

# THE IDENTIFICATION OF MOLECULAR SPECTRA

R.W.B. PEARSE

D.Sc., F.R.A.S.

*Formerly Reader in Spectroscopy,  
Imperial College, London*

and

A.G. GAYDON

D.Sc., F.R.S.

*Emeritus Professor of Molecular Spectroscopy,  
Imperial College, London*

*Formerly Warren Research Fellow  
of the Royal Society, Imperial College, London*

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# *Preface to First Edition*

These tables have been constructed with the aim of facilitating the identification of molecular spectra. Several excellent books have been written dealing with the theory of molecular spectra and some have included collections of molecular constants derived from the analysis of such spectra, yet it has hitherto remained necessary to search through original papers or to calculate the positions of bands from the tables of derived constants in order to identify a given system of bands. This task is usually tedious and sometimes impossible to one without considerable experience.

Originally we prepared for use in the laboratory a list of the wavelengths of the heads of a limited number of band systems which we frequently encountered as impurities in the course of spectroscopic research. This has proved so useful that it seems worth while to extend the list to cover, as far as possible, all known band systems. Since it appears, moreover, that such a list can be of service, not only to pure spectroscopists, but also to those who use spectroscopy as a tool for research in other fields such as astrophysics, chemistry and chemical technology, we have ventured to gather together in book form such information about known band spectra as may assist in their identification.

In the first list the bands were given in order of wavelength; all bands of the systems considered being included. This arrangement was soon found to possess practical disadvantages. A more useful arrangement was obtained by dividing the data into two sections. The advantages of the division are discussed in the introduction preceding the tables.

As a first stage in the compilation of the available data we have been obliged to limit the scope of the tables in several directions. Thus there are limits to the range of spectrum considered and to the complexity of the molecules whose spectra are included. The wavelength region considered is from 10 000 Å to 2000 Å, that is roughly from the photographic infra-red to the ultra-violet limit of quartz spectrographs, except that in a few cases, where the origin of a system lies near the border line, one or two bands have been included which are just outside the range. As to complexity we have endeavoured to include all recorded systems of diatomic molecules, but only those of triatomic and more complex molecules which show well-defined banded structure and are of frequent occurrence in spectroscopic investigations. The absorption spectra of complex organic molecules and of solutions have been omitted.

In addition to the wavelengths of the band heads, the tables include information about the appearance and occurrence of each band spectrum. Though the information thus given is often useful for reference for other purposes, the object of identification has been kept foremost throughout in making decisions relating to the selection and arrangement of material.

For some systems we have found that the existing data are very incomplete. Where these systems are of frequent occurrence we have made new wavelength measurements. In a large number of cases where no estimates of intensities are given in the original paper, but a photograph is included, we have included estimates of intensities made from the photograph. In other cases where the analysis alone is given without mention of the positions and intensities of the most prominent heads, we have located the positions of the heads from the analysis where possible, and if necessary converted the corresponding wave-numbers to wavelengths. In this connection we should like to point out that it would be of great assistance for purposes of identification if authors of papers reporting new band systems would always in future include a brief description of the appearance of the system with wavelengths and intensities of the strongest heads, a few notes on the sources with which it is obtained, and, if possible, publish a photograph with a wavelength scale or a comparison spectrum.

In addition to photographs which we have taken ourselves, we have been very fortunate in having access to numerous spectrograms taken by Professor A. Fowler and his colleagues and students in the Astrophysics Department of the Royal College of Science. Several of the reproductions of common band spectra have been taken from these plates.

Finally, it is with pleasure that we acknowledge our indebtedness to the late Professor A. Fowler for a thorough introduction to the study of spectroscopy and for turning our attention to many of the spectra dealt with herein; to Professor H. Dingle for interest and encouragement in the preparation of these tables; to Dr. W. Jevons, Dr. R. W. Lunt, Dr. E. C. W. Smith, Dr. R. F. Barrow and Dr. R. C. Pankhurst for the use of spectrograms and unpublished data as well as for useful criticism during trial of the tables, and to Mr. E. S. Parke for very valuable assistance in the preparation of the plates. One of us (A. G. G.) is also indebted to the Trustees of the Beit Fellowships for Scientific Research for a special grant, during the tenure of which a large part of the manuscript was compiled.

R. W. B. P.  
A. G. G.

LONDON.  
SEPTEMBER 1940.

## *Preface to Fourth Edition*

The first edition of this book appeared in 1941, the second in 1950, the third in 1963, and, as this sold out quickly, we had it reprinted with a 20-page supplement in 1965. This edition has been very fully revised. The first edition contained information about spectra of around 250 diatomic molecules and 35 polyatomic; this one covers about 490 diatomic and 127 polyatomic. Developments in techniques, such as flash photolysis, and interest in new subjects such as upper-atmosphere chemistry have contributed to the expansion of the amount of data available.

We have done our best to comb the literature up to about the end of 1974. Data listed are based on original papers or, in some cases, on our own measurements, but the compilations edited by B. Rosen *et al.* (*Données Spectroscopiques Relatives aux Molécules Diatomiques*, 1970) and its supplement edited by R. F. Barrow *et al.* (*Diatomic Molecules; A Critical Bibliography of Spectroscopic Data*, 1973), the book by G. Herzberg (*Electronic Spectra of Polyatomic Molecules*, Van Nostrand, 1966) and the Berkeley Newsletters on *Analysis of Molecular Spectra*, prepared regularly by J. G. Phillips and S. P. Davis have been of great value in tracing references to the literature.

Although other works, such as that edited by Rosen, give constants and some data for diatomic molecules, and the book by Herzberg gives molecular constants for polyatomic molecules, this is still the only work aimed primarily at identification, giving both diatomic and polyatomic molecules and including a considerable collection of reproductions of the actual spectra.

A. G. G.  
R. W. B. P.

LONDON.  
AUGUST 1975.

