

Part V

Dust and Molecules in Planetary Nebulae

Photochemistry and Molecular Formation in Planetary Nebulae

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Abstract. Photo-chemical processes in hot neutral gas are summarized that are likely responsible for the destruction and formation of observed molecules in planetary nebulae. According to the hot gas scenario, detected simple molecules such as CN, HCN, C₂H, and HCO⁺ are destroyed in a matter of a week, but are constantly and quickly re-formed.

1. Molecules in Planetary Nebulae

It has been more than 20 years since CO and H₂ were first detected in a planetary nebula (PN) (Mufson et al. 1975; Treffers et al. 1976; also see Black 1983 for an early review on molecules in PNe). Since then, CO has been detected in more than 44 planetary nebulae (PNe) out of 112 in which CO was searched for (Huggings et al. 1996). Molecular hydrogen, too, has been detected in many PNe (Kastner et al. 1996; Latter et al. 1995; Hora et al. 1999; Cox et al. 1997; see Huggins 1993 for an earlier review; also in this proceedings, Bohigas 2002, Garcia-Hernandez et al. 2002, Kelly & Hrivnak 2002, Speck et al. 2002). Several other gas phase molecules (See Table 1) have also been detected in about a dozen PNe (Hasegawa & Kwok 2001; Bachiller et al. 1997; Sahai et al. 1992; Cox et al. 1992; Bachiller et al. 1989; Likkell et al. 1988). The detections have been made in representative, evolved PNe such as the Helix Nebula and the Ring Nebula (Table 1), suggesting that the molecules are present over a significant fraction of the lifetime of a PN. For NGC 7027, the detections also includes OH, CH, CH⁺, C₃H₂, and CO⁺ (Liu et al. 1996; Cernicharo et al. 1997; Liu et al. 1997; Cox et al. 1987; Latter et al. 1993). However, the origins of the detected molecules in PNe are not clear.

Of the observed molecules listed above, HCO⁺ is noteworthy. HCO⁺ is extremely weak or non-detectable in progenitor objects such as IRC+10216 and CRL 2688, but is relatively strong in young PNe with an ionized region such as CRL 618 and NGC 7027. HCO⁺ abundances are similar among several PNe including NGC 6702 and NGC 7293 (Bachiller et al. 1997). The relatively common presence of HCO⁺ suggests that at least one species (and possibly some other species) is newly formed after the post-AGB central star becomes hot. Those who detected HCO⁺ already pointed this out (Deguchi et al. 1990; Cox et al. 1992; Bachiller et al. 1997) and suggested a few scenarios to explain the presence of the detected molecules.

Table 1. Detected Molecules in Planetary Nebulae

Source	Detected Molecules	Main references
NGC 7027	HCO ⁺ , HCN, HNC, CN, C ₂ H, C ₃ H ₂ , OH, CH, CH ⁺ , CO ⁺	Bachiller et al. (1997) See text
NGC 6720	HCO ⁺ , HCN, HNC, CN	Bachiller et al. (1997)
NGC 7293	HCO ⁺ , HCN, HNC, CN	Bachiller et al. (1997)
NGC 6781	HCO ⁺ , HCN, HNC, CN	Bachiller et al. (1997)
M 4-9	HCO ⁺ , HCN, HNC, CN	Bachiller et al. (1997)
NGC 2346	HCO ⁺ , HCN, HNC, C ₂ H	Bachiller et al. (1989)
NGC 6072	HCO ⁺ , HCN, HNC, CN	Cox et al. (1992)
IC 4406	HCO ⁺ , HCN, HNC, CN	Cox et al. (1992)
NGC 6302	HCO ⁺ , HCN, OH(maser)	Sahai et al. (1992)
M 1-16	HCO ⁺ , HCN,	Sahai et al. (1992)
NGC 3132	HCO ⁺	Sahai et al. (1992)
IRAS21282	HCO ⁺ , HCN, CN, C ₂ H	Hasegawa & Kwok

