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MOLECULES IN PLANETARY NEBULAE

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ABSTRACT

It is shown that significant abundances of simple molecules, like H_2, H_2^+, HeH^+, OH, and CH^+, can exist in the transition zones of ionized nebulae. The dominant molecular processes in such regions, where neutral atoms and free electrons mingle at moderately high temperatures, are discussed. Equilibrium abundances of molecules are computed for a model transition zone. It is possible that the observed rotation-vibration lines of H_2 in NGC 7027 arise in such a region. Both HeH^+ and OH will exist in sufficient amounts to radiate detectable lines near 3 μm: The source of undentified lines at 3.28 and 3.4 μm in NGC 7027 is thus not yet clearly established by low-resolution spectra.

Subject headings: infrared: sources — line identifications — molecular processes — nebulae: planetary

I. INTRODUCTION

Molecular hydrogen has recently been detected in NGC 7027 (Treffers *et al.* 1976), and HeH^+ has been suggested (Dabrowski and Herzberg 1977) as the source of unidentified spectral features near 3 μm wavelength in the same nebula (Merrill, Soifer, and Russell 1975). It is important to inquire, then, whether the nebula itself can support detectable amounts of these and other molecules.

It is shown that the conditions of partial ionization and moderate temperature ($10^3 \leqslant T \leqslant 10^4$) expected in the transition zone of a planetary nebula are conducive to the efficient formation of several simple molecules. Molecular ions like H_2^+ and HeH^+, which would not have high abundances in normal interstellar clouds, and familiar species like H_2, CH^+, and OH can occur in significant amounts even in the hostile surroundings of an ionized nebula.

A simple model of a nebular transition zone predicts an amount of H_2 approaching that implied by the lines observed in NGC 7027 (Treffers *et al.* 1976). The lifetime of H_2 against photodissociation is, of course, very short because of the proximity of a hard-ultraviolet radiation source. H_2 is excited about 7 times as fast as it is dissociated, with a yield of about 3 infrared line photons per ultraviolet absorption in the ensuing rotation-vibration cascade; thus a relatively small equilibrium concentration of H_2, when rapidly pumped, becomes readily observable because of large effective line emissivities.

The predicted amount of HeH^+ provides lines of the observed intensity (Merrill *et al.*; Dabrowski and Herzberg 1977) near 3 μm. The identification of HeH^+ on the basis of low-resolution spectra is not certain, however, because OH is predicted to be abundant as well, and because OH also has vibrational transitions at the wavelengths of interest.

II. MOLECULAR PROCESSES

The transition zone of an ionization-bounded nebula is the boundary region in which the fractional ionization of hydrogen decreases from a value near unity to a value near zero. The consequent reduction in heating by photoelectrons results in a decrease in temperature from $T \geqslant 10^4$ K to $T \leqslant 10^3$ K through the zone. In comparison with cold, neutral interstellar clouds, the coexistence of neutral atoms with free electrons and the relatively high temperatures favor formation of H_2 by associative detachment of H^-,

$$H^- + H \rightarrow H_2 + e\,, \qquad (1)$$

following radiative association to form the negative ion

$$H + e \rightarrow H^- + h\nu \qquad (2)$$

(McDowell 1961). The infrared continuum emission, ascribed to thermal emission by hot grains, that is observed in many nebulae may be inconsistent with catalysis on cold grain surfaces as an important source of H_2. In equilibrium, H^- is removed by reaction (1); by photodetachment,

$$H^- + h\nu \rightarrow H + e\,; \qquad (3)$$

and by mutual neutralization,

$$H^- + X^+ \rightarrow H + X \qquad (4)$$

involving an arbitrary positive ion X^+. H_2 is destroyed by photons:

$$H_2 + h\nu + H_2^* \rightarrow 2H + h\nu\,, \qquad (5)$$

$$H_2 + h\nu \rightarrow H_2^+ + e\,. \qquad (6)$$

At the temperatures and densities of interest, collisional dissociation (Aannestad 1973; Gardiner and Kistiakowsky 1961),

