Interstellar Molecular Absorption Lines

A. Dalgarno

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Interstellar molecular absorption lines

By A. Dalgarno, F.R.S.

*Center for Astrophysics, Harvard College Observatory and
Smithsonian Astrophysical Observatory, Cambridge, Massachusetts* 02138, *U.S.A.*

The ultraviolet absorption lines produced in interstellar clouds through the absorption of radiation from early type stars by molecular hydrogen H_2 may be analysed to yield the particle densities and ultraviolet fluxes in the absorbing regions and the absorption by HD may be analysed to determine the proton densities and the ionizing fluxes. The interpretation carries implications concerning the formation of other interstellar molecules, which may be the source of additional absorption lines.

1. Introduction

The observations of ultraviolet interstellar absorption lines with the ultraviolet scanning spectrometer carried on the Copernicus satellite (Rogerson *et al.* 1973) have advanced substantially our understanding of the physical conditions in interstellar space (cf. Morton 1974). Of particular interest is the detection of absorption lines originating in different rotational levels of molecular hydrogen, H_2, and of absorption lines originating in the lowest rotational level of HD. Column densities in the different rotational levels have been derived in the directions towards 28 stars (Spitzer *et al.* 1973; Spitzer & Cochran 1973; Spitzer, Cochran & Hirshfeld 1974) from which relative rotational populations have been derived. The populations may be characterized by two temperatures, the lower temperature being appropriate for the low lying rotational levels and the higher temperature for the upper rotational levels (Spitzer & Cochran 1973; Spitzer *et al.* 1974).

2. Interpretation

The relative overpopulation of the upper rotational levels can be produced by collisional excitation processes, perhaps during the passage of a shock wave (Aannestad & Field 1973), by the molecular formation process (Spitzer & Zweibel 1974) and by ultraviolet fluorescence (Black & Dalgarno 1973*a*). The resulting equilibrium populations depend upon the efficiencies of radiative processes and collisional processes which cause a redistribution of the levels.

Radiative decay occurs by electric quadrupole emission, the rotational quantum number J can change only by two and the lifetimes vary inversely as the fifth power of the frequency. Values of the lifetimes are reproduced in table 1 (Dalgarno & Wright 1972).

The collision frequencies for transitions in which J changes are less securely determined. To within an order of magnitude, a collision frequency of 5×10^{-12} ns^{-1} in a cloud of density n cm^{-3} is probably appropriate for all values of J so that for a density of 100 cm^{-3}, say, the collision times and the radiative times are comparable for $J = 3$. Because the radiative lifetimes vary rapidly with J and the collision rates vary slowly, uncertainties in the collison rates and particle densities do not affect the general conclusions that the low lying J level populations are dominated by collisions and the high lying J level populations are unaffected. Thus the temperature characterizing the lower J populations tends to the kinetic temperature of the

gas; the higher J populations provide a direct measure of their rates of population and the characterization of the upper J distribution by a temperature does not necessarily imply any kind of thermal equilibrium.

Odd and even J levels belong respectively to ortho and para-hydrogen and no sequence of purely radiative processes can convert odd J levels to even J levels with other than negligible efficiency. Collision-induced *ortho-para* conversion by neutral hydrogen atoms has a large activation energy and is very slow at interstellar cloud temperatures. However, Dalgarno, Black & Weisheit (1973) have argued that the proton interchange reaction,

$$H^+ + o - H_2 \ (J = 1) \ \rightarrow H^+ + p - H_2 \ (J = 0), \tag{1}$$
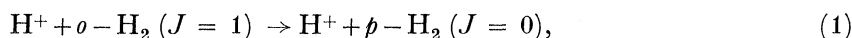
is rapid even at low temperatures, an argument subsequently confirmed by the measurements of Fehsenfeld *et al.* (1973), who obtained a rate coefficient of 1×10^{-9} cm^3 s^{-1} for the analogous proton–deuteron interchange reaction

$$D^+ + H_2 \rightarrow H^+ + HD \tag{2}$$

between 80 and 278 K.

