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COSMIC-RAY–INDUCED PHOTODISSOCIATION AND PHOTOIONIZATION RATES OF INTERSTELLAR MOLECULES

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ABSTRACT

In the Prasad-Tarafdar mechanism, ultraviolet photons are created in the interior of dense interstellar clouds by the impact excitation of molecular hydrogen by secondary electrons generated by cosmic-ray ionization. Detailed calculations of the emission spectrum are described, and the resulting photodissociation and photoionization rates of a wide range of interstellar molecules are calculated.

Subject headings: cosmic rays: general — interstellar: molecules

I. INTRODUCTION

The influence of the ultraviolet photons generated in dense molecular clouds by the secondary electrons produced by cosmic-ray ionization (Prasad and Tarafdar 1983) on the abundances of interstellar molecules has been explored by Sternberg, Dalgarno, and Lepp (1987), who took into account the photons created by the excitation of the $B\,{}^1\Sigma_u^+$ and $C\,{}^1\Pi_u$ states of molecular hydrogen. A more complete description of the cosmic-ray–induced ultraviolet spectrum involving excitation to other singlet and triplet states of H_2 has been given by Gredel, Lepp, and Dalgarno (1987), who employed it in a calculation of the photodissociation rate of CO. We use this spectrum here to derive the internal photodissociation rates of a wide range of interstellar molecules for which photodissociation cross sections are available, and we briefly discuss the effects on the equilibrium chemical composition of dense clouds, extending the models of Sternberg, Dalgarno, and Lepp (1987).

II. THE ULTRAVIOLET SPECTRUM OF H_2

In dense molecular clouds, cosmic rays with energies between 10 and 100 MeV ionize H_2 and generate secondary electrons with a mean energy around 30 eV (Cravens and Dalgarno 1978). Because the fractional ionization is generally low, the secondary electrons lose their energy mainly by exciting, dissociating, and ionizing H_2. The energy degradation process of the secondary electrons was calculated following the method used by Cravens, Victor, and Dalgarno (1975). Excitations to the $B\,{}^1\Sigma_u^+$, $B'\,{}^1\Sigma_u^+$, $B''\,{}^1\Sigma_u^+$, $C\,{}^1\Pi_u$, $D\,{}^1\Pi_u$, and $D'\,{}^1\Pi_u$ Rydberg states and to the valence E, $F\,{}^1\Sigma_g^+$ and $a\,{}^3\Sigma_g^+$ states were included together with excitations into the repulsive $b\,{}^3\Sigma_u^+$ state and into vibrational levels of the ground state.

The cross sections for the excitation into the vibrational levels of the $a\,{}^3\Sigma_g^+$ state and of the excited singlet states were obtained from an analytic representation introduced by Shemansky, Ajello, and Hall (1985). In their formalism, the cross section $\sigma(E)$ is expressed as

$$\sigma(E) = \left[\left(C_0\frac{1}{x^2} + C_5\right)\left(1 - \frac{1}{x}\right) + C_7 \ln x + \sum_{n=1}^{4} C_n(x-1)\exp(-\alpha n x)\right]\Big/ E\,, \quad (1)$$

where $x = E/E_t$ is the ratio of the electron energy E over the threshold energy E_t. Values of C_n and α for the individual vibrational states were provided by Shemanksy (1987). For the excitations into the vibrational levels $v = 1$ and 2 of the $X\,{}^1\Sigma_g^+$ state, the cross sections of Nishimura, Danjo, and Sugahara (1986) and Ehrhardt *et al.* (1968), respectively, were adopted. The electron impact cross sections for the $b\,{}^3\Sigma_u^+$ state of H_2 have been measured by Nishimura and Danjo (1986) and Khakoo *et al.* (1987), and theoretical calculations have been carried out by Baluja, Noble, and Tennyson (1985), Schneider and Collins (1985, 1986), and Rescigno and Schneider (1988). Here, the cross sections of Nishimura and Danjo (1986) were employed. For the total ionization cross sections for H_2 we used the data of Rapp and Englander-Golden (1965), and for the differential cross sections, the data of Opal, Peterson, and Beaty (1971).

