

# HISTORICAL REMARKS ON THE DISCOVERY OF INTERSTELLAR MOLECULES

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## ABSTRACT

Last year was the 50th anniversary of the discovery of the first interstellar molecule, CH, by Swings and Rosenfeld. This discovery was based on optical spectra obtained by Dunham and Adams at Mt. Wilson Observatory. Three years later this discovery was confirmed by the identification of three additional lines of CH by A. McKellar. Furthermore, two other molecules, CN and CH<sup>+</sup>, were identified by McKellar, Douglas and the writer. It was more than twenty years later that the first molecule, OH, was identified by radio astronomical methods followed five years later by the first polyatomic molecule, NH<sub>3</sub>, by Townes and his associates. From then on the history is well known. Now more than 60 interstellar molecules are known and each year more are being observed. Two homonuclear molecules, H<sub>2</sub> and C<sub>2</sub>, have been added by optical methods. Of these H<sub>2</sub> is of course by far the most abundant. Strangely N<sub>2</sub> has not yet been found.

A few remarks are added about the diffuse interstellar lines, still an unresolved puzzle. Also the attention of radio astronomers is called to the possibility of detecting HeNe<sup>+</sup>.

*A. The First Interstellar Molecular Lines.* It is often considered by radio astronomers that the discovery of interstellar molecules is entirely a consequence of radio-astronomical studies. Actually the first observation of interstellar molecules was made twenty-six years before the first molecule was discovered by radio-astronomical methods. Indeed, this year we can celebrate the 50th anniversary of the discovery of the first interstellar molecule. This discovery was made by the Belgian astronomer P. Swings and his colleague the physicist L. Rosenfeld in 1937 on the basis of spectra obtained by Adams and Dunham with the then recently completed coude spectrograph at Mount Wilson Observatory. Dunham and Adams (1937) obtained high-resolution spectra of a number of early type stars, which showed several atomic lines in interstellar absorption, especially those of Ti II in the region 3073–3275 Å. Their remarkable (and unexpected) result was that only those lines appeared in interstellar absorption that came from the very lowest fine-structure level of the ground state <sup>4</sup>F<sub>3/2</sub> of the Ti<sup>+</sup> ion even though in the laboratory there are many other stronger lines coming from the other fine-structure levels of the ground state. This important observation indicated that Ti<sup>+</sup> ions and presumably other atoms and ions will always have plenty of time between collisions to go to the very lowest state even though this involves strongly forbidden transitions.

Dunham and Adams (1937) found in addition to the easily identified lines of

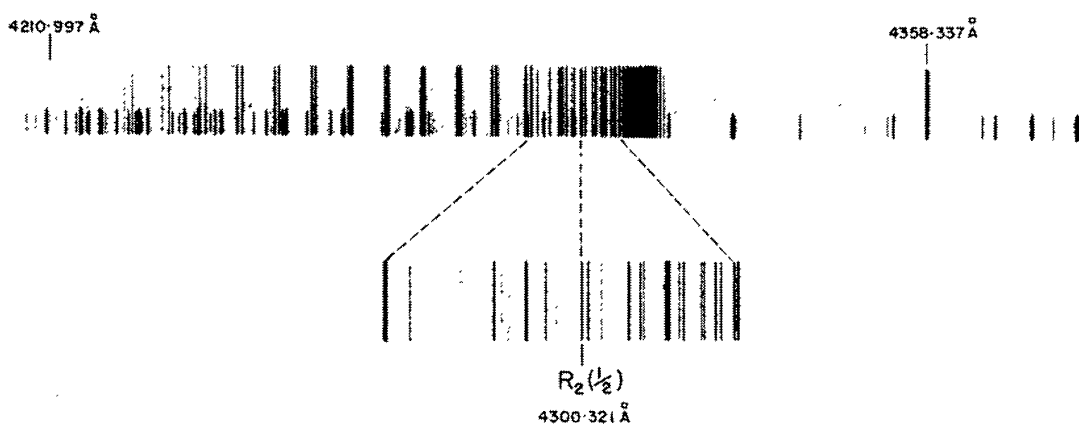


FIG. 1—The  $\text{CH } A^2\Delta - X^2\Pi$  band at  $4315 \text{ \AA}$  obtained from the flame of an ordinary Bunsen burner at high resolution showing the interstellar line at  $4300.3 \text{ \AA}$ .

$\text{Ti}^+$ , several other interstellar lines which they could not identify. In the same year Swings and Rosenfeld (1937), in Liège, Belgium, recognized the wavelength of one of the unidentified lines at  $4300.3 \text{ \AA}$  as agreeing with that of one of the lines in the  $4315 \text{ \AA}$  band of the CH molecule. When they looked closer they realized that the laboratory line with which the interstellar line agreed had as its lower rotational level the very lowest state of the ground state of CH. Figure 1 shows a laboratory spectrum of CH in the region  $4300 \text{ \AA}$  obtained simply from the flame of a Bunsen burner indicating that there are several hundred lines in this band, but the one line marked in the enlarged section of this spectrum with which they identified the interstellar line is the line called  $R_2(1)$  of CH. This coincidence (remembering Adams' and Dunham's results on Ti II and other atoms) made Swings' and Rosenfeld's identification quite secure even though at that point there was only one single line that was identified.