Reaction (1) then tends to bring the $J = 0$ and $J = 1$ level populations into thermal equilibrium at the kinetic temperature of the gas. Observations (Spitzer *et al.* 1974) show that in general the $J = 0$, 1 and 2 levels are indeed characterized by a common temperature. Our discussion therefore implies that there is a source of ionization of hydrogen in the clouds. We shall discuss later those cases for which the temperatures derived from the ratios of the $J = 1$ and $J = 2$ populations to the $J = 0$ population differ.

The populations of the high J levels of the ground vibrational state, $v'' = 0$, measure the efficiencies with which the levels are populated. Except for collisional excitation processes, entry into the J levels occurs by cascading from the higher vibrational levels, $v'' \geqslant 1$, of the ground electronic state, which decay radiatively by quadrupole emission producing an infrared emission spectrum that may be detectable. Some of the radiative lifetimes are reproduced in table 2 (Black & Dalgarno 1975). They are of the order of 2×10^5 to 1×10^6 s and the $v'' \geqslant 1$ levels are unaffected by collisions unless densities of at least 10^4 cm^{-3} occur.

The selection rules are $\Delta J = 0$, ± 2 for each transition in the cascade from $v'' \geqslant 1$ to $v'' = 0$. Thus it is possible in principle to build up a large population of the high J levels of the $v'' = 0$ vibrational level. However, largely because the transition probability varies as the fifth power of the frequency, $\Delta J = -2$ transitions are strongly favoured.

Table 3 reproduces a sample of the results of the solution of the quantum mechanical cascading problem (Black & Dalgarno 1975). The entries in table 3 specify what fraction, $F_v(J, 4)$, of the population of a given rotation-vibrational level (v, J) enters the $v = 0$ level in rotational level $J = 4$.

If the initial population of (v, J) is restricted to $J \leqslant 6$, the fraction $F_4(v, J)$ varies between 0.25 and 0.56. Similar calculations of $F_6(v, J)$ show a variation between 0.03 and 0.33. Since the $J = 4$ lifetime is ten times longer than the $J = 6$ lifetime (cf. table 1), we predict a relative population of $J = 4$ to $J = 6$ between 80 and 20 in harmony with most of the Copernicus data. More detailed comparisons are in progress, but it appears that many of the Copernicus observations are consistent with a model in which the observed rotational levels are produced by radiative cascading from excited vibrational–rotational levels of the ground electronic state, the lower J levels then undergoing modification by collisions.

It remains to determine the mechanisms by which the excited vibrational–rotational levels are populated. One mechanism is established by the observations. The observed absorptions in the Lyman system are followed by spontaneous dipole emission into any one of the vibrational levels of the ground electronic state. Absorptions in the Werner system also are followed by spontaneous dipole emission into the ground state vibrational levels. The rotational selection rule for the fluorescence processes is $\Delta J = 0, \pm 2$.

TABLE 1. RADIATIVE LIFETIMES, τ, OF ROTATIONAL LEVELS J OF
THE GROUND VIBRATIONAL STATE OF H_2

J	τ/s	J	τ/s
2	3.39×10^{12}	6	3.78×10^7
3	2.10×10^9	7	1.70×10^7
4	3.63×10^8	8	8.75×10^6
5	1.02×10^8	9	5.00×10^6

TABLE 2. RADIATIVE LIFETIMES, τ, OF THE EXCITED VIBRATIONAL LEVELS
$v'' \geqslant 1$ OF H_2

	$\tau/10^6$ s		
v''/J	0	5	10
1	1.17	1.26	1.38
2	0.612	0.644	0.815
3	0.422	0.433	0.557
4	0.328	0.329	0.418
5	0.270	0.268	0.330
6	0.234	0.231	0.289
7	0.211	0.207	0.262
8	0.198	0.195	0.251
9	0.184	0.199	0.255
10	0.199	0.200	0.282

TABLE 3. THE FRACTION, $F_v(J, 4)$, OF THE POPULATION OF THE (v, J) LEVEL
THAT CASCADES INTO THE $(0, 4)$ LEVEL

	J					
v	0	2	4	6	8	10
1	0.00000	0.34298	0.32614	0.56033	0.08219	0.03306
2	0.27010	0.24662	0.35992	0.47206	0.22979	0.07159
3	0.28118	0.26363	0.34481	0.39938	0.36142	0.11299
4	0.25776	0.28724	0.31968	0.38100	0.38715	0.17090
5	0.26930	0.29161	0.31111	0.36605	0.38528	0.24120

