MICROWAVE EVIDENCE FOR INTERSTELLAR MOLECULES

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Some time ago, optical astronomy was successful in detecting the first molecular species in interstellar space. However, these have been limited to the three diatomic molecules CH, CH^+, and CN. Consideration of this list made it rather natural, after the development of microwave astronomy, for some attention to be given to a search for OH, which has a rather strong microwave transition. This molecule was first detected, after a considerable search, by Weinreb *et al.* [1]. The analogous Λ-doublet transitions in SH and CH have since been searched for assiduously; failure to detect them does not necessarily mean these radicals are excessively rare in interstellar space, since various unfavorable factors make the search difficult.

Any consideration of polyatomic molecules in interstellar space immediately raises the question as to whether and where such molecules are likely to exist. Of course, they can occur in stellar atmospheres, where they have already been found to a limited extent. But in free interstellar space they are less likely to exist because of slow rates of formation and a rather short lifetime, the latter being typically limited to a few hundred years because of dissociation by ultraviolet radiation from stars. In dust clouds, molecules are more protected from ultraviolet radiation and their formation may be aided by catalysis on the dust grain surfaces. However, here too their lifetimes are limited, being not more than about one million years before condensation on the dust particles. Furthermore, it is not clear how they can escape from the grain surfaces. Hence, without a better understanding of rates and modes of production there is even now no convincing *a priori* theoretical reason why complex molecules must be present in interstellar space. One can only say that if they are present, their most likely location is in the dark dust clouds, which afford protection from dissociating ultraviolet and hence allow longer lifetimes than can occur in other regions of interstellar space. Somewhat more surely, one can expect molecules to be present in transient situations where particles that have condensed are being evaporated, or where more complex chemical condensations are being dissociated. The difficulty in these cases is to know the lifetime and extent of such transient molecular existence. Thus a dark cloud being warmed up by a newly formed star might be favorable. Still another favorable transient situation may be where material is being ejected from some chemical factory like the atmosphere of a star and is not yet dissociated.

Dark clouds offer a particular opportunity to microwave and infra-red work because they have, of course, been largely unavailable to the shorter wavelengths which their dust particles effectively scatter or absorb. A look at photographs of our Milky Way, or of many types of nebulosities and galaxies, show how really abundant are dark dust lanes and blotches. The heavens are full of dark clouds which are readily

De Jager (ed.), Highlights of Astronomy, 359–365. *All Rights Reserved*

available for spectroscopic study only in the longer wavelength regions beyond the visible. The very active searches of these regions at microwave frequencies which began a little less than two years ago have already revealed a substantial list of molecules. Table I gives the list of molecules which have so far been thus detected, and their approximate abundances. The listing for hydrogen molecules represents only an indirect determination, since H_2 has no microwave transition; but it is nevertheless a determination made possible by microwave observations, which will be discussed below. For all other molecules listed, definitely identifiable resonant lines have been seen. Densities given in Table I are for some typical dark clouds. These

TABLE I

Typical abundances of molecular species in dense clouds

Normal molecules	Radicals
$H_2 \geqslant 10^3/cm^3$	$H \lesssim 10/cm^3$
$CO \sim 10^{-1} - 10^{-2}$	$CN \sim 10^{-4} - 10^{-5}$
H_2O?	$OH \sim 10^{-5} - 10^{-6}$
$NH_3 \sim 10^{-3}$	
$HCN \sim 10^{-4}$	
$H_2CO \sim 10^{-4} - 10^{-5}$	
$HCCCN \sim 10^{-5}$	

densities of course vary considerably, and are not the precise values for any one particular dust cloud. In fact, while the molecules listed tend to occur together in the same cloud, there is no one cloud in which every species has been detected. The atomic abundance of hydrogen in some dark clouds has been listed in Table I for comparison. It is clear that most of the gaseous material in these regions is in the form of ordinary stable molecules rather than as atoms or free radicals, and hence rather different from the case of clearer interstellar regions. Furthermore, a substantial fraction of the total C, N, and O atoms are contained in these molecules.

Table I and other results which will be discussed have come from the work of a number of different radio observatories. Included among these are the NRAO observatories at Greenbank and at Kitt Peak, the Hat Creek Observatory of the University of California, the Maryland Point Observatory of the Naval Research Laboratory, Lincoln Laboratory's Haystack antenna, the Onsala Observatory of the Chalmers Institute, and the CSIRO Observatory at Parks. You have the privilege of hearing from a representative of each team that has discovered every individual molecule listed with the exception of OH, which was discovered somewhat earlier than the others by Weinreb *et al.* [1] as already mentioned. You will also hear from Snyder of a molecule which is about to be discovered – he will report an as yet unidentified new line.

