under these conditions nucleation of CO$_2$ on ASW particles becomes favourable between 120 and 123 km. Nucleation of CO$_2$ on ice will occur at temperatures below 80 K for 1 nm particles and below 89 K for 5 nm particles (Figure 3a), but in an increasingly narrow layer when the temperature minimum is less deep.

In summary, heterogeneous nucleation of ASW on MSPs is an effective pathway of producing water ice cloud particles in the upper atmosphere of Venus according to the parameterisation defined by the experiments of Duft et al. (2019). However, due to the limited availability of water vapour, these ASW particles will remain less than around 5 nm in radius, but fill a layer $\sim$5
km thick. The number of heterogeneously nucleating ASW particles will be limited by the concentration of MSPs, but homogeneous nucleation of ASW may provide additional particles (we explore this in section 2.3). If the temperature then decreases sufficiently, CO\textsubscript{2} will nucleate on these nanoscale ASW particles at a temperature dependent on their size. These CO\textsubscript{2} particles have the potential to grow rapidly and this will be explored in section 3.

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**Figure 3.** Probability of heterogeneous nucleation in the atmosphere of Venus. The nucleation probability is defined as the fraction of particles of defined size that nucleate ice in one second.

- **a)** The probability, from our CNT formulation, of H\textsubscript{2}O or CO\textsubscript{2} nucleating on MSPs (0.4 nm radius) or H\textsubscript{2}O ice particles (1 nm and 5 nm radius) as a function of temperature, as well as the onset of particle growth from the KNT model of CO\textsubscript{2} on MgCO\textsubscript{3} MSPs. These values correspond to an altitude of 121.6 km where the pressure was 2.51\times10\textsuperscript{-3} Pa (from the average atmospheric profile for 80-90\textdegree latitude morning terminator in Mahieux et al. (2015)) and a mixing ratio of 1 ppm for H\textsubscript{2}O and unity for CO\textsubscript{2}.

- **b)** The nucleation probability corresponding to the temperature and pressure profiles derived for SOIR profile 691.1, from the 12\textsuperscript{th} March 2008 at 86.6\textdegree latitude from Mahieux et al. (2015). We show the nucleation probabilities according to two potential mechanisms of CO\textsubscript{2} ice particle formation: first, is the direct nucleation of CO\textsubscript{2} on MSP according to KNT (section 2.4), and second, the nucleation of ASW on MSP followed by the nucleation of CO\textsubscript{2} on H\textsubscript{2}O ice (section 2.1 and 2.2).

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### 2.3 Competition between homogeneous and heterogeneous nucleation of ASW

We have shown that both homogenous and heterogeneous nucleation of ASW particles are feasible in the upper atmosphere of Venus. Here we examine which of these two mechanisms is likely to be more important in producing ice particles. In Figure 4 we show the number concentration of ASW particles resulting from both homogeneous and heterogeneous nucleation after 1 hr of constant conditions defined by SOIR profile 691.1. The number that nucleates heterogeneously is defined by the concentration of available MSP particles, which we have set at
100 cm$^{-3}$ here. This number is insensitive to time, since for most of the cloud layer the
probability of nucleation is unity for a 1 second interval. In contrast the number concentration of
particles that nucleate homogeneously increases in proportion with time. For SOIR profile 691.1,
homogeneous nucleation produces around 3 cm$^{-3}$ ASW particles in one hour, whereas
heterogeneous nucleation produces far more (depending on the assumed MSP concentration). If
the cold pocket persisted for a day one would expect (3 cm$^{-3}$ x 24) 72 cm$^{-3}$ ASW particles over
the course of the day. Sedimentation would then deplete the concentration, but there would be a
persistent ASW production until the growth of ASW particles depleted the water partial pressure.
In addition, it might be expected that cloud formation and sedimentation might deplete the MSP
particle population, making homogeneous nucleation relatively more important. Given the
uncertainties in the rate of homogenous nucleation and temperature measurements in Venus’
atmosphere, as well as the MSP concentration, we cannot rule homogeneous nucleation out as
making a significant contribution to the ASW particle population however, if MSP are present
then the calculations indicate that heterogeneous nucleation will produce the majority of ASW
particles in the upper atmosphere of Venus.

Figure 4. The competition between homogeneous and heterogeneous nucleation of ASW
particles assuming conditions remain constant for 1 hour. The number concentration resulting
from heterogeneous nucleation is defined by the product of probability of nucleation and the
number concentration of MSP particles of 0.4 nm (which we assume is 100 cm$^{-3}$). The
temperature and pressure profile correspond to SOIR profile 691.1.

2.4 CO$_2$ particle formation on carbonate MSPs from Kinetic Nucleation Theory

In the section above we established that a plausible mechanism for the formation of CO$_2$ ice
particles is via the nucleation of ASW and the subsequent nucleation of CO$_2$ on those nanoscale
ASW particles. Here we further explore the direct formation of CO$_2$ ice on MSP. In Figure 3a
we showed, based on the data of Nachbar et al. (2016), that nucleation on MSP composed of iron oxides and silica occurred 40 K lower than ASW on MSPs; hence is unlikely to be an important process. However, in a CO₂ rich atmosphere like that of Venus we expect meteoric smoke and MSPs to be composed of metal carbonates rather than oxides (Plane et al., 2018), and hence we need to consider the nucleation of CO₂ ice on metal carbonates. We were not able to find the pertinent physical data for the wetting properties of metal carbonate MSPs, so instead have used KNT. KNT is a bottom-up approach where the kinetics of adsorption and desorption of molecules to a cluster are treated explicitly (Bromley et al., 2016).

In these calculations the INP were assumed to be MgCO₃ and FeCO₃ which have already been discussed as likely MSP building blocks in the analogous atmosphere of Mars (Plane et al., 2018). The size of these seed particles was fixed at a radius of 0.35 nm, corresponding to a single MgCO₃ molecule with three CO₂ molecules bound to it (Plane et al., 2018). Because of the very large dipole moment of MgCO₃ (µD = 11.6 Debye), these CO₂ molecules are strongly enough bound for the MgCO₃(CO₂)₃ complex to be stable at temperatures below 150 K (Plane et al., 2018). Rate coefficients for the addition of subsequent CO₂ molecules up to MgCO₃(CO₂)₄₀ were then calculated using Rice Ramsperger Kassel Markus (RRKM) theory (Gilbert & Smith, 1990) with a solution of the Master Equation based on the inverse Laplace transform method (De Avillez Pereira et al., 1997). Electronic structure theory calculations (Frisch et al., 2016) were used to compute the vibrational frequencies of the small clusters up to n = 4. See Appendix B for details of these calculations and the derivation of the uptake coefficient, γ, for CO₂ attachment to an MgCO₃(CO₂)n cluster, and the rate of evaporation of the new cluster (i.e. MgCO₃(CO₂)n⁺₁ → MgCO₃(CO₂)n + CO₂). Although γCO₂ is estimated to approach unity for cluster sizes larger than n = 15 at temperatures below 150 K (Figure B1a), we limit the value here to γCO₂ ≤ 0.1 to allow for the high pressure limiting attachment rate of CO₂ for MgCO₃(CO₂)n, being lower than the hard sphere collision frequency (Smith, 1980). γCO₂ and the evaporation rate were computed at a pressure of 1.33 x 10⁻⁵ Pa (10⁻⁵ Torr), which is the typical pressure at ~150 km in Venus’ atmosphere (Mahieux et al., 2015). γCO₂ at a lower altitude was then scaled by the relative atmospheric density, up to the limit of 0.1. The evaporation rate was then computed by detailed balance with the CO₂ attachment rate, with an equilibrium constant calculated by statistical mechanics with the partition functions for MgCO₃(CO₂)n⁺₁ and MgCO₃(CO₂)n, using the vibrational frequencies and rotational constants described in the SI. For clusters larger than n = 40, γCO₂ was set to 0.1 at all temperatures below 180 K, and the equilibrium constant (and hence the evaporation rate) estimated from the Antoine relation for gas-phase CO₂ above the solid (Chicko, 2022; Giauque & Egan, 1937).

The conditions under which CO₂ particle growth becomes favourable are indicated in Figure 3. MSPs can provide a site where a CO₂ cluster is stabilised leading to growth of CO₂ particles at temperatures below about 95 K at 122 km. The initial cluster is non-crystalline, but on subsequent growth this material is likely to deposit as crystalline CO₂. However, if heterogeneous nucleation of ASW particles is as effective as indicated by our CNT formulation and the study of Duft et al. (2019), then the majority of MSP particles would already have activated to form nanoscale ASW particles. On the other hand, if the atmosphere were dehydrated by a previous cloud event, then new MSP particles might nucleate CO₂ in preference to ASW. Nevertheless, the most likely route to CO₂ particles is nucleation of CO₂ on ASW particles.
2.5 Planetary wide viability of H\textsubscript{2}O and CO\textsubscript{2} ice particle formation

In order to assess the geographical distribution and occurrence frequency of cloud formation conditions, we have plotted the SOIR profiles from Mahieux et al. (2015), broken down into latitude bands and morning or evening terminator, in Figure 5. The SOIR temperature profiles are then compared to the threshold temperatures at which ASW and crystalline CO\textsubscript{2} become saturated (the phases that are expected to make up clouds) as well as the temperature at which the nucleation rate of ASW on 1.0 nm ASW particles and CO\textsubscript{2} on 5 nm ASW particles is equal to 1 s\textsuperscript{-1} (equivalent to a nucleation probability in 1 s of 0.63).

While there is considerable variability of the temperature profiles, many of the profiles exhibit a minimum around 120-130 km with a value below the temperature required for the nucleation and persistence of both ASW and CO\textsubscript{2} ice particles (see Figure 5 and Figure 6). On average across all latitudes, 64% of the profiles indicate that the atmosphere is supersaturated with respect to ASW in a layer ~5-10 km deep. Nucleation of ASW on MSPs is also possible in 51% of the profiles on average. The sedimentation velocity of a 5 nm ASW particle at 120 km is 0.7 m s\textsuperscript{-1}, hence these particles would form a layer 5-10 km layer thick and have a lifetime with respect to sedimentation on the order of hours. This indicates that clouds composed of nanoscale ASW particles should be a regular feature of the atmosphere of Venus at around 120 km at all latitudes.

Nucleation of CO\textsubscript{2} on ASW particles is also remarkably frequent, occurring in 27% of the profiles on average. The frequency of CO\textsubscript{2} nucleation has a latitude dependence, with ~30-40% of profiles between 60\degree-90\degree dipping below the threshold required for nucleation of CO\textsubscript{2} on 5 nm ASW particles. Even at low latitudes (0-30\degree), ~8% of profiles were sufficiently cold for nucleation of CO\textsubscript{2} on ASW. Hence, CO\textsubscript{2} cloud formation is also relatively frequent at all latitudes. We now turn our attention to the properties and lifetime of these clouds and if they should be observable with contemporary satellite instruments.
Figure 5. Latitude (0-90°) and time of day dependence (morning terminator in purple or evening terminator in green) of saturation point temperature for crystalline CO$_2$ and ASW and of the nucleation activation temperatures (where $J_{\text{het}} = 1$ s$^{-1}$, corresponding to a nucleation probability of 0.63 in 1 s; we show values for nucleation of ASW on 1.0 nm MSP particles and CO$_2$ on 5 nm
ASW particles. Temperature profiles are taken from Mahieux et al. (2015) and the mean morning terminator pressure profiles from the same paper are used to derive the saturation temperatures and the nucleation activation temperatures.

**Figure 6.** Probability of atmospheric temperature falling below the H$_2$O and CO$_2$ frost points, and that required by CNT for particle nucleation above 100 km, using the observed temperature profiles from the data set of Mahieux et al. (2015). The probability is defined as the fraction of individual SOIR profiles where the temperature dropped below the respective frost point or nucleation threshold (see Figure 5). These probabilities are cumulative, meaning that when the SOIR temperature profile being below the CO$_2$ frost point, for example, the atmosphere is also supersaturated with respect to ASW.

### 3 Modelling ice particle evolution in Venus’ upper atmosphere

In order to explore the evolution of the CO$_2$-ice clouds (the VMCs), a 1-dimensional model was constructed which describes the nucleation, growth, sedimentation and sublimation of the ice particles. The model is described in appendix C. The model is initiated with vertical profiles of atmospheric density and temperature determined using the SOIR instrument (Mahieux et al., 2015) that had a deep temperature minimum (< 90 K) so that CO$_2$ would have been highly supersaturated. Figure 3 shows that under these conditions nucleation of CO$_2$ ice particles occurs, either directly on MSPs or on ASW particles that had earlier nucleated on MSPs. Since the concentration of ASW particles depends on the concentration of MSP particles both pathways to formation of CO$_2$ ice particles would produce similar VMCs. Hence, our 1-D microphysical model produces CO$_2$ ice crystals through the direct nucleation on MSP, but the results would be similar for the case where CO$_2$ nucleates on ASW particles. Once CO$_2$ particles are nucleated, the model follows the fate of the particles as they grow, sediment and finally sublimate on entering a warmer region.
Figure 7 shows examples of model output, corresponding to two examples of cloud that can be produced from the observed SOIR temperature profiles. The first example peaks around 120 km with particles around 100-200 nm radius; and the second type persists for longer and peaks around 110 km, with particles that can exceed 2 μm in radius. The first cloud category is produced by deep, but relatively sharp temperature minima above 120 km (e.g. orbit 671.1). In contrast, the much larger particles in the second cloud category are produced by much broader temperature minima, in this case between ~112 and 122 km (e.g. orbit 1581.1). Figure 7b shows the time evolution of the particle size and height, for these two examples. The first cloud only lasts for ~350 s, and the second type lasts for around 1200 s (20 mins). The latter example is the most pronounced cloud that was generated in the model from the SOIR dataset (orbit 1581.1 at 87.3° on the 19th August 2010), but is still relatively short-lived because sedimentation is so rapid in this altitude range. Figure 8 also illustrates a composite of clouds predicted for multiple SOIR profiles at 70-80° and 80-90° bands (north and south), showing that these clouds all have similar features, with small CO₂ particles at higher altitudes that rapidly grow and sediment until they sublime 5-10 km below the cold point. Note that the depth of clouds at 80-90° is generally greater than clouds at 70-80°, as a result of the broader temperature minimum at higher latitudes.
Figure 7. The microphysics of CO$_2$ ice clouds (a) Modelled CO$_2$ particle nucleation, growth, sedimentation and sublimation for the temperature profile of orbit 671.1 at 82.9° (solid lines), and orbit 1581.1 at 87.3° (dashed lines). (b) Time evolution of the radius and height of the CO$_2$ particles ($\gamma$CO$_2 = 0.1$, MSP concentration = 100 cm$^{-3}$).
Figure 8. Modeled particle nucleation, growth and sedimentation of CO$_2$ particles initiated with multiple observed temperature profiles from the dataset of Mahieux et al. (2015) using $\gamma$CO$_2 = 0.1$ at varying latitude ranges.