Molecules including CO and H₂ are destroyed by UV photons with energies lower than 13.6 eV. When exposed to the diffuse interstellar UV radiation field (DISRF), simple molecules are photodissociated in about 200 years. In the vicinity of an O star or a central star of a PN, the UV radiation field is about 10⁴ to 10⁵ times the DISRF. The UV radiation field can be attenuated by dust, where $A_V = 1$ mag corresponds to a reduction of photodissociation rate by a factor of 10. A simple calculation suggests that, for molecules to survive for 1000 years in a PN, the molecular region needs to be protected from UV radiation from the central star by $A_V > 5$ mag (Tielens 1993), which is too large an extinction in an evolved PN. This line of argument also suggests some form of molecular formation in evolved PNe.

When a neutral or molecular region is subjected to a strong UV radiation field, the region is called the photo-dissociation region or the photon dominated region, both of which are used interchangeably and are abbreviated as the PDR. Chemistry that is characteristic to the PDR is referred to as “photochemistry”. The term, however, is often used without presenting or understanding specific processes.

2. Chemical Models

A detailed and quantitative explanation for the presence of the detected molecules requires a so-called “chemical model”, which is a numerical simulation of chemistry. In order to carry out such a chemical simulation, a modeler prepares a database of chemical reactions and their reaction rate constants, a good example of which is the UMIST rate file (Le Teuff et al. 2000). Based on the database, the modeler constructs a set of chemical rate equations that describe the formation and destruction rates of individual species. Typically, 100 to 300 molecular species are considered in a model, and a database consists of 1000 to 3000 reactions. The rate equations are solved either as a time dependent problem or as

a steady state problem. This type of simulation studies of astrochemistry have been carried out since mid-70's, but it is only the past 10 years that chemical models for the PDRs became available.

Most of the chemical models of the PDR have been developed for molecular regions adjacent to galactic HII regions. Most of such models are steady state models with semi-infinite slab geometries. An excellent review on the galactic PDRs and their models is given by Hollenbach & Tielens (1997). The early model on the galactic PDR by Tielens & Hollenbach (1985) focused on thermal budget (UV heating, cooling, and gas temperatures) and H₂ dissociation, and employed a small (41 species, 165 reactions) chemical reaction system. Sternberg & Dalgarno (1995) made an extensive (71 species, 900 reactions) chemical model of the PDR, and pointed out the importance of endothermic reactions.

There is an obvious similarity between the galactic PDRs and the molecular regions of PNe (Tielens 1993). It is natural to apply the knowledge and techniques obtained in the modeling study of the galactic PDRs to the molecular region of a PN. However, there are tight limitations specific to PNe in chemical-modeling the molecular envelope of a PN, and an adaptation of a chemical model designed for a galactic PDR is not straightforward. (1) Size and geometry : A slab model would be a poor approximation. (2) A_V : For most PNe, $A_V < 5$ mag (from the central star to the outer boundary of a PN). (3) Mass : Available gas mass for chemistry is less than $8M_{\odot}$. (4) Density gradient : The r^{-2} density law in PNe. (5) Timescale : The lifetime of an average PN is about 10^4 years, whereas the chemical timescales in galactic molecular clouds are $10^4 - 10^5$ years. (6) A post-AGB system goes through phases with very different physical and dynamical conditions. These difficulties are reviewed by Howe & Williams (1998) and Tielens (1993).

