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FREE RADICALS IN ASTROPHYSICS

par

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FREE RADICALS IN ASTROPHYSICS ⁽¹⁾

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⁽¹⁾ Report presented at the Ninth International Conference on Free Radicals (Banff, Canada, August 25-29, 1969).

This report was prepared and published as a cordial homage to Dr. G. Herzberg, on the occasion of his 65th-anniversary.

INTRODUCTION

The present review covers mainly results obtained during the last twelve years. In 1958 I published in the *Handbuch der Physik* a general exposition on the role played by molecules in stars and, of course, this included the free radicals. I refer to this general text for details on stellar work prior to 1958. The main topics included in this *Handbuch* article were the following :

(1) Presence of radicals (in the gaseous phase) in the atmospheres of the earth, sun, planets, comets, stars and interstellar space. Is there a local thermodynamic equilibrium (LTE) or not?

(2) Information on vibrational and rotational temperatures, chemical compositions, densities, isotopes, physical processes.

(3) Di- and tri-atomic radicals in stars.

(4) The Sun : a typical G2V-star ; its photosphere, spots and chromosphere ; need for further laboratory measurements (λ 's and probabilities) and high resolution scans.

(5) Importance of bands for spectral classification (spectral classes and absolute magnitudes) ; normal stars ; populations I and II ; stars poor (or rich) in H.

(6) Molecules in M-, S- and C stars.

(7) Molecules in variable stars.

(8) Molecular emission mechanisms in stars (especially A10, A1H and CN).

(9) Continuous opacity of molecules.

In the course of the last few years several important reviews have been devoted to the spectra of comets. Hence I shall simply summarize briefly the work in the field of cometary physics.

On the other hand I shall give some detail on a few recent spectacular results, especially those on the role of the hydroxyl radical in interstellar physics. Quite a few puzzles remain outstanding in this domain.

GENERAL CONSIDERATIONS

To a chemist a free radical has a short life and can generally be best identified by spectroscopic means. A radical can exist in isolation; but it reacts and forms stable compounds when it is brought into contact with appropriate species.

Of the several hundred diatomic particles which are known spectroscopically, less than twenty are stable chemical compounds at normal temperature ($< 100^\circ\text{C}$). More than fifty free radical spectra have been observed in the region λ 1,000 to λ 10,000 Å. Fifteen spectra have been studied with high resolution, most of them in Ottawa by Dr. G. Herzberg and his associates. For their major contribution in this field Dr. Herzberg and the Ottawa team deserve the thanks of the astrophysicists. The radicals may reveal themselves as stable compounds (say at $T \geq 1,000^\circ\text{K}$) in the thermal equilibrium. Indeed, it is not always easy to distinguish between molecules and radicals. We may say that a particle with saturated spin is a molecule while a particle with an odd number of electrons is a radical.

In astronomical objects the physical conditions are generally such that radicals and molecules behave identically. Hence whether or not radicals can be called molecules seems often to be largely a matter of taste! There are several reasons for this situation:

- 1) Normally we may consider that there is no wall (except possibly in the case of cometary nuclei and of interstellar solid particles).
- 2) In most astronomical objects the density is low and there are few collisions (not in planets and the central regions of cometary heads).
- 3) In the stellar atmospheres the temperature is often high compared with the chemical experiments. An increase in temperature and a decrease in pressure favor the existence of simple radicals such as NH_2 or OH in thermal equilibrium with the stable molecules NH_3 or H_2O .
- 4) In many cases there is no thermodynamic equilibrium.

In this review I shall consider the important role played in astronomy by a few typical diatomic or triatomic radicals, mainly CN , CH , C_2 , NH , OH , TiO , AlO , ZrO , VO , LaO , YO , AlH ; C_3 , NH_2 , SiC_2 . We shall also consider a few radicals which may possibly play a role in the future.

In certain cosmic objects radicals such as CN , CH , C_2 , etc., may appear conspicuously, while stable molecules do not, simply as a result of the observable spectral region. As an example the stable molecules H_2 , CO , etc., are more abundant than the CN and CH radicals in cool stars but their electronic resonance spectra are in the far ultraviolet while those of CN and CH lie in the ordinary region. On the other hand stable infrared active molecules such as CO show stronger vibration-rotation spectra than the less abundant radicals. Thanks to the space vehicles, including high flying aircraft and balloons, we shall soon be able to extend the

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astronomical spectral range toward the ultraviolet and the infrared. New radicals will be found in absorption or emission.

A close cooperation between experimental and astronomical spectroscopists has led to exciting results in our knowledge of radicals such as C_3 , NH_2 , SiC_2 and CH^+ . High spectral resolution will certainly reveal the presence of new compounds of low abundance in various astronomical objects. A spectacular result in this direction is the recent discovery of HCl and HF (not free radicals!) in Venus.

We shall see later the great importance of spectra of radicals for the determination of abundances of elements such as C, N, O, hence for discussions of nucleogenesis. But already now I wish to stress the need for spectra of several astronomically important radicals such as the hydrides FeH and TiH and a number of oxides. According to Norrish spectra of hydrides such as FeH and TiH can best be obtained by the flash pyrolysis of volatile hydrides or volatile metal alkyls; also in some cases by the isothermal flash photolysis of certain hydrides. There is also a need for additional descriptive data on spectra of radicals such as AlH at higher temperature⁽¹⁾.

Recent theoretical investigations on abundances, based on the molecular bands

The pioneering work on the dissociation equilibria has been made by Rosenfeld (1933), Russell (1934), and Fujita (1935). Major contributions have been made in recent years by the Japanese group under Fujita, teams in India (Vardya), the U.S. (Spinrad, Schadee, ...) and Holland (Schadee, ...). For many years it had been assumed that the very stable CO molecule created the subdivision between M- (or S-) and C-stars. When the ratio C/O is large, the carbon atoms get hold of all the O-atoms to form CO, and no metallic oxide is observed. Vice versa when O/C > 1, no carbon molecule is present. Several important points have been made clear recently :

(i) The relative abundances of the oxides and carbon compounds are extremely sensitive to the ratio C/O (a very small change of C/O perturbs completely the dissociation equilibria).

(ii) In addition to CO, other molecules — including polyatomic molecules and radicals in the coolest objects — play a major role; even solid particles (such as graphite or refractory materials) affect the molecular abundances.

(iii) The effect of the abundance of N on the dissociation equilibria is not negligible (as evidenced by the intensities of the NH and CN bands).

(iv) The detailed interpretation of the molecular spectra of the cool stars implies variations in the ratios H/C/N/O. Actually the dissociation equilibrium equations must fit simultaneously all the observable H, C, N and O compounds.

