Malcolm Walmsley

Astrophysics is a parasite science in some ways. It borrows from the work of others and often adapts results from the physical or chemical literature for its own purposes. Of course, the reverse situation can also occur, where astrophysical observations provide insight into physical or chemical processes both in space and elsewhere. Either way, this requires understanding both from the astronomers and the physicists or chemists about the aims and claims on the other side of the fence. This book aims at facilitating such understanding.

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The book is a compendium of articles discussing laboratory and theoretical work relevant for astrophysicists and will be useful for specialists of the interstellar medium (ISM) and circumstellar envelopes. It may also provide insight into basic physical and chemical processes. In this introduction, I will give a short overview of the interplay between interstellar astronomy and the study of fundamental physical processes. I will also review briefly some current questions of interest in the light of results from the HERSCHEL satellite as well as of the prospects of what may or may not be found with Atacama Large Millimeter Array (ALMA). Finally, I give a brief summary of the subjects treated in this volume.

One reason why astronomical observations can occasionally contribute to basic physics is that it is difficult to achieve in the laboratory pressures comparable to those found in the interstellar medium. A classical example was the discovery by Bowen in 1927 [1] that a series of unidentified lines from nebulae (originally discovered by Huggins in the nineteenth century, the so-called nebulium lines) were in fact forbidden (i.e., electric-dipole-forbidden) transitions of various ionization stages of O and N. These were strong in nebulae (but not in the laboratory) because the densities in ionized interstellar (HII) regions are sufficiently low that radiative decay is faster than collisions. Although they had not been detected in the laboratory, the wavelengths expected for such magnetic dipole transitions could be inferred from combinations with a third level (and thus the laboratory input was indeed critical) and compared with the astronomical results. The agreement was perfect!

Another astronomical identification was the discovery of interstellar molecular ions such as HCO⁺ (the former "X-ogen") in interstellar molecular clouds. This

was first detected at 3 mm (the 1-0 transition) in 1970 by Buhl and Snyder [2], and almost immediately Klemperer [3] realized what it must be. He estimated the bond lengths for HCO⁺ (from HCN and CO⁺) and the rotation constant which corresponded to a prediction for the 1-0 transition differing by 56 MHz from the observed astronomical frequency. I have always been amazed at the insight needed to make that equivalence. In any case, that astronomical result was rapidly confirmed by Woods *et al.* [4] in the laboratory. Moreover, Klemperer's work led to two landmark papers on interstellar chemistry from Solomon and Klemperer [5] and from Herbst and Klemperer [6]. This was the start of ion–molecule chemistry, which had great success in explaining many of the questions brought up by the astronomers exploiting millimeter-wavelength telescopes. Some of this early work is summarized in the review by Winnewisser *et al.* [7].

Astrochemistry has come a long way since the initial phases almost a century ago. One realizes this on reading some of the first papers on the topic. An example of this is the note by Swings and Rosenfeld in 1937 [8] entitled "Considerations regarding interstellar molecules". They were discussing the "new interstellar lines of rather diffuse origin" discovered by Merrill. Others who had contributed to the subject and whom they cite included Russell, Eddington, and Saha! Swings and Rosenfeld discuss a suggestion by Saha [9] that a band at 6283 Å (which later turned out to be a DIB (or diffuse interstellar band and just what these are is still a puzzle) could be due to Na₂ and attempt a calculation (using a modified Saha equation) of the likely abundance of interstellar diatomics. They concluded that CH, OH, NH, CN, and C_2 seem "promising" and make the case for the identification of a line at 4300 Å with CH (which turned out to be correct). They also note the pitfalls in using a Saha-type equation as well as the uncertainties in their estimates of the interstellar radiation density. It was, all in all, a very prescient article based on our present-day knowledge.

From an astronomer's standpoint, however, it may be that the biggest mystery of all is that of the nature, composition, formation, and destruction of dust grains (see Draine [10], Henning [11]). Because of their extinction and scattering properties, but also because of the processes that take place on their surfaces, they cannot be ignored. In different regions, the grains take on different forms; for example, there is good evidence that they grow to centimeter size in the pre-main-sequence (T Tauri) disks. At the other end of the scale, it is clear that nanometer-sized grains and PAHs (polycyclic aromatic hydrocarbons) make a large contribution to the observed extinction in the optical and UV as well as giving rise to spectacular emission features in the near- and mid- infrared (IR). In spite of this, it is clear that there are many gaps in our understanding of interstellar dust, and it may be interesting to mention some of them here. There are also several "mysteries" that need to be resolved before one can say that our grain models are realistic.