$$H_2 + H \rightarrow 3H\,, \qquad (7)$$

may be a competitive process. Dissociation by electron impact excitation of the $b\,^3\Sigma_u{}^+$ state of H_2 will be relatively less important here, judging by the cross sections in Miles, Thompson, and Green (1972). If reactions (1) and (4) dominate the removal of H^- and if equation (7) can be neglected, then the equilibrium concentration, $n(H_2)$, of molecular hydrogen is given approximately by

$$n(H_2) \approx \left\{\frac{(1-x)^2 x k_1 k_2}{(k_5 + k_6)[(1-x)k_1 + xk_4]}\right\} n^2\,, \qquad (8)$$

where $n = n(H) + n(H^+)$ is the total hydrogen density, $n(e) \approx n(H^+) = xn$ is the electron density in terms of the fractional ionization x, and k_i is the rate coefficient of reaction (i). For $x = 0.5$ and typical values of rate coefficients at $T = 10^4$ K, $n(H_2) \approx 10^{-10}n^2$.

Photoionization (reaction [6]) produces $H_2{}^+$ at a rate which decreases drastically with depth through the zone, as ionizing photons are removed by H. Another source of $H_2{}^+$ is radiative association,

$$H^+ + H \rightarrow H_2{}^+ + h\nu\,. \qquad (9)$$

The rate coefficient of reaction (9) in a recent quantum mechanical calculation by Ramaker and Peek (1976) is virtually identical to that in the original semiclassical treatment of Bates (1951) over the relevant temperature range. Dissociative recombination,

$$H_2{}^+ + e \rightarrow 2H\,, \qquad (10)$$

and photodissociation,

$$H_2{}^+ + h\nu \rightarrow H^+ + H\,, \qquad (11)$$

remove $H_2{}^+$. The cross section for photodissociation of $H_2{}^+$ (Dunn 1968) depends upon its degree of vibrational excitation. The larger the vibrational quantum number v, the longer the wavelength at which the cross section peaks. The central star of a planetary nebula emits so many more photons in the far-ultraviolet than in the visible, however, that the dissociation rate computed for $H_2{}^+$ in its lowest state is fairly representative even for a thermal distribution of vibrational state populations at $T = 10^4$ K. An additional destruction mechanism,

$$H_2{}^+ + He \rightarrow HeH^+ + H\,, \qquad (12)$$

is also a significant source of HeH^+. This reaction is substantially endothermic for ground-state $H_2{}^+$; however, it is rapid for $H_2{}^+$ with $v > 3$, states which may be well populated at $T > 5000$ K. Cross sections for reaction (12) have been determined by Chupka, Berkowitz, and Russell (1969) for specific v. When these cross section data are integrated over a Maxwellian velocity distribution and averaged over a thermal distribution of vibrational populations of $H_2{}^+$, we find an approximate representation of the rate coefficient

$$k_{12} \approx 3 \times 10^{-10} \exp(-6717/T)\ \mathrm{cm^3\ s^{-1}}\,.$$

This result is in harmony with the rate measured by Neynaber and Magnuson (1973).

In what follows, the populations of vibrational states of $H_2{}^+$ are assumed to be thermalized at the kinetic temperature. Inelastic collisions with electrons should be able to maintain thermal populations at the densities considered in § III in competition with photodissociation and quadrupole radiative transitions (Bates and Poots 1953). If, however, the rate of reaction (10) is as large as suggested recently by Bottcher (1976), then some excited vibrational states may have nonthermal populations, and the predicted abundances of $H_2{}^+$ and HeH^+ may be overestimates.

