FARADAY LECTURE
(Delivered 30 September 1970)*

Spectra and Structures of Molecular Ions

By G. Herzberg
DIVISION OF PHYSICS, NATIONAL RESEARCH COUNCIL OF CANADA, OTTAWA, CANADA

1 Introduction

The study of the spectra of atomic ions has played an important rôle in the elucidation of the structure of atoms. By removing one or more electrons from an atom and studying the spectra of the resulting ions we obtain clearcut information about the electron configuration of the neutral atom. The observation that the spectrum of the He^+ ion is in every respect similar to that of the neutral H atom, except for a shift by a factor 4 in the frequency scale, was one of the first triumphs of the Bohr theory which predicted this behaviour. The study of the spectra of iso-electronic series such as Na, Mg^+, Al^{2+}, ... first made it possible to assign true principal quantum numbers to the various electronic orbitals and thus to lay a basis for the building-up principle which (together with the Pauli principle) allows an understanding of the periodic system of the elements.

The spectra of *molecular* ions are of similar importance for an understanding of the electronic structure of molecules. Up to now only comparatively few such spectra are known. Whenever they have been observed and analysed they have greatly added to our understanding of the electronic structure and therefore the bonding in the corresponding neutral molecules. For example, if the ground state of the ion has been determined from its spectrum we know immediately which electron (orbital) is the most loosely bound in the neutral molecule, while the excited states of the ion often give us information about the next lowest orbitals. (The recent development of photoelectron spectroscopy is largely aimed at this point.)

In recent years many complicated molecular ions have been studied by means of the electron spin resonance technique in the liquid and solid phases. In this lecture I shall not consider this aspect of the subject of molecular ions but restrict myself to the discussion of simple molecular ions in the gaseous phase.

With one exception (CH^+) all spectra of molecular ions were first observed in emission in electric discharges and only quite recently have a few been observed in absorption. The emission spectrum of the N_2^+ ion occurs in almost any discharge through nitrogen (or air) and is probably the first one that was recognized as a molecular ion spectrum. It is very prominent in the spectrum of the aurora.

---

* The lecture was also given in Oxford, 3rd October, and Dundee, 12th October, 1970.

The spectra of CO^+, N_2^+, CO_2^+, and CH^+ occur fairly strongly in the spectra of comets, particularly comet tails. In interstellar absorption the CH^+ ion was detected some thirty years ago and was, for many years, the only known absorption spectrum of a molecular ion. The possibility that other unidentified features of interstellar spectra may be due to molecular ions and the expectation that molecular ions may be of considerable importance for the chemistry of the interstellar medium provided part of the motivation for the studies of molecular ion spectra carried out in recent years in our laboratory.

Another motive for the study of molecular ion spectra is connected with radiation chemistry and the study of ion molecule reactions. A number of unusual ions such as H_3O^+, CH_5^+ have been observed in these reactions and a study of their structure by means of their spectra seems desirable. Ion molecule reactions are among the fastest reactions known. Therefore the detection of the spectra of some of the ions is beset with considerable difficulties.

2 Experimental Techniques

A. Ordinary Electric Discharges.—The oldest known sources of emission spectra of molecular ions are electric discharges of all kinds. In direct current discharges one observes the well-known positive column and the negative glow and finds that certain molecular spectra predominantly occur in the former and others in the latter. These band systems were called 'positive' and 'negative' bands. If the cathode of the d.c. discharge has one or more holes in it, so that positive ions which are accelerated in the dark space are able to go through the cathode, a positive ray is observed behind the cathode. The observation that 'negative' bands occur in the spectrum of the positive ray even if it occurs in a fairly high vacuum, and that this ray is deflected by electric and magnetic fields in such a

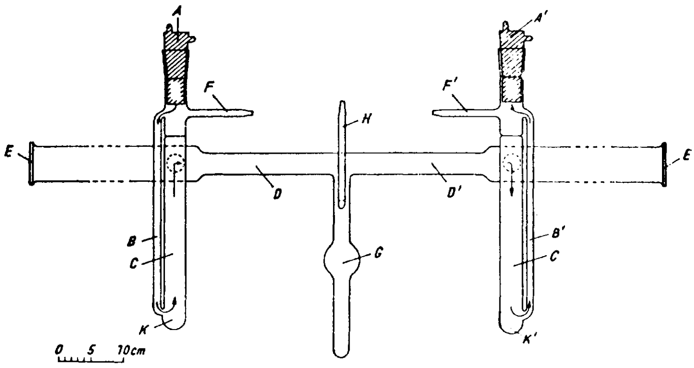

Figure 1 *Schüler tube for the production of emission spectra of organic compounds.*
The arrows indicate the path of the discharge. The tubes BC and B′C′ are cooled with liquid nitrogen. The substance to be investigated is added at G. The discharge is maintained in a carrier gas, usually He

way as to indicate a positive charge, has shown that the 'negative' bands are due to positive ions.[1] In this way spectra of N_2^+, CO^+, and O_2^+ were first identified.

Many different forms of discharge tubes have been developed. As an example, in Figure 1 a tube designed by Schüler[2] is shown; it has proved to be particularly useful for the study of spectra of organic vapours which are prevented from reaching the electrodes by two liquid nitrogen traps as indicated. In such a tube, for example, the emission spectrum of the diacetylene ion ($C_4H_2^+$) has been observed (see Section 4).

In recent years high frequency discharges have often been used as sources not only of the spectra of neutral molecules but also of spectra of positive molecular ions.

B. Electron Impact.—An ideal way to excite molecular spectra is by controlled electron impact. However, the disadvantage of this method is its low intensity.

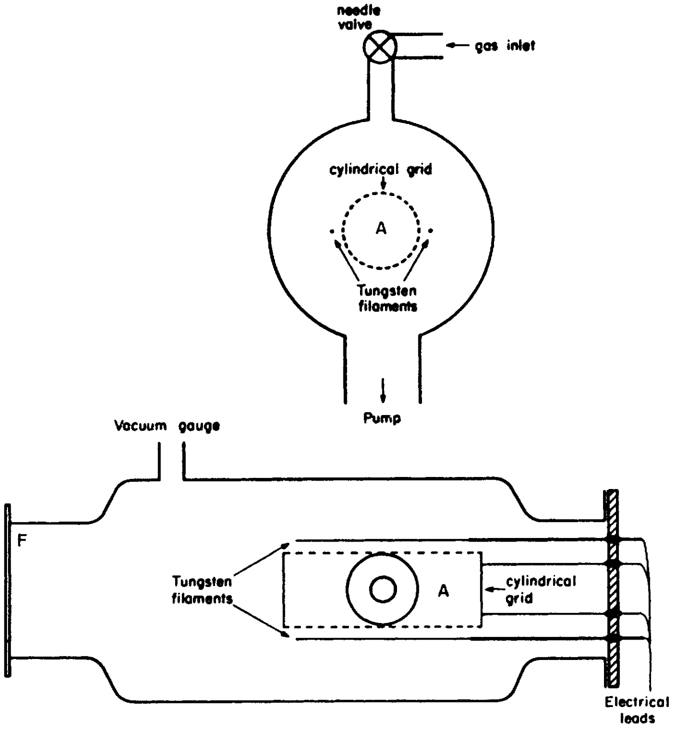

Figure 2 *Low-pressure hot cathode discharge tube of Lutz and Horani.*[3]

Two cross sections are shown. The glow produced in the space A *by the electrons originating from the two filaments and accelerated by the potential difference between filaments and grid is observed through the window* F

---

[1] W. Wien, *Ann. Physik.*, 1922, (4), **69**, 325; 1926, **81**, 994.

[2] H. Schüler, *Spectrochim. Acta*, 1950, **4**, 85.

Lutz and Horani[3] in our laboratory have recently developed a tube that, while not corresponding to controlled electron impact excitation, gives a much better approach to it than an ordinary discharge tube. This tube is shown in Figure 2. It allows the study of molecular spectra at very low pressures where the effect of collisions is greatly reduced and, as a consequence, spectra of molecular ions appear with relatively high intensity.

C. Flash Discharges.—In the sources so far mentioned the concentration of molecular ions is in general quite small and not sufficient for a study of molecular ion spectra in absorption. Much higher concentrations of ions can be obtained in condensed discharges or simply single discharges of a large condenser through the absorption tube; we shall refer to them as flash discharges. Condensed discharges have long been used for the production of emission spectra of molecular ions. During the last few years we have developed the method of flash discharges for the purpose of studying the absorption spectra of molecular ions. Figure 3 shows schematically the experimental arrangement.[4] F is the absorption tube through which a flash discharge is passed using the electrodes E. The flash is produced by the discharge of a condenser C which is charged to a voltage of the order of 10 000 V and connected to the electrodes E through a spark gap G. The gap is triggered by a small pulse from a pulse generator. The continuous background for the absorption experiment is supplied by a second flash tube S which consists of a narrow capillary through which a condenser K of 2 μF is discharged. By means of a second (delayed) pulse from the pulse generator the second flash

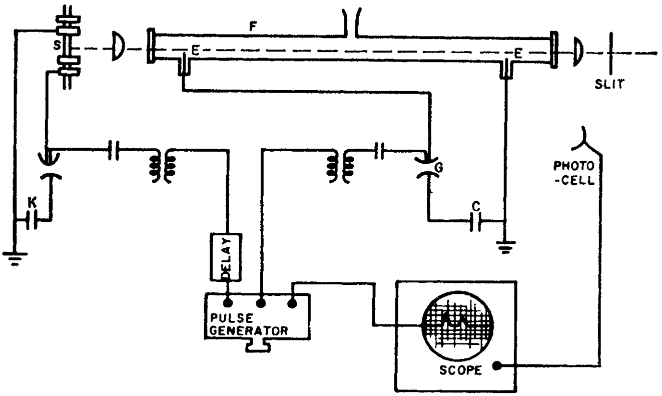

Figure 3 *Flash discharge method for the study of absorption spectra of molecular ions. The plasma to be studied is produced in the absorption tube* F. *The continuous background is supplied by the flash tube* S. *Light from this tube goes through the absorption tube to the slit of the spectrograph at the right*

---

[3] B. L. Lutz and M. Horani, unpublished.

