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CARBON CHEMISTRY OF THE INTERSTELLAR MEDIUM

Anthony C. Danks

Dept. of Physics and Astronomy
Florida International University, USA

ABSTRACT. Molecular hydrogen combines with Carbon to produce a host of molecules in the interstellar medium. In diffuse clouds ($A_V < 2$ mag) a number of diatomics can be studied in the visible ie., CN, CH, CH^+ and C_2.

Modern spectrographs and detectors can yield high quality observations of molecular absorption lines arising in interstellar clouds, seen against background early type stars, resulting in accurate column densities.

Comparison of measured column densities for these molecules with those of atomic and molecular hydrogen, for a large number of lines of sight can yield a wealth of information on formation and destruction of individual species. Such observations provide a testing ground for gas phase chemistry models.

First results show that within the range of column densities observed Log N(CH) = a Log N(H_2) + b where a=0.85 and Log N(CN) α m Log N(H_2) with m=3. This latter result implies CN is a third generation molecule produced by a neutral-neutral reaction C_2 + N. Similarly, CH^+ has been shown to be associated with warm H_2 and is most likely, produced in shock fronts, which provide the necessary energy to make the endothermic reaction,

$$C^+ + H_2 \rightarrow CH^+ + H$$

go. A gas phase network is proposed leading to the production of these molecules.

Key words: CHEMICAL REACTIONS — INTERSTELLAR-MOLECULES

INTRODUCTION

After Hydrogen, Carbon is the most important constituent of the interstellar medium due both to its abundance and its chemical nature. Ground based spectroscopic observations of early spectral type (O,B) stars, embedded in, or behind diffuse (transparent) interstellar clouds, reveal absorption lines of diatomic molecules such as CN, CH, CH^+ and C_2. The only remaining molecule seen from the ground is OH and in addition a number of atomic species. Usually several rotational lines are observed from each molecule and in some cases, lines from several electronic upper states. Measurement of these lines in absorption, at least for bright stars is relatively simple, and the measured equivalent width W_λ can be converted to column densities with a knowledge of oscillator strengths f via the formula,

$$W_\lambda = \frac{\pi e^2}{mc^2}\lambda_{j'j''}N_{j''}f_{j'j''} .$$

The f-values are either determined by calculation or experimentally and are often a source of error. However, comparison of measured column densitites can be made with those of atomic and molecular hydrogen for a large number of lines of sight to yield information on the formation and destruction of a particular species, and provide tests for theoretical models. In the case of C_2 we can use its homonuclear properties to investigate excitation conditions in diffuse clouds (Danks and Lambert 1983; Van Dishoeck and Black 1982). In the case of CN, not only does it play an important role in the gas phase chemistry of interstellar clouds, but it can also be used to monitor the cosmic microwave 3°K emission (Meyer and Jura 1985, 1986; Crane et al.1986; Thaddeus 1972). At slightly higher resolution, these carbon based molecules can be used to determine the isotopic ratio $^{12}C/^{13}C$, usually from the CH^+ lines eg. (Vanden Bout and Snell 1980; Meyer and Jura 1985). Furthermore, as we come to understand the excitation and production mechanisms for these molecules we can use them as diagnostics; ie. the production of CH^+ requires a high temperature most likely, associated with a shock. The presence and strength of CH^+ can then be used to infer the presence of shocks.

For more distant, fainter stars, integration times are longer, with the result that the line and stellar continuum are poorly defined. But in addition the number of clouds along the line of sight increases and it becomes more difficult to unravel the spectra. CaII and NaI are often used to give an indication of the number of clouds along the line of sight (Hobbs 1975).

Lines from different molecules can be considered to arise from the same cloud, if they exhibit the same radial velocity. But this implies they are formed in the same region of the cloud, unaffected by shocks, and furthermore, higher resolution measurements are needed in order to get accurate velocities.