Three years after this identification the presence of CH was strikingly confirmed by the identification by the Canadian astronomer A. McKellar (1940) of several other CH lines in new interstellar spectra obtained by Adams (1941). The CH molecule has three excited electronic states  $A^2\Delta$ ,  $B^2\Sigma^-$ ,  $C^2\Sigma^+$  which are shown in the energy level diagram in figure 2. Transitions from these three excited electronic states to the ground state  $X^2\Pi$  have been observed in the laboratory at  $4315$ ,  $3880$  and  $3140 \text{ \AA}$ . What McKellar realized in 1940 was that there were three lines of the  $B^2\Sigma^- - X^2\Pi$  transition at  $3890.23$ ,  $3886.39$  and  $3878.77 \text{ \AA}$  that arise from the very lowest level of the ground state and all three lines (and no others) are present in Adams' (1941) interstellar spectra. Unlike the  $A^2\Delta - X^2\Pi$  transitions

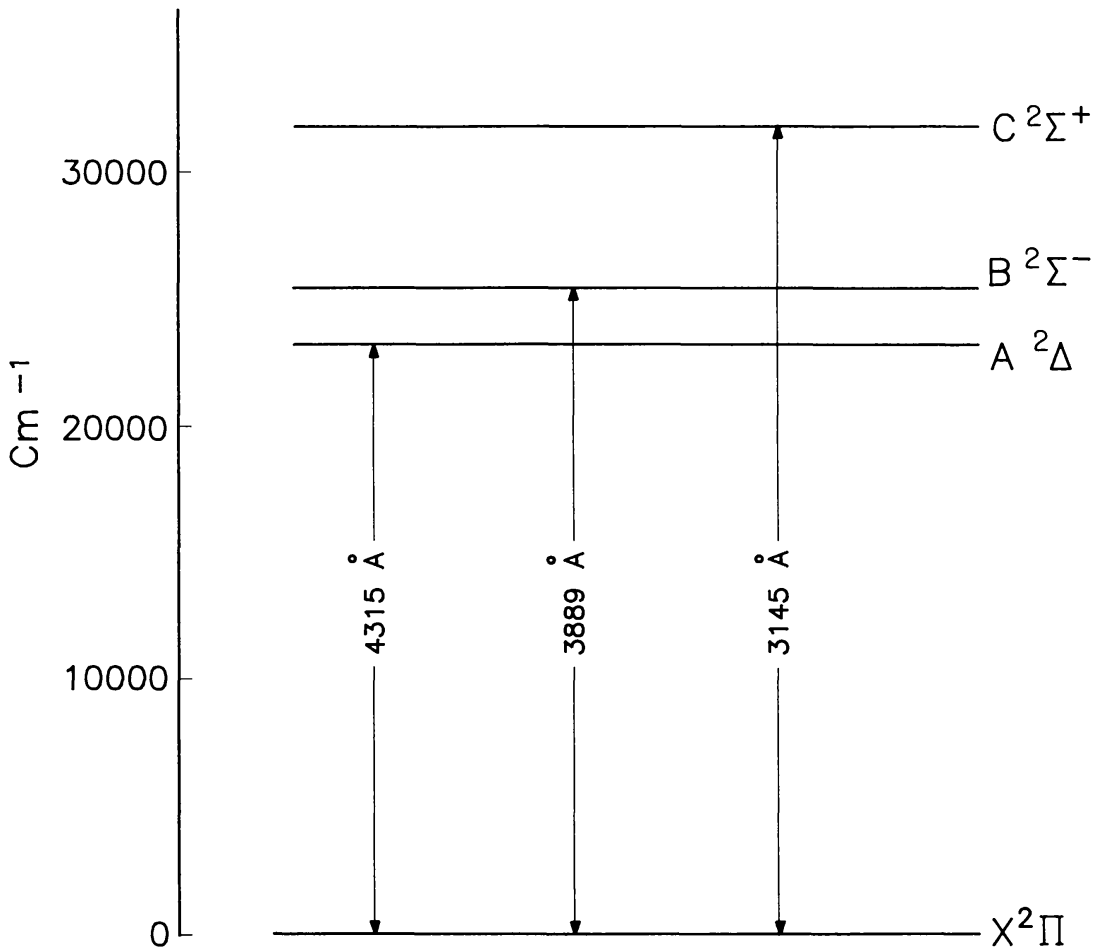


FIG. 2—Low-lying electronic states of CH and transitions between them.

here three lines arise rather than one because in a  $^2\Sigma$  state lower  $J$  values exist than in the  $^2\Delta$  state.

In the same year, 1940, McKellar also identified three further lines in the spectra of Adams (1941) as being due to lines of the  $B^2\Sigma^+ - X^2\Sigma^+$  transition of the CN molecule. The strongest of these lines at  $3874.61\text{\AA}$  is the R(0) line and comes from the lowest rotational level,  $N = 0$ . The other two lines at  $3874.00$  and  $3875.77\text{\AA}$  are the R(1) and P(1) lines with  $N = 1$  which are very much weaker in the interstellar spectra. A much better spectrum than those available to McKellar was recently obtained by Federman, Dank and Lambert (1984). It is shown in figure 3. The fact that in the case of CN two lines from the second lowest rotational level can be seen indicates that the rotational temperature in the interstellar medium is not exactly 0 but, as McKellar estimated, has a value of about 2.3K. This result agrees within its uncertainty with the much later discovery by Penzias and Wilson of the “3 degree” radiation now widely regarded as the residue of the “big bang”.

