Advances in Photochemistry

Volume 5

Editors

W. ALBERT NOYES, JR., Department of Chemistry, University of Texas, Austin, Texas

GEORGE S. HAMMOND, Department of Chemistry, California Institute of Technology, Pasadena, California

J. N. PITTS, JR., Department of Chemistry, University of California, Riverside, California

1968

Interscience Publishers
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Introduction to the Series

Photochemistry first received some systematic attention well over one hundred years ago but it did not receive any great attention until after World War II. Free atoms and free radicals produced by photochemical means have been used for many years to study single steps which may form parts of complex mechanisms, but, in a way, the more fascinating problems of complex molecules which undergo reaction after absorption of radiation, without at any time passing through the stage of atoms and radicals, have only occupied the attention of chemists during recent years.

Progress in photochemistry could only be made following progress in spectroscopy and, in particular, the interpretation of spectra in at least semiquantitative terms, but history has shown that this was not enough. The arrival of new methods of analysis which permit determination of small amounts of products, the development of flash photolysis, nuclear magnetic resonance, and electron spin resonances which can yield valuable information about the natures of intermediate excited states, as well as of atoms and radicals, all have permitted the photochemist to approach the truly fundamental problem of photochemistry: What is the detailed history of a molecule which absorbs radiation?

This series of books entitled *Advances in Photochemistry* will have chapters written by pioneers who are experts. As the late Professor Fermi once said “a state of confusion exists at any frontier.” Frontiers in photochemistry are at times full of confusion and for this reason they are fascinating. The editors have in no sense acted as censors. The authors are free to make any statement they wish which cannot be proved wrong. We hope these volumes will be stimulating and that they will serve the useful purpose of bringing together points of view of photochemists who do not, at present, even always use the same vocabulary.
Contributors to Volume 5

C. S. BURTON
Department of Chemistry, The University of Rochester, Rochester, New York

NORMAN COHEN
Aerospace Corporation, El Segundo, California

GEORGE S. HAMMOND
California Institute of Technology, Division of Chemistry and Chemical Engineering, Pasadena, California

JULIAN HEICKLEN
Department of Chemistry, Pennsylvania State University, University Park, Pa.

G. HERZBERG
National Research Council of Canada, Ottawa, Ontario

J. LEMAIRE
Laboratoire de Chimie Generale, Universite de Nancy, France

W. A. NOYES, JR.
Department of Chemistry, The University of Texas, Austin, Texas

DAVID PHILLIPS
Department of Chemistry, The University, Southampton, United Kingdom

PETER J. WAGNER
Chemistry Department, Michigan State University, East Lansing, Michigan
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The Spectra and Structures of Triatomic Free Radicals*

G. HERZBERG, National Research Council of Canada, Ottawa, Ontario

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I. INTRODUCTION

The idea that free radicals occur in many chemical reactions is as old as the study of the mechanisms of these reactions. However, direct physical evidence for the existence of free radicals and for their presence in certain reactions is comparatively recent. Such evidence has been obtained in recent years by the methods of mass spectrometry, optical spectroscopy, and electron spin resonance spectrometry. The optical method of detecting free radicals has the advantage that it simultaneously supplies information about the structure of the radical. Indeed, in many instances the nature of the free radical has been identified by the structure of the spectrum without any assumptions about the mechanism of the reaction in which it appears.1

Chemists are often inclined to consider a molecule as a free radical when not all free valences are saturated. However, on this basis, molecules like $\text{O}_2$ and NO might have to be considered as free radicals. In order to avoid such difficulties, in the following discussion we shall arbitrarily consider a molecule as a free radical if its lifetime at low

* This paper is the original English version (very slightly modified) of a contribution to a Festschrift in honor of Prof. N. N. Semenoff and published in Russian in the J. All-Union Mendeleev Chem. Soc., 11, 146 (1966).
temperature, even under the most favorable conditions, is short (say, less than 1 sec).