The energy loss of the injected electrons can be expressed in terms of the number of excitations, $\epsilon_i(v')$, of vibrational levels v' of the various electronic states i, produced in the gas by an energetic electron as it slows down. In terms of $\epsilon_i(v')$, the probability $P_i(\nu)$ for the emission of a photon of frequency ν resulting from the radiative decay out of a particular level i, v', J' to a lower j, v'', J'' is given by

$$P_i(\nu) = \sum_{J_0} \frac{\epsilon_i(v')S_{J',J_0}}{\sum_{v',J'} \epsilon_i(v')S_{J',J_0}} \times \frac{A_{v'J',v''J''}}{A_{v'J'}} \times \omega_{J_0}\,, \quad (2)$$

where the first term is the probability of the excitation of the rotational level v', J' in i, S_{J',J_0} is the Hönl-London factor, and

J_0 is the initial rotational level in the $v'' = 0$ level of the ground state of H_2. The second term is the branching ratio describing the probability that the particular transition $v'J' \rightarrow v''J''$ occurs, the weight ω_{J_0} is the fractional population of H_2 in the initial rotational level J_0, and $A_{v'J'}$ is the total transition probability for emission from level $v'J'$. This formula differs from the expression given by Sternberg, Dalgarno, and Lepp (1987), in which absorption oscillator strengths were used for the relative excitation probabilities.

The effective excitation rates $\epsilon_B(v')$ are further enhanced by cascading from excited states which decay to the $B\,^1\Sigma_u^+$ state. The enhanced excitation rates due to cascading were calculated according to

$$\epsilon'_B(v') = \epsilon_B(v') + \sum_v \epsilon_{E,F}(v) \times q_{vv'} , \tag{3}$$

where $q_{vv'}$ are the Franck-Condon factors for the $E,F\,^1\Sigma_g^+$–$B\,^1\Sigma_g^+$ transition and $\epsilon_B(v')$ are the direct excitation rates. For the Franck-Condon factors, the theoretical values of Lin (1974) were adopted.

The transition probabilities for the decay of the vibrational levels of the excited electronic states were obtained from Allison and Dalgarno (1970), Stephens and Dalgarno (1972), Glass-Maujean (1984), Kwok, Dalgarno, and Posen (1985), and Kwok *et al.* (1986). No calculation or measurement exists for the $B''\,^1\Sigma_u^+$–$X\,^1\Sigma_g^+$ and $D'\,^1\Pi_u$–$X\,^1\Sigma_g^+$ transitions. However, the $B''\,^1\Sigma_u^+$ and $D'\,^1\Pi_u$ states have approximately the same equilibrium separation as the $B'\,^1\Sigma_u^+$ and $D'\,^1\Pi_u$ states, respectively, and the branching ratios for transitions to $X\,^1\Sigma_g^+$ state should be similar.

The vibrational levels in the higher lying Rydberg states predissociate. Vibrational levels $v' > 0$ in the $B''\,^1\Sigma_u^+$ state and $v' > 3$ in the $D'\,^1\Pi_u$ state strongly predissociate with efficiencies η near unity (Ajello *et al.* 1984). In the $D\,^1\Pi_u$ state, levels $v' = 3$–8 have predissociation efficiencies around 0.5 (Ajello *et al.* 1984). For them $[1 - \eta_i(v')]$ was included in equation (2) as an additional factor. We calculated the corresponding fluorescence efficiencies $P_i(v)$ for the $D\,^1\Pi_u$–$X\,^1\Sigma_g^+$, $D'\,^1\Pi_u$–$X\,^1\Sigma_g^+$ and $B''\,^1\Sigma_u^+$–$X\,^1\Sigma_g^+$ transitions to be 0.7, 0.4, and 0.07 respectively, in close agreement with those of Ajello *et al.* (1984).