# Introduction

Experience in using the first list which we drew up of band heads arranged in order of wavelength showed that in extending this list to include a large number of molecules it was desirable to modify the system. The Tables for the Identification of Molecular Spectra are therefore divided into two sections.

The first section consists of a list of the most prominent heads of the more persistent and better-known band systems of each molecule. These heads are listed in order of wavelength, with abbreviated information about the direction of degradation of the bands and their appearance, and, of course, the molecule responsible. In earlier editions we made an attempt to include estimates of relative intensity of the heads within the system, listing these intensities under the sources in which the head was likely to be observed; however, since only the most prominent heads of each system were included, most of the intensities were '10' and in many cases information was not really adequate. This information about intensities has therefore been omitted from the first section in this Fourth Edition. This has enabled the table to be set more compactly.

The second section consists of individual lists of band heads for each system of each molecule, accompanied by notes about the occurrence and appearance of the system, the nature of the electronic transition involved, the vibrational assignment of the bands of the system, intensity estimates on a visual scale and references to the source of the data. The lists are arranged in alphabetical order of the chemical symbols of the molecules.

The general considerations leading to this division are briefly as follows. For practical reasons it is preferable to identify the molecular contribution to a given spectrum system by system, rather than band by band. It is the practice to identify the atomic contribution line by line, with the aid of tables of atomic lines in order of wavelength and there is a natural tendency to proceed to identify bands in a similar way. Such a procedure, however, often leads to incorrect identification. In an atom, each change of electronic state gives rise to a line, whereas in a molecule each change in electronic state gives rise to a whole band system. The various bands within the system arise from changes of the vibrational energy of the molecule and in general involve much smaller energy intervals than the electronic changes. Thus in respect of variation of intensity from source to source the bands of one system behave somewhat like the components of a fairly close multiplet, appearing and disappearing together. But whereas the multiplet contains relatively few lines of the whole spectrum, a single band system often contains many heads, perhaps several hundreds, and may comprise all the radiation that is readily excited for that particular molecule. Inclusion of all such bands in a single list leads to a large number of chance coincidences in wavelength. Such coincidences are more troublesome in the case of bands than in the case of lines, since the wavelength recorded for a band head is seldom as precise as that for an atomic line, depending, because of the structure of the head itself, very considerably on the judgement of the observer and on the dispersion used. This makes it much less safe to identify a single band by wavelength alone than it does to identify a single atomic line in this way. Supporting evidence should always be sought. Such evidence can be obtained by considering the system as a whole. The list of Section I has therefore been restricted to a few of the most prominent heads of each system so that it is somewhat analogous to the list of persistent lines of the elements. The purpose of the list is to provide a clue to the identity of an unrecognised system. The most prominent head of the unknown system is selected. This will usually be the front head of the strongest band, but not necessarily the strongest individual head for a multi-headed band. This head is then compared with the Persistent Heads list and a close agreement of wavelength and direction of degradation may suggest that it is a member of a certain system of a given molecule. Reference is then made to the individual list for

that system and the presence or absence of other members is checked. The process is then continued with outstanding heads of the strongest of the remaining unidentified bands, and so on. It is also advisable to look for other systems of the molecules for which systems are found and also for systems of other molecules containing the same elements; thus if a system of  $C_2$  is found and also one of  $N_2$ , it is desirable to look for systems of CN as well as others systems of  $C_2$  and  $N_2$ . Or, again, if a trace of oxygen is suspected, systems of NO and CO may be checked. This procedure often leads to the discovery of weak bands, masked by stronger ones, which would otherwise have passed unnoticed. In following up other systems in this manner, and indeed in all cases where interest lies in the spectrum of a given molecule, the arrangement of Section II is especially convenient.

The actual number and choice of bands which should be included in the two lists is mainly a matter for experience to decide. We have tried to place most emphasis on those molecules which are cosmically abundant or are known to occur readily as impurities. Since the first edition of the book a very large number of new molecular spectra have been reported. In some cases this may almost degenerate to 'stamp collecting'; studies of rare molecules involving unusual combinations of elements form convenient Ph.D. projects for students. However, it is often very difficult to predict what will and what will not be useful. For example the prominence of ZrO bands in some stellar spectra could hardly have been foreseen. Unusual molecules may arise from use of rare elements in transistor materials; development of special laser system may require unusual species; pollution by toxic heavy metals, like cadmium, may involve unusual spectra in their estimation. For common molecules we have tended to give the prominent bands of all known systems; for the rarer species we have usually included only the strongest band or two of the strongest system in the first list of Persistent Heads, and to give all systems but only a few bands of each in the second list, Individual Systems. Some band systems are very extensive, involving many bands of comparable intensity. These present special difficulty and it is not possible readily to identify such systems from the main Persistent Heads table.

It is well to emphasise that in making identifications, the evidence of the presence of atomic lines may be very helpful. To facilitate the checking of the presence of atoms a table of persistent lines of the elements has been included in the Appendix. If it is desired to check the line spectra more fully, recourse should be made to the various tables of atomic lines that are available.

Finally, in as much as direct comparison of photographs is the quickest and most certain way of identification, a number of plates are included showing many of the more frequently encountered band systems. Also those references to papers which contain a useful reproduction of the spectrum are indicated by a dagger, †, following the date.



# Table of Persistent Band Heads

The object of this table is to provide a clue to the nature of the unknown band system as quickly as possible, so that it may be compared directly with the appropriate detailed list or with one of the plates. For this purpose the list contains for all suitable band systems which are of frequent occurrence a few (sometimes only one) of the outstanding band heads, arranged in decreasing order of wavelength.

In this fourth edition the structure of this table has been substantially modified because of the large increase in the number of known band systems. For the simplest systems with strong (0, 0) sequence we have included just this one head. In a greater number of cases we have given the heads of the (0, 1), (0, 0) and (1, 0) sequences. For systems with more open Franck-Condon intensity parabolaes we have had to include more heads, but have kept the number down to the minimum. To include many heads not only makes the table long and expensive to set but increases the risk of chance meaningless coincidences.