[4] G. Herzberg, Invited Talks, International Conference on Spectroscopy, Bombay, 1967, p. 41.

tube can be fired at various times after the main flash tube and thus the absorption spectrum of the plasma produced by the first flash can be investigated. In most instances the spectra of molecular ions require that the second flash occurs within a very few microseconds of the first flash.

In order to ascertain which particular ions are present in the discharge tube and what conditions are best for the production of a high concentration of a given ion, we have connected the tube to a mass spectrometer and are thus able to study the ions produced. Considerable difficulty was encountered in making this system operate because it is not possible to scan the mass spectrum easily, and surface charges near the orifice through which the ions enter the mass spectrometer greatly affect and disturb the mass analysis, but, thanks to the efforts of Drs. Lew and Meinel in our laboratory, a fairly reproducible operation of the mass spectrometer has now been accomplished.

D. Flash Radiolysis.—While some molecular ion spectra have been observed with the flash discharge method, it appears that for many ions the lifetimes are so short that we cannot hope to observe their spectra by this method. We therefore decided to study methods of obtaining absorption spectra of molecular ions on a very much shorter time scale and under conditions that are better controlled than those in a flash discharge. The use of pulse radiolysis (or flash radiolysis) appears to offer such a possibility. In recent years commercial equipment has become available which allows the production of an electron pulse of 10 000 amps lasting for only 3 ns. This equipment, called the Febetron, appears to be a very

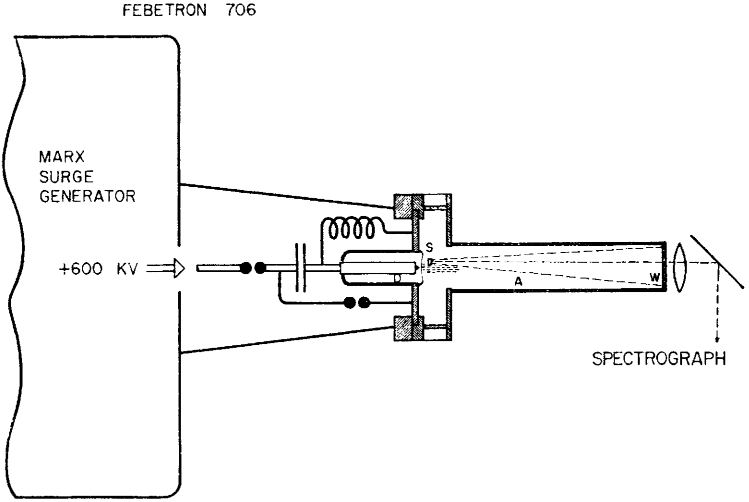

Figure 4 *Flash radiolysis method using a Febetron.*
Only the front end of the Febetron is shown. Electrons emerge from the tube D *into the absorption tube* A. *The scintillator* S *under the impact of part of the electron beam emits a continuous spectrum which acts as the background for the absorption experiment*

powerful tool and is expected to give much information about molecular ion spectra, but at the present time this development is in its infancy. The apparatus is shown schematically in Figure 4. The essential part of the Febetron is a tube D in which, by means of a voltage pulse of 600 kV, electrons are pulled out of the cathode (by field emission) and emerge through a very thin window into the absorption tube A. The problem of a suitable light source of sufficiently short duration has been solved in a preliminary way, following a suggestion by Professor G. Porter, by placing a plastic scintillator in the electron beam. Under the action of electron bombardment the scintillator emits an intense pulse of light which has in a somewhat limited region (varying with the type of scintillator chosen) a continuous spectrum. The duration of the light pulse is of the same order as the duration of the electron current, *i.e.*, 3—5 ns. The scintillator strip covers *ca.* 30—40% of the aperture of the window through which the electron beam emerges.

In the arrangement shown in Figure 4 the cone of light determined by the aperture of the exit window W covers much although not all of the space in which ions are produced by the electron beam. In this arrangement the light pulse is produced at the same time as the ions (strictly speaking a fraction of a nanosecond earlier) and we obtain absorption spectra corresponding to the time of formation of the ions. We have also constructed an optical delay line which allows delaying the entrance of light from the scintillator into the absorption tube by several nanoseconds, but up to now we have not observed any ions living long enough to make the delay line useful.

E. Photoionization.—Many investigations have been carried out in recent years in which ions produced by photons of variable wavelength have been studied in a mass spectrometer. The dependence of the ion current on the wavelength gives direct information about the ionization potential and about excited states of the ion under investigation (see for example the recent work of Chupka and his collaborators[5] on CH_4^+ and $C_2H_4^+$).

F. Photoelectron Spectra.—The field of photoelectron spectroscopy has been developed in recent years for the study of the ground state and the excited states of molecular ions. This method has proved to be of immense value, but in this lecture, devoted mainly to optical spectra, we cannot do full justice to it. Figure 5, taken from an early paper of Turner and May,[6] shows the experimental arrangement for the study of photoelectron spectra: a beam of far-u.v. light passes through the apparatus at A at right angles to the plane of the paper and the photoelectrons produced are analysed in a magnetic field and recorded by an electron multiplier. Usually the helium line 584 Å is used, but spectra have also been obtained with other lines, particularly the He^+ line at 303 Å. The first peak (of highest electron energy) in the photoelectron spectrum corresponds to the

---

[5] W. A. Chupka, *J. Chem. Phys.*, 1968, **48**, 2337; W. A. Chupka, J. Berkowitz, and K. M. A. Refaey, *J. Chem. Phys.*, 1969, **50**, 1938.

[6] D. W. Turner and D. P. May, *J. Chem. Phys.*, 1966, **45**, 471.

ground state of the ion; further peaks (at lower energy of the photoelectrons) correspond to excited states of the ion. In favourable cases the vibrational levels in the various electronic states of the ion can be studied, and for one molecule, H_2, even the rotational levels have been resolved.[7]

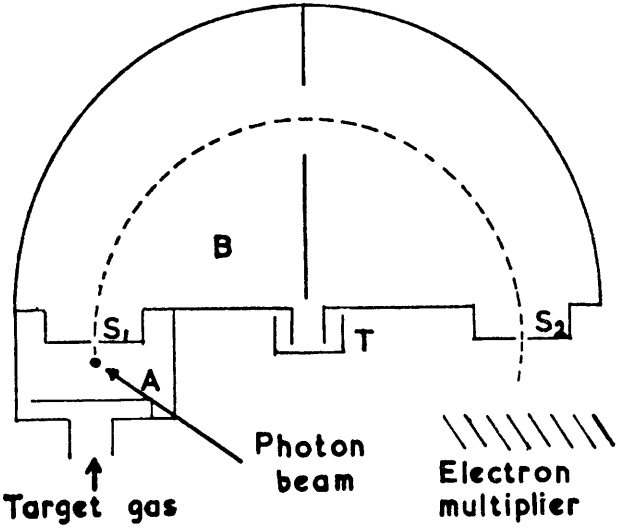

Figure 5 *Apparatus for the study of photoelectron spectra, after Turner and May.*[6]
The photoelectrons are produced at A *by a light beam which is perpendicular to the plane of the paper. A variable magnetic field also perpendicular to the plane of the paper analyses the velocity spectrum of the electrons*

G. Fluorescence Excited By Far-u.v. Light.—Oldenberg[8] was the first to study molecular ion spectra excited in fluorescence by irradiation of the parent mole-

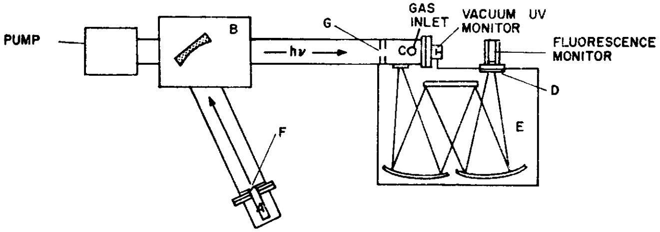

Figure 6 *Apparatus for the study of fluorescence of ions produced by far-u.v. light, after Judge and Weissler.*[9]
The source of far-u.v. light is at A; *it is resolved by the monochromator* B (*entrance slit* F, *exit slit* G) *to produce fluorescence at* C. *The spectrum of the fluorescence is recorded by a second monochromator* E (*exit slit* D)

---

[7] L. Åsbrink, *Chem. Phys. Letters*, 1970 7, 549.
[8] O. Oldenberg, *Z. Physik*, 1926, **38**, 370.

cule with far-u.v. light. This method has recently been greatly improved by Judge, Weissler, and their colleagues.[9] Figure 6 shows their apparatus. The source of u.v. radiation is at A. It is resolved by the Seya monochromator B and produces fluorescence at C. The fluorescence is observed with a high intensity Czerny–Turner monochromator E and recorded by a photomultiplier behind the exit slit D.

