PROCEEDINGS OF THE

Xth COLLOQUIUM SPECTROSCOPICUM INTERNATIONALE

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Foreword

The Xth Colloquium Spectroscopicum Internationale is the first of the Colloquium series to be held in the western hemisphere. For a considerable number of years spectroscopists in the United States had observed with interest the stimulating and informative spectroscopic Colloquia in Europe and actions were begun to have the United States serve as a host for one of the Colloquia. Following the organization of the national Society for Applied Spectroscopy in 1958, the possibility existed for formal invitation to the Colloquium by a representative body in the U. S. A. With the selection of Washington and the year 1962 for the first National Meeting of SAS, both an appropriate location and time were available for the Society to act as host to the Colloquium. Accordingly an invitation was presented at the IXth Colloquium in Lyon in June, 1961 to hold the next Colloquium in the U. S. A. in 1962. The invitation was accepted by the Colloquium group with the informal expression that the even numbered years might be reserved for infrequent meetings of the Colloquium held outside of Europe. This international conference also was sponsored by the University of Maryland, Department of Chemistry, and by the International Union of Pure and Applied Chemistry, through action initiated by its Commission on Spectrochemical and Other Optical Procedures of Analysis.

The Xth Colloquium was held June 18-22, 1962 at the University of Maryland, College Park, Maryland, U. S. A. More than 170 papers, including 24 invited papers, were presented in 27 sessions during the five days. The registration totaled 944, consisting of 807 full participants, 80 associate, and 57 single session registrants, representing 29 countries. In the plan followed for the program, invited lectures were arranged to be given in the morning and early afternoons to present general surveys of research on currently important themes in basic and applied spectroscopy. These lectures were followed by contributed research papers related to the same themes. The general program of papers with abstracts appeared in Applied Spectroscopy, Vol. 16, No. 2, 1962; abstracts of post-deadline papers will be found in the same journal, Vol. 16, No. 5, 1962.

The question of publication of the Proceedings of the Colloquium received considerable attention in the planning stages. While publication of all papers has much appeal, past experience has shown that considerable delays are encountered in publication of the full program, resulting from the large volume of material and difficulties in collecting the manuscripts. Furthermore, it was the opinion of some advisors that papers dealing with original research should be subject to the usual editorial review and published in the existing journals.

For this Colloquium a compromise was adopted in which the invited papers providing broad surveys of important research in spectroscopy and other selected papers of a general nature were scheduled to be published in the Proceedings, and authors of more specialized research papers were referred to the spectroscopic journals. This plan has the advantage of providing a well-knit assembly of authoritative surveys of current spectroscopic research with a minimum time required for publication. The time feature is especially important because of the ever accelerating pace in research in these fields and the pressing need for more rapid communication.

The Chairman of the Program Committee, Dr. Ellis R. Lippincott, and the Secretary of the Conference, Dr. Marvin Margoshes kindly agreed to serve as editors for this volume. With the prompt response of the authors, the diligence of the editors, and the cooperation of the publisher, publication of the Proceedings within a few months was assured. The Organizing Committee for the Colloquium extends its appreciation to the many individuals who made this publication possible.

National Bureau of Standards
Washington 25, D. C.
September 15, 1962

Bourdon F. Scribner
General Chairman
Xth Colloquium

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INTRODUCTION

A large fraction of the observational data of astronomy is obtained by spectroscopic methods, and a similarly large portion of astrophysical theory is devoted to the analysis of spectroscopic data. Any general review of so large a subject must be superficial. The goal of the present review is to describe (1) some of the instrumental problems, and the limitations of the observational techniques, (2) the physical conditions in the sources of the spectra, (3) the peculiarities of the excitation mechanism in various types of astronomical objects, and (4) the chemical composition of the stars, and their relation to nuclear energy generation and the theories of the origins of the chemical elements.