A dominant source of HeH^+ in laboratory discharges is

$$He^* + H_2 \rightarrow HeH^+ + H + e\,, \qquad (13)$$

a reaction in which internal energy in an excited helium atom (usually in the metastable $2\,^3S$ state) is able to cause dissociation and ionization in a collision with H_2 (Mahan 1971). In a low-density plasma like a gaseous nebula, the population of metastable He ($2\,^3S$) is not insignificant. The determination of this population is in itself an intricate problem (Drake and Robbins 1972). The concentration of metastable helium, $n(2\,^3S)$, is given approximately by the balance between the effective rate of recombination to $2\,^3S$,

$$n(e)n(He^+)\alpha(2\,^3S)\ \mathrm{cm^{-3}\ s^{-1}}\,,$$

and the rate of magnetic-dipole transitions to the ground state,

$$A(2\,^3S\text{–}1\,^1S) = 1.27 \times 10^{-4}\ \mathrm{s^{-1}}$$

(Drake 1971). At the appropriate nebular temperatures,

$$n(2\,^3S)/n(He^+) \approx 10^{-9}n(e)\,.$$

In the detailed calculations below, collisional processes have also been included, as in equation (1) of Drake and Robbins (1972).

Dabrowski and Herzberg (1977) have proposed that there is a substantial probability of forming HeH^+ by vibrational inverse predissociation,

$$H^+ + He \rightarrow HeH^{+*} \rightarrow HeH^+ + h\nu\,. \qquad (14)$$

The number of quasi-bound levels of HeH^+ and its large dipole moment suggest a large rate coefficient. Principal destruction processes are expected to be

$$HeH^+ + e \rightarrow He + H\,, \qquad (15)$$

$$HeH^+ + H \rightarrow H_2{}^+ + He\,, \qquad (16)$$

and

$$HeH^+ + h\nu \rightarrow He + H^+\,. \qquad (17)$$

In a molecular region, HeH^+ would also be removed by the rapid reaction

$$HeH^+ + H_2 \rightarrow H_3^+ + He$$

(Johnsen and Biondi 1974).

In the presence of H_2 at high temperatures,

$$O + H_2 \rightarrow OH + H \quad (18)$$

becomes efficient. OH is also formed by inverse predissociation,

$$O + H \rightarrow OH^* \rightarrow OH + h\nu \quad (19)$$

(Smith and Zweibel 1976; Julienne, Krauss, and Donn 1971). OH is removed primarily by photodissociation and by charge transfer with H^+.

At the high temperatures of a nebular transition zone, CH^+ may be formed by the otherwise endothermic reaction

$$C^+ + H_2 \rightarrow CH^+ + H \quad (20)$$

in addition to the conventional direct source

$$C^+ + H \rightarrow CH^+ + h\nu \,. \quad (21)$$

Destruction is presumed to occur rapidly by

$$CH^+ + e \rightarrow C + H \quad (22)$$

(Krauss and Julienne 1973; Bardsley and Junker 1973), by

$$CH^+ + H \rightarrow C^+ + H_2 \,, \quad (23)$$

and by

$$CH^+ + h\nu \rightarrow C^+ + H \,. \quad (24)$$

Reactions similar to (18)–(24) involving nitrogen might result in the formation of NH and NH^+.

It is probably safe to conclude that the preceding discussion identifies those molecules most likely to have substantial abundances in nebular transition zones. Abundant molecules in these circumstances satisfy the following criteria: (1) They arise from the very most abundant elements (H, He, C, N, and O) in appropriate stages of ionization, and (2) they form directly by radiative association or through three intermediate species, H^-, H_2, and H_2^+. These criteria exclude CO; the extended CO line emission observed in the vicinity of NGC 7027 (Mufson, Lyon, and Marionni 1975) most likely arises from surrounding interstellar material that is distinct from that which produces the H_2 lines. Other second-generation species such as H_2O and H_3^+ whose existence requires reactions between two molecules are also excluded from the company of abundant constituents. The chemical processes described above, the adopted rate coefficients, and the references are listed in Table 1.

