# MOLECULES IN PLANETARY NEBULAE

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## 1. INTRODUCTION

The study of molecules in planetary nebulae is still in its infancy; therefore, it is appropriate both to review existing knowledge and to anticipate developments that will arise as the subject matures. Briefly stated, this subject consists of observations of hydrogen, $H_2$, and carbon monoxide, CO, molecules in a very few nebulae; the tentative identification of the hydrogen molecular ion, $H_2^+$; unsuccessful searches for various other species; some theoretical work on molecular processes relevant to planetary nebulae; and the study of molecules in possible precursors of planetary nebulae. Such a facile summary might suggest that molecules are mere curiosities of peripheral interest; on the contrary, it can be asserted that molecular studies of planetary nebulae will yield important new information about their origins, structures, and evolution.

Some of the reasons for studying molecules in nebulae derive from their spectroscopic advantages over atomic species. Molecules are versatile diagnostic probes: they can be coupled to ultraviolet radiation fields through electronic transitions, their vibrational transitions can be excited in shock-heated neutral gas at temperatures $T \simeq 1000$ K, and they can reveal the coldest ($T \simeq 10-100$ K) neutral regions through rotational lines. Molecules are ideally suited for the determination of isotope abundances because a small difference in the mass of a molecule produces a large, and easily observable, difference in the rotational and vibrational structure of its spectrum. With the exception of the microwave line of $^3He^+$ (Rood et al. 1979), atomic spectra are unsuitable for isotope studies of nebulae. Isotope abundances may someday prove as valuable as element abundances in establishing the evolutionary role of planetary nebulae and the properties of the stars that form them. Molecules are particularly useful for studying the neutral gas associated with nebulae: in some cases, this otherwise unobservable material accounts for a large fraction of the total mass of a nebula. The interpretation of the spectra of planetary nebulae has traditionally provided problems of basic interest in atomic physics. There are many molecular processes important in

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nebulae, which may stimulate a similar symbiotic relationship with basic molecular physics. Molecules in the solid phase (i.e. dust grains) are of interest, but are beyond the scope of this brief review.

## 2. OBSERVATIONS AND INTERPRETATION

Mufson et al. (1975) observed CO rotational line emission (J=1-0) associated with NGC 7027 and reported marginal detections in IC 418 and NGC 6543. Knapp et al. (1982) observed the J=2-1 line of CO in the first two objects, but failed to detect it in the third. Zuckerman et al. (1977) searched unsuccessfully for CO in several other nebulae. Thronson (1982a) has made improved measurements of CO J=1-0 in NGC 7027. The CO line profiles in NGC 7027 are broad ($\Delta v$=32 km $s^{-1}$ at the base), with steep wings, suggestive of an expansion velocity of 16 km $s^{-1}$ for the molecular shell. The expansion velocity of the ionized nebula is 5-8 km $s^{-1}$ larger. Thronson observed the isotopic species $^{13}$CO and inferred an abundance ratio $n(^{12}CO)/n(^{13}CO)=36\pm6$, somewhat larger than the value suggested earlier by Mufson et al. This ratio must be regarded as a lower limit if the stronger $^{12}$CO line is optically thick. Thronson argues that if the molecular isotope ratio reflects the overall nuclear abundances in the atmosphere of the star that formed the nebula, and if the carbon/oxygen ratio in the nebula can be used to place an upper limit on the mass of the star (cf. Iben 1981), then the nebula was formed during the asymptotic giant branch phase of a star which began life with approximately 3 $M_{\odot}$. Such arguments are not definitive, but it seems clear that careful studies of isotope abundances in planetary nebulae will provide useful tests of theories of stellar evolution (cf. Finzi and Yahel 1978). Such abundance determinations will also help elucidate the contribution of planetary nebulae to the enrichment of heavy elements in the general interstellar medium. The angular extent of the CO emission in NGC 7027 is 40-50 arcsec (Mufson et al. 1975, Knapp et al. 1982), which is approximately 3 times larger than the mean diameter of the ionized nebula (Becklin et al. 1973). There are several ways to estimate the total neutral mass from CO emission, and all of them require questionable assumptions; however, it seems reasonable to accept Thronson's lower limit $M \geq 0.05\ d^2\ M_{\odot}$, where $d$ is the distance in kpc. The most recent re-examination of the distance to NGC 7027 (Pottasch et al. 1982) suggests that $1 \leq d \leq 1.5$ kpc. Far infrared emission due to cool dust in NGC 7027 ($T_d \simeq 90$ K) is confined to a region smaller than 20 arcsec, and any more extended dust shell must be colder than 35 K (Moseley 1980). Both a search for very cold dust (perhaps at 350 μm as suggested by Moseley) and a better measurement of the CO excitation temperature would help determine the conditions in the extended molecular cloud.