One of these concerns the "large grains." Are there big (1 μ m or larger) grains or "pebbles" out there? Models of the interstellar grain size distribution typically have a power-law size distribution with a cutoff at around 0.5 μ m. Much of the mass is in the largest grains with sizes in the range 0.1–0.5 μ m. However, the Ulysses and Galileo satellites have been directly detecting grains of apparent interstellar origin

with sizes as large as $1 \mu m$ or more (see Draine [12] for a summary). The number of these grains seems to be much larger that what is needed to explain interstellar extinction as well as the limits inferred from the amount of heavy elements depleted from the gas phase. Thus there is a problem, and resolving the controversy will not be easy. At face value, one needs fundamental changes to our generally accepted interstellar grain model, an error in the interpretation of the Ulysses and Galileo measurements, or a large inhomogeneity in the dust distribution close to the heliosphere. Clearly, new measurements of these micrometer-sized particles are needed.

The discrepancy, however, may just be part of our general lack of comprehension about how interstellar grains form and evolve. Why, after all, should there be an upper limit to the interstellar grain size distribution? The answer must lie in how grains are formed, are destroyed, and evolve. We think that grains have their origins in mass loss from giants and planetary nebulae, but it has been known for some time that this cannot compete directly with the grain destruction rate because of supernova shocks. Thus grains are not simply "stardust" but they manage to absorb refractory elements during their roughly billion-year lifetime in the ISM. Presumably, they accomplish this trick in molecular clouds where it also seems likely that they coagulate to form larger grains causing a "flattening" of the UV extinction curve. The details of how this happens are obscure, but it is surely true that finding out the answer will require an improved knowledge of grain surface processes as well as of the processes that destroy grains (sputtering, shattering in shocks, etc.). The complex physics of PAHs and of a variety of "organic grains" must also be part of the answer. It is any case encouraging to learn in the last chapter of this book (Jäger et al. 7) of the progress made in the study of dust formation in giant envelopes.

It is certainly also true that a real advance in our understanding of interstellar dust grain properties will come only with a solution of some of the unsolved puzzles that have bedeviled the subject for the best part of a century (see the recent article by Tielens [13] as well as this volume). One of these puzzles is to find a convincing identification for the well-known 220-nm feature in the extinction curve. It is fairly clear that it is due to a substance or molecular family with aromatic properties, and a possibility is that a family of PAH-type molecules similar to those causing the IR emission features (3.3, 7.6, $11.3 \,\mu$ m, etc.) is also responsible for the 220-nm absorption. However, convincing proof of this is lacking, and small graphitic grains are still a possible contender. The identification of the PAH features themselves is less controversial, but there are still some doubters and one still wonders whether the identification of an individual PAH may prove possible. Could one identify interstellar Coronene and, if so, how?

Another unsolved puzzle is, of course, that of the DIBs. These have resisted identification for almost a century despite the best efforts of many talented people. Again, it seems likely that the solution has to do with large organic molecules and that a large fraction of interstellar carbon is involved. The article by Rice and Maier in this volume discusses possible solutions. These questions are not simply amusing conundrums posed by Mother Nature but questions whose solution

has consequences for the makeup and evolution of interstellar grains. They also probably affect the carbon budget with likely consequences for gas-phase chemistry. One question that has been slightly "forgotten" in recent years is the origin of long-chain carbon compounds such as the cyanopolyynes which are abundant in certain (but not all) dark clouds in the vicinity of the Sun. Their abundance is certainly dependent on the C/O gas phase abundance ratio, and variations in this quantity are likely responsible for variations in the cyanopolyyne abundances. The suspicion is that all these questions are connected.

Will some useful input to these questions come from ALMA, HERSCHEL, Stratospheric Observatory for Infrared Astronomy (SOFIA), and other new instruments? HERSCHEL has already been and gone, and some of its answers were unexpected. Perhaps most unexpected were the results on the ions OH^+ , H_2O^+ , and so on, from HERSCHEL with important contributions from the Atacama Pathfinder Experiment (APEX) (see Gupta *et al.* [14] and Wyrowski *et al.* [15]). Figure 1.1 taken from Gerin *et al.* [16] gives a flavor of the first HERSCHEL results. These ions react with H_2 and hence have a short lifetime in molecular clouds. They, nevertheless, are detectable in diffuse gas (in absorption) and in some photon-dominated regions (PDRs). Their abundance is clearly related to the cosmic ray ionization rate as well as to the relative abundance of atomic and molecular hydrogen. It is amusing (and to some extent unexpected) that some of the main advances brought by HERSCHEL was to diffuse cloud science.