III. A MODEL TRANSITION ZONE

In order to make quantitative predictions of molecule abundances in nebulae, a model transition zone, computed by Flower (1969), has been used as a basic framework. The model has a total density $n = 7000 \text{ cm}^{-3}$, and it is 2.9×10^{17} cm from a central star represented by a blackbody of temperature $T_* = 10^5$ K. Flower has calculated the concentrations of important atoms and ions and the electron temperature as functions of depth through the model zone. We have computed the equilibrium abundances of H^-, H_2, H_2^+, HeH^+, OH, CH^+, and He ($2\,^3S$) as discussed above. This model does not include (1) the effects of charge transfer upon ionization equilibria (cf. Williams 1973), (2) the gas dynamics at the ionization boundary, and (3) the effects of dust upon the transfer of ionizing radiation and upon the formation of H_2. Molecular abundances based on such a model should, however, be quantitatively significant to an order of magnitude or so with respect to a real nebula. The results of the chemical model are shown in Figure 1. Concentrations of the important species are plotted as functions of linear depth through Flower's (1969) transition zone model. The concentrations of H and of free electrons have been reduced by factors of 10^5 for presentation on the same scale. The resulting column densities of H_2, HeH^+, and OH are 5.7×10^{13}, 4.7×10^9, and $1.5 \times 10^9 \text{ cm}^{-2}$, respectively.

The molecular hydrogen in the transition zone radiates through forbidden rotation-vibration transitions in the infrared which are excited in the cascade following ultraviolet absorption and fluorescence (Black and Dalgarno 1976). In the radiation field of interest here, the rate of ultraviolet absorption and fluorescence to bound vibrational levels is 7.0 times the dissociation rate. Each such fluorescent excitation yields about 3 infrared line photons in the subsequent cascade, on average, as long as the excited states decay predominantly through these lines rather than by collisions or by ultraviolet absorption. The upper state ($v = 1, J = 3$) of the 1–0 $S(1)$ line at 2.12 μm is populated at about 0.20 times the dissociation rate given in Table 1. Because the transition probability $A = 3.47 \times 10^{-7} \text{ s}^{-1}$ is roughly 0.1 times the rate of ultraviolet absorptions out of the upper level in this model, only one of every 10 excitations of ($v = 1$, $J = 3$) leads to the emission of an infrared line photon. The received flux in the 1–0 $S(1)$ line from the model nebula at a distance of 1.3 kpc will be 7×10^{-16} ergs $\text{cm}^{-2}\text{ s}^{-1}$. This distance is comparable to that of NGC 7027 (Cahn and Kaler 1971). The linear size of the model nebula and the temperature of its exciting star are also very similar to those inferred for NGC 7027; however, the density in the actual nebula is thought to be almost 10 times higher, $n = 6 \times 10^4 \text{ cm}^{-3}$, as indicated by the strengths of forbidden lines (Miller and Mathews 1972). Since the density of H_2 varies as n^2 (eq. [8]), a model nebula scaled to the conditions in NGC 7027 would be capable of providing a received flux of order 5×10^{-14} ergs $\text{cm}^{-2}\text{ s}^{-1}$ in the 1–0 $S(1)$ line. This flux is 20 times smaller than the observed flux, estimated to be of order 10^{-12} ergs $\text{cm}^{-2}\text{ s}^{-1}$ by Treffers *et al.* (1976). The present calculation is an extreme lower limit, however, because the effects of grains and neutral condensations inside the nebula

