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Spectroscopic Studies of Molecular Structure

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The citation for the 1971 Nobel Prize in Chemistry reads "for contribution to the knowledge of electronic structures and geometry of molecules, especially free radicals" and therefore implies that the prize has been awarded for a long series of studies extending practically over my whole scientific life. I shall try to present in this lecture a few of what I consider to be the more significant results of this work.

It was recognized very early in the development of spectroscopy that the study of molecular spectra is one of the most important tools for the determination of molecular structures. When I began my scientific work it had already been firmly established that band spectra are molecular spectra (in contrast to line spectra, which are atomic spectra) and that a band system such as the one shown in Fig. 1 represents all transitions between the vibrational and rotational levels of two electronic states, that is, corresponds to a single line or a single multiplet in an atomic spectrum.

It was also well known how, by determining the spacing between appropriate bands in a band system, we obtain the vibrational intervals in the upper and lower electronic states, which are simply and directly related to the vibrational frequencies of the molecule in these states and how, by determining the separations of appropriate lines in a given band, we obtain the rotational intervals in these states, which are directly related to the moments of inertia and therefore to the internuclear distances (or in other words the geometrical structures) in the two states.

The fine structure of the rotational lines tells us something about the nature of the electronic states involved, whether they are singlet, doublet, triplet, . . . states, while the nature and number of branches tell us, in the case of linear polyatomic molecules and diatomic molecules, whether the electronic states are of the type Σ^+ or Σ^-, or Π, or Δ.

In the years 1925–28 the work of James Franck (*1*) and Birge and Sponer (*2*) had established how in suitable spectra, where a sufficient number of vibrational levels or the limit of an absorption continuum has been observed, the dissociation energy can be accurately determined.

Diatomic Molecules, Radicals, and Ions

The spectra of a large number of diatomic molecules, radicals, and ions (approximately 600) have been studied by various investigators in the past 50 years. For many of these molecules several band systems have been found, and therefore several (sometimes many) electronic states have been established, allowing a detailed interpretation in terms of molecular orbital theory [see Mulliken's Nobel lecture (*3*)]. If Rydberg series of electronic states are observed (so far only in relatively few cases) it is possible to determine the ionization potential in much the same way as for atoms. In the following I shall describe the results only with regard to a few of the many diatomic systems studied in our laboratory.

H_2, D_2, HD, H_2^+. The simplest molecular systems, H_2 and H^+, are even now the only ones for which ab initio calculations of very high precision can be and have been carried out [Kolos and Roothaan (*4*), Kolos and Wolniewicz (*5*), Hunter and Pritchard (*6*)]. It therefore appeared of considerable interest to improve as much as possible the experimental accuracy of some of the molecular constants. We have attempted to do this for the dissociation energy, the vibrational and rotational intervals in the ground state, and for the ionization potential.

The dissociation energy has been determined from the long wavelength limit of the continuum that joins onto the discrete absorption bands which correspond to transitions from the ground state to an excited electronic state designated *B'* in Fig. 2. This state dissociates into one normal and one excited ($n = 2$) H atom; therefore, the limit of the continuous absorption spectrum occurs at an energy equal to the sum of the dissociation energy of the ground state and the excitation energy of the H atom. As an example Fig. 3 shows a small section of the far ultraviolet absorption spectrum of D_2 near 840 angstroms (Å) under very high resolution taken at liquid nitrogen temperature where the absorption limit is clearly visible (for H_2 the corresponding limit is overlapped by an absorption line which makes it difficult to obtain as precise a limit as for D_2). Subtracting the excitation energy of D (or H) from the

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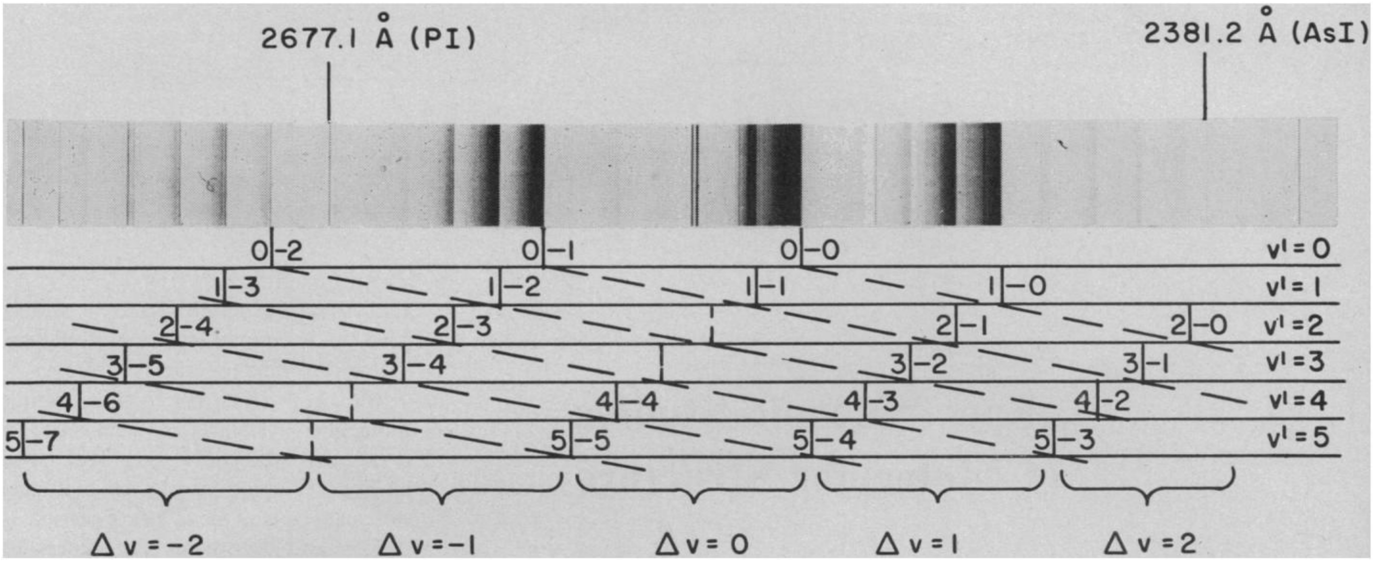
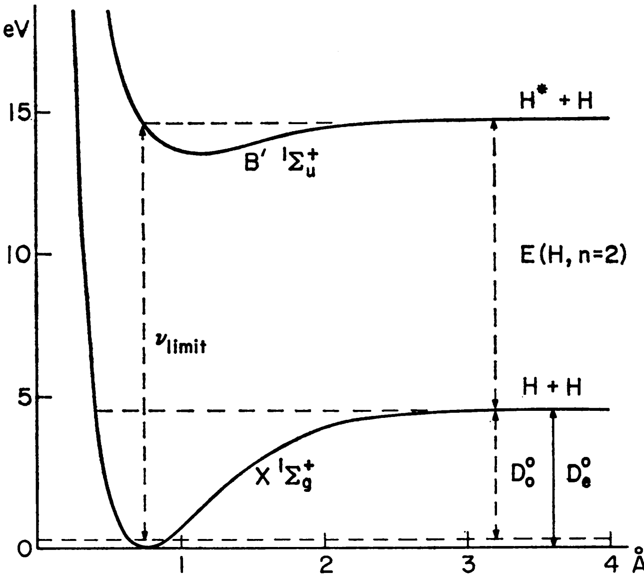


Fig. 1. Band system of the PN molecule. [After Curry, Herzberg, and Herzberg (*62*)]

wave number of the limit and including a very small correction for the rotational barrier at $J = 1$ in the upper state, we have obtained the dissociation energies given in the last column of Table 1, which should be compared with the theoretical values in the second column. The agreement between theory and experiment is clearly very good.

Precise values of the vibrational intervals ΔG and the rotational constants B_v have been obtained for low v values from the Raman spectrum [Stoicheff (*7*)] and the infrared quadrupole spectrum [Herzberg (*8*), Rank *et al.* (*9*)], and for higher v values from the vacuum ultraviolet emission spectrum [Herzberg and Howe (*10*), Bredohl and Herzberg (*11*)]. In Table 2 the observed ΔG values of H_2 are compared with the theoretical values obtained from the Kolos-Roothaan-Wolniewicz potential (*5*). The slight systematic differences are in all probability due to the neglect of the nonadiabatic corrections [see Poll and Karl (*12*) and Bunker (*13*)]. In Fig. 4 the deviations Herzberg (*11*)]. In Table 2 the oblar very small systematic differences are also found for the rotational con-



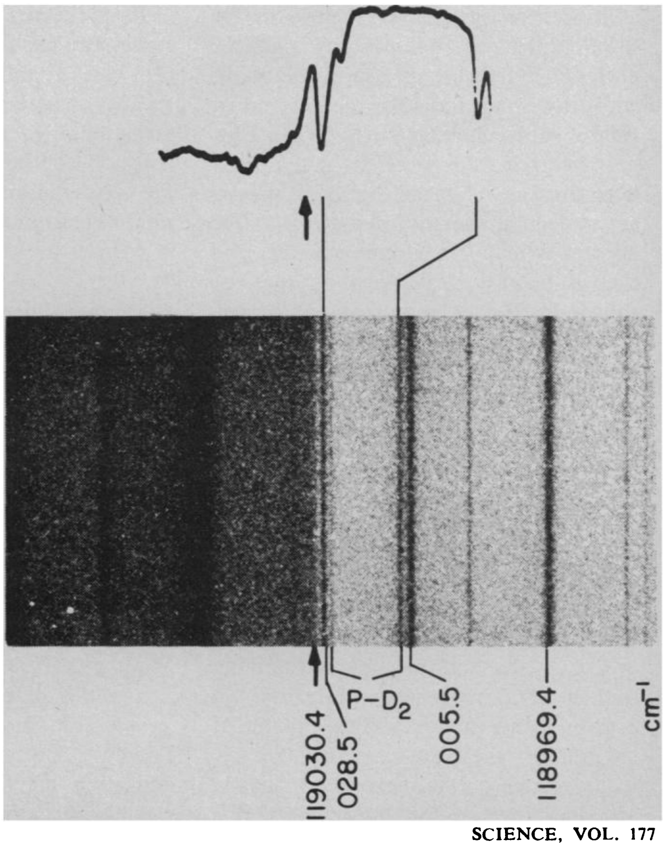
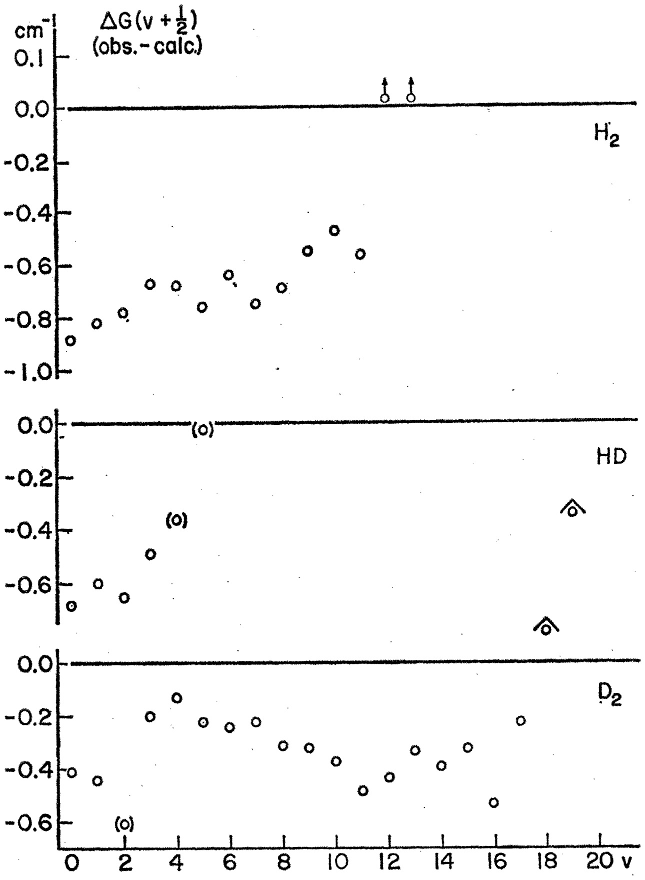


Fig. 2 (left). Potential functions of the ground state ($X\,^1\Sigma_g^+$) and the second excited state ($B'\,^1\Sigma_u^+$) of H_2 showing the relation between the absorption limit and the dissocation energy in the ground state: $D_0^0 = \nu_{\text{limit}} - E\,(H,\ n = 2)$. Fig. 3 (right). Section of far ultraviolet absorption spectrum of D_2 at low temperature showing the absorption limit corresponding to $J'' = 0$. [After Herzberg (*63*)]



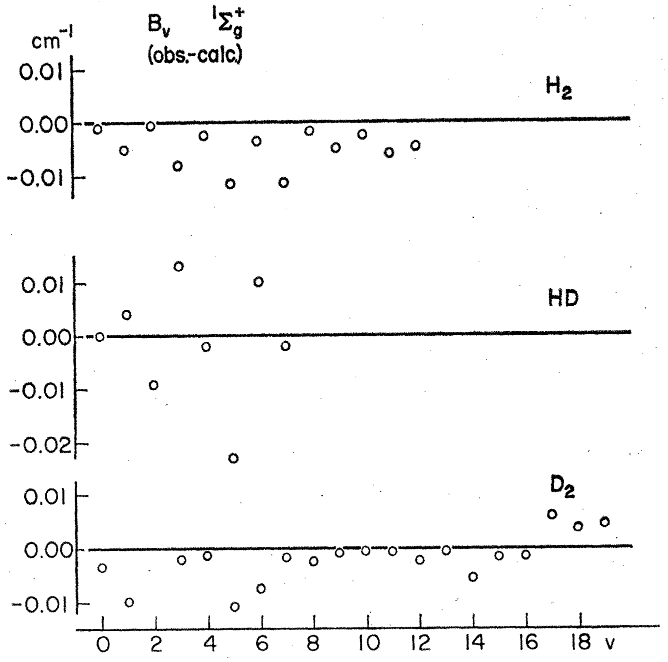


Fig. 4 (left). Deviations of the observed vibrational quanta of H_2, HD, and D_2 from those obtained from theory. Fig. 5 (right). Deviation of the observed rotational constants B_v of H_2, HD, and D_2 from those obtained from theory.

