OBSERVATIONAL CHEMISTRY

C. M. WALMSLEY
University of Cologne
I Physikalisches Institut, Universität zu Köln
Zülpicherstrasse 77
D-50937 Köln
Germany

1. Introduction

Observational Chemistry is a vast topic and I will not attempt to review it in this brief contribution. There are, moreover, several excellent reviews already available (e.g., Irvine et al. 1987; van Dishoeck et al. 1993) which give an overview of molecular abundance determinations. Other discussions of specific aspects of the problem are given by Walmsley and Schilke (1992, 1993), by Mundy et al. (1995), and by van Dishoeck and Blake (1995). In this review, I will consider the specific question of gas–grain interactions in molecular clouds. Specifically, I will review some recent work discussing evidence for depletion of heavy elements onto dust grain surfaces as well as the inverse problem of the mechanisms which cause material deposited onto dust grains to be recycled into the gas phase.

2. Evidence for Depletion of C, N, O, and Si in Molecular Clouds

There is a long standing problem arising from the fact that carbon, nitrogen, and oxygen do not show convincing evidence for depletion onto dust grains in the high density clumps in molecular clouds. For a normal distribution of dust grain sizes, one can estimate the timescale for depletion τ_d (in yrs) as:

$$\tau_d = 10^9/(s\, n(\mathrm{H_2})) \tag{1}$$

where $n(\mathrm{H_2})$ is the molecular hydrogen density in cm^{-3} and s is the sticking coefficient for collisions of molecules with grain surfaces. It has been demonstrated that s is likely to be close to unity for likely physical conditions and grain surface materials (e.g., Leitch-Devlin and Williams 1985).

From equation 1, one derives timescales for depletion of order 10^5 years at typical densities in molecular cloud cores. This is less than current estimates for the dynamical lifetimes of such clumps and it, therefore, seems surprising that there has been little evidence for substantial depletion. Léger et al. (1985) consider explanations for this.

It is important to note that CO, unlike most other observed interstellar molecules, is a majority gas phase species in the sense that it is believed to be the repository of most gas–phase carbon. One finds typically $[CO]/[H_2]$ of order 10^{-4} which is a factor of roughly 6 less than the interstellar carbon abundance. The usual assumption is that the missing 5/6 of the carbon is in the solid state either in the form of graphite or as some refractory organic species. While it is possible that a lot of carbon is locked up in some as yet unobserved gas phase form, it seems unlikely. Theory suggests very strongly that, where dust extinction is sufficiently great that UV radiation is excluded from cloud interiors, most gas–phase carbon will become transformed into CO.

On the other hand, molecules such as CS, NH_3, etc., only contain a small fraction of their constituent elements and hence their abundance does *not* depend linearly on the amount of C, S or N in the gas phase. Their (gas phase) destruction rates may be reduced as a consequence of depletion of (for example) oxygen onto grain surfaces and, hence, they may retain high abundances even when a large fraction of C, N, and O has disappeared into ice (see Pineau des Forêts et al. 1991). Thus measurements of $[CO]/[H_2]$ are a better guide to depletion in dense cores than abundances of other species. Of course in situations where, say, 10^{-4} or less of solar C, N, and O is left in the gas phase, essentially all species will show reduced abundances relative to standard molecular cloud values. But, in general, results from species containing a small fraction of their constituent elements are a bad guide to depletion.

It is in this context that recent observations by Wilson et al. (1995) using the BIMA array to observe $C^{18}O$(1-0) towards NGC 2024 are interesting (see also poster by Mehringer et al., this conference). These authors have a similar synthesised beam to the single dish angular resolution used by Mezger et al. (1988, 1992) to observe the 1.3 mm and 870 μm dust emission. They can thus compare rather well the CO column density with the dust (and by inference hydrogen) column density of Mezger et al. (see also Mauersberger et al. 1992). The BIMA results show rather convincingly that *on the small (0.01 pc) scale*, there is an anti-correlation between $C^{18}O$ emission and dust. The inferred $[CO]/[H_2]$ ratio is of the order of 10^{-5} or lower which is an order of magnitude less than that typically observed in molecular clouds. Although there is considerable uncertainty in hydrogen column densities derived from dust emission and although the kinetic temperature (and hence the $C^{18}O$ partition function) in these high density clumps is also uncertain, the evidence that CO is underabundant seems strong.