A second mechanism is the formation process itself. It is generally assumed that hydrogen molecules are formed on grains (Hollenbach, Werner & Salpeter 1971) though under some physical conditions formation by associative detachment (McDowell 1956) may be more rapid. In both cases, the H_2 molecules are formed in highly excited rotation–vibration levels of the ground electronic state. The rotation–vibration distribution of the molecule when it leaves the grain surface is uncertain but some part of the original vibrational development may persist.

In equilibrium, the efficiency of the formation mechanism of populating excited vibrational levels is directly proportional to the efficiency with which the molecule is destroyed. The molecules

are destroyed by absorption in the Lyman system followed by spontaneous emission into the vibrational continuum (Stecher & Williams 1967) of the ground electronic state and their lifetime is determined by the ultraviolet radiation field to which the molecules are subjected. Thus the efficiencies of both the fluorescence mechanism and the formation mechanism for populating the excited rotation–vibration levels are determined by the intensity of the ultra-violet radiation field, which can therefore be derived from the measurements of the populations of the high J levels. The derived radiation field can be used to calculate the radiative lifetime of the molecule which gives in conjunction with a molecular hydrogen formation rate a value for the density of the cloud.

The transition from low J to high J populations takes place approximately when the radiative and collision times are equal and the derived density can be checked for consistency with the measured rotational populations (or they may be used alternatively to derive a value for the rate coefficient of the grain formation mechanism).

A further test of the proposed fluorescence mechanism would be provided by measurements of absorption from excited vibrational levels. No absorption has been detected and for ζ Oph an upper limit of 1.0×10^{13} cm^{-2} has been obtained for the column densities of hydrogen in the $J = 2, v'' = 1$ rotation–vibrational level (Spitzer *et al.* 1974). The fluorescence model of Black & Dalgarno (1973*b*) predicts a value close to the upper limit.

Column densities of HD have been measured in several directions (Spitzer *et al.* 1974) and of D towards β Cen (Rogerson & York 1973). The ratio of HD to H_2 varies from cloud to cloud but is typically of the order of 10^{-6} and the ratio of D/H towards β Cen, where no H_2 is found, is 1.4×10^{-5}.

Because H_2 is destroyed by a process that is initiated by line absorption, it becomes self-shielding for large column densities (Hollenbach *et al.* 1971). The molecule HD is destroyed by a similar process but its column density is usually so small that self-shielding is not significant. The mean lifetime of HD is accordingly much less than that of H_2. If HD and H_2 are formed by the same process, the value of 10^{-6} for HD/H_2 implies a value of the order of 10^{-3} for D/H (Spitzer *et al.* 1973; Black & Dalgarno 1973*a*; Watson 1973). If the value of D/H measured towards β Cen is typical of the interstellar medium, there must be another source of HD. The probable source is

$$H^+ + D \rightarrow H + D^+ \tag{3}$$

followed by (2) (Dalgarno *et al.* 1973; Black & Dalgarno 1973*a*; Watson 1973). The magnitude of the source depends on the density of the H$^+$ ions which can therefore be derived. For ζ Oph, $n(H^+) = 0.04$ cm^{-3} in the outer regions of the cloud (Black & Dalgarno 1975). Similar studies have been carried out for other clouds (Jura 1974*a*; O'Donnell & Watson 1974) and H$^+$ densities between 10^{-3} cm^{-3} and 10^{-2} cm^{-3} have been derived. The values depend on the ultraviolet radiation intensity adopted in the analysis.

There are clouds in which the temperature characterizing the $J = 0$ and $J = 1$ populations differs from that characterizing the $J = 0$ and $J = 2$ populations so that equilibrium has not been attained. If (1) is the reaction that brings $J = 0$ and 1 into thermal equilibrium, H$^+$ densities between 10^{-3} and 10^{-2} cm^{-3} lead to equilibration times between 10^4 and 10^5 years. However the H$^+$ density decreases with increasing depth into the cloud and a more detailed study is needed to interpret the temperature differences.