Of course, the unique contribution made by HERSCHEL to our understanding of interstellar chemistry has been that of providing reliable information on the distribution and abundance of water. It was already known from the Infrared Space Observatory (ISO), Submillimeter Wave Astronomy Satellite SWAS, and ODIN, as well as from ground-based studies, that gas-phase water H₂O usually contains a minor fraction of the available oxygen (e.g., Bergin *et al.* [17]). On the other hand, it is clear from fairly basic theory that in all molecular regions with temperatures above a threshold of around 300 K, any available atomic oxygen gets converted into water. One knows that such hot molecular regions exist. That is convincingly demonstrated by observations of hot molecular hydrogen seen in both pure rotational transitions (for example, by SPITZER) and in vibrotational lines seen by ground-based work in the near-IR. Does HERSCHEL confirm this?

The jury is still out on this, but the available evidence to date suggests not. The derived water abundance in the hottest layers traced in outflows is often only a few percent of reasonable estimates of the free oxygen abundance. There are, however, considerable uncertainties caused by complex geometry and radiative transport. It is also true that such hot molecular layers in shocked gas associated with outflows are subject to UV radiation fields capable of destroying the water just produced. It certainly seems to be true that the water abundance rises precipitously in shocks even if not to the level expected, and, also, estimating the column density of hydrogen in the water-line-emitting layers is not easy. One thing that has become clear is that photodesorption of water ice caused by incident UV radiation is a key process

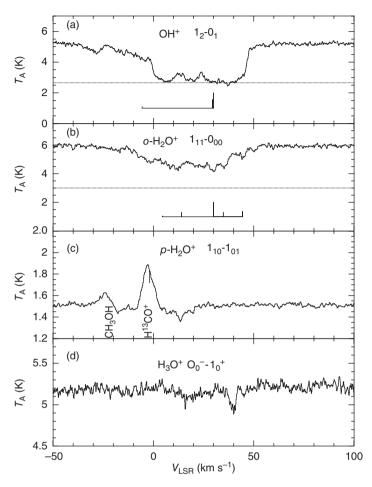


Figure 1.1 HIFI spectra [Reproduced with permission © ESO] of (a) OH⁺, (b) *o*-H₂O⁺, (c) *p*-H₂O⁺, and (d) H₃O⁺ toward the millimeter continuum source G10.6-0.4.

The hyperfine structure of the OH^+ and $o-H_2O^+$ lines is indicated on the upper two panels.

in determining the water abundance as is the (possibly associated) water photodissociation. Of course, H_2O is almost always the major ice constituent and hence this is of more importance for water than for other species. Nevertheless, it seems likely that photodesorption can influence the abundance of methanol and related species, and hence more precise rates for such processes will be needed. The work discussed by Linnartz and collaborators in this volume highlights recent developments in the area.

An example of the importance of understanding photodesorption is provided by the detection of ground-state water transitions toward the nearby (55 pc) disk around the 10 Myr old T Tauri star TW Hya (Hogerheijde *et al.* [18]) using the

HIFI (Heterodyne instrument for the Far Infrared) spectrometer on HERSCHEL. The detected water lines are narrow (1 km s^{-1}) (see Figure 1.2) and are likely from the outer disk at a radius of about 100 astronomical units (AUs) from the central K7 star. This is well beyond the water "snow line" (the radius in the disk outside which water is frozen out onto grain surfaces) and thus the observed lines are likely formed in an outer layer where water can be photodesorbed (more precisely an intermediate layer between the height at which water is photodissociated and that at which it is photodesorbed). The inferred ice reservoir is several thousand times the mass of the Earth's oceans and is thus consistent with suggestions that comets delivered the oceans to Earth. These inferences, however, depend sensitively on the assumed photodesorption yields as well as on grain settling.

