

INVITED DISCOURSES

THE INTERPLAY OF MOLECULAR SPECTROSCOPY AND ASTRONOMY

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Carlyle S. Beals, former Dominion Astronomer of Canada and one of the most distinguished astronomers Canada has produced, died on 2 July, 1979. Carl Beals was not only a great astronomer, known throughout the astronomical world for his studies of Wolf-Rayet stars and many other contributions to astronomy, but he was also a great human person who exercised considerable influence on the development of astronomy in Canada and elsewhere. I should like to dedicate this lecture to the memory of Carl Beals.

A. INTRODUCTION

All information about the composition of stellar atmospheres, of planetary nebulae, of the interstellar medium, of comets, and until very recently also of planetary atmospheres, has come from the study of the spectra of these objects. When looking at the history of the subject it is therefore not surprising to find that there has been a close connection and interaction between laboratory spectroscopy and astronomical spectroscopy. This interplay is obvious to every astronomer for atomic spectroscopy. I only need to remind you of the facts that it was the astronomer H.N. Russell who had a decisive part in the formulation of the language we use to-day in atomic spectroscopy (the Russell-Saunders coupling, etc.), that the laboratory spectroscopist I.S. Bowen first provided the explanation of the nebular lines as forbidden transitions in O^+ , O^{++} , N^+ , etc. and subsequently became so involved in astronomy that he was selected as the first Director of the Mount Palomar Observatory, and that it was the laboratory spectroscopist

Edlén who first recognized on the basis of his laboratory studies the nature of the coronal lines. Here as in many other cases it was the unusual nature of the astronomical conditions, the exceedingly low densities and high temperatures, that caused the appearance of spectral features not normally observed in the laboratory.

The same sort of interplay has occurred between molecular spectroscopy and astronomy but is perhaps less well known. It is the purpose of this lecture to illustrate this interplay by a number of examples and to show that much progress in astronomy is based on laboratory studies in molecular spectroscopy and that conversely certain advances in molecular spectroscopy are based on studies of astronomical spectra.

B. STELLAR ATMOSPHERES

In order to understand the differences of the intensities of molecular features observed in different stars it is necessary to calculate the dissociation equilibrium as a function of temperature and pressure assuming certain abundance ratios of the elements. This was first done by Cambresier and Rosenfeld (1933) and by Russell (1934). For these calculations a knowledge of dissociation energies and other molecular constants is required. Some of these constants, particularly for several of the most important molecules, were in doubt for a long time and made the result of the calculations of the dissociation equilibrium rather uncertain. Indeed, at one time an attempt was made to settle the question of the dissociation energy of CO by establishing which of the two or three possible values for this quantity fitted best with the astronomical observations. The problem of the dissociation energies has now been largely solved by laboratory experiments and the latest values of these constants for some of the astronomically more important molecules are listed in Table I. In this table only the value for CN is still somewhat uncertain.

As an example of the application of these laboratory data I present in Figure 1 the dependence of the dissociation equilibrium on temperature for carbon-rich stars, as given in Fujita's (1970) well-known book. It is seen from this figure that, in addition to many diatomic molecules, there are also a number of polyatomic molecules which are expected to be present at lower temperatures in these atmospheres (involving, of course, the knowledge of some polyatomic dissociation energies not given in Table I). Particularly prominent are HCN, C₂H₂ and CH₄, while others, like H₂O and

Table I. Dissociation energies (D_0^0 in eV) of diatomic molecules

AlH	<3.06	H ₂	4.4781	O ₂ ⁺	6.663
AlO	5.27	HD	4.5138	OH	4.392
C ₂	6.21	H ₂ ⁺	2.6508	OH ⁺	5.0 ₉
CH	3.46 ₅	HCl	4.433 ₆	SH	3.5 ₅
CH ⁺	4.08 ₅	N ₂	9.759 ₄	SiC	4.6 ₄
CN	7.7 ₆	N ₂ ⁺	8.712 ₈	SiH	≤3.06
CO	11.09 ₂	NH	≤3.47	SiO	8.26
CO ⁺	8.33 ₈	NO	6.496 ₈	SO	5.359
CS	7.35 ₅	NO ⁺	10.850 ₆	TiO	6.87
GeO	6.78	O ₂	5.115 ₆	ZrO	7.85

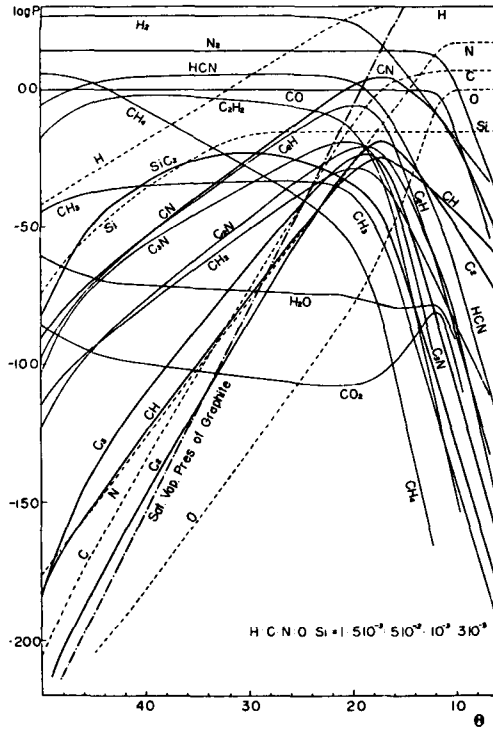


Fig. 1. Dissociation equilibrium in carbon-rich stars after Fujita (1970).

The abscissa is $\theta = 5040/T$, i.e. temperature increases to the right.

CO_2 , are of less importance in these carbon-rich stars. In oxygen-rich stars the predicted abundances are quite different and H_2O , for example, is predicted to be the most abundant of the polyatomic species. An observation of these polyatomic molecules in stellar atmospheres is very difficult and only very few have been definitely assigned. One of these polyatomic species is SiC_2 which was assigned by a laboratory study of Kleman (1956) who reproduced the Merrill-Sanford bands observed in many carbon stars in the laboratory by studying the absorption spectrum of silicon in a carbon tube furnace. He established the carrier of the spectrum by noting the presence of a C-C vibration as well as a C-Si vibration in the vibrational structure of the band system.