The first high-resolution infrared spectrum of NGC 7027 revealed v=1-0 vibration-rotation emission lines of $H_2$ near 2 μm (Treffers et al. 1976). By now, 7 lines in the v=1-0 band have been measured (Smith et al. 1981) and the spatial distribution of the v=1-0 S(1) line emission has been mapped (Beckwith et al. 1980). The excitation energies of the v=1-0 lines are $\Delta E/k \simeq 6800$ K, and the hydrogen molecules thus observed represent a small, but highly-excited, fraction of the molecular gas. The relative strengths of the v=1-0 lines arising in different rotational levels (v=1,J) can be described well by thermal populations at an excitation temperature $T_{ex}$=1100 K in NGC 7027 (Smith et al. 1981). For fully thermalized level populations and an emitting source that fills a 7x7 arcsec beam, the total column density of $H_2$ at this temperature is $N(H_2)=8.9\times10^{19}$ $cm^{-2}$. In ionization-bounded nebulae, a shock front will often precede the ionization front, and produce a compressed layer of neutral gas at an elevated temperature ($T\gtrsim1000$ K). Additional molecule formation processes that are not effective in cold gas become important in shock-heated regions (cf. Dalgarno 1981), and vibrational line emission in $H_2$ can be excited readily (Hollenbach and Shull 1977, Kwan 1977, London et al. 1977). There exist other processes by which nebular molecules can be excited to radiate: in $H_2$, both formation processes and ultraviolet pumping (Black et al. 1981) produce vibrational and rotational lines, and molecules like $CH^+$ and $C_2^-$ can be excited by resonance fluorescence involving nebular emission lines (Gahm et al. 1977). Beckwith et al. (1980) have used a shock model with a steep radial density gradient to account for the excitation of the hot $H_2$ and to estimate the total mass of cooler $H_2$ contained in a volume of the same size as the extended CO emission: the model-dependent result is $M\simeq0.9\ d^2\ M_\odot$. The central star of NGC 7027 is a copious source of ultraviolet photons which can excite vibrational lines by absorption and fluorescence (UV pumping). If UV pumping dominated the excitation, then the v=2-1 lines would be nearly as strong as the well-observed v=1-0 lines (cf. Black and Dalgarno 1976). Smith et al. (1981) placed upper limits on v=2-1 lines and Beckwith et al. (1980) measured the v=2-1 S(1) line at a level much below that expected from pure UV pumping: thus the rates of radiative excitation must be suppressed relative to the rates of collisional excitation. These observations permit a limit to be placed upon the ratio of the UV flux at 1000 Å to the density in the $H_2$ emitting region. The UV flux at the boundary of NGC 7027 can be estimated from the known size and emission measure of the nebula, and it is too large to be consistent with the weak v=2-1 lines, unless there is a significant amount of internal extinction, corresponding to $A_V\simeq0.6$-1.5 mag, between the central star and the emitting region. The observed line strengths in NGC 7027 can be explained without a shocked neutral zone by the combined effects of UV pumping and electron-impact excitation on $H_2$ inside the transition zone of the nebula, provided that the transition zone is thick enough (Black et al. 1981). The spatial distribution of $H_2$ emission, both in NGC 7027 and in NGC 6720 (Beckwith et al. 1978) differs from that of the bulk of the ionized gas, and is consistent with a relatively narrow emitting zone near the boundary. Infrared line emission from $H_2$ has also been observed in the nebulae NGC 6720, BD+30,3639, and Hb 12 (Beckwith et al. 1978). Additional sensitive searches for hot $H_2$ in planetary nebulae are needed.

