Opacities of Molecules and Dust

David R. Alexander¹, Jason W. Ferguson¹, Akemi Tamanai¹,², Julia Bodnarik ¹, France Allard ³, & Peter H. Hauschildt ⁴

1 Department of Physics, Wichita State University, Wichita, KS 67260-0032
2 Zentrum für Astronomie und Astrophysik, TU Berlin, D-10623 Berlin Germany
3 CRAL-ENS, 46 Allee d’Italie, Lyon, 69364 France, Cedex 07
4 Dept. of Physics & Astronomy and Center for Simulated Physics, The University of Georgia, Athens, GA 30602-2451

Abstract.
As progressively lower temperatures are encountered in a stellar atmosphere, first molecules and finally dust grains become important sources of opacity. The abundance of important molecular and solid absorbers depends upon temperature, pressure, and the chemical composition in complex ways which require detailed equation of state calculations. Molecular spectra, which usually contain thousands or millions of spectral lines, are usually treated statistically in the opacity sampling method. Because of the size of modern line lists and the time required to process them, efficient computation of molecular opacity requires careful selection of the wavelengths and the relevant lines.

Molecules begin to affect the equation of state at temperatures of about 5,000 K. By 4,000 K, their contribution to the opacity dominates at many wavelengths. H₂O (in the infrared) and TiO (in the visual) are especially important for temperatures between 3,000 K and 1,500 K. For temperatures below about 1,800 K, some materials begin to precipitate out of the gas phase as small solid particles. Because these small grains are very efficient absorbers and scatterers of light, they dominate the opacity whenever they exist. The thermodynamic and optical properties of these materials is explored. Recent results show that even grains with relatively low abundances, such as Al₂O₃ and CaTiO₃, can have a dramatic impact on the structure of stellar atmospheres. Most atmospheres with $T_{\text{eff}} < 3,000$ K, both giant and dwarf, have grains in their outer layers in sufficient quantity to affect the emergent spectrum.

1. Introduction
Opacity is the engine that drives modeling of the atmospheres of stars, and other radiative environments. As a result, opacity calculations date back to the early years of astrophysics (see, for example, Rosseland 1925). Calculation of opac-
ity requires a detailed knowledge of the chemical state of the material and of the quantum mechanical properties of each significant species that exists in the material. As our understanding of the underlying physics has improved, and as the power available for computing has increased, our ability to compute reasonably accurate and complete opacities for a wide range of physical circumstances has vastly increased. The results of the Opacity Project (Seaton et al. 1994, and references therein) and of OPAL (Iglesias & Rogers 1996, and references therein), which focused on the opacity of high temperature gases, have significantly improved the agreement between models and observations of pulsating stars, helioseismology, and lithium depletion (Rogers & Iglesias 1994).

At lower temperatures, the formation of molecules complicates the computation of the opacity. Both the equation of state and the quantum mechanics of the species become more complex. Since the formation of molecules is favored at high pressures, these effects show up first in main sequence stars. For example, at a pressure of $10^6$ dynes/cm², the atomic hydrogen abundance is altered by as much as 10% at 5,000 K. Even though molecules are not yet a dominant source of opacity under these circumstances, their presence has altered the chemical equilibrium, and therefore the opacity, significantly. For all results and examples discussed in this paper, it has been assumed that thermal and chemical equilibrium exists for all species and that abundances are solar. All results were obtained using the PHOENIX program (Hauschildt, Allard, & Baron 1999; Hauschildt et al. 1999).

At still lower temperatures (below about 1,800 K), solid particles begin to condense from the gas phase. The formation of small solid particles dramatically changes the chemical equilibrium of the remaining gas. Also, many solid particles are efficient absorbers and scatterers of light. Even a small concentration of dust particles can change the opacity by an order of magnitude or more.

Advances in our physical understanding of these molecular and condensation processes, along with rapidly increasing computational power, have allowed us to compute ever more detailed low temperature opacities. Table 1 illustrates the range of improvement in several areas over the past 27 years. Section 2 of this paper will discuss the role of molecules in contributing to the opacity of low temperature objects. Section 3 will focus on the effects of dust particles on the opacity. The effect of dust opacity on stellar atmospheres will be explored briefly in Section 4. Conclusions and the direction of future work will be described in Section 5.