4 Detectability of CO$_2$ ice clouds

We have shown that conditions exist in the upper mesosphere of Venus where CO$_2$ clouds composed of ice particles in the 100s nm to micron sizes can form. We now address the question of whether these VMCs should be observable. The best chance of detection is likely through satellite observations of optical extinction. In this section we evaluate the possibility of detecting these high-altitude clouds in existing datasets by calculating the extinction by CO$_2$ ice particles using Mie theory. Venus Express had a suite of three instruments onboard that profile cloud and haze layers at lower altitudes on Venus. The first two are the UV and near-IR channels of the SPICAV instrument (Spectroscopy for the Investigation of the Characteristics of the Atmosphere of Venus) (although we do not include the near-IR channel in our current analysis). The UV channel has a wavelength range of 118-320 nm, and it performs stellar and solar occultations in addition to nadir and limb observations. The third instrument is SOIR (Solar Occultation in the InfraRed) which measures across the near- to mid-IR from 2.2-4.3 um (or 2200-4400 cm$^{-1}$) in solar occultation only. SPICAV has provided observations of the cloud and haze layers of Venus (Luginin et al., 2016; Wilquet et al., 2012; Wilquet et al., 2009), and SOIR observations were used also by Wilquet et al. (2009, 2012) and (Takagi et al., 2019). (Takagi et al., 2019) observed an increase in aerosol mixing ratio above 100 km, whereas the other studies reported results on clouds and hazes only at altitudes below 100 km. For the purposes of our Mie calculations we have selected the wavelength at 220 nm for SPICAV-UV and at 3320 nm for SOIR; both instruments have a similar detection limit around $1 \times 10^{-5}$ km$^{-1}$ (Wilquet et al., 2009).

We evaluate the detection probability of H$_2$O core (1 nm radius) CO$_2$ shell particles that might form in at an altitude of 120 km by determining the Mie extinction cross sections of individual
particles as a function of radius. We use refractive indices for CO$_2$ taken from Warren (1986), and those for water ice at 220 nm and 3320 nm from Kofman et al. (2019) and Warren and Brandt (2008), respectively. At 220 nm the water ice refractive indices were measured specifically for low density amorphous (LDA) ice at 70 K (Kofman et al., 2019).

In Figure 9 we show the extinction for CO$_2$ particles at varying radii and particle concentrations. Figure 7 shows that CO$_2$ particles often grow into the 100s nm range, hence extinction above the detection limit at both 220 nm and 3320 nm is possible with a sufficiently high number concentration. However, at 220 nm extinction exceeds the detection limit for much smaller particles and for lower number concentrations. For example, for CO$_2$ ice particle concentration of 100 cm$^{-3}$, detection at 220 nm using SPICAV-UV would occur when the particles were larger than ~25 nm, whereas for detection at 3320 nm with SOIR the particles would need to be above ~160 nm.

**Figure 9.** Predicted extinction coefficients in km$^{-1}$ for VMCs with particle radius for different particle concentrations at 220 nm (a) and 3320 nm (b) for CO$_2$ particles with 1 nm radius H$_2$O cores. The dotted line shows the detection limits $1 \times 10^{-5}$ km$^{-1}$ for SPICAV-UV and SOIR at 120 km. The particle concentrations (cm$^{-3}$) are indicated.

We now evaluate the detectability at 220 nm of the clouds modelled in the previous section and the sensitivity of the results to the CO$_2$ uptake coefficient ($\gamma$CO$_2$) and the MSP particle concentration. In the previous section $\gamma$CO$_2$ was set equal to 0.1. Figure 10(a) illustrates the sensitivity of the cloud formation to $\gamma$CO$_2$, for the atmospheric temperature/density profile from orbit 671.1 used previously, and with the MSP particle concentration fixed at 100 cm$^{-3}$ between 110 km and 130 km. As expected, the peak particle size varies with $\gamma$CO$_2$, for example when
CO$_2$ is decreased by a factor of 100 from 0.1 to 10$^{-3}$ the peak particle size only decreases by a factor of ~10, and the peak height is essentially unchanged. This variation has consequences on the detectability of the particles. Figure 10(b) shows the optical extinction at 220 nm of the cloud as a function of CO$_2$ for the same atmospheric profile. The Mie extinction is a strong function of particle size, and so this cloud would be barely detectable (for the SPICAV-UV detection limit of 10$^{-5}$ km$^{-1}$) if CO$_2$ was less than 0.005.

In addition to the particle size, particle concentration plays a role in the detectability of the clouds. In Figure 11 we test the sensitivity of the modelled cloud extinction to the assumed number of MSP particles, with CO$_2$ fixed at 0.1. In this case, the cloud would not be detectable if the MSP number density fell below ~1 cm$^{-3}$. However, the MSP concentration is probably much higher than this because a similar quantity of metal atoms is predicted to be injected via meteorić ablation into the upper atmospheres of Venus and Earth (12.6 and 8.3 tonnes d$^{-1}$, respectively), and the MSP concentration in the terrestrial mesosphere above 75 km is around 2000 cm$^{-3}$, based on rocket-borne charge particle measurements and modelling (Plane et al., 2014).

These sensitivity studies show that even if either the concentration of MSPs or the uptake coefficient CO$_2$ were a couple of orders of magnitude lower than for the standard model run, the resulting CO$_2$-ice clouds would still be detectable. However, it is their very short lifetime of only minutes, which would need to coincide with a satellite observation, which will make the detection of these clouds challenging. The model results of (Listowski et al., 2014) revealed similar short lifetimes for mesospheric CO$_2$ clouds on Mars that were dictated by the duration of the supersaturated cold pockets. They concluded that the scarcity of cloud observations among the hundreds of supersaturated temperature profiles observed by SPICAM was very probably due to the short lifetimes (< 1 - 2 hours) of the cold pockets formed by upward propagating gravity waves, and of the clouds themselves that rapidly evaporate in subsaturated conditions (10-20 minutes) (Listowski et al., 2014). If the cold pockets on Venus are a result of similar gravity waves as on Mars, the cold pocket lifetime of 1-2 hours is a lower limit. According to our simulations (see Figure 8) this cold pocket duration is sufficiently long for a detectable cloud to form, sediment to a subsaturated environment and evaporate (< 20 minutes). Nevertheless, the satellite observation would need to happen exactly at the right time and in the right place to be able to catch these ephemeral clouds.
Figure 7. Sensitivity of (a) CO$_2$ ice particle growth, and (b) optical extinction at $\lambda = 220$ nm, to the CO$_2$ uptake coefficient ($\gamma$CO$_2$) for the conditions of orbit 671.1 ($82.9^\circ$ latitude) from Mahieux et al. (2015). Number density of MSP particles = 100 cm$^{-3}$. The grey line in (b) shows the detection limit ($1 \times 10^{-5}$ km$^{-1}$) of the SOIR instrument onboard Venus Express.
Figure 8. Extinction of CO$_2$ ice particles at $\lambda$ = 220 nm, for a range of MSP particle concentrations for the conditions of orbit 671.1 ($\gamma$CO$_2$ = 0.1) from Mahieux et al. (2015). The grey line shows the estimated detection limit of the SOIR instrument onboard Venus Express.

3. Conclusions

The upper mesosphere of Venus between around 110 and 125 km is frequently cold enough that the atmosphere is supersaturated with respect to both water and CO$_2$ ices. In fact, the supersaturations become sufficiently large that both ASW H$_2$O ice and CO$_2$ ice can nucleate. Based on a combination of classical and kinetic nucleation theory we propose that there is a persistent ASW H$_2$O cloud layer on Venus around 10 km deep centered around 120 km. These ASW particles may form both from heterogeneous nucleation on meteoric smoke particles, or can form homogeneously directly from the vapour phase if the temperature minima persist for longer than a few hours. The ASW cloud particles are unlikely to grow larger than ~5 nm given the limited amount of water vapour present in the upper mesosphere of Venus. Hence, we suggest that there is a persistent sub-visible layer of water ice particles, composed of ASW covering around 50% of Venus at all latitudes. This 50% value is derived assuming the terminator pressure and temperature measurements from SOIR are representative of other times of the Venus day.

We also present evidence that CO$_2$ ice crystals can nucleate on either ASW particles or even bare meteoric smoke particles. At latitudes greater than 60$^\circ$ (N and S) nucleation on ASW particles can occur in more than 30% of the SOIR profiles. Since CO$_2$ is the primary component of Venus’ atmosphere, CO$_2$ particles will grow rapidly to 100s nm in only minutes. However, these clouds will only have a lifetime of ~10-20 minutes since sedimentation is very rapid in the thin upper mesosphere of Venus. These CO$_2$ ice particles are most likely composed of crystalline CO$_2$ ice-I and will likely have a cubic, octahedral or cubo-octahedral shape (Mangan et al.,...
These clouds may also produce halos that are unique to carbon dioxide crystals, as recently suggested for Mars (Ding et al., 2023). To an observer, VMCs might appear similar to cirrus uncinus (mares’ tails) on Earth where nucleation occurs close to the temperature minimum, followed by sedimentation and growth and subsequent sublimation of the ice crystals as they fall into a subsaturated warmer region. Any wind shear would give the fall streaks curvature (uncinus), where falling ice crystals are blown laterally as they sediment.

We have explored if VMCs might be observable with instruments on Venus Express. We find that the extinction will be large enough to observe at both 220 nm (SPICAV) and 3320 nm (SOIR), however the probability of an observation occurring in the 10-20 minutes that a cloud was present would be small. Nevertheless, we recommend that analysis of satellite data should be extended to altitudes where VMCs are predicted to occur, and that VMCs should be a target for future missions to Venus.

Given the strong sedimentation of VMC particles, VMCs have the potential to redistribute material in the upper atmosphere of Venus. Since nucleation of CO$_2$ on ASW with meteoric smoke cores is a likely mechanism for their production, VMCs are likely to transport MSPs to lower altitudes where they will be released in relatively narrow layers on the sublimation of CO$_2$ ice crystals. The formation of CO$_2$ crystals may also lead to the uptake of gas-phase meteoric species, which would also be released in a particulate form as the cloud particles sublimed at the base of the cloud layer (Mangan et al., 2017a). Similarly, VMCs will redistribute water vapour downwards, although the efficiency with which VMCs serve as a ‘cold trap’ will depend on the extent to which ASW particles can quench the supersaturation. On Earth, mesospheric clouds redistribute water downwards, resulting in a layer of enhanced water vapour at the base of the clouds, affecting odd oxygen and hydrogen chemistry (Murray & Plane, 2003; Murray & Plane, 2005). The extent to which VMCs limit the loss of water to space form Venus’ atmosphere should be the subject of more detailed microphysical modelling constrained by observations.

Overall, this work reveals that there is a complex cloud system that forms in the upper mesosphere of Venus around much of the planet, involving both water and CO$_2$ ice particles. We predict a ubiquitous layer of nanoscale water ice particles that forms both homogeneously and heterogeneously and then provides the substrate on which CO$_2$ VMC particles can nucleate. The resulting crystals of CO$_2$ grow rapidly to sizes where they can fleetingly scatter light at a detectable level before sedimenting into a warmer layer where they sublime.
Formation and dissipation of Venusian mesospheric clouds. Meteoric smoke particles nucleate nanoscale amorphous ice particles, followed by the nucleation of CO$_2$ on those particles. The CO$_2$ crystals rapidly grow, probably with a cubic, octoheral or cubo-octohedral shape, then sediment and release the meteoric smoke particles as they sublime in a warmer part of the atmosphere.

Acknowledgments

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Open Research

We have included all relevant equations and physical quantities to reproduce the plots in this paper in the appendicies.
Appendix A. Classical nucleation theory formalism

In this section we describe the nucleation theory we have applied to the atmosphere of Venus for both nucleation of CO\(_2\) and H\(_2\)O phases and give the pertinent parameters in Table 1.

Homogeneous nucleation

The CNT formulation we have chosen to use for homogeneous nucleation is based on the equations set out in Määttänen et al. (2005). The free energy of formation of a spherical cluster of molecules with a radius \(r\) is described by

\[
\Delta F^0 = -\frac{4\pi r^3}{3\nu}kT \ln S + 4\pi r^2 \sigma \tag{A1}
\]

Where \(\nu\) is the molecular volume of the condensed phase, \(\sigma\) is the interfacial energy between the condensed phase and the vapour phase, \(k\) the Boltzmann constant, \(T\) is temperature and \(S\) is the saturation ratio. A cluster is said to reach a critical size when the volume term (the left hand term) starts to dominate over the surface term (the right hand term). At the critical size further growth by addition of monomers results in an increase in stability, hence the critical cluster size and free energy of formation can be derived

\[
r^* = \frac{2\sigma}{kT \ln S} \quad \Delta F^*_{\text{hom}} = \frac{16\pi\nu^3\sigma^3}{3(kT\ln S)^2} \tag{A2}
\]

The homogeneous nucleation rate is defined by an Arrhenius-like expression

\[
J_{\text{hom}} = f_{\delta T}Z_{\text{hom}}\beta_{\text{hom}} c_{1,v} \exp \left( \frac{-\Delta F^*_{\text{hom}}}{kT} \right) \tag{A3}
\]

where \(c_{1,v}\) is the concentration of monomers in the vapour phase. The dimensionless non-isothermal coefficient \(f_{\delta T}\) as described in Feder et al. (1966) accounts for a reduction in the nucleation rate in cases when the atmospheric concentration of the nucleating species comprises a significant fraction of the total atmosphere. Higher collision frequency with the nucleating species compared to the inert carrier gas mean the heat of condensation is not efficiently removed from the cluster, leading to lower \(f_{\delta T}\) values and therefore lower nucleation rates. In the case of water ice nucleation on Venus, given the low H\(_2\)O mixing ratio around 1 ppmv, the isothermal coefficient will be close to 1 and so have a minimal effect on the nucleation rate (Määttänen et al., 2005). Using the lowest value of 0.966 reported by Määttänen et al. (2005) for H\(_2\)O in the comparable case of Mars, increases the nucleation activation temperature by < 0.1 K. Using the lowest non-isothermal value of 0.006 reported for CO\(_2\) ice nucleation (also for Mars) from (Wood, 1999), still only causes an approximate 0.3 K increase.

\(Z_{\text{hom}}\) is the homogeneous Zeldovich factor that accounts for the decrease in rate of cluster formation when there is a finite rate of critical cluster formation and is define as

\[
Z_{\text{hom}} = \sqrt{\frac{\Delta F^*_{\text{hom}}}{3\pi k} \bar{\nu}} \tag{A4}
\]
Where \( n^* \) is the number of molecules in the critical cluster. \( \beta_{\text{hom}} \) describes the rate at which monomers collide with the cluster and is defined as

\[
\beta_{\text{hom}} = c_{1,v} 4\pi r^2 \frac{kT}{2\pi m_m}
\]

where \( m_m \) is the molar mass.

