PHOTODISSOCIATION AND PHOTOIONIZATION PROCESSES

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ABSTRACT. The photodissociation and photoionization processes of species of astrophysical interest are reviewed, with emphasis on recent developments. Depth-dependent photodestruction rates by the interstellar radiation field are presented for a number of atoms and small molecules. The photodissociation processes of CO are discussed with reference to new laboratory data on the absorption cross sections.

1. INTRODUCTION

In any astrophysical region where ultraviolet photons can penetrate, photodissociation and photoionization are major destruction processes of the neutral species. Even for molecular ions, photodissociation can be an important removal mechanism if the fraction of electrons or other negatively charged species in the region is sufficiently low. Photodissociation plays a dominant role in the chemistry of diffuse interstellar clouds and in the outer parts of dense clouds (Eddington 1926; Bates and Spitzer 1951). More recently, it has been realized that cosmic-ray induced photons can significantly affect the chemistry inside dense clouds (Prasad and Tarafdar 1983; Sternberg, Dalgarno and Lepp 1987; Gredel, Lepp and Dalgarno 1987). The outer envelopes of mass-losing stars are exposed to the general interstellar radiation field, so that photodissociation plays an important role in the circumstellar chemistry (Goldreich and Scoville 1976; Omont 1987). Finally, the solar radiation field is responsible for the production of many of the observed radicals in cometary atmospheres (Wurm 1934; Huebner and Carpenter 1979). In order to interpret or predict the observed abundances of molecules in these regions, an accurate knowledge of the photodestruction rates is a prerequisite. This review will be limited mostly to photoprocesses induced by the interstellar radiation field.

2. PHOTODISSOCIATION MECHANISMS

2.1 Small molecules

Although photodissociation is usually referred to as a relatively simple process, it can proceed in various ways. They have been discussed extensively recently by van Dishoeck (1987*a*) and Kirby and van Dishoeck (1988), and will be only briefly reiterated here. The various processes are summarized in Figure 1 for a diatomic molecule. For small

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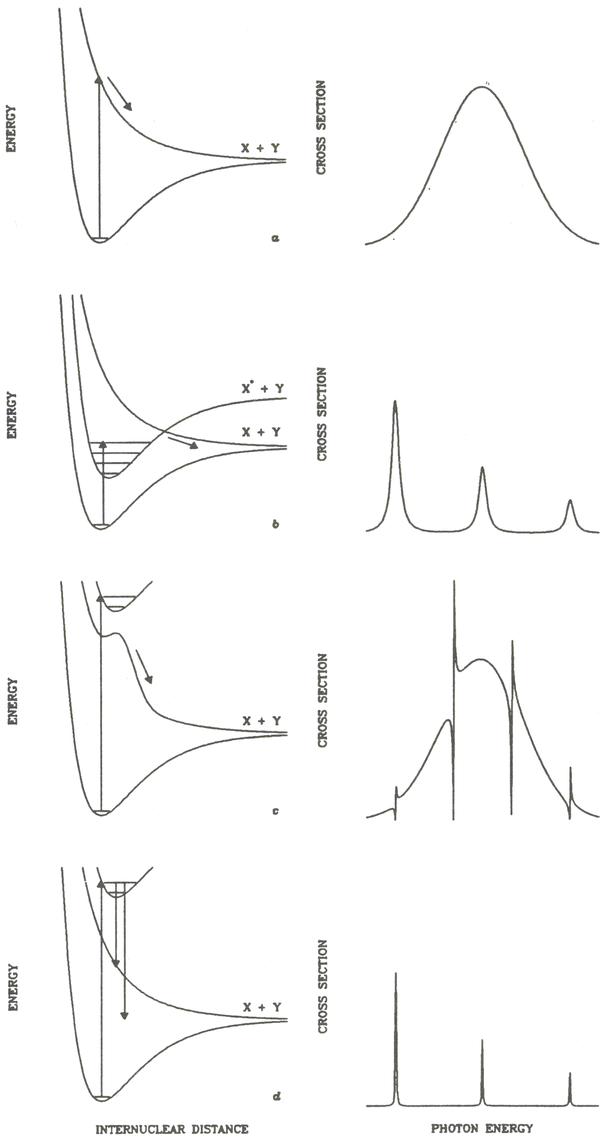

Figure 1. *Potential energy curves and characteristic cross sections for the processes of (a) direct photodissociation; (b) predissociation; (c) coupled states photodissociation; (d) spontaneous radiative dissociation.*

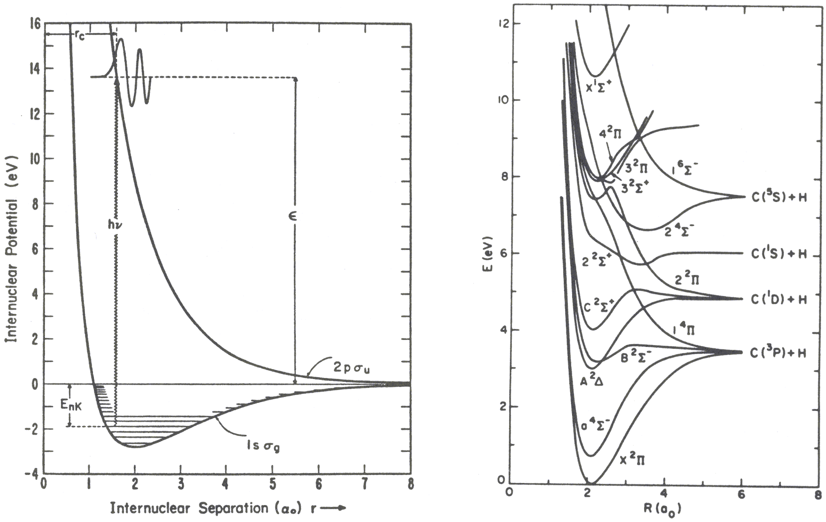

Figure 2. *Potential energy curves for* H_2^+ *(left) and CH (right) (from: Dunn 1968; van Dishoeck 1987b).*

polyatomic molecules, the processes are similar, but more complicated because of the multidimensionality of the potential energy surfaces.

The simplest process of direct photodissociation, illustrated in Figure 1*a*, dominates the photodissociation of a number of small astrophysically important molecules, such as H_2^+, CH^+, NH, and H_2O. The clearest example is provided by the H_2^+ ion for which the potential energy curves are reproduced in Figure 2*a*. A more complicated molecule such as CH (see Figure 2*b*) generally has several low-lying photodissociation channels. In this case, direct photodissociation can occur by absorption into, for example, the $2^2\Sigma^+$ state. The cross section for direct photodissociation is continuous as a function of wavelength, and its shape reflects that of the vibrational wave function for the lower state. The maximum usually occurs close to the vertical excitation energy, indicated by the arrow in Figure 1*a*. Note that the cross section is often negligibly small at threshold. Direct photodissociation can also occur by absorption into the repulsive part of a potential curve which exhibits a bound well at larger distances. A well-known example is provided by the Schumann-Runge continuum of O_2. In this case, the relative amounts of discrete and continuous absorption are very sensitive to small uncertainties in the relative positions of the upper and lower potential curves. An instructive example, illustrated in Figure 3, is provided by the photodissociation of the isovalent CH^+ and SiH^+ ions through the $A^1\Pi$ state. For CH^+, nearly 100% of the absorption cross section occurs into the discrete levels. For SiH^+, however, the curves are slightly displaced, and most of the absorption takes place into the continuum of the A state (Kirby and Singh 1983). Thus the photodissociation of SiH^+ through the A state will be very rapid, whereas for CH^+ it will be negligible.

In indirect photodissociation processes, the initial absorption occurs into a bound discrete excited state which subsequently interacts with the continuum of a final dissociating state. The process of predissociation, in which the bound potential curve is crossed by a repulsive state of a different symmetry, is illustrated in Figure 1*b*. The cross section consists in this case of a series of discrete peaks, broadened by the predissociation process.

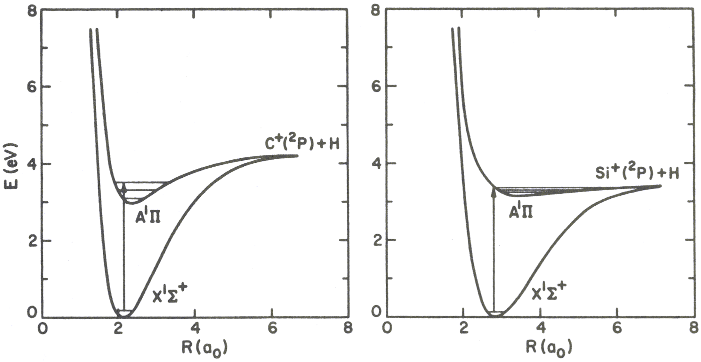

Figure 3. *Comparison of photodissociation of* CH^+ *and* SiH^+ *through the* $A^1\Pi$ *state (from: Kirby and van Dishoeck 1988).*

The photodissociation of the second most abundant interstellar molecule, CO, occurs by this mechanism, and will be discussed in more detail in §6.

The bound levels of an excited state can also couple with the continuum of a dissociative state of the same symmetry, which does not cross the bound state. This process can play an important role in molecules in which e.g., Rydberg–valence interactions cause avoided crossings between excited states. Examples are provided by OH and CH. The shape of the cross section depends on the details of the molecular structure, but it may consist of a continuous background with superposed a series of resonances (cf. Figure 1*c*).