Heap and Stecher (1981) observed anomalous flux distributions in the ultraviolet spectra of central stars of several planetary nebulae, and attributed the depressed fluxes shortward of 1500 Å to absorption by nebular $H_2^+$. Feibelman et al. (1981) presented similar data on other nebulae, and Seaton (1980) noted a flux anomaly shortward of 1500 Å in the central star of NGC 1514, which can probably also be attributed to $H_2^+$. The relative absorption, $\exp\{-N(H_2^+)\ \sigma(\lambda)\}$, using the cross sections $\sigma(\lambda)$ of Dunn (1968a,b), provides an excellent match of the observed flux deficiency if the $H_2^+$ is predominantly in its lowest vibrational state v=0. In NGC 6210, a column density $N(H_2^+)=8\times10^{16}$ $cm^{-2}$ is implied. We will argue below on theoretical grounds that the identification of nebular $H_2^+$ in its ground state is plausible.

Despite careful searches for the 18 cm lines of OH (Silverglate et al. 1979) only one detection of 1612 MHz maser emission, in Vy 2-2, has been reported (Davis et al. 1979). OH emission attributed to NGC 2438 (Turner 1971) was later shown to be due to an unrelated source 6.5 arcmin away (Hardebeck 1972, Goss et al. 1973).

An ionization-bounded nebula will possess a narrow transition zone at its boundary in which the hydrogen goes from being fully ionized to being almost completely neutral. Here, where the concentrations of electrons, protons, and neutral hydrogen atoms are comparable, the conditions are optimal for the formation of $H_2$, $H_2^+$, and $HeH^+$ by gas phase processes. The abundances of such simple molecules inside a steady state nebula have been discussed (Black 1978), and the variety of processes that control the abundance and excitation of $HeH^+$ have been studied (Flower and Roueff 1979, Roberge and Dalgarno 1982). Although $HeH^+$ was suggested as the source of the unidentified emission feature at 3.3 μm in NGC 7027 and other objects (Dabrowski and Herzberg 1977), subsequent observations have indicated that some other species is probably responsible for this broad, intense feature (Scrimger et al. 1978, Tokunaga and Young 1980).

Thronson and Lada (1982) have searched for the J=2-1 rotational line of SiO in seven planetary nebulae without success. While SiO appears to be underabundant in the gas phase relative to CO in NGC 7027, its absence from other nebulae may result from inadequate excitation conditions. Fairly sensitive searches failed to reveal either CH or HCN in NGC 7027 (Sume and Irvine 1977, Zuckerman et al. 1977). Nitrogen is overabundant in some objects, and careful searches for nitrogen-bearing molecules, e.g. CN, HCN, $HC_3N$, and $NH_3$, would be valuable.

Certain evolved stars that possess thick, dusty, molecular shrouds and that show evidence of high rates of mass loss have been identified as "proto-planetary nebulae" (Zuckerman 1978, 1980). Characteristics other than thick molecular envelopes have led to the identification of some emission line objects as the precursors of planetary nebulae (Kwok et al. 1978, Kwok and Purton 1979). These may represent a different evolutionary stage or an entirely distinct population of objects from the proto-planetary nebulae described by Zuckerman. The proto-planetary nebulae are usually distinguished by large infrared fluxes and by strong, broad CO emission lines indicative of expanding clouds (Zuckerman et al. 1976,1977,1978; Lo and Bechis 1976; Knapp et al. 1982). Two proto-planetary nebulae, AFGL 618 and AFGL 2688, exhibit $H_2$ line emission similar to that from NGC 7027 (Beckwith et al. 1978; Thronson 1981, 1982b), and in AFGL 618 the intensity has increased significantly over two years (Beck and Beckwith 1983). In order to understand fully the properties of the precursor stars and the processes by which they form planetary nebulae, it is necessary to determine the total amounts of mass involved and the element abundances. Element abundances (including isotope ratios) can be used to infer the processes of nucleosynthesis at work up to the time of rapid mass loss, and hence to help characterize the evolutionary state of a star when it forms a nebula. Moreover, the C/O abundance ratio is crucial for inferring masses and mass loss rates from observations of CO lines (Zuckerman 1980). In this connection, it is important to recognize that the overall abundances of elements like C and O may be disguised by the manner in which the atoms have been divided up between the gas and the dust. Whether dust grains are enriched in carbon, for example, can sometimes be determined from the 8-13 μm spectra of planetary nebulae (Aitken and Roche 1982 and references therein), and the broad infrared feature at $\lambda>24$ μm that is common to carbon stars and the nebulae IC 418 and NGC 6572 (Forrest et al. 1981). As indicated by the small number of planetary nebulae observed in CO lines, it is fairly rare for a *bona fide* planetary nebula to possess an extensive molecular envelope, while such envelopes are characteristic of the objects identified as proto-planetary nebulae. Evidently molecular processes are most important during the early evolution of the nebula.