Present use of this method of studying the ISM is limited by the number of lines of sight for which accurate H_2 measurements exist. These are primarily the stars observed by Copernicus (Bohlin et al. 1978). Hopefully, future satellites will enlarge the list, e.g. Lyman. Alternatively estimates of the H_2 column density can be inferred from other measurements e.g. E(B-V), this is in itself interesting because as the method comes under closer inspection it is realized that reddening does not scale simply with $N(H_2)$ in all directions in the Galaxy. Never the less, using the above methods we undertook to study the formation and destruction of the molecules C_2 (Danks and Lambert 1983), CH (Danks, Federman & Lambert 1984), CN (Federman, Danks, & Lambert 1986) and CH^+ (Lambert & Danks 1986).

<u>TABLE 1</u>

The molecules observed are listed with wavelengths and transitions.

Molecule	A	Transition
C_2	8740-8809	$A'\pi_u - X'\Sigma_g^+$ (2-0) Phillips
CH	R (1) 4300.3 R (1) 3789	A - X $B^2\Sigma - X^2\pi$ (0-0)
CN	R(1) 3874.61 R(1) 3874.00 P(1) 3875.76	$B^2\Sigma^+ - X^2\Sigma^+$ (0-0)
CH^+	R(0) 4232.5	$A'\pi - X'\Sigma^+$ (0-0)

OBSERVATIONS

Using the 1.4 CAT (Coude Auxilary Telescope) combined with the CES (Coude Echelle Spectrograph) at ESO La Silla, we have studied a large number of lines of sight to investigate the formation and destruction of the molecules C_2 , CH, CN and CH^+.

The CES is a 'state of the art' Coude spectrograph and is described in detail by Enard (1979). But briefly, the instrument is fed by an f/120 beam from an Alt-Alt mounted telescope and converted to f/32.2 by a focal reducer. The instrument employs a prism for predispersion followed by a Littrow mounted echelle grating (204x408mm^2, 79 ℓmm^{-1} Blaze 63° 26'), the light is focused by an f/4.7 camera onto a cooled 1872 element reticon detector, (now replaced by a CCD). All the observations were carried out with a resolving power of approximately 80,000 giving an entrance slit width of 1.7 arcsec on the sky which matched quite well the seeing. In this configuration the spectrograph gives aproximately 30A of spectrum around the chosen wavelength.

Samples of spectra of CH and CN are shown in figure (1).

