of animals," Tinbergen and his colleagues concentrated on the stimulus control of behavior. In both laboratory and field conditions, with butterflies, fish, and birds as subjects, he demonstrated that, by using inanimate models whose properties are systematically varied, experimental demonstration can replace intuitive judgment in deciding which elements of a stimulus complex control a response. New insights into how signaling behavior originates in the course of evolution were summarized, together with a general development of ethological theory in his 1951 book, *The Study of Instinct*, which introduced many English-speaking readers to the subject. Many patterns of social behavior, often with a signaling function, were understood as the outcome of social conflicts, a point of view that Tinbergen, with his wife Elizabeth, has since applied to the genesis of autistic behavior in children.

Perhaps most distinctive in the breadth of Tinbergen's research is his frontal attack in the 1950's and '60's on the problem of adaptiveness, which was for so long the subject of judgments from zoologists' armchairs. However, Tinbergen and his associates demonstrated that one can actually measure in animals preyed upon by others the cost or benefit of such traits as the color of a moth's wings or a bird's eggs, the spines of a three-spined stickleback, habits such as a gull's removal of egg shells from the nest after young have hatched, or living on the edge of a gull colony rather than in the center. The studies of gull behavior illustrate beautifully how an ecological decision made in phylogeny can reverberate through many aspects of the biology of a species. With von Frisch and Lorenz, Tinbergen has expressed the view that ethological demonstrations of the extraordinarily intricate interdependence of the structure and behavior of organisms are relevant to understanding the psychology of our own species. Indeed, this award might be taken not only as fitting recognition of the outstanding research accomplishments of these three zoologists, but also as an appreciation of the need to review the picture that we often seem to have of human behavior as something quite outside nature, hardly subject to the principles that mold the biology, adaptability, and survival of other organisms.

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Interstellar Molecules: New Theory of Formation from Gases

On the first of September, the 27th interstellar molecule was announced, this time sulfur monoxide. It was found with the same instrument used to detect many other molecules—a relatively small radio telescope operated by the National Radio Astronomy Observatory at Kitt Peak, Arizona. That interstellar molecules were discovered at all is a story of near oversight on the part of astronomers (see box), but once they were found at millimeter wavelengths (the radio wavelength the Kitt Peak telescope detects so well) it seemed that every new observation turned up a new molecule.

The pace of discovery was nearly a gallop from 1970 until about 1 year ago. Since then no further molecules except sulfur monoxide have been found, apparently because the limit of sensitivity of the Kitt Peak telescope—with its present electronic configuration—has been reached. In the meantime, the study of interstellar molecules has entered a period of consolidation, in which the scientists who were earlier quite busy simply reporting new findings are beginning to use their results to try to understand the dynamics of interstellar clouds, and others are proposing detailed schemes for the chemistry by which the interstellar molecules might have evolved. A chemical process that has been proposed recently—formation of complex molecules by collisions of ions and simpler molecules in a gas—seems particularly attractive as a working hypothesis, especially in conjunction with an older hypothesis that some molecules are formed on dust grains.

The environment in which interstellar molecules are found is far different from conditions on the earth, even in the laboratory. Some species, like CH, CH^+, OH, H_2, and atomic hydrogen, are found in very diffuse clouds of gas. The density of atomic hydrogen in these clouds is typically only 100 atoms per cubic centimeter; the clouds are transparent and permeated with intense ultraviolet light. But most of the molecular species have been found in a few huge clouds, toward the center of the galaxy and in the constellation Orion, that are opaque to visible or ultraviolet light. (Only the radical OH has been reported in another galaxy. The report has not so far been confirmed.) The clouds appear as dark patches in optical surveys of the sky, and are often associated with a bright nebula that is presumably created and illuminated by hot stars embedded in the cloud.