Following the wavelength we have given a brief indication of the appearance of the head. This always includes the direction of degradation

R degraded to longer wavelengths (red)

V degraded to shorter wavelengths (violet)

or that the band measurement is for the maximum, M, of a headless band, or is the origin, O, of a band with a clear region near the origin and branches spreading in each direction from this origin.

L indicates a very narrow, line-like, feature.

Other remarks in this appearance column are:

CD. Close double head (separation usually less than 5 Å).

CT. Close triple head.

D. Double head.

DCD. Double head, each component a close double.

F. Group of four or more heads.

L. Narrow band resembling an atomic line.

T. Triple head.

wr. Accompanied by weaker head to the red.

wv. Accompanied by weaker head to shorter wavelengths (violet).

We should stress that we have usually given the *first* or most prominent head of the sequence, not necessarily the strongest. Some molecules have very extensive band systems consisting of many bands of comparable intensity and it has not been possible to include these. It often happens that homonuclear molecules have spectra of this type and examples are As<sub>2</sub>, Br<sub>2</sub>, Cl<sub>2</sub>, I<sub>2</sub>, K<sub>2</sub>, Li<sub>2</sub>, Na<sub>2</sub>, P<sub>2</sub>, Se<sub>2</sub>, Te<sub>2</sub>. Some mixed molecules of the same group of the periodic table also tend to give extensive systems, e.g. IBr, ICl, NaK. We have also excluded from this table the very rare molecules, the collector's pieces.

In previous editions we listed intensities, often hypothetical, for the band in each of six sources. However, since we are always selecting just the strongest bands, these intensities were mostly 10 or 9 and not of much help, and since this arrangement took up a lot of space and required a lot of rather arbitrary decisions on our part, we have now dropped the inclusion of intensities from this list of persistent heads.

We have, however, retained the asterisk, \*, to denote those bands which in our experience occur rather frequently as impurities in other spectra.

For those molecules of importance possessing a number of strong systems, such as CO, N<sub>2</sub>, CN, we have given in very abbreviated form an indication of the system following the symbols for the

BrF (*contd.*)

$\lambda$	$I$	$\nu', \nu''$	$\lambda$	$I$	$\nu', \nu''$	$\lambda$	$I$	$\nu', \nu''$
4772.1	2	9, 0	5212.2	6	5, 1	5923.9	10	2, 3
4828.5	2	8, 0	5308.1	8	6, 2	6026	8	3, 4
4891.9	3	7, 0	5396.3	9	5, 2	6153	9	2, 4
4930.0	5	9, 1	5491.5	9	4, 2	6293	10	1, 4
4987.8	4	8, 1	5593.5	9	3, 2	6405	10	2, 5
5055.4	5	7, 1	5693.7	9	4, 3	6554	8	1, 5
5129.4	6	6, 1	5804.1	10	3, 3			

WEAKER SYSTEM,  $1-X^1\Sigma^+$ 

The following are probably the strongest heads:  $\lambda\lambda 5578.1$  (2, 0),  $5499.3$  (3, 0),  $5424.1$  (4, 0),  $5359.8$  (5, 0),  $5307.5$  (6, 0).

## BrO

## ETHYL BROMIDE FLAME BANDS

**Occurrence.** In flame of ethyl bromide and when  $\text{Br}_2$  is added to the oxy-hydrogen flame. They have also been observed in absorption following flash photolysis of  $\text{Br}_2 + \text{O}_2$ .

**Appearance.** Degraded to the red. The  $\nu' = 0$  progression is conspicuous in emission and the  $\nu'' = 0$  in absorption.

**References.** W. M. Vaidya, *Indian Acad. Sci. Proc.*, A, 1, 321 (1938).

E. H. Coleman and A. G. Gaydon, *Disc. Faraday Soc.*, 2, 166 (1947)†.

R. A. Durie and D. A. Ramsay, *Canad. J. Phys.*, 36, 35 (1958)†.

The following are the emission bands from Coleman and Gaydon, with revised  $\nu''$  numbering:

$\lambda$	$I$	$\nu', \nu''$	$\lambda$	$I$	$\nu', \nu''$	$\lambda$	$I$	$\nu', \nu''$
4856	2	1, 11	4349	4	2, 8	4109	4	2, 6
4817	3	0, 10	4270	10	0, 6	4069	5	1, 5
4673	8	0, 9	4225	2	2, 7	4029	3	0, 4
4533	10	0, 8	4186	3	1, 6	3999	3	2, 5
4398	10	0, 7	4147	6	0, 5	3958	3	1, 4

The following are among the strongest absorption bands:

$\lambda$	$I$	$\nu', \nu''$	$\lambda$	$I$	$\nu', \nu''$	$\lambda$	$I$	$\nu', \nu''$
3433.8	9	3, 0	3288.6	10	6, 0	3168.5	10	9, 0
3383.4	10	4, 0	3247.7	10	7, 0	3132.6	9	10, 0
3333.2	10	5, 0	3207.9	10	8, 0	3100.4	8	11, 0

C<sub>2</sub>

The strongest system is the well-known Swan system in the green; this is due to a  $^3\Pi - ^3\Pi$  transition, and two other triplet systems are known (Fox-Herzberg and Ballik-Ramsay). The ground state of  $\text{C}_2$  is a singlet lying  $610 \text{ cm}^{-1}$  below the lowest triplet level, and five singlet systems are known; that found by Mulliken is most readily observed, although the Phillips system in the less accessible near infra-red is probably stronger. The Deslandres-d'Azambuja one is fairly strong.

We have retained the old notation but denoted the lower state of the Swan bands as  $X'^3\Pi_u$  and the lowest singlet as  $x^1\Sigma_g^+$  (formerly  $a^1\Sigma_g^+$ ). Some recent papers use capitals for the singlets and lower case letters for triplets.

