

THE SURPRISING CONSTANCY OF RELATIVE CHEMICAL ABUNDANCES IN DIFFERENT REGIONS OF INTERSTELLAR SPACE – PARTICULARLY FOR FORMALDEHYDE

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Abstract. Many of the places in which radio astronomers search for molecules are located in exotic regions lying near the galactic center, near H II regions or other continuum sources, or in high density regions. Such regions have wide variations in their physical environment. Here we wish to compare two types of region whose environments are thought to be well-understood. One of these is dust clouds; the other is unshielded (from UV) cold clouds in front of bright radio sources. For the sake of interest, we include without comment results for molecular regions near the Galactic center and near Orion A.

Comparison of dust clouds and unshielded clouds is of interest because the volume density differs by a factor of 10^4 or more and the extinction differs by 8 mag. or more. Neither type of cloud lies near H II regions or other sources of intense radiation. Even though their properties differ widely, we will see that the abundances of OH and H₂CO relative to hydrogen are approximately the same in the two. Although this is understandable for OH, no current theory would predict this situation for H₂CO.

1. Dust Clouds

For dark dust clouds we have long known $\tau > 8$ (e.g. Bok, 1956; Heiles, 1968), and $n_{\text{H}_2} > 10^3 \text{ cm}^{-3}$ (Heiles, 1968). However, we now know that the density of molecular hydrogen must be at least the 10^4 cm^{-3} required to collisionally pump the CO molecule which has been observed in emission in dust clouds by Penzias *et al* (1972). The following paragraph argues that the density of H₂ is actually typically near 10^4 cm^{-3} rather than being much larger.

CO is not observed in every dark dust cloud. However, in those clouds showing an observable line its optical depth is always very large, of order 30 (with a large fraction of the cloud's carbon in CO). Thus dust clouds fall into two classes, one which shows a well-saturated CO line and one which shows no lines at all. There are no other apparent differences between the two classes. If a cloud shows no line, it could be either because it has no CO or because the H₂ density is too small to collisionally excite the CO. If the reason is related to the abundance of CO we would be forced to conclude that there are two classes of cloud in which the relative abundance of CO varies by a factor of over 50, with no intermediate cases. It seems much less unreasonable to assume that the H₂ volume density varies by an order of magnitude or so from one

class to the other, the exact value being dependent on the state of dynamical evolution of the particular cloud. Since some clouds show CO and some don't, we would then conclude that the average H_2 density is about 10^4 cm^{-3} , with substantial fluctuations on either side of this value from one cloud to another.

The situation regarding relative abundances in dust clouds has been discussed by Heiles (1971), who assumed $n_{H_2} = 10^3$ rather than 10^4 cm^{-3} . Furthermore, the situation regarding OH and H_2CO was not well known at that time. Since then Heiles (1972, 1973) has derived H_2CO excitation temperatures and Heiles and Gordon (1973) have carefully observed OH, H I, and H_2CO in dust clouds, properly accounting for the differences in telescope beam size. We find that the relative abundance of OH and H_2CO varies substantially, by a factor of at least five, from one position to another within the same dust cloud (Cloud 2 of Heiles (1968) in the Taurus region). There is no correlation of the 21 cm line of H I (seen in self-absorption) with the OH or H_2CO lines. Therefore in speaking of relative abundances of OH and H_2CO we can only take some average value which seems characteristic of the cloud as a whole, realizing that the numbers vary. Furthermore, we should keep in mind that there is no way of measuring the H_2 density directly; thus, we are somewhat unsure of its constancy, and less its reliability. The adopted values of relative abundance, along with physical conditions, are given in Table I.

TABLE I

	Dust clouds	Unshielded cold clouds	Galactic center ^b	Orion A
Hydrogen volume density	$\cong 10^4(H_2)$	$\cong 20(HI)$	$> 10^3(H_2)$	$10^5(H_2)^c$
Optical depth to center	> 4	$\cong 0.5$?	?
ξ^a	10^6	1	?	?
[OH]/[H or H_2]	$\sim 10^{-7}$	$\sim 10^{-7}$	$< 5 \times 10^{-6}$	3×10^{-10d}
[H_2CO]/[H or H_2]	$\sim 3 \times 10^{-10}$	$\sim 2 \times 10^{-9}$	$< 2 \times 10^{-7}$	2×10^{-9c}
[H_2CO]/[OH]	$\sim 2 \times 10^{-3}$	$\sim 2 \times 10^{-2}$	$\cong 4 \times 10^{-2}$	6

^a See text and Watson and Salpeter (1972).