The resulting spectrum was obtained for a neutral gas of H_2 by summing the probabilities for photon emission from the various electronic states i, weighted with the total excitation rate ϵ_i, according to

$$P(v) = \sum_i P_i(v) \times \epsilon_i / R_I , \tag{4}$$

where $\epsilon_i = \Sigma_{v'}\, \epsilon_i(v')$ and R_I is the total number of ionizations. For each 30 eV electron, the total numbers are 0.30, 0.12, 0.02, 0.02, 0.01, 0.01, 0.04, and 0.65 for excitations to the $B\,^1\Sigma_u^+$, $C\,^1\Pi_u$, $B'\,^1\Sigma_u^+$, $D\,^1\Pi_u$, $B''\,^1\Sigma_u^+$, $D'\,^1\Pi_u$, $a\,^3\Sigma_g^+$, and $b\,^3\Sigma_u^+$ states, respectively. For the excitation of vibrational levels in the $X\,^1\Sigma_g^+$ state, the total number is 13.8. The number of ionizations is 0.55 which, together with the primary ionization, yields a value of 1.55 for R_I.

The emission spectrum depends in detail on the rotational populations of the hydrogen molecules, but with the exception of CO, the resulting photodissociation and photoionization rates are little affected. We present in Figures 1 and 2 the emission spectrum for a rotational population in which the molecules are shared between the $J = 0$ and 1 levels in the ratio 1:3. It is shown distributed in bins of 0.1 nm. The spectrum consists of numerous discrete lines superposed on continuum emissions from transitions into the vibrational continuum of the ground state and a continuum emission from the $a\,^3\Sigma_g^+$–$b\,^3\Sigma_u^+$ transition.

III. THE COSMIC-RAY–INDUCED PHOTODISSOCIATION AND PHOTOIONIZATION OF INTERSTELLAR MOLECULES

The photodissociation and photoionization rate R_M of a molecular species M with density $n(M)$ corresponding to a total cosmic-ray ionization rate of ζs^{-1} is given by

$$R_M = \zeta n(M) \int \frac{\sigma_M(v)P(v)}{\sigma_{\text{tot}}(v)}\, dv \ \text{cm}^{-3}\ \text{s}^{-1} , \tag{5}$$

where $\sigma_M(v)$ is the photodissociation or photoionization cross section and $\sigma_{\text{tot}}(v)$ is the total absorption cross section. It may be written in the form

$$\sigma_{\text{tot}} = \sigma_g(1 - \omega) + \sum_M \kappa_M \sigma_M(v) , \tag{6}$$

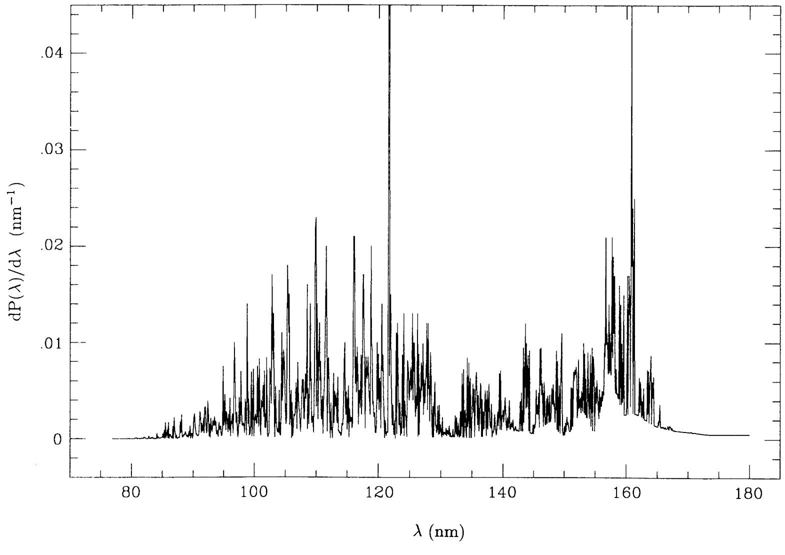

FIG. 1.—The emission spectrum of H_2 between 75 nm and 175 nm shown as numbers of photons emitted per nm. The lines connect the points at intervals of 0.1 nm, each point representing the emission lines falling into the 0.1 nm bin and the continuum emission integrated over the bin.