The enormous range of physical conditions in the sources makes astronomy an important branch of applied spectroscopy, notable at one extreme for high temperatures, low pressures, and nearly complete ionization; at another extreme very high pressure phenomena become important; in some problems, the deviations from thermodynamic equilibrium are very large. There are no standard techniques, no calibrated sources—nature plays a difficult game, sometimes an unfair one, with the investigator. But there is no richer road in astronomy—we are so greatly limited in our experimental techniques that we take gladly what information we can, from the slenderest of clues.

It should be remembered that the faintest objects which are studied spectroscopically have a total flux, at the earth, of less than one photon per cm^2 per second; with a spectral resolution of even 10^3, which can be used on so faint an object, the 200-inch reflector gathers only 40 photons/sec per spectral resolving-power unit and the inefficiency of the slit spectrograph and of the photographic process reduces this number to less than one silver grain per second. Thus, astronomical exposures run from several nights at a dispersion of 400 Å/mm, for a distant galaxy or a faint star, up to relatively short exposures at 1 Å/mm for stars of naked-eye brightness, to snapshots at 0.1 Å/mm for the sun. In general, we still employ photographic techniques, although photoelectric scanning of the spectrum of bright stars at high resolution (≈ 50,000), and of faint stars at low resolution (≈ 500), and image-intensifiers for low resolution spectra are now in regular use and under intensive development. Photography and the atmosphere together limit the spectral region observable to $\lambda 3100$ to $\lambda 8900$.

Infrared scanning of the sun, within the limitations of the transmission of the terrestrial atmosphere, is generally employed to 3μ, and experimental development in the 10μ region is under way. I will omit discussion of far ultraviolet observations from rockets and satellites except to say that spectral emission-line studies of the sun have been carried down to 100Å, in detail, the general intensity distribution charted in the X-ray region, and γ-rays detected from outside the solar system. One very important long wavelength feature is the 21-cm hyperfine transition in the ground states of atomic hydrogen in interstellar space; here the observing techniques are those of radio astronomy. Till now, no other monochromatic radiation has been detected in the long wavelength region, nor are any beyond those of molecular hydrogen expected to be strong; no definite quantitative predictions of the interstellar molecular hydrogen spectrum yet exist.

Among the goals of astronomical spectroscopy are (1) identification of atoms, ions, radicals, and molecules present, (2) the quantitative analysis of stellar atmospheres, (3) the study of the physical conditions in the source of the spectrum, e.g., temperature, electron and gas pressure, magnetic field, state of motion (convection or turbulence) and mass motion. The nature of the excitation process is of the greatest interest; the existence of spectral lines in emission or absorption depends on deviations from complete thermodynamic equilibrium. For example, studies of intensities of the absorption lines across the disk of the sun provide information concerning the temperature gradient in the outer 500 km of the solar atmosphere. The change of the spectrum into emission lines, and the increase of the level of excitation and ionization with height above the solar surface, in the range 10^3 to 10^6 km, reveal the chromosphere and corona, where the temperature ranges from 10^4 to 4×10^6 °K.

THE ASTRONOMICAL BACKGROUND

The variety of densities, temperatures and compositions is so great that one can only say that astrophysics embraces all ranges of density at which spectra can be observed—generally atomic, although molecules dominate the coolest stars, and solids may be responsible for some interstellar bands. A very rough idea of the range of temperature, T, and density, n_H (hydrogen atoms per cm^3) is given in Table 1. The symbols A and E under *Lines* indicate absorption and emission lines. Under *Processes* I list some of the interesting peculiarities in each type of source. The excitation processes will be discussed in detail below, but in general, except for the stellar reversing layers, are dominated by violent deviations from thermodynamic equilibrium. Since hydrogen is dominant in nearly all sources except for planets and comets only its concentration is given. For planets and comets, densities are largely unknown and strongly dependent on which height is being studied. Relative abundances of other elements in interstellar space parallel those in the normal, young stars. The concentration of interstellar compounds is very low, probably about 10^{-6} n_H.

