THE PIONEERING INVESTIGATIONS IN THE FIELD OF THE INTERSTELLAR MOLECULES, 1935–1942*

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In the course of recent years numerous molecules have been discovered in interstellar space. Most of these discoveries were quite unexpected. Until a few years ago, only three interstellar molecules, CH, CH^+ and CN, were known. Almost all the recently discovered interstellar molecules have been found in the radio-region. Several molecules, for example H_2, were also found recently in the vacuum ultraviolet, thanks to the space vehicles.

It has seemed interesting to me to write a history of the first pioneering investigations into interstellar molecules. There still remain an enormous amount of work to be done in this field. Indeed, of the approximately forty diffuse interstellar lines which have been observed – the first having been found around 1935 by P. W. Merrill and C. S. Beals, with most of the others having been discovered by G. H. Herbig in recent years – none has been identified. Not one of the tentative explanations published by Rudkjöping, Unsöld, etc. has been convincing. At this time, as well as 40 years ago, two main orientations have been attempted for the assignments of the diffuse lines, either by solid particles at low temperatures, or by gaseous molecules with predissociation effects or similar complications.

The first diffuse lines discovered by P. W. Merrill about 1935–1936 were entirely unexplained, and still remain so. On the other hand, the very sharp interstellar lines which were found by W. S. Adams and Th. Dunham, Jr have been convincingly assigned to the radicals CH, CH^+ and CN.

In 1935, Henry Norris Russell, in his George Darwin Lecture, had suggested that the diffuse lines ought to be assigned to molecules. Let me quote from Russell's lecture: 'If the temperature of the gas is low enough – more precisely if the rotation of the molecules is little excited – only a few of the band lines observed at room temperature might appear.'

Since 1936–1937, A. S. Eddington, B. Lindblad, O. Struve and others have raised the question of the aggregation of molecules in the form of dust particles, for example ice crystals.

In 1937, in addition to the six diffuse lines observed by Merrill (λλ5780.4; 5796.9; 6203.0; 6263.0; 6283.9 and 6613.9 Å), a very broad band was discovered by C. S. Beals

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(λ4430 Å) and four very sharp lines ($\lambda\lambda$3934.3; 3957.7; 4232.6 and 4300.32). I had guessed that there were coincidences between the interstellar wavelengths λ6613.9–λ6283.9 and the vibration–rotation bands of CO_2 (P. Swings, *Monthly Notices Roy. Astron. Soc.* **97**, 212, 1937), but these coincidences were only numerical. M. N. Saha (*Nature* **139**, 840, 1937) had noticed two coincidences:

Merrill's line λ6283 and Na_2 ($v' = 8$; $v'' = 0$);
Merrill's line λ5780 and NaK ($v' = 5$; $v'' = 0$).

However, these coincidences had no physical meaning, as was shown by Eyster (*Astrophys. J.* **86**, 486, 1937) and by L. Rosenfeld and myself. Indeed, if Saha's coincidences had been of real physical meaning several others should have been found. In my paper published in the *Monthly Notices Roy. Astron. Soc.* in 1937 I had applied to the interstellar molecules the notion of equivalent temperature, introduced in 1917 by Charles Fabry (*Astrophys. J.* **45**, 219, 1917). For the rotational levels the equivalent temperature is low; indeed, for a band of CO_2 (not present in interstellar space) the equivalent temperature T_λ had a width of approximately 2 Å at λ6000 Å. The density of interstellar radiation is equal to the radiation in equilibrium at the equivalent temperature T_λ.

The first interstellar molecule was found in 1937 by L. Rosenfeld and myself (*Astrophys. J.* **86**, 483, 1937); it is the line of the CH-radical (λ4300.32, $^2\Delta \leftarrow {}^2\Pi$). Soon afterwards A. McKellar (*Publ. Astron. Soc. Pacific* **52**, 187, 1940) identified the sharp interstellar lines found by W. S. Adams in June 1940; these are

CH($^2\Sigma \leftarrow {}^2\Pi$), $\lambda\lambda$3886.32; 3878.7 and 3890.15

and

CN($^2\Sigma \leftarrow {}^2\Sigma$), $\lambda\lambda$3874.02 R(1) and 3874.62 R(0).