3 Diatomic Ions

A. Emission Spectra.—In the early development of molecular spectroscopy a number of diatomic ion spectra were studied in emission by various investigators. The following ions are listed in a table of molecular constants[10] published in 1950:

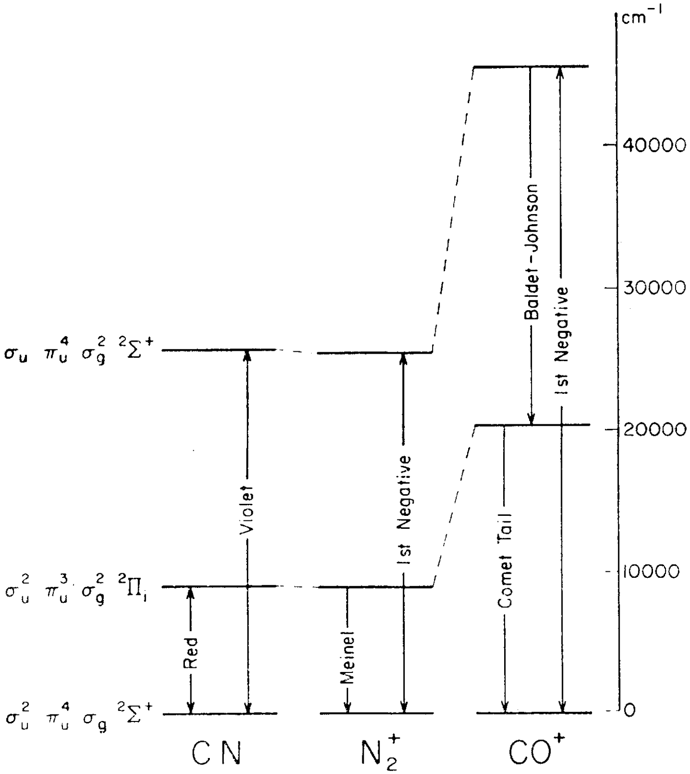

Figure 7 *Electronic energy levels of* N_2^+ *and* CO^+ *compared with those of* CN

---

[9] D. L. Judge and G. L. Weissler, *J. Chem. Phys.*, 1968, **48**, 4590.

[10] G. Herzberg, 'Molecular Spectra and Molecular Structure,' Vol. I, Spectra of Diatomic Molecules, Van Nostrand, New York, 1950.

N_2^+, CO^+, As_2^+
O_2^+, Cl_2^+
BeH^+, MgH^+, ZnH^+, CdH^+, HgH^+
BH^+, AlH^+, CH^+, OH^+
HCl^+, HBr^+.

The lowest electronic states of N_2^+ and CO^+ ions obtained from their spectra and those of the radical CN are compared in the energy level diagrams, Figure 7. It was this comparison that led Hund and Mulliken in the 1920's to the idea of molecular orbitals. The fact that in the two ions the ground state is a $^2\Sigma$ state shows that the most loosely bound electron in the neutral N_2 and CO molecules must be a σ electron, and similarly the fact that the first excited state is $^2\Pi$ and the second excited state $^2\Sigma$ shows that the two next loosely bound electrons are in π and σ orbitals respectively, so that the configurations given in Figure 7 are obtained.

Since 1950 a number of new diatomic ion spectra have been discovered. These are:

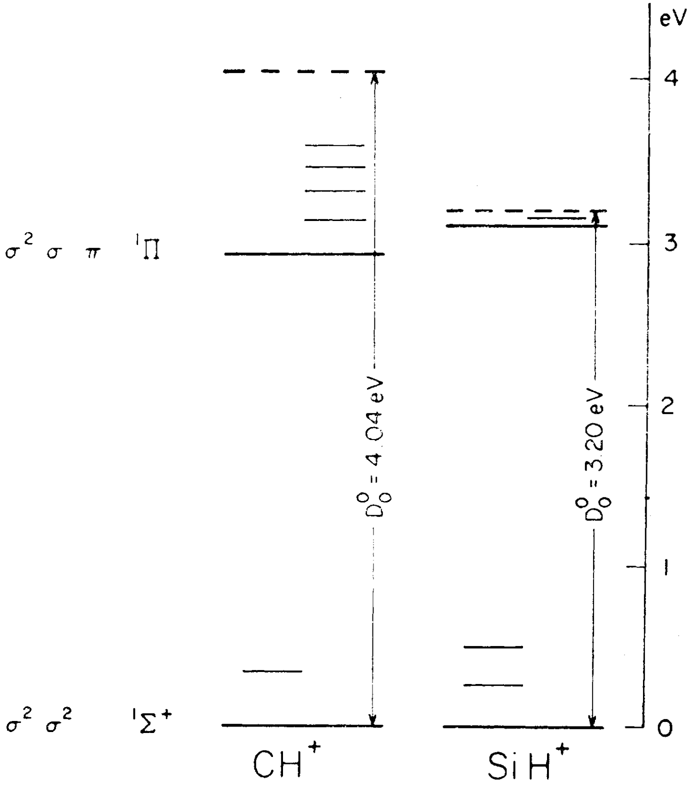

Figure 8 *Observed electronic and vibrational levels of* CH^+ *and* SiH^+

H_2^+, NH^+, SiH^+, PH^+, SH^+
CN^+, NO^+, F_2^+
CS^+, NS^+, PO^+, PF^+
P_2^+, PS^+, AsO^+
N_2^{2+}, C_2^-.

Three of the spectra in this list have been obtained only quite recently. A radiofrequency spectrum of H_2^+ was observed by Jefferts.[11] It is of particular interest since it is a one-electron spectrum which has been predicted quantitatively from first principles. A spectrum of SiH^+ in the visible region was observed by Douglas and Lutz.[12] In Figure 8 the resulting energy levels of SiH^+ are compared with those of CH^+. The observed electronic states are in accord with those expected from the interpretation of the states of the neutral molecules by electron configurations. On the basis of Douglas and Lutz's data Grevesse and Sauval[13] have identified several SiH^+ lines in the solar spectrum, thus for the first time establishing the presence of a molecular ion in a stellar atmosphere.

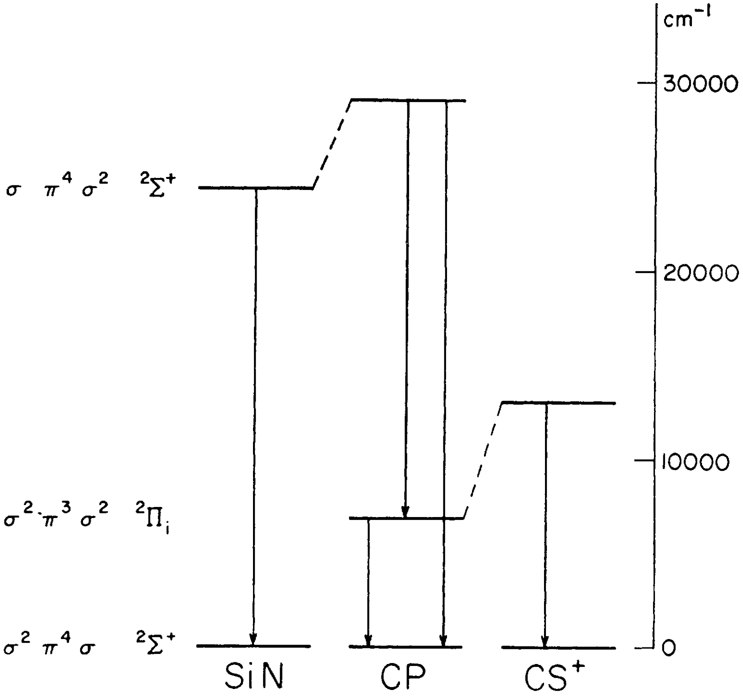

Figure 9 *Electronic energy levels of* CS^+ *compared with those of* SiN *and* CP

---

[11] K. B. Jefferts, *Phys. Rev. Letters*, 1968, **20**, 39; 1969, **23**, 1476.
[12] A. E. Douglas and B. L. Lutz, *Canad. J. Phys.*, 1970, **48**, 247.
[13] N. Grevesse and A. J. Sauval, *Astronomy and Astrophysics*, 1970, **9**, 232.

The CS^+ spectrum was recently observed by Horani[14] in our laboratory. Figure 9 shows a comparison of its energy levels with those of the isoelectronic radicals SiN and CP. The similarity with CO^+ (see Figure 7) is apparent.

The only spectrum of a doubly ionized molecule so far observed is that of N_2^{2+} (Carroll,[15] Carroll and Hurley[16]). It is based on the identification of an emission band at 1590 Å. Its position and structure agree well with theoretical predictions for this ion. It must, however, be admitted that there remains a slight uncertainty about this identification.

B. Absorption Spectra.—For many years CH^+ was the only molecular ion whose spectrum had been observed in absorption. It was observed not in laboratory spectra but in the spectrum of the interstellar medium.[17,18] In the laboratory we succeeded for the first time in 1967 in obtaining absorption spectra of diatomic molecular ions by using the flash discharge technique described earlier.[19] Figure 10 shows absorption bands of N_2^+ and CO^+ obtained in this way. The spectra reproduced were taken with fairly high resolution at a reciprocal dispersion of 1·2 Å/mm. Here it should be remembered that sharp absorption lines require high resolution for their observation. Only the heads of the bands where many lines lie close together can be observed under low resolution also.

Quite recently we have observed the N_2^+ spectrum in absorption by the flash radiolysis technique. Here the time scale is smaller by a factor of several hundred and therefore up to now we have not been able to obtain spectra at high resolution. Figure 11 shows a comparison of spectrograms of the N_2^+ band at 3914 Å as obtained by flash discharge and by flash radiolysis with the same spectrograph. Only the band head at 3914 Å is clearly visible in both spectra. The fine structure lines in the *R* branch which are quite strong in Figure 10 are only barely visible here.[19a]

For reasons to be discussed later we were interested in obtaining a spectrum of the CH_4^+ ion and therefore studied flash discharges in CH_4. Instead of finding the desired spectrum of CH_4^+ we obtained another spectrum of very simple character,[20] part of which is shown in Figure 12. It is readily seen from the structure of this spectrum that it belongs to a diatomic system and represents a Σ–Σ transition. Moreover, the fact that the lines of the *R* branch do not form a simple continuation of the lines of the *P* branch but occur half-way between the positions predicted from this continuation immediately establishes that the

---

[14] M. Horani, to be published.

[15] P. K. Carroll, *Canad. J. Phys.*, 1958, **36,** 1585.

[16] P. K. Carroll and A. C. Hurley, *J. Chem. Phys.*, 1961, **35,** 2247.

[17] W. S. Adams, *Astrophys. J.*, 1941, **93,** 11.

[18] A. E. Douglas and G. Herzberg, *Astrophys. J.*, 1941, **94,** 381; *Canad. J. Res.*, 1942, **A20,** 71.

