

MOLECULES: THEIR ROLE IN ASTRONOMY

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The laboratory spectra of flames, arcs, discharges, and sparks reveal, in addition to continua of various extension, two types of discrete emission: well separated lines emitted by atoms, and closely packed bands produced by molecules. The striking difference in appearance between atomic and molecular spectra is due to the different nature of the energy levels in atoms and in molecules. Atoms possess only electronic energy, whereas molecules have in addition energies of vibration and of rotation. In a molecule, the nuclei vibrate relative to each other, giving rise to quantized vibrational energies, while the whole system rotates around an axis of inertia, thus providing quantized rotational energies. Together with any electronic transition, or even in the absence of such a transition, the vibrational and rotational energies vary according to specific rules of intensity and selection given by wave mechanics. A band, characterized by one or several heads and by series of lines degraded toward the red or toward the blue, corresponds usually to only one specific electronic and vibrational transition, but to all possible rotational transitions. A very complete understanding of the physics of molecular spectra has been reached in recent years, and a wide field of astronomical application has thus been opened.

Molecular spectra are found in a great variety of astronomical sources, the earth's atmosphere, the sun, the planets, comets, stars cooler than those of class F5, novae, and interstellar gas. A general condition for the formation of molecular bands is a moderate or low temperature, since at high temperatures molecules would be dissociated. This condition, however, should not be considered too strictly, because the continuous absorption of molecules like H_2^+ and He_2^+ may play a role in early-type stars. All the observed compounds in celestial gases are associations of cosmically abundant atoms: hydrides, oxides, nitrides, and molecules containing carbon or silicon. Among the carbon compounds, the two isotopic nuclei C^{12} and C^{13} are observed in carbon stars and in comets. Many species of molecules (for example

H_2) are very abundant in astronomical objects, but are not revealed by their discrete spectra which fall in an unobservable region. Yet these molecules manifest their presence either by affecting the abundance of certain free atoms or of other molecules, or by participating in the continuous absorption in the stellar atmospheres. Broad, deep molecular absorption bands affect strongly the colors of the cool late-type stars, making them appear more reddish or bluish than black bodies at the temperatures determined from the atomic lines. Although the continuous opacity of molecules must play an essential role in the late-type stars (and a not negligible role for types as early as A0!), very little theoretical information on the subject is available.

The late-type spectra are very complex, containing thousands of atomic and molecular lines, so that in identifying molecular lines in cool stars one must proceed very cautiously, taking into account the intensities, as well as the coincidences in wave length. A large proportion of the faint lines are still unidentified in the solar spectrum, and it is certain that most of them are of molecular origin. Molecular bands have helped to identify chemical elements which could not be detected by atomic lines. For example, the presence of fluorine was ascertained in the sun and in stars of later type by the discovery of silicon fluoride bands (SiF), long before it was detected in nebulae by the forbidden lines of trebly ionized fluorine atoms. Similarly, there is little doubt that bands of boron oxide (BO) are present in late-type stars, whereas the identification of atomic lines of boron is very doubtful.

Molecular bands are found throughout the astronomical spectral region from λ 3000 (OH) to the far infrared (H_2O , O_3 , CO_2 , ...). In fact, the ultraviolet limit of the astronomical region, slightly to the ultraviolet of λ 3000, is due to absorption by molecules of ozone (O_3) and oxygen (O_2) in the earth's atmosphere. In addition to these, many other atmospheric absorption bands are due to molecules: oxygen (O_2) in the red; water vapor (H_2O) in the yellow, red, and infrared; carbon dioxide (CO_2) in the infrared; ozone (O_3) and several other more complex molecules (such as N_2O_5) also in the infrared; and various

unidentified bands (some probably due to $(O_2)_2$). The atmospheric oxygen bands in the red are especially interesting, since they appear in absorption with great intensity, despite their character of "forbidden" transitions; evidently their intensity is due to the great number of oxygen molecules encountered by light while traversing the earth's atmosphere. "Forbidden" bands of nitrogen (N_2) and probably of oxygen (O_2) are observed in emission in the night-sky spectrum.

All the stellar bands that have been identified belong to neutral diatomic molecules (CN , C_2 , CH , OH , NH , TiO , ZrO , MgH , SiF , BO , ...). Ionized diatomic molecules are found in cometary emission (CO^+ , N_2^+ , CH^+ , OH^+), in interstellar absorption (CH^+), and in the emission of the aurora borealis (N_2^+). Polyatomic compounds are observed in absorption in the earth's atmosphere (O_3 , H_2O , $(O_2)_2$, CO_2 , N_2O_5 , ...), in Venus (CO_2), in the four major planets (methane, CH_4), in Jupiter (ammonia, NH_3); and some should be found in the coolest stars (CH_2 , H_2O , HCN , ...). In addition to these, emission from CH_2 has been observed in comets. All the red and infrared absorption bands of astronomical polyatomic molecules are rotation-vibration spectra, in which no electronic transition is involved. In all the molecular spectra observed, the lower electronic level is the ground electronic state of the molecule.