(v) The infrared CO-absorption is weaker in C-stars, than in M-stars.

(vi) There are great difficulties in determining abundances, on account of lacking f-values, model atmospheres, saturation factors, etc.

⁽¹⁾ At high pressure Van der Waals particles bound by weak polarisation forces may be formed. These particles are of interest in cool dwarf stars of high atmospheric density, a possible example being Ca_2 (absorption peak at $\lambda 4227$ extending in both directions), but these particles are not free radicals.

(vii) The He-stars are H-poor and C-rich ; this applies to the R CrB-stars. Most of the H has been transformed into He, and a fraction of He has been transformed into C¹².

(viii) Observations of the permitted and forbidden lines of C, N, O, S and Si should be pursued in the cool stars ⁽¹⁾; comparison to the sun would be fruitful.

Molecules in the solar photosphere, spots and chromosphere

The sun is a strategically located G2V star (main sequence G2 star). Molecular bands are present, not only in absorption in the solar photosphere and in sunspots, but also in emission in the solar chromosphere.

Most of the identification work in the solar photosphere has been based on the Rowland table, the Utrecht Atlas and the Revised Rowland Table. More fruitful and convincing work will be done in the future on the basis of the better observational data which may be acquired at Kitt Park, Jungfrauoch, Oxford and other modern installations using repeated photoelectric scans. At the present time the status of the solar identifications stands as follows :

- Certain : CO, CN, CH, C₂, NH, OH ;
- Very probable : AlH, MgH, SiH, CaH, TiO ;
- Doubtful : BH, BO, AlO.

Sunspots are richer in molecules ; the bands are easily separated from the atomic lines, on account of their narrow Zeeman effect.

A monumental study of the chromospheric spectrum outside of eclipse has been published recently by A. K. Pierce. It covers the spectral range from λ 3040 to λ 9266 and reveals several hundred lines of C₂ (Swan bands) and CN (violet and red systems). CH, OH and NH do not seem to be present in chromospheric emission.

Spectrum of a representative M Star, β Pegasi (D. Davis)

The molecular bands in the order of decreasing intensities are :

- TiO ;
- MgH, SiH, AlH, CaH ;
- Weak : ZrO, ScO, YO, CrO, AlO, BO, C₂, CH, CN, SiF, SiN ;
- Possible : MgO ;
- Doubtful : BH, PH, FeO, MgF, SrH and SrO.

The presence of CaOH and MgOH is not quite excluded.

Actually this kind of identification work should be repeated with better observational material (e. g. using multiple photoelectric scans) and more accurate laboratory data.

⁽¹⁾ The presence of other forbidden lines (Fe II, Ni II, Fe I, ...) in absorption is not excluded.

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The M and S-Stars

The characteristic molecular bands are :

- typical M : TiO (strongest, 4th period), YO (5th period), CaH, see preceding section ;
- typical S : ZrO (strongest, 5th row), YO, LaO (6th period), SiH, AlH, AlO, CH, CN ;
- intermediate MS : TiO, ZrO, AlO.

The abundances based on the oxides are in agreement with those based on the atomic lines. For the S stars there is an overabundance of the elements $Z \geq 38$, originating from neutron processes. Technetium Tc_{43}^{99} is present in several S stars and also in N stars (19 Piscium).

Unsöld states that the recent calculations on stellar evolution along the red giant branch lead to times which are of the same order of magnitude as the half life of Tc_{43}^{99} , namely 200,000 years.

Spinrad finds no difference of H-abundance in M- and S-stars (using the H_2 -quadrupole lines) but the abundance of H_2O is lower in S stars than in M's.

Typical cases of intermediate spectral classes

Examples of anomalous spectra of late type stars are the following :

(i) Stars showing no ZrO, LaO or other oxides, but having the characteristic line enhancements observed in class S ; sometimes with fairly strong CN, and weak C_2 .

(ii) Certain R stars are not deficient in H, others have weak or absent H and no CH (this includes the R CrB stars, such as RY Sagittarii).

(iii) Stars of halo population II such as HD 26 and HD 201626 have anomalously strong CH-bands (Greenstein and Wallerstein) ; their carbon abundance is 5 or 6 times higher than in normal stars of the same spectral type (ϵ Vir). The other elements, up to Zr^{40} have normal intensities, but the heavier elements (from Ba^{56}) are overabundant (by a factor about 15?).

(iv) The K1 dwarfs HD 75732 and HD 145675 show strong CN and detectable C_2 bands (Greenstein and Oinas). While the objects are essentially main sequence K1 stars, the metallic lines are enhanced. Two explanations are possible : either C/O is greater than 1 (abnormally low abundance of O) or C and O are both enhanced, with C more enhanced than O.

The Ba II (Equivalent normal class : K) and N stars as a temperature sequence

The Ba II stars form a logical higher temperature extension of the N stars (C. P. Gordon). They are characterized by strong Ba II as well as moderately strong bands due to CH, CN and notably C_2 . There is a marked similarity between the Ba II and N stars, except for differences which may be explained by the lower temperature of the carbon stars ; all N-stars have a strong Ba II line λ 4554.

As for the R-stars they show no strong λ 4554. In this regard there is a lack of similarity between the R and N stars, also in regard to the abundances of the other heavy elements.

The R and Ba II stars must have different C/O ratios.

The over-all spectral similarity is greater between the Ba II and the N stars than between the R and N stars. I must, however, make it clear that this is still a controversial matter.

Unidentified bands in M6 or later — and in S-stars (Nassau et al., photographic infrared region)

Puzzling absorptions occur in the M-stars in the regions 7340-7450 and 7865-7974.

Unidentified bands appear also in the S stars (example : R Gygni) in the region λ 7500- λ 8820.

The carbon abundance of population II stars (J. G. Cohen)

In a discussion of the ratio carbon/(elements near the iron peak) the molecular equilibrium must be treated in a refined way ; for example, it must take the stratification and an atmospheric model into account. The CH radical is well adapted to the discussion. The result is that the carbon is not more deficient than the elements in the iron peak, assuming the solar O/Fe ratio. The study was based on the high velocity K-giants HD 6755, HD 103095, HD 19445 and HD 140283 ; the equation of molecular equilibrium was solved for 34 optical depths in the atmosphere.

Behavior of AlO and AlH

The hydride and oxide of Al have furnished extremely valuable information. Forty emission lines observed in long period variables turned out to be due to an inverse predissociation of AlH (G. Herbig) ⁽¹⁾. AlO-absorption is observed in ordinary giants, but is stronger in Mira variables of type Me than in the giants having the same temperature (Keenan et al.). The AlO absorption bands fluctuate greatly from cycle to cycle. AlO appears also in emission in a few Mira stars when these have a relatively low maximum. The relative intensities of the different vibrational transitions show great peculiarities which are explained by overlying absorption features. This results from the stratification in the atmospheres of these cool super-giants.