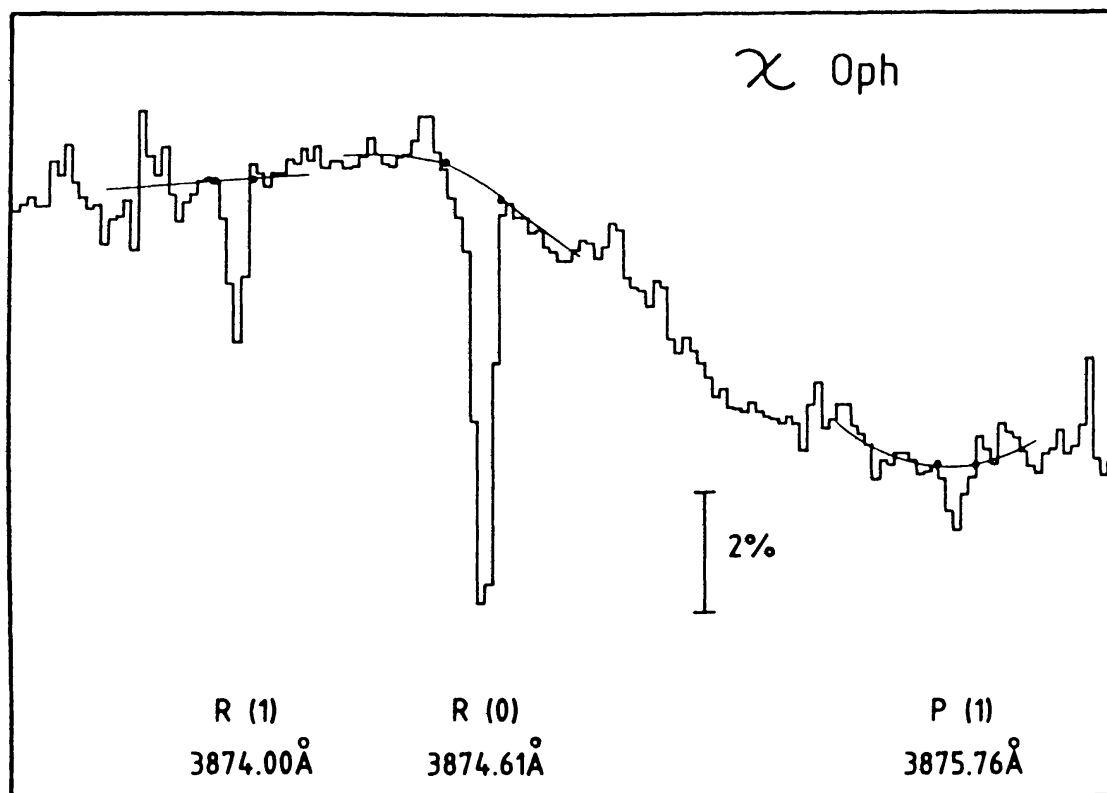


FIG. 3—Interstellar CN lines near 3875 Å in  $\chi$  Oph. after Federman *et al.* (1984). The R(0) and R(1) lines are superimposed on a broad Balmer emission line.

The third electronic transition of CH from the ground state to the  $C^2\Sigma^+$  state was identified only much later, in 1955, by McKellar and Richardson by one line at 3143.2 Å which comes from the lowest  $N = 1$  level of the ground state and is classified as  $Q_2(1) + {}^Q R_{12}(1)$ . It is interesting to realize that the  $C^2\Sigma^+$  upper state is slightly predissociated, that is, in the interstellar radiation field CH is being dissociated. There must therefore be a sufficiently rapid formation process to account for its presence (see Brzozowski, Bunker, Elander and Erman 1976).

In the list of interstellar lines discovered by Adams and Dunham there was still a series of sharp lines starting at 4232.6 Å which had not been identified. Dr. O. Struve, the director of the Yerkes Observatory at that time, organized an informal symposium on the interstellar medium in June 1941 which, among other things, was to deal with the unidentified interstellar lines. Those attending this symposium were, in addition to the members of the Observatory, P. Swings, E. Teller, R.S. Mulliken, H. Beutler and myself. The fact that the unidentified interstellar lines formed a progression of the type often observed in molecular spectra made it clear that they must be molecular in origin. Mulliken, who had just started his important series of papers on the structure of polyatomic molecules, suggested that the carrier of this spectrum might be the  $CH_2$  radical because he had predicted a