Thus, the contention of Mauersberger et al. (1992) and earlier of Mezger et al. (1988) that molecular depletion was occurring in the high density cores in NGC 2024 is confirmed by the new BIMA data from Wilson et al. (1995). It is also interesting to note that a recent $C^{34}S$ map of NGC 2024 by Wiesemeyer et al. (1995) made with the Plateau de Bure Interferometer shows reasonable agreement between the distribution of high density clumps seen in $C^{34}S$ and $C^{18}O$. This suggests that in spite of depletion seen in CO, the [CS]/CO] abundance ratio remains approximately at the canonical molecular cloud value of around $3\,10^{-5}$.

The situation is slightly different for ammonia which has been mapped using the VLA by Gaume et al. (1992) and by Ho et al. (1993) and the $[NH_3]/[CO]$ abundance ratio varies over two orders of magnitude (from 10^{-5} to 10^{-3}) from one position to another in NGC 2024. In at least one case (FIR3), ammonia seems to be coincident with the high density cold clump. Thus ammonia appears to behave differently from CO and CS. One possibility is that ammonia is present in an outer layer of the clump (but see Walmsley and Schilke 1992 for another interpretation).

The NGC 2024 high density clumps are not unique in showing signs of heavy element depletion onto dust grain surfaces. Blake et al. (1995) have recently completed a detailed study of the gas surrounding the "extreme class I source" (i.e., embedded submm–continuum sources) NGC1333/IRAS 4A and B. They find depletion factors of 10–20 for all species including CO in regions where the beam–averaged density exceeds 10^7 cm^{-3}. The molecules may only be present in an outer skin inside of which molecules containing heavy elements have been frozen out (see model calculations by Rawlings et al. 1992).

On the basis of the above studies, one concludes that at densities above 10^7 cm^{-3} depletion becomes important in the sense that $[CO]/[H_2]$ descends to 10^{-5} or smaller values and other molecules appear to behave in analogous fashion. Some depletion is occurring at much lower densities as witnessed by the solid–state CO and H_2O features which are observed to contain a few percent of carbon and oxygen along sight–lines passing through "normal molecular cloud gas" (densities of a few thousand cm^{-3}). Nevertheless, one observes gas whose density is of orders $10^5 - 10^6$ cm^{-3} where the $[CO]/[H_2]$ ratio appears normal. The most impressive evidence for this, perhaps, is the direct measurement of $[CO]/[H_2] = 2.5\,10^{-4}$ towards NGC 2024 IRS2 by Lacy et al.(1994) who observed the near infrared vibration-rotation transitions of both species. The column density $N(H_2)$ in this line of sight is $3.5\,10^{22}$ cm^{-2} and the density must be at least 10^5

cm^{-3}. The dust temperature (which is a critical parameter) is unknown. It would be of considerable interest to obtain abundances for a variety of species towards IRS2.

There is one species, however, which appears to be depleted even at dark cloud densities ($10^4 - 10^5$ cm^{-3}). That is SiO for which the upper limits to the abundance [SiO]/[H_2] in sources such as TMC1 and L183 are of order $3\,10^{-12}$ (Ziurys et al. 1989). This is surprising because SiO is thought to be the major gas–phase form of silicon (Herbst et al. 1989, Langer and Glassgold 1989) and because the solar silicon abundance is [Si/H] $= 3.5\,10^{-5}$. Thus, it appears that silicon is depleted in dark clouds by a factor of at least 10^7 whereas carbon (as one deduces from the CO abundance) is depleted by only a factor of a few. While silicon is depleted more than carbon in diffuse clouds (Sofia et al. 1994), the low upper limit to SiO in TMC1 and L183 suggests that *within the dense core*, depletion is much more effective for silicon than for carbon, nitrogen, etc. One possibility is simply that the sticking coefficient is considerably larger for SiO than for other species. This would then imply a relatively low sticking coefficient for species such as CO and would provide a partial explanation for the low depletion rates of carbon–rich species in general. Another difference between SiO and CO, however, is that the latter can be evaporated at very modest grain temperatures.