Radicals in variable stars

Important physical information (temperature, gravity, abundances) may be gathered, thanks to molecular bands, in a wide variety of variable stars ⁽²⁾, such as :

⁽¹⁾ Lines observed : $A^1\Pi \rightarrow X^1\Sigma^+$; in $v' = 1$, J' from 6 to 12 ;
in $v' = 0$, J' from 17 to 21.

⁽²⁾ The colors are affected by the absorption bands. Example : a star which has very strong absorption bands in the blue-violet region (ex. : C₂) will appear reddened, in comparison with stars of the same effective temperature which have bands in the yellow-red (ex. : TiO).

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- Cepheids (bands of CN, CH, ...);
 - Population II-Cepheids (ex : RU Cam) (bands of C₂, CN, CH);
 - Irregular variables (ex : U Hydrae) (bands of SiC₂, C₃, CaCl);
 - Long period variables (bands of oxides, CN, CH, CO, C₂).
- CN appears in emission in the R CrB-stars near minimum.

Radicals in novae

Novae have occasionally shown absorption bands of radicals, such as CN, C₂ or CH, at phases corresponding to „ temperatures ” apparently too high for molecules. This is certainly due to departures from LTE and to stratification effects. One should even not exclude the possibility of finding some day absorption bands of ionized compounds, such as CH⁺ or SiH⁺ in a nova !

Detection of isotopes in the solar and stellar atmospheres

High resolution spectra have been used for the detection of isotopes : D (no convincing result, except in telluric absorption), He (successful), oxygen (successful in telluric absorption) and Li (successful). Spectra of radicals have been used for :

C (see below C¹²/C¹³), using C₂, CN and CH, possibly also SiC₂;

Mg using MgH (0,0) near λ 5211. (Dispersion 3-4 Å/mm); 10 stars (late types, all luminosity classes); Mg²⁵ and Mg²⁶ are certainly present, their abundance ratio not radically different from the terrestrial ratios, but may be slightly enhanced over the terrestrial abundances.

Kumar has recently studied the relative isotopic abundances of Mg in the sunspot spectrum, using the Q and R branches of the (0-0) and (1-1) bands of MgH. It seems that the heavier isotopes Mg²⁵ and Mg²⁶ are enhanced in the Sun as compared to the Earth;

N using CN (not conclusive);

Si using SiH (no convincing departure);

Ti using TiO (no convincing departure in χ Cygni);

Zr using ZrO in S-stars, 3 Å/mm; a terrestrial isotope ratio is improbable; Zr⁹⁰ may have a lower abundance; but the relative abundances of Zr⁹⁰, Zr⁹¹, Zr⁹², Zr⁹³, Zr⁹⁴, Zr⁹⁶ are still doubtful.

Abundance ratio C¹²/C¹³

The C¹²/C¹³ ratio is of importance in relation to nucleogenesis. Bands which are utilized are C₂ (Swan system); CN (blue and red systems), CH (violet system) and CO (infrared) ⁽¹⁾. We shall consider only recent results. The CNO cycle would give C¹²/C¹³ = 3.4 (or even 2.6 out of equilibrium) ⁽²⁾. There seems to be no con-

⁽¹⁾ Yamashita and Utsumi have also tentatively assigned absorption features of late N stars to isotopic bands of SiC₂ (see section on the SiC₂-radical).

⁽²⁾ The tentative interpretations of the high abundance of C¹³ relative to C¹² are generally based on the existence of a convection zone which brings to the surface of

nection between the abundance of C^{13} and the intensity of the NH band. No C^{13} appears in the H-deficient carbon stars and in the baryum stars. If Li is created in a spallation process, as well as C^{13} , there may be a correlation between the C^{13} and Li abundances; this should be investigated in greater detail.

The photometric determinations of C^{12}/C^{13} in the C-stars are difficult. Observational results range from 2 (ex : Y CVn and WZCas) to more than 100; the terrestrial ratio is 89. Recent observational results are the following :

(i) In the solar photosphere, using very high resolution, a search for the unblended doublet P(58) of the (0,0) band of the violet system of CN does not reveal C^{13} . Using improved laboratory measurements of the isotopic wavelengths, and excellent Jungfraujoch solar tracings, Delbouille, L. Herzberg and Roland conclude that $C^{12}/C^{13} > 40$ in the solar photosphere. Richter and Tonner used $C^{13}H$, and found $C^{12}/C^{13} = 100 \pm 30$ on the basis of the Michigan Atlas. Lambert and Mallia using Oxford Observatory tracings tried to measure a relatively unblended Fraunhofer line of $C^{13}H$ ($A^2\Delta - X^2\Pi$ system) and found $C^{12}/C^{13} = 150 \pm 30$, definitely exceeding the terrestrial value. If confirmed, Lambert and Mallia's result would support the suggestion that the terrestrial C^{13} is the product of spallation processes in the condensing nebula surrounding the contracting sun (Fowler, Greenstein and Hoyle). The observational work should be repeated.

(ii) Search in interstellar absorption — Bortholot and Thaddeus tried to find $C^{13}H^+$ in ζ Ophiuchi, superposing 25 high dispersion (Lick Observatory, 1.3 Å/mm) spectra with the help of a digital computer. This technique should reveal interstellar lines only a few tenths of a mÅ in equivalent width. A new interstellar line is found at 4232.08 ± 0.01 Å; it is possibly the R(0) (0,0) $A^1\Pi - X^1\Sigma$ line of $C^{13}H^+$. The measured equivalent width is $W = 0.68 \pm 0.14$ mÅ. The value thus obtained for C^{12}/C^{13} is 82 (+ 55, - 15). This result should be checked at R(0) (1,0) near 3959 Å, but this line would have only half the intensity of the (0,0) line. Actually photoelectric scanning techniques should be applied to the interstellar lines.

The high C^{12}/C^{13} ratio in interstellar space shows that the C^{13} -rich carbon stars have not appreciably contributed to the CH^+ molecules, at least in the direction of ζ Ophiuchi.