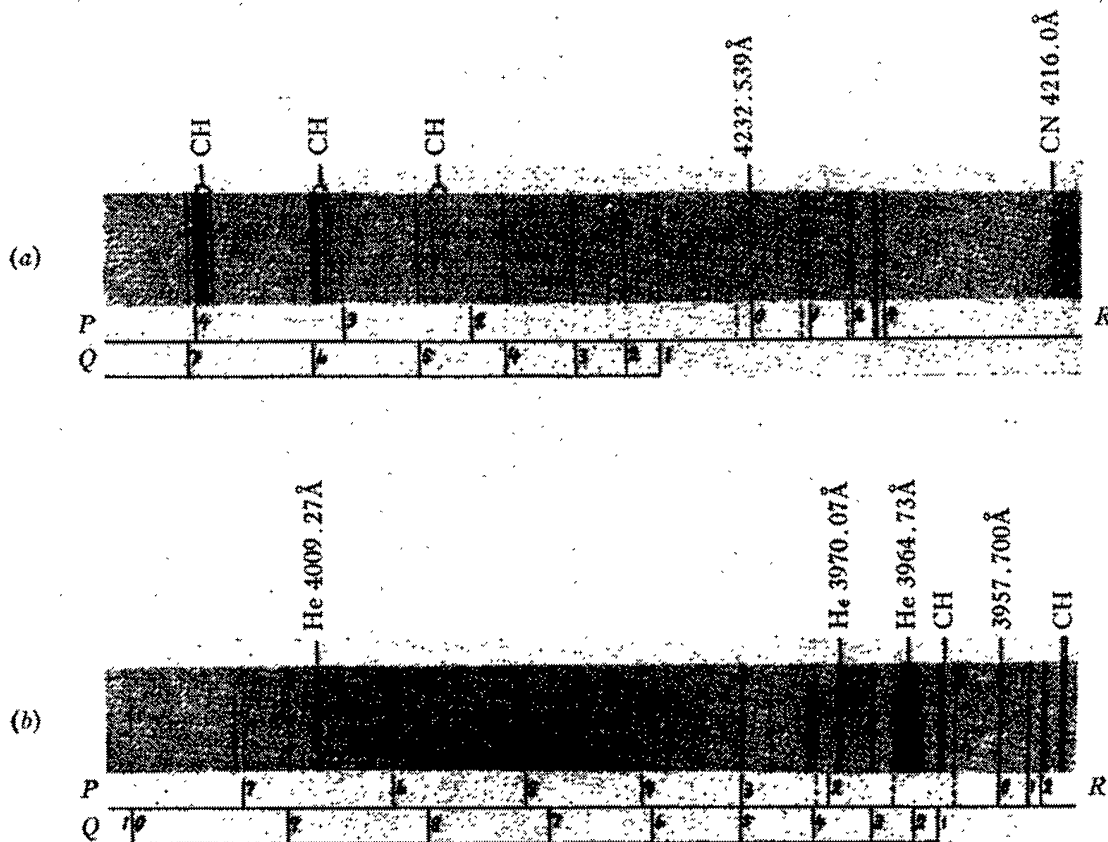


FIG. 4—CH<sup>+</sup> bands in the laboratory after Douglas and Herzberg (1942). (a) 0-0 band, (b) 1-0 band. The R(0) lines are the lines occurring in interstellar absorption.

<sup>1</sup>B<sub>1</sub>-<sup>1</sup>A<sub>1</sub> transition which he estimated to be in just the spectral region near 4000 Å. Other participants doubted that a polyatomic system was likely to be present. Teller and I suggested CH<sup>+</sup> whose spectrum at the time was unknown. From the similarity to the known iso-electronic system BH it seemed likely that CH<sup>+</sup> would have an electronic band system of the required type near 4000 Å.

I returned to Saskatoon from this meeting strongly encouraged to try to produce this spectrum in the laboratory. It so happened that A.E. Douglas, then a graduate student of mine, had a suitable discharge tube ready. On the first try with a mixture of helium and benzene vapour in this tube we were able to observe a new spectrum which turned out to be the spectrum of CH<sup>+</sup> (Douglas and Herzberg 1941, 1942). Part of this spectrum is shown in figure 4. It consists of bands with a simple structure; each band has a single P, Q and R branch in agreement with the predicted structure of a <sup>1</sup>Π - <sup>1</sup>Σ<sup>+</sup> transition as observed for the iso-electronic BH and in accordance with molecular orbital predictions. Most importantly we found that in each of the 0-0, 1-0 and 2-0 bands observed in the laboratory the first line of the R

TABLE I.  
COMPARISON OF LABORATORY AND INTERSTELLAR WAVE-  
LENGTHS OF CH<sup>+</sup> LINES

	R(0) laboratory	Interstellar line	$\Delta$
0-0	4232.539 Å	4232.58 Å	- 0.041
1-0	3957.700	3957.72	- 0.020
2-0	3745.310	3745.330	- 0.020
3-0	(3579.02)	3579.04	- 0.02
4-0	(3447.08)		

branch R(0) agreed accurately with the three unidentified interstellar lines. In Table I the laboratory data on CH<sup>+</sup> are compared with the interstellar measurements. Here the wavelength of the 3-0 band determined indirectly by Douglas and Morton (1968) and the wavelength of the fourth interstellar absorption line has been added.

In this way the presence of the CH<sup>+</sup> ion in the interstellar medium was established in addition to the previously established CH and CN. CH<sup>+</sup> was the first interstellar molecular ion; it was many years later followed by several other molecular ions. It is to be noted that CH<sup>+</sup> was like CH and CN observed in absorption; it was until 1970 the only molecular ion for which an absorption spectrum had been found either in the laboratory or in space.

*B. The First Molecules Discovered by Radio-Astronomical Methods.* A molecule similar to CH, with a <sup>2</sup>Π ground state, is OH. However, its optical resonance lines lie in the region of 3060Å near the edge of transmission of the atmosphere. It is difficult to observe these lines because of the interference of the ozone absorption bands due to our own atmosphere. As soon as the radio frequency spectrum of OH had been measured in the laboratory by Townes and others, attempts were made to observe this radio-frequency spectrum in astronomical sources. It took, however, several years before the first success was obtained and it was only in 1963, that is 26 years after the discovery of CH by optical astronomers, that Weinreb, Barrett *et al.* (1963) observed the first lines of OH. They are near 1665 MHz and represent transitions between the Λ doublet components of the lowest rotational level J = 3/2 of <sup>2</sup>Π<sub>3/2</sub>; they are split by hyperfine structure. Corresponding lines of CH should also have been observable early on but were actually observed ten years later by Rydbeck, Elldér and Irvine (1973). Conversely the optical observation of OH was only accomplished in 1976 by Crutcher and Watson using the line at 3078Å.

