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Nanosilicates and molecular silicate dust species: properties and observational prospects

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Silicate dust is found in a wide range of astrophysical environments. Nucleation and growth of silicate dust grains in circumstellar environments likely involves species with diameters ranging from <1 nm (molecular silicates) to a few nanometers (nanosilicates). When fully formed silicate grains with sizes ~0.1 μm enter the interstellar medium, supernovae shockwaves cause collision-induced shattering which is predicted to redistribute a significant proportion of the silicate dust mass into a huge number of nanosilicates. This presumed population has thus far not been unambiguously confirmed by observation but is one of the main candidates for causing the anomalous microwave emission. By virtue of their extreme small size, nanosilicates and molecular silicates could exhibit significantly different properties to larger silicate grains, which could be of astrochemical and astrophysical importance. Herein, we briefly review the properties of these ultrasmall silicate dust species with a focus on insights arising from bottom-up atomistic computational modelling. Finally, we highlight how such modelling also has the unique potential to predict observationally verifiable spectral features of nanosilicates that may be detectable using the James Webb Space Telescope.

KEYWORDS

cosmic nanosilicates, interstellar dust, ultrasmall grains, circumstellar nucleation, astrophysical dust processing, IR spectra, microwave emission

Introduction

Cosmic dust, consisting mainly of sub-micron sized grains, permeates the interstellar medium (ISM) (Draine, 2003). Although contributing to only 1% of the mass of the ISM, dust has a disproportionately high impact, both astrophysically (e.g., shielding high energy radiation) and astrochemically (e.g., providing adsorption sites for chemical reactions) (van Dishoeck, 2014). The majority of ISM dust grains are formed from silicates (Henning, 2010), which encompass a wide class of solids formed from the interactions between anions based on silicon and oxygen (e.g., SiO_3^{2-}, SiO_4^{4-}) and cations. In astronomical silicates, the cations are mainly magnesium (Mg^{2+}) with a much smaller proportion of iron (Fe^{2+}) (Min et al., 2007). It is usually assumed that most silicate dust has stoichiometric pyroxene or olivine chemical compositions, for which $MgSiO_3$ (enstatite) and Mg_2SiO_4 (forsterite) are the corresponding Mg-based examples. Silicates with intermediate compositions have also been proposed (Fogerty et al., 2016). Observations suggest that the number of dust grains (n_g) in the ISM with respect to their diameter (d) approximately follows an inverse power relationship ($n_g \propto d^{-3.5}$) (Mathis et al., 1977), which massively favours higher populations

of smaller grains. Such a distribution can be rationalised by models which redistribute mass from larger grains into smaller grains by collisional shattering, leading to predictions that ~5% of the silicate dust mass in the ISM should end up in small nanosilicate grains with approximate sizes $d \leq 6$ nm (Jones et al., 1996). Considering infrared (IR) emission observations of the ISM, it has been estimated that small nanosilicates ($d \leq 3$ nm) could account for up to 10% of all silicon in the dust population (Li and Draine, 2001). Even if accounting for only a relatively small fraction of the total silicate dust grain mass in the ISM, nanosilicates could thus potentially dominate dust populations by number. Speculatively extrapolating such predictions would lead to the possibility that nanosilicates could be the most common class of solid object in the Universe. Herein, we focus on the smallest silicate dust species, ranging from molecular silicates containing a few atoms to nanosilicates, with approximate diameters ranging between 1–10 nm. When the dimensions of oxide materials are reduced to the nanoscale new structures and properties can emerge (Bromley et al., 2009). Compared to larger dust grains, nanosilicates are thus likely to have novel and distinct astrophysical and astrochemical impacts. Herein, we provide an overview what is currently known about molecular silicates and nanosilicates from an atomistic level, and how such knowledge can inform us on the prospects for their observational detection.