### Heterogeneous nucleation

The rate of heterogeneous nucleation induced via surface diffusion on a spherical nucleus \( (J_{\text{het}}, \text{a} \) per nucleating particle nucleation rate in units of \( \text{s}^{-1} \)), is given by:

\[
J_{\text{het}} = A_N f_{\text{het}} Z_{\text{het}} \beta_{\text{het}} c_{1,s} \exp \left( -\frac{\Delta F_{\text{het}}^*}{kT} \right)
\]

where \( A_N \) is the surface area of the ice nucleating particle and \( c_{1,s} \) is the concentration of monomers on the particle surface; \( \beta_{\text{het}} \) describes the diffusion of molecules on the particle surface, and the dissociation of a proportion of supercritical clusters is described by the heterogeneous Zeldovich factor \( Z_{\text{het}} \). \( \Delta F_{\text{het}}^* \) is the free energy of forming a critical cluster on the nucleating particle, given by:

\[
\Delta F_{\text{het}}^* = f(m, x) \frac{16\pi\sigma^2 v^2}{3(kT\ln T)^2}
\]

\( \Delta F_{\text{het}}^* \) is calculated relative to the homogeneous barrier \( (\Delta F_{\text{hom}}^*) \) with a reduction in the energy barrier by a factor \( f(m, x) \) as described in Fletcher (1958), where \( x \) is the ratio of the size of the nucleating particle to the size of the critical cluster and \( m \) is the contact parameter (equal to \( \cos \theta \), where \( \theta \) is the contact angle between the ice nucleating particle and the nucleating phase (pertinent values of \( \theta \) are discussed in the following section).

### Table 1. Physical properties of H\(_2\)O and CO\(_2\)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturation vapour pressure</td>
<td>( P_{\text{sat,hex}} = \exp \left( \frac{2312 - 1.6T}{RT} \right) )</td>
<td>(Nachbar et al., 2018)</td>
</tr>
<tr>
<td>Density</td>
<td>940 kg m(^{-3})</td>
<td>(Ghormley &amp; Hochanadel, 1971)</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
<td>Source</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>--------------------------------------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>Surface tension</td>
<td>0.085 J m(^{-2})</td>
<td>Derived from (Duft et al., 2019, pp. author-year)</td>
</tr>
<tr>
<td>Desorption energy on MSP</td>
<td>42 kJ mol(^{-1})</td>
<td>(Duft et al., 2019)</td>
</tr>
<tr>
<td>Vibrational frequency</td>
<td>(10^{13}) s(^{-1})</td>
<td>(Pruppacher &amp; Klett, 1997)</td>
</tr>
<tr>
<td>Mean jump distance</td>
<td>0.32 nm</td>
<td>(Pruppacher &amp; Klett, 1997)</td>
</tr>
<tr>
<td>Contact parameter on MSP</td>
<td>0.999</td>
<td>Duft et al. (2019) suggest (m = 1)</td>
</tr>
<tr>
<td><strong>Ice I(_s)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturation vapour pressure</td>
<td>(\exp(9.550426 - 5723.265/T + 3.53068 \ln(T) - 0.007283327)) (Pa)</td>
<td>(Murphy &amp; Koop, 2005)</td>
</tr>
<tr>
<td>Density</td>
<td>((-1.3103 \cdot 10^{-6} \cdot T^3 + 3.8109 \cdot 10^{-7} \cdot T^2 - 9.2592 \cdot 10^{-5} \cdot T + 0.94040) \cdot 1000) (kg m(^{-3}))</td>
<td>(Murray &amp; Jensen, 2010)</td>
</tr>
<tr>
<td>Surface tension</td>
<td>0.141-0.00015 T (J m(^{-2}))</td>
<td>(Hale &amp; Plummer, 1974)</td>
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<td>Desorption energy</td>
<td>17.5 kJ mol(^{-1})</td>
<td>(Seki &amp; Hasegawa, 1983)</td>
</tr>
<tr>
<td>Vibrational frequency</td>
<td>(10^{13}) s(^{-1})</td>
<td>(Määttänen et al., 2005)</td>
</tr>
<tr>
<td>Mean jump distance</td>
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<td>(Pruppacher &amp; Klett, 1997)</td>
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<tr>
<td>Contact parameter on MSP</td>
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<td>(Saunders et al., 2010)</td>
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<td><strong>CO(_2) crystal</strong></td>
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<td></td>
</tr>
<tr>
<td>Saturation vapour pressure</td>
<td>(1.38 \cdot 10^{12} \exp(-3182.48/T)) (Pa)</td>
<td>(Azreg-Aïnou, 2005)</td>
</tr>
<tr>
<td>Density</td>
<td>(1.72391-0.0002537-0.000002877T^2) (g cm(^{-3}))</td>
<td>(Mangan et al., 2017b)</td>
</tr>
<tr>
<td>Surface tension</td>
<td>0.08 (J m(^{-2}))</td>
<td>(Nachbar et al., 2016; Wood, 1999)</td>
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<tr>
<td>Desorption energy</td>
<td>18.5 kJ mol(^{-1})</td>
<td>(Nachbar et al., 2016)</td>
</tr>
<tr>
<td>Vibrational frequency</td>
<td>(2.9 \cdot 10^{12}) s(^{-1})</td>
<td>(Nachbar et al., 2016)</td>
</tr>
<tr>
<td>Mean jump distance</td>
<td>0.4 nm</td>
<td>(Nachbar et al., 2016; Wood, 1999)</td>
</tr>
<tr>
<td>Contact parameter on ice</td>
<td>0.95</td>
<td>(Glandorf et al., 2002)</td>
</tr>
</tbody>
</table>
### Contact parameter on MSP

<table>
<thead>
<tr>
<th>Contact parameter on MSP</th>
<th>0.78</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Nachbar et al., 2016)</td>
</tr>
</tbody>
</table>

### CO$_2$ liquid

<table>
<thead>
<tr>
<th>Saturation vapour pressure</th>
<th>$101325 \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a = 1353/T - 8.143 \cdot \log(T) + 0.006259 \cdot T^2 + 24.619$</td>
<td>(Dingilian et al., 2020; Michels et al., 1950)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Density</th>
<th>$\ln \left( \frac{\rho'}{\rho_c} \right) = \sum_{i=1}^{4} a_i \left( 1 - \frac{T}{T_c} \right)^{t_i}$</th>
<th>(Dingilian et al., 2020; Span &amp; Wagner, 1996)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1 = 1.9245108; a_2 = -0.62385555; a_3 = -0.32731127; a_4 = 0.39245142; t_1 = 0.34; t_2 = 0.5; t_3 = 10/6; t_4 = 11/6; T_c = 304.1282; \rho_c = 467.6 \text{ kg m}^{-3}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Surface tension | 0.0378 J m$^{-2}$ | Derived from fit to data in Dingilian et al. (2020), see text. |

### Notes on the choice and derivation of physical properties of condensed phases of H$_2$O and CO$_2$

There are significant uncertainties associated with the physical properties of CO$_2$ and H$_2$O under the extremely low temperatures in Venus’s upper atmosphere. Hence, any predictions with CNT need to be taken in the context of these large uncertainties that propagate through into the nucleation rate. For the CNT formulations in this paper we have used a combination of physical properties used in previous nucleation studies and values derived from recent experimental data. The physical properties used in this study are detailed in Table 1. In the cases where physical properties were derived or there was a choice, the methodology and discussion is given below.

**Amorphous solid water:** The homogeneous nucleation of amorphous solid water was determined assuming a water mixing ratio of 1 ppm and the saturation vapour pressure was defined by (Nachbar et al., 2019) and Nachbar et al. (2018). In the past the parameterisation for the saturation pressure from (Murphy & Koop, 2005), where ASW and supercooled water were assumed to be a single continuous phase, was been used. However (Nachbar et al., 2019) show that ASW and supercooled water are two distinct phases of water and have distinct thermodynamics. Nachbar et al. (2018) showed that the vapour pressure of ASW is substantially greater than that predicted by the parameterisation given by (Murphy & Koop, 2005). Surface tension of ASW is not directly measured in the literature, and we used a value that we derived from literature data for the adsorption of ASW on MSPs (Duft et al., 2019); we discuss this
derivation in the heterogeneous section below. We set the non-isothermal constant to unity, which is probably an overestimate, but since we are attempting to identify which mechanisms are possible introducing a highly uncertain term that would reduce the rate would not be helpful.

Using a two-structure model of water (Hruby & Holten, 2004) produce a surface tension value of \( \sim 0.095 \text{ J m}^{-2} \) for water in the temperature regime associated with Venus’ upper mesosphere. Interestingly, they suggest that the temperature dependence of this value below \( \sim 120 \text{ K} \) is weak. In a study where adsorption of ASW onto MSP particles was studied between 128 and 147 K (Duft et al., 2019) found that the surface tension was \( 0.094 \pm 0.011 \text{ J m}^{-2} \). In order to derive a surface tension that was consistent with our CNT formulation we fitted to the data presented in (Duft et al., 2019). They report critical supersaturations where adsorption of water led to ice-activation. We interpreted the saturation at which we see a step change in the nucleation rate as being equivalent to the critical supersaturation reported by (Duft et al., 2019). The nucleation rate is very sensitive to the desorption energy and we have used an average value of 42 kJ mol\(^{-1}\) which is in the range reported by (Duft et al., 2019) for different MSP materials. This desorption energy is somewhat larger than used by (Määttänen et al., 2005) and reflects the strong binding of water molecules to the polar MSP surface. Given the critical cluster is only a few 10s of molecules in size, the assumption that all these molecules experience an enhanced interaction with the surface is reasonable (Duft et al., 2019). We also follow (Duft et al., 2019) in assuming that the MSP is wetted by ASW with \( m = 0.999 \). We fitted to reproduce the critical supersaturations in their Fig 6, yielding a surface tension of \( 0.085 \text{ J m}^{-2} \), which is within the uncertainty of the values reported by (Duft et al., 2019). By constraining our CNT formulation to experimental data down to 120 K, we can have some confidence in the extrapolation to \( \sim 110 \text{ K} \) where we predict nucleation in Venus’ atmosphere.

Liquid CO\(_2\). It is not immediately obvious that liquid CO\(_2\) should play any role in the atmosphere of Venus since bulk liquid CO\(_2\) can only exist at much greater pressures. However, recent experiments and computational studies have demonstrated that the initial cluster to form via homogeneous nucleation has liquid-like properties at temperatures pertinent to the upper atmosphere of Venus (Dingilian et al., 2020) (Halonen et al., 2021). In order to produce a CNT formulation that is consistent with the nucleation rate (and supersaturation) data presented in (Dingilian et al., 2020) we fitted the surface tension to the nucleation rate data between 78 K and 92 K. The average was \( 0.0378 \pm 0.0014 \text{ J m}^{-2} \). (Dingilian et al., 2020) fitted their data using a parameterisation for surface tension based on high-temperature data, that was then extrapolated to the low temperatures of their experiments, producing values of 0.050 to 0.054 J m\(^{-2}\). While there are uncertainties in these physical quantities, the pairing of the surface tension with our formulation of CNT to reproduce the experimentally observed nucleation rates under conditions close to those where clouds may form in Venus’ upper mesosphere gives us some confidence in our results.

Appendix B: Rate coefficients for attachment and detachment of CO\(_2\) molecules to MgCO\(_3\)(CO\(_2\))\(_n\) clusters

Rate coefficients for the sequential addition of CO\(_2\) molecules to MgCO\(_3\)(CO\(_2\))\(_3\), up to MgCO\(_3\)(CO\(_2\))\(_{40}\), were calculated with Rice Ramsperger Kassel Markus (RRKM) theory, using a
solution of the Master Equation based on the inverse Laplace transform method (De Avillez et al., 1997). These MgCO$_3$(CO$_2$)$_n$ + CO$_2$ recombination reactions proceed via the formation of an excited adduct, which can either dissociate back to reactants or be stabilized by collision with a third body to form MgCO$_3$(CO$_2$)$_{n+1}$. The binding energy of each CO$_2$ to the cluster was fixed to 26.6 kJ mol$^{-1}$, which is the heat of sublimation of CO$_2$ at 0 K (Chicco, 2022; Giauque & Egan, 1937). The internal energy of the adduct was divided into a contiguous set of grains with a width of 12 cm$^{-1}$ (which reflects the small binding energy of CO$_2$ to the cluster), each containing a bundle of rovibrational states.

The density of states of the adduct was calculated using the Beyer − Swinehart algorithm (Gilbert & Smith, 1990) for the vibrational modes (without making a correction for anharmonicity). For each MgCO$_3$(CO$_2$)$_n$ cluster these modes were taken to consist of the vibrational modes of MgCO$_3$ (167, 490, 530, 673, 806, 903, 990, 1768 cm$^{-1}$) and the $n$ CO$_2$ ligands (676, 676, 1364, 2400 cm$^{-1}$ for each CO$_2$), calculated at the B3LYP/6-311+g(2d,p) level of theory (Frisch et al., 2016) and assumed to be independent of each other; and a further $5n$ low-frequency modes set to a frequency of 80 cm$^{-1}$. This frequency represents the geometric mean of the frequencies of the “new” vibrational modes that are created when $n$ CO$_2$ molecules cluster with MgCO$_3$. The actual geometric means for $n$ = 2, 3 and 4 are 75.1, 83.2 and 78.5 cm$^{-1}$, respectively, using the data in Table S3 in the SI of Plane et al. (2018). The geometric mean is used because the density of states of the cluster is proportional to the inverse product of the vibrational frequencies (Gilbert & Smith, 1990). A classical densities of states treatment was used for the rotational modes. Since the clusters will be approximately spherical as they grow, the moments of inertia were approximated to be that of a solid sphere about its diameter:

\[ I = 0.4Mr^2 \]  
Eq. B1

where $M$ is the mass of the cluster, and $r$ is the cluster radius assuming a density of 1562 kg m$^{-3}$ for solid CO$_2$ at 195 K.

Each grain associated with the adduct MgCO$_3$(CO$_2$)$_{n+1}$ was then assigned a set of microcanonical rate coefficients for dissociation back to MgCO$_3$(CO$_2$)$_n$ + CO$_2$. These rate coefficients are determined using inverse Laplace transformation to link them directly to $k_{rec}$, which is estimated here as the hard sphere collision frequency between MgCO$_3$(CO$_2$)$_n$ and CO$_2$, with a small $T^{1/2}$ temperature dependence (Smith, 1980). The probability of collisional transfer between grains was estimated using the exponential down model, where the average energy for downward transitions ($\Delta E_{down}$) was set to 600 cm$^{-1}$ which is typical of $M$ = CO$_2$ at 300 K, and treated as independent of temperature (Gilbert & Smith, 1990). The Master Equation, which describes the evolution with time of the grain populations of the adduct, was then expressed in matrix form and solved to yield the rate coefficients for sequential addition of CO$_2$ to the clusters, as a function of temperature (50 – 150 K) at a pressure of 10$^{-5}$ Torr, which is the typical pressure at ~150 km in Venus’ atmosphere (Mahieux et al., 2015).