The determination of the composition of the stars will be discussed later; Table 2 gives a recent compilation by Aller [1]. We shall take such a composition as the standard with which peculiar stars are compared. But except in the most abnormal objects, Table 2 shows that the enormous predominance of hydrogen must control the appearance of the spectra of the stars, either by the strength of its lines, or by its continuous opacity which sets the depth of the atmosphere through which one can observe, and therefore the strength of other lines. Along the main sequence the mass above the photosphere (which is located at optical depth near unity) varies from 0.2 gm/cm^2 at 25000° to 4 gm/cm^2 at 5000°, the temperature of the sun. Surface gravity, and therefore the pressure, decreases from main sequence stars to supergiants. The gas pressure is about 10^5 $dynes/cm^2$ in the sun and drops to 10^2 in a supergiant, while in a white dwarf, the gas pressure reaches 10^9 $dynes/cm^2$. Collisions with neutral hydrogen cause line-broadening, although resonance self-broadening occurs for the strong lines of Ca II, Ca I and Na I at very low temperatures. When hydrogen becomes partially ionized, above 7000°K, collisions with ions and electrons dominate line broadening, and the detailed theory of the hydrogen-line broadening itself has been given by Kolb, Griem and Shen [2].

The observability of lines of a given element depends on many factors besides the abundance. The limitation on the observable spectral region, in particular, requires that subordinate

Table 1

Physical Conditions in Astronomical Sources

Source	Lines	T(°K)	n_H/cm^3	Processes
Interstellar gas	A	50 - 120	0.1 - 100	21-cm emission of H. Lines from lowest energy levels of Na, Ti, Fe, Ca II. Degenerated bands CN, CH; diffuse bands connected with dust, solid state, H_2?
Diffuse nebulae	E	10^4	$10 - 10^5$	Recombination spectra H, He; resonance excitation OIII; collisional excitation leading to forbidden lines of [N II], [O II], [O III]. Shock waves?
Stellar envelopes	E	$5000 - 10^6$	$10^3 - 10^8$	Material ejected from stars due to rotation, tidal forces in binaries, radiation pressure, turbulence. Large scale motions and gaseous streams. Recombination, collisional ionization and excitation. Chromosphere and corona.
Stellar envelopes	A	$10^2 - 10^4$	$10^4 - 10^{10}$	Ejected unstable shell. Mass motions. Metastability enhances population of low energy states; ground state absorption; grades into normal atmosphere.

Table 1—Continued

Source	Lines	T(°K)	n_H/cm^3	Processes
Stellar reversing layer	A	2000 - 75000	10^{12} - 10^{18}	Excitation by radiation or by collisions. Stable, or convective motions. Near-local-thermodynamic equilibrium. Magnetic fields, electric microfields due to plasma. Continuous opacity of H, H^-, and possibly molecules in cooler stars. Molecular bands diatomic, some triatomic radicals.
Comets	E	10^2 - 10^3	?	Excitation by resonance fluorescence of sunlight, radicals and molecules derived from heavier unknown parents. C_2, C_3, NH_2, Na, OH, NH in heads; ions in plasma tail, OH^+, CO^+, CO_2^+, N_2^+, CH^+.
Planets	A	100 - 200	?	Molecules absorbing sunlight; CO_2, NH_3, CH_4, ice, H_2.

Table 2

Normal Stellar Composition of Young Stars and Chondritic Meteorites

Element	log N	Element	log N
H	12.0 v	Ga	2.4
He	11.0 v	Ge	3.2
Li	1.0 v	Rb	2.5
Be	2.2 v	Sr	2.7 v
B	2.9 :	Y	2.4 v
C	8.6 v	Zr	2.5 v
N	8.0 v	Nb	2.0 v
O	9.0 v	Mo	1.9 v
F	6.0 :	Ru	1.4 v
Ne	8.7	Rh	0.8
Na	6.3	Pd	1.2
Mg	7.4	Ag	0.2 :
Al	6.2	Cd	1.5
Si	7.5 v	In	1.2 :
P	5.3 v	Sn	1.5
S	7.3 v	Sb	1.9 :
Cl	6.2 :	Ba	2.1 v
A	6.9	La	1.2 v
K	4.8	Ce	1.3 v
Ca	6.2 v	Pr	0.6 v
Sc	2.8 v	Nd	1.3 v
Ti	4.8 v	Sm	0.9 v
V	3.8 v	Eu	0.5 v
Cr	5.4 v	Gd	1.0 v
Mn	5.1 v	Dy	1.1 v
Fe	6.8	Ho	0.4
Co	4.7	Er	0.8
Ni	5.9	Tm	0.1
Cu	4.5	Yb	0.8
Zn	4.6	Lu	0.0
		Pb	1.8

v = deviations from normal abundances suspected in some types of stars.
: = presence or abundance uncertain.
Rare-earths from chondritic meteorites. Schmitt et al.; other elements solar or stellar, modified from Aller.