The presence of the molecules listed in the dark clouds represents new information which has changed our views. However, this new field of complex molecules is rather different from the new fields of pulsars or quasistellar objects in that the physics (or chemistry) involved is of a known type. This makes it on the one hand a little less exciting, but on the other hand assists us in making the interpretation of observations immediately useful in understanding the conditions where these species are found.

The relative abundances found for most of these various molecules is not very surprising. The more common molecules observed are simple combinations of the more common atoms: hydrogen, then oxygen, carbon, and nitrogen in the ratios 10000:8:3:1. One can be confident, I believe, that other simple combinations such as NO, O_2, N_2 and methane have not been found only because of technical difficulties. O_2, N_2, CH_4 do not have intense microwave lines. O_2 has weak lines, but these are masked by O_2 absorption in the atmosphere. NO has a rotational transition at about 2 mm wavelength which is not easily available, but presumably will be found before long. However, the relative abundance of molecules is not entirely dictated by the relative abundance of atomic constituents. During the last year and a half there has been a minor gold rush in discovery of molecules; many likely candidates have been eagerly searched for – with some found and also some not found. In some cases the unsuccessful searches as well as the successful ones have considerable scientific interest. For at least one molecule found, I believe there is a reason for some surprise. This is the case of HCCCN [2], having four heavy atoms and considerable chemical energy. Many other simpler, and superficially more likely appearing molecules, seem to have less abundance. Pasachoft *et al.* [3] have searched rather carefully for, but not found the molecule ketene. This molecule, H_2CCO, is a rather simple elaboration on formaldehyde, which by contrast is rather abundant. The molecule HCCCN has a larger number of the relatively rare heavy atoms. Another interesting example is thioformaldehyde, the analog of formaldehyde in which O is replaced by S. A search by Evans *et al.* [4] failed to detect this molecule, indicating that its abundance is considerably less by comparison with formaldehyde than the relative cosmic abundance of sulphur to oxygen. Hence specific chemical reactions connected with specific conditions evidently are of importance in whatever chemical factories occur in space. The special chemistry involved should some day provide clues to the processes of formation.

While molecular abundance in a column of gas intercepted by the beam of a radio antenna can frequently be obtained in a straightforward way, determination of abundance is not always straightforward. Those molecules which are seen in emission allow a rather direct measure of the abundance of that species of molecule in a particular state of excitation, if the cloud is not optically thick and not masing. Molecular lines seen in absorption give greater difficulty to an abundance determination, because then the effective temperature for the two states of the transition must be known. If the population of the two molecular states involved in a transition are inverted so that maser action is prominent, one obtains almost no direct information about the molecular abundance. Such is the case for the H_2O line. While H_2O listed in Table I must be fairly abundant, probably more abundant than any of the other polyatomic molecules, and it gives very strong microwave signals, it is clear that the water transition gives strong maser action and affords us almost no way of judging the actual abundance of water.

In addition to abundance information, molecular lines yield velocities and temperatures of the clouds in which they exist. Velocities are determined directly from doppler shifts and widths. Temperatures require a more subtle and hazardous interpretation of line intensities. Ideally, temperatures might be determined from the relative abundance of molecules in two different states which give two different spectral lines.

Figure 1 shows a study of the velocity, number and temperature distribution within a cloud which is some few minutes of arc in diameter [5]. Each square box represents the size of the antenna pattern. Each box contains the molecular density found, the average velocity of that particular part of the cloud, and two different determinations of temperature. The figure represents a preliminary survey, but is revealing. Differences between the two temperature values do not represent simply experimental errors, but rather differences in the effective temperatures of excitation associated with two different processes.