Not only the molecular composition but also certain molecular processes in stellar atmospheres can be studied by comparing laboratory and astronomical data. A striking example is the observation of strong emission lines at certain phases of long period variables like χ Cygni. These were identified by Herbig (1956) on the basis of the laboratory work on AlH. Bengtsson-Knave and Rydberg (1930) observed in the $A \ ^1\Pi - X \ ^1\Sigma^+$ system of this molecule a characteristic predissociation involving a breaking-off of the rotational structure at a fairly low value of the rotational quantum number. Stenvinkel (1939) was the first to observe in the laboratory the inverse process: the emission in a King furnace filled with aluminum and hydrogen of just those lines which are missing in ordinary emission spectra. The same phenomenon occurs apparently in long period variables like χ Cygni: the previously unidentified lines are AlH lines of high J above the normal breaking-off point. In other words, aluminum and hydrogen atoms come together and via a radiationless transition go over into quasi-bound excited states ($A \ ^1\Pi$) which may, in a small percentage of the collisions, lead to emission of the lines in question.

While there are many other examples of inverse predissociation studied in the laboratory that of AlH is as yet the only one observed in stellar atmospheres.

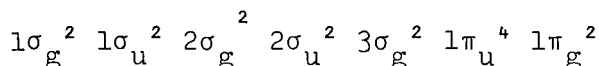
C. PLANETARY ATMOSPHERES

(1) Spectra of the O_2 molecule in the atmospheres of the earth and Venus

The so-called atmospheric oxygen bands have been known ever since solar spectra have been studied in the red region, that is, below 7700 Å. Such studies go back well

over one hundred years but it was only fifty years ago that these features were studied in the laboratory and that the nature of the transition involved was clearly recognized. It was Mulliken (1928) who suggested that the transition is ${}^1\Sigma^- - {}^3\Sigma$ and it was Van Vleck (1934) who recognized that the transition was a magnetic dipole transition similar to some of the nebular lines.

The lowest electron configuration in the oxygen molecule is

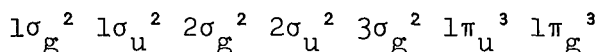


which gives rise to the three states ${}^3\Sigma_g^-$, ${}^1\Delta_g$ and ${}^1\Sigma_g^+$. It is the transition from the ${}^1\Sigma_g^+$ state to the ${}^3\Sigma_g^-$ ground state which accounts for the atmospheric oxygen bands. It is a g-g transition and therefore can occur only because of the magnetic dipole connected with it. The observation of this transition is a nice confirmation of molecular orbital theory which predicted that the triplet state should be the ground state of O_2 and that therefore O_2 should be paramagnetic, as is indeed observed.

The ground electron configuration of O_2 gives, in addition to the ${}^3\Sigma_g^-$ and ${}^1\Sigma_g^+$ states, also a ${}^1\Delta_g$ state which was first observed in liquid oxygen by Ellis and Kneser (1933) and later observed in the solar spectrum at 12500 Å, with its fine structure well resolved (Herzberg 1934). The analysis of the fine structure confirms that this transition is ${}^1\Delta_g - {}^3\Sigma_g^-$ and completes the confirmation of molecular orbital theory for the lowest states of the oxygen molecule.

Recently the two low-lying singlet states of oxygen, especially the ${}^1\Delta$ state, have become of considerable chemical and biological (and even medical) importance as energy carriers, so much so that there was an international conference entirely devoted to the subject in 1977 at Pinawa, Manitoba. I believe it is fair to say that this whole large subject owes its beginning to the interplay between the study of the solar spectrum and molecular spectroscopy.

The first excited electron configuration of O_2 is



which gives rise to the six states ${}^1\Sigma_u^+$, ${}^3\Sigma_u^+$, ${}^1\Sigma_u^-$, ${}^3\Sigma_u^-$, ${}^1\Delta_u$, ${}^3\Delta_u$. Of these states only one, ${}^3\Sigma_u^-$, can combine as an allowed (electric dipole) transition with the ground

state, giving rise to the well-known Schumann-Runge bands which start at 1950 Å and whose adjoining continuum accounts for the opaqueness of the atmosphere, and of air in general, below 1900 Å.

The first application of the long path technique for the study of forbidden transitions yielded the discovery of the forbidden transition from the ground state to the ${}^3\Sigma_u^+$ state of the above set (Herzberg 1932, 1952a). This system, now called A ${}^3\Sigma_u^+ - X {}^3\Sigma_g^-$, and the systems c ${}^1\Sigma_u^- - X {}^3\Sigma_g^-$ and B ${}^3\Delta_u - X {}^3\Sigma_g^-$ discovered later (Herzberg 1953) turned out to be of considerable importance for the understanding of various phenomena in the earth's atmosphere. In particular, the continuum joining on to the first system accounts for the production of free oxygen atoms at fairly low heights and gives rise in the nightglow to the most prominent emission features in the near ultraviolet. The second system, c ${}^1\Sigma_u^- - X {}^3\Sigma_g^-$, has been observed as the most prominent feature in the nightglow of Venus: it was first observed in spectra taken by Venera 9 by Krasnopolsky et al. (1976) and identified and reproduced in the laboratory by Lawrence, Barth and Argabright (1977).

(2) Spectra of CH₄ in the outer planets

The strong absorption bands in the outer planets in the red and yellow regions of the spectrum were first recognized as being due to higher overtones in the rotation-vibration spectrum of CH₄ by Wildt (1932) on the basis of laboratory experiments. With the exception of a simple feature at 1.13 μ (presumably the second overtone of ν_3) all observed absorption bands of CH₄ in the shorter wavelength region have a very complex rotational structure which is not yet understood. One reason for the complexity is the fact that in a spherical top molecule like CH₄ the upper state of, for example, the third overtone, $4\nu_3$ at 8400 Å, on account of anharmonicity decomposes into seven sub-levels: $2A_1 + 2E + F_1 + 2F_2$, of which the two F_2 sub-levels can combine with the ground state. In addition, close by is the level $\nu_1 + 3\nu_3$, which decomposes into $A_1 + F_1 + 2F_2$, and the level $2\nu_1 + 2\nu_3$, which decomposes into $A_1 + E + F_2$ and, finally, the level $3\nu_1 + \nu_3$ which gives rise to only one state, F_2 . All the F_2 components can combine with the ground state so that there is a total of six allowed sub-bands. All of these can perturb one another by Fermi interaction and in addition perturbations with the other nine sub-levels can take place via Coriolis interactions which in a molecule like CH₄ may be quite strong. Thus it is perhaps not too surprising that the higher overtones observed in the spectra of the outer planets have not been analysed.

