

# MICROWAVE SPECTROSCOPY OF ASTROPHYSICAL MOLECULES

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**ABSTRACT.** Recent detections of new molecules in dense interstellar clouds, first detections of certain chemical elements in interstellar molecules, and new information on isotopic fractionation of hydrogen in the interstellar medium are discussed in the context of the need for new laboratory data on transition rest frequencies, reaction rates, and branching ratios.

## 1. Introduction

This brief review will concentrate on some recent results in the chemistry of molecular clouds, in order to provide some examples of areas where new laboratory data are needed. I will not discuss laboratory microwave measurements in themselves. For a more complete description of recent progress, see reviews by Irvine (1988), Irvine and Knacke (1988), Turner and Ziurys (1988), Hjalmarson and Friberg (1988), and Guélin (1985).

The discovery of new molecular constituents in these regions continues apace, with some 13 or 14 new species having been identified in the past couple of years. This brings to about 80 the number of molecular species known in dense clouds and in the envelopes expelled by evolved stars, including molecules with up to 13 atoms and weights up to about twice that of the simplest amino acid, glycine (cf. Irvine, 1988). The striking deviations from chemical equilibrium which characterize the interstellar medium are evident in the considerable number of highly unsaturated species (even in this very "reducing" environment) and in the large number of ions and radicals. The richness of the spectral material with which molecular astrophysicists now have to deal is exemplified by the detection of more than 800 individual transitions in the spectral survey of the Orion molecular cloud carried out at the Owens Valley Radio Observatory (Blake et al., 1987). Interestingly enough, the vast majority of these lines have been assigned to known molecular species. In fact, the proliferation of rotational transitions from asymmetric rotors and their isotopic variants threatens to create a confusion-limited spectrum at short millimeter and submillimeter wavelengths, for the richest molecular sources.

## 2. New Interstellar Molecules

At the time of the last IAU General Assembly, interstellar molecules (excluding near-photospheric species) were known which contained the elements H, C, N, O, S, Si, and probably Cl. Since that time the new 30m IRAM telescope has been used to discover several halides in the envelope surrounding the carbon star IRC+10216, a topic to be discussed later today by Professor Omont (see also Cernicharo and Guélin, 1987); and the first interstellar molecule containing phosphorus has been detected. Although phosphorus is essentially undepleted in diffuse interstellar clouds, it has heretofore been searched for unsuccessfully in denser regions. It is an element of personal interest to all of us, since biological material contains an anomalously high amount of phosphorus relative to terrestrial and cosmic abundances. The detection of PN in several molecular clouds by Ziurys (1987) and by Turner and Bally (1987) is thus an important development. It is important to note, however, that the bulk of the cosmic complement of phosphorus remains undetected in these regions and that the failure to observe PO is puzzling (cf. Thorne et al., 1984).

Abundance comparisons between chemical isomers may provide particularly useful tests of astrochemical models. The classical example is HCN and HNC, where the large HNC abundance in cold clouds has traditionally been one of the main arguments in favor of the importance of ion-molecule chemical schemes (Irvine et al., 1985; Goldsmith et al., 1986). Although the situation is more complicated, the pair  $\text{CH}_3\text{CN}/\text{CH}_3\text{NC}$  is somewhat analogous. The recent detection of the latter species by Cernicharo et al. (1988) in Sgr B2 with an abundance relative to  $\text{CH}_3\text{CN}$  in good agreement with theory is thus an important result.