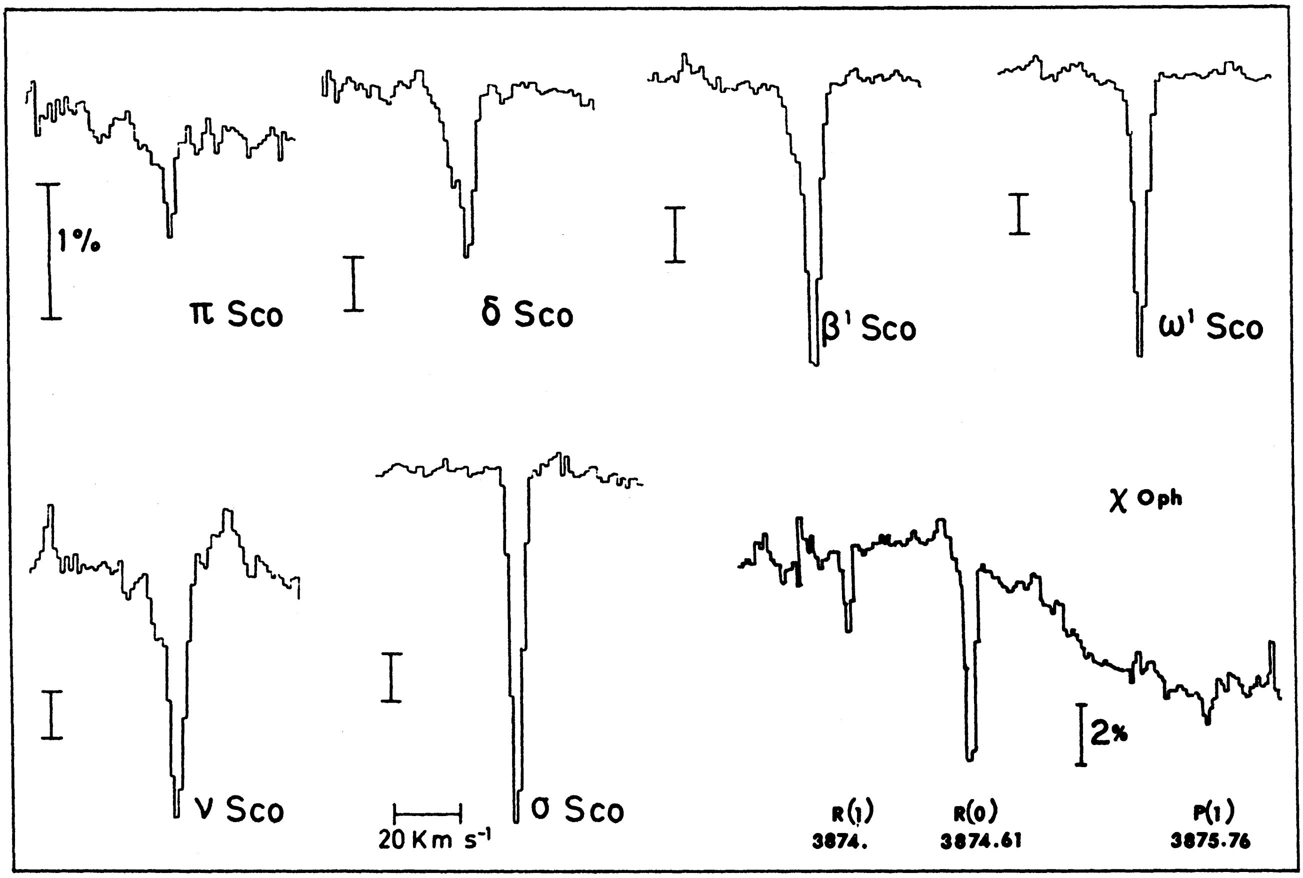


Fig. 1. On top, CH^+ is shown in six stars in Scorpius. Vertical bars correspond to 1% of the continuum. On the bottom CN lines are shown in the spectrum of the Be star χ Oph. The R(0) and R(1) lines are superimposed on a broad Balmer emission line.

CH.

5 The presence of the CH radical in diffuse interstellar clouds was first identified by McKellar (1940) following a suggestion by Swings and Rosenfeld(1937).

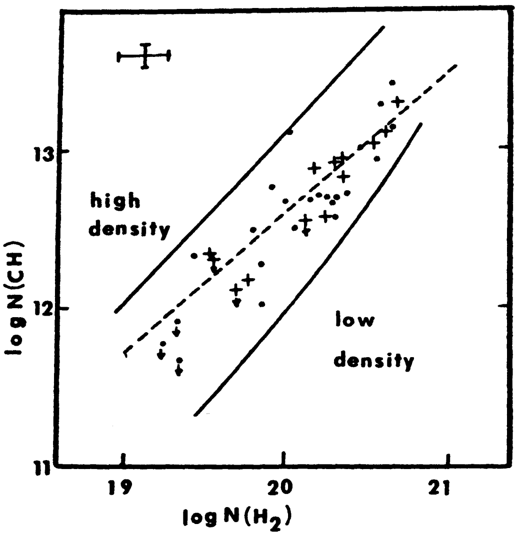
These weak lines are difficult to study photographically, and only recently have detailed studies been carried out using modern spectrographs and detectors (Federman 1982; Danks et al 1984).

The CH A-X R (1) line at 4300.3Å was observed in 29 lines of sight for stars with distances from 140 to 2800pc in the Galactic plane. The conversion of the CH W_λ to the column density N(CH) was achieved with the relation:

$$N(CH) = 1.2x10^{12}W_\lambda cm^{-2} ,$$

with $W_\lambda$in mA. The numerical factor is based on an f-value derived from accurate measurements of the radiative lifetime (Brzozowski et al.1976). In fig(2) we show the tight correlation of N(CH) and H_2 column densities In diffuse clouds the CH chemistry is predicted to be controlled by gas phase reactions with H_2 playing a major role through radiative association of C^+ and H_2, ($C^+ + H_2 \rightarrow CH_2^+ + h\nu$), followed by ion-molecule reactions, ($CH^+ + H_2 \rightarrow CH_3^+ + H$), (Black and Dalgarno 1973; Black et al. 1975). No further reactions with molecular hydrogen are possible at the low temperatures prevailing in the cloud. Dissociative recombination of CH_2^+ and CH_3^+ with electrons produces the neutral CH. The CH radical is destroyed by photo-processes and ion-molecule reactions with C^+ (Federman 1982). Part of this gas-phase chemistry is shown in figure (3).