Finally, the bound excited state can simply decay by spontaneous emission into lower–lying continuum states (see Figure 1*d*). For most molecules, this mechanism plays only a minor role, but it is the dominant photodissociation process of the most abundant interstellar molecule, H_2. The cross section consists in this case of a series of sharp, discrete peaks with widths determined by the natural radiative lifetimes of the levels.

2.2 Large molecules

For larger molecules with a significant number of vibrational degrees of freedom, the density of vibrational levels of the lower electronic states becomes so high that they form a quasi continuum with which the excited electronic states can couple non–radiatively. In this case of internal conversion, the probability is small that all the energy will be located in any specific mode leading to dissociation, and the formation of a highly–excited bound molecule is more likely. The excited molecule can subsequently relax by emission of infrared photons. Alternatively, the excited molecule can fluoresce down to the ground state, or it can undergo intersystem crossing to an electronic state with a different spin multiplicity from which it can phosphoresce down. Statistical arguments suggest that N–atom molecules with $N > 25$ are stable with respect to photodissociation (Duley 1986; Omont 1986; Léger and Puget 1984). Although a considerable amount of experimental data is available on smaller polyatomic molecules such as benzene (Leach 1987), virtually no gas–phase experiments exist on large species to test these theories. Large molecules typically have ionization potentials around 7 eV, so that they can easily be photoionized. Whether a small percentage of the absorptions above the ionization threshold will lead to dissociation, or whether the H atoms on the periphery of a large molecule can be removed efficiently by photodissociation, is still uncertain as well.

3. PHOTODISSOCIATION CROSS SECTIONS

3.1 Theory

The procedure to obtain photodissociation cross sections from theory has been outlined e.g. by Kirby and van Dishoeck (1988). Potential energy curves and transition dipole moments connecting the excited states with the ground electronic state can be obtained from ab initio quantum chemical calculations. As discussed in §2, the potential curves provide insight into the possible photodissociation processes. For direct photodissociation, the eigenvalue equations for the nuclear motion in the ground and excited states can then be solved by numerical integration, and cross sections can be obtained by integration of the product of the vibrational wave functions and the transition dipole moment function over the nuclear coordinate. For indirect processes, the transition moment function is used to compute oscillator strengths for absorption into the discrete upper level. If the coupling of the upper bound level with the final dissociative continuum is weak, a first order perturbation theory can be used to calculate the predissociation rates k^{pr} (in s^{-1}). The predissociation probability η_u is then obtained by comparing k^{pr} with the inverse radiative lifetime of the molecule A^{rad}, $\eta_u = k^{pr}/(k^{pr} + A^{rad})$. If the coupling between the bound and continuum excited states is strong, as often occurs for the case illustrated in Figure 1*c*, the coupled equations for the excited states have to be solved in order to compute the cross sections.

Theory can provide accurate cross sections—i.e., transition energies accurate to better than about 0.3 eV, and oscillator strengths and cross sections to better than 30%—for small molecules in which the number of (active) electrons is at most 30. In practice, reliable calculations are also limited to the lowest 4–5 electronic states per molecular symmetry. For most molecules of astrophysical interest, this range includes the dominant photodissociation channels. An important exception is the CO molecule discussed in §6.

3.2 Experiment

The information obtained from experiment is often complementary to that derived from theory. Laboratory measurements of absorption cross sections have been performed for chemically stable species, such as H_2O, CO_2, NH_3, CH_4, ... Most of these experiments are performed at rather low resolution, where the individual rotational lines are not resolved. Typical examples of measured cross sections are reproduced in Figure 4. For CH_4, various absorption continua are observed, with discrete features superposed at shorter wavelengths. The absorption of NO occurs mostly in discrete bands. Note that often the electronic states responsible for the absorptions have not yet been identified spectroscopically.

The absorption of a photon can result in reemission of another photon, dissociation or ionization of the molecule, and many experiments do not distinguish between these processes. If the photon energy is insufficient to ionize the molecule and if the absorption is continuous, it is likely that photodissociation is the dominant process. In other cases, additional information on the fluorescence and/or ionization cross sections is needed to infer the dissociation probabilities η_u. For some species, the fluorescence cross sections have been measured explicitly. Figure 4*b* compares the absorption and fluorescence results for NO. It appears that for some bands the fluorescence yield is large, whereas for other bands, photodissociation occurs with almost 100% probability. The absorption cross sections for continuous processes measured at low resolution are quite accurate. However, for discrete absorptions, high resolution and low pressures are essential to obtain reliable experimental results, because saturation effects can easily cause orders of magnitude errors. Another

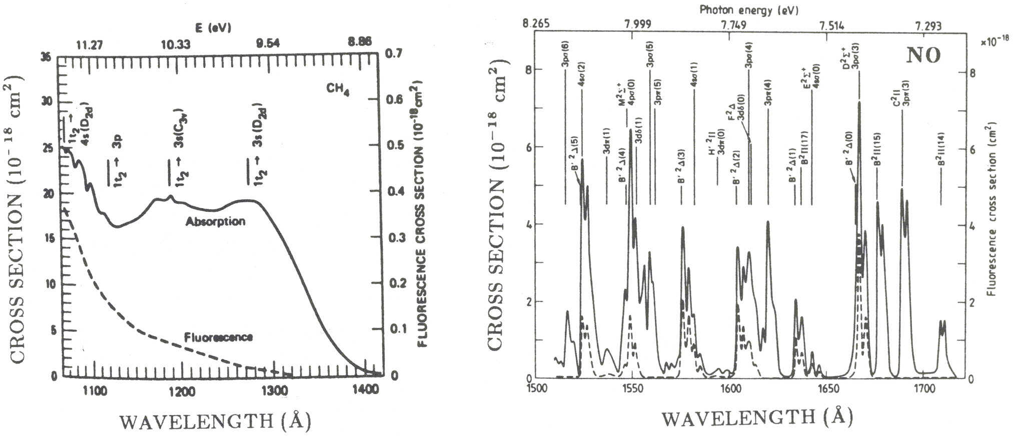

Figure 4. *Measured absorption (full lines) and fluorescence (dashed lines) cross sections for CH_4 (left) and NO (right) (from: Lee and Chiang 1983; Guest and Lee 1981).*

experimental problem arises from the lack of powerful continuous light sources at vacuum ultraviolet (VUV) wavelengths λ <1100 Å. Some beautiful experiments have been performed using VUV lasers, but these are usually limited to only a few specific wavelengths. Measurements using synchrotron radiation are possible, but only very few facilities have spectrographs with sufficiently high resolution (Yoshino *et al.* 1988). Therefore, even for many stable molecules, no reliable cross section data are available at the shortest wavelengths. Experimental data on reactive molecules, such as the radicals CH, OH, C_2H, ... are still extremely limited. Reviews of cross section measurements have been given by Hudson (1971), Robin (1975), Okabe (1978), Ashfold *et al.* (1979), Huebner and Carpenter (1979) and Lee (1984).

3.3 *Photodissociation rates*

The rate of photodissociation k_{pd} of a molecule by absorption from a lower level ℓ into a continuous upper channel u is given by

$$k_{pd}^{cont} = \int \sigma_{u\ell}(\lambda) x_\ell I(\lambda) d\lambda \ \ \mathrm{s}^{-1}, \tag{1}$$

where σ is the cross section for photodissociation in cm^2, x_ℓ is the fractional population in level ℓ, and I is the mean intensity of the radiation measured in photons cm^{-2} s^{-1} Å^{-1} as a function of wavelength λ in Å. For indirect processes, the rate of dissociation by absorption into a specific level of a bound upper state u from the lower level ℓ is

$$k_{pd}^{line} = \frac{\pi e^2}{mc^2} \lambda_{u\ell}^2 \, f_{u\ell} \, \eta_u \, x_\ell \, I(\lambda_{u\ell}) \ \ \mathrm{s}^{-1}, \tag{2}$$

where $f_{u\ell}$ is the line absorption oscillator strength and η_u is the dissociation efficiency of the upper state level which lies between zero and unity. The numerical value of the factor $\pi e^2/mc^2$ is 8.85×10^{-21} in the adopted units. The total photodissociation rate of

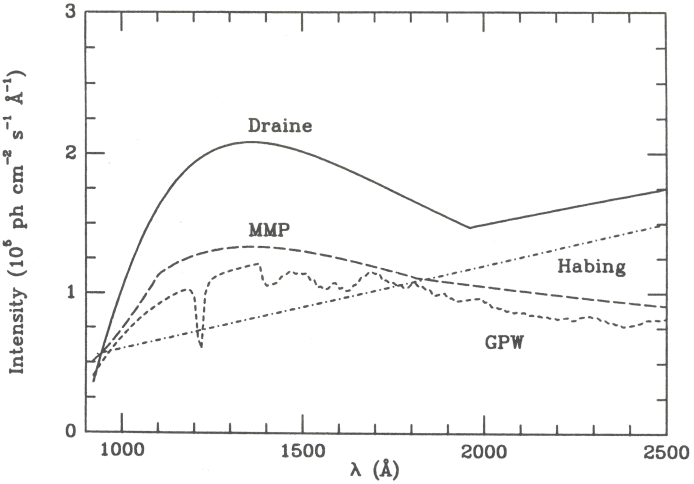

Figure 5. *The intensity of the interstellar radiation field as a function of wavelength cf. Draine (1978) (full line), Mathis et al. (1983) (long–dashed line), Gondhalekar et al. (1980) (short–dashed line) and Habing (1968) (dash–dotted line).*

a molecule is obtained by summation over all possible channels. The effectiveness of each channel depends on the characteristics of the radiation source. Photodissociation channels with large cross sections but at energies of low photon flux may be less significant than channels with smaller cross sections at the peak of the photon flux. In the following, only the interstellar case will be considered.