lines be used, because most resonance lines are in the ultraviolet; for highly ionized atoms this is always true, requiring rocket and satellite spectroscopy. The high excitation potential of observable lines of H, He I, He II (10, 20, 40 ev) make the abundances of these elements uncertain since the Boltzmann factor is very temperature-sensitive. In the sun, the metals are singly ionized, but their low levels are easily observable. Their relative abundances can be well determined, but their ratio to hydrogen is difficult. Elements like C, N, O, also have high excitation potentials, so they are not too well determined. In hot stars, H, He, C, N, O, Ne, Si, are well observed at various stages of ionization, while the metals are too highly ionized.

However, it must be noted that ultraviolet spectra will not be a çure-all. Distant stars are in general unobservable below 1000 A, because of the opacity of the interstellar hydrogen. In addition, in cool stars, the crowding and overlapping of the lines of the metals will make the region below 3000 A almost useless for quantitative purposes, although important for identification and for emission-line study of the hot chromospheres and coronas of the stars. In some ways development of the stellar techniques for high resolution in the near infrared may prove more profitable, because of the comparative simplicity of the atomic spectra and the appearance of new molecular species.

HIGH TEMPERATURE ENVELOPES

Doppler determinations have led to our knowledge of the velocity distribution of the stars, interstellar gas, and distant galaxies, culminating in a value of $cd\lambda/\lambda = 0.46$ for a distant galaxy, the radio source 3C295. But equally important has been the contribution of radial velocities to the determination of stellar masses from the orbits of close spectroscopic binary stars. Less well known, but very significant in the understanding of the high-temperature envelopes of the sun and stars is the existence of convection, "turbulence," stream motions and mass loss in certain types of stars. On the surface of the sun, small, bright, hot granules are observed to rise with speeds near 1 km/sec, in a semi-regular pattern resembling Benard cells. Stars, for which we often observe the integrated result of similar motions on a grander scale, have broadened absorption lines. Loosely described as turbulence, these motions have scales of length up to an appreciable fraction of the stars' radius (macroturbulence) and down to a fraction of the scale height of the reversing layer ($\approx$ 200 km), and velocities from 40 km/sec down to nearly thermal values of 1 to 5 km/sec. They are driven by a convective instability of the stellar plasma. The temperature gradient in most stars is radiative, and depends on the opacity; since hydrogen and metals both contribute to the opacity, the latter is a function of temperature T and pressure P. Given knowledge of the composition of the star and the physics of the opacity, the radiative temperature gradient is found. Convection will occur if

$$\left|\frac{d \ln T}{d \ln P}\right|_{rad.} > \left|\frac{d \ln T}{d \ln P}\right|_{ad.} \qquad (1)$$

The ratio of specific heats of the gas, γ, gives the adiabatic temperature gradient

$$\left|\frac{d \ln T}{d \ln P}\right|_{ad.} = \frac{\gamma - 1}{\gamma}, \tag{2}$$

Therefore, if the radiative gradient is close to the adiabatic one, a change of level of ionization, which will make a substantial change in γ, will drive convection. In stars like the sun, the ionization of hydrogen is responsible, while He and even H_2 ionization zones occur in other types of stars. Such convection may be responsible for stellar light and radius variation such as is found for cepheids and long-period variables.