The network predicts that $n(CH) \alpha n(H_2)$ and this certainly appears to be the case in figure (2). Our data yields a slope of a = 0.85 ±0.15, where Log N(CH) = aLog $N(H_2)$ + b. Two model fits are shown, a low density model cloud with $n = n_H + 2n_{H2} = 150$ cm^{-3} at T = 30°K and a high density model cloud with n = 2500 cm^{-3} at T = 30°K. More details of these calculations are given in Danks, Lambert, and Federman (1984).



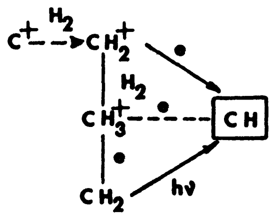


Fig. 2. Log N(CH) vs Log $N(H_2)$. The filled circles are the present data, the crosses are from Federman. The dashed curve is a least squares fit to the data and the two solid curves are the results of the theoretical models described in the text.

Fig. 3. The gas-phase reaction network for the production of CH.

CN.

Our observational exploration of the correlation between CN and H_2 was prompted by the paucity of published data and also by the realization that Nitrogen is predominantly neutral in contrast to Carbon and Oxygen. This difference in the degree of ionization, which reflects the ordering of the ionization potentials of atoms i.e. $I(N) > I(H)$, but $I(C)$ and $I(O) < I(H)$ may be expected to be reflected in the chemistry of CN and the CN-H_2 correlations.

We studied 15 lines of sight for the CN $B^{2+}\Sigma\text{-}X^{2}\Sigma^{+}$ absorption lines. The result of plotting the equivalent width of CN vs H_2 and HI are shown in fig(4).

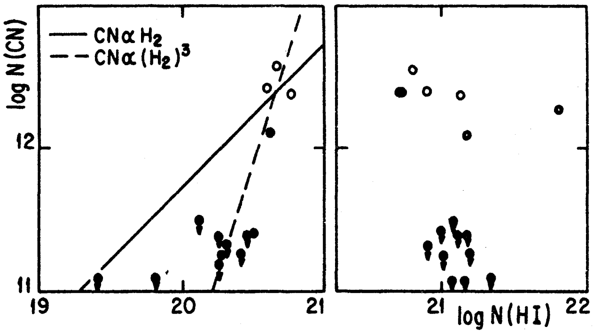


Fig. 4. A comparison of the CN column density with the (left) H_2 and (right) HI column densities given by Bohlin, Savage and Drake (1978); column densities are expressed in the units cm^{-3}. Note that N(CN) α $N(H_2)^3$ is a reasonable fit to the data points (filled circles denote the new observations, open circles those previously published).

Its obvious from the data that no correlation exists with HI where as the relation Log N(CN)αmLogN(H_2) where m=3 is a reasonable fit to the points. This steep dependence of N(CN) on N(H_2) contrasts with N(CH) which varies linearly. This steep increase of the CN density with H_2 suggests CN is a third generation molecule.

This can be understood with simple linear reaction pathways. If we consider the formation of the molecule AH by the reaction $A + H_2 \rightarrow AH + H$, AH destroyed by photodissociation; then the equilibrium density n(AH) is given by:

$$n(AH) = n(A)n(H_2)K_{AH}/G_{AH} = x(A)n(H_2)nK_{AH}/G_{AH}cm^{-3},$$

where K_{AH} is the bimolecular rate constant and G_{AH} is the photodissociation rate. Of course, $G_{AH} = G_{AH}\exp(-\tau_{AH})$with τ_{AH}being the mean optical depth in the UV.

The concentration of species A is $x(A) = n(A)/n$.