The presence of protons in the clouds implies the existence of a penetrating ionizing source,

the magnitude of which can be determined from the HD/H_2 ratio provided the H^+ chemistry can be quantitatively described (Black & Dalgarno 1973a). A possible chemical scheme is summarized in figure 1. Based upon it, Black & Dalgarno (1975) derived an ionizing flux of 2×10^{-17} s^{-1} appropriate to the measured high energy cosmic rays (cf. Spitzer 1968), but considerably smaller than the value of 10^{-15} s^{-1} demanded apparently by the steady state two-component model of the interstellar gas (cf. Dalgarno & McCray 1972). Using a similar chemical scheme, O'Donnell & Watson (1974) have argued that ζ is generally less than 10^{-16} s^{-1} and Jura (1974a) has derived a value of 5×10^{-17} s^{-1} for several clouds.
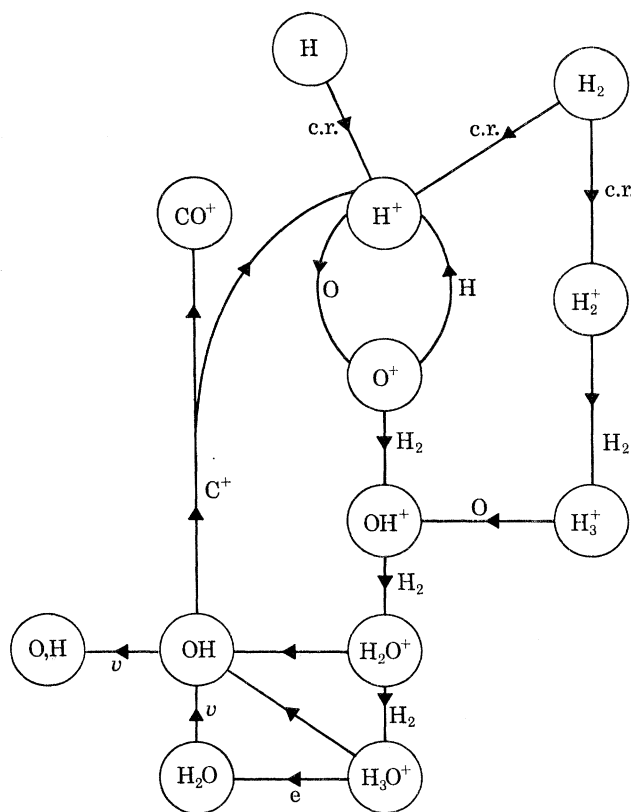

FIGURE 1. Chemical scheme initiated by $H^+ + O \rightarrow H + O^+$.

The presence of H_2 in clouds leads to the formation of other molecules. The chemical scheme of figure 1 shows that the production of a proton in a cloud containing H_2 leads to the production of an OH molecule. Because OH may be destroyed by C^+ in the reaction

$$C^+ + OH \rightarrow CO + H^+ \qquad (4)$$

the H^+ can act like a catalyst and the OH formation rate can exceed the H^+ production rate. There are several important uncertainties in the rate coefficients but adopting the best available estimates, Black & Dalgarno (1973a) predict for ζ Oph a column density of 1.0×10^{13} cm^{-2} of OH molecules, consistent with the upper limit of 8×10^{13} cm^{-2} derived by Herbig (1968). The reaction (4) is an important source of CO, a molecule that has been detected by its interstellar absorption lines (Jenkins et al. 1973).

An interesting example of the influence of H_2 has been noted by Jura (1974b), who pointed out that

$$Cl^+ + H_2 \rightarrow HCl^+ + H \qquad (5)$$

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is exothermic. Subsequent measurements (Fehsenfeld & Ferguson 1974) show that it and

$$HCl^+ + H_2 \rightarrow H_2Cl^+ + H \tag{6}$$

are rapid. The reaction sequence leads to the formation of the molecule HCl. For ζ Oph, the predicted column density is of the order of 10^{12} cm^{-2} (Dalgarno *et al.* 1974).