(3) Detection of H₂ and HD in the outer planets

Teller (1934) in his handbook article mentioned the possibility that H₂, N₂ and O₂ which have no ordinary dipole infrared spectrum may have a quadrupole infrared spectrum; but the intensity of such spectra would be 10⁻⁹ times that of normal dipole spectra. I remembered this remark when two years later I became aware of the problem of detecting hydrogen in the atmospheres of the outer planets and I derived the expected wavelengths of the quadrupole spectrum from the vacuum ultraviolet spectrum of hydrogen (Herzberg 1938). At the same time James and Coolidge (1938) derived from ab initio theory the relative and absolute intensities of the expected lines. At that time no planetary spectra of sufficient resolution were available to detect these lines had they been present.

In 1948 after having set up a long absorbing path at Yerkes Observatory which allowed obtaining the equivalent of 50 km atm I succeeded in observing a few lines of the 2-0 and 3-0 bands of the quadrupole spectrum of H₂ in the laboratory (Herzberg 1949, 1950a). The first observation of some of these lines in Jupiter was made by Kiess, Corliss and Kiess (1960). Later the 4-0 band, which could now be predicted much more accurately from new vacuum ultraviolet laboratory studies, was observed in Jupiter, Saturn and Uranus (Giver and Spinrad 1966, Owen and Mason 1968, Fink and Belton 1969, Owen 1969, Trafton 1973). The 4-0 band has only very recently been observed in the laboratory by Bergstralh, Margolis and Brault (1978) and by Trauger, Mickelson and Larson (1978). Comparison of these laboratory data with the planetary spectra shows that in Jupiter above the cloud layer there are more than 200 km atm of hydrogen and in Uranus 600 km atm.

Even before the first observation of the quadrupole spectrum of hydrogen in Jupiter the pressure-induced dipole spectrum of hydrogen was identified in Uranus on the basis of laboratory experiments at Ottawa. In particular a diffuse absorption feature at 8270 Å, observed by Kuiper in Uranus, represents the S(0) line of the 3-0 band in this pressure-induced spectrum (Herzberg 1952b). Other pressure-induced lines were observed later by Spinrad (1963) (see however Welsh 1969 and Belton and Spinrad 1973). The recent Voyager I spectra show the S(0) and S(1) lines of the pressure-induced rotation spectrum in the far infrared (Hanel et al. 1979).

In 1938 the possibility of observing HD was also mentioned and its predicted spectrum was calculated from

the vacuum ultraviolet data. The first observation of the laboratory infrared spectrum of HD was made in 1950 (Herzberg 1950b) but not until 1973 was one HD line observed in Jupiter by Trauger et al. (1973). McKellar, Goetz and Ramsay (1976) have made careful laboratory measurements of the intensity of the overtones of HD. By comparing the laboratory data for the dipole spectrum of HD and the quadrupole spectrum of H₂ with the Jupiter observations by Trauger et al. and the Saturn and Uranus observations of Macy and Smith (1978) a value of about 5×10^{-5} is obtained for the ratio of deuterium to hydrogen in these planetary atmospheres. A similar value was derived for Jupiter by Beer and Taylor (1973) from the observation of bands of CH₃D.

D. COMETS

(1) Comet head

Almost all spectral features observed in the heads of comets are due to free radicals. Most of these were readily identified since the spectra of these radicals had been available from laboratory studies for a long time. This applies to CN, C₂, CH, NH and OH. An important step in the development of our knowledge about the physical phenomena in comets was the recognition of the fluorescence mechanism for all cometary emissions. This mechanism is demonstrated particularly clearly by the observation of irregularities in the intensity distribution in the rotational structure of cometary bands, as was first demonstrated by Swings (1941, 1943) and McKellar (1942, 1943). Figure 2 shows as an example the CN band at 3883 Å as observed in Comet Bennett (1970 II) by Aikman, Balfour and Tatum (1974). Anomalous minima in the intensity distribution are clearly recognizable, and, according to

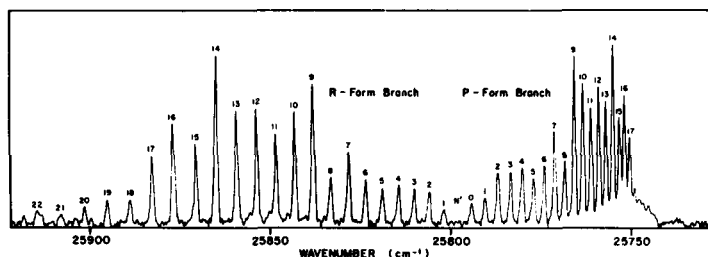


Fig.2. Rotational structure of the 0-0 band of CN at 3883 Å as observed in Comet Bennett (1970 II) by Aikman, Balfour and Tatum (1974).

Swings, are due to the Fraunhofer lines in the solar spectrum which give reduced fluorescence excitation for the particular wavelengths. Indeed shifts of the various anomalous minima are observed depending on the velocity of the comet relative to the sun.

An important problem in the study of comets is the evaluation of the production rates of the observed radicals. The determination of these production rates requires the knowledge of the lifetimes of the upper state or, in other words, the f values of the transitions. Much laboratory work on lifetimes has been stimulated in this way and it is fair to say that these lifetimes are now fairly well known. Table II lists recent values for the more important cometary transitions. Because of uncertainties in the intensities the resulting production rates are known only by order of magnitude. For example, for OH Feldman et al. (1974) give at 1 A.U. for Comet Kohoutek $0.8 \times 10^{29} \text{ sec}^{-1}$, for H $5.4 \times 10^{29} \text{ sec}^{-1}$ while Delsemme and Combi give for H_2O^+ in Comet Bennett $6 \times 10^{26} \text{ sec}^{-1}$ (Delsemme and Combi 1976).