Dense interstellar clouds are principally composed of dust grains and molecular hydrogen. The reddening of starlight passing through the edges of the clouds reveals the presence of dust grains, smaller than a micron in diameter. The fact that molecular emissions are quite intense reveals the presence of a gas with a density of 10^4 to 10^7 molecules per cubic centimeter, but lack of correlation between 21-cm emissions and cloud positions rules out atomic hydrogen, so the gas is thought to be mainly molecular hydrogen. Radio measurements of other molecules indicate that the temperature is probably below 100°K, possibly as low as 20°K. The concentrations of the various complex molecules, relative to that of H_2, are 10^{-3} to 10^{-4} for CO; 10^{-6} to 10^{-7} for NH_3, OH, CS, CH_3OH, and HCN; and even lower for the rest. Because the concentrations of complex molecules are so low, three body collisions, which contribute significantly to chemical reactions at the earth's surface, are completely inconsequential. (Only two body collisions occur.) Therefore, many scientists previously thought gas phase reactions were unimportant.

Instead, until several years ago, most astronomers thought that interstellar molecules formed on the dust grains. Either by physical adsorption or by the stronger process of chemical adsorption, gas particles could be bound to grain surfaces, and despite the great uncertainties about the processes that occur on surfaces, William D. Watson at the University of Illinois, Urbana, and E. E. Salpeter at Cornell University, Ithaca, New York, estimated that simple molecules would almost certainly stick and yet be mobile enough to "find" each other and react. However, Watson and Salpeter concluded that the temperature was probably too low to evaporate any of the molecules from the surface, except possibly molecular hydrogen. Ejection by ultraviolet light is perhaps more important, they suggested, but it would not occur in dense clouds. So a significant problem with the theory of molecular formation on grain surfaces is how molecules might get off the grains once they were formed.

Although the proposal that interstellar molecules form on grains has been widely accepted by astronomers, at least qualitatively, the only molecule everyone agrees must be formed on

Interstellar Molecules Were Found in Spite of the Sages

The search for interstellar molecules has been a sporadic pursuit that has oscillated between periods of boom and bust ever since the radical CH was accidentally discovered in a star spectrum in 1937. A few years afterward the radicals CN and CH^+ were also found with the 100-inch optical telescope at the Mount Wilson Observatory, and then the molecules apparently ran out. Only after radio telescopes were developed, 20 years later, was the next molecule found.

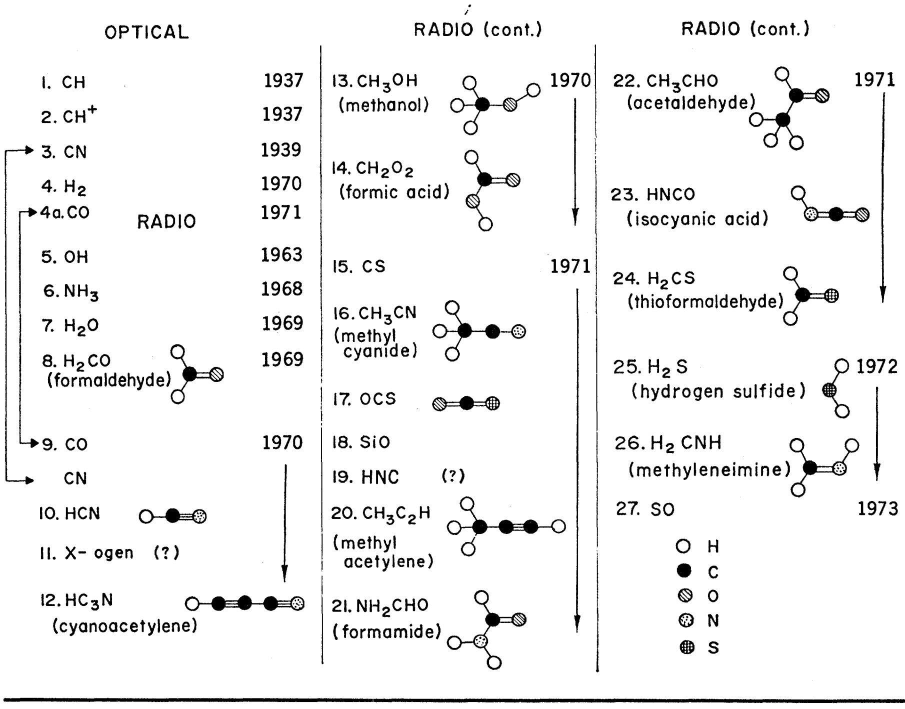
Not only were no further molecules found in the 1940's and 1950's, but most astronomers thought they knew the reason why. The molecules discovered were, after all, not composed of more than two atoms, and only the most abundant atoms at that. Furthermore, the diatomic molecules were scarce (about one to every 10^8 hydrogen atoms), and were particularly unlikely to dissociate in strong ultraviolet light. The conventional wisdom was that more complex molecules would be even less likely to form, and much more likely to break up.