The rotational spectra for the molecules discussed above were well known from laboratory work. In contrast, there continue to be a number of new molecular species for which the first observations of rotational transitions have been made with the radio telescope, and the detected unidentified lines have only subsequently been assigned on the basis of new laboratory measurements. For example, a number of initially unidentified emission lines shared the property of being weak in the rich molecular sources Sgr B2 and IRC+10216, apparently absent in Orion A, but strong in the cold, dark cloud TMC-1. Identification finally came on the basis of collaborative observational work at the Nobeyama Radio Observatory and laboratory spectroscopy at Nagoya University, and resulted in the detection of a new class of molecules, sulfur-containing carbon chains. Two new species were identified,  $\text{C}_2\text{S}$  and  $\text{C}_3\text{S}$  (Saito et al., 1987; Yamamoto et al., 1987). Both cases are unusual relative to previous sulfur-containing organic molecules in molecular clouds in that both are considerably more abundant than the oxygen-containing analogs ( $\text{C}_2\text{O}$  and  $\text{C}_3\text{O}$ ). It has been suggested that this reflects the failure of the  $\text{S}^+$  ion to react with  $\text{H}_2$ , unlike the situation for  $\text{O}^+$  and  $\text{H}_2$ , leaving  $\text{S}^+$  free to insert itself in acetylene and polyacetylene species to produce  $\text{C}_2\text{S}$  and  $\text{C}_3\text{S}$  precursors (Smith et al., 1988). As with much of interstellar sulfur chemistry, however, there is a need for additional laboratory measurements of relevant reaction rates.

Hydrocarbon radicals of increasing length continue to be found in dense clouds: all of the species  $C_nH$  for  $n=1-6$  have now been observed. Interestingly enough, all of these molecules were observed astronomically before the corresponding spectra were studied in the laboratory. The newest addition to the group is  $C_6H$ , identified independently by Suzuki et al. (1986) at the Nobeyama Radio Observatory and Cernicharo et al. (1986) at IRAM and Bonn. Unlike the cyanopolyynes, which show a smooth fall-off in abundance with increasing length, the abundances of these hydrocarbon radicals show large variations which may be related to the ground electronic state. To verify this, laboratory measurements of the appropriate reaction rates are needed.

The first known interstellar hydrocarbon ring,  $C_3H_2$ , has proven to be widespread in the galaxy and promises to be a useful probe of both chemistry and physics in dense clouds (e.g., Madden, Irvine, and Matthews, 1986). It is hypothesized that  $C_3H_2$  is produced by dissociative electron recombination with the precursor ion  $H_3C_3^+$ . As is so often the case, branching ratios among possible exit channels for such a recombination are not known and are extremely important. It is hypothesized that one such channel would lead to  $C_3H$ , the linear form of which has been established in the interstellar medium (Thaddeus et al., 1985). Further information on the stereochemical processes involved are now provided by the identification of cyclic  $C_3H$  in TMC-1, the third ring molecule to be detected astronomically (Yamamoto et al., 1987). In this case laboratory work preceded the astronomical search and detection.

A classic (and highly unusual) example of the interaction of theory, laboratory work, and astronomical observation led a few years ago to the detection of interstellar tricarbon monoxide ( $C_3O$ ); quantum chemical calculations established the structure and stability of this species, enabling accurate laboratory measurements of the rotational spectrum, which in turn allowed the astronomical detection and an accurate abundance determination. The research is also an illuminating example of international cooperation in astronomy, as it involved scientists in Australia, the United States, Canada, Japan, and Sweden (Brown et al., 1985).  $C_3O$  is thought to be produced by a set of reactions which culminate in the radiative association of CO and hydrocarbon ions followed by dissociative recombination (for example, of  $H_3C_3O^+$ ) to produce  $C_3O$ . No direct laboratory measurements of the relevant radiative associations are available, although some inferences on rates can be made from related three-body reactions. Laboratory data are also lacking on the branching ratios for the final dissociative recombination, but some theories would predict that the primary product would be more hydrogenated than  $C_3O$  itself. This led to a search for two isomers of  $H_2C_3O$ , propadienone ( $H_2C=C=C=O$ ) and propynal ( $HC\equiv CCHO$ ). Propynal was successfully detected in the cold cloud TMC-1, which is known as a particularly rich source of acetylene derivatives (Irvine et al., 1988a). The relative abundances of  $C_3O$ , propadienone, and propynal place important constraints on the detailed chemical reactions involved and suggest relevant laboratory measurements.