Table II
Lifetimes (τ in nsec) of upper
states of cometary bands

Molecule	State	τ	Molecule	State	τ
OH	$A^2\Sigma(v=0)$	690	CN	$A^2\Pi(v=1\dots 9)$	680
NH	$A^3\Pi(v=0)$	404		$B^2\Sigma^+(v=0)$	65.6
CH	$A^2\Delta(v=0)$	530	NH ₂	\tilde{A}^2A	8300
	$B^2\Sigma^-(v=0)$	380	CO ⁺	$A^2\Pi(v=1)$	3490
C ₂	$d^3\Pi(v=0)$	170		$B^2\Sigma^+(v=0)$	55
	$D^1\Sigma_u^+(v=0)$	14.6	N ₂ ⁺	$A^2\Pi_u(v=1)$	13900
				$B^2\Sigma_u^+(v=0)$	60.5

Some features in the spectra of heads of comets were not so readily identified. An example is the 4050 Å group which was first observed by Huggins in 1882. Pol Swings in a letter in 1942 called this problem to my attention. Naively, I thought that from the structure of the 4050 group I could deduce that it was probably due to the CH₂ radical. This idea seemed to be further confirmed by

experiments with an interrupted discharge through methane which indeed produced the 4050 group in the laboratory for the first time. Figure 3 shows one of the first spectra compared with a cometary spectrum of Swings. However,

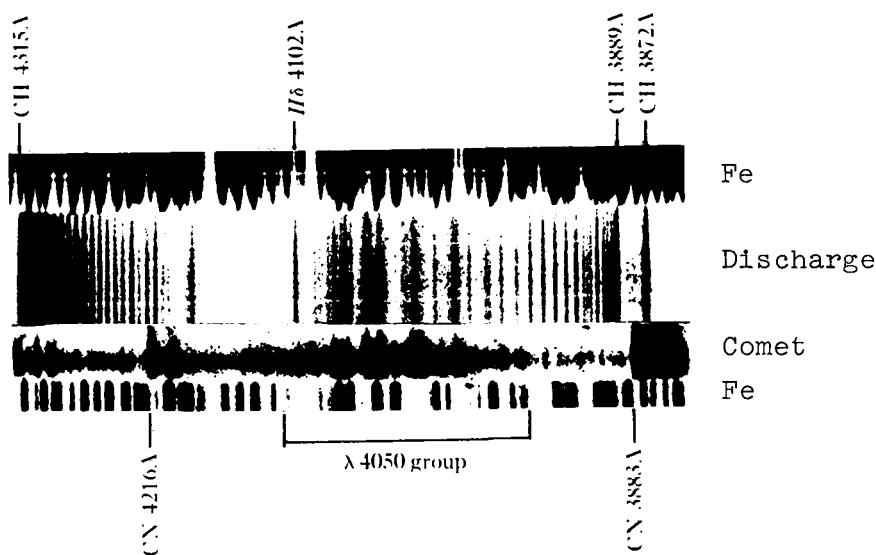


Fig. 3. The 4050 Å group in the laboratory and in comet 1940c after Herzberg (1942).

seven years later it was shown by Monfils and Rosen (1949) that the same spectrum could be obtained with deuterated methane, CD_4 , showing that hydrogen is not part of the molecule that is responsible. Subsequently Douglas (1951) by the use of ^{13}C showed unambiguously that the 4050 group is due to the C_3 radical. Further laboratory work led to a complete analysis of the spectrum (Gausset et al. 1965). The most striking result of this analysis was that the bending frequency in C_3 was extremely low, namely 63 cm^{-1} , causing the complicated vibrational structure (which at one time I thought was rotational structure of CH_2). Since this work on C_3 , stimulated by the cometary problem, many other examples of such low bending vibration in linear molecules have been found.

The mechanism by which C_3 is produced in comets is still a puzzle. It is not known from which parent compound it arises. Strangely, the 4050 group is one of the earliest features observed in the coma when the comet approaches the sun. Another strange fact is that according to Arpigny (1975) the rotational temperature is low, contrary to that of C_2 . That also is a puzzle.

One other polyatomic radical has been clearly observed in the heads of comets, that is, NH_2 whose spectrum has been studied in the laboratory in great detail by Ramsay and his collaborators (1959, 1976, 1978) at Ottawa. In this case the mechanism of production is very simple, namely photodissociation of NH_3 which in the laboratory clearly gives NH_2 and therefore, presumably, also in the coma.

Comet Kohoutek was the first comet which was studied by radio-frequency spectroscopy. By this method several non-radicals have been observed, namely HCN , CH_3CN and H_2O . No laboratory emission spectra of these molecules are known in the visible and ultraviolet regions.

(2) Comet tail

Spectra of the tails of comets were first observed by Deslandres (1907). The strongest features observed at that time could not immediately be identified but Fowler (1909) carried out laboratory studies and showed that these features are due to the CO^+ ion. This system of CO^+ is a ${}^2\Pi-{}^2\Sigma^+$ transition and is now generally known as the comet tail system of CO^+ .

Several other ions were identified later on the basis of earlier laboratory work. It is interesting to note that both CH^+ and OH^+ show only the lines of lowest rotational quantum number. This observation is readily understood since these ions have large dipole moments and therefore a strong rotation spectrum which depopulates the higher rotational levels of the ground state between successive electronic excitations.