2. Molecular Opacities

The molecular chemistry of low temperature astrophysical gases is controlled by the formation of CO and CH₄, as illustrated in Figure 1. For temperatures between about 5,000 K and 800 K, CO controls the equilibrium of molecules. If oxygen is slightly more abundant than carbon, then some atoms of oxygen are left over after CO has used all the available carbon atoms. These left over oxygen atoms are then available to form molecules such as H₂O and TiO, which are efficient absorbers of light in the optical (for TiO) and infrared (for H₂O). The dramatic differences between the observed spectra of M stars and C stars is easily explained as a shift in the abundance ratio of C/O from slightly less
Table 1. Improvements in Low Temperature Opacity Calculations

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>super-saturation</td>
<td>decoupled gas &amp; dust</td>
<td>decoupled gas &amp; dust</td>
<td>gas &amp; dust in equilibrium</td>
<td></td>
</tr>
<tr>
<td>ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Molecular Opacity: straight mean, $2 \times 10^5$ lines + straight mean water, $3 \times 10^7$ lines, $8 \times 10^8$ lines

Dust Opacity: 1 species Rayleigh, 3 species Mie, 4 species CDE, 31 species Mie

Number of Frequencies: 50, 900, 9,000, 25,000

than one to slightly greater than one, which in turn shifts the chemical equilibrium from an emphasis on oxygen-containing molecules to carbon-containing molecules. Below about 800 K (depending upon the pressure), the CO abundance drops precipitously, and is replaced by CH$_4$. Because all the carbon atoms are now locked up in CH$_4$, even more atoms of oxygen are available to form other molecules and dust particles.

Care should be exercised when computing the chemical equilibrium of gases for temperature below 1,000 K. Most of the tabulations of polynomial coefficients for partition functions or equilibrium constants were designed for temperatures between 1,000 K and 6,000 K (Irwin 1981, 1988; Sharp & Huebner 1990). Using those coefficients for temperatures below 1,000 K can lead to significant errors, as shown in Figure 2, compared to the values tabulated in the JANAF (Chase 1998) tables. As modeling has extended to the atmospheres of ever cooler objects, such as brown dwarfs and giant planets, these effects become more and more significant.

The gradually increasing role of molecules in the opacity as the temperature is deceased from 10,000 K is shown in Figure 3. Molecules have become a significant source of opacity at 4,000 K. Continuous sources and the hydrogen lines dominate the opacity at 10,000 K. By 6,000 K, atomic lines begin to dominate at most wavelengths, although the continuous sources continue to provide a "floor" under the opacity which prevents photons from escaping at wavelengths between the lines. At 4,000 K, molecular lines have become important at many wavelengths, while continuous and atomic sources continue to be important.

The temperature dependence of the opacity of a given molecule depends both upon the variation in the absorption per molecule and changes in the abundance of the molecule. This dependence is illustrated in Figure 4 for H$_2$O. As the temperature increases, higher energy states are filled and the opacity between the major absorption bands increases. The absorption at band center changes
Figure 1. Contour plots of the concentration of CO and CH$_4$ as functions of temperature and pressure. Each contour is labeled with log($P_0/P_{gas}$). Note the formation of CO around log $T = 3.7$, the broad plateau in the concentration of CO between log $T = 3.4 - 2.8$, and then the rapid decline in the concentration of CO at log $T = 2.8$ as CH$_4$ begins to

Figure 2. The ratio of the equilibrium constant from Tsuji (1973; solid line) or Sharp & Huebner (1990; dashed line) to that computed directly from the JANAF (Chase 1998) tables for CO and CH$_4$. Large errors occur in the polynomial fits of Tsuji and Sharp & Huebner below their intended range of 1,000 K. These errors are especially important for computation of the CH$_4$ abundance, because it is only significant at these low temperatures.
The monochromatic opacity at several different temperatures, de-resolved to a resolution of $\Delta \lambda/\lambda = 0.007$. In each panel, $\log R = \log(\rho/T_0^3) = -3.0$. Different opacity sources are identified as follows: total opacity (thick solid line), continuous absorbers (thin solid line), hydrogen & helium lines (dotted line), atomic lines (dot-dashed line), and molecules (dashed line).