Table 1. Calculated and observed dissociation energies of hydrogen. The theoretical results are from Kolos and Wolniewicz (*5*) but include small nonadiabatic corrections according to Bunker (*13*).

Molecule	D_0^0 Theoretical (cm⁻¹)	D_0^0 Observed (cm⁻¹)
H_2	36,117.8	$<$ 36,118.3 $>$ 36,116.3
HD	36,405.5	36,406.6 36,405.8
D_2	36,748.2	36,748.9 ± 0.4

Table 2. Observed and calculated vibrational quantum in the ground state of H_2.

v	$\Delta G(v + ½)$ (cm⁻¹) Observed	$\Delta G(v + ½)$ (cm⁻¹) Theoretical
0	4161.14	4162.06
1	3925.98	3926.64
2	3695.24	3696.14
3	3468.01	3468.68
4	3241.56	3242.24
5	3013.73	3014.49
6	2782.18	2782.82
7	2543.14	2543.89
8	2292.96	2293.65
9	2026.26	2026.81
10	1736.66	1737.13
11	1414.98	1415.54
12	1049.18	1048.98
13	621.96	620.16

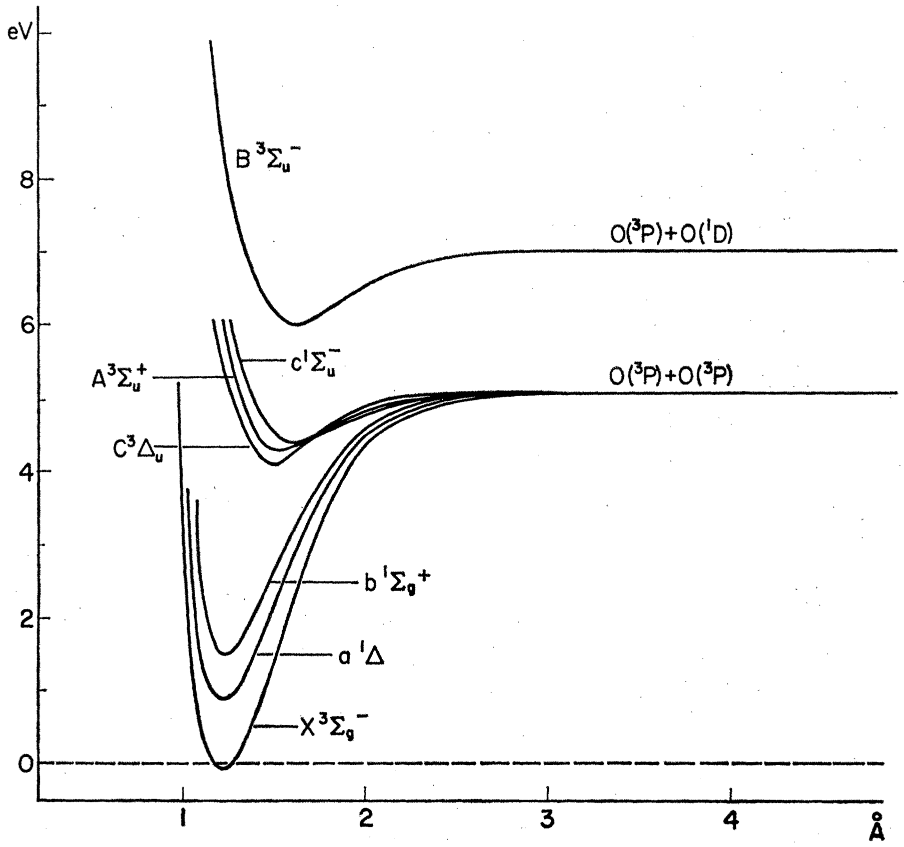


Fig. 6. Potential functions of the ground state and the lower excited states of the O_2 molecule. The state $C\,^3\Delta_u$ in this figure should have designated $A'\,\Delta_u$ to be in accord with Table 3.

stants B_v as shown in Fig. 5. There is little doubt that these small discrepancies, of the order of 100 parts per million, will be fully accounted for once the nonadiabatic corrections have been accurately evaluated.

If one disregards adiabatic and nonadiabatic corrections one obtains from the observed B_v values an internuclear distance for the equilibrium position of 0.74139 and 0.74156 Å for H_2 and D_2 while the theoretical value (the same for both) is 0.74140 Å.

Finally, the detailed study of the Rydberg series of H_2 near 800 Å, which is made somewhat complicated by interesting perturbations, by preionization effects, and small pressure shifts, has led to the following experimental value for the ionization potential of H_2 [Herzberg and Jungen (*14*)]

$$\text{I.P.}(H_2) = 124{,}417.2 \pm 0.4\ \text{cm}^{-1}$$

and a less detailed study by Takezawa (*15*) of D_2, has led, after a pressure shift correction, to the value

$$\text{I.P.}(D_2) = 124{,}745.6 \pm 0.6\ \text{cm}^{-1}$$

The theoretical values, including relativistic and Lamb-shift corrections, are [Hunter and Pritchard (*6*), Jeziorski and Kolos (*16*), Bunker (*13*)]

$$\text{I.P.}_{\text{theor}}\ (H_2) = 124{,}417.3\ \text{cm}^{-1}$$
$$\text{I.P.}_{\text{theor}}\ (D_2) = 124{,}745.2\ \text{cm}^{-1}$$

The agreement is well within the error of measurement, that is, within about 3 parts per million.

From the ionization potentials and the dissociation energies of H_2 and D_2 we obtain, according to the general relation

$$D_0^0(X_2^+) = \text{I.P.}(X) + D_0^0(X_2) - \text{I.P.}(X_2)$$

the following values for the dissociation energies of the ions

$$D_0^0{}_{\text{obs}}\ (H_2^+) \leqslant 21{,}379.9 \pm 0.4\ \text{cm}^{-1}$$
$$D_0^0{}_{\text{obs}}\ (D_2^+) = 21{,}711.9 \pm 0.6\ \text{cm}^{-1}$$

These values may be compared with the theoretical values

$$D_0^0{}_{\text{theor}}\ (H_2^+) = 21{,}379.3\ \text{cm}^{-1}$$
$$D_0^0{}_{\text{theor}}\ (D_2^+) = 21{,}711.6\ \text{cm}^{-1}$$

which are considered to be accurate to $\pm 0.2\ \text{cm}^{-1}$. That the agreement is again very satisfactory is not surprising since $D_0^0(H_2^+, D_2^+)$ are determined by $D_0^0(H_2, D_2)$ and I.P.(H_2, D_2), and for both of the latter quantities very good agreement between theory and experiment was found.

O_2. The study of forbidden electronic transitions, that is, transitions forbidden by the normal selection rules, has greatly aided in the understanding of the electronic structure of diatomic (and polyatomic) molecules. The O_2 molecule is particularly rich in such forbidden transitions. The lowest electron configuration . . . $\pi_u{}^4\,\pi_g{}^2$ gives rise to three states $^3\Sigma_g{}^-$, $^1\Delta_g$, and $^1\Sigma_g{}^+$ of which the first forms the ground state of the molecule. As was first recognized by Van Vleck (*17*), the forbidden transitions from the ground state to the $^1\Delta_g$ and $^1\Sigma_g{}^+$ states can only occur as magnetic dipole (or much more weakly as quadrupole) radiation. Because of the long absorption path in the atmo-

Table 3. Molecular constants of the lower states of the O_2 and S_2 molecules.

	T_0 (cm^{-1})	ω_e (cm^{-1})	D_0 (ev)	r_e (Å)
O_2				
$B\ ^3\Sigma_u{}^-$	49,363.1	700.36	0.9627	1.6049
$A\ ^3\Sigma_u{}^+$	35,007.2	799.07	0.7752	1.5214
$A'\ ^3\Delta_u$	34,320	(611.2)	0.8604	(1.49)
$c\ ^1\Sigma_u{}^-$	32,664.1	794.29	1.0657	1.5174
$b\ ^1\Sigma_g{}^+$	13,120.9	1432.69	3.4887	1.2269
$a\ ^1\Delta_g$	7,882.4	1509.3	4.1382	1.2156
$X\ ^3\Sigma_g{}^-$	0	1580.36	5.1155	1.2075
S_2				
$B\ ^3\Sigma_u{}^-$	31,689	434.0	1.5828	2.1702
$A\ ^3\Sigma_u{}^+$	(22,682)	481.4	(1.55)	
$A'\ ^3\Delta_u$	(21,855)	488.4	(1.66)	2.1506
$c\ ^1\Sigma_u{}^-$				2.15
$b\ ^1\Sigma_g{}^+$		(699.7)		
$a\ ^1\Delta_g$	(5,100)	701.94	(3.73)	1.8978
$X\ ^3\Sigma_g{}^-$	0	725.65	4.3662	1.8892

Table 4. Molecular constants of the known electronic states of CH and CH^+.

State	T_0 (cm^{-1})	$\Delta G(½)$ (cm^{-1})	B_0 (cm^{-1})	r_0 (Å)
CH^+				
$^1\Pi$	109,446	1642.16	11.428	1.2596
$^1\Sigma^+$	85,850	2739.70	13.932	1.1409
CH				
$3d\ ^2\Delta$				
$3d\ ^2\Pi$	72,960			
$3d\ ^2\Sigma^+$				
$3p\ ^2\Pi_r$	64,532		12.6	1.2_0
$3p\ ^2\Sigma^+$			12.17	1.221
$D\ ^2\Pi_i$	58,981	(2800)	13.7	1.12
$C\ ^2\Sigma^+$	31,778	2613	14.25	1.128
$B\ ^2\Sigma^-$	25,698	1795	12.64	1.198
$A\ ^2\Delta$	23,217	2737	14.58	1.115
$X\ ^2\Pi$	0	2732.5	14.19	1.130

Table 5. Diatomic molecules, radicals, and ions studied at the National Research Council of Canada.

H_2, He_2, B_2, C_2, N_2, O_2, F_2, Mg_2, Si_2, P_2, S_2, Cl_2, I_2
LiH, BH, CH, NH, OH, SiH, PH, SH, HCl, HBr, CrH, CuH
BN, CN, PN
CO, NO, PO, SO, IO
BS, CS, SnS
BF, NF, NaF, SiF, PF, KF, RbF
BCl, CCl, SiI, NCl, AlCl
NBr, AlBr, CP, AlC
CH^+, NH^+, SiH^+, PH^+
C_2^-, C_2^+, N_2^+, N_2^{++}, P_2^+, CO^+, CN^+, NO^+

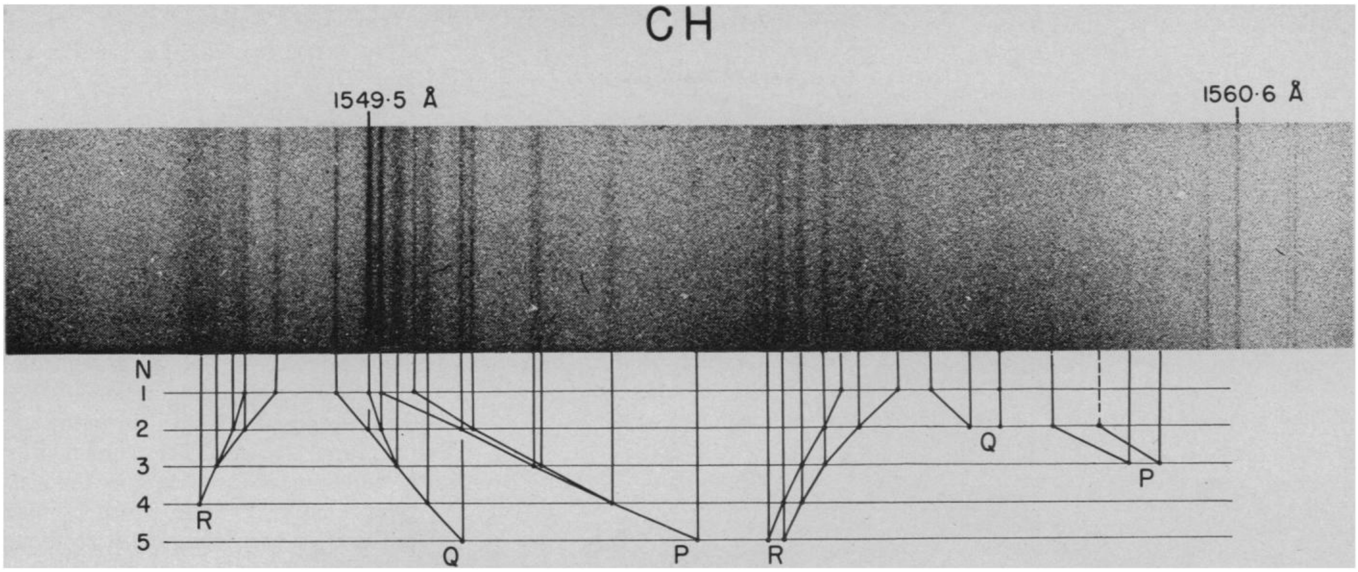


Fig. 7 (above). Section of vacuum-ultraviolet absorption spectrum of CH showing the 0—0 bands of the $E^2\Pi - X^2\Pi$ and $F^2\Sigma$—$X^2\Pi$ transitions. [After Herzberg and Johns (*25*)]

sphere, these forbidden transitions are very prominent in the solar spectrum observed from the ground. In emission they occur strongly in the red and infrared spectrum of the night sky. Even the transition $^1\Sigma_g{}^+$—$^1\Delta_g$, which can occur only as electric quadrupole radiation, has been observed [Noxon (*18*)].