Additional very important information which molecular lines can give is the relative abundance of isotopes. The separation between frequencies of two different isotopic species is typically thousands of times greater than the linewidth. Hence resolution

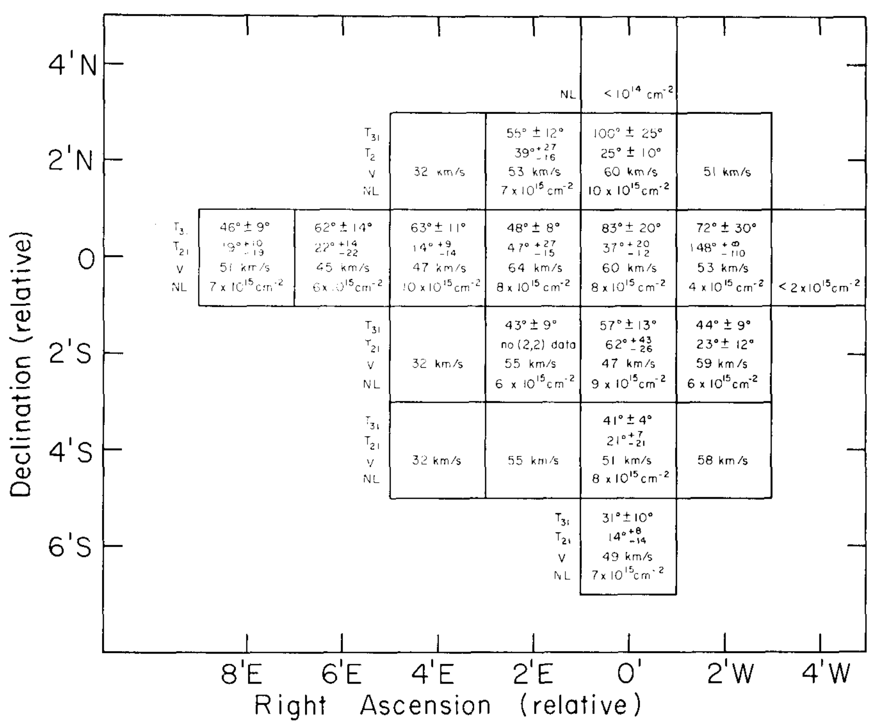

Fig. 1. Distribution and characteristics of ammonia in the Cloud Sagittarius B 2 (Cheung *et al.* [5]).

of isotopic species is not a problem, but one must have enough sensitivity to detect interesting, relatively rare isotopic species. Such determinations are at present troubled with uncertainties in the optical depth, and hence most of them are not yet definitive. However, it is interesting to note that the abundance of O^{18} with respect to O^{16} [6] and the abundance of C^{13} with respect to C^{12} [7, 8] frequently is close to the value which occurs on Earth, for no well-understood reason. In other cases, there is an indication that the C^{13}/C^{12} ratio is substantially higher than on Earth [6] and fairly close to the ratio found in some carbon stars. Such ratios, when determined unambiguously, should be valuable keys to the origins and history of the materials involved.

Molecular excitation has already been used to determine the intensity of the isotropic microwave radiation [9]. The new molecular states recently found add considerable variety to such determinations. Particularly in the region of wavelengths shorter than 5 mm, we have relatively little firm information on the intensity of this isotropic radiation, and there is some evidence that it deviates from the blackbody curve. In the centimeter region, where radiative transitions are frequently somewhat slower than the collision rate, molecular populations tend to equilibrate with collisional energies. But just in the millimeter region and at shorter wavelengths, spontaneous and induced radiative transitions are likely to be so rapid that the relative population of molecular states is determined by the radiation temperature and they may hence give a useful measure of radiation intensity. The limited use of relative abundances of molecular populations determined from microwave transitions which has so far occurred indicates some excited states are more abundant than expected from 3 K blackbody radiation [4]. However, uncertainties in optical depths of the gas clouds observed and problems of optical trapping still require further study before these determinations can be definite.