[19] G. Herzberg, *Pontif. Acad. Sci. Commentarii*, 1968, **2,** 1; Invited Talks, International Conference on Spectroscopy, Bombay, 1967, p. 41.

[19a] Since presenting this lecture I have learned from Dr. M. Clerc that he and B. Lesigne at Saclay have also observed the absorption spectrum of N_2^+ by means of pulse radiolysis produced by a Febetron. Since they used much lower pressures (of the order of 1 mm) they observed a much longer lifetime of the ions, much longer even than that observed by us with the flash discharge technique for which we used pressures of the same order as they did.

[20] G. Herzberg and A. Lagerqvist, *Canad. J. Phys.*, 1968, **46,** 2363.

molecule responsible must have two nuclei of zero spin.[10] From the observation that lines of odd N are missing it follows that the transition is $\Sigma_u^+-\Sigma_g^+$ or possibly, though much less likely, $\Sigma_g^--\Sigma_u^-$.

At first sight the most obvious assumption seems to be that the new spectrum represents a new electronic transition of the C_2 free radical. However, on further investigation it turns out that the rotational and vibrational constants of neither the upper nor the lower state agree with those of any of the many known electronic states of C_2. Further, the theoretically expected electronic energy level diagram of C_2 has no room for additional ${}^1\Sigma_g^+$ and ${}^1\Sigma_u^+$ states (or ${}^1\Sigma_u^-$ and ${}^1\Sigma_g^-$ states) beyond those already observed unless one were to assume that the upper and lower states are highly excited states of C_2, an assumption that is made rather unlikely on account of the fact that these bands are observed in absorption. We were therefore led to enquire whether the new spectrum represented in Figure 12 is perhaps due to a C_2 ion (C_2^+ or C_2^-). In either case it is necessary to assume that the spectrum, which looks like a singlet spectrum, is in fact a doublet spectrum. This assumption is supported by the fact that the lines of high N show an increasing broadening which cannot be accounted for by predissociation (since these bands are also observed in emission) and is probably due to an incipient unresolved doublet splitting.

If the new spectrum is assigned to C_2^+ one finds a similar difficulty to that encountered in assigning it to C_2, namely, that it is very difficult, if not impossible, to find a reasonable place in the expected electronic energy level scheme of C_2^+ for a ${}^2\Sigma_u^+-{}^2\Sigma_g^+$ transition. We were therefore led to ask whether the new spectrum could be due to C_2^-. With that assumption the spectrum can immediately be fitted into the predicted energy level diagram, which is entirely similar to that of N_2^+ given in Figure 7. The whole character of the spectrum, the shading of the bands, the vibrational frequencies in upper and lower state, *etc.*, are indeed very similar to the corresponding quantities of N_2^+.

Further support for the idea that the spectrum in Figure 12 is due to the C_2^- ion came from the observation, by means of the mass spectrometer, that C_2^- is an abundant ion in the flash discharge used for the absorption experiment. Nevertheless none of the arguments so far advanced could be considered as conclusive. However, a year later Milligan and Jacox[21] at the National Bureau of Standards showed that a spectrum observed by many investigators in solid matrices containing C_2 is actually the analogue of our new spectrum and not, as had been assumed up to that time, the analogue of the Swan bands of C_2. By producing electrons in the matrix (obtained by photoionization of Cs) Milligan and Jacox found that the band system is greatly enhanced and in that way they made the interpretation by C_2^- much more likely. Thus in all probability the spectrum shown in Figure 12 represents the first case of a discrete spectrum of a negative molecular ion in the gaseous phase.

Up to now no absorption spectra of diatomic molecular ions other than N_2^+, CO^+, and C_2^- have been observed (see, however, Section 4D).

---

[21] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1969, **51**, 1952.

C. Photoelectron Spectra.—As an example of the photoelectron spectrum of a diatomic molecule we reproduce in Figure 13 the spectrum given by Turner and May[6] for N_2. There are clearly three electronic states revealed by the photoelectron spectrum which agree quantitatively with the three states represented in Figure 7 and derived from the optical spectrum.

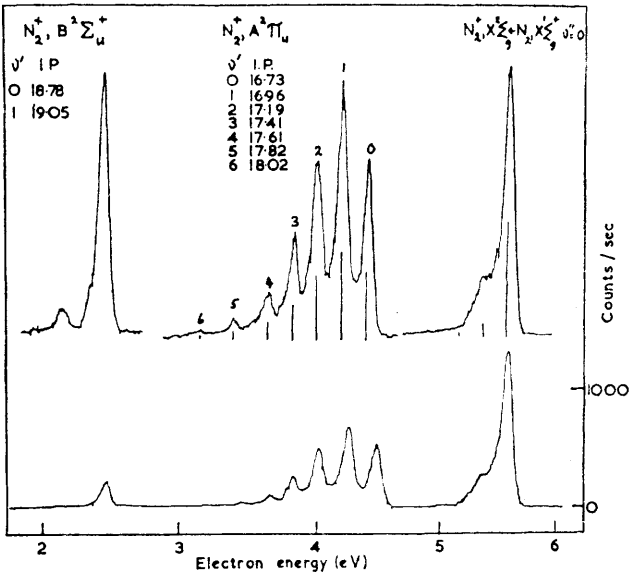

Figure 13 *Photoelectron spectrum of* N_2, *after Turner and May.*[6]

On the abscissa is the electron energy. The peak of highest electron energy corresponds to the ground state ($^2\Sigma_g^+$) *of the* N_2^+ *ion*

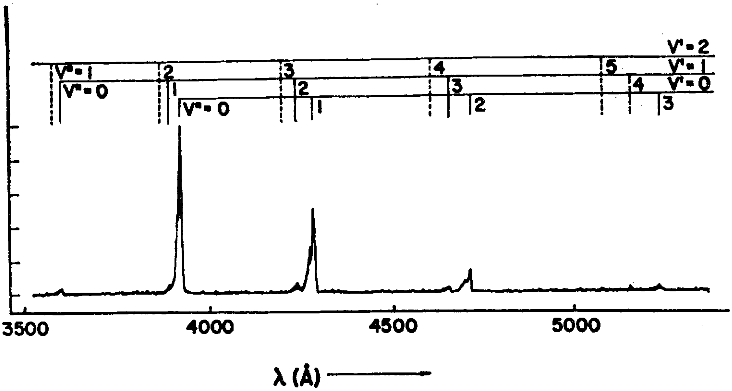

Figure 14 *Fluorescence of* N_2^+ ($^2\Sigma$–$^2\Sigma$) *produced by the irradiation of* N_2 *by light of wavelength* 555 Å, *after Judge and Weissler.*[9]

D. Fluorescence.—In Figure 14 we reproduce a spectrum of N_2^+ obtained by Judge and Weissler[9] by irradiating N_2 with vacuum-u.v. light of 555 Å. It is seen that the progression with $v' = 0$ is by far the strongest, in agreement with the photoelectron result (Figure 13) that the $v = 0$ level of the $B^2\Sigma_u^+$ state predominates greatly over other v values when N_2 is photoionized by the 584 Å line of He. Similar spectra have been obtained of CO^+ and other diatomic ions. They are of interest in connection with phenomena in the upper atmosphere and in the tails of comets where emission spectra of N_2^+ and CO^+ are observed. As for all emission spectra such fluorescence spectra can only be observed if the upper state is not affected by a strong predissociation.

4 Polyatomic Ions

A. Emission Spectra.—Ever since spectra of discharges through CO and CO_2 have been observed two line-like features at 2883 and 2896 Å have been known.[22] In addition, in the 1920's Fox, Duffendack, and Barker[23] recognized that an extensive band system in the region 3800—4900 Å was related to CO_2 and, like the 2890 Å doublet, was probably due to CO_2^+. Mulliken[24] first recognized clearly the interpretation of these spectra in terms of the expected electron configurations of CO_2^+ and, at his suggestion, in his laboratory Bueso-Sanllehi[25] and Mrozowski[26] carried out the first detailed fine structure analysis which proved that CO_2^+ was indeed the carrier. These were the first spectra recognized as those of polyatomic molecular ions.

In Figure 15 we show an energy level diagram of CO_2^+ and compare it with those of the radicals BO_2 and N_3 which were investigated much later.[27,28] The energy level diagram of CO_2^+ establishes the order of the outer orbitals in CO_2. Since in the neutral molecule clearly all orbitals are filled the lowest state of CO_2^+ must arise from configurations in which one electron is missing from a closed shell. Therefore the fact that the ground state of CO_2^+ is $^2\Pi_g$ means that the electron configuration is . . . π_g^3, that is, that the outermost orbital of CO_2 must be a π_g orbital. Similarly, since the first excited state of CO_2^+ is a $^2\Pi_u$ state the second outermost orbital of CO_2 must be a π_u orbital, and since the next excited state is a $^2\Sigma_u$ state the third outermost orbital must be σ_u.

Corresponding to the observed states of CO_2^+ there are several sets of Rydberg series of CO_2 whose limits have energies in exact agreement with the energy levels of CO_2^+ obtained from its spectrum[29] and, in addition, they supply

---

[22] See R. W. B. Pearse and A. G. Gaydon, 'The Identification of Molecular Spectra', 3rd edn., Chapman and Hall, London, 1963.

[23] G. W. Fox, O. S. Duffendack, and E. F. Barker, *Proc. Nat. Acad., Sci., U.S.A.*, 1927, **13**, 302; see also H. D. Smyth, *Phys. Rev.*, 1931, **38**, 2000.

[24] R. S. Mulliken, *J. Chem. Phys.*, 1935, **3**, 720.

[25] F. Bueso-Sanllehi, *Phys. Rev.*, 1941, **60**, 556.

[26] S. Mrozowski, *Phys. Rev.*, 1941, **60**, 730; 1942, **62**, 270; 1947, **72**, 682, 691.

[27] J. W. C. Johns, *Canad. J. Phys.*, 1961, **39**, 1738.