Only slightly as the temperature changes. The abundance of H$_2$O molecules depends critically on the temperature. The resulting total opacity due to H$_2$O displays the combination of these effects. Even though the opacity per molecule at 3,000 K is quite high, there are so few H$_2$O molecules at that temperature that the total opacity is very small. Although other molecules show a similar temperature behavior, most have an abundance peak in a narrow range of temperatures so there is a fall off in opacity at both higher and lower temperatures. In the case of TiO the opacity peaks for temperatures around 1,600 K, and falls off dramatically for temperatures more than about 500 K above or below the temperature of maximum concentration.

The density of lines in a molecular spectrum also plays a critical role in determining the effect of the molecular opacity on the thermal structure of an atmosphere. As shown in figure 5, both CO and H$_2$O have peak absorption per molecule at about the same level. However, the lines of CO are much more widely spaced than are those of H$_2$O. As a result, there are gaps between the lines.
Figure 4. The left panel shows the opacity of H$_2$O per molecule as a function of wavelength. The right panel shows the resulting opacity due to H$_2$O.

of CO which allow photons to escape. Thus, even though CO is usually more abundant than H$_2$O in cool stellar atmospheres, H$_2$O has a greater influence on both the thermal structure of the atmosphere and the emergent spectrum.

While oxides such as H$_2$O, TiO, and CO dominate the spectra of red giant stars, the spectra of red dwarfs and brown dwarfs also contain significant features due to the hydrides. Figure 6 shows that FeH has a significant abundance only at the relatively high pressures that exist in the compact atmospheres of the dwarfs.

Figure 5. The monochromatic opacity per molecule of CO and H$_2$O are shown. The wide swings in the opacity of CO are a result of the widely spaced lines in that spectrum, compared to the strongly overlapping lines of H$_2$O.
3. Dust Opacities

Just as is the case for molecules, the computation of the opacity due to small solid dust particles requires a knowledge of the abundance of the particles as a function of temperature and pressure and the absorption and scattering properties of each particle. The opacity due to a dust species can be computed from

\[
\kappa_\lambda \rho = \pi \sum_i \int_a n_i(a) Q_{\text{ext}}(a, i, \lambda) a^2 \, da
\]

(1)

where \( n_i(a) \) is the number of dust particles of species \( i \) of size \( a \) and \( Q_{\text{ext}}(a, i, \lambda) \) is the total extinction (absorption plus scattering) efficiency of the particle. \( n_i(a) \) depends upon both the chemical equilibrium of species \( i \) and the size distribution of dust particles. Here the size distribution of all dust particles is assumed to be that found for particles in the interstellar medium by Mathis, Rumpl, & Nordsieck (1977). A future paper will explore the effect that other assumptions about the size distribution have on the overall opacity of dust particles. The extinction efficiencies of the particles is computed according to the Mie theory for solid spheres composed of a single, pure substance. Future work will also explore the effect of shape, porosity, and mixtures on the opacity of dust.

The domains of existence of several important dust species in the temperature-pressure plane are shown in Figure 7. Unlike the case for molecules, condensed species have very steep contours as they condense or evaporate. Indeed, the width of the region over which a dust species goes from zero abundance to saturation is much thinner than the lines plotted. As one moves outward to cooler layers in an atmosphere, aluminum oxide (Al\(_2\)O\(_3\) or corundum) is the first significant dust species that appears. Al\(_2\)O\(_3\) exists over a fairly narrow range of temperatures, before it disappears in the competition for aluminum with other
Figure 7. A contour plot of the partial pressure of several condensed species, as before. Al$_2$O$_3$ and CaTiO$_3$ both condense at fairly high temperatures but exist only over a narrow range of temperatures. Mg$_2$SiO$_4$ and Fe condense at lower temperatures but exist over a broader range of temperatures.

species. Even though the cosmic abundance of aluminum is fairly low, Al$_2$O$_3$ increases the overall opacity by as much as a factor of ten (compared to a gas at the same temperature in which dust is not allowed to form). Al$_2$O$_3$ serves a role similar to other continuous absorbers, such as H$^-$, by filling the gaps between molecular lines so that photons cannot escape at wavelengths with low opacity.