4. INTERSTELLAR RADIATION FIELDS

4.1 General background radiation field

Estimates of the intensity of the background interstellar radiation field in the solar neighbourhood due to the ensemble of stars in the Galaxy have been made by Habing (1968), Jura (1974), Draine (1978), Gondhalekar *et al.* (1980; GPW) and Mathis *et al.* (1983; MMP). The various radiation fields for $912 < \lambda < 2500$ Å—the important wavelength region for photodissociation and photoionization—are illustrated in Figure 5. The intensities vanish below 912 Å (13.6 eV) due to absorptions by atomic hydrogen in the vicinity of the stars where the photons originate. The various estimates differ typically by factors of two, so that it is important to refer all photodestruction rates to the same radiation field. In the following, the radiation field of Draine (1978)* will be used at $\lambda < 2000$ Å, augmented

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* Unfortunately, discrepant versions of the Draine (1978) radiation field exist in the literature. These can be traced back to the formula specified by Roberge *et al.* (1981), who did not retain enough significant digits following conversion of units. Therefore, formula (3) in van Dishoeck (1987*a*) is inaccurate and gives intensities that are too large by factors of 2 at $\lambda < 1000$ Å compared with Draine's original formula. The numbers reported in Table 1 of van Dishoeck (1987*a*) were obtained, however, with the correct Draine formula.

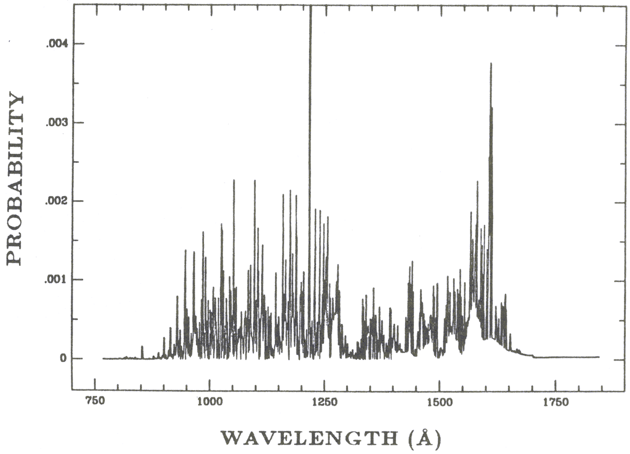

Figure 6. *The emission spectrum of H_2 following excitation by cosmic–ray induced secondary electrons (from: Gredel et al. 1987).*

by a simple formula (cf. van Dishoeck and Black 1982) for λ >2000 Å

$$\begin{aligned} I^o(\lambda) &= 3.2028 \times 10^{15}\lambda^{-3} - 5.1542 \times 10^{18}\lambda^{-4} + 2.0546 \times 10^{21}\lambda^{-5} \quad \lambda < 2000 \text{ Å} \\ &= 7.32 \times 10^{2}\lambda^{0.7} \quad \lambda > 2000 \text{ Å}. \end{aligned} \tag{3}$$

Note that few direct measurements of the interstellar radiation field exist at λ <1100 Å, the important wavelength region for the H_2 and CO photodissociations and C photoionization. As discussed by van Dishoeck and Black (1988), all extrapolations of the measured intensities at longer wavelengths to these short wavelengths are highly uncertain, and the intensities given by formula (3) may well be too large by factors of a few. Thus the photodestruction rates of species which have their dominant channels at short wavelengths are particularly uncertain.

4.2 Lyman α radiation

In interstellar regions subjected to fast shocks, the radiation field may have a very high intensity at 1215.6 Å, because of recombination and collisional excitation of atomic hydrogen leading to Lyman α radiation (Hollenbach and McKee 1979; Neufeld and Dalgarno 1988). It is thus important to know whether a molecule has a photodissociation or photoionization channel at this wavelength. Molecules such as H_2, CO and N_2 cannot be destroyed by Lyman α radiation, whereas other species like OH and H_2O have cross sections of a few times 10^{-18} cm^2 at 1215.6 Å and are thus easily dissociated. Another strong peak in the radiation field in shocks is provided by the C III resonance line at 977 Å.

4.3 Cosmic–ray induced photons

Most models of interstellar clouds assume that the ultraviolet photons of the interstellar radiation field cannot penetrate the inner parts of dense clouds. However, Prasad and Tarafdar (1983) have suggested that a dilute flux of ultraviolet photons can be produced following excitation of H_2 by energetic secondary electrons resulting from cosmic ray ionization of H and H_2. The cosmic ray induced spectrum has been calculated by Sternberg *et al.* (1987), and with more detail recently by Gredel *et al.* (1987). The latter spectrum is reproduced in Figure 6. It consists of a large number of discrete peaks, mostly due to H_2 Lyman and Werner band photons, with a weak underlying continuum. In order to estimate photodissociation rates, coincidences between the cosmic-ray induced photons and the photodestruction cross sections have to be found. A list of cosmic-ray induced photodissociation rates for use in dense cloud models has been given by Gredel (1987). Because of the complicated nature of the process and the lack of high resolution cross sections at short wavelengths, the rates may be quite uncertain, although the large number of lines reduces the sensitivity to some extent.

5. INTERSTELLAR PHOTODISSOCIATION RATES

5.1 Unattenuated photodissociation rates

The photodissociation rates for a number of important astrophysical molecules are summarized in Table 1 for the unattenuated interstellar radiation field given by Draine (1978; Eq. (3)). In order to calibrate the significance of a rate of 3×10^{-10} s^{-1}, say, it is useful to note that this rate corresponds to a lifetime of a molecule of 10^2 years, which is short in comparison with dynamical lifetimes of interstellar clouds (often estimated to be $10^6 - 10^8$ years), and with most other chemical timescales. In particular, destruction of a molecule by reaction with an ion in a cloud of density 10^3 cm^{-3} with a fractional ionization less than 10^{-4} will occur with a characteristic lifetime of 300 years or more.

The rates in Table 1 are based on cross sections which have been derived either from theory, indicated by T, or from experiment, denoted by E. References to the principal sources for the cross sections are indicated. More information can be found in van Dishoeck (1987*a*) and in §5.2. The table includes an indication of the reliability of the results with the notation A (k_{pd} known to better than 50%), B (k_{pd} uncertain up to a factor of two), C (k_{pd} uncertain up to an order of magnitude), and D (no information on cross sections; k_{pd} may be uncertain by orders of magnitude). For some species, Table 1 lists a lower limit to the photodissociation rate, which is obtained by summing the rates through all known channels. This lower limit is often quite accurate. However, higher lying channels may exist for which the cross sections are not yet known. For example, for rates based on experimental results, additional contributions may come from cross sections at $\lambda <1100$ Å, which have not been measured or for which the branching ratios to dissociation and ionization are not known. Rates based on theory may be increased by higher-lying channels below 13.6 eV for which no reliable calculations can be made. In those cases, an additional effective oscillator strength of about 0.1 at $\lambda = 1000$ Å has been assumed for the unknown higher-lying channels, which increases the total rates by $(1 - 2) \times 10^{-10}$ s^{-1}.

Table 1 also includes the most likely products of the photodissociation processes. Note that different products may be obtained for different photodissociation channels. For example, Figure 2*b* illustrates that photodissociation of a simple diatomic molecule like CH may result in C in the ^{3}P, ^{1}D and ^{1}S states, with the two excited species formed predominantly. The relative importance of the photodissociation channels changes with depth into a cloud, so that different products may be dominant at different depths. The photodissociation of polyatomic molecules can result in various fragments, and each of the molecular fragments can be electronically, vibrationally and rotationally excited. Only very limited information is available on the product distributions of polyatomic species as functions of photon energy. If the symmetries of the dissociating states are known, some guesses of the most likely products can be made on the basis of correlation diagrams, but

TABLE 1. Interstellar molecular photodissociation rates (in s^{-1})