Another recent "detective story" leading to the identification of

unassigned interstellar emission lines began with the observation by Thaddeus et al. (1985) that two lines in the Bell Laboratories spectral survey of the galactic center molecular cloud Sgr B2 were harmonically related to each other and to a third line observed in TMC-1 by L. Avery. Subsequent observations at FCRAO, NRAO Green Bank, Onsala, and Nobeyama, and laboratory spectroscopy at Nagoya University, have resulted in the identification of the heaviest non-linear interstellar radical found to date,  $\text{CH}_2\text{CN}$  (Irvine et al., 1988b; Saito et al., 1988). The presence of the unpaired electron as well as the spins of the nitrogen and hydrogen nuclei combine to produce a very complicated spectrum for the lowest rotational transitions. Interestingly enough, the abundance of  $\text{CH}_2\text{CN}$  appears to be significantly greater than that of the closed-shell species  $\text{CH}_3\text{CN}$ , at least in TMC-1. This seems to be consistent with separate routes for the production of these two superficially related species, including perhaps a route to  $\text{CH}_2\text{CN}$  that is analogous to that suggested for the production of the cyanopolyynes (reaction of atomic nitrogen with hydrocarbon ions; e.g., Millar and Freeman, 1984).

### 3. Isotopic Fractionation and High Temperature Chemistry

One of the most characteristic features of interstellar chemistry is the high degree of isotopic fractionation observed for several elements in certain regions. The effect is particularly pronounced for hydrogen, and is reasonably well understood in cold clouds (e.g., Wootten, 1987). Processes that can lead to significant deuterium enhancement in warmer clouds are discussed today by Millar. The effect may provide a link between the formation of the solar system and the molecular cloud where that event occurred, since significant deuterium enhancement is found in the organic components in carbonaceous chondrites (e.g., Epstein et al., 1987).

Although deuterium enhancement is found in virtually every hydrogen-containing interstellar molecule for which data is available (Irvine and Knacke, 1988), the largest effect measured accurately to date may be that in the cyclic species  $\text{C}_3\text{H}_2$ . The  $\text{C}_3\text{HD}/\text{C}_3\text{H}_2$  ratio appears to be as much as 10,000 times the cosmic D/H ratio in cold, dark clouds (Bell et al., 1988; Gerin et al., 1987). It has been suggested that the effect may be enhanced by the preferential loss of H relative to D upon the recombination of the precursor ion  $\text{C}_3\text{H}_2\text{D}^+$ , but laboratory measurements are needed.

Important clues to interstellar chemical processes are provided by the differences in chemical abundances observed under differing physical conditions. Ion-molecule processes are the paradigm for cold, dark clouds. On the other hand, in active star-formation regions a variety of other processes may occur including evaporation of volatile grain mantles and perhaps sputtering of grains themselves (e.g., Blake et al., 1987). Various models of "shock" or high-temperature chemistry have been proposed, and an interesting test appears to be provided by the abundance of the SiO molecule. Unlike the situation for a variety of other molecular species studied, it is unequivocal that SiO is enhanced

by at least two orders of magnitude in dense clumps associated with the supernova remnant IC443, as well as in active regions of massive star formation (Ziurys, Snell, and Dickman, 1988).

#### 4. Conclusion

The observations described above and their interpretations point out the need for laboratory data in a number of areas, including:

- Rotational frequencies for interstellar molecular species on which no data currently exist. This tends to be the case for radicals, ions, and other species which are "unstable" by terrestrial laboratory standards, as well as for heavier molecules which are either of intrinsic interest or whose presence might reasonably be extrapolated from known constituents of molecular clouds.

- In order to determine abundances from observational spectra, dipole moments are needed. These can normally be obtained with contemporary quantum-mechanical computer codes, even for the exotic molecular species characteristic of interstellar chemistry (e.g., recent calculations for C<sub>2</sub>S and cyclic C<sub>3</sub>H; Saito et al., 1987; Yamamoto et al., 1987).

- For a number of important reactions branching ratios among possible exit channels are needed. This is particularly the case for the dissociative recombinations which are the final step in the production of many neutral interstellar molecules. Such measurements would help to resolve discrepancies between theoretical calculations (cf. discussion in Herbst, 1988).

- Reaction rates are currently lacking for many potentially significant reactions, including particularly processes of radiative association, but also for many neutral-neutral reactions. Moreover, measurements at the low temperatures characteristic of molecular clouds are needed in a large number of cases for which only room temperature data are available.

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