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EXTRAORDINARY MOLECULES IN INTERSTELLAR SPACE

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1. INTRODUCTION

In the history of physics, the most fundamental discoveries often resulted from astronomical observations. Such observations have played the role of the Rosetta stone and led to revolutionary developments.

The spectrum of the sun, initially noted by William H. Wollaston[1] in 1802, was studied much more extensively and accurately by Joseph Fraunhofer[2] in 1814 onward and laid the foundation for modern atomic and molecular physics.

The fantastically rich spectrum (576 lines) observed and meticulously drawn by him has started two novel fields. On the one hand it has led to spectroscopy through the study by Bensen and Kirchhoff, and on the other, to identification of the hydrogen spectrum through Ångstrom's laboratory plasma[3] spectroscopy which, together with William Huggins' star spectra,[4] provided the basis for Balmer's formula and in turn for Bohr's quantum mechanics.

The message for the existence of He also came from the sky in 1868 when Pierre Janssen[5] and Joseph Norman Lockyer[5] observed a spectral line during their observations of a solar eclipse and a solar prominence, respectively. There have been numerous other cases of interplay between astronomy and spectroscopy,[7] so much so that until 1952 the Astrophysical Journal had the subtitle "The International Reviews of Spectroscopy and Astronomical Physics".

2. IONS IN SPACE

Although ions are rare species in the earth's atmosphere and in the laboratory, they exist abundantly in certain areas of outer space. This is due to the unusual nature of astronomical conditions such as very high radiative temperature, cosmic ray ionization and exceedingly low densities. Therefore often the spectra of ionic species have been first observed in astronomical objects. Thus, for example, spectra of many highly ionized atoms were first seen in the corona of the sun.[8] Forbidden atomic transitions of O^+, O^{++}, N^+ etc. were initially observed in nubulae and were called nebulium lines.[9] The first spectrum of the CO^+ molecular ion was observed in the tail of comets[10] and is still called the comet tail system. Spectrum of CH^+ was first observed as absorption in diffuse clouds in interstellar space.[11] In all these cases the astronomical observation came first and the laboratory identification followed.

In 1970, with the advent of millimeter wave radio astronomy, laboratory spectroscopists were caught by surprise when a strong emission line unknown in the laboratory and thus named X-ogen was reported in dark clouds in interstellar space.[12] The carrier of this line was later identified[13,14] to be the protonated carbon monoxide HCO^+. Later other species HN_2^+,[15] HCS^+,[16] and $HOCO^+$ [17] have also been detected. The protonated ions belonged to a new category of ions and their spectra had been totally unknown to laboratory spectroscopists in any spectral regions. Also the astronomical objects showing these lines were new. Contrary to other regions of space (such as those mentioned earlier), the interior of dark cloud is at exceedingly low temperature and is well shielded from ionizing ultraviolet radiation. The ionization is done through cosmic ray flux. The area is where new stars are born.

3. ION-MOLECULE REACTIONS

This exciting development has brought about a rapid growth of two fields of science, interstellar chemistry and laboratory ion spectroscopy. In the former, ion-molecule reactions and reactions on dust have been introduced as major chemical processes to produce molecules.[18,19,20] This stimulated detailed laboratory studies of many ion-molecule reaction rates.[21] Now the ion-molecule reaction scheme is used to account for much of the formation of complicated molecules in dark clouds and diffuse clouds.

In dark clouds,[18,19,20] the interstellar ion chemistry starts from cosmic ray ionization of the most abundant species H_2 and He. A cosmic ray proton with energy of say 100 MeV penetrates through a molecular cloud and produces millions of H_2^+ and He^+ in its path. These ions in turn produce H_3^+ and atomic ions X^+ (X = C,N,O) through the ion molecule reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (1)$$

and the charge exchange reaction

$$He^+ + X \rightarrow He + X^+ \qquad (2)$$

respectively. The product ions generate more complicated molecular ions through the universal ion-molecule reactions

$$H_3^+ + X \rightarrow HX^+ + H_2 \quad (3)$$

$$X^+ + H_2 \rightarrow HX^+ + H \quad (4)$$

and

$$X^+ + YZ \rightarrow XY^+ + Z. \quad (5)$$

In diffuse clouds,[22] the initial ionization is more through photoionization. In particular atomic carbon is almost completely ionized by star radiation and is the starting point for production of hydrocarbon ions. It is interesting to note that the universal reaction (4) does not work for C^+ to produce CH^+ and thus the slow radiative association reaction

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu \quad (6)$$

is employed to produce further hydrocarbon ions. While we are still far from having a coherent picture about evolution of interstellar molecules, these considerations give much insight on interstellar chemistry and the chemical conditions of molecular clouds which is the first period of evolution of stars.

4. LABORATORY ION SPECTROSCOPY

Development of laboratory ion spectroscopy stimulated by the discovery of interstellar protonated molecular ions has been equally or even more exciting. Introduction of glow discharge to microwave spectroscopy has enabled laboratory spectroscopists to observe and identify all of the ion transitions reported by radio astronomers.[23] They provided a few molecular ion spectra for astronomers to observe. More recently laser infrared spectroscopic techniques have been very successfully employed to discover many novel spectra of molecular ions, especially astrophysically interesting ones such as H_3^+,[24] H_2D^+,[25] HeH^+,[26] NeH^+,[27] H_3O^+,[28] NH_4^+,[29] $HCNH^+$,[30] CH_3^+,[31] OH^- [32,33] etc. These studies provide very important fundamental information for quantum chemistry, astrophysics and plasma chemistry. Based on these results, spectra of interstellar H_2D^+,[34] $HCNH^+$,[35] and H_3O^+ [36] have been very recently reported. A search for the spectra of H_3^+ has been actively pursued. We are in the middle of a very exciting development.

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