Another group of forbidden transitions in the near ultraviolet corresponds to transitions to states of the configuration . . . $\pi_u{}^3\,\pi_g{}^3$, which give rise to the six states $^1\Sigma_u{}^+$, $^1\Sigma_u{}^-$, $^1\Delta_u$, $^3\Sigma_u{}^+$, $^3\Sigma_u{}^-$, $^3\Delta_u$. Only one of these states can combine with the ground state in an allowed transition, namely, $^3\Sigma_u{}^+$—$^3\Sigma_g{}^-$; this transition, the well-known Schumann-Runge bands, limits the transparency of air in the ultraviolet. Forbidden transitions to three of the other states, $^1\Sigma_u{}^-$, $^3\Sigma_u{}^+$, and $^3\Delta_u$, have been observed [Herzberg (*19*)], of which $^3\Sigma_u{}^+$—$^3\Sigma_g{}^-$ is the best known and is quite prominent in the light of the night sky. Figure 6 shows a potential diagram of the lower electronic states of O_2. The fact that all transitions to the ground state from nonrepulsive states arising from normal atoms ($^3P + {}^3P$) are forbidden accounts for the observation that in the upper atmosphere the radiative recombination of O atoms is very slow indeed. On the other hand, the weak continuous absorption joining onto the $^3\Sigma_u{}^+$—$^3\Sigma_g{}^-$ absorption system ($\lambda < 2440$ Å) gives rise to the production of free O atoms even at fairly low altitudes and thus accounts for the formation of the ozone layer. Thus, the chemistry of the upper atmosphere is greatly affected by the forbidden nature of these transitions, that is, by the electronic structure of the O_2 molecule. In Table 3 some of the molecular

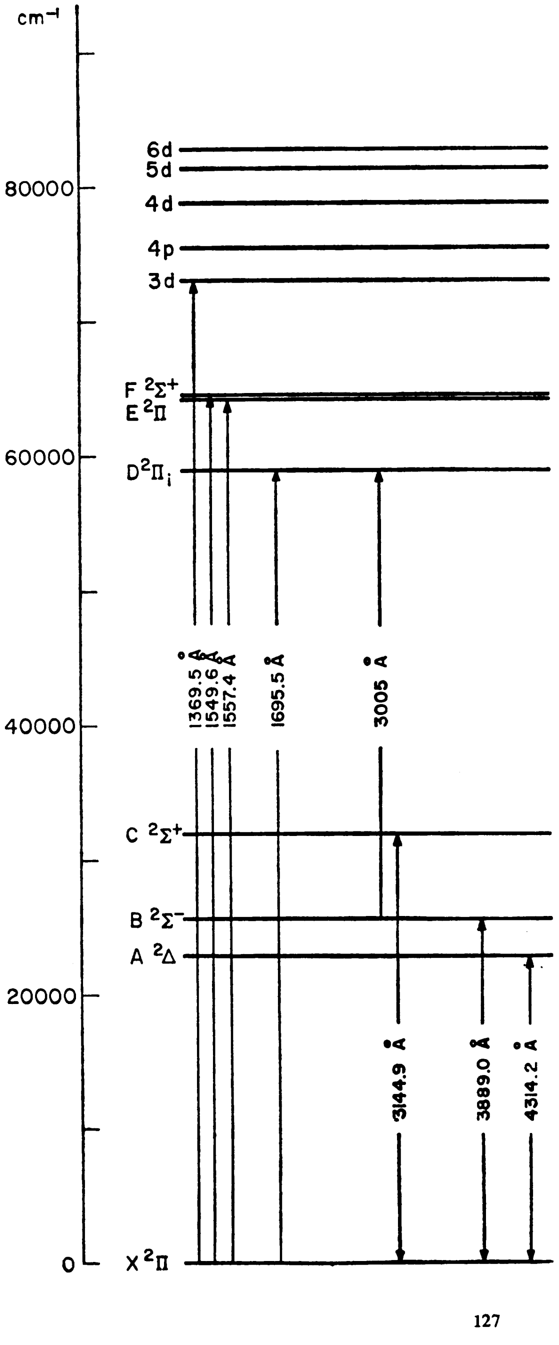


Fig. 8 (right). Energy level diagram of the electronic states of the CH radical showing the observed transitions. The Rydberg transitions are not marked.

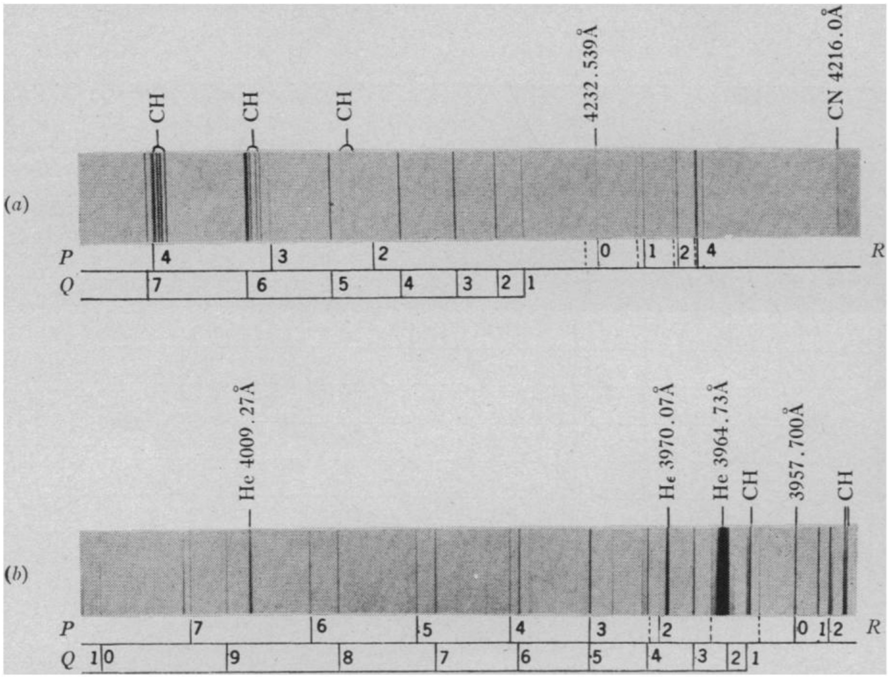


Fig. 9 (left). Two emission bands of CH$^+$ [after Douglas and Herzberg (*29*)]. The interstellar lines are the $R(0)$ lines.

constants of O_2 are summarized and compared with those of S_2. In S_2 the analogues of the forbidden transitions of O_2 have not yet been observed.

Many studies of forbidden transitions in other molecules have been made but will not be discussed here [see Herzberg (*20*)].

CH and CH$^+$. The visible and near ultraviolet emission spectrum of the CH radical has been known ever since spectra of an ordinary Bunsen burner have been taken. That the well-known bands at 4314 and 3889 Å really belong to CH was established, of course, only after the theory of diatomic spectra was sufficiently developed [Heurlinger (*21*), Heurlinger and Hulthén (*22*), Hulthén (*23*)]. The band at 3145 Å, later discovered by Hori (*24*) in electric discharges, has the same lower state as the other two, the $^2\Pi$ ground state of the molecule. While the ground state has the electron configuration $\sigma^2\sigma^2\sigma^2\pi$, the three excited states have the configuration . . . $\sigma\pi^2$. This configuration, in addition to $^2\Sigma^-$, $^2\Delta$, and $^2\Sigma^+$, also gives rise to a $^4\Sigma^-$ state, which, however, has not yet been observed even though it is expected to be a stable and fairly low-lying state.

The CH radical is a very reactive radical which under most conditions has a very short lifetime. It is for this reason that its absorption spectrum has been observed and studied in detail only fairly recently [Herzberg and Johns (*25*)]. This study has revealed a number of new transitions in the vacuum ultraviolet of which Fig. 7 gives an example. Indeed, a whole Rydberg series was found, which allowed an accurate determination of the ionization potential (10.64 ev). In addition, the

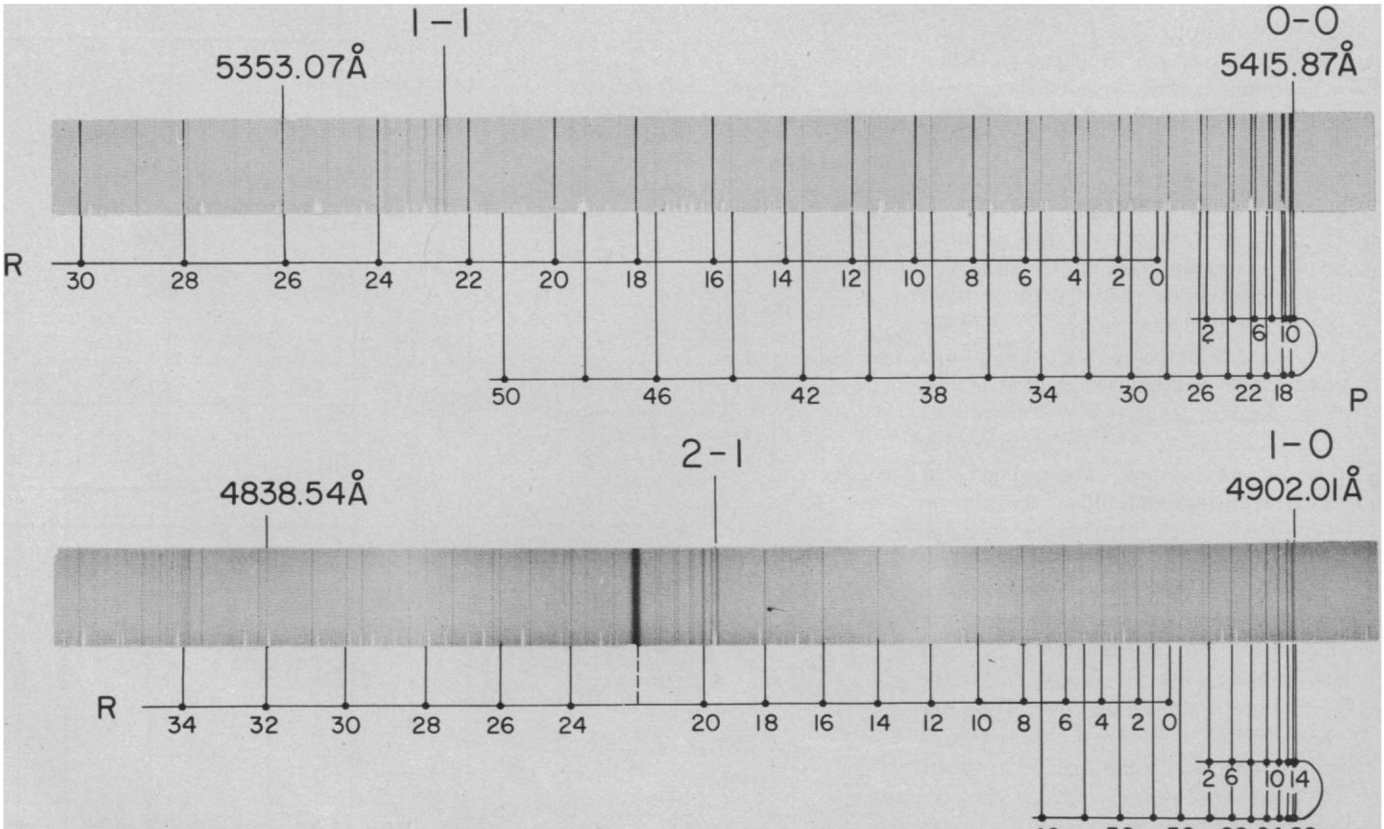


Fig. 10. Absorption spectrum of the C_2^- ion. [After Herzberg and Lagerqvist (*30*)]