There have been only about ten or so attempts to construct chemical models for PNe. Black (1978, 1983) presented a photochemical model for the ionization front where atoms and electrons mingle. Howe, Millar, & Williams (1992) built a time dependent model for the initial chemical phase with a relatively small chemical network. Later, Howe, Hartquist & Williams (1994) constructed a steady state chemical model for a globule in a PN with a large chemical network and found it difficult to obtain a model with a high HCO⁺ abundance. Tielens (1993) presented PDR models including NGC 7027 with an emphasis on physics and with a small chemical system. Natta & Hollenbach (1998) constructed time-dependent, thermal-dynamical evolutionary models of the neutral envelopes of PNe without the chemistry part. Their work lays bases for future chemical modeling (such as identifying photopumping and photodissociation of H₂ as dominant heating mechanisms that give rise to $T_k \sim 1000$ K and predicting the density distribution at a given evolutionary stage) and shows current technical limitations in incorporating a chemical system into an otherwise comprehensive model of the evolution of PNe. Yan et al. (1999) constructed a steady state, thermal-chemical model of the PDR of NGC 7027 in a semi-infinite slab approximation and fitted the *ISO* observations. This work demonstrates that hot gas chemistry is a viable explanation for molecular formation in PNe. In contrast to these models, Hasegawa, Volk, & Kwok (2000) built steady-state models with emphases on chemistry and radiative transfer, but without thermal or dynamical equations. According to Justtanont et al. (2000), Latter & Tie-

lens will present more sophisticated thermal-chemical models of PNe in various evolutionary stages in the near future. Woods et al. (2002 in this proceedings) present time-dependent chemical models of CRL 618, an extremely young PN in its initial ionization phase, with a large chemical database. Ali et al. (2001) constructed time-dependent chemical models of dense globules in NGC 6781 and NGC 7293, where the assumed gas temperature is 15 K and the chemistry is driven by high energy events such as X-ray ionization of molecules.

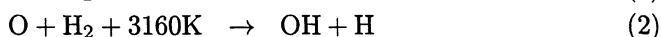
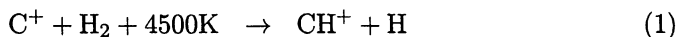
3. A Chemical Model for NGC 7027

A chemical model by Hasegawa et al. (2000) is presented here to illustrate the characteristics of photochemistry in hot gas. This is a steady state chemical model in which 106 atomic and molecular species are considered based on a reaction database consisting of 1530 gas-phase chemical reactions. A set of chemical rate equations are solved for molecular abundances at each of 91 radial grid points. Neither Lyman continuum nor X-ray photons are assumed in this model. Instead, a gas temperature of 800 K is assumed near the inner boundary of the model neutral envelope. The photodissociation rates of molecules were estimated based on the UV (< 13.6 eV) radiation field, which were determined by solving the spherical radiative transfer with dust opacities (Volk & Kwok 1997).

Figures 1a and 1b show model molecular abundances. In this model, most heavy elements are either atomic or ionized, only small fractions of them going into molecules. Hydrogen is half molecular and half atomic. Nevertheless, the model predicts significant abundances of HCO^+ , CO^+ , HCN, CN, CH, CH^+ , and OH, mostly in good agreement with observations. The most important aspect in Figures 1a and 1b is that the abundances of heavy molecules are enhanced near the inner boundary (facing the HII region), not in the outer part where the UV radiation field is much lower. The high molecular abundances are caused by the high gas temperature of 800 K near the inner boundary and not by the high density. Figure 2a shows the density and temperature distributions assumed for the model neutral envelope.

Figure 2b illustrates the effect of gas temperature on molecular abundance. In this figure, the model HCO^+ abundances are plotted for 3 models which have been calculated with the same parameter values except that the gas temperatures are different (800 K, 400 K, and 100 K) near the inner boundary. Gas temperatures higher than 400 K not only result in enhanced HCO^+ abundances, but also are necessary to explain the observed HCO^+ abundance (Hasegawa & Kwok 2001). Similar enhancements at higher gas temperatures occur to CO^+ , HCN, OH, H_2O .