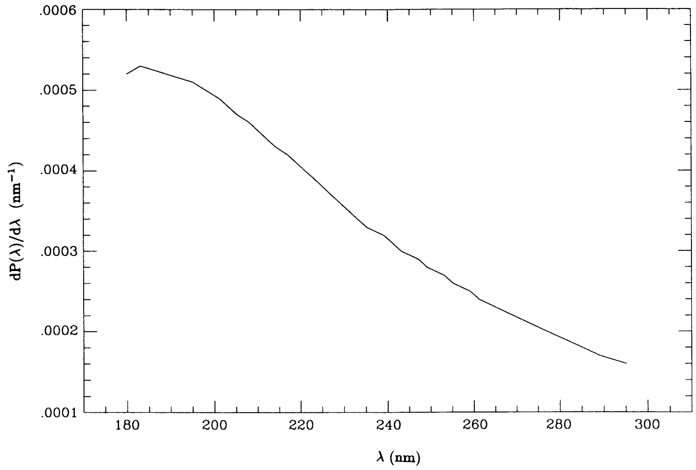

FIG. 2.—The emission spectrum of H_2 between 175 nm and 300 nm

where $\sigma_g = 2 \times 10^{-21}$ cm^2 is the grain extinction cross section per hydrogen nucleus, ω is the grain albedo, and $\kappa_M = n(M)/n_H$. In practice, for molecules in interstellar clouds, with the exception of CO (Gredel, Lepp, and Dalgarno 1987), σ_{tot} is dominated by $\sigma_g(1 - \omega)$ and for them we may write

$$R_M = \frac{\zeta n(M)}{1 - \omega} p_M \text{ cm}^{-3} \text{ s}^{-1} , \tag{7}$$

where the efficiency p_M is given by

$$p_M = \int \frac{\sigma_M(\nu)P(\nu)}{\sigma_g} d\nu . \tag{8}$$

The cosmic-ray–induced photodissociation and photoionization efficiencies p_M of 37 molecules are presented in Table 1. It includes most interstellar molecules for which at least some data on the absorption cross sections in the ultraviolet are available. For several species, there are no experimental data,