In the atmospheres of stars that form planetary nebulae, high densities enable three-body processes to control molecular abundances; hence the abundances of many species approach their thermodynamic equilibrium values. These abundances may be frozen into the gas at some stage as the atmosphere expands. Relevant theoretical studies include those of Goldreich and Scoville (1976), Scalo and Slavsky (1980), McCabe et al. (1979), Clegg and Wootten (1980), Lafont et al. (1982), and Huggins and Glassgold (1982). Later, as the nebula expands and the optical depth of the molecular envelope decreases, the molecules become exposed to the destructive effects of the ambient interstellar radiation from outside and the intense ultraviolet radiation of the central star from inside. If the typical molecular lifetime becomes smaller than the nebular lifetime, then the molecular abundances will be determined by a statistical equilibrium of two-body processes.

Previous theoretical work has concerned the processes by which molecules form inside nebulae and models to explain their excitation. The photochemistry of a dense molecular shell close to a very hot central star still requires careful study: preliminary results of such an investigation are discussed in the following section. There is also a great need for detailed theoretical models of transition zones of nebulae in which charge transfer processes and the effects of dust have been fully incorporated.

## 3. DISCUSSION

Some problems concerning the abundance and excitation of molecules in planetary nebulae can be discussed in terms of simple models of the ionized nebulae and their surrounding molecular envelopes. Consider an idealized model in which the ionization front expands more rapidly than the molecular envelope. In the reference frame of the ionization front, molecules of initial density $n_o$ $cm^{-3}$ flow with relative velocity $v_o$ across the front into an ionized region of uniform electron density $n(e)$ and temperature $T_e \simeq 10^4$ K. Outside the ionization boundary, the molecules are completely shielded from H-ionizing photons ($h\nu > 13.6$ eV). The abundant species of particular interest, $H_2$ and CO, are special in that dissociation by less energetic photons ($h\nu < 13.6$ eV) occurs through line absorptions. Dissociation is rapid only into depths where these lines remain unsaturated; at greater depths the destruction rate decreases greatly and $H_2$ and CO molecules effectively shield themselves. Once they enter the nebula, the molecules will be exposed to large ionizing fluxes and to hot positive ions, and their lifetimes against destruction will be short, $\tau \simeq 10^5$-$10^6$ s. The principal reactions that affect the abundances of $H_2$, CO, and their ions, $H_2^+$ and $CO^+$, inside the nebula are summarized in the table, together with their rates. Photoionization rates assume a blackbody stellar radiation field of temperature $T_* = 3.29 \times 10^5$ K and a ratio of nebular radius to stellar radius $R_o/R_* = 5.7 \times 10^7$. The rates of charge transfer of $H^+$ with ground-state $H_2$ and CO have been estimated from the measured rates of the reverse processes (Karpas et al. 1979). Theory suggests that the low energy cross sections for dissociative recombination of $H_2^+$ (reaction 3) increase by an order of magnitude as the vibrational state of $H_2^+$ goes from v=0 to v=1 and from v=1 to v=2 (Zhdanov 1980, Derkits et al. 1979). The adopted rate coefficient, $k_{dr}$, represents an average over the states v=0,1,2 (Auerbach et al. 1977), and it is almost certain to be excessively large for ground-state $H_2^+(v=0)$. The rate $k_{dr}$ for $CO^+$ is from Mentzoni and Donohoe (1969), and all collisional rates in the table are evaluated at $T_e = 10^4$ K. The destructions of $H_2$ and CO by reactions 1 and 2 are the sources of the ions $H_2^+$ and $CO^+$. The rates of processes like photodissociation and e-impact dissociation, which form neutral products, are factors of at least 10 smaller than those of reactions 1 and 2 at the temperatures and radiation fields of interest (cf. Black 1978). The ions have even shorter lifetimes than their parent molecules. For a uniform spherical nebular