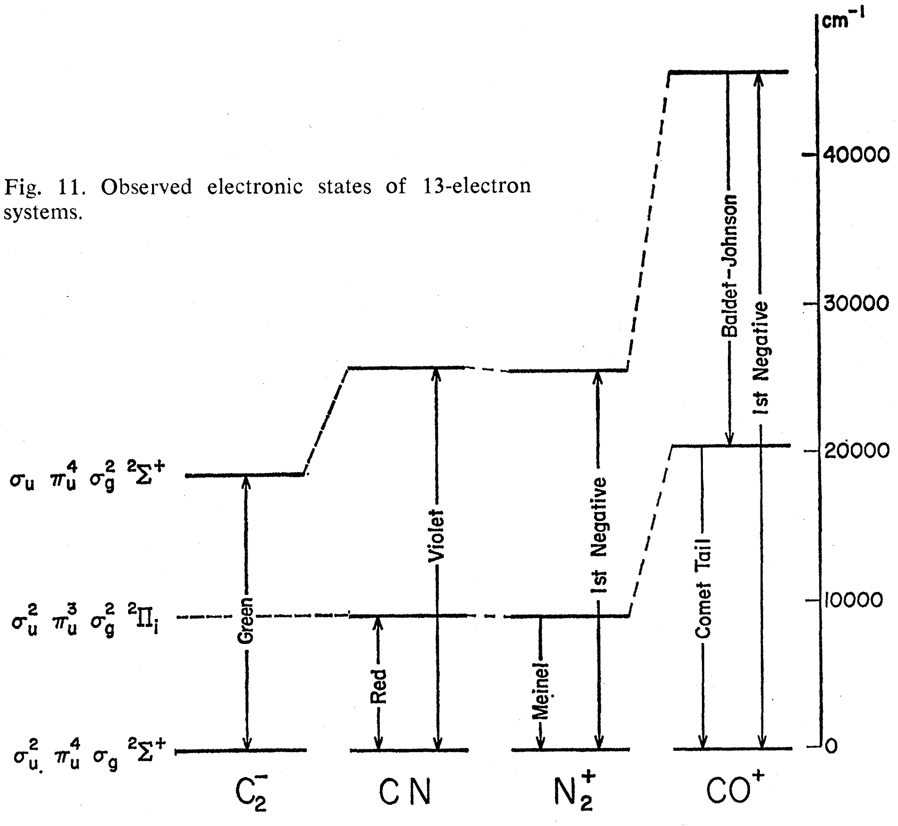


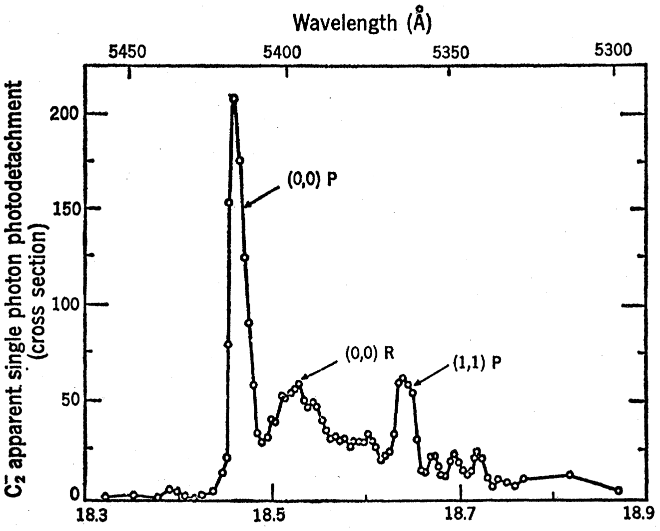
Fig. 11. Observed electronic states of 13-electron systems.

value for the dissociation energy was slightly refined in this work, and much evidence of predissociation in all excited states except the $^2\Delta$ state was obtained. Figure 8 shows a diagram of the observed electronic states of CH, and Table 4 gives some of the principal molecular constants.

The CH radical was the first molecule recognized in the interstellar medium [Swings and Rosenfeld (*26*), McKellar (*27*)]. The lifetime of CH under the action of the interstellar radiation field is relatively short (about 30 years) because of the predissociation that has been shown to occur in all absorption systems of CH except the longest wavelength one ($^2\Delta$—$^2\Pi$). It is therefore somewhat surprising that CH is present in sufficient concentration to show its absorption spectrum.

The ion CH^+ has also been observed, first in interstellar absorption [Adams (*28*)] and then in emission in the laboratory [Douglas and Herzberg (*29*)]. The observed transition is the expected $\sigma\pi\,^1\Pi$—$\sigma^2\,^1\Sigma$ transition. The molecular constants are included in Table 4. Figure 9 shows a laboratory spectrum. The interstellar lines [$R(0)$ lines coming from the lowest rotational level] are marked. In spite of much effort we have not yet been able to observe this spectrum *in absorption* in the laboratory.

C_2^-. A few years ago, in an attempt to observe absorption spectra of CH_4^+, CH_3^+, CH_2^+, and CH^+ by using flash discharges through CH_4, we observed a new, very simple spectrum shown in Fig. 10 [Herzberg and Lagerqvist (*30*)]. The analysis was very easy and showed immediately and conclusively that the carrier of this spectrum must be the C_2 radical or one of its ions. It seemed impossible to fit this transition into the known system of energy levels of C_2. Therefore, and because of the similarity with N_2^+, we suggested that the spectrum belongs to the C_2^- ion (that is, represents the first discrete spectrum of a negative molecular ion) even though the required doublet structure



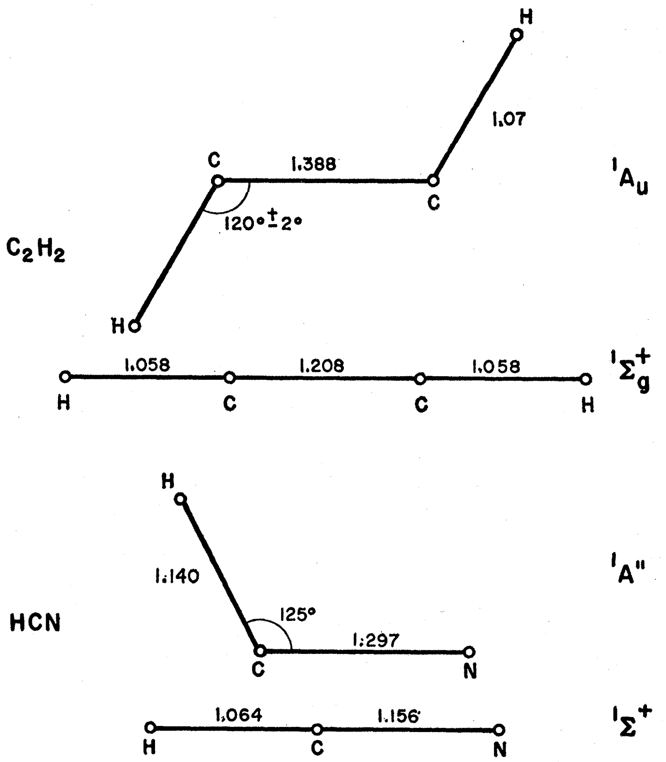


Fig. 12 (left). Photoionization spectrum of a C_2^- beam produced by two-photon absorption of a tunable laser beam. [After Lineberger and Patterson (32)] Fig. 13 (right). Geometrical structures of C_2H_2 and HCN in their ground and first excited states. [Ingold and King (*64*), Innes (*65*), Herzberg and Innes (*66*)]

Table 6. Bond angles in the ground states of triatomic dihydrides.

BH_2	CH_2	NH_2	H_2O	AlH_2	SiH_2	PH_2	H_2S
131°	136° (triplet) 104° (singlet)	103.3°	105.2°	119°	92.1° (singlet)	91.5°	92.2°

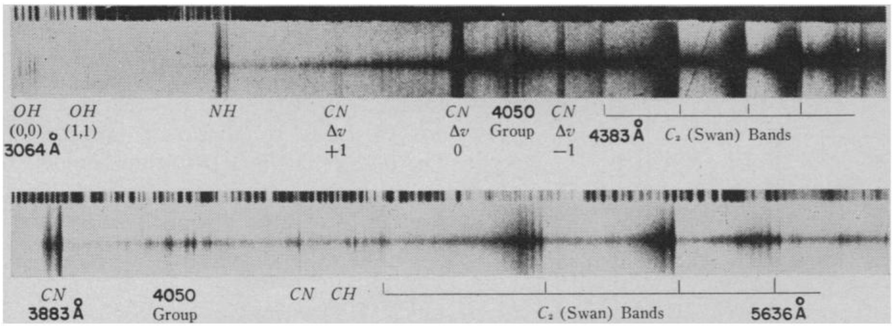


Fig. 14. Spectrum of comet Cunningham (1940 c). [After Swings (*67*)]

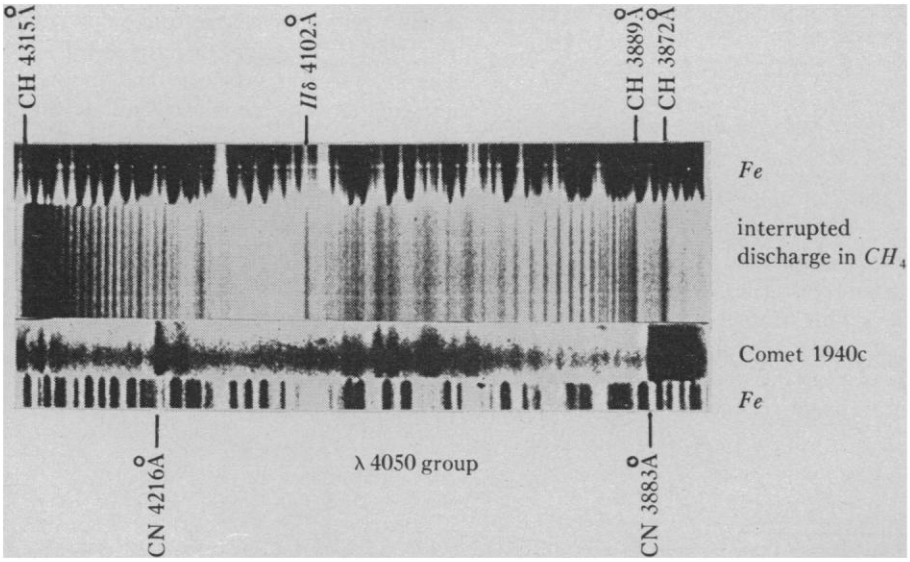


Fig. 15. The 4050-Å group in the laboratory and in a comet. [After Herzberg (*36*)]

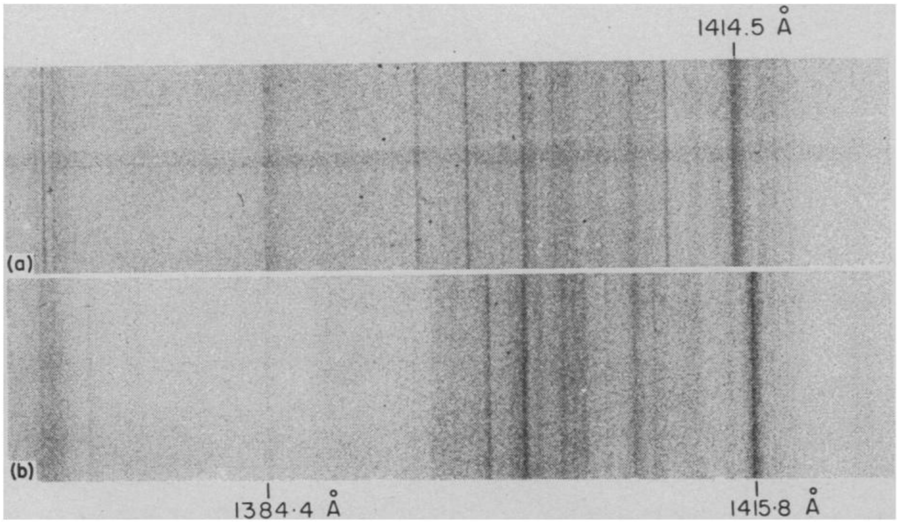


Fig. 16. Absorption spectra of flash-photolyzed (a) diazomethane and (b) deuterated diazomethane. [After Herzberg (*43*)]

of the spectrum was not very clearly recognizable.

In Fig. 11 the observed electronic energy levels of N_2^+, CN, and CO^+ are compared with those of the new transition. All these molecules or ions have 13 electrons. Comparisons such as this historically formed the starting point of molecular orbital theory. Here the comparison serves to strengthen the suggestion that the new transition belongs to a 13-electron system, that is, C_2^-. This suggestion was strikingly confirmed first by the work of Milligan and Jacox (*31*) on the analogous spectrum observed in a solid matrix, since it is considerably strengthened by the addition of an electron donor like Cs; and recently even more conclusively by the work of Lineberger and Patterson (*32*), who photoionized a C_2^- beam by a two-photon absorption of a tunable laser beam and found, as shown in Fig. 12, a photoionization exactly at the wavelengths of the new absorption bands.