As early as 1955, Charles H. Townes speculated that water vapor might be found with a radio telescope, but the fact that it is not diatomic made most scientists pessimistic. It is no coincidence that the molecule most radio astronomers bet on finding was the radical OH, also diatomic and composed of the most abundant elements in the universe. After several unsuccessful searches, conducted before the microwave frequency was well established, OH was found in 1963 by astronomers at the Lincoln Laboratories, Massachusetts Institute of Technology. Townes was at MIT at the time, and the MIT radio facilities included a small telescope designed to look for water vapor in the venusian atmosphere, in addition to the large one that detected OH, but apparently no one looked for water beyond the solar system.

The OH radical was observed throughout our galaxy, but most astronomers—with exceptions such as David Buhl and Lewes Snyder, who postulated in 1967 that water emissions would be seen—expected that even if water vapor were present the signal would be very weak. Townes and his colleagues were intent on finding ammonia (the first maser, invented by Townes, was an ammonia maser), and discovered it in 1968 at Berkeley. Very soon afterward they found water vapor at nearly the same wavelength (1.3 centimeters). Then in 1969 formaldehyde was found at 6.2 centimeters with the 140-foot telescope of the National Radio Astronomy Observatory (NRAO), and the idea that most interstellar molecules would be diatomic surely died.

Ammonia, water, and formaldehyde were found in very dense clouds, composed of dust grains and molecular hydrogen, where no one had previously thought to look. Such regions are very different from the areas where CH is found because the dust completely blocks out ultraviolet light, and the molecular hydrogen collides with more complex molecules so frequently that they are excited and easily seen in radio emissions (also the reason water vapor is seen).

The effect of the dense concentration of molecular hydrogen in the clouds also causes millimeter wave emissions to generally be stronger than centimeter wave emissions, with which radio astronomers are more familiar. The technology for detecting millimeter waves was generally not available in the 1960's, but in 1970 Arno A. Penzias and R. W. Wilson at the Bell Laboratories, working with scientists at NRAO, perfected a millimeter wave receiver and attached it to the NRAO 36-foot telescope, and then a great many more molecules were quickly identified. The 27 molecules discovered to date are indicated at the left, by formula and structure.—W.D.M.



grains is H_2. Two hydrogen atoms cannot combine without a third body around to carry off the energy released by binding (the possible photon transitions are spin forbidden). Dust grains act as the third body. But beyond the certainty about H_2, it is very difficult to make predictions about chemical reactions on grain surfaces, and possibly more difficult to test. No laboratory techniques are generally available; as one scientist noted, the chemistry of heterogeneous reactions is a formidable problem.

The chemistry of gas phase reactions is much better known, of course. The combination of neutral molecules by radiative association (reaction with photon emission) was originally thought to be the most important process. But the reaction rates proved to be too slow because the chemical activation energy necessary for neutral molecule reactions acts as a barrier to formation of more complex molecules. Most reactions between ions and neutral molecules have no such barrier, however. Thus heavier ions can be built from lighter ones by reactions such as

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$
$$H_3^+ + CO \rightarrow HCO^+ + H_2$$

Of course, ions can recombine with electrons (estimated at a density of 10^{-7} cm^{-3} in the dense clouds) to form neutral molecules and thus end a reaction pathway. For instance, HCO^+ might either react to transfer a proton to another molecule, or recombine with an electron to form carbon monoxide and atomic hydrogen.

William Klemperer and Eric Herbst at Harvard University, Cambridge, Massachusetts, and William D. Watson at Illinois have independently developed schemes for the genesis of some of the complex molecules in dense clouds, starting with the two reactions above. They assume that the source of ionization is the flux of cosmic rays at energies of 100 million electron volts and above. Though the ionization rate from that flux is small ($\sim 10^{-17}$ sec^{-1}), it would be sufficient to make an ion-molecule reaction scheme work.