These enhancements at high gas temperatures are caused by gas-phase chemical reactions with an endothermicity or activation energy. Figure 3a shows chemical pathways at 800 K leading to HCN, CN, OH, H_2O , CO, CO^+ , and HCO^+ , where endothermic reactions are indicated by dashed arrows. Those key reactions are :



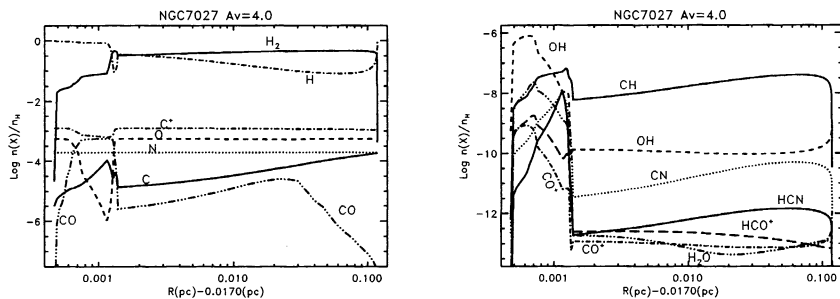


Figure 1. (a - left) (b - right) Model molecular abundances in the neutral envelope of NGC 7027. R is the distance from the central star. Adapted from Hasegawa et al. (2000).

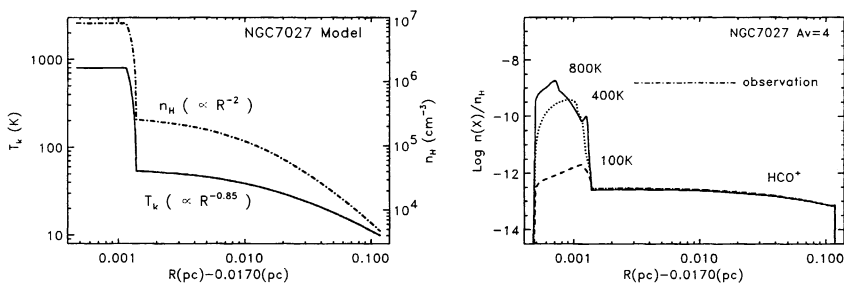
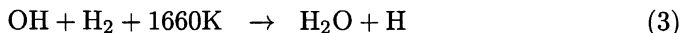


Figure 2. (a - left) The density and temperature distributions assumed in the 800 K model. (b - right) Model HCO^+ abundances in 3 models with the same parameter values except T_k near the inner boundary (the left part in the figure). The horizontal dashed line indicates the observed HCO^+ abundance in NGC 7027 by Hasegawa and Kwok (2001). The relative abundances of other observed species have similar strong dependences on T_k .



At high temperatures, those endothermic reactions efficiently return C^+ and O (both of which are end-products of photodissociation of molecules) into chemical circulation. Once CH^+ and OH are formed, successive gas-phase reactions efficiently generate more complex molecules regardless of gas temperature, efficiently incorporating N (another end-product of photodissociation of molecules) into molecules. Notice that ion-molecule reactions and neutral-neutral reactions are equally important. At temperatures lower than 400 K, those endothermic reactions are negligibly slow, and the end-products of photodissociation are not efficiently converted to molecules.

In Figure 3b, chemical timescales in the steady-state chemical model are compared with the dynamical time for NGC 7027. For the inner, hot region,

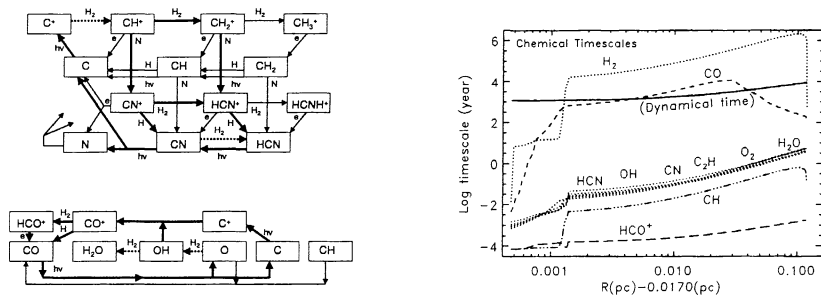


Figure 3. (a) Chemical pathways leading to CN and HCN (top) and to OH, H₂O, CO⁺, and HCO⁺ (bottom). (b) Chemical timescales in the steady-state model and the dynamical time in NGC 7027.

the chemical timescales are sufficiently shorter than the dynamical time that the steady-state approximation is a reasonable representation of chemistry. For the outer part, the steady-state approach is a poor approximation for H₂ and CO. Except for H₂ and CO, molecules are photodissociated in 0.1 to 10 years throughout the model neutral envelope (the chemical timescales in Figure 3b are mostly photodissociation timescales).