For the purpose of atmospheric modelling, it is customary to use the uptake coefficient, $\gamma$. This was calculated as ratio of the recombination rate coefficient to the collision rate of CO$_2$ with a sphere of radius $r$.
\[ \gamma = \frac{k_{rec}[\text{CO}_2]}{(0.25 \bar{A})} \]  

where \( k_{rec} \) is the recombination rate coefficient, \( \bar{c} \) is the mean collision speed between \( \text{MgCO}_3(\text{CO}_2)_n \) and \( \text{CO}_2 \), and \( A \) is the surface area of the cluster \( (4\pi r^2) \). \( \gamma \) is illustrated as a function of \( n \) and \( T \) in Figure B1(a). Note that \( \gamma \) does not exceed unity, which is a good test of the Master Equation calculation.

Finally, the rate of dissociation of the cluster i.e. \( \text{MgCO}_3(\text{CO}_2)_{n+1} \rightarrow \text{MgCO}_3(\text{CO}_2)_n + \text{CO}_2 \), was calculated by detailed balance with the recombination rate coefficient, where the equilibrium constant is calculated by statistical mechanics with the partition functions for \( \text{MgCO}_3(\text{CO}_2)_{n+1} \) and \( \text{MgCO}_3(\text{CO}_2)_n \) using the vibrational frequencies and rotational constants described above. The equilibrium constant is within 20% of that given by the Antoine relation (Chicko, 2022; Giauque & Egan, 1937) for clusters larger than \( n = 30 \) and \( T > 140 \) K (where the Antoine relation is valid). The dissociation rate, i.e., the evaporation rate, is shown as a function of \( n \) and \( T \) in Figure B1b.
Figure B1. (a) $\gamma$CO$_2$ as a function of temperature and number of CO$_2$ molecules clustered around a meteoric smoke particle. (b) Rate of evaporation (units: molecule s$^{-1}$) of CO$_2$ from an MSP-(CO$_2$)$_n$ cluster, as a function of temperature and the number of CO$_2$ molecules ($n$).
Appendix C: Details of the microphysical model

In order to explore the evolution of the CO$_2$-ice clouds, a 1-dimensional model was constructed which describes the nucleation, growth, sedimentation and sublimation of the ice particles. For this simple cloud model we describe the production of CO$_2$ particles using the KNT theory presented in section 2.4. Hence, we implicitly assume that nucleation occurs on MSP, probably MgCO$_3$ and FeCO$_3$. Although we expect very similar results in terms of growth, sedimentation and lifetime of cloud particles if nucleation occurred on ASW particles which in turn nucleated on MSPs.

When the concentration of MSPs is larger than ~ 1000 cm$^{-3}$, the production of large CO$_2$ particles with radii of a few hundred nm starts to deplete significantly the background CO$_2$ density (this effect is accounted for in the model). Because the CO$_2$ ice clouds are short-lived, coagulation of ice particles is neglected.

The sedimentation velocity of the MgCO$_3$(CO$_2$)$_n$ clusters and CO$_2$ ice particles, $w_i$, can be estimated using a form of Stokes’ law describing a spherical particle falling through a stationary fluid:

$$w_i = \frac{2(\rho_p-\rho_{air})}{9\mu} g r_i^2 C_{scf}$$  \text{Eq. C1}

where $\rho_p$ and $\rho_{air}$ are the particle density (taken to be the density for solid CO$_2$, which is 1562 kg m$^{-3}$ at 195 K) and the air density, respectively; $\mu$ is the dynamic viscosity of CO$_2$ at the atmospheric temperature and pressure; $g$ is the gravitational constant (8.87 m s$^{-2}$ for Venus); and $r_i$ is the particle radius. $C_{scf}$ is the Cunningham slip correction factor accounting for the effects of drag on small particles, and is estimated from equation Eq.B2, where $\lambda$ is the mean free path of the CO$_2$ molecules, and $A_1$, $A_2$ and $A_3$ are dimensionless coefficients:

$$C_{scf} = 1 + \frac{\lambda}{r_i}\left( A_1 + A_2 \exp\left(\frac{-A_3 r_i}{\lambda}\right) \right)$$ \text{Eq. C2}

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Ephemeral Ice Clouds in the Upper Mesosphere of Venus

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Key Points:

- The upper mesosphere of Venus is frequently supersaturated with respect to both amorphous solid water and crystalline carbon dioxide ice
- There is a persistent layer of nano-scale amorphous solid water particles encircling Venus
- Short-lived carbon dioxide ice clouds sporadically form in the upper mesosphere
Abstract
The conditions in Venus’ upper mesosphere at around 120 km have some similarities to the upper mesosphere of Earth and Mars where ice clouds form. Here we show, using published satellite products and numerical modelling, that the upper mesosphere of Venus is sufficiently cold that both H$_2$O and CO$_2$ can condense to form particles. In fact, we show that there is likely to be a competition between the direct nucleation of particles from the gas phase (homogeneous nucleation) and the nucleation on meteoric smoke particles (MSPs, heterogeneous nucleation). Amorphous solid water particles (ASW) are likely to nucleate first, resulting in clouds of nanometer-sized particles at around 120 km globally. The temperatures can then become sufficiently low that CO$_2$ particles can nucleate either on MSPs or on ASW particles (>30% of the time poleward of 60°). Since the main component of the atmosphere is CO$_2$ these particles will grow and sediment on a timescale of 10-20 minutes. Mie calculations show that these Venusian mesospheric clouds (VMCs) should be observable by contemporary satellite instruments, although their short lifetime means that the probability of detection is small. We suggest that VMCs are important for the redistribution of meteoric smoke and may serve as a cold-trap, removing some water vapour from the very upper mesosphere of Venus, through the growth and sedimentation of cloud particles, and possibly reducing the loss of water to space.

Plain Language Summary
Venus is renowned for extreme heat at the surface and clouds composed of sulphuric acid encircling the planet; however, there are regions of Venus’ atmosphere that are sufficiently cold to harbour ice clouds. In fact, the temperatures frequently fall to below 100 K at around 120 km altitude and under the right conditions we have shown that ice clouds composed of both water and carbon dioxide ices can form. We have used published data from satellites that orbit Venus to show that clouds composed of nanometer sized water ice particles may encircle the planet. The temperatures are so low in this part of Venus’ atmosphere that the ice in these water ice particles likely lacks any crystalline structure, that is, it has an amorphous (liquid-like) structure. Furthermore, when the temperature falls below about 90 K, we have shown that carbon dioxide ice crystals can form on top of water ice crystals. Since the atmosphere of Venus is mainly made of carbon dioxide, these carbon dioxide crystals grow and fall rapidly. If we were lucky enough to see one of these short-lived sporadic clouds it would look a bit like a mares’ tail cloud on Earth.

1 Introduction
The plausibility of ice clouds in Venus’ atmosphere has been discussed as early as the 1950s (Menzel & Whipple, 1954). Through differing analyses of infrared absorption seen at 3 μm from high altitude balloon measurements in the 1960s, both Bottema et al. (1965) and Pollack and Sagan (1968) suggested water ice clouds could explain the observed absorbances, although a rebuttal by Rea and O’Leary (1968) suggested this was possible only if the ice particles were submicron in size. Turco et al. (1983) expanded on these predictions, suggesting that water ice clouds may be present in two layers: one between 80 and 100 km, resulting from freezing of sulphuric acid haze droplets; and another layer at Venus’ mesopause (~120 km) consisting of water ice nanoparticles, possibly nucleated on meteoric dust particles.
Since the prediction of water ice clouds on Venus by Turco et al. (1983), our understanding of both the physics of ice cloud formation in planetary atmospheres and the structure and dynamics of the Venusian atmosphere have increased greatly. A range of satellite observations of lower altitude (≤ 100 km) sulphuric acid haze layers have since been made (Titov et al., 2018), and recent observations by instruments onboard the Venus Express satellite have highlighted extreme temperature minima in Venus’ upper atmosphere (Mahieux et al., 2015).

Figure 1 illustrates an example of a typical cold temperature profile (green line) from the Solar Occultation in the InfraRed (SOIR) instrument onboard the Venus Express satellite (Orbit 669.1, taken at 81.6° latitude on the 19th February 2008 from Mahieux et al. (2015)). This profile includes the coldest region in Venus’ atmosphere, with temperatures below 100 K from 118 – 125 km, and a temperature minimum of 64 K at 121 km. The blue line in Figure 1 shows the saturation temperature for H₂O with respect to amorphous solid water (ASW), assuming a water vapour concentration of 1 ppmv (the expected range in the Venusian upper atmosphere is 0.56 – 2.45 ppmv (Chamberlain et al., 2020)). This highlights that the atmosphere is sometimes significantly supersaturated with respect to ASW within the cold pocket. We show here the saturation (frost) point associated with ASW, rather than the stable crystalline hexagonal phase of ice I (ice Ih), because under these conditions in the upper atmosphere any ice formed should be amorphous (Mangan et al., 2021). The Turco et al. (1983) prediction of water ice clouds was based on an assumed water vapour concentration of 10 ppm at slightly lower altitudes than the example shown in Figure 1, but with a much higher temperature minimum of 110 K; this led to a many orders of magnitude smaller supersaturations than those shown in Figure 1. These atmospheric conditions for water ice evoke comparisons to Polar Mesospheric Clouds (PMCs) on Earth (Plane et al., 2015), and water ice clouds observed in the upper atmosphere of Mars (Stcherbinine et al., 2020). On Mars, upper mesospheric clouds are also thought to redistribute H₂O, although the process is not as effective as it might be if the growth of ice particles can quench the supersaturation (Fedorova et al., 2020); nevertheless ice cloud formation and sedimentation of ice crystals will limit the amount of water transported vertically.

Figure 1 also shows the saturation temperature for crystalline CO₂ ice (phase I), the phase that we expect cloud particles to be composed of under conditions in the upper mesosphere of Venus (Mangan et al., 2017b), even if nucleation occurs through a different phase. The primarily CO₂ atmosphere of Venus is sufficiently dense and the cold pocket sufficiently cold that the atmosphere is also supersaturated with respect to CO₂ ice around the temperature minimum at 121 km. These atmospheric conditions are again comparable to the Martian upper atmosphere, where gravity wave-induced cold pockets enable deposition of the primary atmospheric constituent, producing populations of micron-sized CO₂ ice particles (Listowski et al., 2014; Plane et al., 2018). At the time of Turco et al. (1983), CO₂ ice clouds were not considered as a possibility, given that the first confirmed observations of high-altitude CO₂ ice clouds on Mars were not made for another 20 years (Montmessin et al., 2006), and the temperature minima reported by Turco et al. (1983) were insufficient to produce supersaturated conditions with respect to CO₂ ice.

Despite being higher on Venus, if H₂O and/or CO₂ ice clouds formed around this temperature minimum they would exist in a region with striking similarities to the mesospheric clouds observed on Mars, quite possibly with similar nucleating particles available. Hence, building on the predictions of water ice clouds by (Turco et al., 1983), we propose that ice clouds,
comprising both H\textsubscript{2}O and CO\textsubscript{2} ice, may form in Venus’ upper atmosphere at around 120 km in altitude. In this paper, using the more extensive database of measurements for the Venus atmosphere that are now available, and applying our improved knowledge of high-altitude clouds on Earth and Mars, we examine the formation, growth and composition of H\textsubscript{2}O and CO\textsubscript{2} ice clouds, and their detectability, in the upper atmosphere of Venus.

Figure 1. Atmosphere of Venus showing known and proposed cloud layers. General atmospheric profile (black) extracted from Palen et al. (2019). The temperature profile from orbit 669.1 (green) is taken from Mahieux et al. (2015). Saturation temperatures shown for H\textsubscript{2}O with respect to amorphous solid water (blue) and CO\textsubscript{2} with respect to crystalline CO\textsubscript{2} (red). The water saturation ratios were calculated using the Nachbar et al. (2019) parameterisation for ASW in combination with the vapour pressure over hexagonal ice (Murphy & Koop, 2005). The frost point for crystalline CO\textsubscript{2} ice was calculated using saturation vapour pressure parameterisation from Azreg-Aïnou (2005). The altitude range over which meteoric ablation occurs is taken from Carrillo-Sánchez et al. (2020).

2. Nucleation of H\textsubscript{2}O and CO\textsubscript{2} particles in Venus’ mesosphere

To evaluate the feasibility of nucleation of H\textsubscript{2}O and CO\textsubscript{2} ice particles in Venus’ upper atmosphere we employ two theoretical approaches: Classical Nucleation Theory (CNT) and Kinetic Nucleation Theory (KNT). Atmospheres can exist in a metastable state where the partial pressure of some condensable component is greater than the equilibrium vapour pressure of a condensed phase (or phases) (Murray & Jensen, 2010). An atmosphere can persist in a supersaturated state because there is a free energy barrier to nucleation of a new phase related to the creation of a new interface. Nucleation can either occur spontaneously (homogeneous nucleation), or can occur at lower supersaturations on the surface of suitable particles. These ice-nucleating particles (INPs) stabilise the cluster of the condensed phase through favourable interactions with the surface. In cold clouds in Earth’s mesosphere (Murray & Jensen, 2010), there is thought to be a competition between homogeneous and heterogeneous nucleation, and the balance between the mechanisms results in clouds with very different hydrometeor size...
distributions. Sometimes heterogeneous nucleation occurring at lower supersaturations than
those required for homogeneous nucleation leads to the depletion of the supersaturation as the ice
particles grow, thus preventing homogeneous nucleation from occurring. But, if the cooling rate
is sufficiently rapid then homogeneous as well as heterogeneous nucleation can occur (Murray &
Jensen, 2010).

In the upper mesosphere of Venus there are at least two condensable materials, CO\textsubscript{2} and H\textsubscript{2}O.
The stable form of both of these materials is crystalline under the conditions on Venus, but it is
unlikely that the critical cluster is made up of the stable phase. In many nucleating systems the
initial phase to nucleate is a metastable phase that has a smaller surface energy penalty than the
stable phase (Mullin, 2001). The metastable phase may subsequently relax to the stable phase. In
the case of water homogeneously nucleating from water vapour, measurements clearly show that
it is the liquid phase that nucleates at temperatures to below 200 K, even though the liquid phase
rapidly converts to crystalline ice under those conditions (Wölk et al., 2013). At below around
120 K, deposition of water on a surface results in amorphous solid water (ASW); hence, the
nucleating phase was probably amorphous but at these low temperatures the kinetics of
transformation to the stable phase were too slow for it to occur on the experimental time scale
(mins-hours) (Duft et al., 2019; Mangan et al., 2021). Similarly, for CO\textsubscript{2} recent experiments and
molecular dynamics studies show that the initial phase to nucleate is a liquid-like form of CO\textsubscript{2}
between 75 and 92 K (Dingilian et al., 2020; Halonen et al., 2021).