The chain of reactions that could proceed from ionized H_2 is only one of several possible chains. Others could proceed from ionized helium, carbon, and oxygen. But the hydrogen reactions appear to be so basic that Watson and Klemperer both think that the whole ion-molecule scheme is unlikely to be correct if HCO^+ is not present in the dense clouds.

Klemperer has suggested that an unidentified molecular transition at 89.190 gigahertz (3.4 mm), usually called X-ogen, might be evidence for HCO^+. But because HCO^+ is an ion, no one has measured its radio transitions. The best that has been done is to calculate the transition frequency. Klemperer made an estimate of the principal radio transition that was consistent with the observed frequency, and more recently Henry F. Schaefer at the University of California, Berkeley, and his associates have increased the believability that X-ogen is HCO^+ by making a complete calculation of the molecular orbitals. They found that the calculated and observed frequencies are consistent within 0.2 Ghz. However, 0.2 Ghz is a very large range to scan.

If the isotopic species of HCO^+ with ^{13}C replacing ^{12}C were found, it would be much stronger evidence that the ion is really present in interstellar clouds. David Buhl at the National Radio Astronomy Observatory, Charlottesville, and Lewes Snyder at the University of Virginia, Charlottesville, have looked for HCO^+ but didn't find it at the frequency expected.

The question whether HCO^+ is found in clouds that are rich with other molecules is still unanswered, but the very fact that ion-molecule formation could be debunked by the failure to find HCO^+ or other intermediate species illustrates the advantage of the ion-molecule scheme as a working hypothesis. Another advantage is that the rates of ion-molecule reactions can often be measured in the laboratory. Particularly for the reactions thought to produce diatomic molecules in interstellar clouds, a considerable body of chemical knowledge is available because many of the same species are constituents of the earth's upper atmosphere. But researchers trying to explain the heavier interstellar molecules have very little information on relevant reaction rates.

An extensive ion-molecule reaction scheme that predicts species as complex as formaldehyde was recently proposed by Herbst and Klemperer, who included more than 100 reactions and predicted the abundances of about 35 species. They propose that H_3CO^+ is formed by radiative association of HCO^+ and H_2, and that when it subsequently recombines formaldehyde (H_2CO) is formed a large fraction of the time.

$$H_3CO^+ + e^- \rightarrow H_2CO + H$$
$$\text{or } CO + 3H$$

The scheme also accounts for the observation of HCN, NH_3, and H_2O. But the subsequent study of the formaldehyde prediction in the laboratory indicates how severely theorists constructing ion-molecule schemes are restricted by lack of data. E. E. Ferguson and associates at the National Oceanic and Atmospheric Administration's Environmental Research Laboratories, Boulder, Colorado, have found that the form of H_3CO^+ which is produced in ion-molecule reactions may be destroyed by collision more often than by recombination with an electron, and the most likely products from recombination would be HCO and H_2. So a different explanation for formaldehyde may be needed. A. Dalgarno at the Harvard College Observatory, Cambridge, Massachusetts, thinks that the reactions of neutral CH_3 and ionized CH_3^+ with atomic oxygen produce formaldehyde in diffuse clouds. (No one knows whether molecules produced in diffuse clouds could migrate into dense clouds.)

While there are many attractive features about the ion-molecule theory, at this point most of the arguments that support it—or the theory of formation on grains—are based on estimates of what physical processes are likely. It should be remembered, according to Snyder, that neither theory has been verified by observational tests. The point of view of Salpeter, who is a theorist, is that ion-molecule schemes are just as important as grain surface schemes, and should not have been overlooked for so long. He thinks that the ion-molecule reactions reshuffle the molecules that were produced on the grains.

To prepare for future observations, a new receiver will be installed at the Kitt Peak telescope in the spring of 1974, and after that a resurgence in the number of discoveries may be expected. The new receiver should be 250 times as sensitive to weak millimeter wave signals as the receiver that started the molecule discovery boom in 1970. So heavier molecules, rare isotopic species, or possibly even more radio transitions that are not known in terrestrial chemistry may be found. Three of the four unidentified transitions found so far were discovered by accident, so no one knows how many more to expect.

Even though a new and highly workable hypothesis for interstellar molecule formation is developing rapidly, it appears that the observations will stay ahead of the theory for some time to come.—William D. Metz