^b See Rank, D. M., *et al.* (1971)

^c See Thaddeus *et al.* (1971).

^d See Goss (1968).

2. Unshielded cold Clouds in Front of Bright Radio Sources

The observational situation has been recently reviewed by Davies and Matthews (1972). Several distinct clouds at different velocities typically lie in front of these sources. Total optical extinctions are reasonably well-known and the edge-to-edge optical extinction per cloud is usually less than 1 mag. Hydrogen volume densities are not too uncertain because the sources have been observed interferometrically in the 21 cm line (see Clark, 1965), and of course column densities of all species are determined easily given a reasonable estimate of the excitation temperature. The possibility

that H_2 exists in these regions is poor from a theoretical standpoint (Hollenback *et al.*, 1971), although no observations exist; we neglect this possibility.

Davies and Matthews (1972) find a possibly significant dependence of relative molecular abundance on the hydrogen column density. However, since their observed range of molecular abundance amounts to less than the variation found in dust clouds mentioned above, we question the statistical significance of their derived variation. More sensitivity in measuring weak molecular adsorption features in the sources should decide the issue, and one of us (CH) is presently conducting such measurements. We have taken representative values from Davies and Matthews (1972) and list them in Table I along with the values for dust clouds.

3. Discussion: Comparison with Watson and Salpeter (1972)

The differences in density and UV extinction between the two types of region compared herein are explicitly and succinctly summarized in terms of the parameter introduced by Professor Salpeter earlier today:

$$\xi = \frac{n_{\text{H}}}{100} e^{2.5\tau_{\text{vis}}},$$

where n_{H} is the atomic or molecular hydrogen volume density cm^{-3} and τ_{vis} is the visible extinction to the cloud center in magnitudes. The value of this parameter is about 1 for the unshielded cold clouds in front of radio sources, and about 10^6 for dark dust clouds (although as pointed out by Watson and Salpeter (1972), this value may be an overestimate if the clouds are not spherical in shape).

The parameter ξ is a measure of the ratio of the binary collision rate to the intensity of UV starlight. Relative abundances will correlate well with this parameter if indeed these processes are the relevant ones for molecular formation and destruction. The data of Table I indicate that the relative abundances do not correlate with this parameter, but instead are approximately the same for unshielded and shielded clouds; furthermore, the higher relative abundance of H_2CO in unshielded clouds, if real, is quite surprising. The only existing theory which might possibly account for these abundances is that of Watson and Salpeter (1972).

3.1. OH

Watson and Salpeter (1972) conclude that formation on grains followed nearly instantaneously by UV photoejection is the most efficient production mechanism in unshielded ($\xi \cong 1$) and moderately shielded ($\xi < 10^4$) clouds. Destruction occurs mainly by exchange reactions with C^+ if carbon is mainly ionized ($\xi < \xi_0 \cong 100$) and otherwise by exchange reactions with other species. Thus the equilibrium relative abundance of OH is independent of density within the two regimes of ξ . For $\xi < \xi_0$, $[\text{OH}]/[\text{H}] \cong 3 \times 10^{-8}$; for $\xi > \xi_0$, $[\text{OH}]/[\text{H}] \cong 2 \times 10^{-7}$. For $\xi > 10^4$, UV radiation becomes too weak for photoejection so that grains are expected to accrete molecules with a resultant decrease in molecular abundances relative to hydrogen.

Observational data in Table I are not drastically different from these theoretical predictions. The apparent discrepancy for unshielded cold clouds should not be taken seriously because the derived OH abundance varies linearly with the assumed excitation temperature. The data in Table I from Davies and Matthews (1972), was derived assuming an excitation temperature of 10 K. This value is equal to the upper limit derived by Rogers and Barrett (1968) for the OH in front of Cas A, and is therefore certainly too large (but not by more than a factor of three!).