Species	Products	k^o_{pd} L.L.[a]	k^o_{pd} Draine[a]	k^o_{pd} MMP[b]	α_2[c]	β_2[c]	γ_2[d]	γ_3[d]	Acc[e]	Ref[f]	
H_2	H+H	...	5.0(-11)	4.0(-11)	[g]	[g]	[g]	[g]	A	1	T
H_2^+	H+H^+	...	5.7(-10)	3.8(-10)	3.913	4.106	1.85	0.72	A	2	E,T
H_3^+	...	...	<1(-12)	<1(-12)	...	...	...	...	A	3	T
HeH^+	He^++H	...	<1(-12)	<1(-12)	...	...	...	...	A	4	T
CH	C+H	8.0(-10)	9.5(-10)	6.6(-10)	2.815	3.089	1.15	0.82	A	5	T
CH^+	C+H^+	...	3.2(-10)	2.5(-10)	5.760	5.604	2.5	0.94	A	6	T
CH_2	CH+H	5.0(-10)	7.2(-10)	4.9(-10)	3.543	3.813	1.67	0.79	C	7	T
CH_3	CH_2+H	...	5.0(-10)	3.2(-10)	3.567	3.792	1.88	0.67	D	8	T
CH_4	$CH_2+H_2/2H$	...	1.2(-9)	8.1(-10)	4.233	4.387	2.15	0.76	A	9	E
C_2	C+C	1.8(-10)	2.3(-10)	1.7(-10)	4.658	4.789	2.09	0.75	B	10	T
C_2H	C_2+H	2.0(-10)	5.1(-10)	3.4(-10)	3.676	3.881	1.89	0.67	C	11	T
C_2H_2	C_2H+H	...	3.2(-9)	2.1(-9)	3.536	3.750	1.84	0.71	B	9	E
C_2H_4	$C_2H_2+H_2/2H$	...	3.0(-9)	2.0(-9)	3.479	3.730	1.67	0.73	C	12	E
C_3	C_2+C	...	3.8(-9)	2.5(-9)	2.950	3.186	1.80	0.60	C	13	T
c–C_3H_2	C_3H+H	...	1.9(-9)	1.2(-9)	2.920	3.157	1.79	0.67	C	14	T
OH	O+H	...	4.2(-10)	2.9(-10)	3.815	4.028	1.72	0.77	A	15	T
OH^+	O^++H	...	1.1(-11)	8.5(-12)	5.862	5.658	2.8	1.05	A	16	T
H_2O[h]	OH+H	...	8.0(-10)	5.5(-10)	3.895	4.120	1.70	0.76	A	9,17	E
O_2	O+O	...	7.9(-10)	5.3(-10)	3.286	3.534	1.76	0.66	A	18	E
HO_2	OH+O	4.7(-10)	6.7(-10)	4.4(-10)	3.808	4.075	1.76	0.77	C	19	E,T
H_2O_2	OH+OH	...	9.4(-10)	6.2(-10)	3.756	3.967	1.82	0.71	B	9	E
O_3	O_2+O	...	1.9(-9)	1.2(-9)	3.301	3.559	1.46	0.75	B	20	E
CO	C+O	...	2.0(-10)	1.8(-10)	[g]	[g]	[g]	[g]	B	21	E
CO_2	CO+O	...	8.7(-10)	6.5(-10)	5.333	5.291	2.5	0.90	C	22	E
HCO	CO+H	...	1.1(-9)	1.0(-9)	2.028	2.285	0.8	0.50	C	23	T
H_2CO	$CO+H_2/2H$	...	1.0(-9)	6.7(-10)	3.457	3.689	1.74	0.74	B	24	E
CH_3OH	H_2CO+H_2	...	1.4(-9)	9.4(-10)	3.758	3.975	1.76	0.71	C	25	E
NH	N+H	...	5.0(-10)	3.3(-10)	3.727	3.942	1.97	0.68	A	26	T
NH^+	N^++H	...	5.4(-11)	3.9(-11)	3.398	3.693	1.39	0.99	C	27	T
NH_2	NH+H	5.8(-10)	7.4(-10)	5.0(-10)	3.476	3.737	1.63	0.83	B	28	T
NH_3[j]	NH_2+H	...	1.1(-9)	7.8(-10)	3.842	4.055	1.79	0.74	A	9	E
N_2[k]	N+N	5.0(-11)	2.3(-10)	2.1(-10)	6.435	6.022	3.82	1.20	C	29	E
NO	N+O	...	4.7(-10)	3.3(-10)	3.838	4.090	1.71	0.72	B	9	E
NO_2	NO+O	...	1.4(-9)	9.1(-10)	3.473	3.715	1.70	0.73	B	9	E
N_2O	N_2+O	...	1.9(-9)	1.2(-9)	3.836	4.023	2.05	0.72	B	30	E
CN[k]	C+N	1.5(-10)	3.0(-10)	2.5(-10)	5.860	5.656	3.07	1.05	C	31	T
HCN	CN+H	...	1.5(-9)	1.1(-9)	4.450	4.565	2.08	0.79	B	9	E
HC_3N[i]	C_3N+H/C_2H+CN		5.6(-9)	3.6(-9)	3.157	3.383	1.84	0.64	B	32	E
CH_3CN	CH_3+CN	...	2.4(-9)	1.6(-9)	4.206	4.354	2.04	0.76	B	33	E
HCℓ	Cℓ+H	...	9.8(-10)	6.5(-10)	3.713	3.928	1.79	0.72	A	34	T,E
NaCℓ	Na+Cℓ	4.8(-10)	3.8(-9)	3.6(-9)	1.565	1.764	0.90	0.90	C	35	E,T

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[a] *Unattenuated rates using the Draine (1978) radiation field; L.L. indicates lower limit;* [b] *As a, but with the Mathis et al. (1983) radiation field;* [c] *Exponential fit parameters α and β cf. Eqn. (5) for grain model 2 and $A_V^{tot}=1$ mag;* [d] *Exponential fit parameters γ cf. Eqn. (4) for grain models 2 and 3, respectively;* [e] *Estimated accuary of rate, see text;* [f] *References for cross sections; E=experiment, T=theory;* [g] *Depth dependence dominated by self-shielding and H, H_2 shielding, see text;* [h] *Branching ratio to $O+H_2$ is about 10%;* [i] *Products highly uncertain;* [j] *Branching ratio to $NH+H_2$ is about 30%;* [k] *Depth dependence affected by H, H_2 shielding, effective γ may be much higher.*

TABLE 1. Interstellar molecular photodissociation rates (cont'd)

Species	Products	k^o_{pd} L.L.[a]	k^o_{pd} Draine[a]	k^o_{pd} MMP[b]	α_2[c]	β_2[c]	γ_2[d]	γ_3[d]	Acc[e]	Ref[f]	
SH	S+H	2.8(-10)	9.7(-10)	6.5(-10)	3.281	3.536	1.42	0.67	C	36	T
SH^{+}[i]	S^{+}+H	...	2.5(-10)	1.9(-10)	4.158	4.416	1.8	0.96	C	36	T
H_2S	SH+H	...	3.1(-9)	2.0(-9)	3.716	3.935	1.87	0.69	A	37	E
CS	C+S	2.5(-10)	9.7(-10)	6.3(-10)	3.637	3.828	2.03	0.71	C	36	E
CS_2	CS+S	...	6.1(-9)	4.2(-9)	3.447	3.715	1.74	0.74	B	9,38	E
COS	CO+S	...	3.7(-9)	2.4(-9)	3.186	3.434	1.69	0.75	B	9	E
SO	S+O	...	3.7(-9)	2.4(-9)	3.753	3.949	1.95	0.74	B	39	E
SO_2	SO+O	...	1.9(-9)	1.2(-9)	3.768	3.961	1.88	0.73	B	9	E
SiH	Si+H	1.5(-9)	2.8(-9)	1.9(-9)	2.802	3.095	1.10	1.03	B	28,40	T
SiH^{+}	Si^{+}+H	2.0(-9)	2.6(-9)	2.5(-9)	1.824	2.050	0.86	0.84	A	41	T
PH	P+H	...	5.8(-10)	3.8(-10)	3.204	3.440	1.73	0.72	C	36	T
PH^{+}[i]	P^{+}+H	...	1.4(-10)	1.1(-10)	2.923	3.206	1.2	0.84	C	36	T
LiH	Li+H	...	5.1(-9)	3.5(-9)	2.351	2.597	1.21	1.21	A	42	T
NaH	Na+H	...	7.3(-9)	5.2(-9)	2.206	2.442	1.13	0.94	A	42	T
MgH	Mg+H	3.3(-11)	5.0(-10)	3.3(-10)	2.914	3.160	1.45	0.61	C	43	T
AℓH	Aℓ+H	2.0(-9)	3.2(-9)	3.7(-9)	1.193	1.342	0.77	0.74	C	44	T

References: (1) Allison and Dalgarno 1970; Stephens and Dalgarno 1972 ; (2) Dunn 1968 ; (3) Kulander and Bottcher 1978 ; (4) Roberge and Dalgarno 1982; (5) van Dishoeck 1987b; (6) Kirby et al. 1980; (7) Römelt et al. 1981; (8) Herzberg 1961; Macpherson et al. 1985; (9) Lee 1984; (10) Pouilly et al. 1983; (11) Shih et al. 1977, 1979; (12) Zelikoff and Watanabe 1953; (13) Römelt et al. 1978; (14) van Hemert et al. 1988; (15) van Dishoeck and Dalgarno 1983, 1984; (16) Saxon and Liu 1986; (17) Watanabe and Zelikoff 1953; Watanabe and Jursa 1964; (18) Huebner et al. 1975; Yoshino et al. 1983; Smith et al. 1984; Gies et al. 1981; (19) McAdam et al. 1987; Lee 1982; Langhoff and Jaffe 1979; (20) Molina and Molina 1986; Tanaka et al. 1953; Ogawa and Cook 1958a; (21) see §6; (22) Lewis and Carver 1983; NaKata et al. 1965; (23) Bruna et al. 1976; (24) Suto et al. 1986; Mentall et al. 1971; (25) Salahub and Sandorfy 1971; Nee et al. 1985; Ogawa and Cook 1958b; (26) Kirby and Goldfield 1988; (27) van Dishoeck 1986; (28) Saxon et al. 1982; (29) Carter 1972; (30) Zelikoff et al. 1953; (31) van Dishoeck 1986; Lavendy et al. 1987; (32) Connors et al. 1974; (33) Nuth and Glicker 1982; Suto and Lee 1985; (34) van Dishoeck et al. 1982; Nee et al. 1986; (35) Silver et al. 1986; Zeiri and Balint-Kurti 1983; (36) see §5.2; (37) Lee et al. 1987; (38) Cook and Ogawa 1969a; (39) Nee and Lee 1986; Phillips 1981; (40) Lewerenz et al. 1983; (41) Kirby and Singh 1983; (42) Kirby and Dalgarno 1978; (43) Kirby et al. 1979; (44) Matos et al. 1987.

these estimates are usually limited to the best characterized lowest-lying channels, which may not dominate the photodissociation.