Study of [O I] and CN in the bright red giants (Conti, Greenstein, Spinrad, Wallerstein and Vardya, and others)

The intensity of CN is very sensitive to the abundance ratios C/N/O, while [O I] is sensitive to C/O, because of the formation of CO molecules near the top of the photosphere. Strong CN may be expected in giants if C/O is greater than 1/1.6 (in which case [O I] would be weakened), or if the abundance of N is abnormally high ⁽¹⁾.

the carbon stars elements generated by nuclear reactions, in particular the CNO cycle, taking place in the central parts of the stars. However these interpretations are not quite convincing, as an observed ratio C^{13}/C^{12} as low as 2 seems to require spallation mechanisms in the superficial layers.

According to Fowler a value lower than 2.6 would give evidence for the early production of carbon in supermassive stars, in which C^{13} is usually produced in excess of C^{12} . The CNO cycle alone is not adequate to account for the variations in the relative abundances of H, C^{12} , C^{13} , N and O in the carbon stars.

⁽¹⁾ A search for [N I] may be useful, but difficult (see the papers on [N I] in solar absorption).

In « normal » red giants (ϵ Vir, γ Tau, α U Ma, μ Psc, ...) the observations of CN and [O I] agree with the predictions on the basis of solar abundances. But there are two types of peculiar red giants :

(i) the high-velocity *weak-CN* giants (ex : α Boö, γ Leo A and B, HD 148897, ...) in which [O I] is approximately twice as strong as predicted ; the ratios O/C and O/metals must be higher than in the normal red giants ;

(ii) the *strong CN* red giants (ex : α Ser) : [O I] is half as strong as predicted. The C/O ratio must be increased to 1/1.4 instead of 1/1.6.

Griffin has also compared the red CN system and the [O I] lines of α Boö and α Ser (both K2 giants). Arcturus has stronger [O I] and weaker CN than α Ser.

The C_3 -radical

The strong group of cometary emissions near λ 4050, which remained puzzling for 60 years, is now convincingly assigned to the C_3 -radical. It seems rather certain that C_3 is also responsible for the absorption bands near λ 4000 in the coolest carbon stars, also for their continuum shortward of λ 4200.

The isotopic effect of C^{13} helped greatly in disentangling the complex laboratory spectrum of C_3 : the complexity is partly due to the very low frequency (63 cm^{-1}) of the bending vibration in the ground electronic state of C_3 . As a result many vibrational levels are populated in the carbon stars and in cometary heads.

The SiC_2 -radical

The Merrill-Sanford bands of the coolest carbon stars remained a mystery for several decades until Kleman in Ottawa found them in emission in a King furnace charged with silicone and was able to assign them to SiC_2 . The same bands were also found later in absorption at low temperature by Verma in the flash photolysis of phenyl silane. Much remains to be done on this spectrum, especially in replacing C^{12} by the isotope C^{13} and in comparing the laboratory spectra with the Merrill-Sanford bands of late type carbon stars having different C^{12}/C^{13} ratios. Y. Yamashita and K. Utsumi have assigned several absorption features in RY Draconis and Y Canum Venaticorum to $Si-C^{12}C^{13}$, $Si-C^{13}C^{12}$ and $Si-C^{13}C^{13}$. The isotopic bands involving Si^{30} seem to be absent in these spectra.

There seems to be no correlation between the intensity of SiC_2 bands and the spectral type, C as well as R-N. Could there be a luminosity effect? This is not excluded. The abundance of SiC_2 depends on the abundances of the other molecules containing silicon.

When taking the C_3 spectrum by the flash photolysis of diazopropyne ($HC_2 \cdot CHN_2$) in the region λ 3100 — λ 3700 bands appear which probably belong to C_3H_2 ($HCCCH$), which cannot be easily separated from the overlapping C_3 bands in the long λ -part.

It is hoped that this new band system will be analyzed. There are strong unidentified absorption bands in the region λ 3300 — λ 3800 of the very late carbon stars, such as YCVn, especially at $\lambda\lambda$ 3418, 3480, 3595, 3700 and 3790. Their assignment to C_3H_2 is not entirely excluded, although polyatomic molecules such as C_3H_2 are probably not abundant in stellar atmospheres.

Abundances in G- and K-stars

Stars of spectral type later than about G5 often exhibit a considerable diversity in chemical abundances, even for the same spectral and luminosity classes. Greenstein and Oinas have studied two K dwarfs (ρ' Cancri and HD 145675, spectral type KO V or KI V) with enhanced bands of molecular carbon; their discussion is to a great extent based on the bands of CN, C₂ and CH, which are enhanced in the two strong-metallic-line stars. The spectra indicate a ratio C/O \simeq 1. The forbidden lines [O I] are not seen. A search for [C I] is desirable and is being carried at McDonald Observatory.

Vibration and rotation temperatures; transition probabilities

Temperature determinations have been made spectroscopically for all kinds of astronomical objects. In the case of comets the determinations of rotational temperatures have little physical meaning, on account of the low densities.

The important work of Nicholls, Dalby, Jeunehomme, Lawrence, Hesser, Zare Remy, etc. should be continued, in order to gain more accurate and complete results on radiative lifetimes, oscillator strengths and Franck-Condon factors for radicals of astronomical interest. Among the latest publications in this field, we may mention the determination of the lifetimes of NH, SiH, SiD by W. H. Smith, of OH by R. N. Zare.

Infrared spectra of cool stars

A good example is the high resolution infrared spectrum of Arcturus, obtained by P. and J. Connes, and studied by a team of the University of Texas. It covers the region 11407-25129 Å (or 8766-3978 cm⁻¹), with a resolution 0.1 to 0.3 cm⁻¹. 1038 stellar lines have been measured, of which 60 % are identified. 300 CO-lines have been found, including C¹³O¹⁸. Spectrograms of red stars obtained by P. and J. Connes in the region from 1.1 to 2.5 μ are also studied by a group at the University of Toulouse. Among the identifications in K — M and C stars one should expect vibration-rotation transitions of CH, OH, CN, ... Determinations of temperature, line broadening, turbulence and departures from local thermodynamic equilibrium may be based on such excellent high resolution material.

However, low resolution observations may be of help too, for example for temperature determinations and comparison with the models of cool atmospheres. Such observations may be conveniently made from high flying aircraft (such as the NASA Convair) or from high altitude balloons.

We may expect polyatomic radicals and molecules, not only in very cool stars, but also in many peculiar objects which reveal low temperature features or a high intensity in the infrared (symbiotic objects, quasars, Seyfert galaxies, planetary nebulae, Of-stars, Be-stars, etc.). More sensitive infrared receivers and more refined mechanical, optical and electronic equipment have rendered the investigation of the infrared region much more fruitful and practical than a few years ago.