C<sub>2</sub> (contd.)SWAN SYSTEM, A<sup>3</sup>Π<sub>g</sub> — X'<sup>1</sup>Π<sub>u</sub>

**Occurrence.** These bands are of very frequent occurrence in sources containing carbon. They are especially strongly developed in the greenish inner cone of a Bunsen or Meker burner flame, and in discharge tubes with high current density through hydrocarbon and other organic vapours. They also occur in a carbon arc, in active nitrogen reacting with organic vapours, in discharge tubes through He + CO, and in both emission and absorption in shock tubes and furnaces. They have been reported in reactions between alkali metals and organic halides (e.g. Na + CCl<sub>4</sub>). They are a prominent feature of comets and carbon-type stars.

**Appearance.** Degraded to the violet. Marked sequences of single-headed bands. See Plate 9.

**References.** R. C. Johnson, *Phil. Trans. Roy. Soc., A*, 226, 157 (1927).

D. C. Tyte, S. H. Innanen and R. W. Nicholls, *Identification Atlas of Mol. Spectra*, 5, York Univ. (1967)†.

J. G. Phillips, *Astrophys. J.*, 108, 434 (1948).

E. D. Bugrim, A. I. Lyutyi, V. S. Rossikhin and I. L. Tsikora, *Opt. Spectrosc.*, 19, 292 (1965).

K. S. Kini and M. I. Savadatti, *J. Phys.*, B, 2, 307 (1969).

The following are all the main heads:

λ	I	ν', ν"	λ	I	ν', ν"	λ	I	ν', ν"
6677.3	1	2, 5	5923.4	1	5, 7	4737.1	9	1, 0
6599.2	1	3, 6	5635.5	8	0, 1	4715.2	8	2, 1
6533.7	2	4, 7	5585.5	8	1, 2	4697.6	7	3, 2
6480.5	2	5, 8	5540.7	6	2, 3	4684.8	4	4, 3
6442.3	2	6, 9	5501.9	4	3, 4	4680.2	1	6, 5
6191.2	3	0, 2	5470.3	2	4, 5	4678.6	2	5, 4
6122.1	4	1, 3	5165.2	10	0, 0	4382.5	2	2, 0
6059.7	3	2, 4	5129.3	6	1, 1	4371.4	4	3, 1
6004.9	3	3, 5	5097.7	1	2, 2	4365.2	5	4, 2
5958.7	2	4, 6						

*Tail Bands*

Some weak 'tail bands', degraded to the red have been observed by Phillips and by Bugrim *et al.*, λλ4996.7 (13, 12), 4911.0 (12, 11), 4836.1 (11, 10), 4770.1 (10, 9), 4255.0 (11, 8), 4197.1 (10, 7) and 4147.9 (9, 6). The bands with origins at 4734 (9, 8), 4395 (8, 6) and 4123 (8, 5) are headless. Kini and Savadatti record 12 more weak heads.

*High Pressure Bands*

These occur in condensed discharges through CO at relatively high pressures (10 to 100 torr) and some special sources. They were initially treated as a separate system, but are now known to be part of the Swan system with ν' = 6 selectively excited, probably by the reaction C + C<sub>2</sub>O = C<sub>2</sub> (A<sup>3</sup>Π) + CO. They may occur without the ordinary Swan bands being present.

They are degraded to the violet, and under small dispersion usually appear double headed, perhaps due to anomalous rotational intensity distribution, but with larger dispersion the shorter wavelength head becomes less definite.

**References.** R. C. Johnson and R. K. Asundi, *P.R.S.*, 124, 668 (1929).

A. Fowler, *Mon. Not. R. Astr. Soc.*, 70, 484 (1910)†.

J. G. Fox and G. Herzberg, *P.R.*, 52, 638 (1937).

C. Kunz, P. Harteck and S. Dondas, *J. Chem. Phys.*, 46, 4157 (1967).

$C_2$  (contd.)

In the following table the longer wavelength heads are by Johnson and Asundi, and the shorter, where given, by Fowler.

$\lambda$	$I$	$\nu', \nu''$	$\lambda$	$I$	$\nu', \nu''$	$\lambda$	$I$	$\nu', \nu''$
7852.5	4	6, 11	5434.9	5	6, 7	4093	2	6, 3
—	—	—	5413	2	—	—	—	—
7083.2	6	6, 10	5030	2	6, 6	3619.5	1	6, 1
—	—	—	5015	1	—	—	—	—
6442.3	8	6, 9	4680.2	15	6, 5	3419	1	6, 0
6420	4	—	4663	6	—	—	—	—
5899.3	10	6, 8	4368.8	7	6, 4	—	—	—
5878	5	—	4353	3	—	—	—	—

FOX-HERZBERG SYSTEM,  $B^3\Pi_g - X'^3\Pi_u$ 

*Occurrence.* Weakly condensed discharge through helium containing benzene vapour.

*Appearance.* Shaded to red.

*Reference.* J. G. Fox and G. Herzberg, *P.R.*, 52, 638 (1937).

J. G. Phillips, *Astrophys. J.*, 110, 73 (1949)†.

$\lambda$	$\nu', \nu''$	$\lambda$	$\nu', \nu''$	$\lambda$	$\nu', \nu''$
*3283	0, 6	2772.1	1, 3	2527.9	3, 2
*3129	0, 5	2731.5	0, 2	2486.3	2, 0
**2987	0, 4	2698.8	2, 3	2429.9	3, 0
2896.4	1, 4	2656.3	1, 2	2378.2	4, 0
**2855	0, 3	2589.0	2, 2	—	—

\* Probably fairly strong.

\*\* Strong band.

BALLIK-RAMSAY, FAR INFRA-RED SYSTEM,  $A'^3\Sigma_g^- - X'^3\Pi_u$ 

*Occurrence.* Emission from carbon-tube furnace. The system is likely to be strong in most sources but is too far in the infra-red to have been recorded so far from flames, etc.