The list of molecules in Table 1 is far from complete, but contains most small species of astrophysical interest for which some information is available in the vast molecular and chemical physics literature. A list of photodissociation rates for larger molecules has been compiled by Herbst and Leung (1986). As emphasized by them, data for large species are sparse and incomplete. It appears from Table 1 that the unshielded rates for most polyatomic molecules are large, about 10^{-9}–10^{-8} s^{-1}. However, at the depth into a cloud where the abundances of the larger molecules become significant, the cosmic ray induced photodissociation rates are probably more relevant.

Compared with the photodissociation rates listed by Black and Dalgarno (1977), most of the rates listed in Table 1 are significantly larger. This is partly due to the fact that the radiation field of Draine (1978) is a factor of two more intense than that adopted by Black and Dalgarno in the ultraviolet (cf. Figure 5). Further increases are due either to contributions from channels which were not recognized before, or to improved experimental data. The photodissociation rates in the unattenuated radiation field specified by Mathis *et al.* (1983) are included in the table for comparison, and are typically smaller by 40%.

The photodissociation rates for isotopic species are expected to be similar to those of the principal species if the photodissociation proceeds mostly by the direct mechanism. However, if indirect processes dominate, differences may occur if the predissociation of the isotopic variety starts at a different energy level with a different oscillator strength than that of the main species. In addition, depth–dependent effects may occur if the predissociating lines of the principal molecule do not shield those of the isotopic species. Examples are provided by HD and the isotopic varieties of CO (cf. §6).

5.2 Recent developments

Molecules for which information on the photodissociation cross sections has recently become available and/or which were not yet discussed by van Dishoeck (1987*a*) will be reviewed briefly below. The important case of CO will be discussed separately in §6.

Potential energy curves and transition dipole moment functions for the NH molecule have been computed by Goldfield and Kirby (1987). The photodissociation cross sections into the excited $^3\Sigma^-$ and $^3\Pi$ states give rise to an unshielded rate of about 5×10^{-10} s^{-1} (Kirby and Goldfield 1988), which is comparable to that of OH, and about a factor of two smaller than that of CH (van Dishoeck 1987*b*). The photodissociation rate of NH^+ is based on cross sections calculated by van Dishoeck (1986). Although many of the excited electronic potentials are repulsive, most of them have vertical excitation energies larger than 13.6 eV, so that the destruction by interstellar radiation is not very rapid.

A large photodissociation rate had been suggested for the CN molecule by Lavendy *et al.* (1984). As pointed out by van Dishoeck (1986), the limited size of these computations may have led to an overestimate of the rate. More recent computations by Lavendy *et al.* (1987) indicate a rate of about 7×10^{-10} s^{-1}, whereas the results of van Dishoeck (1986) suggest $k_{pd} \approx 3 \times 10^{-10}$ s^{-1}. The photodissociation occurs primarily at short wavelengths, $\lambda <$1050 Å, in harmony with the fact that no CN photodissociation is observed experimentally for $\lambda >$1060 Å (Nee and Lee 1985).

The electronic structure of molecules involving second row atoms is often similar to that of the corresponding first row species. Nevertheless, subtle differences can occur in the photodissociation processes. For example, the photodissociation of SiH^+ through the lowest $A^1\Pi$ channel is much more effective than that of CH^+, as discussed in §2.1 and illustrated in Figure 3. As a consequence, the photodissociation rate of interstellar SiH^+ is about an order of magnitude larger than that of CH^+. In general, the potential energy curves of molecules involving second row atoms are shifted to lower energies compared with the first row species. Thus, photodissociation channels that are inaccessible at $\lambda >$912 Å in the latter case may contribute significantly to the photodissociation of the second row molecules. For example, the excited repulsive $^3\Pi$ and $^3\Sigma^-$ states are expected to contribute significantly to the photodissociation of interstellar SH^+, whereas they cause negligible photodissociation in the case of OH^+. The transition moments are probably of similar magnitude in the two cases. Since the intensity of the interstellar radiation field also increases with wavelength, the photodissociation of second row molecules will usually proceed more rapidly than that of the first row species.

The SH photodissociation rate was estimated on the basis of potential curves computed by Bruna and Hirsch (1987), together with transition moments for similar states of OH obtained by van Dishoeck and Dalgarno (1983). Note that photodissociation of interstellar SH can also occur by absorption into the $A^2\Sigma^+$ (v'=0) level, which is strongly predissociated throughout (Friedl *et al.* 1983). The interstellar SH^+ photodissociation rate was obtained by shifting the cross sections computed by Saxon and Liu (1986) for OH^+ by 200 Å to longer wavelengths.

The photodissociation of interstellar CS, SiO and SiS probably proceeds by processes similar to those for CO, with the difference that the dissociation energies and ionization thresholds are smaller by 3–4 eV. High resolution spectra of CS at VUV wavelengths (Stark *et al.* 1987*a*) show many diffuse bands. In particular, the strong B–X (0,0) and C–X (0,0) bands of CS are rapidly predissociated, in contrast with CO. If the oscillator strengths for these bands in CS are similar to those of CO, the photodissociation rate of interstellar CS must be significantly larger than that of CO. The SiO and SiS photodissociation rates are probably similar to that of CS. Photoabsorption cross sections for SO have recently been measured by Nee and Lee (1986) and Phillips (1981). Photodissociation of interstellar S_2 is expected to be at least as rapid as that of O_2.

Detailed potential energy curves of lower electronic states of PH and PH^+ have been computed by Bruna *et al.* (1981). The rate estimated for PH assumes that the cross sections to the repulsive $^3\Sigma^-$ and $^3\Pi$ states are similar to those of NH, but shifted to longer wavelengths. Photodissociation of PH^+ can occur already through the low-lying $1^2\Sigma^-$ and $1^2\Sigma^+$ states, which are bound in the case of NH^+. The PH^+ photodissociation rate is therefore expected to be at least as large as that of NH^+.

The lower limit to the photodissociation rate of interstellar AlH is based on potential curves and transition moments computed by Matos *et al.* (1987). Additional contributions from higher-lying states are expected to further increase the rate. The photofragmentation of various alkali–halides, including the KCl and NaCl molecules recently discovered in circumstellar envelopes (Cernicharo and Guélin 1987), has been investigated theoretically by Zeiri and Balint-Kurti (1983). Measurements of photodissociation cross sections for NaCl have been performed by Silver *et al.* (1986).

The photodissociation of HO_2 in the 1700–2700 Å range has been investigated experimentally by McAdam *et al.* (1987) and Lee (1982), and theoretically by Langhoff and Jaffe (1979). Little is known about possible photodissociation processes at higher energies. The photodissociation rate of interstellar HCO is based on potential curves and oscillator strengths computed by Bruna *et al.* (1976), and is still highly uncertain.

The photodissociation rate of c–C_3H_2 is based on preliminary results of calculations by van Hemert *et al.* (1988), and assumes that the strong absorptions around 1500 Å lead to dissociation of the molecule. The photodissociation of CH_3 can occur through several of the excited states found by Herzberg (1961), but no information is available on cross sections for these transitions, except at 2164 Å (MacPherson *et al.* 1985). The ionization potentials of both species lie around 10 eV, so that photoionization may be effective. Note that the uncertainties in the branching ratios for dissociation vs. ionization affect the estimated photodissociation rates of many small hydrocarbons such as CH_2, CH_3 and C_2H, which have ionization potentials around 10–11 eV. In Table 1, it has been assumed that at least 50% of the absorptions above the ionization threshold lead to ionization of the molecules.

5.3 Depth–dependent photodissociation rates

The intensity of the interstellar radiation field—and consequently the photodissociation rates—decreases with depth into an interstellar cloud due to several factors. First, the grains present in the cloud will scatter and absorb the photons with a cross section that varies almost inversely with wavelength. The amount of continuum attenuation at each depth into the cloud depends on the extinction, the albedo and the scattering phase function of the grains (Sandell and Mattila 1975; Roberge, Dalgarno and Flannery 1981), only the first of which is sometimes known accurately at ultraviolet wavelengths. Current models of interstellar grains (Draine and Lee 1984; Chlewicki and Greenberg 1984) favor a relatively low albedo $\omega_\lambda \approx 0.4$ and a rather forward scattering asymmetry parameter $g_\lambda \approx 0.6$–0.9 at $\lambda < 1500$ Å. Second, the intensity of the radiation field at $\lambda < 1100$ Å may be further diminished by the opacity due to H_2 and C in the clouds. The rates for molecules like CO and CN for which the photodissociation occurs primarily at $\lambda < 1100$ Å will be particularly affected. Finally, if the photodissociation of a molecule is dominated by discrete absorptions and if its abundance is sufficiently high, the dissociating lines will become saturated and the molecule will shield itself against dissociation deep in the cloud.