Meinel (*33*) in our laboratory has recently observed the spectrum of C_2^+. Other diatomic molecules, radicals, and ions studied in our laboratory are listed in Table 5. For all these systems, information about their geometrical structure (internuclear distances), vibrational frequencies in various electronic states, and about their electronic structure has been obtained. Much work on these molecules and many other molecules which we have not studied has proceeded in many laboratories throughout the world, notably here in Stockholm in Professor Lagerqvist's laboratory.

Polyatomic Molecules, Radicals, and Ions

General remarks. In polyatomic molecules and radicals there are, in general, several geometrical parameters which are required to describe their structures (rather than one, r_e, for diatomic molecules). For a large number of stable molecules these parameters have been determined in their ground states by the techniques of infrared, Raman, and microwave spectroscopy. In excited electronic states these parameters can only be obtained by a detailed study of electronic band systems in absorption or emission. In many cases it has been found that the shape (point group) of the molecule in an excited state is different from its shape in the ground state. For example, the molecules C_2H_2 and

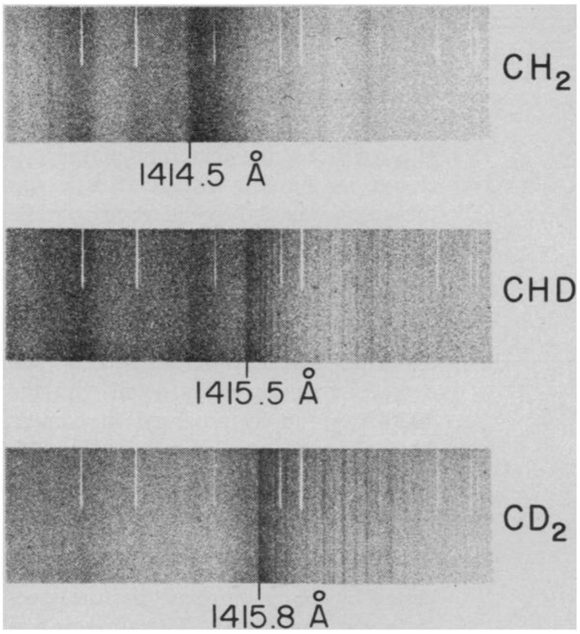


Fig. 17. High-resolution absorption spectra of flash-photolyzed normal and deuterated diazomethanes (*43*).

HCN, well known to be linear in their ground states, are found to be strongly bent in their first (singlet) excited states, as shown in Fig. 13. It is clear that this behavior throws an interesting light on the way in which the electronic structure determines molecular shape.

For polyatomic free radicals and ions one is dependent both for the ground states and the excited states on the study of electronic spectra to obtain the shapes and the geometrical parameters. Only for a few radicals have microwave and infrared spectra been obtained in the gaseous state. Not infrequently, just as for stable molecules, electronic spectra of radicals are diffuse or even continuous, in which case no information about geometrical structure can be obtained. The BH_3 radical may be such a case. An additional difficulty in the interpretation of free-radical spectra is the problem of identification, that is, the problem to which particular radical an observed spectrum belongs. As an example of these difficulties I should like to discuss the history of the discovery of the spectra of CH_2 and C_3.

CH_2 and C_3. In 1941 the Belgian astronomer Swings wrote to me about a problem that had arisen in the interpretation of the spectra of comets. Figure 14 shows the spectrum of a comet. In this spectrum the emission bands of CN, C_2, CH, NH, and OH can be clearly seen, but in addition there is a group of bands near 4050 Å whose origin nobody had been able to identify at that time. On the basis of the structure of this spectrum, I thought I could eliminate the possibility that it was due to a *diatomic* free radical. Rather, the 4050-Å group appeared to me like a perpendicular band of a nearly symmetric top molecule, and because of the wide spacing of the subbands I concluded (*34*) that it must be due to a nonlinear molecule XH_2 with a bond angle of the order of 140°. The most likely identification appeared to be CH_2, particularly since at that time Mulliken (*35*) had just predicted a spectrum of CH_2 to occur in the region 4000 to 4500 Å. Since CH was known to be present in comets, the identification of the 4050-Å group as due to CH_2 seemed eminently reasonable.

On the basis of these considerations I proceeded to do some laboratory ex-

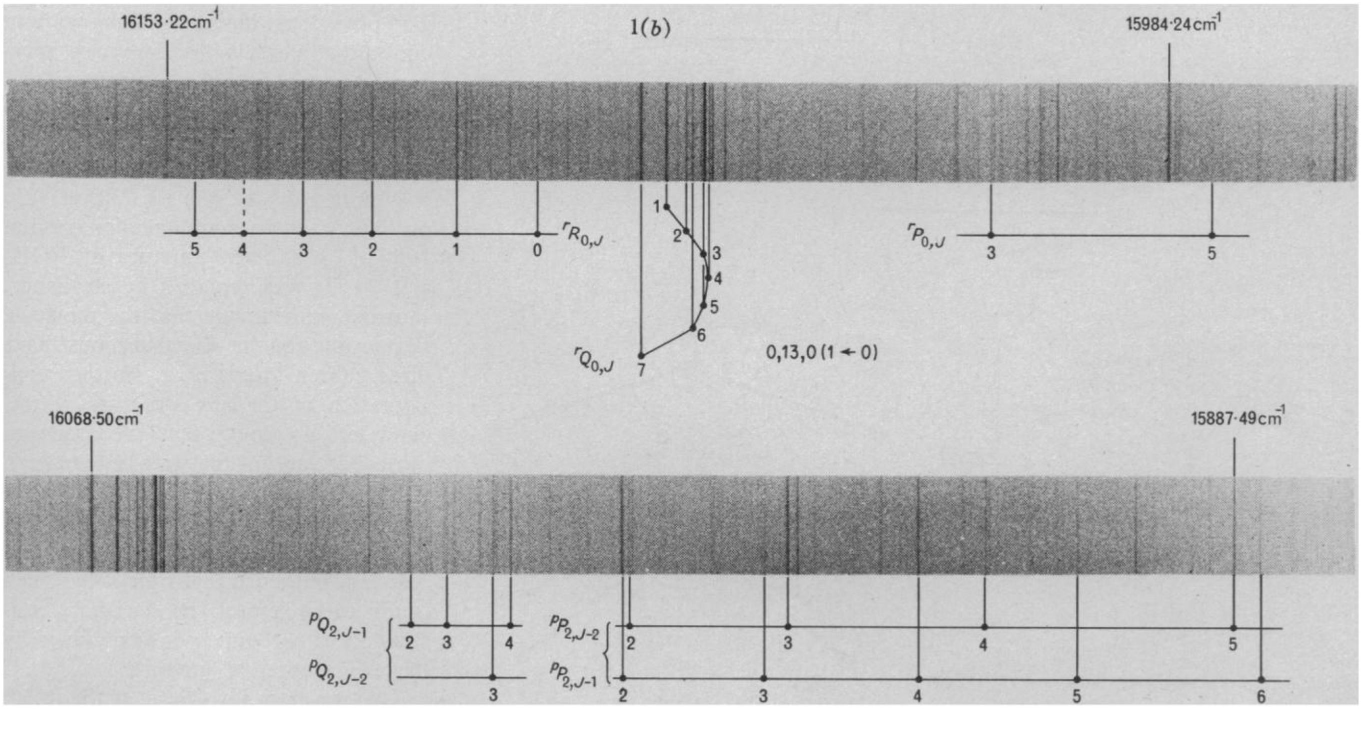


Fig. 18. Two subbands (1—0 and 1—2) of the 0 13 0—0 0 0 band of the red absorption system of CH_2.

Table 7. Molecular constants in the ground states of linear triatomic nonhydrides. N is the number of valence electrons.

Molecule	State	ΔG (cm^{-1})	B_0 (cm^{-1})	r_0 (Å)	N
C_3	$^1\Sigma_g^+$	63.1	0.4305	1.277	12
CCN	$^2\Pi_r$	(325)	0.3981		
CNC	$^2\Pi_g$	321	0.4535	1.245	13
NCN	$^3\Sigma_g^-$	(423)	0.3968	1.232	
CCO	$^3\Sigma^-$	379.4	0.3851		14
NCO	$^2\Pi_i$	(539)	0.3894		
N_3	$^2\Pi_g$		0.4312	1.182	15
BO_2	$^2\Pi_g$	464	0.3292	1.265	
CO_2	$^1\Sigma_g^+$	667.4	0.3902	1.162	16

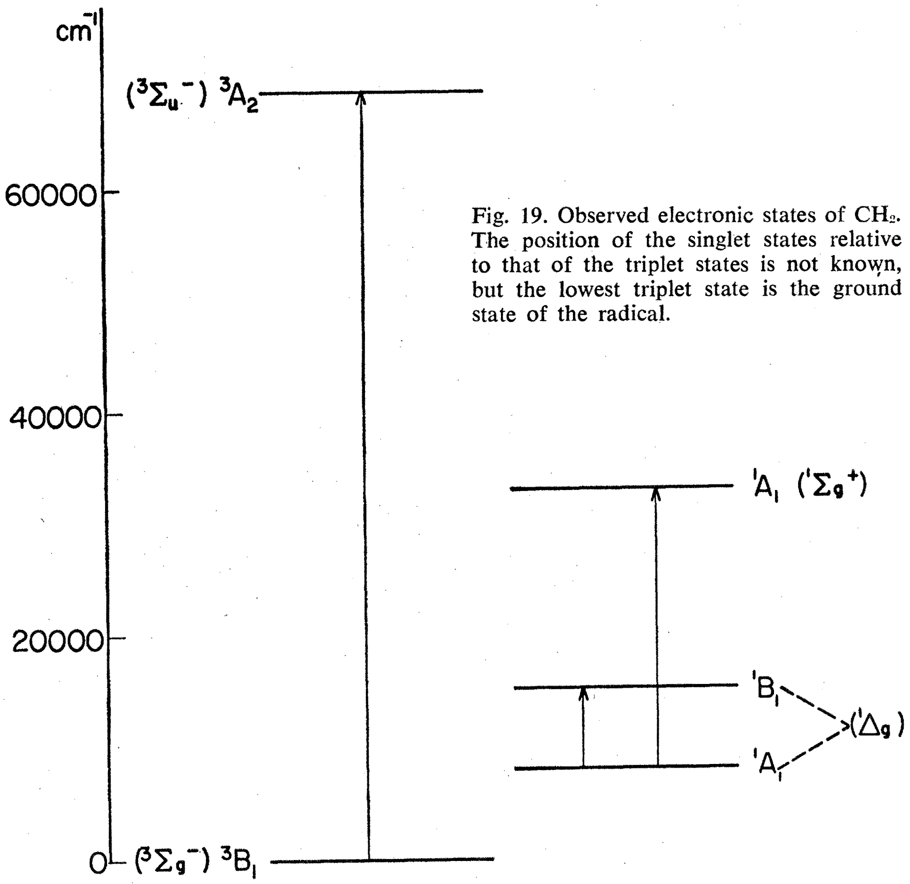
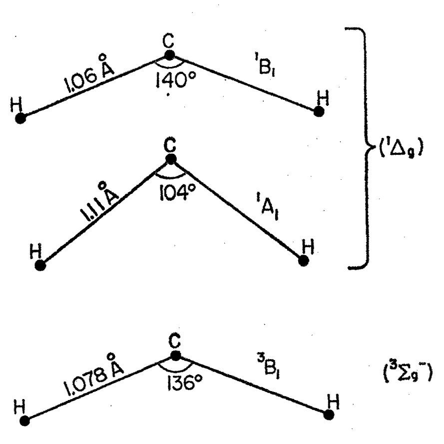


Fig. 19. Observed electronic states of CH_2. The position of the singlet states relative to that of the triplet states is not known, but the lowest triplet state is the ground state of the radical.



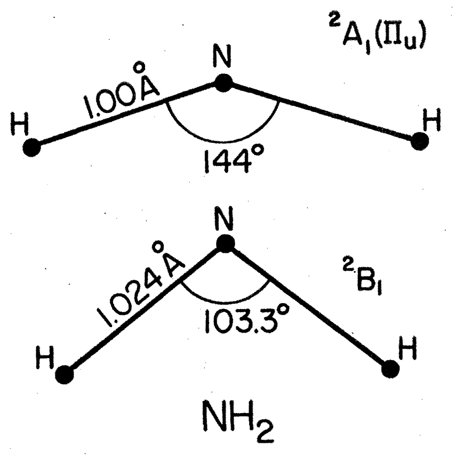


Fig. 20 (left). Geometrical structure of CH_2 in the three lowest states. Fig. 21 (right). Geometrical structure of NH_2 in the two known electronic states.

periments. I tried the obvious, passing a discharge through methane (CH_4) in the hope of obtaining in this discharge a spectrum of CH_2. While the continuous discharge through methane showed only well-known features such as CH and H_2, I noticed that the color of the discharge in the first instant after it was turned on was slightly different from the later color. I therefore took a spectrum with the discharge turned on and off repeatedly. On this spectrum, in addition to the bands of CH, a new feature appeared precisely at 4050 Å which agreed in almost every detail with the 4050-Å group as observed in comets. This agreement is shown in Fig. 15. Thus, for the first time [Herzberg (*36*)], the 4050-Å group of comets had been observed in the laboratory, and this had been done by choosing conditions suggested by the assumption that the spectrum was due to CH_2. Therefore, it was perhaps excusable that I felt confirmed in my belief that this spectrum was due to CH_2.