If the reaction $AH + A \rightarrow A_2 + H$ is a minor competitor to photodissociation of AH, and is followed by $A_2 + B \rightarrow AB + A$ with photodissociation of both A_2 and AB as the leading destructive processes for these molecules then the equilibrium density of AB is $n(AB) = x(A)^2x(B)n(H_2)n^3(K_{AH}/G_{AH})(K_{A2}/G_{A2})(K_{AB}/G_{AB})cm^{-3}$.

Clearly, the molecule AB is third generation with a steeper dependence on the gas density and optical depth than AH a first generation molecule.

In particular, n(AB) is proportional to $n^3n(H_2)\exp(3\tau)$ for $\tau_{AH}\cong\tau_{AB}\cong\tau_{A2}\cong\tau$.

Ion-molecule reaction networks for the production of CN below 70°K are very inefficient and rate constants for neutral-neutral reactions are a factor of 10 greater in these conditions. The two neutral-neutral pathways for CN production are CH+N, and C_2 + N and the observed steep dependence of CN on H_2 suggests the latter is the important one. The proposed production network is shown in fig(5). The CN radical is thus the first observable molecule with a heavy atom that requires neutral-neutral reactions for its formation in diffuse clouds. Other molecules i.e. CH, CH^+, CO and probably OH are understood in terms of ion-molecule reactions.

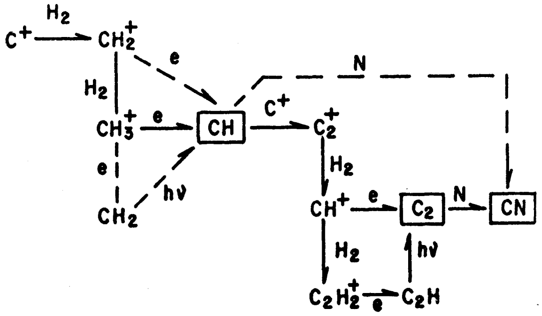


Fig. 5. The gas-phase chemistry leading to the production of CN. Channels of lesser importance are shown by dashed lines. Destruction of CH, C_2 and CN occurs primarily by photodissociation.

If C_2+N dominates, as is necessary to reproduce the steep dependence of CN on H_2, then CN is a third generation neutral molecule:

$$CH \rightarrow C_2 \rightarrow CN .$$

The CN radical is the first such molecule measured in difffuse clouds (A < 1 mag). Our model fits are shown in fig(6) for two cases, high and low density clouds. The low density case has an average density of $n=150cm^{-3}$, T=55°K and the high density case has parameters of $n=2500cm^{-3}$and T=30°K. Details of the model calculations are given in Federman, Danks & Lambert (1984).
At higher gas densities and in the inner regions of the most opaque clouds, gas phase reactions may compete with photodissociation. In fact, we have tested this relationship over a very small range of H_2 column densities. As pointed out earlier H_2 measurements are not available for fainter stars. However, correlations between CH, C_2 and CN can be compared for higher cloud densities (A >>1). Here several problems arise, first as the cloud's density increases, we may move away from gas phase chemistry, as temperatures decrease and dust density increases. But also correlations become less evident as observations of more distant stars introduce errors in the equivalent widths of the lines.

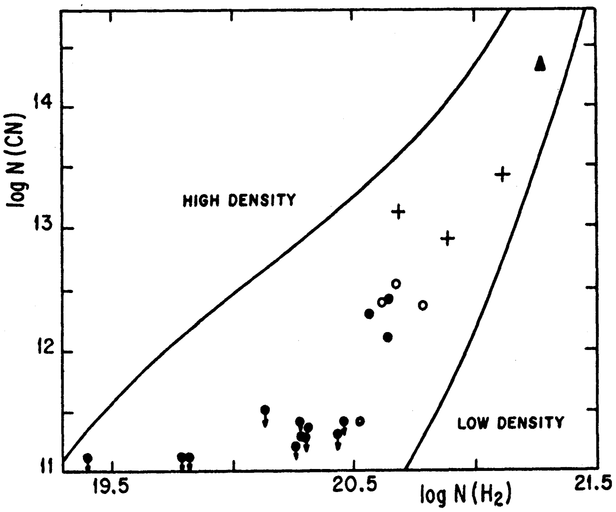


Fig. 6. Predictions and observations in the Log N(CN) - Log N(H_2) plane. The two solid curves are the results of the theoretical models described in the text. Filled circles are from observations by Federdam et al. 1984, open circles published observations, and Δ is HD 29647.