It is usually assumed that the contributions of line and continuum attenuation are separable. The depth dependence of the photodestruction rates due to grain attenuation can be computed by solving the equations of radiative transfer for specified grain properties and geometry of the cloud. If the cloud is assumed to have a plane–parallel geometry with radiation incident on both sides of the cloud, the depth–dependent rates depend strongly on the total extent of the cloud. The results for clouds with a total visual extinction A_V^{tot} are usually represented by single exponential decays to the centers

$$k_{pd} = C \exp(-\gamma A_V) \ \ \mathrm{s}^{-1}. \tag{4}$$

For thicker clouds, $A_V^{tot} > 5$ mag, this representation is accurate to within a factor of a few at all depths. For typical diffuse clouds with $A_V^{tot}=1$ mag, more accurate fits may be provided by bi–exponential decays

$$k_{pd} = C \exp(-\alpha A_V + \beta A_V^2) \ \ \mathrm{s}^{-1}. \tag{5}$$

Depth–dependent photodissociation rates have been computed for most species listed in Table 1 adopting grain models 2 and 3 of Roberge *et al.* (1981) for clouds with total visual extinctions ranging from 1 to 30 mag. Of the two grain models, model 2 gives results that are closest to those obtained with the grain properties recommended by Chlewicki and Greenberg (1984). The results for the exponents α and β for a typical diffuse cloud with $A_V^{tot}=1$ mag illuminated from both sides are presented in Table 1 for grain model 2, together with the exponents γ for a dense cloud with $A_V^{tot}=20$ mag. The latter exponents are also appropriate for a cloud exposed to radiation from one side only. The exponents α and β listed in Table 1 should not be used beyond a depth of 0.5 mag. The single exponents γ range from 1.5 to 3.5 with grain model 2. The exponent is small for species like NaH and SiH^+ for which the photodissociation occurs principally at longer wavelengths, whereas it is large for molecules like CN and N_2, which only photodissociate at the shortest wavelengths. The effective exponent for the latter species will be even larger if the attenuation due to H_2 and C is taken into account. For the more forward scattering grain model 3, γ is decreased to about 0.7–1.2. Results for γ with grain model 3 are included in Table 1. Note that the depth dependence of the rate of each photodissociation channel varies with wavelength: lower–lying photodissociation channels become relatively more important than higher–lying channels deep inside a cloud. It may thus be that the photodissociation of a molecule is dominated by a high–lying channel at the edge, whereas deeper inside a low–lying channel is most important. In those cases, the single exponential fit is particularly bad, and differences of 0.5 or more in γ are found if the total thickness of the cloud is varied from 2 to 20 mag. The factor C in Eqs. (4) and (5) is about half the unattenuated photodissociation rate if the cloud is illuminated on both sides by half the intensity specified by Eq. (3), so that in the absence of the cloud the unattenuated rates are recovered.

Expressions for the attenuation due to line shielding have been given by Hollenbach, Werner and Salpeter (1971), Federman, Glassgold and Kwan (1979) and van Dishoeck and Black (1986). In practice, self–shielding is taken into account only for the H_2, HD

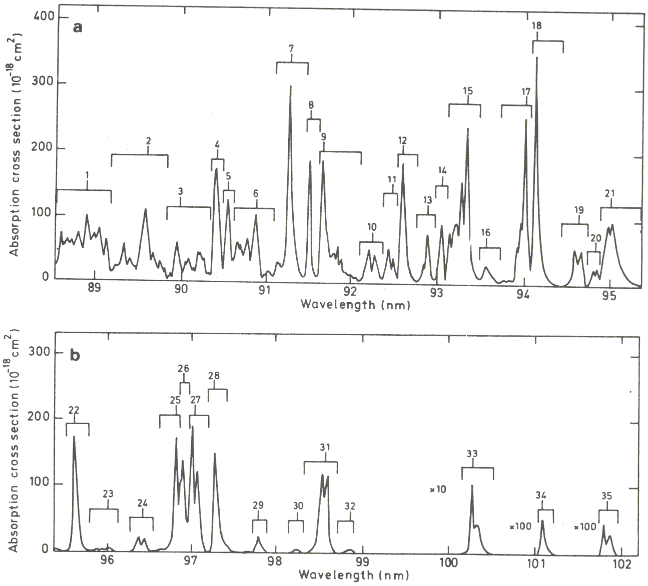

Figure 7. *CO absorption cross sections measured by Letzelter et al. (1987)*

and CO molecules. In applications in which the fine details of the depth dependences can be ignored, the shielding functions can be approximated by those of a representative single line with an appropriate scaling factor to account for the absolute value of the rate. Such simple expressions have been given by van Dishoeck (1987*a*) for H_2, and by Mamon, Glassgold and Huggins (1988) for CO. In addition, van Dishoeck and Black (1988) have presented a simple representation of the photodissociation rates of CO and its isotopes as functions of total CO and H_2 column densities.

6. PHOTODISSOCIATION OF INTERSTELLAR CO

The most important recent development with respect to photodissociation is that the photodissociation of CO is finally reasonably well understood. This has been accomplished mostly by the detailed laboratory measurements of photoabsorption cross sections and line positions by Letzelter *et al.* (1987) and Yoshino *et al.* (1988). The photodissociation processes of interstellar and circumstellar CO based on the new experimental data have been discussed in considerable detail by Letzelter *et al.* (1987), Viala *et al.* (1988), Mamon *et al.* (1988) and van Dishoeck and Black (1988), and only the most important aspects will be summarized here. Apart from being the second most abundant molecule, CO also illustrates well the difficulties in the determination of accurate cross sections at short wavelengths (cf. §3), as well as the many complications that arise in the calculation of depth-dependent rates (cf. §5).

The dissociation energy of CO is 11.09 eV, so that photodissociation can take place only at $\lambda < 1118$ Å. Although it has been clear for some time that the CO photodissociation is dominated by discrete absorptions, it was previously thought to occur mostly through the $C^1\Sigma^+$–$X^1\Sigma^+$ (1,0) and $E^1\Pi$–$X^1\Sigma^+$ (0,0) bands at 1063 and 1076 Å respectively (Bally

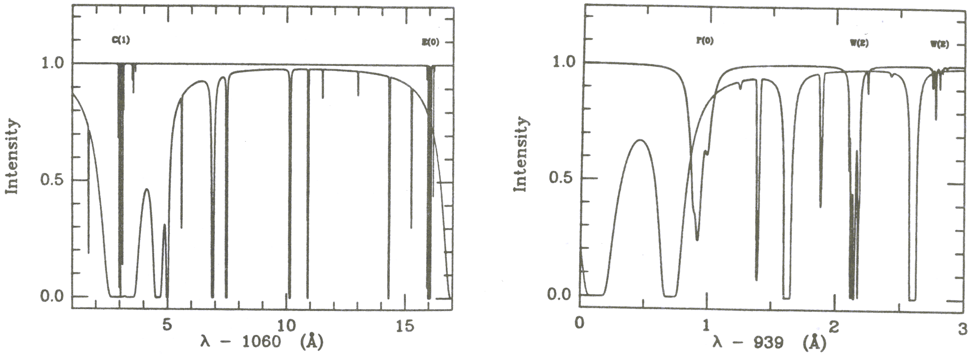

Figure 8. *Parts of the simulated high-resolution absorption spectrum of CO (full lines) and H and H_2 (dotted lines) at the center of the ς Oph cloud (from: van Dishoeck and Black 1988).*

and Langer 1982; Glassgold, Huggins and Langer 1985). Experiments by Fock, Gürtler and Koch (1980) indicated that many more excited states may contribute to photodissociation of the molecule at shorter wavelengths, but accurate determinations of the cross sections had to await the measurements by Letzelter *et al.* (1987). Part of the resulting absorption spectrum is reproduced in Figure 7, and cross sections for individual bands have been listed by Letzelter *et al.* They are significantly larger than those obtained in earlier experiments due to underestimates of the saturation effects in the older work. Note, however, that the resolution of 0.15 Å in the Letzelter *et al.* spectrum is not yet sufficient to resolve the rotational structure of the bands. Experiments at the 20 times higher resolution of 0.007 Å have recently been performed by Yoshino *et al.* (1988), and indicate that some of the cross sections given by Letzelter *et al.* may still be too low by a factor of about two. Since many of the absorptions involve high Rydberg states, no accurate theoretical calculations are possible. An additional uncertainty in the calculation of CO photodissociation rates is provided by the predissociation probabilities η_u for the upper states. The experiments of Letzelter *et al.* suggest that all η_u are close to unity, except for the C–X (1,0) and E–X (0,0) states, but most of the experiments refer to rather high rotational levels. The question remains whether the lower rotational levels are rapidly predissociated as well, as is assumed in all current models. With the new experimental data, the unshielded photodissociation rate of CO in the Draine (1978) radiation field is 2.0×10^{-10} s^{-1}. This rate is a factor of 40 larger than that adopted e.g. by Black and Dalgarno (1977) and Glassgold *et al.* (1985).