3.2. H₂CO

Watson and Salpeter (1972) find that H₂CO formation occurs efficiently only on grains. The rate of this process is limited by the rate at which a saturated molecule and a radical can find each other on a grain surface, since they are usually much more likely to instead encounter an H atom on the surface. However, if H₂ preponderates in the gas phase it will also preponderate on the grain surface and since radicals are much less likely to react with H₂ the formation rate of H₂CO is enhanced under such conditions. For large values of ξ CO radicals hitting dust grains will likely form H₂CO by two H-attachment reactions. Therefore, under all conditions the formation rate is proportional to the collision rate. Since destruction occurs by interaction with UV, the equilibrium abundance is given by

$$[\text{H}_2\text{CO}]/[\text{H or H}_2] \cong 10^{-9} \xi \eta,$$

where η is an efficiency factor accounting for the above-mentioned difficulty with hydrogen atoms on the grain surface. For unshielded regions ($\xi < 30$) $\eta \cong 0.03$, while for moderately shielded regions η can be taken as unity. This leads to relative abundances $[\text{H}_2\text{CO}]/[\text{H}]$ of 10^{-11} for unshielded regions and 10^{-5} for the dust cloud in Table I (taking $\xi = 10^4$ instead of 10^6 to generously allow for a possible nonspherical dust cloud (see Watson and Salpeter, 1972)).

Here the discrepancy between theory and observation is serious. It cannot be ascribed to uncertainties in the excitation temperatures. For the unshielded clouds, Davies and Matthews (1972) assumed an excitation temperature of 3 K for the H₂CO, which is certainly correct to within a factor of two (Roberts and Gordon, 1971). The excitation temperature for H₂CO in dust clouds is known, in some cases, to within 20% (Heiles, 1972). Furthermore, the smaller relative abundance of H₂CO in dust clouds as compared with that in unshielded clouds is completely contradictory to theoretical expectations; although one might wish to explain it on the basis of grain accretion in clouds with $\xi > 10^4$, one would then expect that OH would be similarly depleted, which is just not the case.

In order that the H₂CO abundance be so large in the unshielded region, where the volume density is small, its formation process must be concerned with some agent other than binary collisions. The photo-destruction rate in unshielded regions is so large (Steif *et al.*, 1972) that the lifetime of a given molecule is less than 100 yr. It is therefore tempting to conclude that UV is also responsible for forming these molecules, since its intensity varies by a factor of about 10^4 between dust clouds and the unshield-

ed clouds. Perhaps interaction of UV with grains can form H_2CO at a sufficient rate. If so, grain lifetimes would be limited to $\sim 10^8$ yr in typical regions of interstellar space; alternatively, perhaps the grains could be only a temporary source of supply, their ability as molecule sources being restricted to a special surface condition.

The problem of the large H_2CO abundance in unshielded regions is not new; a comparison similar to the present one was made earlier by Heiles (1971). It is a vexing one, however, because it illustrates our lack of ability to make even qualitative predictions about some molecular abundances. It is interesting to speculate on the possibility that, given the data in Table I, the process which is most important in H_2CO formation occurs only outside of dust clouds and that the H_2CO observed at present in dust clouds was formed long ago and is 'frozen in'. Present abundances would then be more a result of historical accident than statistical equilibrium at the present. The large variations in $[\text{OH}]/[\text{H}_2\text{CO}]$ found by Heiles and Gordon (1973) would not be inconsistent with this picture. If this is the case, our inability to detect H_2CO and OH in unshielded clouds which do not happen to lie in front of radio sources would be due to its excitation temperature rather than its low relative abundance.

Finally, we note that OH is more abundant relative to hydrogen in our two classes of cloud than in Orion A, and not necessarily less abundant than in the galactic center. The relative abundance of H_2CO in Orion A is the same as in our clouds, again, the situation with the galactic center is unclear. It seems that the old concept that dust clouds, H II regions, and the galactic center sources are regions in which prodigious molecule formation occurs – i.e., 'molecule factories' – must be abandoned, at least for OH and H_2CO .

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