The radio observation of OH encouraged several radio astronomers to consider the possibility of identifying lines of polyatomic molecules in the radio frequency

TABLE II.  
FIRST MOLECULES DETECTED BY RADIO-FREQUENCY METHODS

Molecule	Year	$\nu$ (MHz)	Transition
OH	1963	1665	$\Lambda$ -doubling; $J = 3/2$
NH <sub>3</sub>	1968	23694	(1,1) inversion
H <sub>2</sub> O	1969	22235	$5_{23}-6_{16}$ rotation
H <sub>2</sub> CO	1969	4830	$1_{10}-1_{11}$ K doubling
CO	1970	115271	1-0 rotation
HCN	1970	88632	1-0 rotation
HC <sub>3</sub> N	1970	9098	1-0 rotation

region. The first success, as is well known, was obtained by Townes and his colleagues in 1968 with NH<sub>3</sub> and shortly thereafter with H<sub>2</sub>O, both in emission. Soon after that Snyder *et al.* observed formaldehyde (H<sub>2</sub>CO) in absorption and from then on several new molecules were found each year. One of the most important and abundant is CO. In Table II the first molecules found in the radio region are listed.

*C. Homonuclear Molecules.* For all practical purposes, radio-frequency methods are powerless to detect homonuclear molecules like H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> in the interstellar medium. Optical methods can be applied only when there are suitable excited electronic states; in all but one case this makes it necessary to take the spectra from outside our own atmosphere, that is, by rocket or satellite-based spectrometers. The first identification of H<sub>2</sub> was made in 1970 by Carruthers (1970) by means of rockets. Much higher resolution in the vacuum ultraviolet was obtained by means of the *Copernicus* satellite by the Princeton group (Spitzer, Drake, Jenkins, Morton, Rogerson and York 1973). One of their spectra is shown in figure 5 and is compared with a laboratory spectrum obtained at N.R.C. The comparison of the two spectra leaves no doubt that there are large amounts of H<sub>2</sub> in the interstellar medium. In this case because of the very strongly forbidden nature of rotational transitions the spectrum shows not only the R(0) lines but also higher rotational lines.

The intensity of the hydrogen absorption is so large that even the isotopic molecule HD can be observed (Morton 1975). At N.R.C. at the time we had new measurements of the HD laboratory spectrum (Dabrowski and Herzberg 1976) and it was satisfying to see that the new measurements compared with the astronomical data left no doubt that HD was present.

As a laboratory spectroscopist I had always told my colleagues that the infrared quadrupole rotation-vibration spectrum of H<sub>2</sub> was useless to detect H<sub>2</sub> in

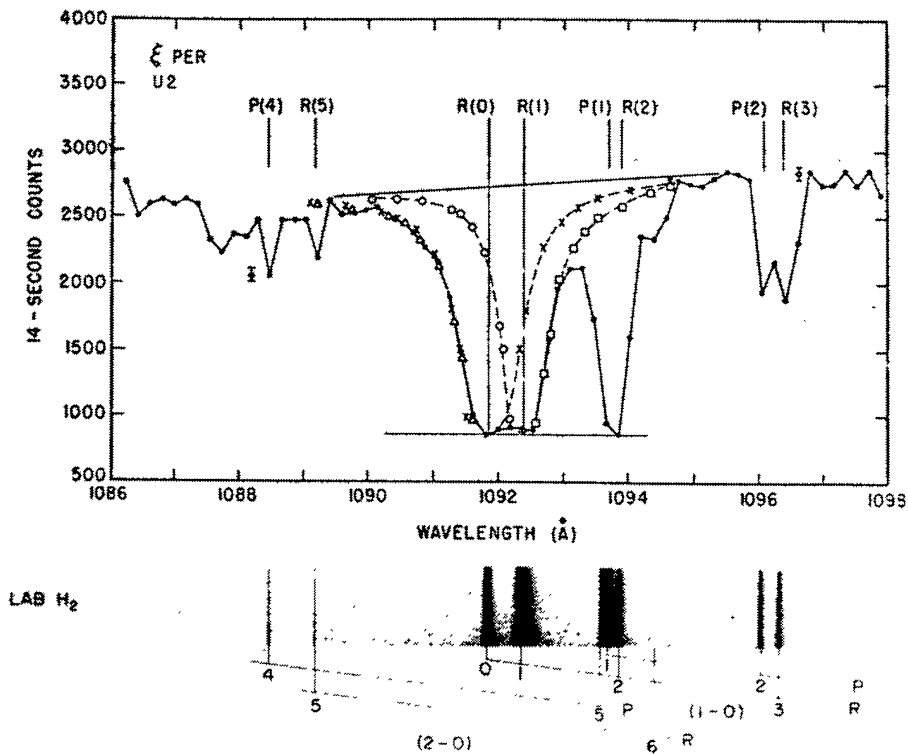
INTERSTELLAR  $H_2$ 

FIG. 5— $H_2$  absorption bands near  $1090 \text{ \AA}$  in interstellar space after Spitzer *et al.* (1973) and in the laboratory.