TABLE 1

COSMIC-RAY–INDUCED PHOTODISSOCIATION AND PHOTOIONIZATION EFFICIENCIES p_M OF INTERSTELLAR MOLECULES

SYSTEM	PRODUCTS	p_M a	p_M b	CROSS SECTION SOURCE
C_2	C + C	228	237	1
CH	C + H	756	730	2
CH^+	$C + H^+$	183	176	3
CN	C + N	9122	10580	4
OH	O + H	522	509	5
O_2	O + O	730	751	6, 7
	$O_2^+ + e$	88	117	8, 9
NO	N + O	427	482	10, 11
	$NO^+ + e$	430	494	10
HCl	H + Cl	448	610	12
H_2O	H + OH	979	971	13
CO_2	CO + O	1464	1708	14
	$CO_2^+ + e$	0	0	15
H_3^+	$2H + H^+$	0	0	16
HCN	CN + H	2986	3114	17, 18
HCO	H + CO	313	421	19
	$HCO^+ + e$	1152	1169	20
OCS	CO + S	5371	5360	13
	$OCS^+ + e$	1246	1444	13
C_3	$C_2 + C$	1099	1119	20
H_2S	$H_2 + S$	5072	5154	21
	$H_2S^+ + e$	1555	1696	21
SO_2	SO + O	1995	1884	22
NH_2	NH + H	81	80	23
	$NH_2^+ + e$	610	649	20
NH_3	$NH_2 + H$	1325	1315	24, 25
	$NH + H_2$	541	541	26
	$NH_3^+ + e$	543	576	26, 27
CH_2O_2	$CH_2O_2^+ + e$	610	649	20
	HCO + OH	262	249	28, 29, 30
CH_3N	$HCN + H_2$	4805	4982	20
CH_4	$CH_2 + H_2$	2272	2339	31, 32
CH_4O	$H_2CO + H_2$	2980	3168	33, 34
CH_4O	$CH_3 + OH$	1559	1504	35
	$CH_4O^+ + e$	1431	1433	36
	$CH_3O^+ + H + e$	73	99	20
CH_5N	HCN + H + 2H	1489	1409	37
	$CH_3N + 2H$	20	19	37
	$CH_3 + NH_2$	711	670	37
	$CN + 2H_2 + H$	387	367	37
	$CH_5N^+ + e$	1099	1119	20
C_2H_2	$C_2H + H$	5118	5155	38, 39
	$C_2H_2^+ + e$	1180	1309	40
C_2H_2O	$CH_2 + CO$	948	913	24, 41
	$C_2H_2O^+ + e$	1204	1218	20
C_2H_3N	$CH_3 + CN$	4899	4756	18
	$C_2H_3N^+ + e$	1907	2245	18
C_2H_4	$C_2H_2 + H_2$	3762	3700	42
	$C_2H_4^+ + e$	692	778	42
C_2H_4O	$CH_3 + CHO$	543	527	43
	$CH_4 + CO$	543	527	43
	$C_2H_4O^+ + e$	1099	1119	20
CH_3OCH_3	$H_2CO + CH_4$	1717	1714	44
	$C_2H_6O^+ + e$	1099	1119	20
C_2H_5OH	$C_2H_5 + OH$	4191	4307	33, 36
	$C_2H_5OH^+ + e$	2548	2736	20, 36
C_3HN	$C_2H + CN$	1804	1727	45
C_3H_4	$C_3H_3 + H$	3425	3284	40, 46, 47
	$C_3H_4^+ + e$	5127	5305	40
C_3O	$C_2 + CO$	6864	6609	48
C_4H_2	$C_4H + H$	1802	1730	49, 50, 51
	$C_2H + C_2H$	1802	1730	49, 50, 51
	$C_4H_2^+ + e$	1099	1119	20, 49, 50, 51
H_2CO	$CO + H_2$	2737	2659	52
HNCO	NH + CO	2462	2361	53

NOTE.—In the column headed p_M, values headed by "a" are calculated ignoring reabsorption of resonance line photons, while values headed by "b" are calculated using on-the-spot approximation to take account of resonance line photons.