| | Reaction | Rate |
|---|---|---|
| 1. | $H_2 + h\nu \rightarrow H_2^+ + e$ | $k_{pi} = 1.4 \times 10^{-6}$ $s^{-1}$ |
| | $CO + h\nu \rightarrow CO^+ + e$ | $k_{pi} = 8.6 \times 10^{-6}$ $s^{-1}$ |
| 2. | $H_2 + H^+ \rightarrow H_2^+ + H$ | $k_{ct} = 7.7 \times 10^{-11}$ $cm^3\ s^{-1}$ |
| | $CO + H^+ \rightarrow CO^+ + H$ | $k_{ct} = 8.0 \times 10^{-11}$ $cm^3\ s^{-1}$ |
| 3. | $H_2^+ + e \rightarrow H + H$ | $k_{dr} = 8.9 \times 10^{-9}$ $cm^3\ s^{-1}$ |
| | $CO^+ + e \rightarrow C + O$ | $k_{dr} = 1.1 \times 10^{-7}$ $cm^3\ s^{-1}$ |

boundary of radius $R_o$, the expressions governing the densities of these molecules as functions of distance $r$ from the central star are just those used to describe density distributions in the coma of an idealized comet (Haser 1957). The distance scale must be reversed, however, because the nebular molecules flow inward from the boundary, rather than outward from the nucleus. In the cases of interest, the molecules are confined to a very thin ($\Delta r \simeq \tau v_o < 10^{13}$ cm) zone near the boundary; therefore, $y \equiv R_o - r << R_o$, and the number densities of molecule X ($=H_2$ or CO) and its ion $X^+$ are given approximately by

$$n(X) = n_o(X) \exp(-\beta(X)y) \tag{1}$$

$$n(X^+) = n_o(X)\ \beta(X)\ \{\exp(-\beta(X)y) - \exp(-\beta(X^+)y)\}/\{\beta(X^+)-\beta(X)\}\ . \tag{2}$$

The factors $\beta$ are given by $\beta(X) \simeq (k_{ct}\ n(e) + k_{pi})/v_o$ cm$^{-1}$ and $\beta(X^+) = k_{dr}\ n(e)/v_o$ cm$^{-1}$, when it is assumed that the systematic inflow velocities of the initial and product species are equal and independent of $y$. This approximation permits useful simplifications, but is not strictly valid. The initial density will be $n_o(H_2) \simeq 200\ n(e)$ for a molecular shell at T=100 K in approximate pressure balance with an ionized nebula at $T_e=10^4$ K. The corresponding initial density of CO can be at least as large as $n_o(CO) \simeq 4\times10^{-4}\ n_o(H_2)$, even if half the carbon is in grains. We adopt $v_o$=10 km s$^{-1}$. The resulting column densities, $N(X) = \int_0^\infty n(X)\ dy$ cm$^{-2}$, computed from equations (1) and (2) are $2\times10^{18}$, $2\times10^{16}$, $4\times10^{14}$, and $7\times10^{11}$ cm$^{-2}$, for $H_2$, $H_2^+$, CO, and $CO^+$, respectively. The column densities are quite insensitive to the value of $n(e)$ in the range $10^3$-$10^5$ cm$^{-3}$, because a decrease in $n_o(H_2)$ is largely compensated by a decrease in $\beta$ in the integration over path length $y$.