Calcium titanate (CaTiO$_3$), the next species to form, plays a somewhat different role. Because titanium has a very low abundance, CaTiO$_3$ is never a dominant opacity source. However, the condensation of CaTiO$_3$ takes TiO out of the gas phase, greatly reducing the opacity due to that important visual absorber. The condensation of CaTiO$_3$ will thus have profound effects on the emergent spectrum of a star if it occurs at an appreciable optical depth.

Both magnesium and iron are an order of magnitude more abundant than aluminum or calcium. When species containing those materials begin to condense (such as Fe, MgSiO$_3$, and Mg$_2$SiO$_4$), their absorption and scattering completely dominates the opacity. These species also exist over a wider range of temperatures than is typical of the high temperature condensates. FeS finally replaces Fe at about 700 K, although the magnesium silicates remain abundant to even lower temperatures.

While the opacity of dust particles is essentially continuous, there are absorption features in their response to light. Figure 8 shows the opacity per grain core of several common condensates. A grain core is one molecular unit of the
Figure 8. The monochromatic opacity per grain core for several common condensates is shown.

grain. Note that the peak absorption per core shown in this figure is much greater than the absorption of molecules shown in Figures 4 and 5. The familiar 10 μm absorption peak of the silicates is apparent, as are the sharper absorption peaks at 12.6 μm and 20 μm of Al₂O₃.

Figure 9 illustrates the increasing role of dust grains on the overall opacity at lower temperatures. At 1,400 K, grains have created a floor under the molecular opacity, which prevents photons from escaping at wavelengths between molecular lines. At 1,000 K, grains have significantly raised the opacity at most wavelengths, even where molecular bands are strong. Another perspective on the effects of dust particles on the overall opacity is shown in the plot of the Rosseland mean opacity shown in Figure 10. After the opacity minimum is reached at 2,500 K, the first rise in the opacity, caused by molecular absorption of H₂O and TiO, increases the opacity by two orders of magnitude. The condensation of Al₂O₃ increases the opacity by another 1.5 dex. Another increase in opacity of similar magnitude occurs at about 1,150 K, when iron and the silicates condense. Perhaps the most surprising feature of this figure is that carbon grains condense at 430 K, because so much oxygen has been removed from the gas phase that the C/O ratio of the gas has become greater than one.

4. Dust in Stellar Atmospheres

Because the condensation of solid particles is favored at high pressures, that is, occurs at higher temperatures when the pressure is greater, it is not surprising that the effect of dust is very strong in the atmospheres of cool main sequence stars. The fact that brown dwarfs extend the temperature sequence to much
Figure 9. The monochromatic opacity at several different temperatures, as in Figure 3. Different opacities sources are identified as follows: total opacity (thick solid line), atomic lines (dot-dashed line), molecules (dashed line), and dust (thin solid line).

lower temperatures merely exaggerates this effect. Figure 11 illustrates this effect for models at three effective temperatures. The “Cond” models have included the effect of dust formation in the equation of state, but have not included any dust opacity. Such models might simulate the effect of grains settling out of the upper atmosphere of the star. “Dusty” models include the full effect of dust formation in both the equation of state and in the opacity. Grain formation is turned off in the “Dustless” models. The effect of dust condensation is quite strong in the $T_{\text{eff}} = 2,500$ K models, and overwhelming in the 1,600 K models. When compared to observations, the 1,600 K “Dusty” model shows much too strong dust opacity while the “Cond” model fits the observations reasonably well, suggesting that dust has indeed settled from the atmosphere (Allard 2001).