Boron compounds

The cosmic abundance of boron is still rather uncertain. One might have expected

to obtain results on the basis of boron compounds. A few years ago I did not succeed in finding BN in solar absorption on the basis of the Utrecht Atlas, but better solar material is now available. The cases of BH and BO should also be rediscussed, first in the sun and sunspots, then in cooler stars. Engvold has searched for the bands of BH and BO in sunspots, but he has not found them, despite the high quality of the observational material. The bands of BN would still be much weaker than BH and BO. A search in very cool stars is still desirable ; observational material of a quality higher than that used by D. Davis may now be available.

HS in the ultraviolet

The $A^2\Sigma - X^2\Pi$ transition of HS falls near λ 3240, and may be found in cool stars, or possibly in the sun and the major planets. Seven other electronic transitions, all with lower level $X^2\Pi$, fall in the region from λ 1234 to λ 1673. Their detection will not be easy ! No infrared absorption has been found as yet.

Opacity problems

Many important theoretical, experimental and observational investigations have been devoted to the opacity of compounds in cool stars. Opacity effects are sometimes very striking in carbon stars. Bands may appear anomalously strong or weak relative to others, simply on account of variations in the continuous opacity.

It may be mentioned here that CaH (λ 8385) and MgH (λ 5211) have a negative absolute magnitude effect.

Laboratory investigations of radicals of astronomical interest

Twenty years ago practically nothing was known of the spectra of gaseous polyatomic radicals, with the possible exception of HCO and NH_2 . The tremendous progress in this field is due to a considerable extent to the Ottawa group.

Several polyhydride radicals which have been studied recently, especially by the Ottawa School, have been of great interest to astronomers ⁽¹⁾. Others will most probably have an astronomical interest some day, possibly in the far ultraviolet or in the infrared.

The NH_2 radical (responsible for the α -bands of ammonia) has been wonderfully analyzed, thanks to the isotopic effects with deuterium and N^{15} . It explained many emission features of comets. It will probably be found in the outer atmospheres of the major planets, which are rich in NH_3 ; possibly also in interstellar space and in the atmospheres of very cool stars.

The CH_3 radicals should be found in astronomical objects some day, possibly in high resolution spectra of the major planets which are rich in methane ; possibly also in comets or in interstellar space. It has been studied in detail, including the isotopic effects (D and C^{13}). One of the CH_3 bands of the system near 1500 Å has discrete rotational fine structure, while the other bands are diffuse. Rydberg series have been found shortward of λ 1500, also a diffuse band at λ 2160.

⁽¹⁾ The free radicals have led to the development of gas lasers which are used in space experiments, but this point will not be considered here.

The CH_2 radical may be found some day in comets, in the major planets, in cool stars or in interstellar space. Rydberg series of diffuse triplet bands start at λ 1415. Weak singlet absorption bands cover the region λ 4900 to λ 9200. They may be looked for on high resolution spectra of the major planets. The lower state of the singlet system is not necessarily the ground state. NH_2 , CH_2 , CH_3 may be found some day in emission in the aurorae of Venus or the major planets.

The SiH_2 radical is similar to CH_2 ; it is found in the flash photolysis of phenyl silane (SiH_4); it appears near λ 3250 and in the region λ 4800 — λ 6500. The presence of SiC_2 in cool stars leads to the suggestion that SiH_2 may also be found in cool stars (¹).

Other polyhydride radicals, such as BH_2 and PH_2 have been studied in considerable detail in Ottawa; they may help, some day, in determining the cosmic abundances of boron and phosphorus.

Several mono-hydride polyatomic radicals which have been studied recently may become useful in astronomical identifications. Among them:

- HCO (in absorption from λ 4500 to λ 7500);
- HNO (in emission and absorption, from λ 5500 to λ 10,000);
- HCOO (in emission in region 3500 — 4400);
- HN CN , HSiCl , HSiBr , etc.

The electronic spectrum of HO_2 has not been located yet; but HO_2 is present in the infrared. It should provide important astronomical applications.

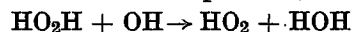
Recently studied radicals which do not contain H are: NCO , BO_2 , NO_3 , N_3 , NCN , NCS . They have not been located in astronomical objects yet.

The recently studied spectra of N_2O^+ and CS_2^+ have not yet been found in cosmic sources but may eventually.

New electronic vibrational and rotational analyses have been made recently on NH , SH , BH , BO , BN , SiH , SiN , SiCl , CH^+ , SiH^+ , TiO , LaO , CaCl , etc. To be kept informed on all the recent progress and on the investigations under way, we recommend the spectroscopic news letters published initially by Jenkins and Phillips, and now by Phillips and Davis; these Berkeley colleagues deserve our sincere gratitude.

Low temperature stabilisation of free radicals

Important results have been obtained by trapping radicals in matrices at low temperature, especially by H. P. Broida and his collaborators. We cannot exclude the possibility that similar phenomena take place in the solid cometary nuclei and particles and in the interstellar dust. The low temperature stabilisation of free radicals is astronomically interesting for radicals such as NH , OH , CH , CN , C_3 , NH_2 , HCO , HNO , NCO , possibly also CH_2 , CN_2 , HCN_2 . The trapped species may give rise to chemical synthesis at low temperature, an example being:



For many years the possibility has been mentioned that radicals such as C_3 and OH may be trapped in the icy cometary layers. The interstellar grains may also provide an ideal surface on which atoms can join.

(¹) SiH_3 has not been found in the flash photolysis giving SiH_2 and SiH .

Actually free radicals seem to be trapped in meteorites, but this problem will not be discussed here.

Cometary spectra

The comets and the interstellar matter provide certainly the most exciting examples of astrophysical applications of free radicals. In the case of the comets we summarize briefly here the most recent results on the profiles of the emission bands of the coma, which contains only neutral radicals ⁽¹⁾ : OH, NH, CN, CH, C₃, C₂, NH₂ ⁽²⁾.

The electronic band systems show very complex profiles which are due to the fluorescence excitation by the solar radiation, account being taken of the Fraunhofer lines, the radial velocity of the cometary nucleus, the local radial velocities within the head, and the distributions on the lower rotational and vibrational levels.

A satisfactory interpretation of the rotational intensity distributions in the cometary emissions requires accurate solar wavelengths and profiles (of the integrated disc) and accurate laboratory wavelengths of the lines of the molecular transitions under consideration. The dispersion of the cometary spectra must be sufficient : 20 Å/mm is hardly sufficient to separate the rotational lines in the R branch of CN (0,0). The cometary profiles of a specific band vary from one point of the coma to another, as a result of the variations in radial velocity and of the distribution on the rotational levels. The cometary band which is best adapted to a detailed quantitative discussion of the fluorescence excitation mechanism is the (0,0) transition of the violet system ²Σ — ²Σ of CN. However the fluorescence mechanism has also been discussed, in a less quantitative fashion, for all the other cometary radicals.