Due the extreme small sizes of nanoscale grain species it is often extremely difficult to characterise them experimentally. Here, atomistic level computational modelling can play an essential role in providing realistic nanoscale structural models and atomic/electronic level insights, which would be otherwise unobtainable (Bromley et al., 2014). Atomistically detailed nano-models can subsequently be used to calculate properties (e.g., atomic and electronic structures, chemical reactivity, spectroscopy), which can be compared with, and used together with, any available experimental/observational data. Even when the latter is unavailable, such bottom-up computational modelling can provide detailed predictions and helpful insights which can help to guide future experimental/observational research. In Figure 1 we show a range of ultrasmall silicate species for which atomistic computational modelling has provided a wealth of astronomical relevant information. Below we summarise results from selected studies on molecular silicates (<1 nm diameter) and nanosilicates with respect to: i) nucleation, ii) energetic processing, iii) chemical interactions and iv) spectroscopic signatures.
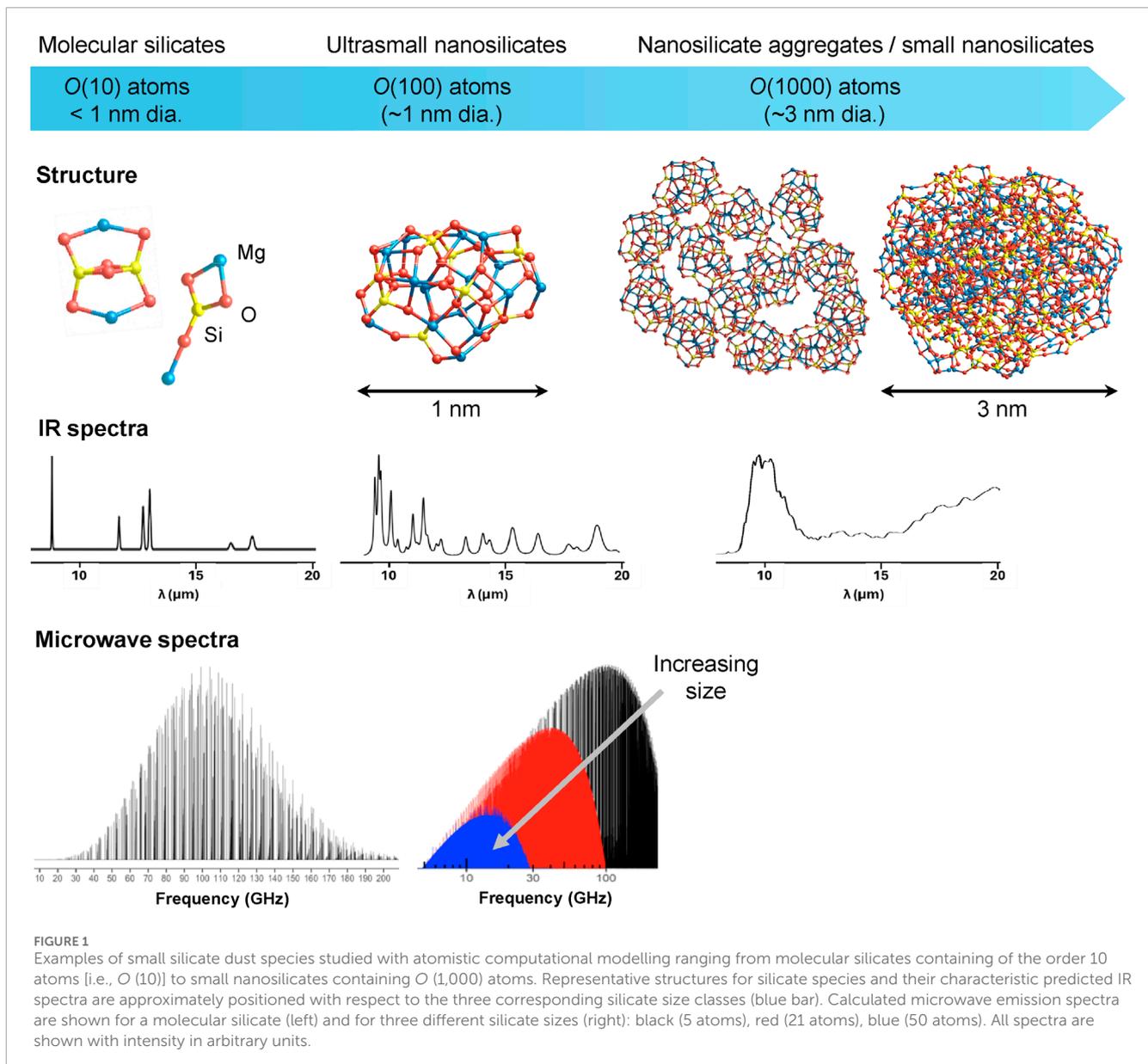
Nucleation and molecular silicates