REFERENCES.—(1) Pouilly *et al.* 1983; (2) van Dishoek 1987; (3) Kirby *et al.* 1980; (4) Lavendy, Gandara, and Robbe 1984; (5) van Dishoek and Dalgarno 1984; (6) Ogawa and Ogawa 1975; (7) Gibson *et al.* 1983; (8) Matsunaga and Watanabe 1967; (9) Brion *et al.* 1979; (10) Watanabe, Matsunaga, and Sakai 1967; (11) Guest and Lee 1981; (12) van Dishoek, van Hemert, and Dalgarno 1983; (13) Lee 1984; (14) Lewis and Carver 1983; (15) Nakata, Watanabe, and Matsunaga 1965; (16) Kulander and Bottcher 1978; (17) Lee 1980; (18) Nuth and Glicker 1982; (19) Bruna, Buenker, and Peyerimhoff 1976; (20) Herbst and Leung 1986; (21) Watanabe and Jursa 1964; (22) Suto, Day, and Lee 1982; (23) Saxon, Lengsfield, and Liu 1983; (24) Okabe 1978; Suto and Lee 1983; (26) Samson, Haddad, and Kilcoyne 1987; (27) Watanabe 1954; (28) Bell, Ng, and Walsh 1975; (29) Style and Ward 1952; (30) Calvert and Pitts 1966; (31) Lee and Chiang 1983; (32) Mount, Warden, and Moos 1977; (33) Harrison, Cederholm, and Terwilliger 1959; (34) Sahalub and Sandorfy 1971; (35) Nee, Suto, and Lee 1985; (36) Ogawa and Cook 1958; (37) Gardner 1981; (38) Suto and Lee 1985; (39) Wu and Judge 1985; (40) Nakayama and Watanabe 1964; (41) Braun, Bass, and Piling 1970; (42) Zelikoff and Watanabe 1953; (43) Lake and Harrison 1959; (44) Harrison and Price 1959; (45) Connors *et al.* 1974; (46) Stief, De Carlo, and Payne 1971; (47) Hamai and Hirayama 1979; (48) Kim and Roebber 1966; (49) Georgieff and Richard 1958; (50) Heller and Milne 1978; (51) Okabe 1981; (52) Suto, Wang, and Lee 1987; (53) Okabe 1970.

and theoretical values of the photoabsorption cross sections were adopted. References to the cross sections used in the calculations are given in Table 1. For many molecules the data are fragmentary, especially as regards the identity of the dissociation products. The available data often refer to total absorption and in such cases we have made arbitrary estimates of the probabilities of dissociation. Carbon monoxide requires special consideration. The CO photodissociation rates have been calculated by Gredel, Lepp, and Dalgarno (1987).

The cosmic-ray–induced photodissociation and photoionization efficiencies will be modified by the absorption by H_2 of those lines which are produced by transitions terminating in rotational levels of the lowest vibrational state. An accurate estimate of their effect can be made by adopting an on-the-spot approximation in which it is assumed that the emitted photon is immediately absorbed after which the excited state emits again into the various vibrational levels of the ground state. The efficiencies that result are also listed in Table 1. The effects of reabsorption are usually small.

IV. THE STEADY STATE ABUNDANCES OF INTERSTELLAR MOLECULES

We briefly explore the effects of the cosmic-ray–induced photons on the abundances of interstellar molecules, using a version of the chemistry of Sternberg, Dalgarno, and Lepp (1987), modified by the incorporation of the rate coefficients of dissociative recombination recommended by Bates (1986, 1987) and Millar *et al.* (1988), and with the addition of reactions involving nitrogen, mostly taken from Prasad and Huntress (1980) and Anicich and Huntress (1986).

We present results for a uniform cloud of total hydrogen density $n_H = 10^4$ cm^{-3}, a temperature of 50 K, abundances relative to H_2 for carbon of 1.46×10^{-4}, for oxygen of 3.52×10^{-4}, and for nitrogen of 4.5×10^{-5}, a cosmic-ray ionization rate of $\zeta = 10^{-17}$ s^{-1}, a total metal abundance ratio relative to hydrogen of 1.5×10^{-8}, and an albedo ω of 0.5.

The calculated steady state abundances of several interstellar compounds are presented in Table 2. To separate the effects of the supply of carbon atoms by photodissociation of CO, we show first the results obtained without it. The major source of carbon atoms is then the reaction

$$C^+ + NH_3 \rightarrow C + NH_3^+$$

measured by Marquette *et al.* (1985), and the major sink,

$$C + O_2 \rightarrow CO + O\ .$$

The cosmic-ray photons enhance the abundance of OH and of O and diminish that of H_2O. They substantially reduce the abundance of the more complex species because photodissociation is an effective destruction process at many points in the formation sequence (Sternberg, Dalgarno, and Lepp 1987).