Heterogeneous nucleation requires the presence of particles on which nucleation might occur.
The most likely candidate for particles that might serve as ice-nucleating particles (INPs) for ice
clouds on Venus are nm-sized Meteoric Smoke Particles (MSPs). MSPs form from the
recondensation of metallic compounds (oxides, hydroxides and carbonates) formed from the
ablation of metals such as Fe, Mg and Na from cosmic dust particles entering an oxidizing
planetary atmosphere such as Venus (Plane et al., 2015). Current predictions for Venus by
Carrillo-Sánchez et al. (2020) show that ablation should occur between 100 and 125 km, peaking
around 115 km (Figure 1). This altitude range happens to coincide with the cold pocket (Figure
1). In the following sections we use CNT and KNT to test the likelihood of both homogeneous
and heterogeneous nucleation of both CO\textsubscript{2} and H\textsubscript{2}O particles in the upper mesosphere of Venus.
Note that there are also significant concentrations of HCl in Venus’ upper mesosphere,
approaching 1 ppm around 110 km and therefore ~ 1 – 10% of the H\textsubscript{2}O mixing ratio (Mahieux et
al., 2015). HCl may therefore play a role as a condensable vapour, though this is likely to be as a
minor enhancement of that of H\textsubscript{2}O.

2.1 Homogeneous nucleation of CO\textsubscript{2} and H\textsubscript{2}O particles

Homogeneous nucleation directly from the vapour phase can occur under extreme conditions and
it has been suggested that it may be important in the Earth’s mesosphere (Lübken et al., 2009;
Murray & Jensen, 2010). Given the conditions in the upper mesosphere of Venus are extremely
cold, it is worth considering if H\textsubscript{2}O or CO\textsubscript{2} particles might nucleate homogeneously. We have
used a Classical Nucleation Theory (CNT) formulation described by (Määttänen et al., 2005).
The equations and the choice of parameterisations of physical quantities are set out in Appendix
A. Key physical quantities have been updated to be consistent with the latest experimental and
theoretical studies. This includes the use of a parameterisation of the vapour pressure of ASW
from Nachbar et al. (2019), who showed that ASW is not simply the low temperature extension
of supercooled liquid water and is in fact a distinct phase of water. We also derived a self-consistent interfacial energy for the liquid CO$_2$–vapour interface, based on measurements of homogeneous nucleation in a supersonic nozzle (Dingilian et al., 2020), and the ASW–vapour interfacial energy from studies of water uptake onto trapped nano-scale meteoric smoke analogues (Duft et al., 2019) (note that by self-consistent we mean that the interfacial energy is derived using the CNT and physical constant chosen in this paper, and then these CNT models are extrapolated to the conditions on Venus).

Nucleation rates (events per unit volume per unit time) for crystalline and amorphous/liquid-like phases of H$_2$O and CO$_2$ are shown in Figure 2a for an altitude of 121.6 km and a total pressure of 2.52 x 10$^{-3}$ Pa (taken from the mean profiles derived from SOIR data in Mahieux et al., 2015)). We assumed a water mixing ratio of 1 ppm and the CO$_2$ mixing ratio was taken as unity (in practice it is around 0.96). We also show, in Figure 2b, $J_{\text{hom}}$ for one of the coldest temperature profiles in the SOIR dataset, 691.1 from the 12th March 2008 at 86.6° latitude from Mahieux et al. (2015), where the temperature minimum was 63 K at 121.6 km.

As expected, homogeneous nucleation of crystalline H$_2$O and CO$_2$ are very slow. In contrast, the homogeneous nucleation of ASW and liquid-like CO$_2$ might perhaps contribute to cloud particle populations. The nucleation rate for ASW is appreciable in this region, and is relatively insensitive to temperature with values of around 10$^{-2}$ cm$^{-3}$ s$^{-1}$ at 63 K, which would produce ~1 cloud particle per cm$^3$ in 100 s. While there are uncertainties in the physical constants that go into the calculation of $J_{\text{hom}}$, $J_{\text{hom}}$ in this ‘plateau regime’ has a relatively weak temperature dependence (Figure 2a) and is therefore insensitive to those uncertainties. Since the plateau value of $J_{\text{hom}}$ is defined by the rate of formation of ASW clusters, which in turn is related to the H$_2$O monomer concentration, this limit should be well defined and it is unlikely that the true $J_{\text{hom}}$ of ASW is many orders of magnitude larger (or smaller). The same cannot be said for $J_{\text{hom}}$ for liquid CO$_2$ at around 120 km in the atmosphere of Venus. $J_{\text{hom}}$ for liquid CO$_2$ has a very strong temperature dependence above ~60 K; hence, uncertainties in temperature and various physical quantities can have a substantial effect on the nucleation rate. For example, while $J_{\text{hom}}$ is relatively small at 63 K, peaking at 10$^{-5}$ cm$^{-3}$ s$^{-1}$ (Figure 2b), a shift of only 3 K to lower temperatures would increase $J_{\text{hom}}$ to ~1 cm$^{-3}$ s$^{-1}$. This would produce 100 particles per cubic centimetre in 100 s. Similarly, an interfacial energy only 15% smaller would also increase $J_{\text{hom}}$ by more than five orders of magnitude. On this basis one should certainly not rule out homogeneous nucleation of liquid CO$_2$ particles, which would then rapidly convert to crystalline CO$_2$ ice.

To summarise, the role of homogeneous nucleation in clouds at around 120 km in the atmosphere of Venus, we can state that nucleation of crystalline particles cannot occur, whereas homogeneous nucleation of ASW and liquid CO$_2$ is feasible. The resulting CO$_2$ particles would likely rapidly crystallise, as was observed in experiments (Dingilian et al., 2020), whereas ASW would likely persist in an amorphous state (Mangan et al., 2021). The nucleation of ASW would proceed at a rate of up to 10$^{-2}$ to 10$^{-3}$ cm$^{-3}$ s$^{-1}$ in layers of ~4 km wide, depending on the shape of the temperature profile, whereas nucleation of CO$_2$ might produce very high number concentrations in very narrow layers at the locus of the temperature minimum, owing to the very strong temperature dependence of $J_{\text{hom}}$. 
Figure 2. Homogeneous nucleation rates in the atmosphere of Venus. Panel a shows $J_{\text{hom}}$ for CO$_2$ and H$_2$O particles in both an amorphous/liquid and crystalline form for an altitude of 121.6 km where the pressure was 2.51x10$^{-3}$ Pa (from the average atmospheric profile for 80-90º latitude AM (AM refers to the morning terminator) in Mahieux et al. (2015)) and a mixing ratio of 1 ppm for H$_2$O and unity for CO$_2$. Panel b shows the corresponding $J_{\text{hom}}$ values corresponding to the temperature and pressure profiles derived for SOIR profile 691.1, from the 12th March 2008 at 86.6º latitude from Mahieux et al. (2015).

2.2 Heterogeneous nucleation of CO$_2$ and H$_2$O particles

For mesospheric water ice clouds on Earth and Mars, the primary ice-nucleating particles for both planets are thought to be MSPs (Hervig et al., 2021; Plane et al., 2018). In Venus’ atmosphere, metals such as Fe, Mg, Si and Na are modelled to ablate from dust particles of mostly cometary origin (within the altitude range shown in Figure 1 Carrillo-Sánchez et al. (2020). The metal atoms become oxidized and then polymerize into MSPs (Plane et al., 2018). To the best of our knowledge, no other particle sources are available above 100 km in Venus’ atmosphere. Hence, MSPs are a likely candidate for nucleation of both CO$_2$ and H$_2$O particles.

The CNT formulation we adopt here has been used previously to evaluate nucleation of CO$_2$ and H$_2$O in Mars’ upper atmosphere (Listowski et al., 2014; Listowski et al., 2013; Määttänen et al., 2005; Määttänen et al., 2007; Mangan et al., 2017b; Nachbar et al., 2016), but here we have updated the physical constants (see Appendix A). For CO$_2$ we use CNT to model the nucleation of crystalline ice on iron oxide or silica MSPs, and also on water ice. In addition, we use the KNT approach to study nucleation of CO$_2$ on metal carbonates, which are a more likely composition of MSPs in the CO$_2$ atmosphere of Venus (Plane et al., 2018). Since the KNT approach is somewhat different to CNT, we introduce it separately in section 2.4. Note that in
Venus’ atmosphere these metallic carbonates and oxides may be partially converted to metal chlorides by the large concentrations of HCl present (Mahieux et al., 2015). However, electronic structure theory calculations of the kind described in Section 2.4 show that polar metal chlorides would be even more effective nuclei for CO$_2$ and H$_2$O, if they form. Figure 3a shows the probability of nucleation in one second as a function of temperature for the four potential nucleation pathways based on CNT. Three of these pathways involve MSPs (0.4 nm radius): nucleation of ice I$_h$ is defined by the experiments of (Saunders et al., 2010) who quantified ice nucleation on MSP analogues in a cloud chamber at temperatures down to 180 K, reporting $m = 0.985$ at 190 K ($\theta = 10^\circ$); nucleation of ASW on MSPs is defined by the experiments of (Duft et al., 2019) who studied absorption and particle growth kinetics between 128 and 147 K, showing ASW was indeed the phase to nucleate under these conditions and surface adsorption of water resulting in an $m$ of $\sim 1$; and nucleation of CO$_2$ on MSPs composed of iron oxides or silica was defined by (Nachbar et al., 2016) between 64 and 73 K, reporting $m = 0.78 \pm 0.02$. In addition, we illustrate the nucleation of CO$_2$ on H$_2$O ice particles of 1 nm and 5 nm radius, where nucleation was defined experimentally by (Glandorf et al., 2002) between 130 and 140 K, finding $m = 0.95$. Details of each of these CNT formulations are given in Appendix A.

Inspection of the nucleation probabilities in Figure 3a shows that the nucleation of ASW on 0.4 nm MSPs is most favourable, with nucleation probability increasing from an infinitely small value to unity on decreasing the temperature by only a few degrees. This occurs at a saturation ratio with respect to ASW of $\sim 250$, and larger MSPs would be expected to nucleate at even lower supersaturations. A nucleation probability of unity means that 100% of 0.4 nm MSP particles would activate to form ASW particles, hence consuming all MSPs before CO$_2$ or ice I$_h$ might nucleate on them. If the MSP particle concentrations were 100 cm$^{-3}$, then a cloud of 100 ASW particles would nucleate and grow. These particles would only grow to a few nanometers given the availability of H$_2$O in the rarefied upper atmosphere of Venus. If the atmosphere were to become sufficiently cold, the curves in Figure 3a suggest that CO$_2$ might then nucleate on these small ASW particles. CO$_2$ is much more abundant than H$_2$O, and these particles would then grow rapidly (this is explored in more detail in Section 3 below).

We examine heterogeneous nucleation corresponding to a specific SOIR profile (691.1) in Figure 3b. The probability of nucleation in one second is shown for the nucleation of ASW on MSP and for CO$_2$ on ice. We do not show the probability of nucleation of ice I$_h$ or CO$_2$ on MSP because according to these calculations all the MSP would be activated to form ASW particles long before the saturation was great enough for these other pathways to become active. It can be seen in Figure 3b that a broad layer of nanoscale ASW particles will form between 118 km and 125 km. The ASW saturation point is around 120 K at 122 km, hence these ASW particles will persist until the temperature goes above this threshold or when they slowly sediment out of the layer. SOIR profile 691.1 is a particularly cold profile and under these conditions nucleation of CO$_2$ on ASW particles becomes favourable between 120 and 123 km. Nucleation of CO$_2$ on ice will occur at temperatures below 80 K for 1 nm particles and below 89 K for 5 nm particles (Figure 3a), but in an increasingly narrow layer when the temperature minimum is less deep.

In summary, heterogeneous nucleation of ASW on MSPs is an effective pathway of producing water ice cloud particles in the upper atmosphere of Venus according to the parameterisation defined by the experiments of Duft et al. (2019). However, due to the limited availability of water vapour, these ASW particles will remain less than around 5 nm in radius, but fill a layer $\sim 5$
km thick. The number of heterogeneously nucleating ASW particles will be limited by the concentration of MSPs, but homogeneous nucleation of ASW may provide additional particles (we explore this in section 2.3). If the temperature then decreases sufficiently, CO$_2$ will nucleate on these nanoscale ASW particles at a temperature dependent on their size. These CO$_2$ particles have the potential to grow rapidly and this will be explored in section 3.

**Figure 3.** Probability of heterogeneous nucleation in the atmosphere of Venus. The nucleation probability is defined as the fraction of particles of defined size that nucleate ice in one second.

- a) The probability, from our CNT formulation, of H$_2$O or CO$_2$ nucleating on MSPs (0.4 nm radius) or H$_2$O ice particles (1 nm and 5 nm radius) as a function of temperature, as well as the onset of particle growth from the KNT model of CO$_2$ on MgCO$_3$ MSPs. These values correspond to an altitude of 121.6 km where the pressure was 2.51×10$^{-3}$ Pa (from the average atmospheric profile for 80-90° latitude morning terminator in Mahieux et al. (2015)) and a mixing ratio of 1 ppm for H$_2$O and unity for CO$_2$.

- b) The nucleation probability corresponding to the temperature and pressure profiles derived for SOIR profile 691.1, from the 12th March 2008 at 86.6° latitude from Mahieux et al. (2015). We show the nucleation probabilities according to two potential mechanisms of CO$_2$ ice particle formation: first, is the direct nucleation of CO$_2$ on MSP according to KNT (section 2.4), and second, the nucleation of ASW on MSP followed by the nucleation of CO$_2$ on H$_2$O ice (section 2.1 and 2.2).

### 2.3 Competition between homogeneous and heterogeneous nucleation of ASW

We have shown that both homogenous and heterogeneous nucleation of ASW particles are feasible in the upper atmosphere of Venus. Here we examine which of these two mechanisms is likely to be more important in producing ice particles. In Figure 4 we show the number concentration of ASW particles resulting from both homogeneous and heterogeneous nucleation after 1 hr of constant conditions defined by SOIR profile 691.1. The number that nucleates heterogeneously is defined by the concentration of available MSP particles, which we have set at
100 cm\(^{-3}\) here. This number is insensitive to time, since for most of the cloud layer the probability of nucleation is unity for a 1 second interval. In contrast the number concentration of particles that nucleate homogeneously increases in proportion with time. For SOIR profile 691.1, homogeneous nucleation produces around 3 cm\(^{-3}\) ASW particles in one hour, whereas heterogeneous nucleation produces far more (depending on the assumed MSP concentration). If the cold pocket persisted for a day one would expect (3 cm\(^{-3}\) x 24) 72 cm\(^{-3}\) ASW particles over the course of the day. Sedimentation would then deplete the concentration, but there would be a persistent ASW production until the growth of ASW particles depleted the water partial pressure. In addition, it might be expected that cloud formation and sedimentation might deplete the MSP particle population, making homogeneous nucleation relatively more important. Given the uncertainties in the rate of homogeneous nucleation and temperature measurements in Venus’ atmosphere, as well as the MSP concentration, we cannot rule homogeneous nucleation out as making a significant contribution to the ASW particle population however, if MSP are present then the calculations indicate that heterogeneous nucleation will produce the majority of ASW particles in the upper atmosphere of Venus.