[28] A. E. Douglas and W. J. Jones, *Canad. J. Phys.*, 1965, **43**, 2216.

[29] See G. Herzberg, 'Molecular Spectra and Molecular Structure,' Vol. III, Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand-Reinhold, New York, 1966, p. 500f.

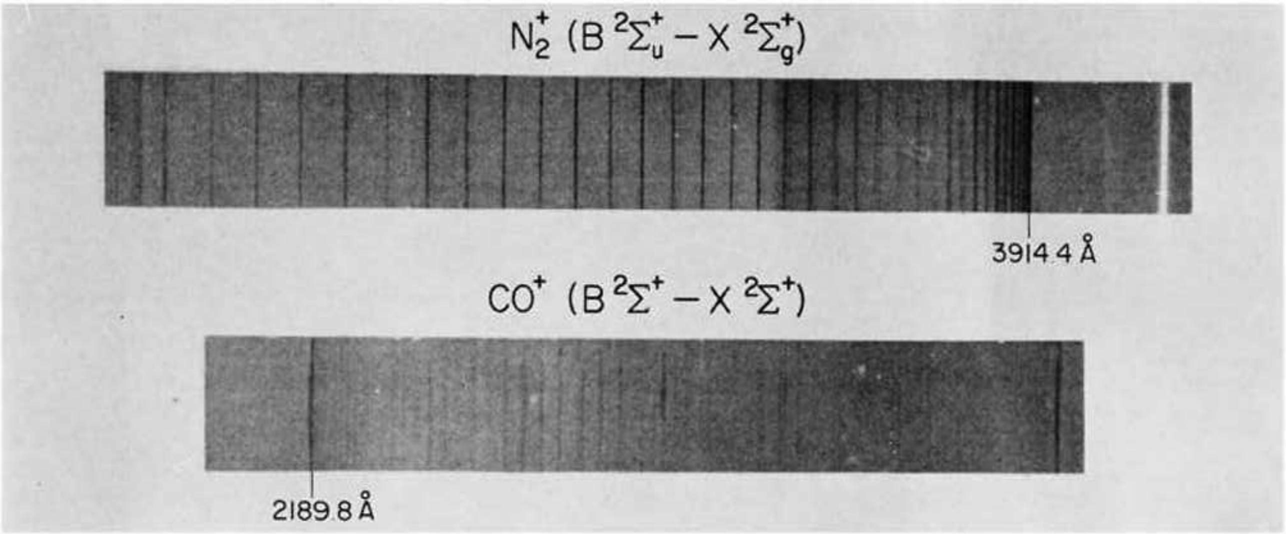

Figure 10 *Absorption spectra of* N_2^+ *and* CO^+ *obtained by the flash discharge technique. Only the strongest band of* N_2^+ *at* 3914 Å *and of* CO^+ *at* 2190 Å *is shown. Other bands of the same band systems have also been observed*

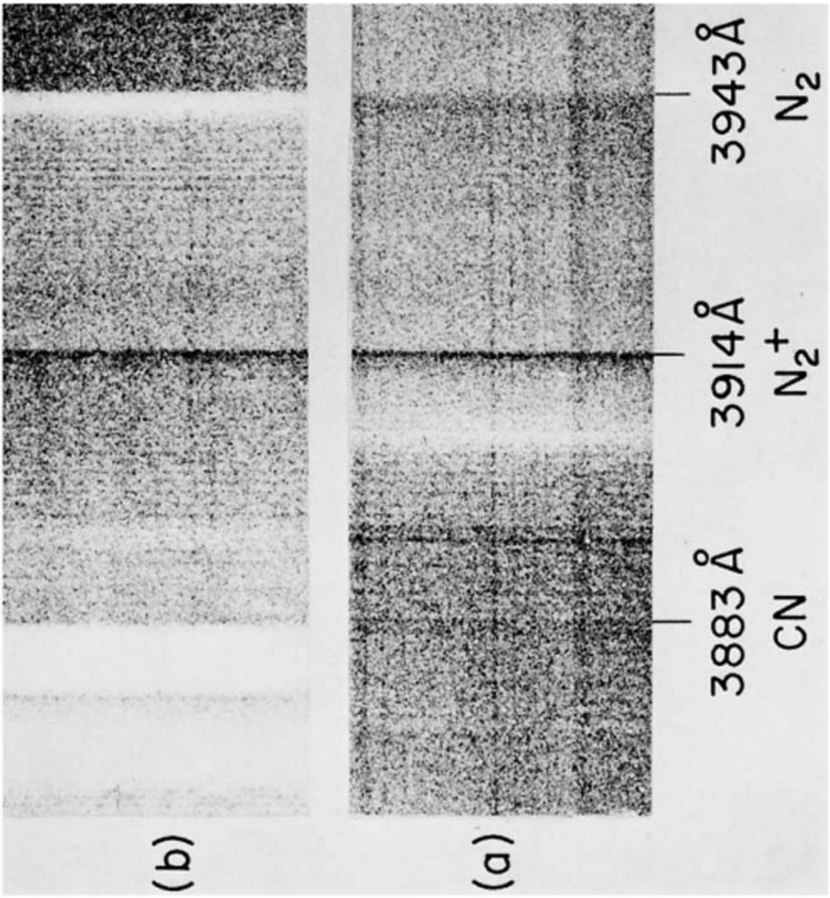

Figure 11 *Comparison of absorption spectra of* N_2^+ *by* (a) *the flash discharge* (b) *the flash radiolysis techniques.*

In the flash radiolysis spectrum emission bands of neutral N_2 *(second positive group) and, as an impurity, those of* CN *occur strongly*

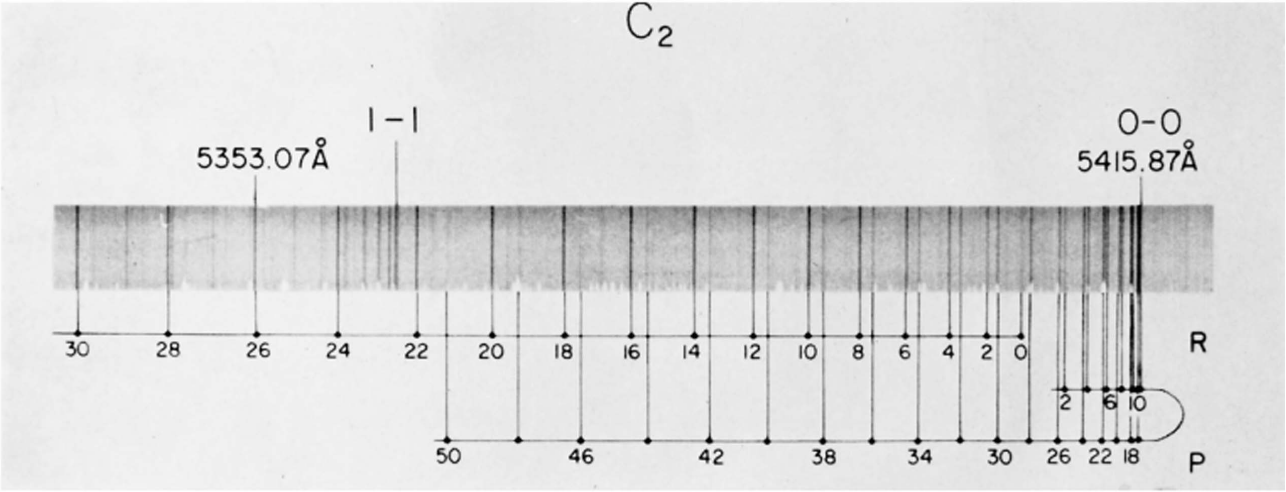

Figure 12 *Part of absorption spectrum of the C_2^- ion, after Herzberg and Lagerqvist.*[20] *The 0–0 and 1–1 bands are shown. The rotational lines are marked only for the 0–0 bands*

Figure 16 *Emission band observed in a discharge through* H_2S *and probably due to* H_2S^+

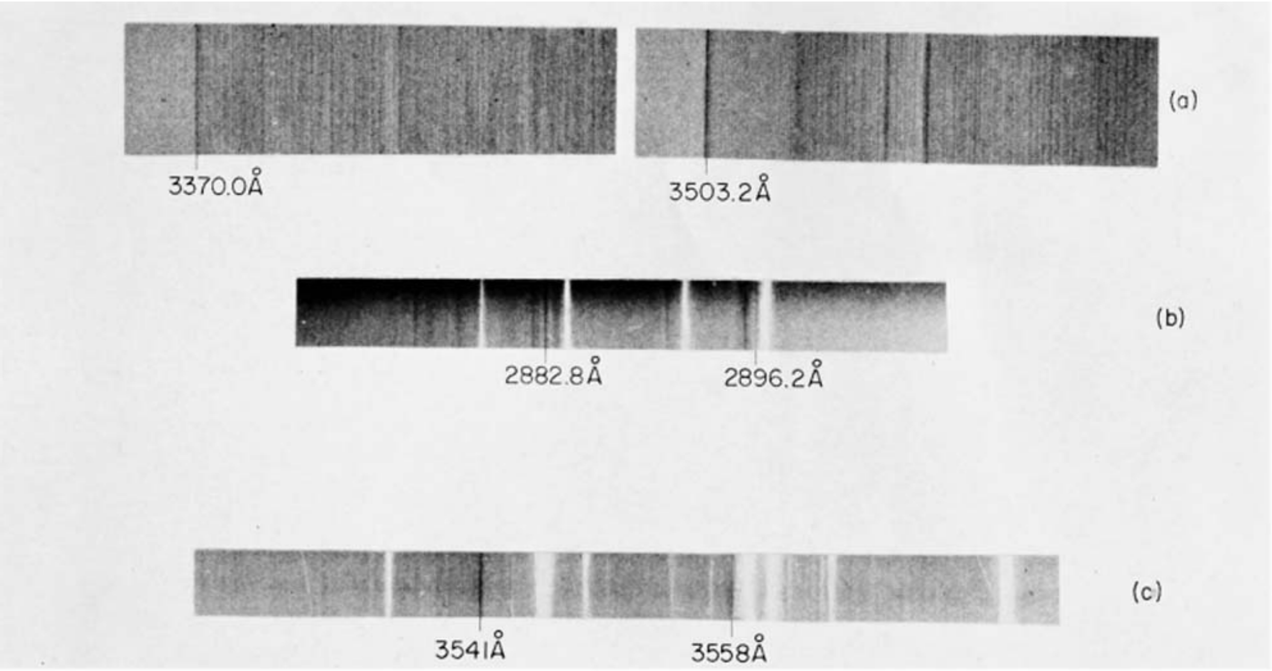

Figure 17 *Absorption spectra of the* CO_2^+ *and* N_2O^+ *ions obtained by the flash discharge method In* (a) *are reproduced two bands of the* $^2\Pi$–$^2\Pi$ *system of* CO_2^+, *in* (b) *the* 0–0 *band of the* $^2\Sigma$–$^2\Pi$ *system of* CO_2^+, *in* (c) *the* 0–0 *band of the* $^2\Sigma$–$^2\Pi$ *system of* N_2O^+