The above considerations illustrate, in several different ways, the importance of understanding excitation processes. Quite characteristically, molecules in interstellar space are not in thermal equilibrium with all their surroundings. Factors which are important in their excitation are collisions, spontaneous emission, the isotropic radiation, radiation trapping, and higher frequency radiation such as infra-red. Particularly crucial are the rates of collisions and those for spontaneous emission or transitions stimulation by isotropic radiation. These radiation processes and collisions frequently have comparable rates, and since the ambient radiation and the kinetic energy of colliding particles represent very different temperatures, the amount of molecular excitation is critically dependent on these relative rates. The relative rates frequently even determine whether the molecule can be seen at all. For example, ammonia comes into equilibrium with the isotropic microwave radiation in a time of about one year, i.e. the rate at which a stimulated radiative process occurs at about one centimeter wavelength. Hence upper and lower levels of the NH_3 transition would come into equilibrium with the isotropic radiation and take on its temperature if there were no other more frequent disturbances. If the NH_3 levels come into equilibrium with the microwave radiation, it is quite impossible to detect NH_3 in emission, because an antenna could see only radiation of a uniform temperature, and hence of course no resonant line. Ammonia is in fact seen and hence must undergo disturbances about as rapid as the induced transitions, about once per year. The only reasonable source of such disturbances are collisions with neutral molecules, and it is from this conclusion that one deduces the density of hydrogen molecules to be as large as about $10^3/\mathrm{cm}^3$. The case of HCN is more extreme than ammonia, since its high frequency and large dipole moment make its time for equilibrating with the isotropic radiation about one hundred times faster, or only a few days. If we would attribute its evident deviation from the isotropic radiation temperature to hydrogen molecules, this makes the density in those regions where HCN is observed somewhat higher than $10^3/\mathrm{cm}^3$. It need not be as much as one hundred times higher, but H_2 molecules must either be substantially higher than $10^3/\mathrm{cm}^3$ or there must be electrons at a density somewhat greater than $1/\mathrm{cm}^3$ which would alternatively serve the purpose of keeping the HCN out of equilibrium with the isotropic radiation.

The regions in which molecules such as HCN exist are not well identified or understood, although there are substantial indications that most molecules typically exist in dense clouds. We know at least that complex molecules which are found generally coincide in direction with known clouds. Furthermore, doppler velocities of molecules found in the same direction generally coincide, so that they presumably exist in the same clouds. However, correlation between density of dust and occurrence of molecules, and the extent to which some molecules exist outside of substantial dust concentrations has not yet been examined in any detail.

The two processes of collisions and stimulated emission in the simple form outlined above by no means end the rich variety of phenomena which are important to molecular excitation in interstellar space. There are many metastable states, for example, with radiative lifetimes very much longer than what has been indicated – in some cases longer than the age of the universe – and for these, collisions are also frequently very ineffective in making transitions. There are two-or-more step processes which may produce excitation temperatures far from those of other systems with which the molecule interacts. An example is the divergence from any distribution describable by a positive temperature which evidently occurs in interstellar maser action. OH 'masers' have been known for some time – cases where rather localized regions of OH emit abundant radiation of intensity and characteristics which cannot be due to thermal radiation and must be associated with the coherent amplification of microwaves by molecular resonances. More recently it has been found that in certain regions water vapor also strongly amplifies microwave radiation at its resonance. In fact, water would not otherwise be visible if it were not 'masing'. Water has no suitable level for microwave observation in the cool clouds because its microwave transition involves levels with excitation energies of about 450 wave numbers, and these levels rapidly decay radiatively to lower states. Water can exist in these states in any abundance only in localized gases of high energy and density. If such a gas radiated at thermal levels rather than amplifying, it would subtend such a small fraction of an antenna beam that it could not be detected at all. Very long baseline measurements recently completed [10] show that some of these regions are smaller than an AU – comparable in size with a large star, or a planetary gas cloud around a star. Because the amplified radiation is in fact enormously intense, water is rather commonly seen in these localized regions of high excitation, and their study should give insight into such arenas where possibly stellar formation or explosions are occurring.

Finally, let us consider briefly some of the future needs in this area. Clearly, we are coming into a period where there is considerable need not only for further discoveries of individual molecules or transitions, but for careful, systematic, studies and correlations which will tell us in more detail some of the answers to the questions raised by the present brief and exploratory work. We also need badly to increase the spectral range over which good observations can be made. Observations are now made fairly easily in the centimeter and decameter region, and with difficulty to wavelengths of a few millimeters. There clearly are many important molecular lines in the short millimeter region and on into the infra-red. These waves also penetrate the dust clouds and infra-red would easily give better angular definition than is now available if it could be used to examine molecular species and their various excitation conditions. The use of infra-red on down in wavelength to a few microns seems to provide very promising tools, though ones which are not easy to develop properly. Along with the extension of the spectral range over which studies can be made, must come, of course, better and more telescopes suitable for these wavelengths, high resolution spectrometers, and a variety of new detectors.

Acknowledgements

Work partially supported by NASA Grant NGL-05-003-272 and National Science Foundation Grant GP-14356.

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DISCUSSION

Gold: The argument that certain molecules would quickly get into equilibrium with the isotopic background radiation is dependent on this radiation having a black-body spectrum. This is not certain. Could the radiation seen not be due to a non-thermal part of the background radiation?