The destructive effects are mitigated when the photodissociation of CO is initiated. The photodissociation of CO is a much larger source of neutral carbon atoms than the charge transfer reaction of C^+ with NH_3 and the fractional abundance of C is increased by two orders of magnitude. The increase in the carbon atom abundance is reflected in enhanced abundances of the hydrocarbon species.

Large molecules, if they exist in significant amounts in dense interstellar clouds, also enhance the abundances of the complex hydrocarbons (Lepp and Dalgarno 1988). The addition of a large molecule component with an abundance relative to hydrogen of 10^{-7} yields in our model chemistry the steady state concentrations given in Table 2. With the inclusion of the photodissociation of CO as a source of neutral carbon, the additional source of C atoms from charge transfer to large molecules and from mutual neutralization to large molecular negative ions (Lepp and Dalgarno 1988) has but small consequences.

We also list in Table 2 the maximum abundances that are obtained if we assume the cloud evolves with uniform density and temperature from an initial state in which the hydrogen is molecular, carbon is singly ionized, and oxygen and nitrogen are in the form of neutral atoms. Because the time scales of the internal photodissociation and photoionization processes are longer than the time scales to form molecules, given that the hydrogen is initially molecular, the maximum abundances are not significantly affected by the presence of the internally generated photons.

TABLE 2

FRACTIONAL ABUNDANCES $n(y)/n_H$ AT STEADY-STATE (SS) AND AT MAXIMUM (max) FOR VARIOUS CLOUD MODELS

COMPOUND	CASE A[a]		CASE B[b]		CASE C[c]		CASE D[d]	
	SS	Max	SS	Max	SS	Max	SS	Max
O	7.9(−5)	3.5(−4)	1.2(−4)	3.5(−4)	1.2(−4)	3.5(−4)	1.1(−4)	3.5(−4)
OH	3.3(−9)	3.3(−9)	1.4(−8)	1.4(−8)	1.3(−8)	1.3(−8)	1.4(−8)	1.4(−8)
H_2O	5.4(−5)	7.0(−5)	2.5(−5)	2.6(−5)	2.5(−5)	2.6(−5)	2.5(−5)	2.6(−5)
O_2	3.7(−5)	3.7(−5)	3.1(−5)	3.1(−5)	3.0(−5)	3.0(−5)	3.3(−5)	3.3(−5)
C^+	1.8(−10)	1.5(−4)	4.3(−10)	1.5(−4)	4.4(−10)	1.5(−4)	4.2(−10)	1.5(−4)
C	4.5(−9)	9.2(−5)	6.5(−9)	9.2(−5)	6.1(−7)	9.2(−5)	7.9(−7)	1.2(−4)
C_2H_2	4.2(−9)	9.6(−7)	7.2(−11)	2.7(−7)	7.5(−10)	2.7(−7)	1.9(−9)	2.8(−7)
CH_4	6.6(−8)	1.3(−5)	9.6(−9)	2.7(−6)	9.5(−8)	2.7(−6)	1.7(−7)	4.4(−6)
C_2H	1.5(−10)	1.2(−6)	4.2(−11)	1.2(−6)	4.2(−10)	1.2(−6)	8.3(−10)	9.0(−7)
C_3H_2	2.1(−11)	6.6(−7)	8.8(−13)	6.3(−7)	9.4(−12)	6.7(−7)	1.2(−12)	3.1(−7)
NH_3	4.7(−8)	4.7(−8)	4.4(−8)	4.4(−8)	4.1(−8)	4.1(−8)	3.3(−8)	3.3(−8)
HCN	1.9(−10)	4.2(−7)	2.7(−10)	4.2(−7)	1.2(−9)	4.2(−7)	6.0(−10)	2.1(−7)

[a] No photons; no large molecules (LM).

[b] Photons but no dissociation of CO; no LM.

[c] Photons; no LM.

[d] Photons; LM at $n(LM)/n_H = 10^{-7}$.

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