Figure 4. The competition between homogeneous and heterogeneous nucleation of ASW particles assuming conditions remain constant for 1 hour. The number concentration resulting from heterogeneous nucleation is defined by the product of probability of nucleation and the number concentration of MSP particles of 0.4 nm (which we assume is 100 cm\(^{-3}\)). The temperature and pressure profile correspond to SOIR profile 691.1.

2.4 CO\(_2\) particle formation on carbonate MSPs from Kinetic Nucleation Theory

In the section above we established that a plausible mechanism for the formation of CO\(_2\) ice particles is via the nucleation of ASW and the subsequent nucleation of CO\(_2\) on those nanoscale ASW particles. Here we further explore the direct formation of CO\(_2\) ice on MSP. In Figure 3a
we showed, based on the data of Nachbar et al. (2016), that nucleation on MSP composed of iron oxides and silica occurred 40 K lower than ASW on MSPs; hence is unlikely to be an important process. However, in a CO$_2$ rich atmosphere like that of Venus we expect meteoric smoke and MSPs to be composed of metal carbonates rather than oxides (Plane et al., 2018), and hence we need to consider the nucleation of CO$_2$ ice on metal carbonates. We were not able to find the pertinent physical data for the wetting properties of metal carbonate MSPs, so instead have used KNT. KNT is a bottom-up approach where the kinetics of adsorption and desorption of molecules to a cluster are treated explicitly (Bromley et al., 2016).

In these calculations the INP were assumed to be MgCO$_3$ and FeCO$_3$ which have already been discussed as likely MSP building blocks in the analogous atmosphere of Mars (Plane et al., 2018). The size of these seed particles was fixed at a radius of 0.35 nm, corresponding to a single MgCO$_3$ molecule with three CO$_2$ molecules bound to it (Plane et al., 2018). Because of the very large dipole moment of MgCO$_3$ ($\mu_D = 11.6$ Debye), these CO$_2$ molecules are strongly enough bound for the MgCO$_3$(CO$_2$)$_n$ complex to be stable at temperatures below 150 K (Plane et al., 2018). Rate coefficients for the addition of subsequent CO$_2$ molecules up to MgCO$_3$(CO$_2$)$_{40}$ were then calculated using Rice Ramsperger Kassel Markus (RRKM) theory (Gilbert & Smith, 1990) with a solution of the Master Equation based on the inverse Laplace transform method (De Avillez Pereira et al., 1997). Electronic structure theory calculations (Frisch et al., 2016) were used to compute the vibrational frequencies of the small clusters up to $n = 4$. See Appendix B for details of these calculations and the derivation of the uptake coefficient, $\gamma$, for CO$_2$ attachment to an MgCO$_3$(CO$_2$)$_n$ cluster, and the rate of evaporation of the new cluster (i.e. MgCO$_3$(CO$_2$)$_{n+1}$ $\rightarrow$ MgCO$_3$(CO$_2$)$_n$ + CO$_2$). Although $\gamma$CO$_2$ is estimated to approach unity for cluster sizes larger than $n = 15$ at temperatures below 150 K (Figure B1a), we limit the value here to $\gamma$CO$_2$ $\leq$ 0.1 to allow for the high pressure limiting attachment rate of CO$_2$ for MgCO$_3$(CO$_2$)$_n$, being lower than the hard sphere collision frequency (Smith, 1980). $\gamma$CO$_2$ and the evaporation rate were computed at a pressure of $1.33 \times 10^{-3}$Pa ($10^{-5}$ Torr), which is the typical pressure at ~150 km in Venus’ atmosphere (Mahieux et al., 2015). $\gamma$CO$_2$ at a lower altitude was then scaled by the relative atmospheric density, up to the limit of 0.1. The evaporation rate was then computed by detailed balance with the CO$_2$ attachment rate, with an equilibrium constant calculated by statistical mechanics with the partition functions for MgCO$_3$(CO$_2$)$_{n+1}$ and MgCO$_3$(CO$_2$)$_n$, using the vibrational frequencies and rotational constants described in the SI. For clusters larger than $n = 40$, $\gamma$CO$_2$ was set to 0.1 at all temperatures below 180 K, and the equilibrium constant (and hence the evaporation rate) estimated from the Antoine relation for gas-phase CO$_2$ above the solid (Chicko, 2022; Giauque & Egan, 1937).

The conditions under which CO$_2$ particle growth becomes favourable are indicated in Figure 3. MSPs can provide a site where a CO$_2$ cluster is stabilised leading to growth of CO$_2$ particles at temperatures below about 95 K at 122 km. The initial cluster is non-crystalline, but on subsequent growth this material is likely to deposit as crystalline CO$_2$. However, if heterogeneous nucleation of ASW particles is as effective as indicated by our CNT formulation and the study of Duft et al. (2019), then the majority of MSP particles would already have activated to form nanoscale ASW particles. On the other hand, if the atmosphere were dehydrated by a previous cloud event, then new MSP particles might nucleate CO$_2$ in preference to ASW. Nevertheless, the most likely route to CO$_2$ particles is nucleation of CO$_2$ on ASW particles.
2.5 Planetary wide viability of H₂O and CO₂ ice particle formation

In order to assess the geographical distribution and occurrence frequency of cloud formation conditions, we have plotted the SOIR profiles from Mahieux et al. (2015), broken down into latitude bands and morning or evening terminator, in Figure 5. The SOIR temperature profiles are then compared to the threshold temperatures at which ASW and crystalline CO₂ become saturated (the phases that are expected to make up clouds) as well as the temperature at which the nucleation rate of ASW on 1.0 nm ASW particles and CO₂ on 5 nm ASW particles is equal to 1 s⁻¹ (equivalent to a nucleation probability in 1 s of 0.63).

While there is considerable variability of the temperature profiles, many of the profiles exhibit a minimum around 120-130 km with a value below the temperature required for the nucleation and persistence of both ASW and CO₂ ice particles (see Figure 5 and Figure 6). On average across all latitudes, 64% of the profiles indicate that the atmosphere is supersaturated with respect to ASW in a layer ~5-10 km deep. Nucleation of ASW on MSPs is also possible in 51% of the profiles on average. The sedimentation velocity of a 5 nm ASW particle at 120 km is 0.7 m s⁻¹, hence these particles would form a layer 5-10 km layer thick and have a lifetime with respect to sedimentation on the order of hours. This indicates that clouds composed of nanoscale ASW particles should be a regular feature of the atmosphere of Venus at around 120 km at all latitudes.

Nucleation of CO₂ on ASW particles is also remarkably frequent, occurring in 27% of the profiles on average. The frequency of CO₂ nucleation has a latitude dependence, with ~30-40% of profiles between 60°-90° dipping below the threshold required for nucleation of CO₂ on 5 nm ASW particles. Even at low latitudes (0-30°), ~8% of profiles were sufficiently cold for nucleation of CO₂ on ASW. Hence, CO₂ cloud formation is also relatively frequent at all latitudes. We now turn our attention to the properties and lifetime of these clouds and if they should be observable with contemporary satellite instruments.
Figure 5. Latitude (0-90°) and time of day dependence (morning terminator in purple or evening terminator in green) of saturation point temperature for crystalline CO$_2$ and ASW and of the nucleation activation temperatures (where $J_{het} = 1$ s$^{-1}$, corresponding to a nucleation probability of 0.63 in 1 s; we show values for nucleation of ASW on 1.0 nm MSP particles and CO$_2$ on 5 nm
ASW particles). Temperature profiles are taken from Mahieux et al. (2015) and the mean morning terminator pressure profiles from the same paper are used to derive the saturation temperatures and the nucleation activation temperatures.

Figure 6. Probability of atmospheric temperature falling below the H$_2$O and CO$_2$ frost points, and that required by CNT for particle nucleation above 100 km, using the observed temperature profiles from the data set of Mahieux et al. (2015). The probability is defined as the fraction of individual SOIR profiles where the temperature dropped below the respective frost point or nucleation threshold (see Figure 5). These probabilities are cumulative, meaning that when the SOIR temperature profile being below the CO$_2$ frost point, for example, the atmosphere is also supersaturated with respect to ASW.

3 Modelling ice particle evolution in Venus’ upper atmosphere

In order to explore the evolution of the CO$_2$-ice clouds (the VMCs), a 1-dimensional model was constructed which describes the nucleation, growth, sedimentation and sublimation of the ice particles. The model is described in appendix C. The model is initiated with vertical profiles of atmospheric density and temperature determined using the SOIR instrument (Mahieux et al., 2015) that had a deep temperature minimum (< 90 K) so that CO$_2$ would have been highly supersaturated. Figure 3 shows that under these conditions nucleation of CO$_2$ ice particles occurs, either directly on MSPs or on ASW particles that had earlier nucleated on MSPs. Since the concentration of ASW particles depends on the concentration of MSP particles both pathways to formation of CO$_2$ ice particles would produce similar VMCs. Hence, our 1-D microphysical model produces CO$_2$ ice crystals through the direct nucleation on MSP, but the results would be similar for the case where CO$_2$ nucleates on ASW particles. Once CO$_2$ particles are nucleated, the model follows the fate of the particles as they grow, sediment and finally sublimate on entering a warmer region.
Figure 7 shows examples of model output, corresponding to two examples of cloud that can be produced from the observed SOIR temperature profiles. The first example peaks around 120 km with particles around 100-200 nm radius; and the second type persists for longer and peaks around 110 km, with particles that can exceed 2 μm in radius. The first cloud category is produced by deep, but relatively sharp temperature minima above 120 km (e.g. orbit 671.1). In contrast, the much larger particles in the second cloud category are produced by much broader temperature minima, in this case between ~112 and 122 km (e.g. orbit 1581.1). Figure 7b shows the time evolution of the particle size and height, for these two examples. The first cloud only lasts for ~350 s, and the second type lasts for around 1200 s (20 mins). The latter example is the most pronounced cloud that was generated in the model from the SOIR dataset (orbit 1581.1 at 87.3° on the 19th August 2010), but is still relatively short-lived because sedimentation is so rapid in this altitude range. Figure 8 also illustrates a composite of clouds predicted for multiple SOIR profiles at 70-80° and 80-90° bands (north and south), showing that these clouds all have similar features, with small CO₂ particles at higher altitudes that rapidly grow and sediment until they sublime 5-10 km below the cold point. Note that the depth of clouds at 80-90° is generally greater than clouds at 70-80°, as a result of the broader temperature minimum at higher latitudes.
Figure 7. The microphysics of CO$_2$ ice clouds (a) Modelled CO$_2$ particle nucleation, growth, sedimentation and sublimation for the temperature profile of orbit 671.1 at 82.9° (solid lines), and orbit 1581.1 at 87.3° (dashed lines). (b) Time evolution of the radius and height of the CO$_2$ particles ($\gamma$CO$_2 = 0.1$, MSP concentration = 100 cm$^{-3}$).
Figure 8. Modelled particle nucleation, growth and sedimentation of CO\(_2\) particles initiated with multiple observed temperature profiles from the dataset of Mahieux et al. (2015) using \(\gamma_{CO_2} = 0.1\) at varying latitude ranges.

4 Detectability of CO\(_2\) ice clouds

We have shown that conditions exist in the upper mesosphere of Venus where CO\(_2\) clouds composed of ice particles in the 100s nm to micron sizes can form. We now address the question of whether these VMCs should be observable. The best chance of detection is likely through satellite observations of optical extinction. In this section we evaluate the possibility of detecting these high-altitude clouds in existing datasets by calculating the extinction by CO\(_2\) ice particles using Mie theory. Venus Express had a suite of three instruments onboard that profile cloud and haze layers at lower altitudes on Venus. The first two are the UV and near-IR channels of the SPICAV instrument (Spectroscopy for the Investigation of the Characteristics of the Atmosphere of Venus) (although we do not include the near-IR channel in our current analysis). The UV channel has a wavelength range of 118-320 nm, and it performs stellar and solar occultations in addition to nadir and limb observations. The third instrument is SOIR (Solar Occultation in the InfraRed) which measures across the near- to mid-IR from 2.2-4.3 um (or 2200-4400 cm\(^{-1}\)) in solar occultation only. SPICAV has provided observations of the cloud and haze layers of Venus (Luginin et al., 2016; Wilquet et al., 2012; Wilquet et al., 2009), and SOIR observations were used also by Wilquet et al. (2009, 2012) and (Takagi et al., 2019). (Takagi et al., 2019) observed an increase in aerosol mixing ratio above 100 km, whereas the other studies reported results on clouds and hazes only at altitudes below 100 km. For the purposes of our Mie calculations we have selected the wavelength at 220 nm for SPICAV-UV and at 3320 nm for SOIR; both instruments have a similar detection limit around \(1 \times 10^{-5}\) km\(^{-1}\) (Wilquet et al., 2009).

We evaluate the detection probability of H\(_2\)O core (1 nm radius) CO\(_2\) shell particles that might form in at an altitude of 120 km by determining the Mie extinction cross sections of individual
particles as a function of radius. We use refractive indices for CO$_2$ taken from Warren (1986), and those for water ice at 220 nm and 3320 nm from Kofman et al. (2019) and Warren and Brandt (2008), respectively. At 220 nm the water ice refractive indices were measured specifically for low density amorphous (LDA) ice at 70 K (Kofman et al., 2019).

In Figure 9 we show the extinction for CO$_2$ particles at varying radii and particle concentrations. Figure 7 shows that CO$_2$ particles often grow into the 100s nm range, hence extinction above the detection limit at both 220 nm and 3320 nm is possible with a sufficiently high number concentration. However, at 220 nm extinction exceeds the detection limit for much smaller particles and for lower number concentrations. For example, for CO$_2$ ice particle concentration of 100 cm$^{-3}$, detection at 220 nm using SPICAV-UV would occur when the particles were larger than ~25 nm, whereas for detection at 3320 nm with SOIR the particles would need to be above ~160 nm.

We now evaluate the detectability at 220 nm of the clouds modelled in the previous section and the sensitivity of the results to the CO$_2$ uptake coefficient ($\gamma$CO$_2$) and the MSP particle concentration. In the previous section $\gamma$CO$_2$ was set equal to 0.1. Figure 10(a) illustrates the sensitivity of the cloud formation to $\gamma$CO$_2$, for the atmospheric temperature/density profile from orbit 671.1 used previously, and with the MSP particle concentration fixed at 100 cm$^{-3}$ between 110 km and 130 km. As expected, the peak particle size varies with $\gamma$CO$_2$, for example when
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$\gamma$CO$_2$ is decreased by a factor of 100 from 0.1 to $10^{-3}$ the peak particle size only decreases by a factor of $\sim$10, and the peak height is essentially unchanged. This variation has consequences on the detectability of the particles. Figure 10(b) shows the optical extinction at 220 nm of the cloud as a function of $\gamma$CO$_2$ for the same atmospheric profile. The Mie extinction is a strong function of particle size, and so this cloud would be barely detectable (for the SPICAV-UV detection limit of $10^{-5}$ km$^{-1}$) if $\gamma$CO$_2$ was less than 0.005.