However, in 1949 Monfils and Rosen (*37*) at Liège repeated our experiment but replaced the hydrogen by deuterium. The spectrum that they observed was identical in every detail with the spectrum that I had observed, whereas, of course, small isotope shifts would have been expected had this spectrum been due to CH_2. Dr. Douglas and I at Ottawa immediately repeated this experiment using much higher resolution and confirmed the result of the Belgian physicists, thus establishing without doubt that neither the cometary spectrum nor the laboratory spectrum was due to CH_2. Douglas (*38*) then proceeded to find the true carrier of this spectrum by using methane with ^{13}C in it (supplied by the late K. Clusius). He observed that the main emission band at 4050 Å in a 50-50 mixture of $^{12}CH_4$ and $^{13}CH_4$ was replaced by six bands, showing immediately that the molecule responsible for this spectrum must have three carbon atoms in it. Further consideration of the fine structure of this band left no doubt that the spectrum must be due to the free C_3 radical. At the time when Douglas established this conclusion, the C_3 radical had not even been postulated in any chemical reaction, but since that time it has been found to be one of the dominant constituents of carbon vapor as obtained by the evaporation of graphite.

The question now arose, if the 4050-Å group is not due to CH_2, where is the true spectrum of CH_2—or does such a spectrum not exist? It was almost 10

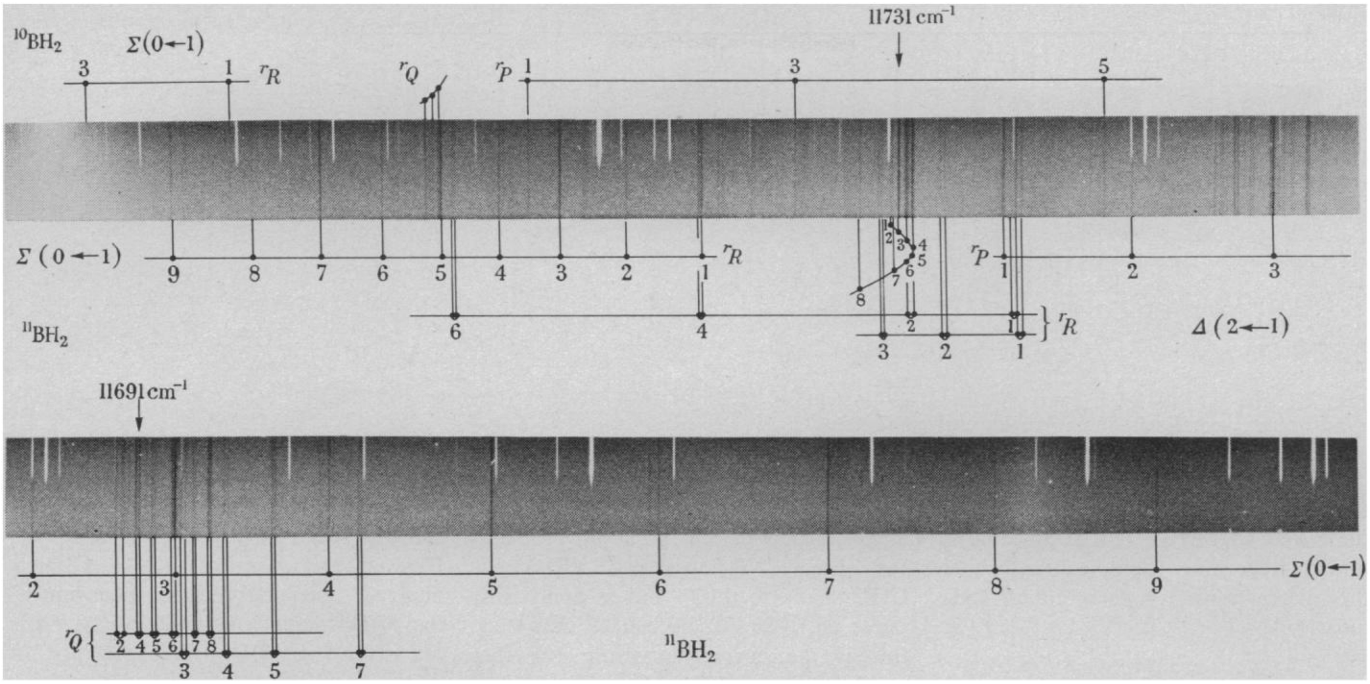
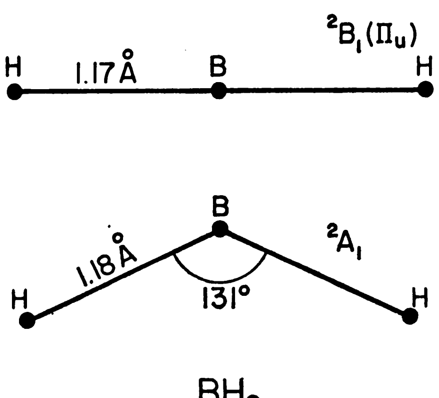


Fig. 22. Subbands of the BH_2 bands near 8520 Å, after Herzberg and Johns (*46*). Lines of $^{10}BH_2$ are marked above, those of $^{11}BH_2$ below the spectra.

years after the identification of the carrier of the 4050-Å group before a spectrum of CH_2 was found. From photochemical evidence, it was well known that there are two molecules which on photolysis give CH_2—namely, ketene (CH_2CO) and diazomethane (CH_2N_2). Since the latter compound is rather explosive, we began by studying the continuous photolysis of ketene and, when that failed, by turning to flash photolysis, which had in the meantime been developed [Norrish and Porter (*39*)]. Even though we extended our search into the vacuum ultraviolet, we did not find a spectrum of CH_2. As a last resort we decided that we should try diazomethane in spite of its hazardous properties. Almost the first absorption spectrum of flash-photolyzed diazomethane showed a new transient feature (of a lifetime of about 10 μsec), which turned out to be the spectrum of CH_2. We did not observe this particular feature in the flash photolysis of ketene because ketene itself absorbs strongly at this particular wavelength.

We were fortunate in being able to obtain immediately, with the help of Dr. Leitch at Ottawa, a quantity of deuterated diazomethane and in this way were able to verify, as shown by Fig. 16, that the new feature, at 1415 Å, actually does shift when hydrogen is substituted by deuterium. Thus, at least we were sure that the molecule or radical responsible for this feature contained hydrogen, but of course this observation did not yet prove that the radical was CH_2.

Spectra taken at high resolution in partially or fully deuterated diazomethane showed three different positions for the principal band depending on the deuterium concentration. These spectra, reproduced in Fig. 17, show for two of the isotopes a clear and simple fine structure. For CD_2 there is in addition a characteristic intensity alternation indicating a symmetric position of the



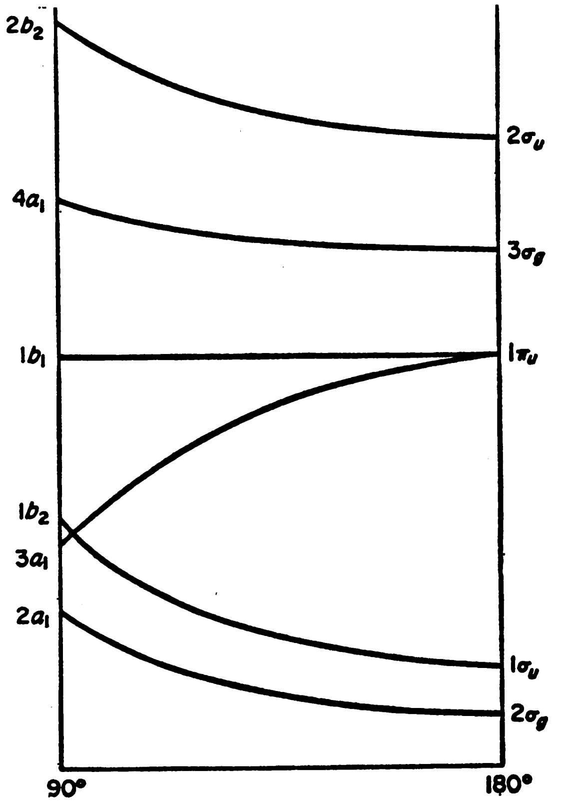


Fig. 23 (left). Geometrical structure of BH_2 in the two known electronic states. Fig. 24 (right). Walsh diagram for XH_2 molecules. The variation of the orbital energies in going from a bond angle of 90° to 180° is shown.

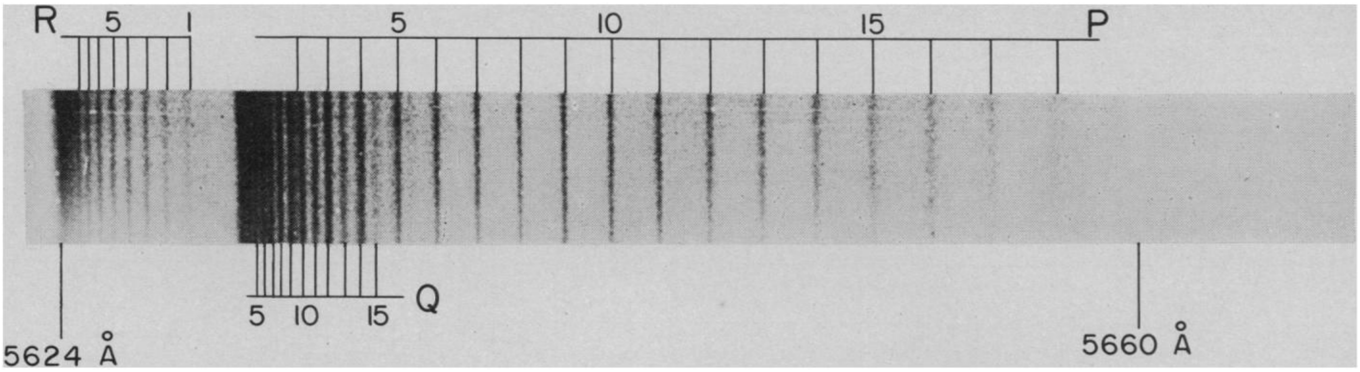


Fig. 25. The 0 11 0—0 0 0 band of the $\tilde{A}$—$\tilde{X}$ system of HCO at 5624 Å, after Herzberg and Ramsay (*48*). Only the 0—1 subband is observed. Each line is an unresolved doublet.

two D atoms. The simple structure of the bands suggests that the molecule is linear. According to molecular orbital theory the ground state of linear CH_2 must be

$$\ldots \sigma_g{}^2 \pi_u{}^2 \, {}^3\Sigma_g{}^-$$

and in agreement with that the odd lines are strong in the CD_2 band. We concluded, therefore, that the ground state of CH_2 is a triplet state and that the molecule is linear even though the triplet splitting was not resolved.

During the last year several theoretical calculations (*40*) as well as electron-spin resonance studies (*41*) of CH_2 and CD_2 in inert matrices have strongly suggested that CH_2 in its lowest triplet state is not linear. If that is so the molecule is a symmetric top, and in addition to the $K = 0$ subband in the vacuum ultraviolet spectrum there should be several other subbands with $K \neq 0$. In 1960 the nonobservation of these subbands was considered as strong evidence that the molecule is linear. However, in view of the new evidence from electron spin resonance one must consider the possibility that the $K \neq 0$ subbands are so strongly predissociated that they escape observation [Herzberg and Johns (*42*)]. Indeed a calculation of the bond angle from the observed B_0 values of CD_2 and CHD leads to 136° and a bond distance of 1.078 Å. We believe now that this is the correct structure for the ground state of CH_2.

In addition to the vacuum-ultraviolet spectrum a series of bands with complicated fine structure were found (*43, 44*) in the red and photographic infrared, of which Fig. 18 gives an example. This spectrum was analyzed as that of an asymmetric top and corresponds to a second modification of CH_2 with zero spin (singlet CH_2). Its lifetime is shorter than that of the first (triplet) modification, suggesting that the latter represents the ground state. In Fig. 19 an energy level diagram of the observed states is shown. The energy difference of the lowest singlet and triplet state is uncertain. It should be noted that the observed low-lying states are precisely those predicted from the electron configuration (${}^3\Sigma_g{}^-$, ${}^1\Delta_g$, ${}^1\Sigma_g{}^+$) for the linear conformation.

In Fig. 20 the geometrical structure of CH_2 in the lowest states is illustrated graphically.

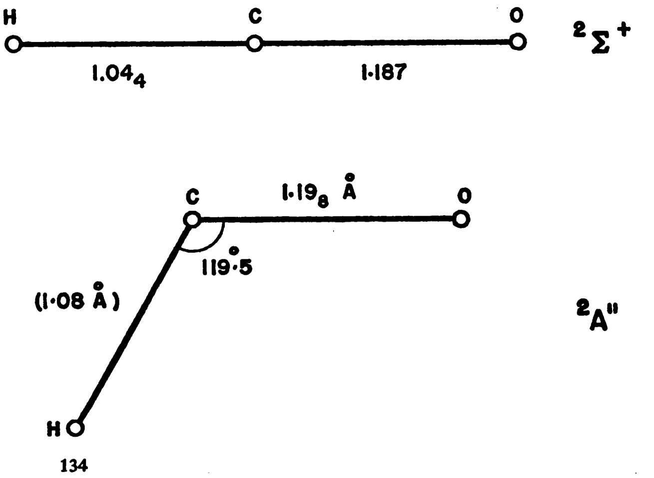


Fig. 26. Geometrical structure of HCO in the two known electronic states.