TABLE 1

MOLECULAR PROCESSES

Reaction	Rate Coefficient	Reference
$H + e \rightarrow H^- + h\nu$	3.9×10^{-15} (T = 10000)	3
$H^- + H \rightarrow H_2 + e$	2.7×10^{-9} (T = 10000)	4
$H^- + X^+ \rightarrow H + X$	$4 \times 10^{-6}\ T^{-1/2}$	5
$H^- + h\nu \rightarrow H + e$	5.34×10^{-6} [1+0.33 exp(−1.4 x 10^{-18}N(H))]	6,1
$H_2 + h\nu \rightarrow H + H$	4.69×10^{-7} [1+0.241 exp(−5.68 x 10^{-18}N(H))]	7,1
$H_2 + h\nu \rightarrow H_2^+ + e$	3.75×10^{-6} exp(−4.61 x 10^{-19}N(H))	8,1
$H_2 + H \rightarrow H + H + H$	$2 \times 10^{-7}\ T^{-1/2}$ exp (−52000/T)	9
$H^+ + H \rightarrow H_2^+ + h\nu$	(2.325 T − 1375) x 10^{-20} (T $\gtrsim$ 5000)	10
$H_2^+ + h\nu \rightarrow H^+ + H$	1.81×10^{-6}	11,1
$H_2^+ + e \rightarrow H + H$	$4.2 \times 10^{-8}\ T^{-1/2}$	12
$H_2^+ + He \rightarrow HeH^+ + H$	3.0×10^{-10} exp (−6717/T)	13,1
$H_2^+ + H \rightarrow H^+ + H_2$	10^{-11} ?	2
$H^+ + He \rightarrow HeH^+ + h\nu$	10^{-18}	2,14,17
$He^* + H_2 \rightarrow HeH^+ + H + e$	10^{-9}	2,15
$HeH^+ + e \rightarrow He + H$	10^{-8}	2,16
$HeH^+ + H \rightarrow H_2^+ + He$	10^{-10}	17,19
$HeH^+ + h\nu \rightarrow He + H^+$	1.81×10^{-6}	2,18
$O + H \rightarrow OH + h\nu$	5.0×10^{-19}	20
$O + H_2 \rightarrow OH + H$	3×10^{-14} T exp(−4480/T)	21
$OH + h\nu \rightarrow O + H$	9.42×10^{-7}	20,1
$OH + H^+ \rightarrow OH^+ + H$	10^{-9}	22
$C^+ + H_2 \rightarrow CH^+ + H$	2×10^{-10} exp(−4640/T)	23,2
$C^+ + H \rightarrow CH^+ + h\nu$	1.27×10^{-17} (T = 1000)	24
$CH^+ + H \rightarrow C^+ + H_2$	$7.5 \times 10^{-15}\ T^{1.25}$	25
$CH^+ + e \rightarrow C + H$	10^{-7}	26
$CH^+ + h\nu \rightarrow C^+ + H$	6.28×10^{-8}	27

*Rate coefficients of two-body processes are in $cm^3\ s^{-1}$. Rates of photon processes are in s^{-1} and are appropriate for a blackbody radiation field of temperature T_r = 100,000K and dilution factor 1.21×10^{-14}. N(H) is the column density, cm^{-2}, of atomic hydrogen.

REFERENCES.—(1) This work. (2) Estimate. (3) Dalgarno and Kingston 1963. (4) Browne and Dalgarno 1969. (5) Dalgarno and McCray 1973; Petersen *et al.* 1971. (6) Macek 1967; Doughty *et al.* 1966. (7) Stecher and Williams 1967; Dalgarno and Stephens 1970. (8) Ford *et al.* 1975; Crasemann *et al.* 1974; Kaplan and Markin 1973. (9) Aannestad 1973. (10) Ramaker and Peek 1976; Bates 1951. (11) Dunn 1968. (12) Dubrovskii and Obedkov 1967. (13) Chupka *et al.* 1969. (14) Dabrowski and Herzberg 1977. (15) Mahan 1971. (16) Atreya *et al.* 1974. (17) Hutchins 1976. (18) Assumed to be similar to the rate of photodissociation of H_2^+. (19) Rutherford and Vroom 1973. (20) Smith and Zweibel 1976. (21) Oppenheimer 1975. (22) Herbst and Klemperer 1973. (23) Maier 1967. (24) Abgrall *et al.* 1976, extrapolated to higher temperatures. (25) Solomon and Klemperer 1972. (26) Bardsley and Junker 1973; Krauss and Julienne 1973. (27) Assumes an effective oscillator strength $f = 0.01$ at 950 Å (cf. Solomon and Klemperer 1972).