TW Hya has been the subject of intense study with HERSCHEL, and another surprise was the detection by Bergin *et al.* [19] using the Photodetector Array Camera and Spectrometer (PACS) of the 1-0 rotational transition of hydrogen deuteride (HD) at 112 μ m. This is important because it provides constraints on the disk gas mass (and hence on the gas-to-dust ratio). One knows much more about dust than about gas in such young disks, and what one does know about the

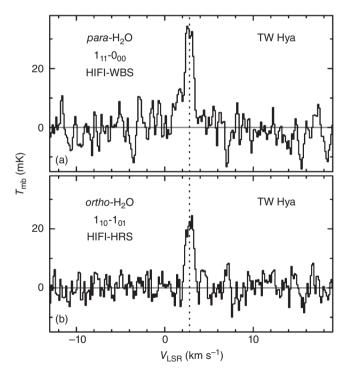


Figure 1.2 HIFI spectra [from [18], copyright 2011 © permission from American Association for the Advancement of Science] of water ground-state lines toward the

nearby pre-main-sequence disk TW Hya. The observed gas-phase water suggests the presence of an ice reservoir of several thousand Earth oceans in this object.

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gas (as in the case of water mentioned above) often just concerns a thin surface layer. This is partly true also for HD (the J = 1 level is 128 K above ground) and most of the emission comes from inside 80 AU. However, the conclusion seems to be that the disk is relatively massive and that the gas-to-dust ratio may not be far from the canonical ISM value of 100. But certainly this is an area where SOFIA can potentially make important discoveries.

Another interesting result from HERSCHEL has come from the work on the 69-µm Forsterite feature in the emission from circumstellar disks around Herbig Ae stars by Sturm *et al.* [20]). Interstellar silicate dust is essentially amorphous, and the silicate emission from pre-main-sequence star disks is mainly from amorphous silicates. However, features from crystalline dust were found with ISO, and much work on shorter wavelength features was carried out with the SPITZER spectrometer. All of this, together with the HERSCHEL observations, puts limits both on the temperature and the iron-to-magnesium abundance ratio in the emitting grains. One finds that the crystalline silicates are iron-poor and magnesium-rich and this is found also in the emission from débris disks such as β Pic. If this is true for the crystalline silicates, it may also hold for the amorphous silicates. Where is the iron if it is not in the silicates? Could a large fraction of interstellar dust be in the form of "iron filings"?

Results using ALMA are beginning to arrive, but we surely have had only a taste of what is to come. As one perhaps should expect, the first results have focused on protostellar disks and inner envelopes. For example, it is becoming possible to establish the location of the "CO snow line" in some nearby disks such as that around TW Hya. This has now been imaged by Qi *et al.* [21] in the N₂H⁺(4-3) transition showing a ring of about 20–30 AU in radius (see Figure 1.3).

Since N_2H^+ is known to react rapidly with CO, it is thought that this ring must be due to CO freeze-out onto grain surfaces and consequently to N_2H^+ enhancement. CO itself is seen at much smaller radii. This observation will certainly be surpassed when full ALMA is in operation, but we are already seeing signs of what can be achieved.

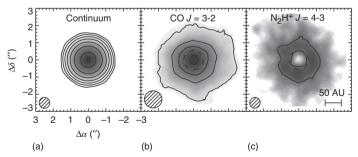


Figure 1.3 Images taken with ALMA (a,c) and with the sub-millimeter array (SMA (b)) of disk emission from the young premain-sequence star TW Hya. (a) shows the 372-GHz dust continuum emission and (b) emission in the CO(3-2) line. (c) shows

an image in N_2H^+ (4-3) where the dashed circle marks the best fit inner radius of the N_2H^+ ring (the hypothesized CO snow line). (Reprinted with permission from AAAS, Ref. [21].)

ALMA will impinge upon our understanding in a variety of ways, and it is beyond the scope of this short foreword to discuss all of them. The fact that one can get linear resolutions of better than 100 AU in some nearby objects suggests [21] a host of possible observations. It is also true that the increased sensitivity will allow fundamental advances in diffuse cloud chemistry using the well-honed techniques (absorption toward background quasi-stellar objects (QSOs, etc.) which have been used so effectively with the Institut de Radioastronomie Millimeterique IRAM instruments. Gravitational lenses seen in absorption at high redshift will certainly be another source of interesting results. And, of course, there will be surprises. All of these will certainly need new input from physicists and chemists.

What sort of input would astronomers like to have from the laboratory? Modern astrophysics needs both high-quality measurements of physical processes and high-quality simulations of the chemical processes that affect the abundances of the observed interstellar molecules. One also needs laboratory measurements of the optical properties and other characteristics of interstellar grains. The latter is a vast topic but it is worth noting that our understanding of the formation of the first galaxies depends critically on the characteristics of the grains observed at high redshift and their differences with the modern Milky Way variety. Molecular hydrogen forms (as a rule) on grain surfaces, and its formation is critically dependent on grain characteristics as well as on physical conditions (gas and grain temperature, for example). All of these topics are covered in the present volume, which explores recent advances in laboratory astrochemistry spanning a large range from molecular spectroscopy via gas-phase chemistry to grain formation processes and grain properties.