Comet Kohoutek brought another exciting example of the interplay between laboratory spectroscopy and astronomical observation. Benvenuti and Wurm (1974) of Asiago Observatory were the first to communicate to us photographic infrared spectra of the tail of this comet which had two unidentified doublets. These had been independently obtained by Herbig (1973). At that time Dr. Lew (1973, 1976) in our laboratory had just observed and analysed the laboratory spectrum of H_2O^+ . In the laboratory the spectrum of H_2O^+ shows several thousand lines in the red part of the spectrum but comparison with the new cometary features showed that the latter were identical with the lowest temperature lines of H_2O^+ . Later at smaller distances of the comet many more lines of H_2O^+ were observed by Herbig, Wehinger and Wyckoff (Wehinger et al. 1974) leaving no doubt that H_2O^+ was correctly identified as an important constituent of comet tails. The spectrum shown in Figure 4 illustrates well the characteristic

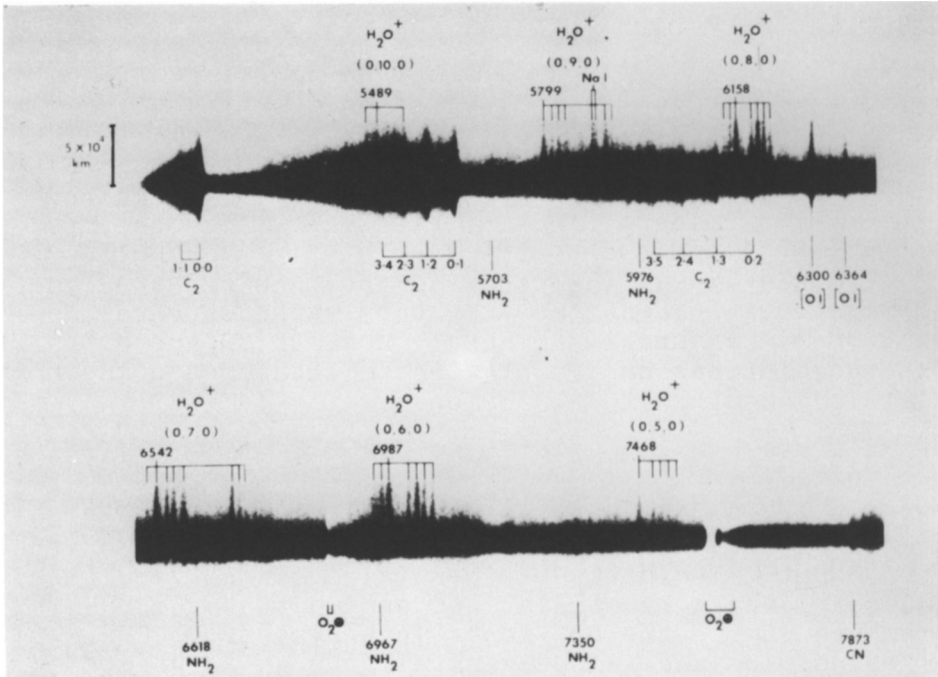


Fig.4. Spectrum of comet Kohoutek taken 1974
Jan.10.7 UT at Wise Observatory in
Israel, after Wehinger et al. 1974.

structure of the spectrum of H_2O^+ : successive bands of the main progression have alternately different structures as required for a molecule which is linear in the excited and strongly bent in the ground state. Incidentally, in the same spectrum NH_2 can be seen in the coma. The NH_2 bands are all very close to the corresponding H_2O^+ bands. This is because H_2O^+ and NH_2 have the same number of electrons and their spectra are therefore very similar.

The observation of H_2O^+ in Comet Kohoutek and subsequent comets nicely confirms Fred Whipple's "dirty ice" model of the comet nucleus.

Stimulated by the results on H_2O^+ we have carried out work on NH_3^+ in the laboratory. A spectrum near 2300 \AA has been observed although it has not yet been fully analysed. It will be interesting to know whether the new features occur in the tails of comets. So far no tail spectra near 2300 \AA are available.

E. INTERSTELLAR MEDIUM, NEBULAE

(1) Early history

The first molecule detected in the interstellar medium was the CH radical. Swings and Rosenfeld (1937) noticed that one of the unidentified interstellar lines observed by Dunham (1937) and Adams (1941) at 4300.3 \AA coincides with the single line of lowest J in the CH band at 4315 \AA . This band occurs for example in the spectrum of an ordinary Bunsen burner. Figure 5 shows such a spectrum where the line in question has been marked. The coincidence in this

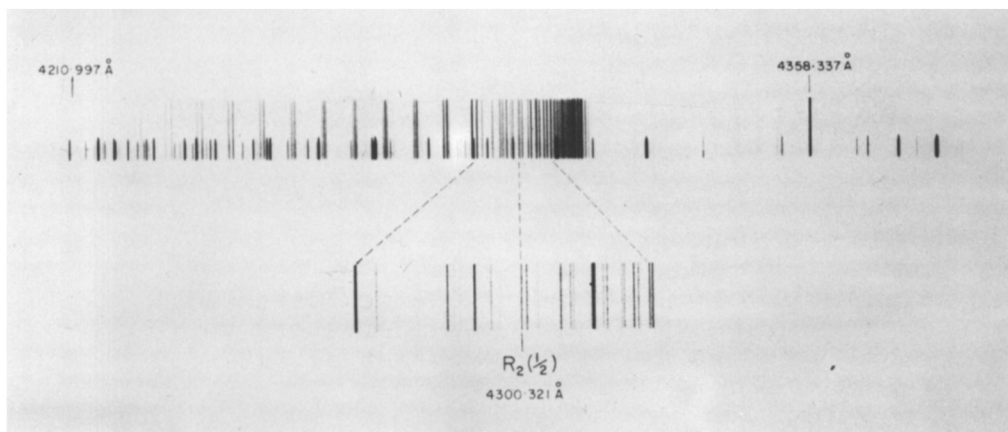


Fig.5. The CH band at 4315 \AA obtained from the flame of an ordinary Bunsen burner at high resolution showing the interstellar line at 4300.3 \AA .

case while very significant indeed would perhaps not have sufficed to convince everyone that CH is present but A. McKellar in 1941 identified three other CH lines in the spectra of Adams which belong to the next electronic transition of CH near 3890 \AA . All three lines arise from the lowest rotational level of CH in the ground state. McKellar at that time also identified two lines of CN near 3883 \AA , the R(0) and the R(1) lines. Indeed from the intensity ratio of the R(0) and R(1) lines he derived a temperature of 3° K for the interstellar medium, anticipating in a way the later discovery of the 3° radiation.