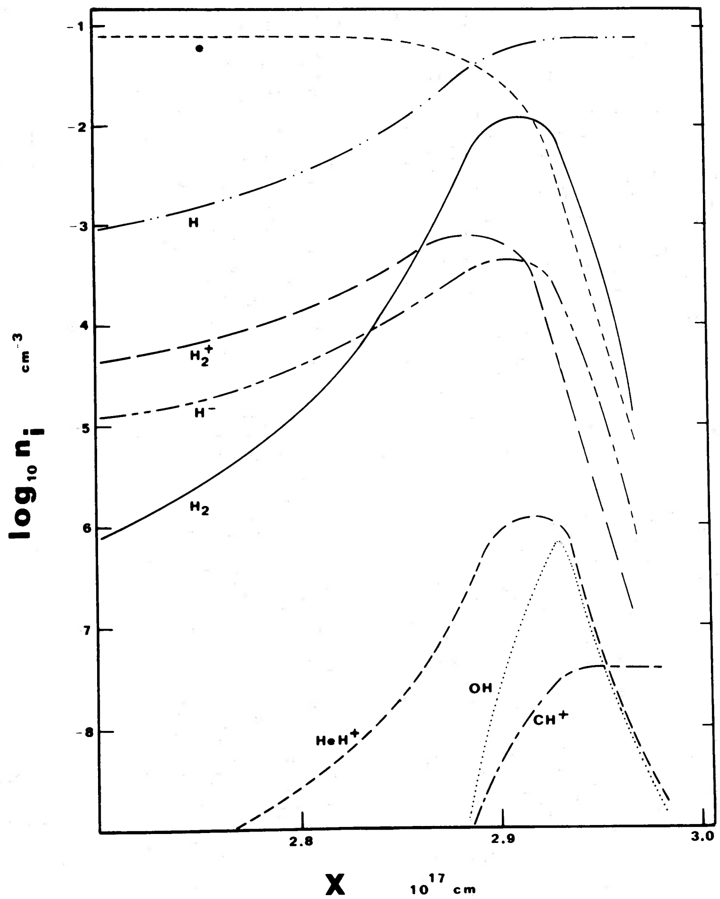

FIG. 1.—Computed molecule concentrations in the model transition zone. Density in cm^{-3} is plotted as a function of linear distance from the central star in units of 10^{17} cm. The densities of electrons and hydrogen atoms have been reduced by a factor of 10^5 for presentation on the same scale.

have not been taken into account. Telesco and Harper (1977) find that most of the far-infrared emission from NGC 7027 can be attributed to grains at temperatures of 120 K or less, present in a gas to dust ratio less than $\sim$200 by mass. According to Barlow and Silk (1976), such grains might also contribute to the formation of H_2, and their presence will certainly increase the lifetimes of the molecules as a result of ultraviolet extinction. The likely existence of neutral condensations inside the nebula might increase the effective size of regions of radiating molecules. A detailed model of the transition zone and neutral regions in NGC 7027 will be necessary before a decision can be made as to whether the observed H_2 line emission can be explained quantitatively.

In order for collisional excitation by electrons or protons at $T = 9000$ K and $n(H^+) \approx n(e) = 10^4$ cm^{-3} to rival the emissivity in the 1–0 $S(1)$ line due to ultraviolet fluorescence, the appropriate inelastic cross section at 1 eV impact energy must be at least of the order of 10^{-17} cm^2. A lower density would require a proportionally higher cross section. Such a large cross section appears to be ruled out by direct measurement in the case of electron impact (Crompton, Gibson, and McIntosh 1969). Vibrational excitation by proton impact is likely to have cross sections of order 10^{-18} cm^2 or less at 1 eV, based upon comparison with accurate calculations of inelastic Li^+–H_2 collisions (Schaefer and Lester 1975). Neutral atom encounters are surely negligible in comparison (Heidner and Kasper 1972).