Let us notice that the difference between the rotational levels of the two lines of CN is only 0.00042 eV. McKellar believed that λ3934.3 was due to NaH, but this assignment is not correct.

The sharp lines $\lambda\lambda$4232.08, 3957.72, 3745.39 and 3579.94 had still to be identified. These were found to be due to CH^+. It is interesting to quote from an article by Paul Ledoux, published in *Popular Astronomy* (**49** (N. 10), 1941), entitled 'A Summary of the Symposium on Interstellar Lines at the Yerkes Observatory, on June 30, 1941'. It seemed probable to assume that the four sharp lines belong to the same molecule and that the potential energy curve in the excited electronic state must be very shallow (dissociation energy of the order of 1 eV). The molecule ought to be a hydride, such as BH, and it was tempting to think of CH^+. A few days after the Yerkes Symposium, Prof. G. Herzberg, who had taken part in the discussions, obtained the spectrum of CH^+ in his laboratory, in collaboration with A. E. Douglas, using a discharge in helium with a trace of C_6H_6. The interstellar lines were indeed due to CH^+. Just as for BH the spectrum of CH^+ is a transition $^1\Pi \leftarrow {}^1\Sigma$. The astronomers had thus led to the discovery of a new molecule CH^+ which later played an important role in the physics of interstellar space and of the comets.

In a paper published in 1942 (P. Swings, *Astrophys. J.* **95**, 270, 1942; 'Considerations Regarding Cometary and Interstellar Molecules') I discussed the properties of the observed cometary band emissions and interstellar absorptions, including the dissociation and ionization equilibrium of CH, CN, CH^+ and C_2. In the study of the molecular dissociation equilibrium, account must be taken of the fact that the photodissociation starts only from the lowest level while the formation by capture leads to any excited level. This correction factor suggested by R. Oppenheimer (private communication) amounts to about 10^3 in the case of CH^+. In my first estimate of molecular abundances (1937), only the dilution factor was introduced. Using the Oppenheimer factor, the molecular abundances (for example, that of CH) turn out to be comparable to those of the neutral atoms, such as calcium.

At the 1937 Paris Astrophysical Symposium on Interstellar Matter, several reports were devoted to the constituents of space (P. Swings, *Ann. d'Aph.* **1**, 39, 1938). At that time certain considerations on molecules (H_2, OH, CaH, etc.) were considered. As a comparison the interstellar lines of Ti^+ were considered; these started upward from the lowest level $a^4F_{3/2}$ only; no line started from $a^4F_{5/2}$ although the difference between $a^4F_{3/2}$ and $a^4F_{5/2}$ amounted only to 0.012 eV.

Let us consider a few additional aspects of the problems related to the diffuse interstellar lines. The role of the solid particles has been considered by numerous scientists. For example, around 1939 the following papers by M. Désirant and P. Swings ('Les raies ou bandes d'absorption interstellaire non encore identifiées et leurs rapports avec l'optique des corps solides aux très basses températures', *Ciel et Terre* **55**, 161, 1939); P. Swings and Y. Öhman ('The Origin of Unidentified Interstellar Absorption Lines', *Observatory* **62**, 150, 1939).

In order to assign the diffuse (yet fairly narrow) lines, the solid particles must be at very low temperature, a condition which is fulfilled in interstellar space. The interactions between the constituents must be weak; this excludes the metals in the crystalline state and the ionic crystals.

In the paper by Swings and Öhman several references concern the amorphous state, especially the investigations by J. Kramer who studied the solids obtained by condensation at low temperature. I have not found any convincing research of the kind published by Kramer around 1939. As a matter of fact, H. Beutler (private communication) did not consider that the results by Kramer were convincing. We hope that the identification of the diffuse interstellar lines will eventually be found, providing thus a new means of analysis of interstellar space and the dark clouds. Forty years after 1935 the diffuse interstellar lines remain as mysterious as ever.