Most silicate dust is thought to originate in the circumstellar envelopes of oxygen-rich M-type asymptotic giant branch (AGB) stars. Here, the excess oxygen strongly binds with abundant silicon atoms, leading to the formation of silicon monoxide (SiO) molecules (González Delgado et al., 2003). The formation of silicates should involve several chemical processes which enable the incorporation of Mg (and Fe) and the increase of a 1:1 silicon-to-oxygen stoichiometry in SiO monomers to that found in silicates (e.g., $MgSiO_3$, Mg_2SiO_4). These required chemical transitions suggest that silicate nucleation pathways likely involve

complex homogeneous molecular processes in the gas phase and heterogeneous processes on existing grains. Based on typical elemental abundances and physical conditions in a circumstellar silicate dust condensation zone (1,000–1,200 K, 0.1–0.001 Pa), the available chemical pathways for silicates are likely dictated by the abundance of stable oxygen-containing molecules (H_2O, OH and SiO), while Mg is stable in atomic form (Gail and Sedlmayr, 1986; Gail and Sedlmayr, 1998). Systematic searches using accurate computer modelling can reveal molecular silicate species resulting from the chemical reactions of these components which are stable under such conditions (Goumans and Bromley, 2012). Using this data, a general alternating oxidation/metal-incorporation silicate nucleation scheme has been proposed and validated in detailed kinetic nucleation theory models of dust formation in supernovae (Sarangi and Cherchneff, 2013) and AGB stars (Gobrecht et al., 2016), see Figure 2. At the high temperatures in circumstellar environments, the initial production of small silicon oxide molecules [e.g., $(SiO)_2$, Si_2O_3] is most difficult and is a bottleneck to subsequent nucleation (Bromley et al., 2016; Andersson et al., 2023). It is thus likely that the very first species that initiate circumstellar silicate nucleation are, as yet unidentified, extremely stable refractory seeds (e.g., Ti-based (Jeong et al., 2003; Goumans and Bromley, 2013; Plane, 2013) or Al-based (Gobrecht et al., 2022; Gobrecht et al., 2023) oxide species). We note that this does not rule out homogeneous SiO nucleation being involved in silicate dust formation in lower temperature environments [e.g., cold dense clouds (Krasnokutski et al., 2014), around Mira-type variable stars (Gail et al., 2016)].

At the end of their growth phase around evolved stars, silicate dust grains are thought to attain a typical radius of ~0.1 μm before they enter the ISM. The morphology of these grains is unknown but will depend on the efficiency of nucleation and growth, and the availability of monomeric species. For example, the highly inefficient monomeric-based growth of SiO_x grains can leads to a high number of nanosized particles, which can condense into larger fractal aggregates (Kimura et al., 2022). For silicates, laboratory studies show that dust formation often also proceeds via primary particles of a few nanometres in radius (i.e., nanosilicates), followed by rapid growth through agglomeration producing a smaller number of large fractal-like particles (Saunders and Plane, 2006). A similar nanosilicate aggregation process could potentially also play a role in dust (re)formation in the ISM (Rimola and Bromley, 2021). Relative to more spherical compact grains, such nanosilicate aggregates (see Figure 1) possess high surface areas and porosities which could have astrochemical implications (Potapov et al., 2024).

Energetic processing of silicate dust

Newly formed silicate dust from evolved AGB stars is thought to be Mg-rich, with an olivinic chemical composition (Dorschner et al., 1995) and with ~10% being crystalline (Molster et al., 2002). From analysis of IR spectra, the extent of crystallinity of silicates in the ISM is estimated to be between 0%–5% by mass (Kemper et al., 2004; Li et al., 2007), suggesting that the original crystalline fraction of the grain population is amorphized in the ISM. Laboratory experiments have shown that amorphisation of silicates could