The depth-dependence of the absorption rate in each line is controlled by self-shielding, by shielding by coincident lines of H and H_2, and by dust attenuation. In order to account for the first two effects, van Dishoeck and Black (1988) have simulated the full absorption spectrum of CO at each depth into the cloud. Line positions were based on published analyses of the well-studied transitions and unpublished spectra by Stark *et al.* (1987*b*). Line widths were estimated from high-resolution spectra on the basis of the diffuseness of the bands. Since the predissociation rates are rapid, $A^{pr} \approx 10^{11} - 10^{12}$ s^{-1}, the lines are intrinsically very broad with line widths of 2–20 km s^{-1} in Doppler velocity units. Figures 8*a* and *b* contain two small portions of the absorption that would be produced by CO and by H and H_2 at the center of a diffuse cloud such as that toward ς Oph. It is clear that some bands like the C–X (1,0) band at 1063 Å are coincident with strong H or H_2 features, and are effectively blocked by them. Figure 8*b* also illustrates that the predissociation rates

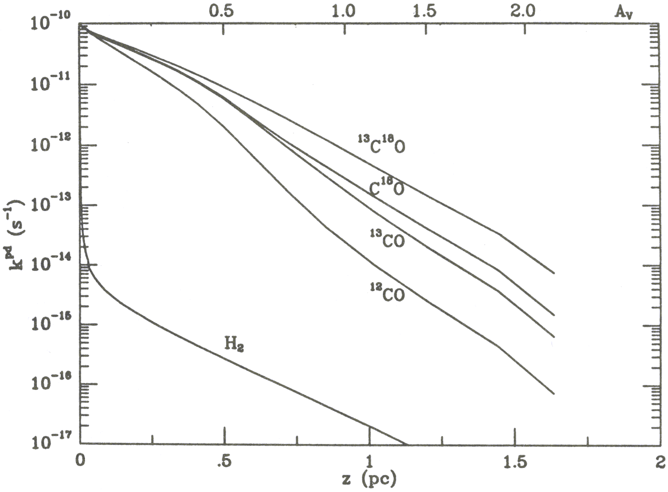

Figure 9. *Photodissociation rates of CO and its principal isotopes as functions of depth into a cloud with a total visual extinction of 5 mag (from: van Dishoeck and Black 1988).*

for some bands, such as that at 940 Å, are so large that the rotational structure becomes indistinct, even at a rotational excitation temperature of only 4 K.

The depth dependence of the CO photodissociation rate is shown in Figure 9 for a model cloud with a total visual extinction A_V^{tot}=5.2 mag, a total hydrogen density of 1000 cm^{-3} and a temperature of 15 K, exposed to the normal interstellar radiation field cf. Draine (1978). Grain model 2 of Roberge *et al.* (1981) was adopted. The CO photodissociation rate decreases rapidly with depth into the cloud due to self-shielding and shielding by H and H_2. The variation is, however, not as drastic as that of the H_2 photodissociation rate, as illustrated in the figure.

The calculation of the depth dependence of the photodissociation rate of the isotopic varieties ^{13}CO, $C^{18}O$ and $^{13}C^{18}O$ is complicated by the fact that lines in (0,0) bands can be effectively shielded by ^{12}CO inside the cloud, but not lines in (v',0) bands with $v' \geq 1$, owing to the larger isotope shift when a non-zero vibrational quantum number is involved. Unfortunately, the majority of the absorption bands at $\lambda <1000$ Å shown in Figure 7 have not yet been identified spectroscopically, although reasonable guesses have been made by van Dishoeck and Black (1988). The depth-dependent rates of the isotopic species included in Figure 9 are therefore still uncertain, but appear to be larger than those of ^{12}CO inside a cloud by up to an order of magnitude. This isotope-selective photodissociation, originally recognized by Bally and Langer (1982), competes with ion-molecule exchange reactions in establishing the fractionation of the isotopic species, as discussed by Glassgold *et al.* (1985) and van Dishoeck and Black (1988).

From Figures 8*a* and *b*, it is clear that there are many coincidences between the CO photodissociation transitions and the broad lines of H_2 arising in the lowest rotational levels. In order to compute the cosmic ray induced CO photodissociation rate inside a dense cloud, coincidences between the CO absorption lines and the H_2 emission lines presented in Figure 6 have to be found. Note that these emission lines are much narrower than the broad absorption lines, so that the coincidences need to be nearly exact. Gredel

TABLE 2. Ionization potentials of selected species

Species	I.P. (eV)	Ref.	Species	I.P. (eV)	Ref.	Species	I.P. (eV)	Ref.
H_2	15.43	1	OH	13.0	1	SiH	8.0	1
CH	10.64	1	H_2O	12.62	2	SiO	11.43	1
CH_2	10.40	2	O_2	12.06	3	SH	10.43	1
CH_3	9.83	3	O_3	12.67	3	S_2	9.36	1
CH_4	12.55	3	HO_2	11.53	2	CS	11.34	1
C_2	12.15	1	NH	13.1	1	SO	10.29	1
C_2H	11.0	4	NH_2	11.4	2	H_2S	10.47	2
C_2H_2	11.41	2	NH_3	10.15	2	HCl	12.74	1
C_2H_4	10.50	2	N_2	15.58	1	PH	10.2	6
C_3	12.1	3	NO	9.25	1	PN	11.85	1
CO	14.01	1	NO_2	9.78	2	NaH	6.9	7
CO_2	13.79	5	N_2O	12.89	2	CH_3CN	12.19	3
HCO	9.88	2	CN	14.17	1	CH_3OH	10.83	3
H_2CO	10.88	2	HCN	13.59	3			

References: (1) Huber and Herzberg 1979; (2) Herzberg 1966; (3) Rosenstock et al. 1977; (4) Shih et al. 1977; (5) Cossart–Magos et al. 1987; (6) Bruna et al. 1981; (7) Langhoff 1985.

et al. (1987) have found about 60 close coincidences, resulting in a fairly large cosmic ray induced photodissociation rate of CO.

7. PHOTOIONIZATION PROCESSES AND CROSS SECTIONS

Absorption of a photon with an energy above the lowest ionization threshold can result both in photoionization and in photodissociation of a molecule. The photoionization can produce either a stable molecular ion in its ground or excited electronic state, or it can result in dissociation of the ion into a charged and a neutral fragment. Photoionization can also occur by absorption into excited Rydberg states lying above the first ionization potential, followed by autoionization:

$$\begin{aligned} XY + h\nu &\rightarrow XY^+ + e && \text{photoionization} \\ &\rightarrow X^+ + Y + e && \text{dissociative photoionization} \\ &\rightarrow XY^{**} \rightarrow XY^+ + e && \text{autoionization} \end{aligned} \tag{6}$$

The photoionization cross section is finite at threshold and generally consists of a smooth background with superposed resonances due to interactions with Rydberg states of the neutral molecule. Information about the cross sections can be obtained both from theory and experiment. On the theoretical side, the calculation is complicated by the description of the wave function of the electron in the field of the molecular ion XY^+. The various theoretical methods have recently been summarized e.g. by Langhoff (1985) and Lucchese and McKoy (1983). Extensive calculations have been performed mostly for common species such as H_2, N_2, CO and NO, for which direct comparison with experiments is possible. Although the computations give reasonable results at higher energies, they often fail to reproduce the detailed structure near threshold, the region of astrophysical interest.

Many different experimental techniques have been applied to obtain total and partial photoionization cross sections (see e.g. Hudson 1971; Sandorfy, Ausloos and Robin 1974;

TABLE 3. Interstellar atomic photoionization rates

Species	λ_{ion} (Å)	k^o_{pi} (s^{-1}) Draine[a]	k^o_{pi} (s^{-1}) MMP[b]	α_2[c]	β_2[c]	γ_2[d]	γ_3[d]	Ref.
H	911.75	...	...	...	...	...	...	
H^-	16420	1.1(-7)	1.4(-7)	0.302	0.329	0.17	0.17	1
He	504.3	...	...	...	...	...	...	
Li	2299	3.5(-10)	2.3(-10)	3.557	3.820	1.70	0.71	2
C	1101	3.0(-10)	2.2(-10)	5.426	5.336	2.96	0.99	3
N	853	...	...	...	...	...	...	
O	910.5	...	...	...	...	...	...	
Na	2413	1.5(-11)	1.0(-11)	3.769	3.996	1.78	0.72	4
Mg	1622	7.9(-11)	5.1(-11)	3.091	3.335	1.67	0.70	5
Al	2071	4.7(-9)	3.2(-9)	3.456	3.740	1.68	0.76	6
Si	1521	3.1(-9)	2.0(-9)	3.488	3.704	1.91	0.67	7
P	1182	1.0(-9)	7.0(-10)	4.786	4.832	2.65	0.88	8,9
S	1197	5.9(-10)	4.4(-10)	5.193	5.180	2.58	0.90	10
Cℓ	956	9.5(-11)	9.6(-11)	6.695	6.192	4.01	1.25	11
K	2856	2.9(-11)	1.9(-11)	3.429	3.684	1.65	0.75	12
Ca	2028	3.4(-10)	2.3(-10)	3.353	3.627	1.68	0.82	13
Ca^+	1044	2.3(-12)	1.8(-12)	5.895	5.665	3.33	1.09	14
Ti	1818	2.3(-10)	1.5(-10)	3.943	4.132	1.95	0.72	9
Cr	1832	1.5(-9)	9.8(-10)	3.282	3.535	1.70	0.76	9
Mn	1668	3.3(-11)	2.2(-11)	2.971	3.228	1.66	0.75	8,9
Fe	1575	2.8(-10)	1.8(-10)	3.204	3.427	1.86	0.67	15
Co	1577	5.4(-11)	3.5(-11)	3.039	3.278	1.73	0.73	9
Ni	1624	9.8(-11)	6.4(-11)	3.027	3.270	1.70	0.74	9
Zn	1320	4.4(-10)	3.0(-10)	5.116	5.081	2.43	0.94	16
Rb	2986	2.7(-11)	1.8(-11)	3.396	3.656	1.42	0.74	17