In addition to the particle size, particle concentration plays a role in the detectability of the clouds. In Figure 11 we test the sensitivity of the modelled cloud extinction to the assumed number of MSP particles, with $\gamma$CO$_2$ fixed at 0.1. In this case, the cloud would not be detectable if the MSP number density fell below $\sim$1 cm$^{-3}$. However, the MSP concentration is probably much higher than this because a similar quantity of metal atoms is predicted to be injected via meteoric ablation into the upper atmospheres of Venus and Earth (12.6 and 8.3 tonnes d$^{-1}$, respectively), and the MSP concentration in the terrestrial mesosphere above 75 km is around 2000 cm$^{-3}$, based on rocket-borne charge particle measurements and modelling (Plane et al., 2014).

These sensitivity studies show that even if either the concentration of MSPs or the uptake coefficient $\gamma$CO$_2$ were a couple of orders of magnitude lower than for the standard model run, the resulting CO$_2$-ice clouds would still be detectable. However, it is their very short lifetime of only minutes, which would need to coincide with a satellite observation, which will make the detection of these clouds challenging. The model results of (Listowski et al., 2014) revealed similar short lifetimes for mesospheric CO$_2$ clouds on Mars that were dictated by the duration of the supersaturated cold pockets. They concluded that the scarcity of cloud observations among the hundreds of supersaturated temperature profiles observed by SPICAM was very probably due to the short lifetimes ($< 1 - 2$ hours) of the cold pockets formed by upward propagating gravity waves, and of the clouds themselves that rapidly evaporate in subsaturated conditions (10-20 minutes) (Listowski et al., 2014). If the cold pockets on Venus are a result of similar gravity waves as on Mars, the cold pocket lifetime of 1-2 hours is a lower limit. According to our simulations (see Figure 8) this cold pocket duration is sufficiently long for a detectable cloud to form, sediment to a subsaturated environment and evaporate ($< 20$ minutes). Nevertheless, the satellite observation would need to happen exactly at the right time and in the right place to be able to catch these ephemeral clouds.
Figure 7. Sensitivity of (a) CO$_2$ ice particle growth, and (b) optical extinction at $\lambda = 220$ nm, to the CO$_2$ uptake coefficient ($\gamma$CO$_2$) for the conditions of orbit 671.1 (82.9° latitude) from Mahieux et al. (2015). Number density of MSP particles $= 100$ cm$^{-3}$. The grey line in (b) shows the detection limit ($1 \times 10^{-5}$ km$^{-1}$) of the SOIR instrument onboard Venus Express.
Figure 8. Extinction of CO$_2$ ice particles at $\lambda = 220$ nm, for a range of MSP particle concentrations for the conditions of orbit 671.1 ($\gamma_{CO_2} = 0.1$) from Mahieux et al. (2015). The grey line shows the estimated detection limit of the SOIR instrument onboard Venus Express.

3. Conclusions

The upper mesosphere of Venus between around 110 and 125 km is frequently cold enough that the atmosphere is supersaturated with respect to both water and CO$_2$ ices. In fact, the supersaturations become sufficiently large that both ASW H$_2$O ice and CO$_2$ ice can nucleate. Based on a combination of classical and kinetic nucleation theory we propose that there is a persistent ASW H$_2$O cloud layer on Venus around 10 km deep centered around 120 km. These ASW particles may form both from heterogeneous nucleation on meteoric smoke particles, or can form homogeneously directly from the vapour phase if the temperature minima persist for longer than a few hours. The ASW cloud particles are unlikely to grow larger than ~5 nm given the limited amount of water vapour present in the upper mesosphere of Venus. Hence, we suggest that there is a persistent sub-visible layer of water ice particles, composed of ASW covering around 50% of Venus at all latitudes. This 50% value is derived assuming the terminator pressure and temperature measurements from SOIR are representative of other times of the Venus day.

We also present evidence that CO$_2$ ice crystals can nucleate on either ASW particles or even bare meteoric smoke particles. At latitudes greater than 60° (N and S) nucleation on ASW particles can occur in more than 30% of the SOIR profiles. Since CO$_2$ is the primary component of Venus’ atmosphere, CO$_2$ particles will grow rapidly to 100s nm in only minutes. However, these clouds will only have a lifetime of ~10-20 minutes since sedimentation is very rapid in the thin upper mesosphere of Venus. These CO$_2$ ice particles are most likely composed of crystalline CO$_2$ ice-I and will likely have a cubic, octahedral or cubo-octahedral shape (Mangan et al.,
These clouds may also produce halos that are unique to carbon dioxide crystals, as recently suggested for Mars (Ding et al., 2023). To an observer, VMCs might appear similar to cirrus uncinus (mares’ tails) on Earth where nucleation occurs close to the temperature minimum, followed by sedimentation and growth and subsequent sublimation of the ice crystals as they fall into a subsaturated warmer region. Any wind shear would give the fall streaks curvature (uncinus), where falling ice crystals are blown laterally as they sediment.

We have explored if VMCs might be observable with instruments on Venus Express. We find that the extinction will be large enough to observe at both 220 nm (SPICAV) and 3320 nm (SOIR), however the probability of an observation occurring in the 10-20 minutes that a cloud was present would be small. Nevertheless, we recommend that analysis of satellite date should be extended to altitudes where VMCs are predicted to occur, and that VMCs should be a target for future missions to Venus.

Given the strong sedimentation of VMC particles, VMCs have the potential to redistribute material in the upper atmosphere of Venus. Since nucleation of CO$_2$ on ASW with meteoric smoke cores is a likely mechanism for their production, VMCs are likely to transport MSPs to lower altitudes where they will be released in relatively narrow layers on the sublimation of CO$_2$ ice crystals. The formation of CO$_2$ crystals may also lead to the uptake of gas-phase meteoric species, which would also be released in a particulate form as the cloud particles sublimed at the base of the cloud layer (Mangan et al., 2017a). Similarly, VMCs will redistribute water vapour downwards, although the efficiency with which VMCs serve as a ‘cold trap’ will depend on the extent to which ASW particles can quench the supersaturation. On Earth, mesospheric clouds redistribute water downwards, resulting in a layer of enhanced water vapour at the base of the clouds, affecting odd oxygen and hydrogen chemistry (Murray & Plane, 2003; Murray & Plane, 2005). The extent to which VMCs limit the loss of water to space form Venus’ atmosphere should be the subject of more detailed microphysical modelling constrained by observations.

Overall, this work reveals that there is a complex cloud system that forms in the upper mesosphere of Venus around much of the planet, involving both water and CO$_2$ ice particles. We predict a ubiquitous layer of nanoscale water ice particles that forms both homogeneously and heterogeneously and then provides the substrate on which CO$_2$ VMC particles can nucleate. The resulting crystals of CO$_2$ grow rapidly to sizes where they can fleetingly scatter light at a detectable level before sedimenting into a warmer layer where they sublimate.
Figure 12. Formation and dissipation of Venusian mesospheric clouds. Meteoric smoke particles nucleate nanoscale amorphous ice particles, followed by the nucleation of CO$_2$ on those particles. The CO$_2$ crystals rapidly grow, probably with a cubic, octohedral or cubo-octohedral shape, then sediment and release the meteoric smoke particles as they sublime in a warmer part of the atmosphere.

Acknowledgments

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Open Research

We have included all relevant equations and physical quantities to reproduce the plots in this paper in the appendicies.
Appendix A. Classical nucleation theory formalism

In this section we describe the nucleation theory we have applied to the atmosphere of Venus for both nucleation of CO$_2$ and H$_2$O phases and give the pertinent parameters in Table 1.

Homogeneous nucleation

The CNT formulation we have chosen to use for homogeneous nucleation is based on the equations set out in Määttänen et al. (2005). The free energy of formation of a spherical cluster of molecules with a radius $r$ is described by

$$\Delta F_0 = -\frac{4\pi r^3}{3\nu}kT \ln S + 4\pi r^2 \sigma$$  \hspace{1cm} \text{Eq. A1}$$

Where $\nu$ is the molecular volume of the condensed phase, $\sigma$ is the interfacial energy between the condensed phase and the vapour phase, $k$ the Boltzmann constant, $T$ is temperature and $S$ is the saturation ratio. A cluster is said to reach a critical size when the volume term (the left hand term) starts to dominate over the surface term (the right hand term). At the critical size further growth by addition of monomers results in an increase in stability, hence the critical cluster size and free energy of formation can be derived

$$r^* = \frac{2\nu\sigma}{kT \ln S} \quad \Delta F^*_\text{hom} = \frac{16\pi\nu^2\sigma^2}{3(kT\ln S)^2}$$  \hspace{1cm} \text{Eq. A2}$$

The homogeneous nucleation rate is defined by an Arrhenius-like expression

$$J_\text{hom} = f_{\delta T}Z_\text{hom}\beta_\text{hom}c_{1,v}\exp\left(\frac{-\Delta F^*_\text{hom}}{kT}\right)$$  \hspace{1cm} \text{Eq. A3}$$

where $c_{1,v}$ is the concentration of monomers in the vapour phase. The dimensionless non-isothermal coefficient $f_{\delta T}$ as described in Feder et al. (1966) accounts for a reduction in the nucleation rate in cases when the atmospheric concentration of the nucleating species comprises a significant fraction of the total atmosphere. Higher collision frequency with the nucleating species compared to the inert carrier gas mean the heat of condensation is not efficiently removed from the cluster, leading to lower $f_{\delta T}$ values and therefore lower nucleation rates. In the case of water ice nucleation on Venus, given the low H$_2$O mixing ratio around 1 ppmv, the isothermal coefficient will be close to 1 and so have a minimal effect on the nucleation rate (Määttänen et al., 2005). Using the lowest value of 0.966 reported by Määttänen et al. (2005) for H$_2$O in the comparable case of Mars, increases the nucleation activation temperature by $< 0.1$ K. Using the lowest non-isothermal value of 0.006 reported for CO$_2$ ice nucleation (also for Mars) from (Wood, 1999), still only causes an approximate 0.3 K increase.

$Z_\text{hom}$ is the homogeneous Zeldovich factor that accounts for the decrease in rate of cluster formation when there is a finite rate of critical cluster formation and is define as

$$Z_\text{hom} = \sqrt[3]{\frac{\Delta F^*_\text{hom}}{3\pi k \cdot \sigma^2}}$$  \hspace{1cm} \text{Eq. A4}$$
Where $n^*$ is the number of molecules in the critical cluster. $\beta_{\text{hom}}$ describes the rate at which monomers collide with the cluster and is defined as

$$\beta_{\text{hom}} = c_{1,v} A \pi r^{*2} \frac{kT}{2\pi m_m} \quad \text{Eq. A5}$$

where $m_m$ is the molar mass.

**Heterogeneous nucleation**

The rate of heterogeneous nucleation induced via surface diffusion on a spherical nucleus ($J_{\text{het}}$, a per nucleating particle nucleation rate in units of $s^{-1}$), is given by:

$$J_{\text{het}} = A_N \delta_{\text{het}} Z_{\text{het}} \beta_{\text{het}} c_{1,v} \exp \left( -\frac{\Delta F^*_{\text{het}}}{kT} \right) \quad \text{Eq. A6}$$

where $A_N$ is the surface area of the ice nucleating particle and $c_{1,v}$ is the concentration of monomers on the particle surface; $\beta_{\text{het}}$ describes the diffusion of molecules on the particle surface, and the dissociation of a proportion of supercritical clusters is described by the heterogeneous Zeldovich factor $Z_{\text{het}}$. $\Delta F^*_{\text{het}}$ is the free energy of forming a critical cluster on the nucleating particle, given by:

$$\Delta F^*_{\text{het}} = f(m,x) \frac{16\pi \sigma^2 v^2}{3(kT \ln \tau)^2} \quad \text{Eq. A7}$$

$\Delta F^*_{\text{het}}$ is calculated relative to the homogeneous barrier ($\Delta F^*_{\text{hom}}$) with a reduction in the energy barrier by a factor $f(m,x)$ as described in Fletcher (1958), where $x$ is the ratio of the size of the nucleating particle to the size of the critical cluster and $m$ is the contact parameter (equal to $\cos \theta$, where $\theta$ is the contact angle between the ice nucleating particle and the nucleating phase (pertinent values of $\theta$ are discussed in the following section).

**Table 1. Physical properties of H$_2$O and CO$_2$**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ASW</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturation vapour pressure</td>
<td>$P_{\text{sat,hex}} = \exp \left( \frac{2312 - 1.6T}{RT} \right)$</td>
<td>(Nachbar et al., 2018)</td>
</tr>
<tr>
<td>Density</td>
<td>940 kg m$^{-3}$</td>
<td>(Ghormley &amp; Hochanadel, 1971)</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
<td>Source</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>---------------------------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>Surface tension</td>
<td>0.085 J m$^{-2}$</td>
<td>Derived from (Duft et al., 2019, pp. author-year)</td>
</tr>
<tr>
<td>Desorption energy on MSP</td>
<td>42 kJ mol$^{-1}$</td>
<td>(Duft et al., 2019)</td>
</tr>
<tr>
<td>Vibrational frequency</td>
<td>$10^{13}$ s$^{-1}$</td>
<td>(Pruppacher &amp; Klett, 1997)</td>
</tr>
<tr>
<td>Mean jump distance</td>
<td>0.32 nm</td>
<td>(Pruppacher &amp; Klett, 1997)</td>
</tr>
<tr>
<td>Contact parameter on MSP</td>
<td>0.999</td>
<td>Duft et al. (2019) suggest $m = 1$</td>
</tr>
<tr>
<td>Ice I$_h$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturation vapour pressure</td>
<td>$\exp(9.550426 - 5723.265/T + 3.53068 \ln(T) - 0.007283327T)$ (Pa)</td>
<td>(Murphy &amp; Koop, 2005)</td>
</tr>
<tr>
<td>Density</td>
<td>$(-1.3103 \cdot 10^6 \cdot T^3 + 3.8109 \cdot 10^7 \cdot T^2 - 9.2592 \cdot 10^5 \cdot T + 0.94040) \cdot 1000$ (kg m$^{-3}$)</td>
<td>(Murray &amp; Jensen, 2010)</td>
</tr>
<tr>
<td>Surface tension</td>
<td>0.141-0.00015T (J m$^{-2}$)</td>
<td>(Hale &amp; Plummer, 1974)</td>
</tr>
<tr>
<td>Desorption energy</td>
<td>17.5 kJ mol$^{-1}$</td>
<td>(Seki &amp; Hasegawa, 1983)</td>
</tr>
<tr>
<td>Vibrational frequency</td>
<td>$10^{13}$ s$^{-1}$</td>
<td>(Määttänen et al., 2005)</td>
</tr>
<tr>
<td>Mean jump distance</td>
<td>0.32 nm</td>
<td>(Pruppacher &amp; Klett, 1997)</td>
</tr>
<tr>
<td>Contact parameter on MSP</td>
<td>0.985</td>
<td>(Saunders et al., 2010)</td>
</tr>
<tr>
<td>CO$_2$ crystal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturation vapour pressure</td>
<td>$1.38 \cdot 10^{12} \exp(-3182.48/T)$ (Pa)</td>
<td>(Azreg-Aïnou, 2005)</td>
</tr>
<tr>
<td>Density</td>
<td>$1.72391-0.0002537-0.00000287T^2$ (g cm$^{-3}$)</td>
<td>(Mangan et al., 2017b)</td>
</tr>
<tr>
<td>Surface tension</td>
<td>0.08 (J m$^{-2}$)</td>
<td>(Nachbar et al., 2016; Wood, 1999)</td>
</tr>
<tr>
<td>Desorption energy</td>
<td>18.5 kJ mol$^{-1}$</td>
<td>(Nachbar et al., 2016)</td>
</tr>
<tr>
<td>Vibrational frequency</td>
<td>$2.9 \cdot 10^{12}$ s$^{-1}$</td>
<td>(Nachbar et al., 2016)</td>
</tr>
<tr>
<td>Mean jump distance</td>
<td>0.4 nm</td>
<td>(Nachbar et al., 2016; Wood, 1999)</td>
</tr>
<tr>
<td>Contact parameter on ice</td>
<td>0.95</td>
<td>(Glandorf et al., 2002)</td>
</tr>
</tbody>
</table>
Contact parameter on MSP  | 0.78  | (Nachbar et al., 2016)