FIGURE 1
Examples of small silicate dust species studied with atomistic computational modelling ranging from molecular silicates containing of the order 10 atoms [i.e., O (10)] to small nanosilicates containing O (1,000) atoms. Representative structures for silicate species and their characteristic predicted IR spectra are approximately positioned with respect to the three corresponding silicate size classes (blue bar). Calculated microwave emission spectra are shown for a molecular silicate (left) and for three different silicate sizes (right): black (5 atoms), red (21 atoms), blue (50 atoms). All spectra are shown with intensity in arbitrary units.

result from impacts from high velocity ions in supernovae shocks and heavy ions in cosmic rays (Demyk et al., 2001; Jäger et al., 2003a; Bringa et al., 2007). However, it is often overlooked that, below a certain size, nanosilicate grains are inherently not able to maintain long range crystalline order, thus being effectively amorphous. Energetically stable ultrasmall nanosilicates (≤1 nm diameter) of pyroxene and olivine composition have been confirmed to be inherently non-crystalline by accurate quantum chemical calculations (Maciá Escatller et al., 2019). Computational modelling of larger nanosilicate grains up to approximately 5 nm diameter, still show that amorphous structures obtained by thermal annealing are more energetically stable than crystalline nanograins (Zamirri et al., 2019). Aggregates formed from nanosilicate building blocks will thus also tend to be amorphous. Indications of crystallinity have been inferred in laboratory produced silicate grains with diameters of a few 10 s of nm, indicating a possible lower grain size for maintaining crystalline order (Ishizuka et al.,

2015). Generally, the fact that crystallinity is only possible in larger silicate grains should be considered when interpreting observed spectra.

In the diffuse ISM, dust grains are subject to energetic processing by supernovae shockwaves which lead to shattering in grain-grain collisions. Shattering leads to a redistribution of mass from a smaller number of larger grains into a larger number of smaller grains tending to lead to an abundance of nanosized grains (Jones et al., 1996). For porous nanosilicate aggregates, such processing would likely lead to disaggregation. Smaller grains are also more resilient than larger grains to shattering which could help them persist in the harsh conditions of the diffuse ISM (Jones et al., 1994). Shockwave-induced collisions and other processes can also lead to vaporization of grain mass into the gas phase (i.e., dust destruction). Models of grain processing typically predict that the estimated dust destruction rate in the ISM is significantly more than the stardust production rate (Slavin et al., 2015). This situation is clearly at odds with the observed

FIGURE 2
Possible thermodynamically viable initial steps in silicate dust nucleation starting from the SiO dimer (i.e., Si_2O_2) up to the pyroxene dimer (i.e., $Mg_2Si_2O_6$) molecular silicate. Steps show incorporation of Mg or O (via H_2O or OH) with respect to the previous step. The lowest energy structure is shown for all molecular species. See Goumans and Bromley (2012) for more details.

heating has been estimated to be up to ~1000 K (Draine and Li, 2001), with, as yet, unknown consequences for astrochemistry. We note that molecular silicates and ultrasmall silicates are found to be surprisingly structurally stable in molecular dynamics simulations at such elevated temperatures where they exhibit only small conformational changes (Mariñoso Guiu et al., 2021a; Oueslati et al., 2015). The temperature and emissivity of stochastically heated nanograins depends on the rates of UV energy absorption and subsequent IR emission, which, in turn is intimately linked to their specific heat capacity. Typical estimates of stochastic heating employ empirical fits to bulk silicate heat capacities (Draine and Li, 2001; Camps et al., 2015). The heat capacity of a system depends on the range of available vibrational modes, which is dramatically affected by size constraints in nanosized solids. Accurate quantum chemical calculation of vibrational modes in ultrasmall nanosilcates have shown that empirically fitted models tend to underestimate the stochastic heating of small nanosilicates by tens of Kelvin (Mariñoso Guiu and Bromley, 2022). This could imply that ultrasmall nanosilicates could be easier to detect by their IR emission than previously expected.

The strong UV field in the ISM can also lead to ionisation of small dust grains. Due to the dominance of photoelectric electron ejection over recombination in very small grains in the ISM, small nanosilicates are also likely to be positively ionized by their interaction with high energy UV photons (Weingartner and Draine, 2001). UV-induced charging of small grains has been suggested as a way to enhancing their role as seed species for dust (re)nucleation in the ISM (Zhukovska et al., 2016). Cationic molecular silicates have also been produced in cluster beam experiments and their structures and properties elucidated by quantum chemical calculations (Mariñoso Guiu et al., 2022). These studies also suggest that ionised molecular silicates could act as sinks for oxygen depletion, potentially contributing to the unresolved problem of the "missing" oxygen in the ISM (Whittet, 2010).