An interesting new development in the context of silicon depletion is the detection by Greaves et al. (1995) of SiO in absorption in the spiral arm clouds along the line of sight towards W49 and SgrB2 which are thought to have densities of a few thousand cm^{-3}(i.e., intermediate between the ζOph cloud where silicon is depleted by a factor 20, and sources like TMC1 and L183). Greaves et al. find [SiO]/[H_2] of order 10^{-10} consistent with the idea that silicon depletion increases rapidly with increasing density.

3. Molecules in hot cores and outflows

A considerable amount of work has gone into abundance determinations in the Orion hot core and other regions with analogous properties. One motivation for this has been the idea that there is an early phase in the evolution of a massive star (prior to the switch–on of a compact HII region) where the embedded object heats up the surrounding molecular gas to temperatures at which icy mantles on dust grain surfaces can evaporate. One then observes objects such as the Orion hot core with temperatures well above 100 K, densities above 10^7 cm^{-3} and column densities in the range $10^{24} - 10^{25}$ cm^{-2}. Example are the hot cores in SgrB2-N, G10.47, G31.4, G34.26, and of course Orion (see Walmsley and Schilke 1993 for a more detailed discussion). These objects have the characteristic that relatively saturated (hydrogenated) species such as NH_3, CH_3OH, CH_3CN, C_2H_5CN, and CH_2CHCN are found to have abundances an order of magnitude or more larger than those determined in cold dark dust clouds.

The interpretation has been that these molecules are manufactured on grain surfaces due mainly to reactions with atomic hydrogen which is expected to be both mobile and reactive. Then (due to the formation of an embedded O–B star), the grains heat up causing evaporation of the icy mantles. The constituents of the mantles are ejected into the gas phase and stay there for more than 10^4 years until gas phase chemistry reasserts itself and establishes new steady state abundances. Model calculations of the evolving chemistry for a variety of scenarios have been carried out by Brown et al. (1988), Charnley et al. (1992), and by Caselli et al. (1993).

A characteristic of their results is that one expects water and ammonia in hot cores to contain a considerable fraction of the available oxygen and nitrogen respectively. Thus one expects abundances for these species of order 10^{-4} relative to H_2. It has been known for some time, however, that the ammonia abundance in hot cores is more like $10^{-5} - 10^{-6}$ and it is becoming clear (Gensheimer et al. 1995; Zmuidzinas (this Symposium) that the situation for water is similar. This creates a serious problem for the case of water whose solid state abundance is directly measured (see van Dishoeck et al. 1993) and seems to be an order of magnitude larger than the H_2O abundance measured in hot cores. Thus, water in the solid state does not seem to be simply transformed into gas phase water in the hot core.

There are many possible explanations for this including the comforting one that the uncertainties in the various measurements are such that the "discrepancy" should not be taken seriously. While this may be true, one should perhaps consider alternate possibilities. One is that in the core which precedes the "turn-on" of the embedded O–B star, the grain mantle composition is fundamentally different from that seen in regions which one can detect in the 3 μm ice feature. If for example, most oxygen in the pre–hot–core–mantle was in the form of O_2, the low gas phase water abundance would be comprehensible. But then presumably, one would expect to see evidence for O_2 which does not seem to be forthcoming. All this underlines the fact that we are still unsure what form most of the oxygen is in, in molecular clouds in general and in hot cores in particular.