*Appearance.* Marked sequences. Degraded to longer wavelengths.

*Reference.* E. A. Ballik and D. A. Ramsay, *Astrophys. J.*, 137, 61 (1963).

Sequence heads, 24745 (0, 1), 17675 (0, 0), 14075 (1, 0) and 11724 Å (2, 0).

MULLIKEN SYSTEM, 2313 Å,  $d^1\Sigma_u^+ - x^1\Sigma_g^+$ 

*Occurrence.* Emission in carbon arc, oxy-acetylene flame and discharge tubes containing hydrocarbons. Also in absorption.

*References.* R. S. Mulliken, *Z. Elektrochem.*, 36, 603 (1930).

J. G. Fox and G. Herzberg, *P.R.*, 52, 638 (1937).

O. G. Landsverk, *P.R.*, 56, 769 (1939).

G. Messerle, *Z. Naturforsch.*, 23 A, 470 (1968).

The headless (0, 0) band with single P and R branches spreading out from the origin at 2312.7 Å is by far the strongest. Other weaker bands have been recorded. Origins:

$C_2$  (contd.)

$\lambda_0$	$\nu', \nu''$
2414.8	0, 1
2316.8	3, 3
2315.4	2, 2
2314.0	1, 1
2312.7	0, 0

PHILLIPS NEAR INFRA-RED SYSTEM,  $b^1\Pi_u - x^1\Sigma_g^+$ 

*Occurrence.* Originally found in heavy-current discharges, but now known to be a strong feature in most systems including arcs and flames.

*Appearance.* Degraded to longer wavelengths with clear sequences. Strong Q branches and weaker P and R branches.

*References.* J. G. Phillips, *Astrophys. J.*, **107**, 389 (1948)†.

E. A. Ballik and D. A. Ramsay, *Astrophys. J.*, **137**, 84 (1963).

R heads:

$\lambda$	$\nu', \nu''$	$\lambda$	$\nu', \nu''$
15484.1	0, 1	8750.8	2, 0
12070.2	0, 0	8108.2	5, 2
10147*	1, 0	7907.7	4, 1
8980.5	3, 1	7714.6	3, 0

\* Band origin

DESLANDRES-D'AZAMBUJA SYSTEM,  $c^1\Pi_g - b^1\Pi_u$ 

*Occurrence.* Condensed discharge through CO, CO<sub>2</sub> or C<sub>2</sub>H<sub>2</sub>, or through argon containing H<sub>2</sub> using carbon electrodes. In spark through liquid alcohol. In carbon arc in H<sub>2</sub> under high temperature conditions.

*Appearance.* Degraded to shorter wavelengths. Single headed.

*References.* R. C. Johnson, *Nature*, **125**, 89 (1930).

G. H. Dieke and W. Lochte-Holtgreven, *Z.P.*, **62**, 767 (1930).

G. Herzberg and R. B. Sutton, *Canad. J. Res.*, **40**, 74 (1940).

G. Messerle and L. Krauss, *Z. Naturforsch.*, **22A**, 2015 (1967).

This is a weak system. Intensities are relative to the strongest band of this system.

$\lambda$	<i>I</i>	$\nu', \nu''$	$\lambda$	<i>I</i>	$\nu', \nu''$	$\lambda$	<i>I</i>	$\nu', \nu''$
4102.3	9	0, 1	3852.2	10	0, 0	3587.6	7	3, 2
4068.1	6	1, 2	3825.6	5	1, 1	3399.7	5	2, 0
4041.8	3	2, 3	3607.3	8	1, 0	3398.1	5	3, 1
4026.9	1	3, 4	3592.9	7	2, 1			

*Tail Bands*

Herzberg and Sutton obtained the following from an uncondensed discharge through He + C<sub>6</sub>H<sub>6</sub>.

They are degraded to the red:

3689.0 (6, 5), 3617.9 (5, 4), 3599.3 (4, 3), 3431.9 (5, 3).

MESSERLE-KRAUSS BANDS,  $c^1\Pi_g - b^1\Pi_u$ 

This is a weak system, observed mainly by its perturbations of overlapping Deslandres-d'Azambuja bands. The following are band origins. Degraded to the red:

$C_2$  (contd.)

$\lambda_0$	$I$	$v', v''$	$\lambda_0$	$I$	$v', v''$
3779.6	weak	4, 6	3586.0	strong	0, 2
3691.5	weak	3, 5	3405.7	strong	1, 2
3672.7	mod.	5, 6	3396.1	strong	0, 1
3627.0	strong	2, 4			

FREYMARK BANDS,  $e^1\Sigma_g^+ - b^1\Pi_u$ 

*Occurrence.* Discharge through acetylene and probably in other sources.

*Appearance.* Degraded to shorter wavelengths. Apparently single headed, with clear sequences.

*Reference.* H. Freymark, *Ann. Phys. (Lpz.)*, 8, 221 (1951)†.

Heads ( $\lambda_h$ ) or origins ( $\lambda_0$ ):

$\lambda_h$	$I$	$v', v''$	$\lambda_h$	$I$	$v', v''$	$\lambda_0$	$I$	$v', v''$
2218.2	9	0, 1	2072.4	6	1, 0	2087.1	5	4, 3
2216.6	7	1, 2	2075.6	6	2, 1	2096.9	4	5, 4
2142.9	10	0, 0	2081.2	5	3, 2			
2142.6	1	1, 1						

 $C_2^*$ MEINEL SYSTEM, 2490 Å,  $2\Sigma_g^- - 2\Pi_u$ 

*Occurrence.* Absorption following a flash discharge through  $C_2H_2$ .

*Appearance.* Slightly degraded to the red. The only known band, the (0, 0), has a Q head at 2490.5, with P and R branches extending away from this.

*Reference.* H. Meinel, *Canad. J. Phys.*, 50, 158 (1972)†.