Other dihydrides. Several years before the spectrum of CH_2 was observed Dressler and Ramsay (*45*) at Ottawa observed and analyzed the spectrum of the NH_2 radical obtained by the flash photolysis of NH_3. The spectrum is quite complicated since the molecule is an asymmetric top and its analysis by Dressler and Ramsay represented a very considerable accomplishment. The experience gained by them was of great help in the analysis of the singlet spectrum of CH_2 referred to earlier. Figure 21 shows the structure of NH_2 derived from the spectrum.

More recently, Dr. Johns and I [see (*46*)] obtained the spectrum of BH_2 by the flash photolysis of BH_3CO. This spectrum lies in the same region as that of NH_2. Figure 22 shows a section of the spectrum showing the ${}^{10}B$–${}^{11}B$ isotope shift, and Fig. 23 shows the resulting structure. Table 6 summarizes the information on bond angles observed in these and other dihydrides.

Several years before these structures were spectroscopically established Walsh (*47*) gave some rules for the prediction of such structures on the basis of certain semiempirical assumptions about the molecular orbitals in these systems. In the Walsh diagram for XH_2 molecules shown in Fig. 24 the predicted energies of the lowest orbitals are plotted as a function of the bond angle (going from 90° to 180°). The orbitals designated $2a_1$ and $1b_2$ (or $2\sigma_g$ and $1\sigma_u$) favor slightly the linear conformation, while the orbital $3a_1$, which arises as one component of $1\pi_u$, strongly favors the bent conformation. The other orbital $1b_1$ arising from $1\pi_u$ favors neither conformation. In the ground state of BH_2 the electron configuration is

$$(2a_1)^2 \; (1b_2)^2 \; 3a_1$$

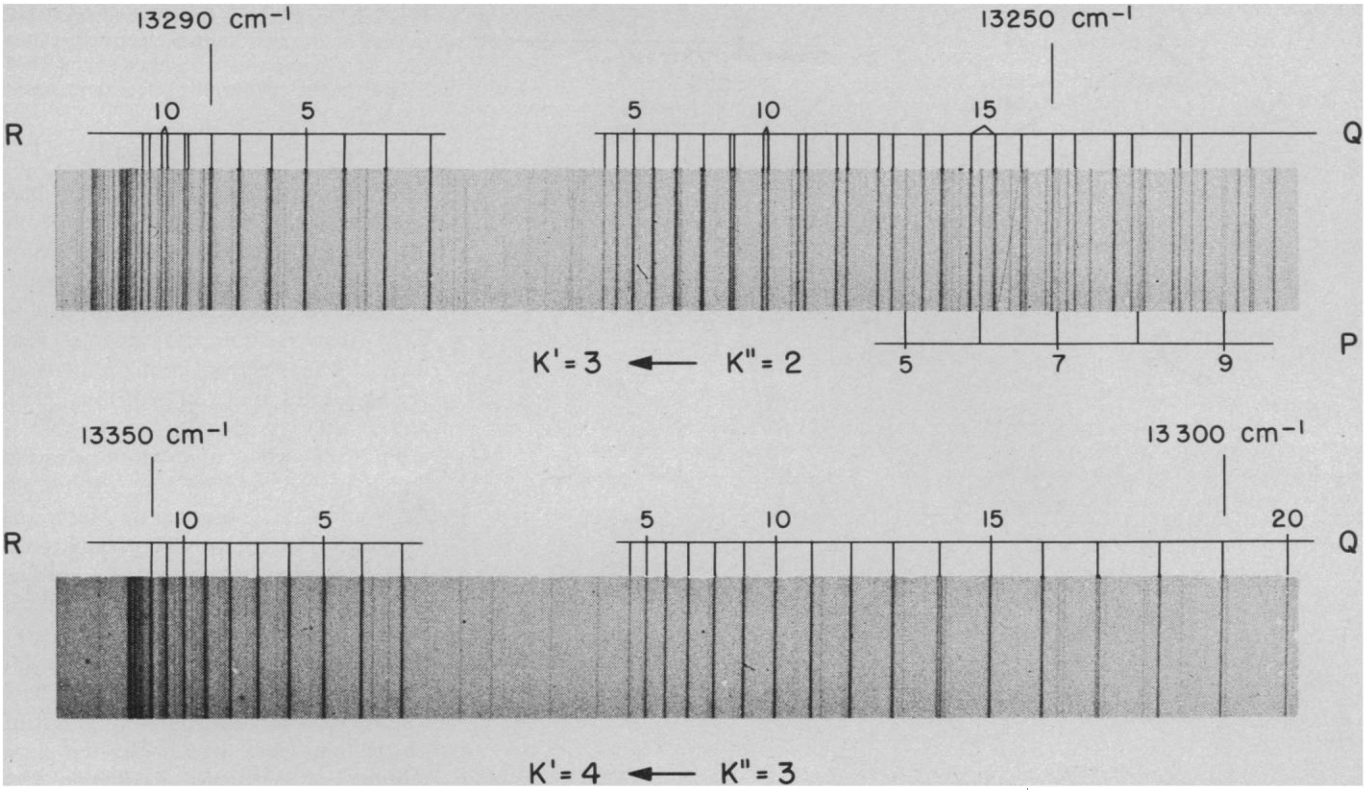


Fig. 27. Two subbands of the 0 0 0—0 0 0 band of the $\tilde{A}$—$\tilde{X}$ system of the HNO radical. [After Dalby (*49*)]

and therefore in this state the molecule is bent (see Table 6); but in the first excited state

$$(2a_1)^2\,(1b_2)^2\,1b_1$$

there is no tendency for bending, and the molecule is predicted to be linear in agreement with observation. In a similar way the other molecules of Table 6 can be treated: Two electrons in the $3a_1$ orbital always lead to strong bending with an angle of about 105° as in the ground state of H_2O.

Triatomic monohydrides. A number of triatomic radicals with one H atom have been studied. The first was HCO of which Fig. 25 shows one of the absorption bands [Herzberg and Ramsay (*48*)]. Here again there is a striking change of shape in the electronic transition as shown in Fig. 26. Moreover, this is another case (the first to be recognized) in which only one K value, here $K'' = 1$, appears since in the upper state (where the molecule is linear) all levels with $l \neq 0$ are strongly predissociated.

The spectra of HNO [Dalby (*49*)] and HCF [Merer and Travis (*50*)], shown in Figs. 27 and 28, are examples of cases in which the radicals are bent in both upper and lower states and no predissociation occurs, that is, several subbands of different K are observed. The geometrical structures resulting from the analysis of these spectra are shown in Figs. 29 and 30.

The most recent radicals studied in this group are HNF [Woodman (*51*)] and HSiI [Billingsley (*52*)], for which Figs. 31 and 32 show the resulting structures. The radical HNF is one of the first examples of an asymmetric top in which the spin doubling is fully resolved and analyzed.

Triatomic nonhydrides. Among triatomic nonhydrides the C_3 radical has already been discussed. It is linear in both the upper and the lower state of the only known electronic transition, which is of type $^1\Pi_u$—$^1\Sigma_g{}^+$. In the excited state ($^1\Pi_u$) there is a strong interaction between electronic and vibrational angular momentum (Renner-Teller effect) leading to considerable

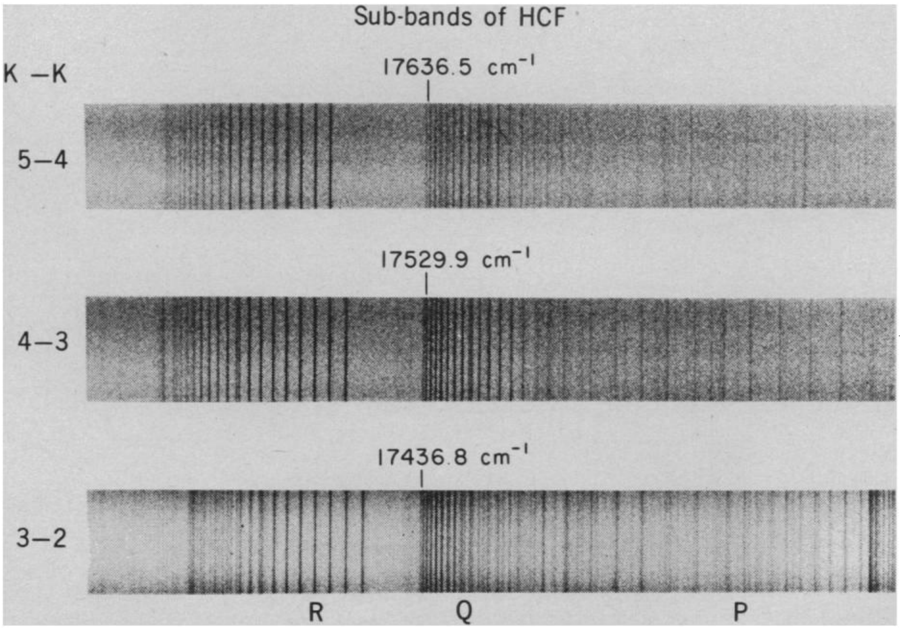


Fig. 28. Subbands of the 0 0 0—0 0 0 and of the $\tilde{A}$—$\tilde{X}$ system of the HCF radical. [After Merer and Travis (*56*)]

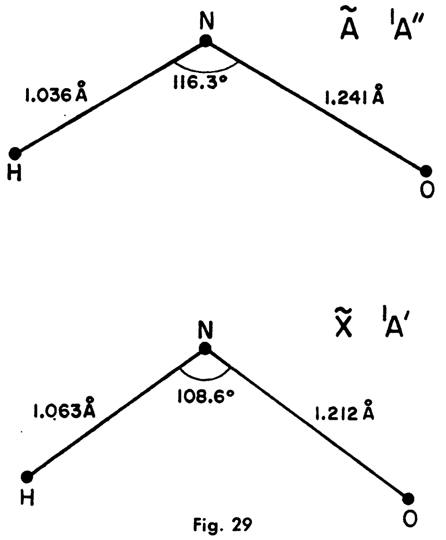


Fig. 29

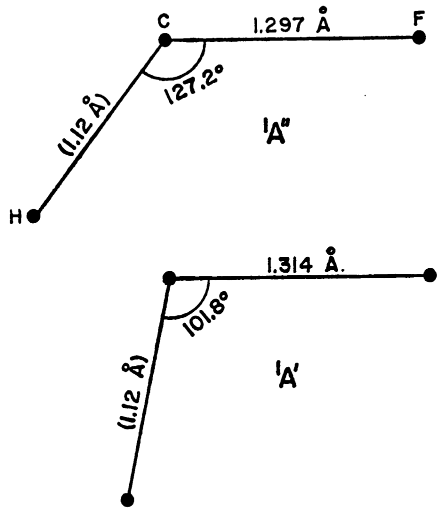


Fig. 30

Fig. 29. Geometrical structure of the HNO radical in the two known electronic states. Fig. 30. Geometrical structure of the HCF radical in the two known electronic states.

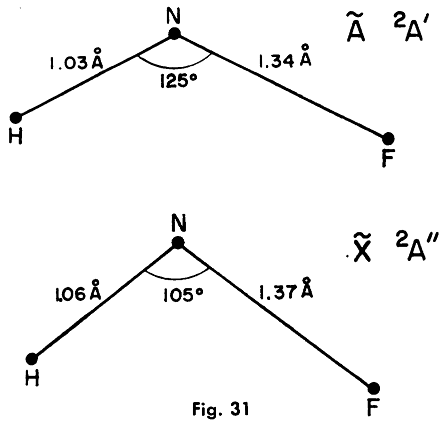


Fig. 31

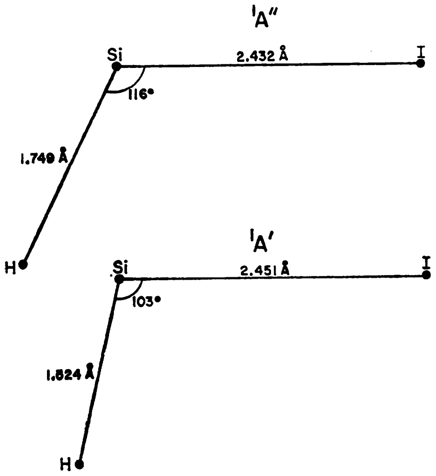


Fig. 32

Fig. 31. Geometrical structure of the HNF radical in the two known electronic states. Fig. 32. Geometrical structure of the HSiI radical in the two known electronic states.