astronomical objects other than planetary atmospheres because of the very low intensity of this highly forbidden transition. It came therefore as a considerable surprise to me when in 1976 infrared astronomers observed several lines of this quadrupole spectrum in emission in the Orion nebula and later in many other sources including other galaxies. The possibility of such emission becomes clear when one realizes that at the extremely low density in interstellar space each  $H_2$  molecule once excited to higher rotational and vibrational levels will have sufficient time to make these forbidden transitions. Therefore the intensity depends only on the excitation mechanism. The excitation is generally considered to be by the shock waves which arise in the formation of new stars and cause excitation of vibrational levels with  $v > 0$ . Figure 6 shows a beautiful spectrum obtained by Connes and colleagues (Davis *et al.* 1980) showing the Q branch of the 1-0 band of  $H_2$  in Orion. Figure 7 shows an observation of the S(1) line of the same spectrum in the galaxy N.G.C. 6240 (Joseph, Wright and Wade 1984).

The  $C_2$  molecule has an absorption in the visible region namely the Phillips bands which represent a  ${}^1\Pi_u - {}^1\Sigma_g^+$  transition. Several lines of this transition near  $8750 \text{ \AA}$  were found in 1978 by Chaffee and Lutz. Up to now neither  $N_2$  or  $O_2$  has



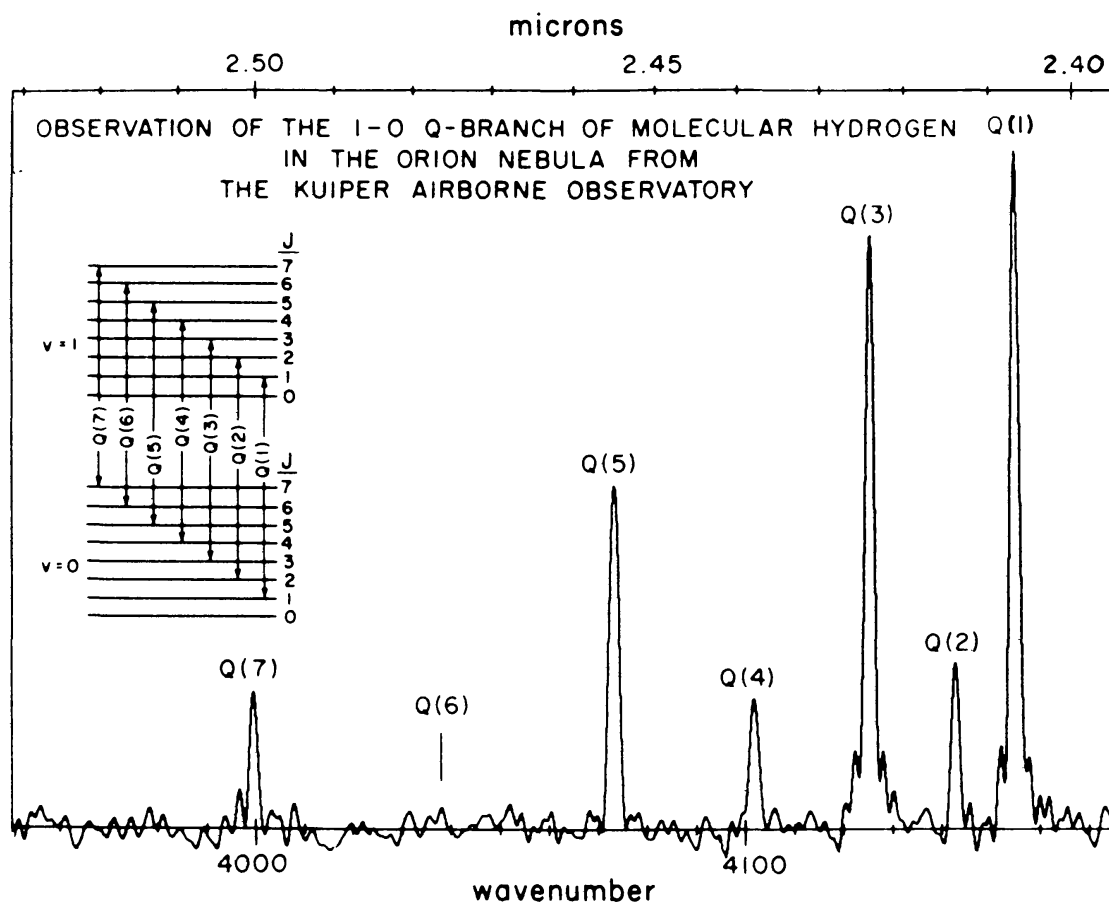


FIG. 6—Infrared emission of the Q branch of the 1-0 quadrupole  $H_2$  band in the Orion nebula, observed by Davis *et al.* (1980).

been observed in interstellar clouds even though they must surely be present. But of course the abundance is smaller by a factor of 1000 than that of  $H_2$  and they are therefore difficult to observe. On the other hand, CO, first observed in the radio frequency region has been observed in the vacuum ultraviolet by Jenkins *et al.* (1973). Figure 8 shows a comparison of one of their spectra with a laboratory spectrum of the  $C^1\Sigma^+ - X^1\Sigma^+$  transition.

*D. Diffuse Interstellar Lines.* There is another jubilee that we might celebrate in 1987 and that is the 50th anniversary of the discovery of the diffuse interstellar lines by Merrill, Sanford, Wilson and Burwell (1937). The strongest of these diffuse interstellar lines and the first one to be discovered occurs at  $4430\text{\AA}$ . In 1938 it was confirmed in a detailed study by Beals and Blanchet and thus it also has a Canadian aspect. Figure 9 shows an old spectrum in which this feature is prominent.