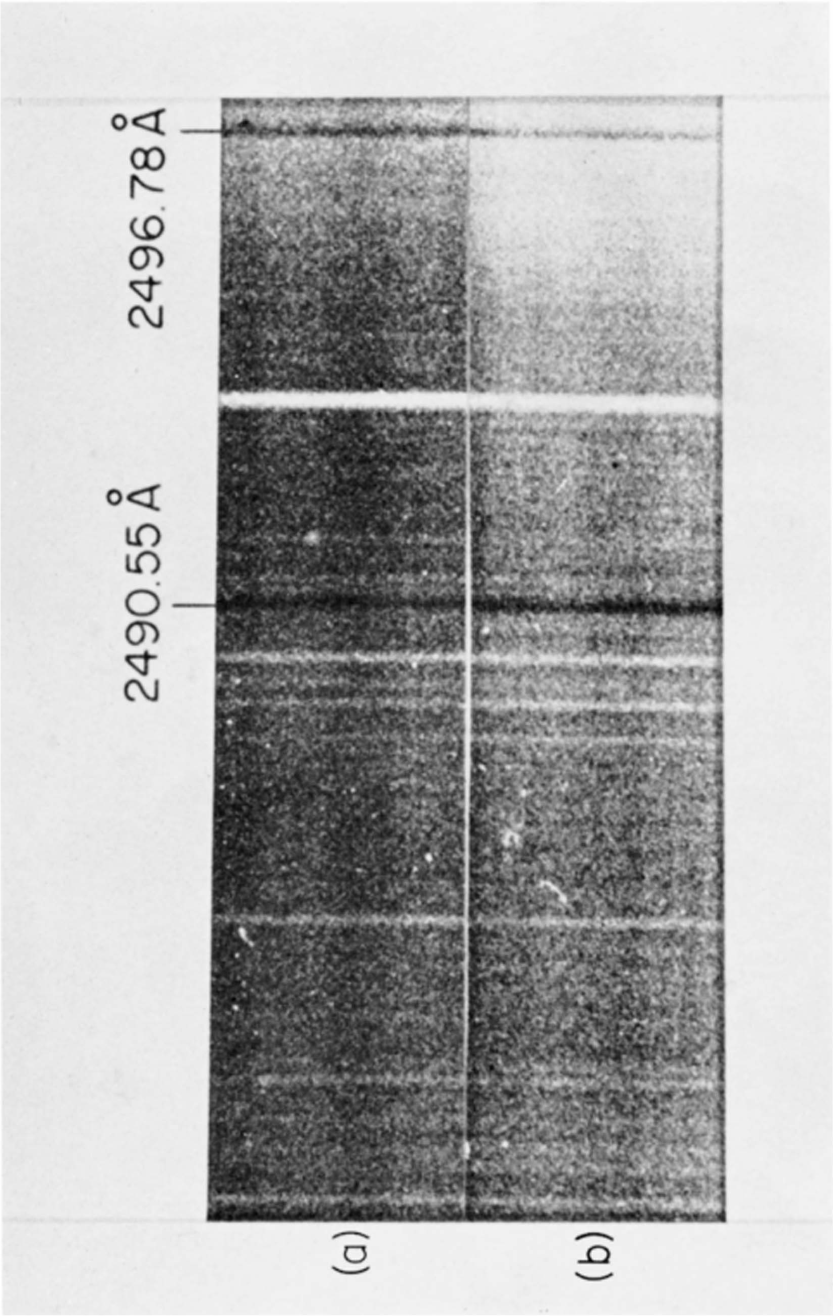

Figure 21 *Absorption spectra of flash discharges in* (a) *a* 10:1 He–C_2H_2 *mixture* (b) *a* 10:1 He–C_2D_2 *mixture.*

The feature at 2490·55 Å *is the line-like* Q *branch of a band, some of whose other branches are just visible to the left and right of this feature. The line marked* 2496·78 Å *is a* B I *line which occurs in the source due to the use of a* BN *liner* evidence[30] for a third excited state of CO_2^+ which, from theoretical arguments about the orbitals, is believed to be a $^2\Sigma_g^+$ state. It is included in Figure 15.

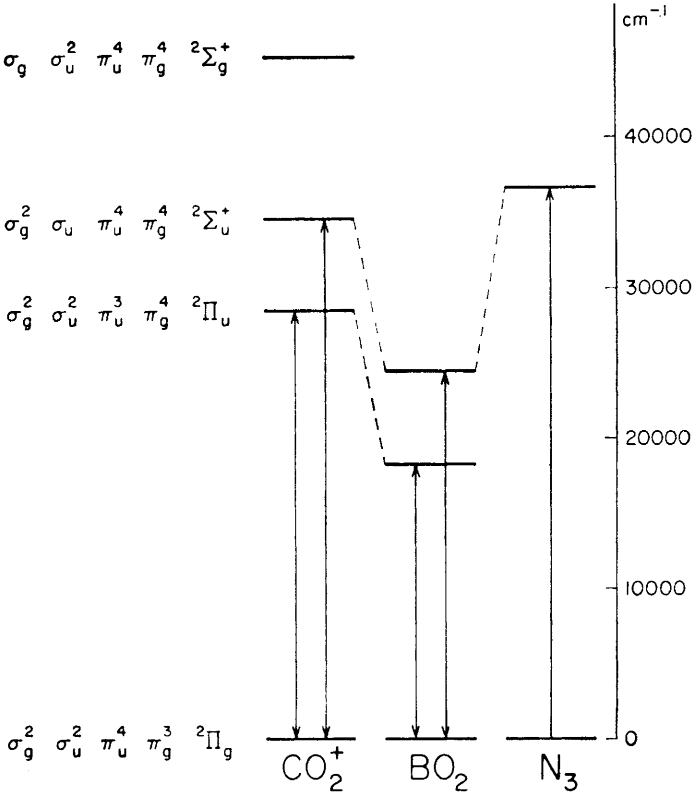

Figure 15 *Electronic energy levels of* CO_2^+ *compared with those of* BO_2 *and* N_3

Callomon, Leach, and their collaborators[31–34] have found and analysed spectra similar to that of CO_2^+ for CS_2^+, N_2O^+, and COS^+. For the unsymmetrical ions (N_2O^+ and COS^+) the order of the excited $^2\Pi$ and $^2\Sigma$ states is reversed and therefore we must conclude that for the corresponding neutral molecules the order of the π and σ orbitals is reversed.

Another polyatomic ion spectrum (the only other one known until this year)

---

[30] Y. Tanaka, A. S. Jursa, and F. J. Leblanc, *J. Chem. Phys.*, 1960, **32**, 1199.

[31] J. H. Callomon, *Proc. Roy. Soc.*, 1958, **244**, 220.

[32] J. H. Callomon, *Proc. Chem. Soc.*, 1959, p. 313; J. H. Callomon and F. Creutzberg, Invited Talks, International Conference on Spectroscopy, Bombay, 1967, p. 143.

[33] M. Horani and S. Leach, *Compt. rend.*, 1959, **248**, 2196.

[34] S. Leach, *J. chim. phys.*, 1964, **61**, 1493; M. Horani, S. Leach, J. Rostas, and G. Berthier, *J. chim. phys.*, 1966, **63**, 1015.

is that of the diacetylene ion ($C_4H_2^+$). Schüler and Reinebeck[35] observed in the special tube mentioned earlier (Figure 1) a strong discrete spectrum between 5000 and 6000 Å in discharges through benzene, naphthalene, ethylene, acetylene, diacetylene, and other hydrocarbons. They called this spectrum the T system. This spectrum was fully analysed by Callomon[36] in 1956 and was shown to be due to a $^2\Pi_u$–$^2\Pi_g$ transition of the $C_4H_2^+$ ion. From the observed type of the lower state we must conclude that the most loosely bound orbital in C_4H_2 is a π_g orbital and from the type of the upper state that the next most loosely bound orbital is a π_u orbital. Since in neutral diacetylene all orbitals are completely filled the transition in $C_4H_2^+$ must therefore correspond to $\pi_u^3\ \pi_g^4\ {}^2\Pi_u \rightarrow \pi_u^4\ \pi_g^3\ {}^2\Pi_g$. Two Rydberg series observed in diacetylene have limits whose energy difference agrees exactly with the energy difference of the upper and lower state of the T spectrum, confirming the assignment of this spectrum to $C_4H_2^+$.

The first new emission spectrum of a polyatomic molecular ion in a number of years was recently found by Horani[37] in our laboratory who observed by means of the special discharge tube described earlier (Figure 2) a spectrum which is in all probability due to the H_2S^+ ion. Figure 16 shows one of the bands that have been observed. The structure of this spectrum is exceedingly complicated but is very similar in character to the known spectra of PH_2 and NH_2. A full analysis has not yet been accomplished but there is little doubt that the spectrum really is due to H_2S^+. We have tried to observe the corresponding spectrum of H_2O^+ under similar conditions but up to now have failed to do so.