Chemical processing of silicate dust

Processing from ion irradiation (e.g., protons, He^+) in supernovae shocks also induces chemical tranformations in silicate dust grains in the ISM. From early laboratory studies of the effect of the solar wind on lunar surface silicate material, two important intertwined chemical processes were established to be the result of proton-iradiation: (i) the formation of hydroxyls (Zeller et al., 1996), and (ii) the depletion of magnesium and oxygen through preferential sputtering (Keller and McKay, 1997). Confirmation of these results has come from more recent experiments (Demyk et al., 2001; Jäger et al., 2003b; Bringa et al., 2007) and from analysis of interplanetary dust (Bradley, 1994). Hydroxylated silicate grains formed by such processing could also be relevant as potential reservoirs of water during the formation of planetary systems (Djouadi et al., 2011).

Starting from Mg-rich olivine nanograins, sputtering of magnesium and oxygen would tend to lead to a transformation towards a pyroxene-like chemical composition. Elevated levels of pyroxene (relative to the initial dominance of olivine) is consistent with estimates of the amorphous pyroxene fraction of the grain

abundance of dust in the ISM. The discrepancy probably reflects the large uncertainties in our estimates of dust lifetimes, based on our current understanding of dust formation/destruction (Jones and Nuth, 2011).

Through their interaction with the strong ultraviolet (UV) radiation field in the ISM, dust grains with sizes of only a few nanometres are also susceptible to sporadic temperature spikes (Duley, 1973). Stochastically heated nanosilicate grains with 10 nm diameters are expected to exhibit temperature fluctuations up to 20–40 K, which is predicted to have a significant impact on their role in astrochemical processes (Cuppen et al., 2006; Chen et al., 2018). For ultrasmall nanosilicates possessing only a few tens of atoms (≤1 nm diameter) the fluctuations in temperature from stochastic

population in the ISM (Kemper et al., 2004), and with the pyroxene-rich environments of protostars (Demyk et al., 1999). Combining chemical processing with energetic processing (i.e., shockwave-induced shattering and ionisation), the extreme end result would be molecular pyroxene-based cations (e.g., $MgSiO_3^+$). Higher proton-induced sputtering could potentially lead to extreme reduction of Mg^{2+} and hydroxyl formation from H^+ implantation, leading to $(Si_xO_yH_z)^+$ species. By approximately mimicking silicate dust grain processing occurring in the diffuse ISM by ablation/cooling of a mixed Si/Mg source in the presence of O_2, clusters based on discrete ionized pyroxene monomers ($MgSiO_3^+$) were readily formed (Mariñoso Guiu et al., 2022). Similar experiments, using a pure Si source and a small amount of water vapour, led to the production of small $(Si_xO_yH_z)^+$ clusters with one or two -OH groups (de Donato et al., 2024). This indicates that such ionised molecular silicate species could also be a common result of energetic and chemical processing in the ISM. More speculatively, such experiments could also suggest that molecular silicate formation from hot gas phase atoms could directly compete with dust destruction during energetic processing.

Quantum chemical calculations have also shown that formation of Si-OH groups is highly energetically favourable on pyroxene nanosilicates (Goumans and Bromley, 2011) and $(SiO_2)_N$ nanoclusters (Jelfs et al., 2013; Maciá Escatller et al., 2017). Such hydroxylation is likely to be a precursor stage to the subsequent formation of water ice mantles. However, UV irradiation is known to reduce hydroxylation of silica surfaces (Imai et al., 1996) and lead to water photodesorption. As such, high degrees of nanosilicate hydroxylation and water ice mantle growth are only likely to occur in interstellar clouds that are opaque enough to shield the intense UV field of the ISM. Bare nanosilicates (i.e., without mantles) been predicted to be able to promote dissociation and/or formation of H_2 molecules (Kerkeni and Bromley, 2013). Other theoretical studies have shown that such chemical processes can be significantly affected by the low degree of hydroxylation likely to be possible in the diffuse/translucent ISM (Kerkeni et al., 2017; Kerkeni et al., 2019).