A large number of attempts have been made to identify the origin of these

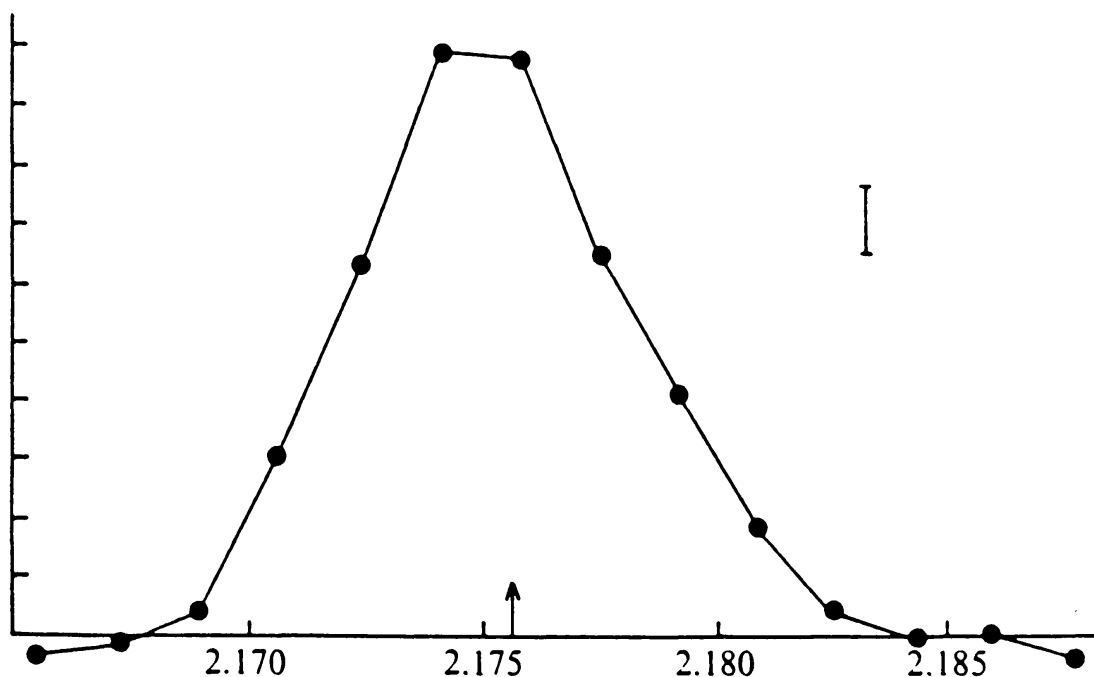


FIG. 7—S(1) line of the 1-0 quadrupole band of  $H_2$  observed in the luminous infrared galaxy N.G.C. 6240 by Joseph *et al.* (1984). The arrow shows the wavelength of the  $2.122 \mu\text{m}$  S(1) line red shifted to the radial velocity of the galaxy.

diffuse interstellar lines (or bands). There are now perhaps one or two hundred different explanations but up to now none of them has been generally accepted. Until a few years ago most astronomers favoured the idea that the lines originate from interstellar dust. I myself have always favoured the molecular origin of these lines and believe that their diffuseness is caused by predissociation of the molecule responsible. A variation of this idea has been suggested by the late A.E. Douglas (1977) who thought it more likely that the diffuseness is caused by “internal conversion” in a somewhat larger molecule. Recently Léger *et al.* (1986) suggest that they have found the solution in the assumption that the diffuse bands are due to polycyclic aromatic hydrocarbons or their ions. I have not been able to follow their argument nor have I been able to see how such complicated molecules can form in interstellar space in sufficient numbers to give rise to fairly strong absorption features. Note also that radio astronomers thus far have not found even a single aromatic molecule.

If the molecule responsible for the diffuse interstellar lines would be a simple neutral molecule it would surely have been identified long ago. Therefore I have looked for possible spectra of molecular ions since many of them are incompletely known or not known at all. The photoelectron spectrum of a molecule gives information about the energy levels of the corresponding ion. I have found one ion  $\text{HCOOH}^+$  which has according to the photoelectron spectrum, energy levels