CH^+.

This ion is the most common molecule detected in the diffuse clouds, yet its chemistry is far from understood, (Black 1978). Basically, the molecule is destroyed very quickly, i.e., in cool atomic H, $CH^+ + e \rightarrow C+H$ or by H atoms $CH^+ + H \rightarrow C^+ + H$. Similarly in cool H_2, $CH^+ + H_2 \rightarrow CH_2^+ + H$, all these reactions keep the predicted CH^+ density to 1% of the observed density, (Watson 1974; Black and Dalgarno 1973). It is necessary then to find a production mechanism faster than the destruction rate, and this is the reaction $C^+ + H_2 \rightarrow CH^+ + H$, but this reaction is endothermic and requires therefore warm gas $T = 10^3$ K, leading Elitzur and Watson (1978,1978)to propose production in the passage of a shock. We investigated 65 lines of sight, in the CH^+ 4232 A line and correlation of Log $N(CH^+)$ vs Log N(HI) and Log $N(H_2)$ in fig(7) illustrate the problem.

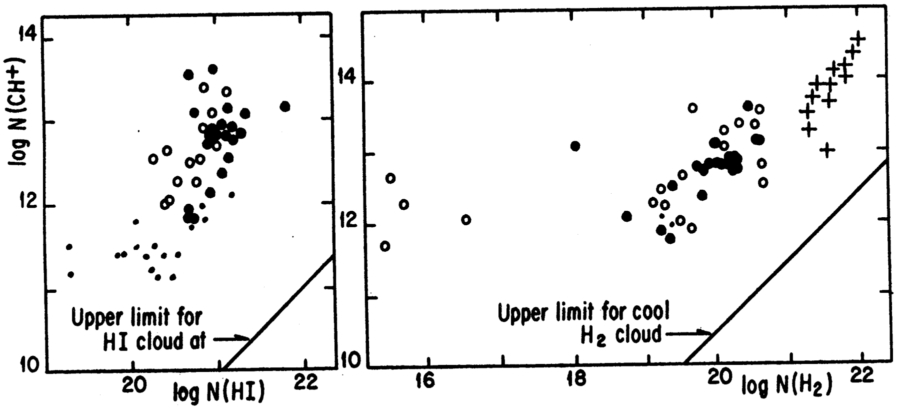


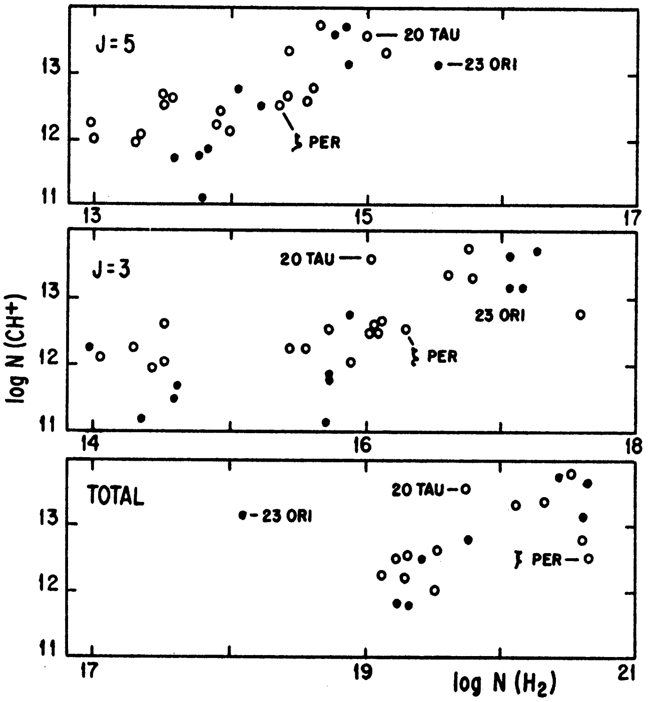
Fig. 7. On the left are shown the column densities of CH^+ and HI. Large symbols correspond to detections of CH^+, smaller to upper limits. The solid dots are our data, the open ones are taken from the literature. The right hand side shows the column densities of CH^+ and H_2. The crosses refer to measurements of highly reddened stars, for which $N(H_2)$ was deduced using E_{B-V}.