The observable properties of these molecules depend upon their degree of vibrational and rotational excitation. The homonuclear species $H_2$ and $H_2^+$ lack permanent dipole moments and thus have long radiative lifetimes in excited states (cf. Black and Dalgarno 1976, Posen et al. 1982). $H_2$ will be substantially excited in nebulae. $H_2^+$, however, will exist primarily in v=0 because it is formed preferentially in that state by charge transfer and because excited molecules are removed rapidly by dissociative recombination. Indeed, if realistic, v-dependent rates of dissociative recombination are used, a ratio of populations n(v=0)/n(v=1) >25 is expected, and the total column density will be increased to $N(H_2^+) \simeq 10^{17}$ cm$^{-2}$, in harmony with the value suggested by the observations of Heap and Stecher (1981). Both CO and $CO^+$ will exist mostly in v=0, and the rotational populations of the latter should be subthermal because of its large dipole moment and very rapid dissociative recombination.

We conclude that the identification of $H_2^+$(v=0) in nebulae is plausible. If the identification is correct, $H_2^+$ must be accompanied by observable concentrations of $H_2$, CO, and $CO^+$. The predicted column density of nebular $H_2$ is 40 times smaller than that ascribed to a shocked neutral layer in NGC 7027 (Smith et al. 1981, Beckwith et al. 1980) and could have escaped detection through infrared emission lines. The nebular $H_2$ will, however, produce ultraviolet absorption lines in the spectra of central stars: e.g., $N(H_2)=2x10^{18}$ cm$^{-2}$ at $T=10^4$ K will yield an equivalent width W=0.2 Å (including curve of growth effects) in the $B^1\Sigma_u^+-X^1\Sigma_g^+$ 0-3 R(7) line at 1298.2 Å. Ultraviolet absorption lines of CO have been sought, but not detected, in the spectrum of the central star of IC 418 (Clavel and Flower 1980). The quoted upper limit, N(CO) $\lesssim 3x10^{14}$ cm$^{-2}$, is similar to the model prediction; therefore, a more sensitive search for CO in nebulae suspected of harboring $H_2^+$ might prove fruitful. Because of its subthermal excitation, the small amount of $CO^+$ might be detectable, either by the comet tail $(A^2\Pi-X^2\Sigma^+)$ lines in absorption against the central star, or by millimeter wavelength rotational lines. It is interesting that rotational lines of $CO^+$ have been observed towards the Orion Nebula (Erickson et al. 1981), and that $CO^+$ has been suggested as the source of possible absorption bands in the spectra of several stars in and near the Orion Trapezium (Tamura and Ishii 1977). The flow of molecules from the Orion Molecular Cloud into the nebula is expected to produce nebular molecules in the manner outlined above for planetary nebulae: perhaps the $CO^+$ rotational lines in Orion can be explained in this way also. Searches for $CO^+$ in planetary nebulae would be interesting.

A simplified photochemical model has been constructed for predicting the abundances of H, $H_2$, C, $C^+$, CO, OH, and other simple species as functions of distance through the molecular envelope (details will be published elsewhere). The distances beyond the ionization front at which hydrogen becomes mostly $H_2$ and carbon becomes mostly CO are sensitive to the total density of the envelope. These models can be compared with observational data on the envelope around NGC 7027. Pottasch et al. (1982) observed no H 21 cm line and derived a strong limit $N(H)<1.2x10^{20}$ cm$^{-2}$ and a weak (model-dependent) limit $N(H)\lesssim(2-4)x10^{19}$ cm$^{-2}$. The CO column density is $N(CO)\gtrsim 2x10^{17}$ cm$^{-2}$ (Thronson 1982a). These constraints are satisfied by the model only if $n=n(H)+2n(H_2)>4x10^5$ cm$^{-3}$ (strong H limit) or $n>10^6$ cm$^{-3}$ (weak H limit) near the boundary. Beyond the C/CO transition distance, the density can decrease without serious effects on the abundances until the molecules become exposed to unattenuated galactic background radiation that enters from outside. An additional constraint is supplied by an upper limit on the intensity of the C 76α radio recombination line (Bignell 1974). At low temperatures, $T\simeq 20$ K, implied by the excitation temperature of CO (Thronson 1982a) and the relative sizes of the CO envelope and far IR emitting region (Moseley 1980), the limit $\int n(e)\, n(C^+)\, dr < 3.2$ cm$^{-6}$ pc requires a model with $n>2x10^6$ cm$^{-3}$ near the boundary. At densities this high, the important chemical timescales are short compared with a nebular lifetime, and steady-state abundances are realistic. At lower densities, more elaborate time-dependent models will be required.