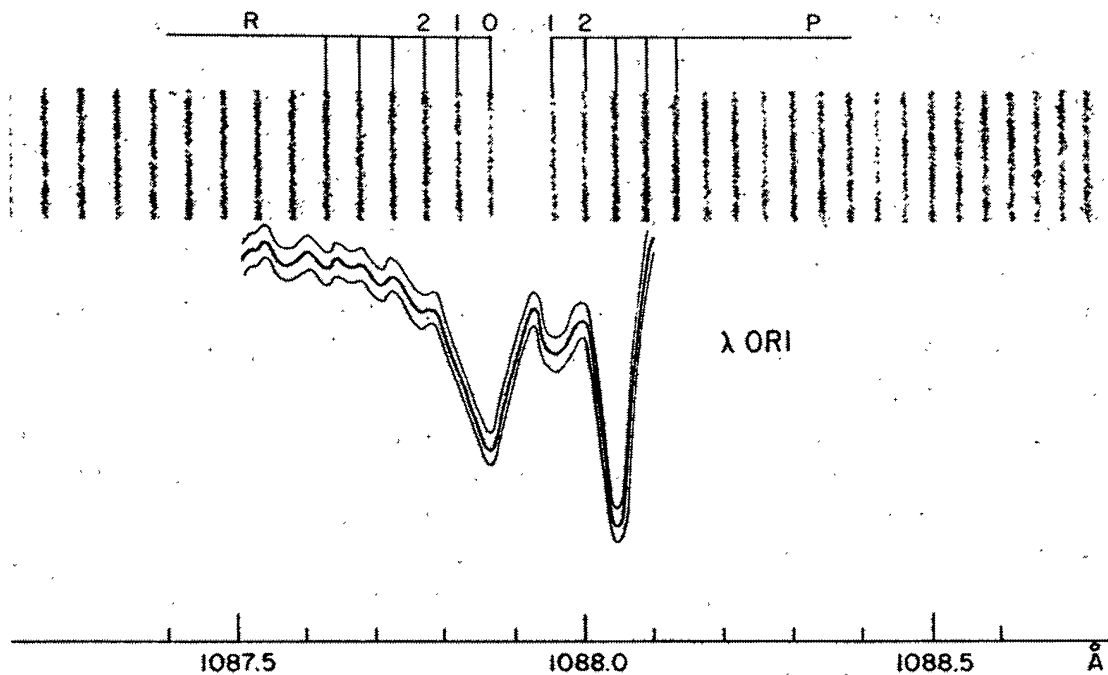


FIG. 8—0-0 band of the  $C^1\Sigma^+ - X^1\Sigma^+$  transition of CO as observed by Jenkins *et al.* (1973) in the spectrum of  $\lambda$  Ori, compared with a high resolution laboratory spectrum obtained at N.R.C. The sharp line at 1088.05 Å, which is not CO, has yet to be identified.

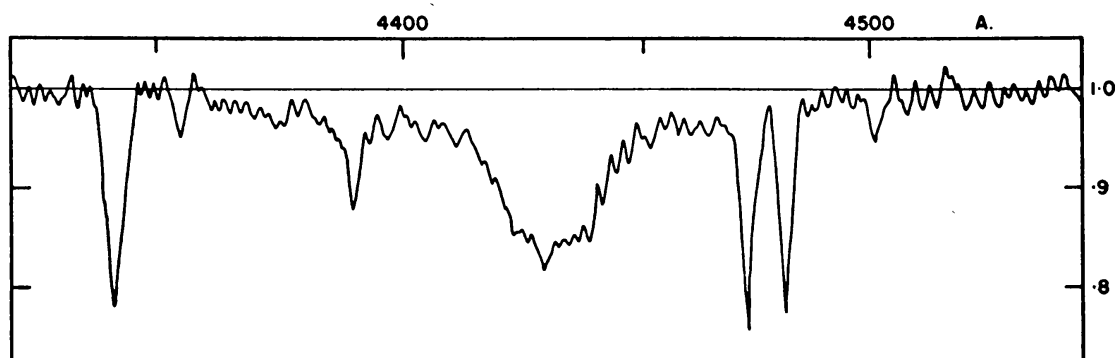


FIG. 9—Diffuse interstellar band at 4430 Å after Wilson (1958).

which might give rise to the two strongest features at 4430 Å and 2250 Å. Experiments at the Max-Planck Institute for Quantum Optics are in progress to test this hypothesis but so far have not led to a definite answer. It is perhaps relevant to mention that formic acid ( $HCOOH$ ) as well as protonated  $CO_2$ , that is  $COOH^+$ , have been observed in interstellar clouds and that the formation of the formic acid ion from  $COOH^+$  needs only the addition of one hydrogen atom. The question

would be whether such a radiative combination process would be sufficiently fast to account for the formation of  $\text{HCOOH}^+$ ; according to the hypothesis of predissociation as the cause of diffuseness, the ions would be dissociated every time a light quantum is absorbed within the line width of the diffuse lines.

*E. Conclusion.* In concluding this brief historical survey I would like to call to the attention of radio astronomers a molecular ion which is likely to play an important role in interstellar clouds, namely  $\text{HeNe}^+$ . The optical emission spectrum of this ion was studied in some detail ten years ago in this laboratory (Dabrowski and Herzberg 1978). Unfortunately the nature of the spectrum is such that it is not possible to determine directly the molecular constants of the lowest vibrational level of the ground state. In the laboratory, transitions take place from an excited state  $\text{B}^2\Sigma^+$  to the  $\text{A}^2\Pi$  state and to the  $\text{X}^2\Sigma^+$  ground state. However on account of the Franck-Condon principle only higher levels of the ground state are reached. For these higher levels very precise constants are known but for lower levels one is dependent on extrapolation. In interstellar clouds there is plenty of time to go from the higher to the lower levels of the ion and therefore it should be possible to see this ion in microwave or infrared absorption. Perhaps some ingenious method will be found in the laboratory to improve the extrapolation of the molecular constants, or theoretical work might lead to a satisfactory prediction. At any rate, in view of the high relative abundance of helium and neon it seems very likely that  $\text{HeNe}^+$  is present.

In concluding I would like to congratulate Grote Reber on this 50th anniversary of his great work which has led to many of the fine results we have nowadays on interstellar molecules. I would also like to express the hope that our radio astronomy group at N.R.C. will have much success in their work with the James Clerk Maxwell Telescope which is just beginning to make observations in the sub-millimeter wavelength region.

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