B. Absorption Spectra.—The study of the absorption spectrum of a molecular ion is important not only because it establishes which is the ground state of the ion with more certainty than does the emission spectrum but, more importantly, because it allows the observation of excited states of the ion which are subject to predissociation and therefore do not give rise to emission spectra.

By means of the flash discharge method we have been able to obtain the two known band systems of CO_2^+ in absorption as well as the $^2\Pi$–$^2\Pi$ bands of N_2O^+ and the $^2\Sigma$–$^2\Pi$ bands of CS_2^+. Figure 17 shows some of the spectra obtained. Naturally it was hoped that it would be possible to observe in absorption higher excited states of these ions, which have not been seen in emission, but this aim has not yet been accomplished.

Many other ions have been looked for by means of the flash discharge method, such as H_3^+, H_2O^+, H_3O^+, $C_2H_2^+$, CH_4^+, CH_3^+, CH_2^+, and NH_3^+. While in the search for H_2O^+ a new absorption band was found near 7200 Å it has so far been impossible to identify the carrier of this band and no spectra of the other ions mentioned have been found. This lack of success is in all probability connected with the occurrence of fast ion–molecule reactions which remove the wanted ions from the discharge before observation is possible. Of course, recombination with electrons also removes ions at a rapid rate so that only the

---

[35] H. Schüler and L. Reinebeck, *Z. Naturforsch.*, 1951, **6a**, 160, 270; 1952, **7a**, 285.
[36] J. H. Callomon, *Canad. J. Phys.*, 1956, **34**, 1046.
[37] M. Horani, unpublished.

first few microseconds after the flash offer any chance of observing molecular ion absorption. By improving our mass spectrometer which is attached to the flash tube we hope to bring the ions formed under better control and in this way to obtain eventually the desired spectra. At the same time the flash radiolysis method, which operates on a much shorter time scale, will allow us to study absorption spectra of very short-lived, that is, very reactive, ions.

C. Fluorescence.—The $^2\Pi$–$^2\Pi$ bands of CO_2^+ have been studied in fluorescence by Judge, Bloom, and Morse[38] using far-u.v. light in the region 715—700 Å. Figure 18 gives an example of their spectra. By varying the exciting wavelength, uncertainties in the vibrational analysis of the CO_2^+ spectrum have been cleared up. No new spectra have as yet been discovered by this method.

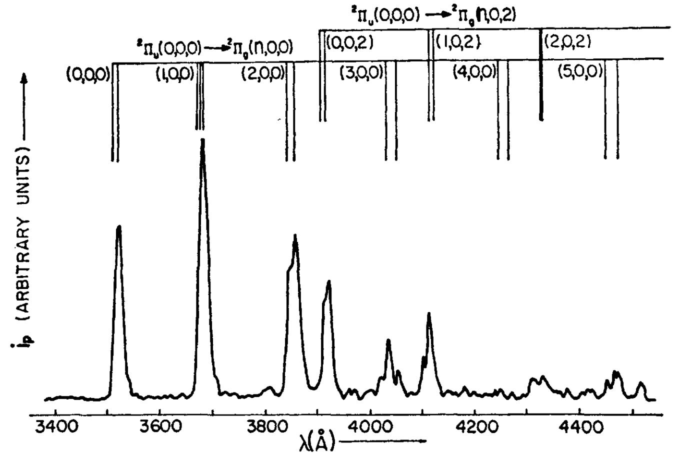

Figure 18 *$^2\Pi$–$^2\Pi$ Bands of CO_2^+ obtained in fluorescence by irradiating CO_2 with light of wavelength 715 Å, after Judge, Bloom, and Morse.*[38]

Since λ715 Å corresponds to the 000 level of the upper $^2\Pi_u$ state, only bands with this upper level occur in fluorescence

D. Photoelectron Spectra.—The photoelectron spectrum of CO_2 studied by Brundle and Turner[39] accurately reflects the three states of CO_2^+ obtained from the optical spectrum and in addition confirms the fourth state derived indirectly from the Rydberg series of CO_2. Figure 19 shows this photoelectron spectrum. The four electronic states are readily identified. However, it is not possible from the photoelectron spectrum to say anything about the nature of the electronic states.

In a similar way the photoelectron spectrum of diacetylene studied by Baker

---

[38] D. L. Judge, G. S. Bloom, and A. L. Morse, *Canad. J. Phys.*, 1969, **47**, 489.

[39] C. R. Brundle and D. W. Turner, *Internat. J. Mass Spec.*, 1969, **2**, 195.

and Turner[40] shows the two states that form the upper and lower state of the T spectrum as well as two further states at 6·44 and 9·6 eV above the ground state.

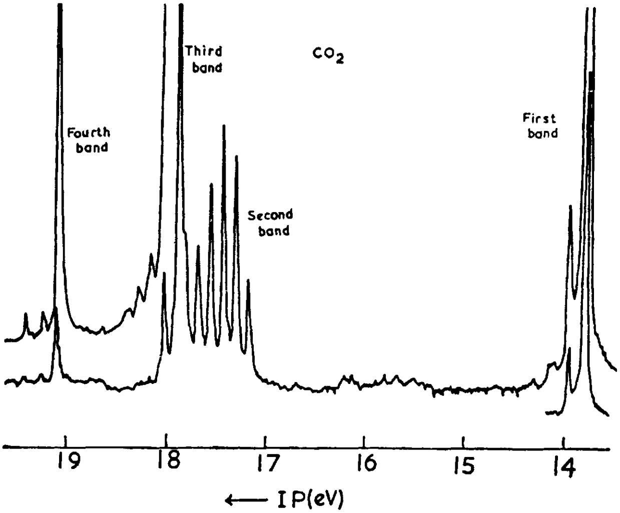

Figure 19 *Photoelectron spectrum of* CO_2 *obtained with the* He *line* 584 Å, *after Brundle and Turner.*[39]

The abscissa scale gives the energy above the ground state of CO_2. *The group of photoelectrons of highest energy at the right corresponds to the electronic ground state* $^2\Pi_g$ *of* CO_2^+ *and its vibrational levels. The second group, consisting of a fairly long progression, corresponds to the* $^2\Pi_u$ *excited state. It is overlapped by a strong peak corresponding to* $^2\Sigma_u^+$ *(see Figure* 15). *The peak at* 19 eV *corresponds to the* $^2\Sigma_g^+$ *state previously derived from Rydberg series of* CO_2

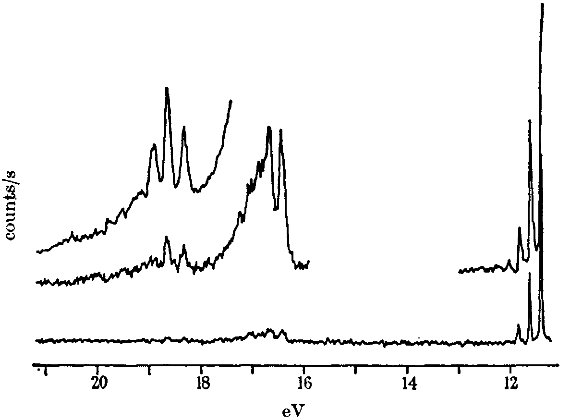

Figure 20 *Photoelectron spectrum of* C_2H_2 *obtained with the* He *line* 584 Å *by Baker and Turner*[40]

---

[40] C. Baker and D. W. Turner, *Proc. Roy. Soc.*, 1968, **A, 308**, 19.

The knowledge of the photoelectron spectrum can be of great help in predicting the absorption spectrum of a molecular ion. For example, the photoelectron spectrum of acetylene shown in Figure 20 and taken from the paper by Baker and Turner[40] shows that there is an excited state of this ion at 4·96 eV above the ground state. Correspondingly we must expect an absorption band of the acetylene ion very close to 2500 Å. Similarly in HCN^+ from the photoelectron spectrum one would expect an absorption feature at 2271 Å. Dr. Meinel in our laboratory looked for the absorption spectra of $C_2H_2^+$ by the flash discharge technique after having ascertained by means of the mass spectrometer the best conditions for a high concentration of this ion. He found an absorption feature at 2490 Å, as shown in Figure 21(a), but when he studied the corresponding spectrum obtained with C_2D_2 he found an identical absorption band, as shown in Figure 21(b). This result shows that the observed spectrum cannot be due to $C_2H_2^+$. We suspect that the observed spectrum is due to the C_2^+ ion whose spectrum is as yet unknown but this conclusion remains to be verified.[41]

Price,[42] Turner,[43] and Pullen *et al.*[44] have investigated the photoelectron spectrum of CH_4^+. This spectrum is shown in Figure 22 as excited by the 304 Å

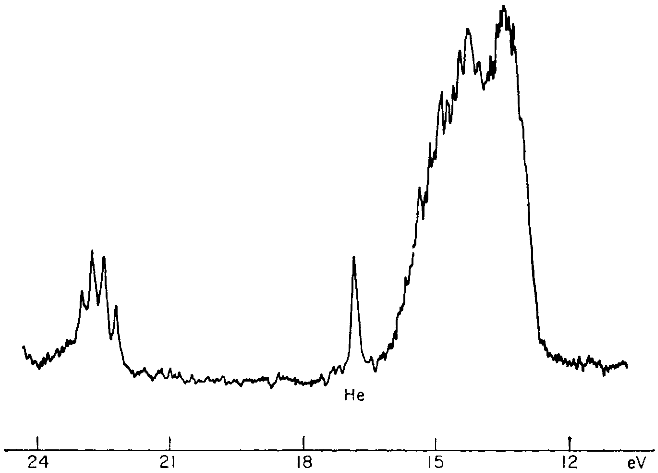

Figure 22 *Photoelectron spectrum of* CH_4 *obtained with the* He^+ *line* 304 Å *by Price.*[42] *The abscissa scale gives the energy above the ground state of* CH_4*. The peak marked* He *corresponds to photoelectrons from* He, *not* CH_4

---

[41] Since this was written studies with ^{13}C have indeed confirmed that the spectrum shown in Figure 21 is due to the C_2^+ ion.