When the molecular bands are observed in emission, they are excited either by a pure fluorescence mechanism as in comets, by chemiluminescence as in the night sky, or by electron impacts as in the aurora borealis. The molecules revealed by absorption bands may be more or less in thermodynamical equilibrium as in stellar atmospheres, or they may be in conditions which depart considerably from such an equilibrium as in interstellar gas. In stellar atmospheres we may assume a Boltzmann distribution in the vibrational and rotational levels, and use the intensity distributions among the vibrational and rotational transitions to determine the excitation temperature ("vibrational" or "rotational" temperature), a method which has been applied successfully to the sun and to late-type stars. In interstellar gas, considerations of equilibrium are excluded, and great care has to be exercised in discussing theoretically the

dissociation and ionization of interstellar molecules. The astronomical molecular problems are thus concerned with a wide variety of physical questions.

Because of the low temperature, the molecular bands in the late-type stars may actually become intense enough in certain spectral regions to obliterate almost completely the atomic absorption lines. In many long-period variables of very low temperature, atomic emission lines are observed along with strong molecular absorption. How these bright lines are excited is still a mystery. For some lines, effects of chemiluminescence have been suggested as the source. For others, the very striking selectivities observed among the atomic transitions suggest a mechanism of monochromatic excitation. At any rate there is no doubt that the molecules play an essential role in stimulating the atomic emission.

The intensity of molecular bands provides the essential means of classifying late-type stars in absolute magnitude, as well as in spectral type; strong bands of *TiO*, *ZrO*, and carbon compounds characterize the M, S, and carbon stars respectively. Many theoretical discussions have been concerned with the dissociation equilibrium of molecules in stellar atmospheres, and with the resulting abundances for various spectral types and absolute magnitudes. In general the agreement between theory and observation is fairly satisfactory, considering the scarcity of data on the continuous opacity in the late-type stars. Yet, a number of questions remain. If, as is always done, we assume a thermodynamical equilibrium, the difference between the M and the R and N stars must be attributed to different chemical constitutions. In the M stars, oxygen must be abundant relative to carbon, while the opposite is required for the R and N stars. Such a subdivision, however, into carbon and oxygen atmospheres does not appear in the earlier spectral types, and differences in chemical constitution should be assumed only as a last resort. It may be that the subdivision of cool stellar atmospheres into *TiO*, *ZrO*, and *C₂* types is due to physical (instead of chemical) conditions. Actually, the stellar radiation reaching a specific outer layer of a late-type star has already been transformed in the deeper layers; this transformation may have resulted in the

absorption of specific spectral regions. If a molecule AB can be dissociated only by the absorption of radiations in this depleted spectral region, a higher abundance will be built up than in conditions of thermodynamical equilibrium. In other words, the molecular abundance obtained from the dissociation equilibrium should be multiplied by a correcting factor α , which represents the effect of the departure of the dissociating radiation from the black-body distribution ($\alpha \geq 1$ or ≤ 1). Such a factor α may have a great importance on the outskirts of novae (where CN and C_2 have been observed), in the outer regions of red stars, in the interstellar gas, in all extended stellar atmospheres, and in the solar chromosphere. In comparing the relative abundances of two molecules and in discussing the behavior of a molecular abundance with respect to temperature and gravity, the α factors may become as important as the molecular abundances obtained in thermodynamical equilibrium. We may think that the "normal" conditions of late-type atmospheres are those in which the TiO bands are conspicuous. For very specific physical conditions affecting the dissociating radiations, $\alpha(TiO)$ may be reduced whereas $\alpha(ZrO)$ may be increased, thus producing atmospheres of the S type. Identical considerations may apply to the R and N stars, and, in this connection, a comparative investigation of the OH bands in M and R and N stars would be very fruitful (but difficult!). Evidently similar factors affect the ionization of molecules in interstellar space or in comets.

It is hoped that this very sketchy account will show the importance of astronomical research in the molecular field at the present time. One of the most urgent needs is the extension of astronomical observations toward the infrared. The help of the physicists is needed for additional investigations of bands of astronomical interest, giving intensities as well as further descriptions of the bands.

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