Figure 3b suggests that, in the actual envelope, H₂ in the cold, outer part are mostly remnants from the AGB atmosphere, and that the steady-state model probably overestimates HI abundance. Indeed, the observed HI upper limit is $N(\text{HI}) < 1 \times 10^{20} \text{ cm}^{-2}$ in NGC 7027 (Pottasch et al. 1982), whereas the model predicts $N(\text{HI}) = 4 \times 10^{21} \text{ cm}^{-2}$. Likewise, the actual amount of CO will be higher than the model predicts in the outer, cold region, since there is not enough time to photodissociate CO and reduce the CO abundance to a steady-state level.

4. Discussion – What is Photochemistry ?

The model presented in the previous section has a shortcoming arising from the steady-state approximation as Figure 3b illustrates. Attempts should be made in the future to develop a time-dependent chemical model. For the inner part, which probably corresponds to the hot molecular region detected with *ISO* (Liu et al. 1996) in NGC 7027, the model gives us some insight into what is actually happening in the hot molecular region.

The picture emerging from the *ISO* observation and the models by Yan et al. (1999) and by Hasegawa et al. (2000) is summarized as follows. (1) The strong UV radiation rapidly destroys heavy molecules but at the same time heats up the gas to about 1000 K. (2) The high gas temperature makes endothermic reactions efficient and drives the chemistry, resulting in rapid re-formation of molecules from atoms and atomic ions. (3) Heavy molecules characteristic of

carbon-rich (or oxygen-rich) gas are quickly destroyed, and oxygen (or carbon) based molecules can be formed through the re-formation process. So-called “photochemistry” or “PDR chemistry” is probably summarized this way, where more specific processes have been given in the previous section. In this picture, heavy molecules in the hot regions in PNe do not survive more than a week (100 years for CO), but are constantly re-formed. What we observe in PNe is the average of the rapid destruction and re-formation cycle. The chemical processes described in the previous section are similar to those for the galactic PDRs (Sternberg & Dalgarno 1995).

The picture presented above is yet to be tested, although comparisons with observations of NGC 7027 are encouraging (Hasegawa & Kwok 2001). Also, it is yet to be seen whether the hot-gas chemistry is applicable to more evolved PNe (globules in the Helix nebula, for example). So far, CO ($J = 1 - 0, 2 - 1$) observations do not indicate a rotational temperature higher than 100 K (Bachiller et al. 1997) in NGC 6720, NGC 6781, or NGC 7293. But then, CO ($J = 1 - 0, 2 - 1$) observations in NGC 7027 show no hint of $T_k \sim 1000$ K detected with *ISO*.

If the gas temperature is lower than 400 K in molecular gas in the torus or a globule in above-mentioned PNe, the hot-gas photochemistry will not work. An alternative mechanism that could drive the chemistry at low temperatures is X-ray ionization (Deguchi et al. 1990; Ali et al. 2001; Justtanont et al. 2000). If X-ray ionization is the dominant driving mechanism of chemistry, the chemical pathways will be different from Figure 3a (Ali et al. 2001).

The steady-state approach is clearly inadequate to deal with the initial ionization phase (CRL 618), in which remnant molecules from the AGB phase, photodissociation products, and ionized molecules all co-exist and react in a rapidly evolving physical environment. So far, only Howe et al. (1992) and Woods et al. (2001) have made time-dependent models of the initial evolutionary phase of PNe. The chemistry in this phase cannot be simply described as photo-chemistry. This is an exciting but challenging problem in astrochemistry, awaiting for future study.

Acknowledgments. Some part of this presentation was carried out in collaboration with Kevin Volk and Sun Kwok.

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