**CO$_2$ liquid**

Saturation vapour pressure  | $=101325 \cdot 10^{-A}$  
$A = \frac{1353}{T} - 8.143 \cdot \log(T) + 0.006259 \cdot T + 24.619$  | (Dingilian et al., 2020; Michels et al., 1950)

Density  | $\ln\left(\frac{\rho'}{\rho_c}\right) = \sum_{i=1}^{4} a_i \left(1 - \frac{T}{T_c}\right)^{t_i}$  
$a_1 = 1.9245108; a_2 = -0.62385555; a_3 = -0.32731127; a_4 = 0.39245142; t_1 = 0.34; t_2 = 0.5; t_3 = 10/6; t_4 = 11/6; T_c = 304.1282; \rho_c = 467.6 \text{ kg m}^{-3}$  | (Dingilian et al., 2020; Span & Wagner, 1996)

Surface tension  | 0.0378 J m$^{-2}$  | Derived from fit to data in Dingilian et al. (2020), see text.

### Notes on the choice and derivation of physical properties of condensed phases of H$_2$O and CO$_2$

There are significant uncertainties associated with the physical properties of CO$_2$ and H$_2$O under the extremely low temperatures in Venus’s upper atmosphere. Hence, any predictions with CNT need to be taken in the context of these large uncertainties that propagate through into the nucleation rate. For the CNT formulations in this paper we have used a combination of physical properties used in previous nucleation studies and values derived from recent experimental data. The physical properties used in this study are detailed in Table 1. In the cases where physical properties were derived or there was a choice, the methodology and discussion is given below.

**Amorphous solid water:** The homogeneous nucleation of amorphous solid water was determined assuming a water mixing ratio of 1 ppm and the saturation vapour pressure was defined by (Nachbar et al., 2019) and Nachbar et al. (2018). In the past the parameterisation for the saturation pressure from (Murphy & Koop, 2005), where ASW and supercooled water were assumed to be a single continuous phase, was been used. However (Nachbar et al., 2019) show that ASW and supercooled water are two distinct phases of water and have distinct thermodynamics. Nachbar et al. (2018) showed that the vapour pressure of ASW is substantially greater than that predicted by the parameterisation given by (Murphy & Koop, 2005). Surface tension of ASW is not directly measured in the literature, and we used a value that we derived from literature data for the adsorption of ASW on MSPs (Duft et al., 2019); we discuss this
derivation in the heterogeneous section below. We set the non-isothermal constant to unity, which is probably an overestimate, but since we are attempting to identify which mechanisms are possible introducing a highly uncertain term that would reduce the rate would not be helpful.

Using a two-structure model of water (Hruby & Holten, 2004) produce a surface tension value of ~0.095 Jm\(^{-2}\) for water in the temperature regime associated with Venus’ upper mesosphere. Interestingly, they suggest that the temperature dependence of this value below ~120 K is weak. In a study where adsorption of ASW onto MSP particles was studied between 128 and 147 K (Duft et al., 2019) found that the surface tension was 0.094 ±0.011 J m\(^{-2}\). In order to derive a surface tension that was consistent with our CNT formulation we fitted to the data presented in (Duft et al., 2019). They report critical supersaturations where adsorption of water led to ice-activation. We interpreted the saturation at which we see a step change in the nucleation rate as being equivalent to the critical supersaturation reported by (Duft et al., 2019). The nucleation rate is very sensitive to the desorption energy and we have used an average value of 42 kJ mol\(^{-1}\) which is in the range reported by (Duft et al., 2019) for different MSP materials. This desorption energy is somewhat larger than used by (Määttänen et al., 2005) and reflects the strong binding of water molecules to the polar MSP surface. Given the critical cluster is only a few 10s of molecules in size, the assumption that all these molecules experience an enhanced interaction with the surface is reasonable (Duft et al., 2019). We also follow (Duft et al., 2019) in assuming that the MSP is wetted by ASW with \(m\) of 0.999. We fitted to reproduce the critical supersaturations in their Fig 6, yielding a surface tension of 0.085 J m\(^{-2}\), which is within the uncertainty of the values reported by (Duft et al., 2019). By constraining our CNT formulation to experimental data down to 120 K, we can have some confidence in the extrapolation to ~110 K where we predict nucleation in Venus’ atmosphere.

**Liquid CO\(_2\).** It is not immediately obvious that liquid CO\(_2\) should play any role in the atmosphere of Venus since bulk liquid CO\(_2\) can only exist at much greater pressures. However, recent experiments and computational studies have demonstrated that the initial cluster to form via homogeneous nucleation has liquid-like properties at temperatures pertinent to the upper atmosphere of Venus (Dingilian et al., 2020) (Halonen et al., 2021). In order to produce a CNT formulation that is consistent with the nucleation rate (and supersaturation) data presented in (Dingilian et al., 2020) we fitted the surface tension to the nucleation rate data between 78 K and 92 K. The average was 0.0378 ± 0.0014 J m\(^{-2}\). (Dingilian et al., 2020) fitted their data using a parameterisation for surface tension based on high-temperature data, that was then extrapolated to the low temperatures of their experiments, producing values of 0.050 to 0.054 J m\(^{-2}\). While there are uncertainties in these physical quantities, the pairing of the surface tension with our formulation of CNT to reproduce the experimentally observed nucleation rates under conditions close to those where clouds may form in Venus’ upper mesosphere gives us some confidence in our results.

**Appendix B: Rate coefficients for attachment and detachment of CO\(_2\) molecules to MgCO\(_3\)(CO\(_2\))\(_n\) clusters**

Rate coefficients for the sequential addition of CO\(_2\) molecules to MgCO\(_3\)(CO\(_2\))\(_3\), up to MgCO\(_3\)(CO\(_2\))\(_{40}\), were calculated with Rice Ramsperger Kassel Markus (RRKM) theory, using a
solution of the Master Equation based on the inverse Laplace transform method (De Avillez & Pereira et al., 1997). These MgCO$_3$(CO$_2$)$_n$ + CO$_2$ recombination reactions proceed via the formation of an excited adduct, which can either dissociate back to reactants or be stabilized by collision with a third body to form MgCO$_3$(CO$_2$)$_{n+1}$. The binding energy of each CO$_2$ to the cluster was fixed to 26.6 kJ mol$^{-1}$, which is the heat of sublimation of CO$_2$ at 0 K (Chicco, 2022; Giauque & Egan, 1937). The internal energy of the adduct was divided into a contiguous set of grains with a width of 12 cm$^{-1}$ (which reflects the small binding energy of CO$_2$ to the cluster), each containing a bundle of rovibrational states.

The density of states of the adduct was calculated using the Beyer – Swinehart algorithm (Gilbert & Smith, 1990) for the vibrational modes (without making a correction for anharmonicity). For each MgCO$_3$(CO$_2$)$_n$ cluster these modes were taken to consist of the vibrational modes of MgCO$_3$ (167, 490, 530, 673, 806, 903, 990, 1768 cm$^{-1}$) and the $n$ CO$_2$ ligands (676, 676, 1364, 2400 cm$^{-1}$ for each CO$_2$), calculated at the B3LYP/6-311+g(2d,p) level of theory (Frisch et al., 2016) and assumed to be independent of each other; and a further 5$n$ low-frequency modes set to a frequency of 80 cm$^{-1}$. This frequency represents the geometric mean of the frequencies of the “new” vibrational modes that are created when $n$ CO$_2$ molecules cluster with MgCO$_3$. The actual geometric means for $n$ = 2, 3 and 4 are 75.1, 83.2 and 78.5 cm$^{-1}$, respectively, using the data in Table S3 in the SI of Plane et al. (2018). The geometric mean is used because the density of states of the cluster is proportional to the inverse product of the vibrational frequencies (Gilbert & Smith, 1990). A classical densities of states treatment was used for the rotational modes. Since the clusters will be approximately spherical as they grow, the moments of inertia were approximated to be that of a solid sphere about its diameter:

$$I = 0.4Mr^2$$

Eq. B1

where $M$ is the mass of the cluster, and $r$ is the cluster radius assuming a density of 1562 kg m$^{-3}$ for solid CO$_2$ at 195 K.

Each grain associated with the adduct MgCO$_3$(CO$_2$)$_{n+1}$ was then assigned a set of microcanonical rate coefficients for dissociation back to MgCO$_3$(CO$_2$)$_n$ + CO$_2$. These rate coefficients are determined using inverse Laplace transformation to link them directly to $k_{rec}$, which is estimated here as the hard sphere collision frequency between MgCO$_3$(CO$_2$)$_n$ and CO$_2$, with a small $T^{1/2}$ temperature dependence (Smith, 1980). The probability of collisional transfer between grains was estimated using the exponential down model, where the average energy for downward transitions ($\Delta E$)$_{down}$ was set to 600 cm$^{-1}$ which is typical of M = CO$_2$ at 300 K, and treated as independent of temperature (Gilbert & Smith, 1990). The Master Equation, which describes the evolution with time of the grain populations of the adduct, was then expressed in matrix form and solved to yield the rate coefficients for sequential addition of CO$_2$ to the clusters, as a function of temperature (50 – 150 K) at a pressure of 10$^{-5}$ Torr, which is the typical pressure at ~150 km in Venus’ atmosphere (Mahieux et al., 2015).

For the purpose of atmospheric modelling, it is customary to use the uptake coefficient, $\gamma$. This was calculated as ratio of the recombination rate coefficient to the collision rate of CO$_2$ with a sphere of radius $r$:
\[ \gamma = \frac{k_{\text{rec}}[\text{CO}_2]}{(0.25 \bar{c} A)} \]  

Eq. B2

where \( k_{\text{rec}} \) is the recombination rate coefficient, \( \bar{c} \) is the mean collision speed between \( \text{MgCO}_3(\text{CO}_2)_n \) and \( \text{CO}_2 \), and \( A \) is the surface area of the cluster \( (4\pi r^2) \). \( \gamma \) is illustrated as a function of \( n \) and \( T \) in Figure B1(a). Note that \( \gamma \) does not exceed unity, which is a good test of the Master Equation calculation.

Finally, the rate of dissociation of the cluster i.e. \( \text{MgCO}_3(\text{CO}_2)_{n+1} \rightarrow \text{MgCO}_3(\text{CO}_2)_n + \text{CO}_2 \), was calculated by detailed balance with the recombination rate coefficient, where the equilibrium constant is calculated by statistical mechanics with the partition functions for \( \text{MgCO}_3(\text{CO}_2)_{n+1} \) and \( \text{MgCO}_3(\text{CO}_2)_n \) using the vibrational frequencies and rotational constants described above. The equilibrium constant is within 20% of that given by the Antoine relation (Chicko, 2022; Giauque \\& Egan, 1937) for clusters larger than \( n = 30 \) and \( T > 140 \text{ K} \) (where the Antoine relation is valid). The dissociation rate, i.e., the evaporation rate, is shown as a function of \( n \) and \( T \) in Figure B1b.
Figure B1. (a) $\gamma_{CO_2}$ as a function of temperature and number of CO$_2$ molecules clustered around a meteoric smoke particle. (b) Rate of evaporation (units: molecule s$^{-1}$) of CO$_2$ from an MSP-(CO$_2$)$_n$ cluster, as a function of temperature and the number of CO$_2$ molecules ($n$).
Appendix C: Details of the microphysical model

In order to explore the evolution of the CO\(_2\)-ice clouds, a 1-dimensional model was constructed which describes the nucleation, growth, sedimentation and sublimation of the ice particles. For this simple cloud model we describe the production of CO\(_2\) particles using the KNT theory presented in section 2.4. Hence, we implicitly assume that nucleation occurs on MSP, probably MgCO\(_3\) and FeCO\(_3\). Although we expect very similar results in terms of growth, sedimentation and lifetime of cloud particles if nucleation occurred on ASW particles which in turn nucleated on MSPs.

When the concentration of MSPs is larger than \(\sim 1000\ \text{cm}^{-3}\), the production of large CO\(_2\) particles with radii of a few hundred nm starts to deplete significantly the background CO\(_2\) density (this effect is accounted for in the model). Because the CO\(_2\) ice clouds are short-lived, coagulation of ice particles is neglected.

The sedimentation velocity of the MgCO\(_3\)(CO\(_2\))\(_n\) clusters and CO\(_2\) ice particles, \(w_i\), can be estimated using a form of Stokes’ law describing a spherical particle falling through a stationary fluid:

\[
w_i = \frac{2(\rho_p - \rho_{\text{air}})}{9\mu} g r_i^2 C_{\text{scf}}
\]

where \(\rho_p\) and \(\rho_{\text{air}}\) are the particle density (taken to be the density for solid CO\(_2\), which is 1562 kg m\(^{-3}\) at 195 K) and the air density, respectively; \(\mu\) is the dynamic viscosity of CO\(_2\) at the atmospheric temperature and pressure; \(g\) is the gravitational constant (8.87 m s\(^{-2}\) for Venus); and \(r_i\) is the particle radius. \(C_{\text{scf}}\) is the Cunningham slip correction factor accounting for the effects of drag on small particles, and is estimated from equation Eq.B2, where \(\lambda\) is the mean free path of the CO\(_2\) molecules, and \(A_1, A_2\) and \(A_3\) are dimensionless coefficients:

\[
C_{\text{scf}} = 1 + \frac{\lambda}{r_i} \left( A_1 + A_2 \exp\left(\frac{-A_3 r_i}{\lambda}\right) \right)
\]

References