1.1

The Contents of this Volume

This book brings us up to date with some of the puzzles that have inspired laboratory spectroscopists over the years. The most ancient concerns the origin of the DIBS, which, as mentioned earlier, were discovered roughly 90 years ago and are still unidentified despite a plethora of suggestions. The contribution by Rice and Maier in Section 2.1 in this volume discusses some possible solutions to this conundrum. There are other puzzles, such as the dissociative recombination rate of the ion H_3^+ , that are crucial for the chemistry and appears now to have been resolved (see the contribution of Geppert, Wolf, and Glosik in Section 3.2). The latter question affects our understanding of how ion chemistry works and of to what extent ions are responsible for processes such as deuterium fractionation (see discussion by Asvany and Schlemmer in Section 3.4). A combination of astronomical observation and laboratory work is surely the way to proceed in this area.

But the most fundamental puzzles perhaps involve surface science and, in particular, molecular hydrogen formation. First, one should note that molecular hydrogen is not always formed on grain surfaces, and, indeed, in the early universe (where initially there are no grains) H_2 presumably has to form in the gas phase (see the discussion of negative ion chemistry by Kreckel and Savin in Section 3.5). However, once dust has formed, there seems little doubt that molecular hydrogen forms on grains, but how it does it and on which sort of grains (or nanoparticles) has been the source of much controversy. The best astronomical measurements (see the discussion of Hornekaer in Section 5) give some guidance, but the main conclusion one draws is that the estimates of Salpeter and coworkers in the 1960s and 1970s were very prescient. Getting beyond that to understand, for example, the relative importance of the Eley–Rideal and Langmuir–Hinshelwood mechanisms in various astrophysical situations has proven difficult (see contributions by Hornekaer and Price in Section 5.2 as well as by Herbst in Section 5.5). Another aspect is the effect of the different surfaces (ice or silicate or carbonaceous), which becomes important in differing locales (see contribution by McCoustra *et al.* in Section 5.3).

Of course, molecular hydrogen is not the only species which forms on dust grain surfaces although for many years, it was assumed tacitly that this was the case. That assumption was made for the "lack of a better" alternative, or because it was unclear what rates were applicable on grain surfaces (though the early work of Allen and Robinson [22] provided a guide). These days it is clear that, for example, water, methanol, and carbon dioxide can form on grain surfaces (see the contribution of Isokoski and collaborators who also discuss some of the early ideas in this area). Can complex organic molecules (e.g., prebiotic species) form in this manner? Relatively complex species such as glycolaldehyde are found in the "hot core" region SgrB2(N), and the circumstances (high temperature such that ices desorb) are suggestive of surface formation. The models to date are consistent with this, but there is presently no convincing explanation of the patterns of complex species observed.

One essential input for the millimeter astronomers interpreting observations of sources like SgrB2(N) is reliable spectroscopic data. The increasing sensitivity of modern telescopes (in particular the potential of ALMA) has had the consequence that one reaches the confusion limit where line-blending dominates the spectrum and where many of the observed transitions are due to vibrationally excited states. Separating out the "weeds" due to species such as methanol and ethyl cyanide from the "transitions of interest" has rendered clear identification of emission from new molecules extremely challenging. The contribution by Müller in Section 2.4 describes some of what has been done both in the laboratory and astronomically. I might add that in all of this the availability of the CDMS (Cologne Database for Molecular Spectroscopy) database has been invaluable.

Molecular line intensities and profiles are used as probes of the physical characteristics of the clouds and stellar envelopes where the lines are formed. As in the case of the forbidden lines from ionized gas, level populations are non-Boltzmannian and are determined by competition between collisional excitation and radiative decay. Thus one needs accurate computations of state-to-state rates for the observed species, and this in turn requires accurately determined potential energy surfaces as well as computations of the various cross sections. One also

needs laboratory measurements of the cross sections to verify the computations, and some recent experimental results are described in the contribution by Parker and Wiesenfeld in Section 3.3.