Spectroscopic signatures of nanosilicates

Microwave emission

The best current observational evidence for the presence of nanosilicates is from their proposed role as the source of the anomalous microwave emission (AME) (Hensley and Draine, 2017; Hoang et al., 2016). The AME is a broad foreground ISM feature centred at around 30 GHz which is most likely to originate from a population of fast spinning nanosized grains with a sufficiently large dipoles (Ali-Haïmoud et al., 2018). Quantum chemical modelling has shown that nanosilicates (unlike most carbonaceous species) have high inherent dipoles. As such, it would only require 1% of the available silicon dust mass to be in ultrasmall nanosilicates to make them a viable source of the AME (Maciá Escatller and Bromley, 2020). Similar studies have shown that this results still holds if we consider weak hydroxylation of the nanosilicates (Mariñoso Guiu et al., 2021b). The lack of distinct features in

AME spectra means that a definite assignment to nanosilicates is difficult. However, for small molecular silicates with specific structures and high dipoles, the microwave emission spectrum would be more detailed and potentially assignable to specific species (e.g., pyroxene monomers) (Maciá Escatller and Bromley, 2020; Valencia et al., 2020). See Figure 1 for a comparison of microwave emission spectra expected for small molecular silicates and ultrasmall nanosilicates.

IR spectra

Interpretations of silicate dust IR observations typically employ laboratory-based measurements of bulk silicate samples. Such measurements confirm the typically-observed IR spectra of silicate dust characterised by two broad peaks at 9.8 μm (Si-O stretching mode) and 18–20 μm (O-Si-O bending mode) (Jäger et al., 2003b; Henning, 2010). Experimental IR spectra of laboratory produced silicate grains with diameters of a few 10 s of nm also show these characteristic modes (Ishizuka et al., 2015). For much smaller molecular silicates, IR spectra can also be obtained using cluster beam experiments. Here, the spectra exhibit sharp individual peaks which allow for accurate assignments of structure and composition via quantum chemical calculations. Clearly, between these two extremes there should be a size-dependent transition of the IR spectra of silicate dust.

Calculations suggest that the emergence of bulk-like double-peaked IR spectra should emerge for non-porous nanosilicate grains with diameters ≥5 nm (Zamirri et al., 2019), or upon aggregation of ultrasmall nanosilicates (Rimola and Bromley, 2021). This implies that the IR spectra of smaller nanosilicates should have specific non-bulk-like IR spectra, as explicitly confirmed by accurate quantum chemical modelling for ultrasmall nanosilicates. A summary of the size-dependency of IR spectra of small silicates is shown in Figure 1. As populations of ultrasmall silicates are expected to be extremely numerous, their cumulative IR spectra may be observationally discernible from the dominant IR signal of larger silicates. We note that the highly sensitive spectrometers of the Mid-IR instrument (MIRI) on the James Webb Space telescope (JWST) are well suited to probe the signature wavelength range for silicates (i.e., approximately between 8–20 μm). Using accurately calculated individual IR spectra of 10 s of ultrasmall nanosilicates, characteristic IR spectra of populations of ultrasmall nanosilicates with pyroxene and olivine compositions have been produced. Assuming that the silicate dust population has 3%–10% of its mass of Si in ultrasmall nanosilicates, several small but distinct influences on the bulk-like silicate IR spectra are predicted (e.g., increased intensity slightly above and below 9.8 μm) (Zeegers et al., 2023). In principle, such subtle effects should be detectable with JWST observations using MIRI, which should thus be able to confirm and/or place limits on the nanosilicate content of the diffuse ISM.

Summary

In summary, we highlight the importance of molecular silicates and nanosilicates in the formation and processing of larger silicate

dust grains. It is expected that these ultrasmall species should be prevalent in the ISM where their astrochemical influence could be highly significant. While currently lacking direct observational conformation of nanosilicates, we show the role that atomistic bottom-up computational modelling, often together with laboratory experiments, can play in providing detailed insights into these species. Looking to the future, we expect that the combination of computational modelling and detailed observations will be indispensable for confirming the presence and assessing the abundance of nanosilicates in the ISM and other astrophysical environments.

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SB: Conceptualization, Funding acquisition, Writing–original draft, Writing–review and editing.

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