The assignment to  $C_2^*$  is probable but not quite certain;  $C_2^-$  is a possibility.

 $C_2^-$ HERZBERG-LAGERQVIST SYSTEM, 6000–4800 Å,  $2\Sigma^- - 2\Sigma$ 

*Occurrence.* In emission and in absorption from flash discharges through  $CH_4$ , and in a shock tube.

*Appearance.* Marked sequences of single-headed bands. Degraded to the violet.

*References.* G. Herzberg and A. Lagerqvist, *Canad. J. Phys.*, 46, 2363 (1968)†.

W. S. Cathro and J. C. Mackie, *J. Chem. Soc. Faraday Trans. II*, 69, 237 (1973)†.

P heads with own estimates of intensity:

$\lambda$	$I$	$v', v''$	$\lambda$	$I$	$v', v''$	$\lambda$	$I$	$v', v''$
5984.8	4	0, 1	5363.3	6	1, 1	4833.8	5	3, 2
5912.7	5	1, 2	4902.0	6	1, 0	4804.5	3	4, 3
5844.6	2	2, 3	4866.4	6	2, 1	4779.1	2	5, 4
5415.9	10	0, 0						

 $C_3$ 

## THE 4050 Å COMET-HEAD GROUP

This group was at one time attributed to  $CH_2$  but later work using deuterium and  $C^{13}$  proved that the emitter is  $C_3$ .

**C<sub>3</sub> (contd.)**

**Occurrence.** Originally observed in the heads of comets, the group was later observed in various laboratory sources, including discharges through flowing hydrocarbons or between carbon electrodes in H<sub>2</sub> + Xe, or in a graphite hollow-cathode discharge. Also in rich hydrocarbon flames, hydrocarbon/fluorine flames, in shock waves and in absorption and emission in a carbon-tube furnace. The most detailed work has been done on flash-photolysis absorption (and fluorescent emission) of diazomethane.

**Appearance.** A complex group of narrow red-degraded bands. The appearance depends a lot on the dispersion used, rotational structure being observed at large dispersion. The main head is at 4049.77 Å and is always prominent. Another head at 4072.4 is usually quite clear. The wavelength measurements in comets (Swings), flames (Kiess and Bass) and flash photolysis (Gausset *et al.*) do not agree at all well.

**References.** P. Swings, *Mon. Not. R. Astr. Soc.*, **103**, 92 (1943).

A. E. Douglas, *Astrophys. J.*, **114**, 466 (1951)†.

N. H. Kiess and A. M. Bass, *J. Chem. Phys.*, **22**, 569 (1954)†.

K. Clusius and A. E. Douglas, *Canad. J. Phys.*, **32**, 319 (1954).

L. Gausset, G. Herzberg, A. Lagerqvist and B. Rosen, *Astrophys. J.*, **142**, 45 (1965)†.

Gausset *et al.* list about 80 red-degraded heads between 4100 and 3440 Å in flash photolysis of diazomethane. The following are extracted from this list:

λ	I	λ	I	λ	I	λ	I
4098.5	1	3990.8	6	3935.8	3	3793.5	3
4072.4	6	3983.1	4	3925.9	3	3656.8	3
4049.8	10	3970.9	4	3914.5	3	3619.7	3
4038.4	4	3965.9	3	3879.4	3	3524.9	3
4018.3	4	3949.1	4				

The C<sub>3</sub> molecule is linear and a full analysis has been made. The transition is <sup>1</sup>Π<sub>u</sub> - <sup>1</sup>Σ<sub>g</sub><sup>+</sup>.

**CBr**

**Occurrence.** Absorption following flash photolysis of organic bromides.

**References.** R. N. Dixon and H. W. Kroto, *Trans. Faraday Soc.*, **59**, 1484 (1963)†.

W. J. R. Tyerman, *Spectrochim. Acta.*, **26a**, 1215 (1970).

**3052 Å SYSTEM, A<sup>2</sup>Δ - X<sup>2</sup>Π**

**Appearance.** Double-headed bands, degraded to shorter wavelengths, but Q<sub>1</sub> heads are diffuse due to predissociation.

Heads from Dixon and Kroto:

λ	ν', ν''	remarks
3060.0	1, 1 Q <sub>2</sub>	weak head
3052.3	0, 0 Q <sub>2</sub>	strong head
3023.0	1, 1 Q <sub>1</sub>	weak maximum
3014.5	0, 0 Q <sub>1</sub>	strong maximum

**2500 Å SYSTEM, PROBABLY B<sup>2</sup>Σ<sup>+</sup> - X<sup>2</sup>Π**

Two diffuse bands at 2526 and 2496 Å observed by Tyerman.

**CF<sub>2</sub>** (*contd.*)

$\lambda$	<i>I</i>	$\lambda$	<i>I</i>	$\lambda$	<i>I</i>
3214.1	6	2866.1	6	2675.5	6
3197.5	4	2852.5	6	2652.4	6
3053.7	5	2799.8	8	2628.5	9
3038.1	5	2774.2	5	2595.0	9
3022.8	5	2761.2	5	2550.6	8
2921.3	6	2749.1	8	2518.6	9
2893.5	7	2711.3	9	2487.8	9
		2688.1	5	2457.6	7

The following are the strongest bands, observed by Margrave and Wieland in absorption:

$\lambda$	<i>I</i>	$\lambda$	<i>I</i>
2118.7	3	2062.5	5
2101.7	3	2045.3	7
2099.9	4	2042.8	6
2083.3	3	2028.4	7
2079.5	5	2011.3	8
2063.5	6	2008.0	7

**CH**

Bands of CH are readily excited during the combustion of hydrocarbons and in electrical discharges where carbon and hydrogen are present. They are also observed in many astrophysical sources. Three systems are known in the regions of 4300 Å, 3900 Å and 3143 Å respectively. Their intensities decrease in the order in which they are given, the third usually being much the weakest.