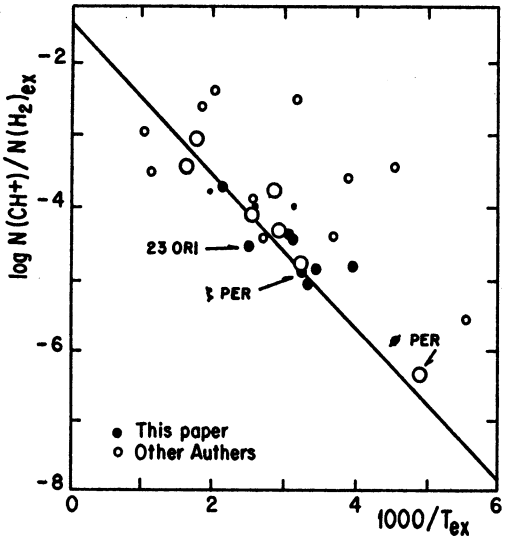
However by plotting Log $N(CH^+)$ vs Log $N(H_2)$ for specific J states its seen that a correlation begins to appear for the high J states, i.e., the region producing CH^+ is associated with the warm H_2, figure (8). To illustrate the effect better the states J = 3 to 5 were converted in to a Boltzmann temperature or excitation temperature T_{ex} and these results are shown in figure (7). The slope of the line corresponding to $T_{formation}$ = 2500 ±200°K, or an activation energy of 0.22eV. This is less than the energy necessary to make the endothermic reaction "go". But of course, our crude T_{ex} is not $T_{kinetic}$ of the gas. Due to cascading $T_{ex} < T_K$ and the ratio $T_K = \alpha T_{ex}$ gives $\alpha = 1.8$. This correlation Log $N(CH^+)/N(H_2)_{ex} = 2500/T_{ex}$ provides strong evidence that CH^+ is formed in warm gas where the reaction $C^+ + H_2 \rightarrow H$ is effective.

Shocks are the most probable sites providing zones of warm H_2 in which this reaction can work. In fact to produce the observed $N(CH^+)/N(H_2)$ ratio we need only 2% of the H_2 along the line of sight with T = 1000°K or 0.1% at T = 3000°K. This small % of warm H_2 would be in keeping with shock heating. Details of those models are given in Lambert and Danks (1986).

C_2.

Interstellar C_2 molecules were discovered by Souza and Lutz (1977); from observations of the 1-0 band of the Phillips system. Since then observations have concentrated on the 2-0 system at 8760 A, (Chaffee and Lutz 1978; Hobbs and Cambell 1982). In addition, the 0-0 band of the Mulliken system at 2312 A has been reported (Snow 1978).





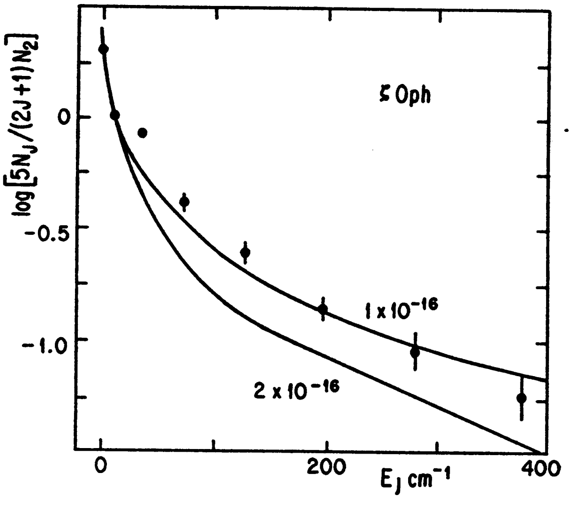


Fig. 8. Shows the correlation of CH^+ and H_2 for rotational levels J = 3 and 5. Note the correlation improves towards high J, ie., higher Texcitation.