In addition to these identifications there were four unidentified lines in Adams' spectra between 4232 and 3579 Å which formed a clear progression. At a meeting at Yerkes Observatory in 1940 the possible origins of these lines were discussed at great length. Eventually Edward Teller and I came to the conclusion that these lines must be due to CH^+ . Fortunately at this time Alec Douglas, then a graduate student of mine at the University of Saskatchewan, had a discharge tube set up for some other purpose which we could immediately apply to this problem and within a week we obtained (Douglas and Herzberg 1941, 1942) a spectrum of CH^+ in which the R(0) lines of the 0-0, 1-0 and 2-0 bands agreed exactly with those observed by Adams. Figure 6 shows the first two bands. Much later Douglas and Morton

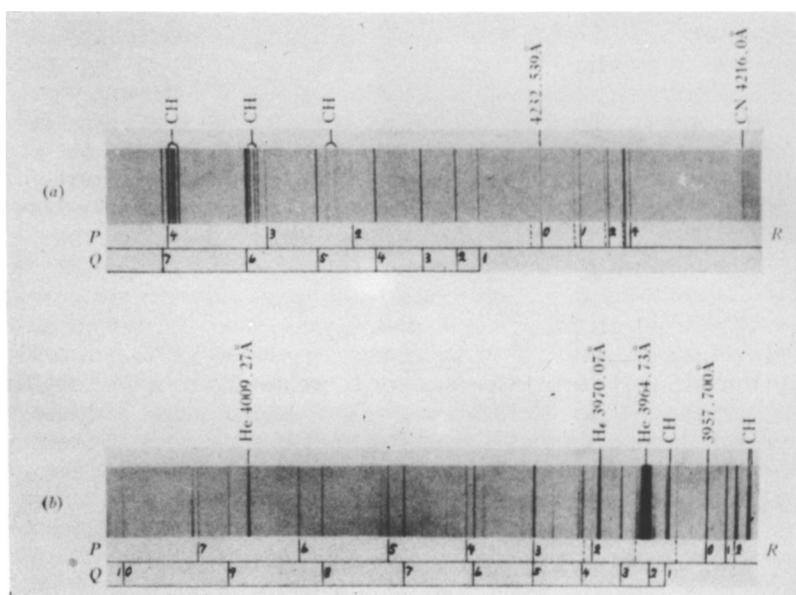


Fig.6. CH^+ bands in the laboratory after Douglas and Herzberg (1942). (a) 0-0 band, (b) 1-0 band. The R(0) lines are the lines occurring in interstellar absorption.

(1960) also identified the line at 3579 Å as the R(0) line of the 3-0 band. In Table III the wavelengths of the interstellar lines are compared with those measured in the laboratory. CH^+ was the first interstellar ion and it was observed in absorption. Indeed for many years it remained the only molecular ion that was observed in absorption.

Table III. Comparison of laboratory and interstellar wavelengths of CH^+ lines

	R(0) laboratory	Interstellar line	Δ
0-0	4232.539	4232.58	-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)		

In the identification of CH^+ as an interstellar ion the interplay between laboratory spectroscopy and astronomical observation was particularly important and striking. On the other hand for the first molecules detected by radio-astronomy the corresponding laboratory spectra were all known long before. This applies to OH, discovered in 1963, NH_3 in 1968, H_2O and H_2CO in 1969, CO in 1970, and several others. As is well-known, carbon monoxide turned out to be the most abundant molecule next to H_2 .

(2) New molecules and ions

Soon after the initiation of the field of radio and microwave detection of molecules in interstellar space a number of strong unidentified lines were found in several molecular clouds. The first was a line at 89190 MHz, observed by Buhl and Snyder (1970). It was suggested by Klemperer at the 1970 IAU meeting that this line represents the 1-0 transition of HCO^+ but it was several years before this interpretation was finally established beyond doubt. It took the observation of H^{13}CO^+ and of DCO^+ , as well as the laboratory observation by Woods et al. (1975) which came more than five years after the first astronomical observation. On the basis of the astronomical observations it is possible to derive the geometric structure of HCO^+ . It is a linear molecule with $r(\text{CH}) = 1.10_0 \text{ \AA}$ and $r(\text{CO}) = 1.10_0 \text{ \AA}$. We have tried at Ottawa to obtain optical spectra of this molecular ion but so far have failed to find any.

The second molecule first identified by radio-astronomical observations was C_2H (Tucker, Kutner and Thaddeus 1974). In this case the observed fine structure and hyperfine structure made the identification on the basis of the astronomical data alone practically certain, but actually Claude Woods has again observed this spectrum in the laboratory in his studies of microwave absorption of

electric discharges. Long before C_2H was considered for astronomical reasons we had carried out at Ottawa a number of studies to obtain the optical spectrum of this free radical by means of flash photolysis and other methods. These attempts were continued more recently, jointly with D.A. Ramsay, but have not led to positive results. There are, however, observations of C_2H in solid matrices both in the infrared and in the ultraviolet.

The third group of unidentified lines, near 93173 MHz, was shown by Turner (1974), Green et al. (1974) and Thaddeus and Turner (1975) to be due to the N_2H^+ ion. Here the two-fold hyperfine structure due to the inner and the outer nitrogen nucleus makes the identification quite definite, but again Woods and his associates [Saykally et al. (1976)] have observed the same transitions in the laboratory.

More recently Guélin and Thaddeus (1977) have observed two doublets at 89055 and 98949 MHz which they identified as the 9-8 and 10-9 transitions of $C\equiv C-CN$. At IAU Symposium No. 87 at Mont Tremblant Thaddeus reported the observation of C_4H .

Another and very definite and interesting identification is that of the cyanopolyacetylenes by Kroto, Oka, Avery, Broten and MacLeod (Avery et al. 1976, Kroto et al. 1978, Broten et al. 1978) at Ottawa. These identifications started out from laboratory work by Kroto and his students on cyanodiacetylene, a linear molecule. From these laboratory data various expected radio-frequency lines accessible to radio telescopes could be predicted and were indeed found, first at the Algonquin Radio Observatory. Subsequent laboratory work of Kroto and his students resulted in the laboratory observation of a spectrum of cyanotriacetylene which was immediately found in Heiles' Cloud. Finally, by extrapolation of the various cyanopolyacetylenes, it was possible to predict the positions of the lines of cyanotetraacetylene and this molecule was also detected. It represents the largest molecule yet observed in interstellar space. The cyanoacetylenes have large dipole moments and are therefore detectable in fairly small amounts. Nevertheless the slowness of the decrease of the observed abundances with the number of acetylene groups is striking.