Another type of explanation for the low observed water abundance in hot cores is that the process of evaporation itself needs to be considered. The process of warm–up is presumably not instantaneous. While warm–up is taking place, the mobility and reactivity of a variety of species on the grain surfaces is enhanced. The less polar portions of the mantle should evaporate first and will be mobile for a short time prior to evaporation. If there are "stored radical sites" on the grain such as envisaged by Greenberg

TABLE 1. Comparison of Abundances (rel. to H_2) in the L1157 Outflow and the Orion Hot Core

	Orion	L1157
NH_3	$6\,10^{-7}$	$1.3\,10^{-6}$
CH_3OH	$3\,10^{-7}$	$7\,10^{-6}$
SiO	$2\,10^{-7}$	10^{-7}

and collaborators (e.g., Greenberg 1989), these may be capable of powering reactions which, for example, destroy water. Then the start-up conditions for hot core chemistry may be different than envisaged in the model calculations.

Yet another possibility is that the ices come off the grains in shocks. There have been a series of recent studies showing evidence for enhanced abundances of particular molecules in outflows from young stars. The surprise was that the list of molecules found to have enhanced abundances in outflows is rather similar to that of the molecules with enhanced abundances in hot cores. For example, there has been considerable recent work on the L1157 flow (see e.g. Bachiller et al. 1995; Mikami et al. 1992; Umemoto et al. 1992; Tafalla and Bachiller 1995). These results show that in the blue lobe of the L1157 flow, ammonia and methanol are enhanced by rather similar amounts to that estimated for the Orion hot core. Table 1 gives a comparison of the different abundance estimates from the literature. While more data for more species are clearly needed, there appears to be a similarity between Orion hot core abundances and L1157 blue lobe abundances. This suggests that in both cases, the contents of grain mantles have been returned recently to the gas phase. However, this speculation needs to be tested by obtaining more detailed information on the L1157 outflow as well as towards similar sources.

In the case of L1157, presumably shocks are responsible for the ejection of grain mantles since the dust temperature is thought to be low. Moreover, one observes SiO in the L1157 flow and SiO is thought to be a shock indicator (see above and Martin–Pintado et al. 1992). Hence, one may have conditions similar to those envisaged by Flower and Pineau des Forêts (1995) who find that their C-shock models can explain a small amount of SiO ejection with shock velocities as low as 25 km s^{-1}. Another possibility (see Mackay 1995) is that there is a small amount of silane (SiH_4) mixed in to the icy mantle which, subsequent to ejection in the shock, gets processed by gas phase reactions to SiO. Testing this would require a search for other silicon–containing species towards outflow sources such as L1157.

A completely different approach to studying abundances in hot outflow material is that adopted by Carr et al. (1995) who have observed mid–infrared absorption lines of a variety of species towards the bright ($2\,10^4$ $L_\odot$) outflow source GL2591. They compare their data to an earlier CO study by Mitchell et al. (1989) and find an enhancement by two orders of magnitude in the HCN abundance close to the hot young star relative to that found in the surroundings (using mm lines). This is reminiscent of the Orion hot core where HCN is also enhanced (see Schilke et al. 1992) and again suggests that icy mantle material is returning to the gas phase in this source.

Finally, I note that there are some interesting puzzles to do with sulfur chemistry whose solution is almost certainly relevant to understanding the chemistry of shocks and outflows. SO and SO_2 are known to show enhanced abundances in outflows (see e.g., Serabyn in this proceedings; Helmich et al. 1994) but it is unclear whether the explanation lies in surface or in gas phase processes. The phenomenon does *not* seem to correlate well with high abundances for SiO. Moreover, McMullin et al. (1993) present maps of the Orion South concentration showing different distributions for CH_3OH, SO_2, and SiO. All of these three molecules are thought to be formed in shocks but the data suggest that we are going to be forced to distinguish between different types of shocks.

4. Conclusions

The aim of this short review has been to show that there is considerable progress being made both in determining in which localities matter is disappearing onto grain surfaces and where it is reappearing. In both cases, a lot of work is still needed to understand the physical processes involved. Clearly, direct measurements of the species of interest in the solid state will help also. It seems likely that results from ISO may help here but one can already conclude that even in the post-ISO era, we will be to some extent dependent upon gas phase abundance measurements to know what is happening in the solid state.

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