In summary, even though only a few molecules have been observed in a small number of planetary nebulae, the existing observations augur well for future molecular studies of planetary nebulae and their precursors.

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OSTERBROCK: What is the evidence that the $H_2$ v = 1 → 0 emission is concentrated near the boundary of NGC 7027? What is meant by the boundary - that of the ionized region or that of the ionized, high density region?

BLACK: The spatial distribution of the S(1) line intensity was mapped by Beckwith et al. (1980) with resolution adequate to show a marked contrast with the distribution of most of the atomic line emission but inadequate to define precisely the $H_2$ emitting region. The observations are consistent with a narrow emitting zone near the boundary of the ionized region.

REAY: Using the U.K. Infrared Flux Collector (Hawaii), my colleagues and I have detected $H_2$ S(1) v = 1 → 0 emission from NGC 6302 at one position only, near the centre where the (so far undetected) central star would be expected to be. Flux levels $\simeq 5 \times 10^{-18}$ W $cm^{-2}$ $\mu m^{-1}$.

BLACK: This is extremely interesting, particularly in view of the detection of H I 21 cm line absorption in the same direction (L.F. Rodriguez and J.M. Moran, contributed poster paper, this volume). Further study of the distribution of neutral gas associated with NGC 6302 may help to partly explain the complicated dynamical structure of the nebula.

CLEGG: At UCL, we have just completed a survey of the ultraviolet fluxes from about twenty PN central stars with the IUE satellite. However, we were not able to confirm the detection of $H_2^+$ absorption by Heap, Stecher and others. In particular, many stars cooler that about 50 000 K show line blanketing between 1200 Å and 1500 Å.

HEAP: Yes, I agree that the effect of line blanketing can be important, although this should be diminished in a differential analysis, which we did. Another source of uncertainty in the identification of $H_2^+$ in NGC 6210 is the extinction by dust internal to the nebula.

ZUCKERMAN: I have been using the 20 m radiotelescope at Onsala (Sweden) with Olofsson and Johansson (Onsala), Rieu (Meudon) and Sopka (Maryland) to study HCN in Red Giant stars and a few PN. We have detected weak J = 1 → 0 HCN emission from NGC 7027. This is the first time that a polyatomic molecule has been seen in a PN environment. There has been some controversy in the literature as to whether NGC 7027 is oxygen-rich (O/C > 1) or carbon-rich (C/O > 1). The detection of HCN shows reasonably conclusively that the envelope is carbon-rich or S-type (C/O $\approx$ 1) since this molecule is expected to have an extremely small abundance in an oxygen-rich environment. Observation of HCN in Red Giant stars is consistent with this expectation.

BLACK: This is very encouraging news, and I hope that more such observations will be made. The absence of thermal Si O emission (Thronson and Lada, 1982) would also seem to support C/O $\gtrsim$ 1 in the envelope of NGC 7027.

KALER: There is evidence that C → N conversion takes place on the AGB which affects the $^{12}C/^{13}C$ ratio. It is very important to observe this ratio in high N-abundance nebulae such as NGC 2440. However, the observed CO may relate to an earlier stellar wind, and the measured $^{12}C/^{13}C$ ratio may not reflect that in the nebular proper. Have you any comments?

BLACK: I agree that the molecular material may often have been ejected earlier than most of the nebular gas. The significance of the molecular isotopic abundance ratios cannot be established without more and better observations. Attempts to measure isotope abundances of other elements, such as N, although very difficult, should be made.

MATHIS: You showed processes for producing $H_2$ by gas-phase reactions. Do these dominate the production of $H_2$ in PN? Do you still believe that $H_2$ is produced almost entirely on grains in the general interstellar medium?

BLACK: Although it is uncertain, inside nebulae the dust may be too hot for $H_2$ to form on dust at a sufficiently high rate to compete with gas-phase processes. In cool, extended molecular envelopes, on the other hand, formation of $H_2$ on dust grains probably dominates, although the formation time scale can be long compared with a nebular lifetime if the density is low. Gas-phase processes are totally inadequate to account for the large amounts of $H_2$ observed in the general interstellar medium, but are probably responsible for most other molecules.