**4300 Å SYSTEM, A<sup>2</sup>Δ—X<sup>2</sup>Π**

**Occurrence.** In sources where carbon and hydrogen are present together such as flames of hydrocarbons, the carbon arc in hydrogen, discharge tubes under a great variety of conditions and in active nitrogen when a hydrocarbon is introduced. It is also observed in emission from the heads of comets and in absorption in the Sun's atmosphere. Difficult to detect in absorption, but has been recorded in flash photolysis and the reaction zone of flames. Also in stars and inter-stellar space.

**Appearance.** Degraded to the violet. Usually the (0, 0) band is the only one to appear. The (1, 1) and (2, 2) are overlaid by this (0, 0); a line-like feature at 4324 Å is the piled up Q branch of the (2, 2). The (0, 0) shows strong Q heads and the lines of the P branch can be traced to about 4385. Both branches consist of narrow doublets. See Plate 4.

**References.** L. Gerö, *Z.P.*, 118, 27 (1941)†.

N. H. Kiess and H. P. Broida, *Astrophys. J.*, 123, 166 (1956)†.

C. E. Moore and H. P. Broida, *J. Res. Nat. Bur. Stand.*, A, 63, 19 (1959).

A. M. Bass and H. P. Broida, *Nat. Bur. Stand. Monograph*, No. 24 (1961).

$\nu', \nu''$	<i>Q Heads</i>	<i>I</i>	<i>P Heads</i>	<i>I</i>
0, 1	4890.0	2	4941.2	1
1, 2	4857.6	0	4913.5	0
2, 2	4324	6		
0, 0	4314.2	10	(4385)	5



## CH (contd.)

3900 Å SYSTEM,  $B^2\Sigma - X^2\Pi$ 

*Occurrence.* Similar to the 4300 Å system.

*Appearance.* Degraded to the red. The (0, 0) band has a very open rotational structure. Other bands are obtained rather more readily than for the 4300 system, but rotational structure of bands with  $v' = 1$  is curtailed by predissociation. The (2, 1) band is usually absent, due to predissociation, but has been observed by Durie. See Plate 4.

*References.* C. E. Moore and H. P. Broida, *J. Res. Nat. Bur. Stand., A*, 63, 19 (1959).

R. A. Durie, *Proc. Phys. Soc., A*, 65, 125 (1952)†.

A. M. Bass and H. P. Broida, *Nat. Bur. Stand. Monograph*, No. 24 (1961).

$v', v''$	Q Heads	I	R Heads	I
1, 2			4495.5	1
1, 1	4036	0	4025.3	2
0, 0	3889.0	5	3871.3	6
1, 0	3635	0	3627.2	2

3143 Å SYSTEM,  $C^2\Sigma^+ - X^2\Pi$ 

*Occurrence.* Similar to the above, but favoured by a higher temperature. More readily observed in absorption.

*Appearance.* The (0, 0) and (1, 1) bands have been reported. The branches consist of doublets. The Q branches are at first degraded to the violet, then at the sixteenth member form a second head and turn to the red. This last head is the most intense.

*References.* T. Hori, *Z.P.*, 59, 91 (1930)†.

T. Heimer, *Z.P.*, 78, 771 (1932).

$v', v''$	Q Heads
1, 1	3156.6 maximum
0, 0	3144.9 deg. V 3144.1 deg. V 3143.4 deg. R

CH<sup>+</sup>DOUGLAS-HERZBERG SYSTEM,  $A^1\Pi - X^1\Sigma$ 

*Occurrence.* Discharge, especially in hollow cathode, through helium with a trace of benzene or acetylene.

*Appearance.* Open rotational structure, with single P, Q and R branches. Degraded to the red; heads not well developed.

*References.* A. E. Douglas and G. Herzberg, *Canad. J. Res., A*, 20, 71 (1942)†.

A. E. Douglas and J. R. Morton, *Astrophys. J.*, 131, 1 (1960)†.

As the heads are not well developed, we list the Q(1) lines as well; these are close to the origins. No intensities are available, but the (0, 0) and (1, 0) bands are probably strong.

$v', v''$	R Heads	Q(1)	$v', v''$	R Heads	Q(1)
0, 1	4775.9	4794.0	1, 0	3954.4	3962.1
1, 1	4433.8	4444.4	3, 1	3967.1	3972.5
0, 0	4225.3	4237.6	2, 0	3743.7	3749.2
2, 1	4171.1	4178.4	4, 1	3806.1	3810.6

## OH

The 3064 Å system of OH occurs very readily and is one of the commonest and best known band systems. A weak system has been found in the visible, and another in the ultra-violet, 2530–2250 Å. The rotation-vibration bands in the red and infra-red are known as the Meinel bands.

3064 Å SYSTEM,  $A^2\Sigma^+ - X^2\Pi$ 

**Occurrence.** In emission from almost all sources where water vapour is present, such as flames, arcs and discharge tubes. Also in absorption in flames, flash photolysis, etc.

**Appearance.** Degraded to the red. Four main heads  $R_1$ ,  $R_2$ ,  $Q_1$  and  $Q_2$ ; the  $Q_2$  is rather overlapped. There is also a weak  $^5R_{21}$  head. See Plate 4.