At very low densities, as was generally considered until a short time ago, no collision — hence no chemical reaction — occurs. The distribution on the rotational levels results entirely from the fluorescence mechanism, combined with the pure rotational and vibration-rotation transitions. In the best case of the CN (0,0) band the stationary state leads to a system of 30 equations with 30 unknowns, which may be handled easily by an electronic computer. It is also possible to study the variations of the relative intensities with nucleocentric distance. Irregular motions within the coma are observed, in addition to regular motions. This problem was studied extensively by Cl. Arpigny.

It was, however, found by D. Malaise that the cometary profiles could not be fully explained under the assumption that the distribution on the rotational levels is due exclusively to the fluorescence excitation mechanism. It was indeed found that the rotational distribution is due, in many cases, much more to collisions (i. e. Boltzmann distribution) than to radiation (fluorescence). The relative importance of the collisional and radiative effects varies from one object to another, and, obviously, with the nucleocentric distance and local conditions. Malaise found that the total density of the gas is often 3 or 4 orders of magnitude greater than what is currently adopted in the literature.

Attempts have been made at calculating the synthetic profiles of the main

⁽¹⁾ The important discovery of the C₂ spectrum (affinity : 3 to 4 eV) should find applications in comets ; C₂ is very abundant in the evaporation of graphite. Main bands : λ 5416 and λ 4902 (G. Herzberg).

⁽²⁾ In Sun-grazing comets, strong atomic lines are observed. The red [O I] doublet has appeared in many comets ; so has Na I.

bands of C_3 in comets, on the assumption of the resonance-fluorescence mechanism. This is a difficult task as we know little about the transition probabilities in C_3 . Moreover, we would need cometary spectra of higher resolution (say 4 Å/mm). The transition studied in comets was mainly (000-000) of ${}^1\Pi_u - {}^1\Sigma_g^+$. It seems that the Fraunhofer lines affect the cometary profiles very little, on account of the crowded character of the C_3 spectrum (60 lines in a region only 10 Å wide). It seems that the rotational temperature is low, from 50 to 200° K.

Interstellar radicals

For three decades, until six years ago, our knowledge of the chemical composition of the interstellar matter progressed rather slowly, from the observational as well as the theoretical points of view. Until 1963, the following atoms and radicals were known to be present in interstellar space :

H, Ca^+ , Na, Ca, Fe, K, Ti^+ ;

CH, CH^+ , CN.

The resonance lines of C, N, O and their ions, and of the H_2 and CO molecules are located shortward of λ 3000, hence could not be observed except from space vehicles. Except for CN the atoms and radicals revealed only the transitions whose lower level was the lowest atomic sublevel or molecular rotational state. The CN radical revealed lines corresponding to a rotational temperature of approximately 3° K (i. e. the T of the blackbody radiation observed in the whole universe). A recent search for interstellar C_2 was conducted in vain by G. Münch who scanned ζ Ophiuchi through a Fabry-Perot interferometer around λ 8757.6, R(0) of (2,0) of the Phillips system of C_2 ; at least no line stronger than 5 mÅ could be detected.

Exciting recent discoveries have been made in the microwave and radio regions (in addition to the 21 cm — H line), and have given rise to scores of important publications. These discoveries concern :

- the hydroxyl radical OH ;
- the hydrogen lines 109 α and 158 α , and similar He I lines ;
- water vapor (H_2O) ⁽¹⁾, ammonia (NH_3) ⁽¹⁾, formaldehyde H_2CO ⁽¹⁾, possibly methane CH_4 ⁽²⁾.

We shall give some detail on the hydroxyl radical, which was the first to reveal striking maser effects.

Many teams have concentrated their observational and theoretical work on the interstellar radicals and molecules, especially the groups at Berkeley, Cal Tech, Harvard, M.I.T., NRAO, Parkes (CSIRO), Jodrell Bank, Onsala (Sweden).

Pumping mechanisms of all types (including collisional) have been applied to OH, H_2O , NH_3 , H_2CO ; a few will be discussed later on in the case of OH.

Certain H_2O sources seem to be associated with H II-regions in the same way as OH, but seem to display a more extreme range of velocities.

⁽¹⁾ Wave lengths or frequencies :

H_2O : 1.348 cm ; 22.2351 GHz ; $5_{23} - 6_{16}$;
1.64 mm ; 183.3096 GHz ; $2_{20} - 3_{13}$;

NH_3 : 1.25 cm ;

H_2CO : 6.21 cm ; 4830 MHz ; $1_{11} - 1_{10}$.

⁽²⁾ R(0) of CH_4 in infrared spectrum of α Orionis.

The recent discovery of interstellar NH_3 , H_2O , H_2CO (and possibly CH_4) demonstrates that clouds of polyatomic molecules can be formed and subsist in interstellar space. NH_3 , H_2O and H_2CO are not always found in the same regions (1). CH — whose resonance electronic transitions are known to be present in interstellar space — has not yet been detected in the radio- or microwave region (2).

Interstellar SH (similar to OH) has not been detected yet ; its main frequencies are :

<i>F-transitions</i>	<i>Frequencies</i>
2,2	111.54 MHz
1,1	111.22 MHz
2,1	122.60 MHz
1,2	100.16 MHz

Sulphur has a much lower cosmic abundance than oxygen, approximately one fiftieth, if the solar relative abundances are adopted.

About 30 diffuse interstellar absorption lines have been found in the photographic region, mainly by G. Herbig and are still completely unidentified. Their diffuseness differs for all lines ; the equivalent widths range from 20 Å (λ 4430) to 0.1 Å. Two hypotheses are being defended with regard to the assignment of these puzzling absorptions. Many astrophysicists consider that the cold dust particles are responsible for the fuzzy stationary lines. Others, among them Dr. G. Herzberg, favor the assignments to gaseous molecules ; the widths of the lines would be due to various predissociation (or possibly preionization) effects. The discovery of interstellar H_2O , NH_3 and H_2CO give greater weight to Dr. Herzberg's view. Molecules mentioned (3) are CH_4^+ , NH_4 , H_3O , CH_3^+ , CH_2^+ , H_3^+ , C_2^- , etc. As Dr. Herzberg has often stated, this problem is a challenge to the molecular spectroscopists ! Thus far no positive result has been obtained in this field, but I would be surprised if the Ottawa group would not reach interesting information, for example on the basis of absorption spectra of flash discharges.

