

tional Astronomical Union met in Paris in 1935 with Dr. Schlesinger as its president, he was appointed an officer in the French Légion d'Honneur.

Dr. Schlesinger was completely devoted to his science and also very conscious that the results of the present time owe much to the work of the past. He was anxious to pay this debt and to do his full share of work that would be useful in the future. In 1922, he made the need for better star positions the subject of his address as retiring president of the American Astronomical Society. His address was concluded as follows: "We may be sure that astronomers of our own day will fulfill in some way the obligations imposed upon them by the needs of their science, as fully and as unselfishly as have their predecessors." Truly it can be said of Frank Schlesinger that he did fulfill these obligations as fully and as unselfishly as any astronomer of the past or the present.

YALE UNIVERSITY OBSERVATORY, AUGUST, 1943.

The Physical Chemistry of Comets*

By P. SWINGS

In recent years considerable attention has been devoted by astronomers to the general problem of the relative abundances of the various atoms and molecules in celestial objects, in other words to their chemical constitution. The observational data are the intensities of the atomic lines and of the molecular bands present in the spectra; the next step is the interpretation of the observed intensities in terms of abundances.

The problem is especially interesting, but at the same time particularly difficult, in the case of the comets, and it illustrates in the most striking fashion, the usefulness of a close collaboration between astronomers, physicists, and chemists.

First, what are the observational data? A cometary spectrum consists of emission bands of molecules superposed over a solar spectrum, due to the reflection or scattering by the solid or gaseous particles present everywhere in the comet but especially abundant in the nucleus. The relative intensity of the solar spectrum and of the bright bands depends on the distance of the comet from the Sun. Comets observed at very large heliocentric distances have only revealed a solar spectrum indicating that they contain then relatively few gaseous molecules emitting in the observed spectral region. Yet a renewed, thorough investigation of this spectroscopic problem should be of primary interest in the light of the recent results on the polyatomic molecules of comets. At small heliocentric distances, not only do we find molecular bands, but even the yellow lines of the sodium atom appear.

*Address given at the May meeting of the Sigma Xi Chapter of the California Institute of Technology, Pasadena, California.

Considerable resemblance exists between the spectra of different comets. But even for comets having the same excitation, *i.e.*, observed at the same distance from the Sun, there may occasionally occur striking differences in the relative intensities of the solar spectrum and the emission bands, as well as in the relative intensities of the bands due to different molecules. This indicates that the comets do not all possess exactly the same chemical constitution.

What are the molecules identified in cometary spectra? Much progress has been made in the course of the last three years, and we have now the following list of identified molecules: OH, NH, CN, CH, CH⁺, C₂, CO⁺, N₂⁺, CH₂, NH₂, and probably OH⁺. All the strong emission features of comets are now identified, and further additions will require new observations in the red and infrared regions.

What is the mechanism of excitation of the emission bands of these molecules? Are they emitted as a result of electron collisions, or through some process of photodissociation by solar light, or as a pure fluorescence excited by solar radiation? It is possible to decide unambiguously in favor of the latter mechanism, *i.e.*, the pure fluorescence, in the following way. If a specific molecular line can be excited only in a wavelength coinciding with a strong absorption line of the solar spectrum, little energy will be available in the Sun for this particular excitation, and the corresponding cometary line will be weak or even absent. This is actually what we observe: for example, the cometary bands of cyanogen have a very peculiar, irregular intensity distribution, unlike anything obtained in a laboratory discharge. On the other hand, the cometary band structure can be fully explained on the basis of a fluorescence excited by the complex solar radiation. Physicists will undoubtedly correlate this observation with the complex superposition of resonance doublets observed in the laboratory fluorescence spectra of diatomic molecules, such as I₂, Br₂, S₂, Se₂, Te₂, etc., when they are excited by non-monochromatic radiation. And indeed the two observations are essentially identical, except for the fact that densities are so low in comets that we never have to fear collisional effects! Actually most cometary molecules live their whole life, until photodissociation or photoionization occurs, without encountering a single collision.

At first sight it might seem strange that a low temperature object, such as a comet, may contain molecules like CH, NH, OH, etc., that are not considered as chemically stable. But this is, of course, due to the low densities, prevailing in comets. Once a CH radical has been formed by photodissociation of a more complex chemically stable molecule, it will not have the slightest chance to re-combine in a collisional process.

How do these chemically unstable molecules originate? The gaseous atmosphere of a comet is formed by the liberation of molecules which were occluded in the solid particles. These parent molecules must of

course be chemically stable compounds. From the observed emission bands we gather that the following occluded compounds must be present in the cometary solids: H_2O , NH_3 , CH_4 , C_2N_2 , N_2 , CO or CO_2 . Although this is about all that we can say with any degree of confidence at the present time, it seems rather tempting to relate the cometary problem to the chemical constitution of the occluded gases found in meteorites by heating or breaking them in vacuum. We know that meteorites also reveal CH_4 , CO_2 , N_2 , etc. It might not be entirely legitimate to identify the two types of objects; yet a comparison is very useful. It is well established, for example, that the occluded gases of the stone and iron meteorites do not have the same chemical compositions. As a working hypothesis we may thus at least consider that the differences between individual comets might be related to the differences between meteorites.

The different types of molecules have very different distributions in a cometary atmosphere. Whereas CH , CH_2 , and NH_2 are concentrated very near the nucleus, OH extends farther out, NH still farther, and CN and C_2 are found all over the head. The ionized molecules are found especially in the tail, up to very large distances from the nucleus; yet in the head, they are found only very close to the nucleus. The extension of a molecule is of course the product of its average velocity by its average lifetime. Some molecules such as CO^+ and N_2^+ have very small initial velocities, but extremely long lives; others, such as CH or C_2 , have large velocities, and intermediate cases are also observed. The initial velocities cannot be due to thermal agitation, since molecules of nearly the same mass, such as CN and CO^+ , have very different initial velocities. Hence these velocities must result from the photodissociation of the parent molecules.

As for the average lifetime of a specific molecule before photodissociation or photo-ionization occurs, this depends not only on the physical characteristics of the molecule but also on the solar energy available in the spectral region considered. For example, if the CO^+ and N_2^+ ions are produced by the photo-ionization of CO and N_2 , the solar radiation required lies beyond $\lambda 900 \text{ \AA}$, *i.e.*, beyond the Lyman limit. We do not know how the Sun radiates in this spectral region. But we do know that practically all the hydrogen atoms are in their ground state in the solar atmosphere; hence the Lyman absorption lines, and the Lyman absorption continuum must be extremely strong. As a result we may have to think of other possible mechanisms of formation of CO^+ and N_2^+ , such as photodissociation of parent molecules into a positive and a negative ion, or photo-ionization in several steps via intermediate levels, or ionization by impact of solar electrons.

To discuss in detail the physico-chemical problems of comets we need: additional laboratory or theoretical data on the oscillator strengths of the abundant molecules; physico-chemical information on the dissociation and ionization properties of these molecules; more precise data on