The very large dipole moment of HeH^+ allows for vibrational transitions of considerable strength even though this molecule is rather less abundant than H_2, which, however, can radiate only forbidden lines in the infrared. Dabrowski and Herzberg (1977) have shown that the predicted emission spectrum can match fairly well the positions and shapes of features at 3.09 and 3.4 μm observed in NGC 7027 (Merrill *et al.*). This emission can include contributions from radiative association (reaction [14]) as well as from direct collisional excitation. The strongest feature in the 1–0 band of HeH^+ at 3.09 μm will produce a received flux from the model region described above of order 10^{-9} ergs cm^{-2} s^{-1}, on the basis of the calculated line strength data of Dabrowski and Herzberg (1977). The observed flux in the 3.09 μm feature of NGC 7027 is 4×10^{-10} ergs cm^{-2} s^{-1} (Merrill *et al.*). A detailed calculation of the complete HeH^+ spectrum at high temperature will be required in order for one to determine whether the broad 3.4 μm feature can also be matched. It is important to note that the $\Delta v = 1$ progression in the vibrational spectrum of OH produces bands in the same spectral region. Using extrapolations of the thermally averaged transition probabilities of Mies (1974), we predict for the model nebula a maximum received flux of 4×10^{-10} ergs $cm^{-2}\ s^{-1}$ in the 3–2 band of OH at 3.09 μm. The 4–3 and 5–4 bands of OH lie at 3.25 and 3.43 μm, respectively, and could contribute to the other feature as well. At present, then, it is not possible to ascribe the 3 μm spectral features exclusively to HeH^+ on the basis of low-resolution spectra. On the other hand, both HeH^+ and OH are expected to be sufficiently abundant in nebulae like NGC 7027 to produce infrared lines of the requisite intensity.

Grasdalen and Joyce (1976) have observed the 3.28 and 3.4 μm features in NGC 7027 at somewhat higher resolution, $\lambda/\Delta\lambda \approx 300$, than did Merrill *et al.* They note difficulties with corrections for atmospheric absorption at these wavelengths but suggest that the 3.28 μm feature is complex. They have proposed CH^+ as a possible source of the feature. Our work indicates that CH^+ is much less likely than HeH^+ or OH to be the correct identification, on the bases of abundance and line strength.

Spectra of great sensitivity and high resolution will be required in order to establish any identification for such infrared lines. In addition, as a test of the transition zone hypothesis, it will be necessary to calculate in detail the strengths of the emission lines of H_2, HeH^+, and OH at high temperature from a model region appropriate for NGC 7027.

The recombination spectrum of $H_2{}^+$ (reaction [9]) in the far-ultraviolet may eventually be detectable. The formation of $H_2{}^+$ by radiative association in the model nebula is necessarily accompanied by emission around 1000 Å with a predicted total flux of 1.4×10^{-12} ergs $cm^{-2}\ s^{-1}$. This flux will be spread across a relatively broad spectral range, but it is encouraging that lines at this intensity level have already been detected at $\lambda \geqslant 1500$ Å in NGC 7027 (Bohlin, Marionni, and Stecher 1975).

Finally, we note that the discussion of chemistry at the boundaries of planetary nebulae applies just as well to the transition zones of H II regions such as the Orion Nebula. The structure of the zone of an H II region produced by a rather cooler exciting star will differ in detail, but the conclusions of this paper will remain qualitatively similar. The recent detections of rather intense infrared lines of H_2 toward the Orion Nebula (Gautier *et al.* 1976; Joyce and Grasdalen 1976) raise the question of whether the mechanism discussed above can also account for the strong lines in Orion. Further work on this is in progress.

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