The hydroxyl radical (4) in interstellar space (5)

We shall discuss this problem in some detail. The ground electronic state of OH is $^2\Pi_{3/2}$; the levels are doubtlessly double on account of the Λ doubling, resulting from the interaction of the electronic orbital angular momentum with the rotation of the radical. Moreover, the hyperfine splitting due to the spin of the proton doubles again the levels, so that 4 levels and 4 lines are present instead of one (fig. 1). The

(1) Complex chemical processes may actually take place in the interstellar dust clouds. Certain molecules may also be protected from the dissociating ultraviolet radiation.

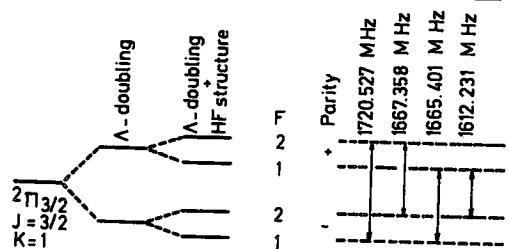
(2) The Λ doublet transition of CH is probably not known with sufficient accuracy in the laboratory. H_2^+ has not yet been observed either.

(3) On account of the high cosmic abundance of H , poly-hydrides are favored.

(4) The OH -radical plays a major role in geophysics (vibration-rotation emission bands in nightglow, varying with the solar cycle, seasons and geomagnetic disturbances). OH is also essential in the reactions in gases, flames, discharges, antiknock processes (see Norrish's Nobel Lecture).

(5) My thanks are due to Dr. B. J. Robinson and to Eric Gérard for valuable information on this section.

Lowest rotational state of OH and the four transitions near λ 18 cm



Relative strengths in thermodynamic equilibrium : 1:9:5:1
 The frequencies were first measured by Townes and his collaborators in 1959

Fig. 1

$2\Pi_{3/2}$ and $2\Pi_{1/2}$ levels

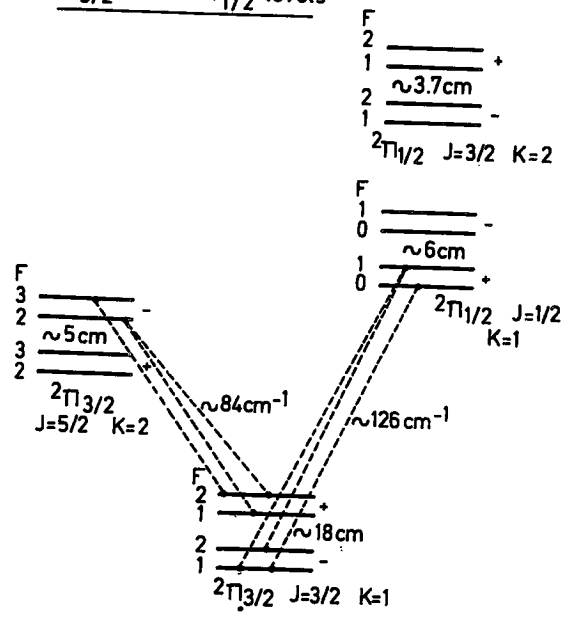


Fig. 2

$2\Pi_{3/2}, J=5/2, K=2$ levels and corresponding transitions

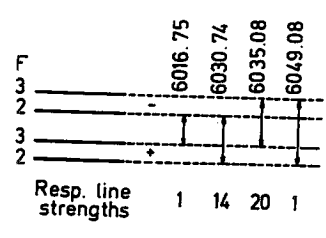


Fig. 3

four transitions have been observed for 6 years in absorption near 18 cm ⁽¹⁾, or in emission or both, sometimes with very queer relative intensities; their interpretation rests on the assumption of a natural maser effect.

Figures 1, 2 and 3 describe four of the lowest rotational states, and the corresponding transitions; emissions near 5 cm ($3 \rightarrow 3$, $2 \rightarrow 2$, ${}^2\Pi_{3/2}$, $J = 5/2$, figure 3), 6 cm (${}^2\Pi_{1/2}$, $J = 1/2$) and 3.7 cm (${}^2\Pi_{1/2}$, $J = 3/2$) have been detected. There is no detailed correspondence among the features near 18 cm, 6 cm, 5 cm and 3.7 cm. Of course there are still other possible transitions, and there is little doubt that they will soon be found.

The first absorption by OH was discovered at M.I.T. by S. Weinreb et al. in 1963 ⁽²⁾ at the strong radio source Cassiopeia A. Actually I. S. Shklovsky had first suggested that the Λ doublet transitions of simple diatomic molecules might be detected in the interstellar medium. The team at Parkes soon found the 4 components, but the relative intensities did not follow the expected ratio 1 : 9 : 5 : 1 (see figure 1). The OH distribution did not match well the distribution of hydrogen.

Beginning on May 11, 1965, many investigators (especially the teams at Berkeley, Harvard and CSIRO) observed the emission of OH. This was first detected in the H II-regions ⁽³⁾. The OH-lines have complex profiles, on account of the large number of clouds having different radial velocities. Beginning in the Fall of 1965 the strong polarization of the OH-emissions was found: sometimes linear (up to 100 %) (W42, NGC 6334 A, 6334 B, ...), usually circular (more than 90 %), or elliptical. However, there are also a few unpolarized features, as in W51. No polarization is observed in any absorption line, down to very low limits.

Soon the OH-emission was observed in many objects, beside the H II-regions ⁽⁴⁾: near supernova-remnants or the galactic center (emission only in the satellite lines at 1612 MHz and 1720 MHz, the two other lines appearing in absorption; or emission in 1720 MHz only, the other three lines appearing in absorption); near infrared stars or nebulae (emission strongest in the satellite 1612 MHz, weak emission in 1665 MHz, unpolarized, small angular sizes); near thermal radio sources (emission in the satellite 1612 MHz, more than an order of magnitude stronger than in 1665 MHz; no detectable line in 1720 MHz). The absorption and emission components are separated both spatially and in radial velocity.

The polarization, profiles and relative intensities differed in the various types. The observed phenomena suggested a natural maser effect, the maser gain being sometimes very high. Different pumping processes were considered; they will be mentioned later on. Recently time variations in intensity and polarization have been observed, especially by the Berkeley, Cal Tech, Harvard, Parkes and Onsala groups (W49, W75S, NGC 6334) ⁽⁵⁾. Such variations, which may amount to 100 %, could yield valuable information on the relaxation times (from days to months) of the maser mechanisms.

⁽¹⁾ Until 1967 the radiation was mainly observed in the 1665 and 1667 MHz frequencies, less or not at all in 1612 and 1720. These observations were always near H II-regions. The $O^{16}H$ radical has also been observed, the corresponding ratio O^{16}/O^{18} being approximately the same as on the earth (~ 490).