(3) Molecules without dipole moment

Molecules like H_2 , N_2 , C_2 , CO_2 , C_2H_2 , C_2H_4 and others can not be discovered by radio-astronomical methods because the dipole moment is strictly zero. On the other hand

molecules like CH_4 , CH_3 and C_2H_6 which also have no dipole moment in the equilibrium position may develop a very small dipole moment with increasing rotation on account of centrifugal distortion. Fox and Jennings (1978) claim the observation of CH_4 by such forbidden radio-frequency transitions but this claim has not yet been generally accepted.

The hydrogen molecule can be readily detected by vacuum ultraviolet absorption using spectrometers on rockets or on artificial satellites. Extensive laboratory data for H_2 are available. In Figure 7 as an example a record from Copernicus observations [Spitzer et al. (1973)] is compared with a laboratory spectrum obtained in Ottawa and shows clearly the strong presence of H_2 lines in interstellar absorption.

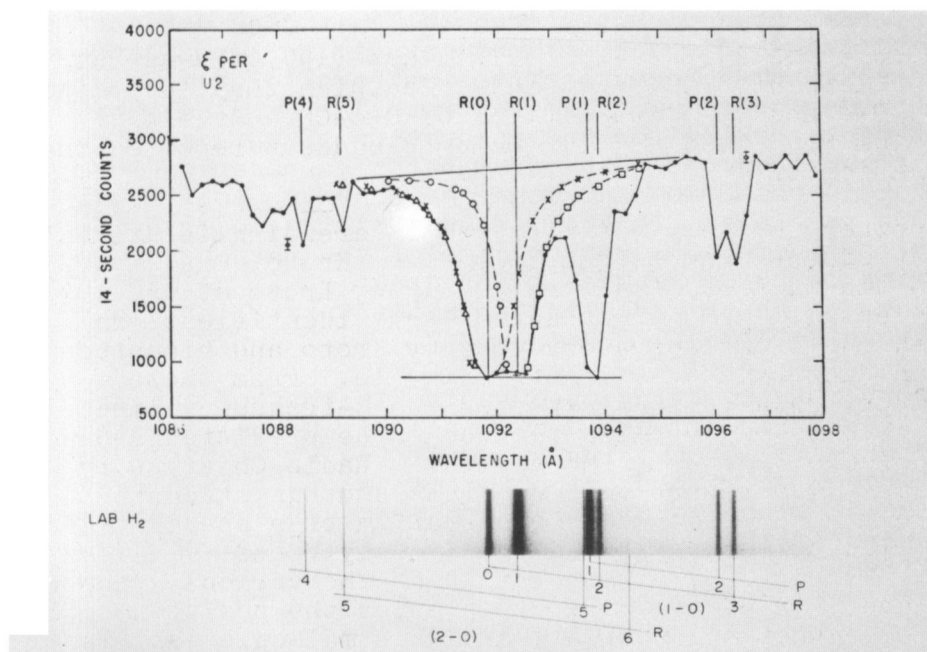


Fig.7 H_2 absorption bands near 1090 \AA in interstellar space after Spitzer et al. (1973) and in the laboratory.

The amounts of H_2 found in this way are so large that it is even possible to detect HD. In this case new laboratory data at Ottawa (Dabrowski and Herzberg 1976) give much better agreement with the Copernicus observations (Morton 1975) than the earlier extrapolated data. Table 4 shows the comparison.

Table IV. HD in the interstellar medium

Band	$\lambda_{\text{int.}}$ (ζ Oph.)	$\lambda_{\text{lab.}}$
3-0	1066.272	1066.2712
4-0	1054.288	1054.2855
5-0	1042.845	1042.8471
6-0	1031.920	1031.9091
7-0	1021.452	1021.4534
	\AA	\AA
	(Morton)	

As already mentioned in the discussion of planetary atmospheres, molecular hydrogen while it does not have an ordinary infrared spectrum does have an infrared quadrupole spectrum. Because of the extremely low intensity of this quadrupole spectrum interstellar H_2 cannot be detected by looking for the absorption of this spectrum. However the quadrupole spectrum has been observed in emission in the Orion and other nebulae by Gautier, Fink, Treffers and Larson (1976). This striking observation throws considerable light on some of the phenomena occurring in these nebulae. For example, it points to the existence of shock waves in certain interstellar clouds (see Beckwith 1979).

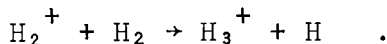
Another interesting observation is that of infrared absorption of acetylene, C_2H_2 , in a circumstellar cloud around IRC+10.216° by Ridgway, Hall, et al. (1976). Many other molecules without dipole moments could be discovered in this way since laboratory data are available but the abundances of these molecules may be insufficient for detection.

(4) Molecular ions not yet observed

The observation of three molecular ions (CH^+ , HCO^+ and N_2H^+) and the fact that ion-molecule reactions are known to be very fast has led several groups to suggest that ions play a major role in the chemistry of interstellar clouds and in particular in the formation of interstellar molecules (Herbst and Klemperer 1973, Watson 1973). Therefore further theoretical and laboratory work on molecular ions seems important. At Ottawa we have tried to do our share of such work.

Because of the high abundance of H_2 it is expected

that H_3^+ is an important ion in the interstellar medium even though its presence has not yet been established by observation of its spectrum. When H_2 is ionized either by photons or cosmic rays H_3^+ is immediately formed by way of the exothermic and fast ion-molecule reaction



Ab initio calculations have shown that the H_3^+ ion has no discrete visible or ultraviolet absorption spectrum. All excited electronic states are unstable. Therefore H_3^+ can be detected only by its infrared spectrum. Even in the laboratory such an infrared spectrum has not yet been identified with certainty. Carney and Porter (1976) have predicted the positions of the principal emission or absorption bands. In our laboratory we have looked for the infrared emission spectrum of H_3^+ in a hollow cathode discharge in hydrogen and have indeed found lines at the positions predicted by Carney and Porter; in fact they are the strongest predicted infrared transitions, but in the same spectrum there are also a number of H_2 lines and it is difficult to ascertain conclusively that the lines coincident with the predicted lines of H_3^+ are really due to H_3^+ . Work on this problem is continuing in our laboratory.