We turn finally to the problem of CH and CH$^+$ whose presence in the interstellar medium was established decades ago by the observation of the visual interstellar absorption lines. The conventional theory (Bates & Spitzer 1951; Solomon & Klemperer 1972) for the formation of CH$^+$ and CH is difficult to sustain quantitatively. An alternative theory (Black & Dalgarno 1973 *b*) invokes the reaction

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu \tag{7}$$

to initiate the sequence summarized in figure 2 (Dalgarno, Oppenheimer & Black 1973). The theory has been discussed by Watson (1974), who argues from the laboratory study of Fehsenfeld, Dunkin & Ferguson (1974) that the reaction is probably too slow. The experiments refer to collisions in the ground state potential of CH$_2^+$. The proposed reaction refers to collisions in the excited state potential. The chemical scheme of figure 2 implies a substantial concentration of CH$_3^+$ and a search for absorption lines of CH$_3^+$ would provide a critical test of the chemistry.
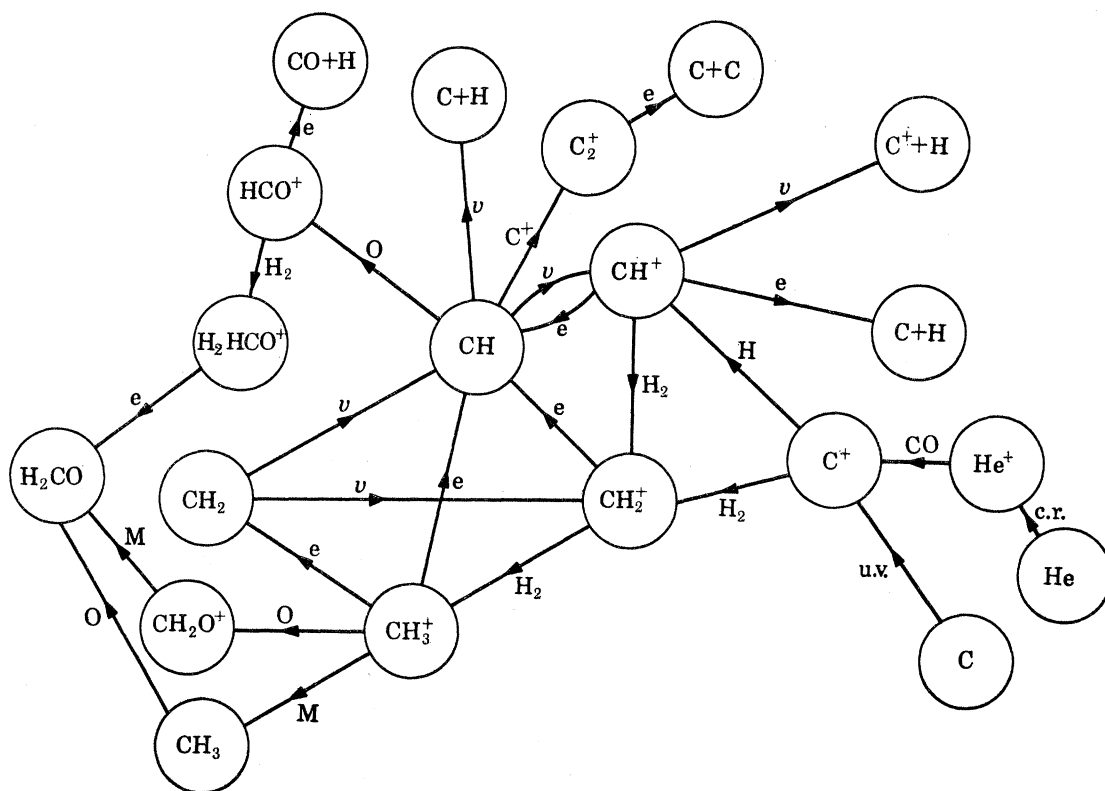

FIGURE 2. Chemical scheme initiated by $C^+ + H_2 \rightarrow CH_2^+ + h\nu$.

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