⁽²⁾ The technique is simple in principle: the aerial is pointed at a known powerful radio source and one looks for a decrease in the received power at the OH frequencies.

⁽³⁾ The radio-regions were listed by G. Westerhout at Leiden, W1 to W82.

⁽⁴⁾ About a third of the H II-regions has associated OH-emission. The polarization is strong; the line width and the angular sizes are small.

⁽⁵⁾ No change of velocity has been found.

The OH sources which coincide with infrared objects (such as in the Orion Nebula, or at the cool stars listed by the Cal Tech scientists (1)) have little polarization.

It was becoming urgent to estimate the sizes and exact positions of the OH-emissions. Radio interferometers were employed. First, links of about 1 km (at M.I.T. and Cal Tech). Then a link of 13 km, or 74,400 wave lengths (M.I.T. and Harvard). Later on a baseline of 127 km (Jodrell Bank and Malvern). Then NRAO — Arecibo; then M.I.T. — NRAO (845 km). Eventually very long baseline interferometers (VLBI) were used. There was no connection between the receiving elements. The signals were recorded carefully at each telescope, then brought together and combined using atomic frequency standards. A 1420 MHz transition of H maintained stability of the clocks of 10^{-13} (over a day their time is accurate to better than 0.01 microsecond).

In January 1968 a VLBI connecting 4 stations was installed; this interferometer gave 6 possible baselines. The locations were: Hat Creek (Calif.), Green Bank (W. Va.), Lincoln Lab (Mass.) and Onsala (Sweden). The 6 baselines ranged from 845 km to 7700 km in length, or 4.7 to 42.10^6 wavelengths. It was possible to measure the diameters to a few 10^{-3} seconds of arc. One feature in W3 has an apparent diameter (2) of $0.0045''$. Other VLBI's were used later on. Diameters of the order of 0.01 second of arc were found for features in W3. Actually certain sources are not yet resolved with the VLBI's.

The high brightness temperature and the polarization preclude generally an explanation in terms of a thermal mechanism. In most cases a pumping process must populate the upper energy levels of the Λ doublet, giving rise to a maser gain, of the type which Charles Townes invented in the early 1950's.

The main questions which then arise are:

What are the source and the pump, and how are they related in space? This problem has been the object of scores of papers since 1967.

We may consider various *optical* pumping models with far infrared trapping:

(i) Near ultraviolet ($\lambda \sim 3100 \text{ \AA}$), leading to the excited electronic state $A^2\Sigma$; the UV may come from an O-star (say, at $50,000^\circ$) or an H II-region, or from a shock protostar (say, at 4000° K) (3); the photons cascade down to the ground state and overpopulate the upper Λ doublet levels.

(ii) Near infrared ($\lambda \sim 2.8 \mu$) vibration-rotation; may be due to an infrared star or a shock protostar (say at 1000° K) (4);

(iii) Far infrared (84 and 126 cm^{-1} , see figure 2) rotational transitions; may be due to infrared nebulae or heated dust (say at 100° K);

(iv) Relativistic particles (originating in the remnants of a supernova?) whose

(1) Nine of the listed stars revealed OH-emission.

(2) The sizes measured by the interferometers may actually be the sizes of the input signal sources, not necessarily the dimensions of the OH-clouds. A source, as small in angular diameter as W3 or W49 should scintillate strongly when close to the sun; these scintillations have actually been observed at CSIRO when Sag B2 was 5° from the sun.

(3) A shock protostar is a dense, self-gravitating region in the process of collapse; a spherical shock wave may be formed and converge towards the center.

(4) Shklovsky suggested that protostars or young stars in the process of formation may be capable of pumping infrared radiation into an OH-cloud.

close passage near a nucleus gives rise to ultraviolet radiation (« near field interaction »).

We may have instead a *chemical* pumping, such as :

- $O + H \rightarrow OH(A^2\Sigma)$ (pre-association at $T \sim 1000 - 3000^\circ K$) ;
- or fast collision of an H-atom with H_2O , dissociation of water, and formation of rotationally excited OH : $H + H_2O + 4.5 eV \rightarrow OH + 2H$ (at, say $10,000^\circ K$, the leading edge of a shock front) ;
- or excitation of OH rotation by H ($< 100^\circ K$), electrons or nuclei ;
- or $H^+ + O^- \rightarrow OH \text{ exc.} + h\nu$.

These mechanisms of trapping the radiation, by cascade, on the lowest rotational states may establish non-equilibrium populations and explain the observed relative intensities ⁽¹⁾. The infrared pumping produces maser emission at 1612 MHz (near infrared process) and at 1720 MHz (far infrared) in cool OH-clouds, while 1665 and 1667 appear in sufficiently hot or turbulent clouds.

The amount and the temperature of the OH radical in a dust cloud are respectively of the order of 10^{-6} radical per cm^3 and T from 2° to 6° (?). There is, however, hardly any case where a single excitation temperature may apply to the 4 components which always behave differently in intensity and polarization.

The emissions of H_2O at λ 1.35 cm, NH_3 at 1.25 cm and H_2CO at 6.21 cm are similar to OH in radial velocities and distribution. Actually most H_2O sources at 1.35 cm lie very close to the OH sources at 18 cm, but a few have been found where no OH can be detected. The OH and H_2O profiles have no similarities. H_2CO absorption is observed in many more sources than those showing OH emission or absorption.

Much remains to be done, theoretically as well as observationally ; for example, in relation to the excitation and kinetic temperatures, (and the relation to maser gain), the magnetic fields, the protostars, the radial velocities, the relations of OH with very cold objects, as well as with the H_2O and other molecular sources, and the recombination H-lines, such as 109α , etc. The line widths are thought to be narrowed by the high maser gain ; some cases with wider lines are explained by much reduced maser narrowing. The polarization and spatial distributions of the different types of OH-emission sources correspond to different types of excitation ; certain sources have not yet been « categorized ». Within an OH-cloud the penetration of the ultraviolet radiation produces first an anti-inversion, then (more deeply) a progressive inversion. What does really vary in the OH-emission? Is it the intensity, the position or the polarization? Could the OH-frequency be calculated ⁽²⁾ or measured experimentally? A close collaboration of astrophysicists with hertzian spectroscopists is imperative.

⁽¹⁾ Whether an inversion (« maser effect ») or an anti-inversion (increased absorption relative to thermodynamic equilibrium) occurs, depends on the detailed stationary state, hence on the pumping process. A really satisfactory and complete theoretical treatment is not yet available.

⁽²⁾ The only accurate and simple calculation of a microwave frequency is that for H (λ 21 cm).

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