**References.** W. W. Watson, *Astrophys. J.*, **60**, 145 (1924)†.

D. Jack, *P.R.S.*, **115**, 373 (1927)†; **118**, 647 (1928); **120**, 222 (1928).

T. Tanaka and Z. Koana, *Proc. Phys. Math. Soc. Japan*, **15**, 272 (1933).

C. E. Moore and H. P. Broida, *Nat. Bur. Stand. J. Res.*, **A**, **63**, 279 (1959).

G. H. Dieke and H. M. Crosswhite, *J. Quant. Spectrosc. Rad. Transfer*, **2**, 97 (1962).

A. Stoebner and R. Delbourgo, *J. Chim. Phys.*, **64**, 1115 (1967).

$\nu', \nu''$	$^5R_{21}$	$R_1$	$R_2$	$Q_1$	$Q_2$	$I$
3, 0	—	2444	—	—	—	0
2, 0	—	2608.5	2613.4	2613.4	2622.1	3
3, 1	—	2677.3	2683.1	2681.8	2691.1	2
1, 0	—	2811.3	2816.0	2819.1	2829.0	6
2, 1	—	2875.3	2880.6	2882.3	2892.7	3
3, 2	—	2945.2	2951.2	2951.2	2962.4	1
0, 0	3021.2	3063.6	3067.2	3078	3089	10
1, 1	—	3121.7	3126.4	—	—	1
2, 2	—	3184.8	3190.2	3195.9	3208.7	1
0, 1	—	3428.1	3432.1	3458.5	3472.1	2
0, 2	—	—	3847	—	3934.7	0
1, 3	—	—	3902	—	3975.5	1
2, 4	—	—	—	—	4021.8	0

Under some conditions (e.g. low-pressure hydrogen flame) bands with  $\nu' = 2$  are enhanced by an inverse predissociation process.

VISIBLE SYSTEM (SCHULER AND WOELDIKE) 5800–3700 Å,  $B^2\Sigma^+ - A^2\Sigma^+$ 

**Occurrence.** This is a very weak system occurring in discharges through water vapour. It probably occurs in sun-spots.

**Appearance.** Open P and R branches; strongly degraded to the red.

**References.** H. Schuler and L. Reinebeck, *Z. Naturforsch.*, **A**, **4**, 560 (1949).

R. F. Barrow and A. R. Downie, *Proc. Phys. Soc.*, **A**, **69**, 178 (1956).

A. Michel, *Z. Naturforsch.*, **129**, 887 (1957).

S. Benoist, *Ann. Phys. (Paris)*, **10**, 363 (1955)†.

P. Felenbok, *Ann. Astrophys.*, **26**, 393 (1963)†.

No intensities are available but the (0, 7) and (0, 8) are relatively strong. R heads:

$\lambda$	$\nu', \nu''$	$\lambda$	$\nu', \nu''$	$\lambda$	$\nu', \nu''$
5534.1	1, 9	4957	1, 7	4336.6	0, 5
5480.3	0, 8	4729.7	0, 6	4216.4	1, 5
5123.5	0, 7	4587.3	1, 6	3864	0, 4

## OH (contd.)

ULTRA-VIOLET SYSTEM (SCHÜLER-MICHEL-BENOIST) 2550–2250 Å,  $C^2\Sigma^+ - A^2\Sigma^+$ 

*Occurrence.* A very weak system observed in high frequency and other discharges through water vapour. Found in sun spots.

*Appearance.* Probably open P and R branches only; degraded to red.

*References.* S. Benoist, *Ann. Phys. (Paris)*, **10**, 363 (1955).

A. Michel, *Z. Naturforsch.*, **A**, **12**, 887 (1957).

C. Carlone and F. W. Dalby, *Canad. J. Phys.*, **47**, 1945 (1969)†.

R heads from Michel and from Carlone and Dalby, with the latter authors values of  $\nu'$ :

$\lambda$	$\nu', \nu''$	$\lambda$	$\nu', \nu''$
2682.9*	0, 9	2464.7	1, 7
2599.6*	1, 9	2333.9	3, 7
2544.7*	1, 8	2248.6	3, 6

\* These may be relatively strong.

MEINEL (VIBRATION-ROTATION) BANDS ( $X^2\Pi$ )

*Occurrence.* In spectrum of the night sky, and in reactions of ozone with atomic hydrogen or with acetaldehyde. Under these conditions bands with  $\nu' = 8$  and 9 are strong. Also in oxyhydrogen flames, when bands with lower  $\nu'$  are excited.

*Appearance.* Degraded to longer wavelengths. In cool sources, such as the night sky glow, the Q branch is strongest, with a few R lines closing up towards a weak head 20 to 50 Å on the short-wave side, and resolved P lines on the long-wave side. In hotter laboratory sources the R heads are better developed.

*References.* A. B. Meinel, *Astrophys. J.*, **111**, 555 (1950)†.

J. D. McKinley, D. Garvin and M. J. Boudart, *J. Chem. Phys.*, **23**, 784 (1955)†.

G. Dejardin, J. Janin and M. Peyron, *Cahiers de Phys.*, **46**, 1 (1953).

A. M. Bass and D. Garvin, *J. Mol. Spec.*, **9**, 114 (1962)†.

B. J. Finlayson, S. S. Gaffney and J. N. Pitts, *Chem. Phys. Lett.*, **17**, 22 (1972).

R heads from Bass and Garvin in  $H + O_3$  reaction; Q heads from older references. Intensities are our estimates from Broida and Garvin's plate:

$\lambda_R$	$\lambda_Q$	$I$	$\nu', \nu''$	$\lambda_R$	$\lambda_Q$	$I$	$\nu', \nu''$
9946	10000	3	9, 5	6665.0		3	10, 4
9652.0		2	3, 0	6463.8		5	6, 1
9310.1	9400	8	8, 4	6235.4	6258	10	9, 3
8761.3	8829.4	7	7, 3	6137.0		3	5, 0
8281.0	8344	5	6, 2	5666.3		7	8, 2
7850.0	7918.5	6	5, 1	5541.1		5	7, 1
7714.7	7755.8	10	9, 4	5530.6		3	10, 3
7462.2	7529.1	3	4, 0	5188.5		5	9, 2
7238.0	7284.2	6	8, 3	4629.4		3	7, 0
6828.9	6879	8	7, 2				

## OH\*

3565 Å SYSTEM,  $A^3\Pi - X^3\Sigma^-$ 

*Occurrence.* Electrodeless and high-frequency discharges through water vapour at low pressure.