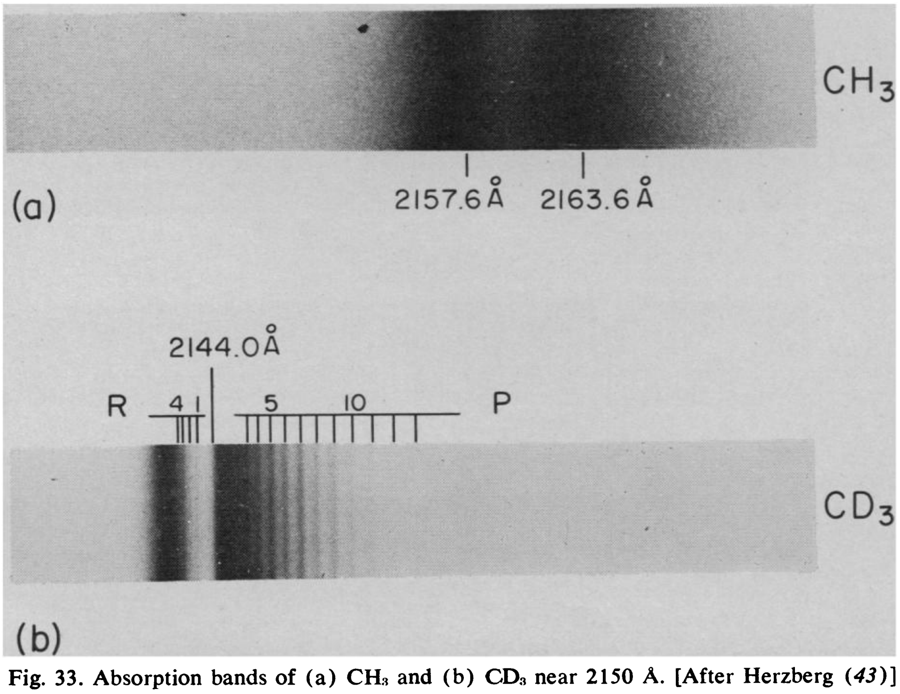


Fig. 33. Absorption bands of (a) CH_3 and (b) CD_3 near 2150 Å. [After Herzberg (*43*)]

anomalies in the spacing of the vibrational levels. In the ground state ($^1\Sigma_g{}^+$) the bending frequency is surprisingly small, only 63 cm^{-1}. The corresponding force constant is 1/100 of that in CO_2, that is, the molecule is very floppy. The electron configurations of the two states are . . . $(1\pi_u)^4\ (3\sigma_u)\ (1\pi_g)$ and . . . $(1\pi_u)^4\ (3\sigma_u)^2$.

Radicals with one more electron which has to go into a π_g orbital are CCN and CNC, observed by Merer and Travis (*53*) at Ottawa. The NCN molecule, with two electrons in the π_g orbital and therefore with $^3\Sigma_g{}^-$ ground state, was studied by Travis and myself (*54*), the isoelectronic molecule CCD by Devillers and Ramsay (*55*). We have looked for the corresponding spectrum of the ion $N_3{}^+$, which has the same number of electrons. Ledbetter (*56*) found a complicated absorption band in flash discharges through nitrogen which is not otherwise identifiable, but proof that it belongs to $N_3{}^+$ has not yet been obtained. Several radicals and ions with three electrons in the π_g orbital have been studied by various investigators.

Table 7 summarizes the molecular constants for the ground states of this group of molecules. Note the strong increase of the bending frequency ν_2 as a function of the number of π_g electrons.

CH_3 and $CH_4{}^+$. The spectrum of the methyl radical was easier to obtain than that of methylene (*43*). First by the flash photolysis of $Hg(CH_3)_2$ and later by that of many other methyl-containing compounds, a spectrum consisting of two diffuse peaks near 2160 Å was obtained, as shown in Fig. 33a. For CD_3 a simple (even though still diffuse) fine structure is observed (Fig. 33b), which yields the conclusion that CD_3 is planar (or very nearly planar) in its ground state and that the C–D distance is 1.079 Å. In addition, several Rydberg series have been observed in the region 1500 to 1280 Å which yield accurate values for the ionization potential [I.P.(CH_3) = 9.843 ev].

The electron configurations of the two lowest states of CH_3, assuming D_{3h} symmetry, are

$$. . .\ (1e')^4\ (1a_2'')\ {}^2A_2''$$

$$. . .\ (1e')^3\ (1a_2'')^2\ {}^2E'$$

The transition between these two states should lie in the visible region, but for planar CH_3 it is a forbidden transition and so far has not been observed. The upper states of all observed transitions are Rydberg states of the type

$$\ldots (1e')^4\ nsa_1';\ nda_1';\ nde''$$

The spectrum of SiH_3 is, of course, expected to be very similar to that of CH_3, but in spite of considerable effort we have not yet been able to observe it. Thus, it is still an open question whether SiH_3 is planar or nonplanar in its ground state, although the latter appears more likely.

A molecular system with the same number of electrons as CH_3 is the CH_4^+ ion. If CH_4^+ were tetrahedral like CH_4 its ground state would have the electron configuration

$$(1a_1)^2\ (2a_1)^2\ (1f_2)^5\ {}^2F_2$$

that is, would be a triply degenerate state. However, according to the Jahn-Teller theorem, in such a triply degenerate state the equilibrium conformation cannot be the symmetrical tetrahedral one. Theoretical calculations [see, for example, Dixon (*57*)] suggest that CH_4^+ has a D_{2d} structure and that the electron configurations of the two lowest electronic states derived from $2F_2$ are

$$(1a_1)^2\ (2a_1)^2\ (1e)^4\ (1b_2)\ {}^2B_2$$
$$\ldots\ldots\ldots\ (1e)^3\ (1b_2)^2\ {}^2E$$

If, instead, CH_4^+ had C_{3v} symmetry (that is, one C–H bond longer than the other three) the states ${}^2A_1$ and ${}^2E$ with electron configurations even more similar to those of the two low-lying states of CH_3 would result. But now the transition between these two low-lying states is not forbidden. That these two low-lying states of CH_4^+ exist has been conclusively shown by photoelectron spectroscopy. Figure 34 shows the photoelectron spectrum as observed by Price (*58*). The two maxima at the right correspond to photoelectrons with CH_4^+ left in one or the other of the two states. The allowed transition between these two states would lie in the visible region but has not yet been observed.

One reason (in addition to its intrinsic interest) why we have spent considerable effort to observe this spectrum is its possible astrophysical importance. It is possible that the diffuse interstellar lines (which represent the last major identification problem in astronomical spectroscopy) may be due to this transition in CH_4^+, the diffuseness being due to predissociation of the upper state (the dissociation energy of CH_4^+ is only about 1 ev). Since CH_4 is almost certainly present in the interstellar medium it would not be surprising if a sufficient stationary concentration of CH_4^+ arises for the appearance of the ${}^2E$—${}^2B_2$ transition.

HNCN. As a final example I should like to mention a radical which, like many others, was observed in the flash photolysis of diazomethane, namely HNCH [Herzberg and Warsop (*59*)]. As shown in Fig. 35 a particularly simple spectrum arises, a textbook example of

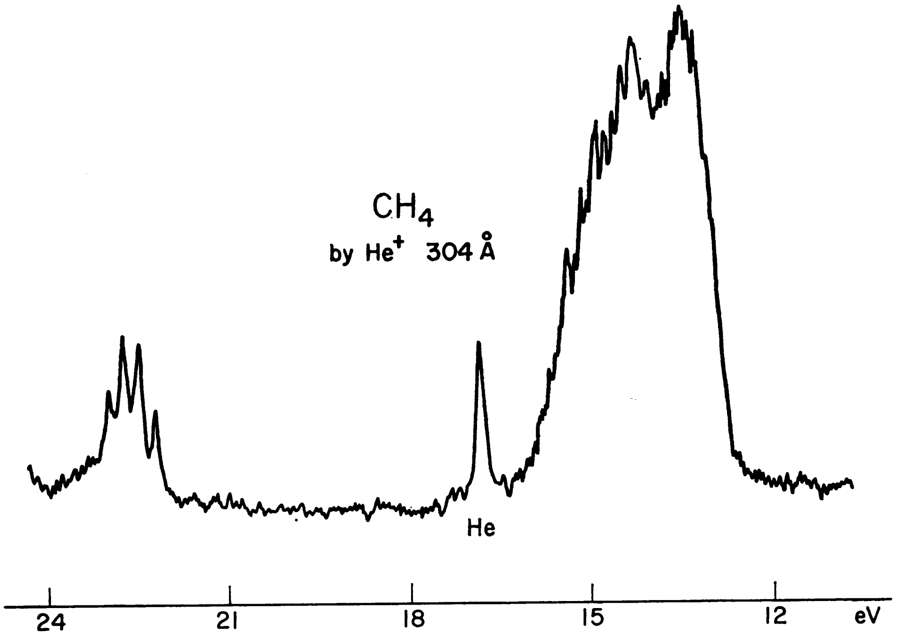


Fig. 34. Photoelectron spectrum of CH_4 obtained with the He^+ line at 304 Å by Price (*58*).

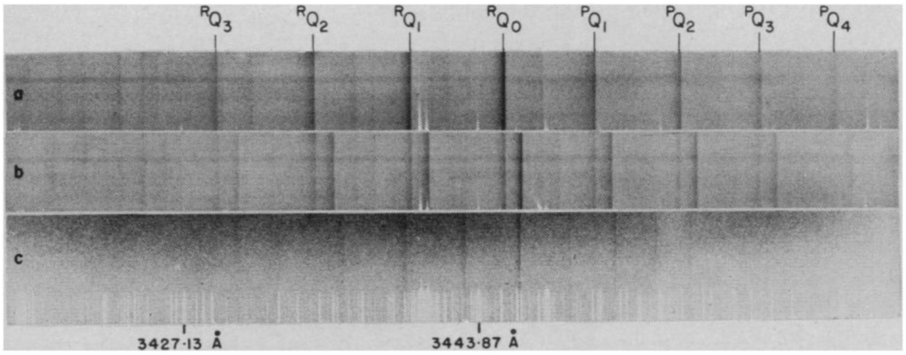
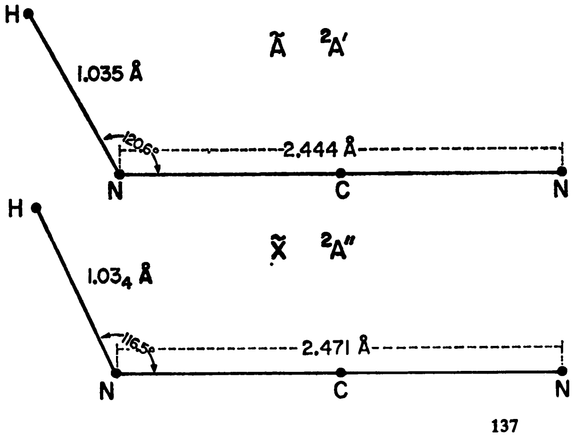


Fig. 35. The 0—0 band of the $\tilde{A}$—$\tilde{X}$ system of the HNCN radical at 3440 Å in absorption. [After Herzberg and Warsop (*59*)]

Fig. 36. Geometrical structure of HNCN in the two known electronic states.



a perpendicular band of a nearly symmetric top, consisting of a series of almost equidistant subbands. The large separation of the subbands indicates that the heavy atoms lie very nearly on a straight line while the H atom lies off that line. Isotope effects with D and ^{13}C show that only one hydrogen and one carbon atom is present. Figure 36 shows the derived structure; the position of the C atom cannot be accurately determined from the present data.

Conclusion

In the preceding discussion I have not described any of the techniques used in our work since the principal method, the flash photolysis technique, was described by Norrish and Porter (*39*) in their Nobel lectures. We have more recently developed two methods for the study of spectra of molecular ions: the flash discharge technique, which is closely related to the flash photolysis technique, and the flash radiolysis (or pulse radiolysis) technique, in which a powerful pulse of electrons is sent through the absorption cell and produces many ions. Both methods have been described in more detail in my Faraday lecture (*60*). The results obtained with the second method have as yet been very sparse, but we hope to overcome some of the difficulties and obtain absorption spectra of ions such as $C_2H_2^+$, HCN^+, CH_4^+, CH_3^+, CH_2^+, H_3O^+, H_2O^+, $C_6H_6^+$, and many others about which nothing is known at present. The information so obtained would be of immense help for a deeper understanding of the electronic structure of these ions as well as the corresponding neutral molecules. The new methods of tunable lasers as shown by Patel and his collaborators (*61*) promise to give infrared spectra of radicals and ions about which up to now very little is known. For example, the vibrational frequencies in the ground state of CH_2 are unknown at present. These few remarks may suffice to indicate that a great deal remains to be done in the study of the geometrical and electronic structure of radicals and molecular ions.

The work described in this lecture could not have been accomplished without the effective help and independent work of many collaborators. The list of references gives the names of most of them. I should like to single out particularly the constant support by most valuable criticisms and suggestions which I have had from Dr. A. E. Douglas, now my successor as director of the Physics Division of the National Research Council. I should also like to acknowledge the devoted help I have had for 20 years from Mr. J. Shoosmith who carried out all the experimental work with great efficiency, energy, and skill. In receiving the Nobel Prize I am deeply aware of the debt I owe to all these collaborators and technical assistants for their continued help and support.

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