Fig. 9. Ratio of the column densities of CH^+ and 'excited' H_2 vs the H_2 excitation temperature.

Fig. 10. Relative populations of the rotational levels for the ξ Oph cloud derived from equivalent width measurements are show with predictions by Van Dishoeck and Black 1982. This is a 2-cloud model, with two values for the excitation cross-section σ_0.

Like H_2 this homonuclear molecule allows us to study the competition between collisional and radiative excitation of the rotational states. Radiative excitation which occurs via electronic excited states, is controlled by the intensity of the interstellar radiation field and in general, results in a rotational temperature in excess of the kinetic temperature. A thorough analysis of the excitation equilibrium has been carried out by Van Dishoeck and Black (1982). The model shows that the rotational temperature increases up the rotational ladder as the hot diffuse radiation wins its competition with the cool gas. Our results for χ Oph, ρ Oph A and ξ Oph indeed show that the rotational population is not described by a single temperature, figure (9). The populations are consistent with a competition between collisional and radiative excitation.

SUMMARY

Almost all our knowledge of diffuse interstellar clouds comes from visible spectroscopy and from satellite observations in UV. Unlike the dark clouds where many new molecules have been found over the past 10 years, most of the molecules studied here are simple diatomics known since 25 years or more. Advances in this field have come in part from new detectors and instruments capable of doing near spectrophotometry, but also from the merging of chemists and astronomers producing gas-phase models of the intersteller medium.

For the future, in ground based spectroscopy we can search for new molecules, such as SH^+, a possible candidate in MHD shocks, which could give new information on weak interstellar magnetic fields. Many of the molecules discussed, have transitions in other wavelength regions, i.e. there is the C_2 Mulliken $D'\Sigma^+ - X'\Sigma_g^+$ system in the UV. Initial calculations show this line should be easily detected using the HRS on space telescope, see Danks & Lambert (1983). Furthermore the CN red system $\pi - \Sigma$ transition has been detected in several stars in the near infrared and hasn't been fully investigated to date.

As we move to denser clouds, increasing extinction, we move from the domain of diffuse to dark clouds. The cloud becomes optically thick to exciting radiation from embedded and nearby stars, the inner cloud temperature dropping and large complex molecules forming. These are identified at radio frequences. Carbon probably still plays an important role in the formation of the complex molecules, ie. $CO + H_2 \rightarrow H_2CO$ etc. However, the density of particle matter, dust, is higher and gas phase chemistry may break down. The domain between diffuse and dark clouds is an interesting region for future study.

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Anthony C. Danks: Dept. of Physics and Astronomy, Florida International University, Tamiami Campus, Miami, FL 33199, USA.

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QUASI-STATISTICAL SOLUTION OF EARLY HOMOGENEOUS NUCLEATION PHASES

S.C.F. Rossi and P. Benevides-Soares

Instituto Astronômico e Geofísico
Universidade de São Paulo, Brasil

ABSTRACT. Time-dependent nucleation processes have been a challenging problem, for which no general solution is available so far. Partial solutions have been obtained by various authors with a handful of simplifying assumptions. Apart from physical hypothesis, which are generally accepted and will not be discussed here, actual solutions are based on assumptions of a numerical and algebraic nature, whose validity and consequences remain to be established.

This paper is concerned with the numerical aspects of the problem, specially in the small cluster region, and within physical constraints which are adequate for astrophysical environments. Most important of these is the temperature time-dependence, which is assumed to be sufficiently slow to allow the definition of a quasi-statical process. We show that for clusters smaller than a limiting size, the time derivative of the ratio between the actual and equilibrium concentrations may be neglected. As a consequence the system of differential equations becomes a set of algebraic non linear equations. The solution of the algebraic approximation is shown to approximate very closely the numerical integration gives good estimates for the time-constants of the concentrations variation.

Key words: NUMERICAL METHODS

P. Benevides-Soares and S.C.F. Rossi: Universidade de São Paulo, Instituto Astronômico e Geofísico, Caixa Postal 30627, 01051 São Paulo SP, Brasil.

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Sistema Solar

Solar System