As a by-product of the search for H_3^+ we have obtained in the laboratory a Rydberg spectrum of neutral H_3 and D_3 (Herzberg 1979). Figure 8 shows one of the emission bands of H_3 as well as the corresponding one of D_3 near 5600 Å. This spectrum is produced in the process of recombination of H_3^+ ions with electrons. The lower state predissociates into $H_2 + H$ (or $D_2 + D$) and causes the lines of the 5600 Å band to be fairly diffuse (much more so for H_3 than for D_3). The proof that this spectrum really is due to H_3 (or D_3) in a Rydberg state comes from the observed rotational structure in the D_3 band which yields a structure of D_3 almost identical with the predicted structure of D_3^+ , as would be expected, since the Rydberg electron in D_3 (or H_3) does not have a significant effect on the bonding.

The emission of the H_3 spectrum occurs during the dissociative recombination of H_3^+ and this recombination has already been assumed by Watson, Herbst and Klemperer and others to be the eventual fate of H_3^+ in the interstellar medium. The H_3 spectrum must therefore appear in emission in suitable interstellar clouds in which the concentration of H_3^+ is high enough. Searches for this emission have already been made at Victoria.

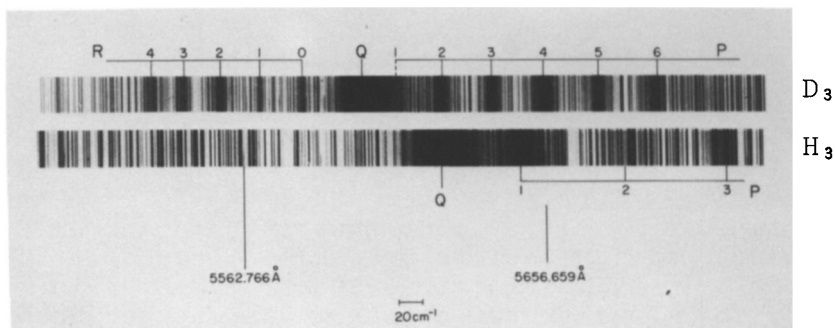


Fig.8. Rydberg spectrum of H_3 and D_3 in a hollow cathode discharge in H_2 and D_2 respectively.

Another ion that may well be important in the interstellar medium is HeH^+ . The ground state of this system is quite stable: it has a dissociation energy of 1.845 eV. From data in the literature we have calculated the ordinary infrared spectrum of this ion which should be fairly strong because the dipole moment is large (Dabrowski and Herzberg 1977). In addition we have calculated the recombination spectrum which occurs on account of inverse predissociation. While our own efforts in the laboratory to obtain this spectrum have thus far been unsuccessful I understand that the Arizona group has very recently observed by the ion-beam laser-beam method the first transition in the HeH^+ infrared spectrum.

Still another spectrum that might be of importance in the interstellar medium is the spectrum of $HeNe^+$ which we have recently studied in considerable detail in the laboratory (Dabrowski and Herzberg 1978). As shown by the potential functions in Figure 9 derived from our analysis of the spectrum, the ground state is fairly stable with a dissociation energy of 0.6 eV and an infrared spectrum should be observable at 1140 cm^{-1} . The visible spectrum

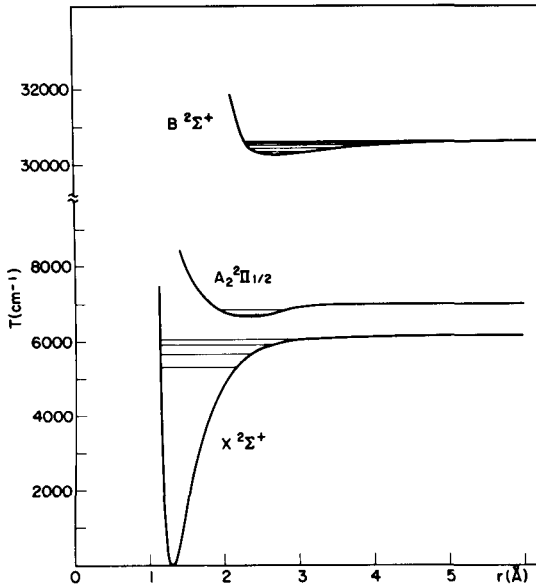


Fig.9. Potential functions of the three observed states of HeNe^+ .

near 4200 \AA that we analysed can not appear in absorption since it does not involve the lowest vibrational level of the ground state. If HeNe^+ existed in the interstellar medium it would eventually reach the lowest vibrational level of the ground state and would give rise to a microwave doublet near 173555 MHz . Unfortunately the accuracy of this prediction is not very great but it seems to be worthwhile looking for this line.

F. CONCLUSION

In this lecture I have tried to show that the frequent and intimate interplay between laboratory spectroscopy and astronomical observation is responsible for a great deal of progress both in molecular spectroscopy and in astronomical problems. Clearly this interplay is continuing. One problem in which this interplay will be especially important is the problem of the diffuse interstellar lines, perhaps the last outstanding major identification problem. Much of the work in our laboratory was stimulated by the desire to solve this problem even though so far without success. Until quite recently almost all astronomers assumed that the diffuse interstellar lines are due to the interstellar dust. For many years, as a

lone prophet in the wilderness, I favoured the idea that these lines are due to interstellar molecules and that they are broad because of predissociation. A number of recent astronomical papers (see for example Sneden et al. 1978) have thrown some doubt on the dust idea. The recent observation of the large cyanopolyacetylenes in the interstellar medium has caused A.E. Douglas (1977) to suggest that such molecules or even simpler ones (C_n) may be the carriers of the diffuse lines, and that the diffuseness is due to perturbations by high vibrational levels of the ground state (as in internal conversion of aromatic molecules). The solution of this important problem will certainly open new vistas in astronomy and molecular physics.

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