Energy transport by convection can be computed from the temperature fluctuation in the convective elements, $\Delta T/T$, their velocity and pressure. In the sun, the velocities are subsonic, $\Delta T/T \approx 0.05$, and the energy thus transported as pressure waves is a non-negligible fraction of the solar output. The important fact, however, is that pressure waves, running through the outer low density envelope, gain velocity because of the conservation of energy. As they approach the velocity of sound, i.e., as $M(= v/v_s) \rightarrow 1$, the production of noise becomes important, and most of this sound energy, E_s, is converted into heat. For isotropic turbulence, when M is not large,

$$E_s = 19\rho <v^2>^{3/2} M^5 \text{ erg/cm}^2 \text{ sec}, \tag{3}$$

where $<v^2>$ is the mean-square turbulent velocity. In the region where solar granulation appears, $\rho \approx 10^{-6}$ gm/cm^3, with $<v^2>^{1/2} \approx 2 \times 10^5$ cm/sec, (M = 0.2), we find $E_s \approx 10^6$ erg/cm^2 sec, about 10^{-4} of the radiant energy of the solar photosphere, 10^{10} erg/cm^2 sec. This small fraction, however, is ample to account for the phenomena of solar activity, the chromosphere (10^4 °K) and the low density corona (10^6 °K). Biermann and Lüst [3] give a rough estimate of the energy involved in high-temperature, nonthermal, or particle radiation from the sun, reproduced in Table 3. Violent activity involves large fluxes for short periods, as in solar flares. While these numbers are highly uncertain, they are in the range of the acoustic noise energy, or the transport of energy by the granules, so that they may be different aspects of the same phenomena. Larger units of mass transport have also been suggested, e.g., spicules. Of course, still a different mechanism is present in the form of the moving magnetic fields of the sunspots, flares, prominences and ejected plasma. But the energies in the magnetic fields may

Table 3

Solar Non-Thermal Energies

(ergs/cm² sec)

Type	Radiation		Particles	
	U.V.	Radio Freq.	Normal	Relativistic
Average	10^5	10^{-1}	10^5	--
Active Regions	$>10^6$	1 - 10	10^6	--
Flares	$10^8 - 10^{10}$	$10^2 - 10^3$	$10^7 - 10^9$	$10^7 - 10^8$

also have the convective plasma transport as their fundamental energy source, and magnetic lines of force may be merely a coupling mechanism, and provide the locale for particle acceleration.

A non-thermal source of local heating gives a temperature or level of ionization corresponding to about $1 - 4 \times 10^6$ °K in the sun, i.e., about 400 ev. Strong forbidden emission lines of [Fe X], [Fe XIV], [Ca XV] are found in the corona. If all energy densities are in rough equipartition, characteristic values are $U_{mag.} = B^2/8\pi = U_{thermal} = 3/2\, n_H kT = U_{kin.} = 1/2\, n_H m_H v^2$. At typical conditions in the lower solar corona, $n_H = 10^8/cm^3$, $T = 10^6$ °K, $\langle v^2 \rangle^{1/2} = 100$ km/sec (approaching random motions observed) and the magnetic field strength is 1 gauss (not far from the solar general dipole field). Magneto-hydrodynamic velocities are $v_A = B(4\pi\, n_H m_H)^{-1/2} = 300$ km/sec. The spectroscopy of such a source, very far from equilibrium between matter and radiation density, is extremely interesting, and the rocket and satellite results will be of great interest. Ultraviolet permitted lines from high ionization levels have already been detected, and X-ray radiation traced far beyond the energies suggested by the above elementary considerations. Some double stars containing red giants, as well as ordinary novae at certain stages of their evolution, show emission-line spectra similar to that of the solar corona, ranging from [Fe II] to [Fe XIV]. One recurrent nova showed forbidden lines from as low as [O I] (low temperature) to [Ca XV] (very high temperature). Permitted emission lines up to OVI occur near faint, hot stars which are nuclei of planetary nebulae, i.e., which have ejected large quantities of gas with velocities up to 100 km/sec. Thus we often find superposed on the normal and absorption-line spectra of stars, emission-line features as evidence for a hot circumstellar envelope. Since the solar corona is only 10^{-6} as bright as the sun, such objects must display these non-thermal features on an enormously greater scale than does the sun.