Another fundamental input for our understanding of interstellar chemistry is a set of credible photodissociation rates. It is, of course, a challenge to understand how one forms interstellar molecules, but equally important is to know how they are destroyed. In the diffuse interstellar gas, but also in the so-called PDRs, the main destruction process is often photodissociation by the ambient UV field (in the case of the PDRs, the UV photons originate in nearby hot stars). In practice, most photodissociation rates are computed at least for small species but, of course, laboratory work has provided important checks on theory. van Dishoeck and Visser in Chapter 4 provide a useful overview of the techniques used as well as some insight into some of the complications that occur in the astrophysical context (an example is line self-shielding in cases such as CO). In this context, the databases provided by the Leiden group have been invaluable to the community.

In all of the discussions of molecular complexity in the interstellar medium, the role played by the PAHs is clearly of great importance. It is worth stressing that the PAH's near- and mid-IR features dominate the spectra of many well-studied galactic and extragalactic objects (planetary nebulae, galactic nuclei, PDRs, young stellar objects, etc.). Nanoparticles matter! PAH characteristics are described in the contribution by Oomens, Pirali, and Tielens in Section 2.3 and UV spectroscopy by Carpentier *et al.* in Section 2.2. Their importance is underlined by the fact that they are thought in many situations to take up a large fraction (several percent) of the available carbon. How is it possible for one single family to do this? There is no good answer to this, but certainly good laboratory data on both ionized PAHs and various PAH modifications are needed. One of the interesting questions is whether PADs (deuterated PAHs) are abundant and can affect the amount of deuterium in atomic or molecular (HD) form.

If carbon-based nanoparticles exist, why not also Si-based nanoparticles? Huisken and collaborators in Section 6.7 discusses the possibility that photoluminescence from such particles may be observable. It might even account for the "extended red emission" or ERE seen toward some reflection nebulae.

For astronomers, however, the properties of the classical 0.1-µm-sized dust particles are of primary importance. This is because of both the importance of extinction in the visible and near-IR and the observed dust emission at wavelengths ranging from the far-IR to 1 mm. In particular, the results from the PLANCK and HERSCHEL satellites have led to increased interest in the long-wavelength emissivity. Such measurements often give us our most reliable estimates of cloud masses and column densities. It is, therefore, appropriate that Chapters 6 and 7 of this volume are devoted to studies of classical dust.

A description of our present knowledge of ISM, circumstellar, protoplanetary, and solar system dust is given in the contribution by Henning in Section 6.1, while laboratory techniques for measuring grain optical properties are discussed by Mutschke in Section 6.2. Laboratory techniques for measuring the IR spectra of amorphous silicates are considered by Mutschke and Zeidel in Section 6.3 and

for crystalline silicates by Koike in Section 6.4. Crystalline silicates are found in comets and protoplanetary disks, and we have seen earlier the potential of the observations of crystalline features for understanding grain composition.

The apparent predominance of silicate dust brings up the question of the role played by other oxides in the formation and evolution of cosmic dust. This is discussed in the contribution by Posch and Zeidler in Section 6.5, who point out the role a variety of oxides (SiO, FeO, Al_2O_3 , etc.) can play as intermediaries in the formation of silicate dust in circumstellar shells. Some hints about how this might work are given by observations of inclusions in meteorites. A large fraction of interstellar dust, however, is formed of either graphite or HACs (hydrogenated amorphous carbon) and it is clear that one therefore needs accurate optical constants for such substances. Mutschke's second chapter (Section 6.6) deals with this topic as well as with the characteristics of related species such as SiC. An open question here is whether one of these materials can account for the prominent "bump" at 220 nm seen in the interstellar extinction curve; some of the proposed solutions to this problem are discussed.

A clear need is a comprehensive model of the formation, evolution, and destruction of interstellar dust particles. A partial answer to this is given in Section 7.1 by Gail, who reviews present knowledge of the formation of dust in the shells surrounding asymptotic-giant-branch (AGB) stars and supergiants. This requires separate discussion of the oxygen-rich stars producing silicates and of the carbon stars forming soot and other carbon-rich solids. Can one mimic grain formation processes in the laboratory? Such possibilities are discussed in Sections 7.2, 7.4 by Jaeger and Section 7.3 by Rietmeijer and Nuth. The grains that one actually observes in the ISM have, however, been subject to shocks as well as irradiation by cosmic rays and UV. These processes are discussed in Section 7.5 by Jaeger and Mennella. The spectroscopic characteristics of the grains change under irradiation, for example, the 220-nm feature shifts. One is surprised at the relative constancy of the band wavelength in the observed extinction curves.

This compendium will be useful to both students and experts. It serves both as an introduction to several topics and as a summary of recent results in the field. Most importantly perhaps, it gives different points of view on some of the open questions both from the astrophysical standpoint and from that of the laboratory physicist.

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