It is somewhat more surprising that dust particles can also form in the atmospheres of red giant stars, where the pressure is many orders of magnitude smaller. Our calculations suggest, however, that all red giant models with $T_{\text{eff}} \leq 3,000$ K will have dust present (Ferguson et al. 2001). Figure 12 shows, however, that grains only exist in the optically thin layers of red giant models. The effect of the dust is to cool the outer layers of the model, by as much as 200 K,
while causing a very modest backwarming deeper in the model. Because the grains only exist in the optically thin portion of the atmosphere, that effect on the emergent spectrum of the star is rather small. Figure 13 shows that the principle effect of dust occurs in the TiO bands, because the condensation of CaTiO$_3$ removes some titanium from the gas phase and, therefore, causes a reduction in the gaseous TiO abundance. The “Cond” models show a slight depression of the flux due to the increased opacity of the grains.

5. Conclusions

A great deal of progress has been made in recent years in the calculation of low temperature opacities. The availability of much more complete and accurate molecular line lists, coupled with computers fast enough to include monochromatic molecular opacities through opacity sampling, has dramatically improved the comparison of model spectra with observations. Model spectra can now be used to diagnose reliably the physical properties of observed stars. Nevertheless, additional molecular data is still needed. Line lists for several hydrides are badly needed to model accurately the cool dwarfs. Present methane line lists are woefully inadequate for modeling the coolest brown dwarfs, although several groups are presently working on this task (Freedman & Schwenke 2001; Jørgensen, these proceedings; Borisyov et al., these proceedings).

There are similar gaps in our knowledge of the optical properties of many grain species. There are no optical constants available for the high temperature condensate CaTiO$_3$. It is presently included through its chemical analogue, SrTiO$_3$, and even that species is missing crucial data in the near-IR. There is also no data for $\lambda < 2\mu$m for MgAl$_2$O$_4$, the condensate that replaces Al$_2$O$_3$ at
Figure 11. The emergent spectra for several different models. The surface gravity of each model is $10^{5.5} \text{cm s}^{-2}$. "Dustless" models (solid lines) have dust turned off in both the equation of state calculation and in the opacity. "Cond" models (dashed lines) include dust condensation in the equation of state, but not in the opacity calculation. "Dusty" models (dotted lines) include dust in both the equation of state and in the opacity.

about 1,200 K. There are also a great variety of silicate materials for which no data exist.

Many additional effects regarding the absorption and scattering due to grains should also be explored. The effect of different size distributions of grains should be examined. Porous and inhomogeneous grains are much more likely to form than the solid, homogeneous spheres presently assumed. The thermal history of the gas is also likely to affect which species are present. For example, once an element condenses into a high temperature condensate, it becomes essentially unreactive when the gas cools to a lower temperature, even though another species may be in chemical equilibrium at the lower temperature. All of these effects are under investigation, and will be reported in future work.

Acknowledgments. Low temperature astrophysics at Wichita State University is supported by NASA EPSCoR grant NCC5-168, NASA LTSA grant NAG5-3435, NSF grant EPS-9874732, and matching support from the State of Kansas. PHH acknowledges support by NASA grants NAG5-9396, NAG5-9222, NAG5-8425, and NAG5-3619, and NSF grants AST-0086246 and AST-920704, as well as HST-GO-08617.09A and GO-0-1013C to the University of Georgia. FA acknowledges support from Pôle Scientifique de Modélisation Numérique at ENS-Lyon.
Figure 12. The thermal structure of model atmospheres of several red giant stars are shown. For each model $M_\odot = 1.0$ and $\log L_\odot = 3.5$. The curves are labeled with the $T_{\text{eff}}$ of the model. Solid lines are models in which grain condensation has been turned off; dashed lines are “Dusty” models that include the effect of dust in both the equation of state and in the opacity.

References

Freedman, R. S. & Schwenke, D. W. 2001, BAAS, 33, 40.10
Figure 13. The emergent spectrum of the 2,500 K models shown in Figure 12 are shown in the upper panel. At this scale, differences between the models are not perceptible. The lower panels show the flux ratio of models with grains included relative to the grainless models. Solid lines represent "Dusty" models while dashed lines are "Cond" models. Each panel is labeled with the $T_{\text{eff}}$ of the models. The thin vertical lines marks the center of the TiO band at 0.59 $\mu$m.