[a–d] *See footnotes to Table 1.*

References for cross sections: (1) Wishart 1979; (2) Caves and Dalgarno 1972; Serrao 1982; (3) Cantù et al. 1981; Burke and Taylor 1979; Hoffmann et al. 1983; (4) Butler and Mendoza 1983; (5) Bates and Altick 1973; Preses et al. 1984; Mendoza and Zeippen 1987; (6) LeDourneuf et al. 1975; Kohl and Parkinson 1973; Roig 1975; (7) Chapman and Henry 1972b; (8) McGuire 1968; (9) Reilman and Manson 1979; (10) Chapman and Henry 1972a; Dill et al. 1975; (11) Brown et al. 1980; Ruščić and Berkowitz 1983; (12) Weisheit 1972; Sandner et al. 1981; (13) Scott et al. 1983; McIlrath et al. 1972; Carter et al. 1971; (14) Black et al. 1972; (15) Kelly 1972; Lombardi et al. 1978; Tondello 1975; Hansen et al. 1977; (16) Marr and Austin 1969; (17) Weisheit 1972; Suemitsu and Samson 1983.

Samson 1976; Berkowitz 1979; Brion and Thomson 1984; Gallagher *et al.* 1988 and references cited), although still only few high resolution measurements exist around threshold. Information on the branching ratios to photoionization and photodissociation is still incomplete at low energies, and is based mostly on the older high resolution measurements. The experiments for species such as H_2, CO and O_2 suggest that the quantum yield for photoionization is more than 50% around threshold if no major change in configuration occurs during the ionization. If the transition is highly non–vertical, as is the case for CH_4 and NO_2, the photoionization yield can be very small around threshold. At higher energies —typically about 20 eV for molecules of astrophysical interest— the ionization efficiency approaches unity. The percentage of absorptions leading to dissociative photoionization is usually low at threshold, $<$5–10 %, but increases with increasing photon energy. The probability for formation of an ion–pair $X^+ + Y^-$ is also usually small at low energies,

TABLE 4. Interstellar molecular photoionization rates

Molecule	λ_{ion} (Å)	k^o_{pi} (s^{-1}) Draine[a]	k^o_{pi} (s^{-1}) MMP[b]	α_2[c]	β_2[c]	γ_2[d]	γ_3[d]	Ref.
CH	1164	7.6(-10)	5.5(-10)	5.311	5.247	2.84	0.97	1
CH_4	980	6.8(-12)	6.9(-12)	6.733	6.217	4.04	1.26	2,3
C_2	1020	4.1(-10)	3.4(-10)	6.171	5.853	3.54	1.14	4
C_2H_2 ...	1087	3.3(-10)	2.5(-10)	5.713	5.547	3.12	1.04	2,3
C_2H_4 ...	1181	4.1(-10)	3.1(-10)	5.447	5.370	2.77	0.95	2,3
C_2H_6 ...	1064	2.0(-10)	1.6(-10)	6.013	5.751	3.28	1.10	2,3
O_2	1027	7.7(-11)	6.8(-11)	6.366	5.978	3.73	1.18	5
H_2O	984	3.3(-11)	3.1(-11)	6.531	6.088	3.85	1.21	6,7
NH_3	1220	2.8(-10)	2.0(-10)	5.134	5.117	2.70	0.93	8,9
NO	1345	2.6(-10)	1.9(-10)	5.092	5.107	2.32	0.86	10
NO_2	1268	1.5(-10)	1.1(-10)	5.585	5.464	2.77	0.99	11
N_2O	962	1.9(-10)	1.9(-10)	6.688	6.188	4.00	1.25	12
H_2S	1185	7.1(-10)	5.1(-10)	5.023	5.027	2.69	0.91	7,13
CS_2	1232	1.7(-9)	1.2(-9)	5.239	5.198	2.62	0.93	14,15
COS	1109	7.0(-10)	5.4(-10)	5.592	5.471	2.96	1.00	16
HCl	973	8.7(-11)	8.2(-11)	6.535	6.087	3.89	1.22	17
H_2CO ..	1142	4.7(-10)	3.5(-10)	5.369	5.304	2.82	0.96	18
P1[e]	950	1.8(-11)	1.8(-11)	6.707	6.200	4.05	1.25	
P2	1000	5.9(-11)	5.1(-11)	6.339	5.962	3.70	1.18	
P3	1100	1.9(-10)	1.4(-10)	5.503	5.393	3.00	1.00	
P4	1200	3.7(-10)	2.6(-10)	4.893	4.930	2.58	0.88	
P5	1300	5.7(-10)	3.9(-10)	4.413	4.537	2.26	0.79	
P6	1500	9.8(-10)	6.6(-10)	3.791	3.995	1.95	0.69	

[a–d] See footnotes to Table 1. [e] Rates obtained assuming a constant cross section of 10^{-17} *cm*^{2} *and an ionization threshold given by* λ_{ion}.

References to cross sections: (1) Barsuhn and Nesbet 1978; (2) Hudson 1971; (3) Metzger and Cook 1964; (4) Padial et al. 1985; (5) Matsunaga and Watanabe 1967; (6) Haddad and Samson 1986; (7) Watanabe and Jursa 1964; (8) Samson et al. 1987; (9) Watanabe and Sood 1965; (10) Watanabe et al. 1967; (11) Nakayama et al. 1959; (12) Cook et al. 1968; (13) Lee et al. 1987; (14) Cook and Ogawa 1969a; (15) Carnovale et al. 1981; (16) Cook and Ogawa 1969b; (17) Faegri and Kelly 1982; (18) Mentall et al. 1971.

although e.g. $NO^+ + O^-$ can be produced from NO_2 already at 1145 Å.

Reviews of atomic ionization cross sections have been given by Burke (1976), Roberge *et al.* (1981), Mendoza (1983), Keenan (1984) and Péquinot and Aldrovandi (1986).

8. INTERSTELLAR PHOTOIONIZATION RATES

Photoionization of atoms and molecules by the interstellar radiation field can occur only if their lowest ionization potential is less than 13.6 eV. The ionization potentials of a number of molecules of astrophysical interest are collected in Table 2. The table lists the lowest ionization threshold, wherever data are available. Note that this threshold may be substantially lower than the vertical ionization potential of the molecule. For example, for CH_4, the ionization threshold is about 12.5 eV, whereas the vertical ionization potential is 14.2 eV. Thus, the photoionization cross section of CH_4 is extremely small at threshold, and becomes substantial only at energies larger than 14.2 eV, resulting in a negligible interstellar photoionization rate. Most simple molecules have their ionization threshold below 13.6 eV. On the other hand, important molecules such as $H_2(v=0)$, CO, CN and N_2 cannot be photoionized in interstellar clouds. Photoionization of H_2 out of vibrationally excited levels $v \geq 4$ can take place at wavelengths longer than 912 Å (Ford *et al.* 1975), and may be important in some astrophysical environments (Black and van Dishoeck 1987). In planetary nebulae, where the radiation field extends beyond 13.6 eV, photoionization of H_2 $(v=0)$, CO and N_2 becomes possible (Black 1983).

Tables 3 and 4 list the resulting photoionization rates in the unattenuated interstellar radiation field of Draine (1978; cf. Eq. (3)) for a number of important atomic and molecular species. Although many of the atomic cross sections and rates are accurately known, the rates for most molecules are uncertain by at least a factor of two. An order of magnitude estimate of the photoionization rates of species not listed in Table 4 can be obtained by assuming a constant cross section of 10^{-17} cm^2 above the (vertical) ionization threshold. Some prototypical calculations for different thresholds are included at the bottom of Table 4. Comparison with rates for species for which the cross sections are known shows that the assumption of $\sigma_{\rm ion} = 10^{-17}$ cm^2 most likely results in an underestimate of the rate by a factor of a few. The variations of the photoionization rates with depth for the cases discussed in §5.3 are included as well. It is expected that virtually all of the molecular ionizations lead to the formation of a stable molecular ion.

9. CONCLUDING REMARKS

Substantial progress has been made in the last decade in our understanding of the photodissociation and ionization processes of small molecules. In particular, the experiments by Letzelter *et al.* (1987) and Yoshino *et al.* (1988) have finally removed most of the uncertainties in the photodissociation of one of the dominant interstellar molecules, CO. Nevertheless, there are still many simple molecules of astrophysical interest such as the radicals CH_2, C_2H, CH_3, HCO ... and the ions HCO^+, CH_2^+, CH_3^+, N_2H^+, ... for which only little is known about the photodissociation or ionization. Information on the photodissociation of larger molecules is still sparse and incomplete, not only with respect to cross sections, but also regarding the possible photodissociation products. Detailed theoretical calculations on smaller species and experiments on larger molecules are needed to remove these uncertainties. In addition, the stability of very large molecules with respect to photodissociation urgently needs to be investigated experimentally.

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