[42] W. C. Price, in 'Molecular Spectroscopy', ed. P. W. Hepple, Inst. Petroleum, London, 1968, p. 221.

[43] D. W. Turner, 'Molecular Photoelectron Spectroscopy', Wiley-Interscience, London, 1970.

[44] B. P. Pullen, T. A. Carlson, W. E. Moddeman, G. K. Schweizer, W. E. Bull, and F. A. Grimm, *J. Chem. Phys.*, 1970, **53**, 768.

line of He^+. There is a double maximum of the first group of photoelectrons (at the right in Figure 22), showing that there is a low-lying excited state in addition to the ground state. The existence of these two states is readily understood. If the CH_4^+ ion had tetrahedral symmetry its electron configuration would be $1a_1^2 2a_1^2 1f_2^5$ which would yield a triply degenerate ($^2F_2$) ground state. However, such a state would be subject to a large Jahn–Teller interaction and as a result there would be two low-lying states whose nature would depend on the kind of deformation produced by the Jahn–Teller interaction. Several independent theoretical studies[45] predict the conformation of CH_4^+ to have D_{2d} symmetry and the two low-lying states would therefore be $^2B_2$ and ^2E. If the conformation had C_{3v} symmetry the resulting states would be $^2A_1$ and ^2E. In absorption it should be possible to find a transition between these two states which is an allowed transition for either symmetry and whose position could be predicted if the photoelectron spectrum were better resolved. Actually a recording of the photoelectron spectrum by Lindholm and Åsbrink[46] at extremely high resolution showed a rather indistinct structure, probably due to predissociation. Nevertheless, experiments are in progress in our laboratory to obtain the absorption spectrum of CH_4^+ because of its possible astronomical importance (see Section 5).

It is interesting to note that the second excited state of the CH_4^+ ion, revealed by the photoelectron spectrum Figure 22, is 9·7 eV above the ground state of the ion. There is no alternative but to assign this second excited state to the excitation of the 2*s* electron or, in other words, to the state $1a_1^2 2a_1 1f_2^6\ ^2A_1$. It is surprising that this state lies so high. This observation illustrates the rather drastic nature of the approximation made in the valence bond treatment of CH_4 in which 2*s* and 2*p* electrons of the carbon atom are considered as degenerate and where this 'degeneracy' is used to form tetrahedral orbitals representing mixtures of 2*s* and 2*p* atomic orbitals. The molecular orbital treatment does not have this difficulty.

5 Applications to Astrochemistry

Many molecular ions play an important rôle in the upper atmosphere of the earth, that is, in the ionospheric layers. As already mentioned, in the spectrum of the aurora the N_2^+ ion is very prominent, but N_2^+ as well as other ions, O_2^+, NO^+, H_2O^+ and NO_2^-, have been detected mass spectrometrically in the ionospheric layers even when no aurora is present.[47]

The upper atmospheres of other planets would be expected to contain similar layers in which molecular ions play a great rôle. In the recent flight of Mariner 6 Barth and his collaborators[48] have observed in the spectrum of the upper

---

[45] R. Pearson, *J. Amer. Chem. Soc.*, 1969, **91**, 4947; G. S. Handler and H. W. Joy, *Internat. J. Quantum Chem.*, 1970, **3S**, 529; F. A. Grimm and J. Godoy, *Chem. Phys. Letters*, 1970, **6**, 336; J. Arents and L. C. Allen, *J. Chem. Phys.*, 1970, **53**, 73; R. N. Dixon, *Mol. Phys.*, 1971, **20**, 113.

[46] E. Lindholm and L. Åsbrink, unpublished.

[47] See H. E. Newell, jun., in 'Physics of the Upper Atmosphere', ed. J. A. Ratcliffe, Academic Press, New York, 1960.

[48] C. A. Barth, C. W. Hord, J. B. Pearce, K. K. Kelly, G. P. Anderson, and A. I. Stewart, *J. Geophys. Res.*, April, 1971.

atmosphere of Mars, in addition to the Cameron bands of CO, clear indications of the $^2\Sigma$–$^2\Pi$ and $^2\Pi$–$^2\Pi$ bands of CO_2^+. Their spectrum is reproduced in Figure 23. Since CO_2 is the principal constituent of the atmosphere of Mars its photo-

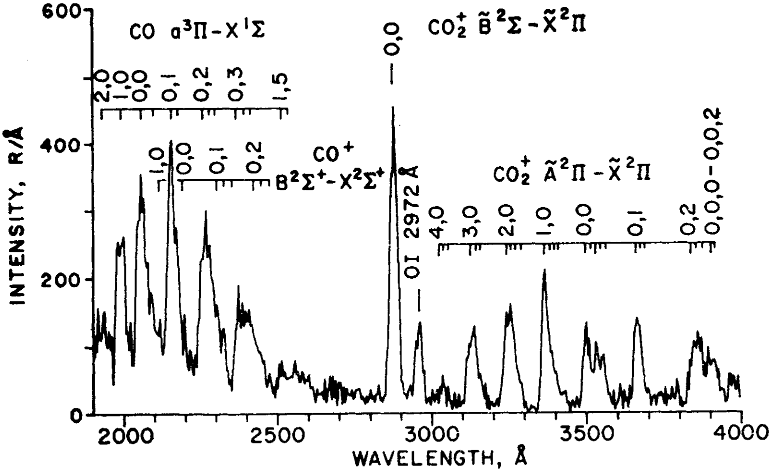

Figure 23 *Ultraviolet spectrum of the upper atmosphere of Mars, after Barth* et al.[48]

ionization in the upper layers of the atmosphere by solar u.v. radiation is bound to occur, thus accounting for the presence of CO_2^+. In a similar way, in the upper atmosphere of Jupiter the ions H_2^+, H_3^+, and CH_4^+ are expected to play a rôle since the principal constituents of the atmosphere are H_2 and CH_4, but their presence has not yet been detected. It is well known that CH_4^+ reacts very rapidly with H_2 or CH_4 to form CH_5^+, and according to Libby CH_5^+ may start the formation of higher hydrocarbons.[49]

As was pointed out in the Introduction, molecular ions play a great rôle in comets, particularly in the comet tails where the most prominent feature is CO^+, but in addition N_2^+, CO_2^+, and CH^+ have been observed. All these ions are, of course, formed by photoionization by the u.v. radiation from the sun. The gas density in the tail is so low that collisions play no rôle at all and thus in many ways we have a very simple chemical situation.

Finally, I would like to stress the importance of molecular ions in the chemistry of the interstellar medium. CH^+ was the first ion to be established,[18] in 1941. It is probable that other molecular ions are present, since in interstellar space the reaction time for ion–molecule reactions and the recombination time is extremely long (the time between collisions is of the order of 10—100 years). The ions H_2^+, H_3^+, N_2^+, and CN^+ are almost certainly present (in addition to CH^+)

---

[49] In an unpublished lecture at the Fiftieth Anniversary of the National Research Council of Canada (1966) Professor Libby expressed this situation dramatically by suggesting that 'it rains crude oil' in the atmosphere of Jupiter.

but only N_2^+ could be detected in the readily accessible region. The concentration of N_2^+ is clearly insufficient to produce the well-known bands shown in Figure 10.

Klemperer[50] has recently suggested that an unidentified radio-frequency line at 89190 MHz is due to the HCO^+ ion, which is a likely ion to be present because of the known presence of H_2CO.

Other unidentified features are the diffuse interstellar lines which extend from 6300 to 4400 Å. There are now 26 such lines with widths varying from 0·1 to 20 Å. Although most astronomers seem to believe that these diffuse lines are due to some impurity in the interstellar dust, I have advanced the suggestion[51] that they are lines of a radical or ion in the interstellar gas which are broadened because of predissociation. The CH_4^+ ion appears to be a good candidate for being responsible for this spectrum because its dissociation energy is only of the order of 1 eV and because, as we have seen earlier, on the basis of the photoelectron spectrum an absorption spectrum is expected in the visible region. Moreover, there is little doubt that CH_4 is a constituent of the interstellar medium even though, unlike NH_3 and H_2O, it has not yet been positively identified[52] since it does not give rise to a radiofrequency spectrum. At any rate, because of the possible importance of CH_4^+ in the interstellar medium a determined effort is being made in our laboratory to find its spectrum. If CH_4^+ is present it would lead, in collisions with H_2 or CH_4, to the formation of CH_5^+ and probably to the further reactions suggested by Libby for the upper atmosphere of Jupiter. The process of condensation and eventual formation of larger aggregates in the interstellar medium is still little understood. More information about molecules and molecular ions in the interstellar medium might be expected to lead to a better understanding of these phenomena.

6 Conclusion

The subject of spectra and structures of simple molecular ions is developing rapidly. Apart from its importance for the understanding of molecular structure it is important for radio-chemistry, for plasma physics, and for astronomy. In this field of study a close interaction between chemistry, physics, and astronomy is important and quite sophisticated considerations in each field are required for an understanding of the observed phenomena.

I thank Professors Price and Barth for the use of Figures 22 and 23 and Professor Lindholm and Dr. Åsbrink for supplying a high resolution photoelectron spectrum of CH_4.

---

[50] W. Klemperer, *Nature*, 1970, **227**, 1230.

[51] G. Herzberg, *Mém. Soc. R. Sci. Liège*, 1955, **15**, 291; *J. Opt. Soc. Amer.*, 1965, **55**, 229; International Astronomy Union Symp. No. 31, 1967, p. 91.

[52] Two small dips in Connes' i.r. spectrum of α Orionis may well be due to interstellar CH_4 but this remains to be confirmed; see G. Herzberg, International Astronomy Union Joint Discussion on Interstellar Molecules, in the press.