Almost all spectroscopic studies of free radicals have been carried out in the visible and ultraviolet regions, and as a consequence only those radicals that have discrete spectra in these regions have been amenable to detailed investigation. Our inability to find any spectroscopic evidence for certain radicals, such as BH₃, C₂H, CF₃, and others, in spite of their almost certain presence under the conditions of our experiments, is probably due to the fact that these radicals have no stable excited states, and therefore give rise only to (weak) continuous absorptions, which are difficult to detect and identify. (If CH₄ were a free radical, it would be exceedingly difficult to detect spectroscopically, since it has only continuous absorptions except, of course, in the infrared.)

It is only very recently that attempts to obtain infrared spectra of free radicals have been successful. As these infrared studies are further developed, they promise to fill many of the gaps left by ultraviolet investigations, both with regard to radicals studied (since all radicals must have a discrete infrared spectrum), and with regard to the fundamental frequencies of the ground state, which in most cases are difficult to obtain from ultraviolet absorption spectra.

In this paper, a brief summary of the spectroscopic work on triatomic free radicals in the visible and ultraviolet regions is presented, including recent unpublished work from this laboratory.*

II. EXPERIMENTAL METHODS

The great majority of the spectra to be discussed here have been observed in absorption only. Most of these absorption spectra have been obtained by the flash photolysis technique, but a few have been studied in thermal equilibrium at high temperature or in the afterglow of an electric discharge. A much smaller fraction of the radical spectra has been observed in emission, either in flames (NH₂, NCN, HNO, HPO, BO₂) or in thermal emission (SiC₂) or in electric discharges (NH₂, C₃, BO₂, CF₂, SiF₂).

The flash photolysis method was first described by Norrish and Porter and independently developed by at least two other groups

* A more detailed presentation of the general field of electronic spectra of polyatomic molecules may be found in Herzberg.²a
of investigators. A high intensity flash is produced by the discharge of a condenser of high capacity through a tube of $\frac{1}{2}$-2 m in length and 10-20 mm in diameter. This discharge tube is placed close to the absorption tube which is filled with the parent compound. The flash produces photodecomposition of the parent compound. The primary and some of the secondary products of the photo-reaction are free radicals which are, however, present only for a very short time, 10-1000 $\mu$sec, after the beginning of the photolysis flash. If an absorption spectrum is taken during this short interval of time, the spectra of the radicals may be observed. For this purpose a second flash produced by a much smaller discharge tube provides a continuous background of the absorption spectrum. This source flash is electronically timed to follow the photolysis flash within the desired small and variable time interval. In this way, many absorption spectra of free radicals have been obtained. In some cases, spectra of free radicals are observed in fluorescence during flash photolysis. This fluorescence is produced by the action of the light from the photolysis flash on the radicals formed by the action of the first part of this flash.

More recently the flash discharge method has been developed. Here the parent compound is introduced into the flash tube, which serves at the same time as the absorption tube. A mild flash obtained by discharging a condenser of about 1 $\mu$F dissociates the parent molecule and thus produces free radicals.

A considerable increase in the sensitivity of detection of weak free radical spectra can be obtained by passing the light from the source flash through the absorption tube several times, according to the method of White. By this method, an increase of the absorbing (or emitting) path by a factor of up to 100 can be easily obtained. Furthermore, it must be remembered that in absorption the sensitivity of detection for weak sharp lines increases with the resolving power of the spectrograph used. For this reason, large grating spectrographs have been used almost exclusively in our laboratory for the study of free-radical spectra.

We shall divide the triatomic radicals thus far studied into three groups: dihydrides, monohydrides, and nonhydrides.

III. DIHYDRIDES

The first polyatomic free-radical spectrum observed by the flash photolysis technique was that of NH$_2$. This radical appears in the
photolysis of ammonia as a primary product according to the reaction

$$\text{NH}_3 + h\nu \rightarrow \text{NH}_2 + \text{H}$$

The absorption spectrum observed was identical with the so-called $\alpha$ bands of ammonia, long known as emission bands in oxy-ammonia flames and discharges through ammonia. The spectrum is a many-line spectrum which was analyzed only after several years of effort by Dressler and Ramsay. Figure 1 shows the structure of the molecule in the upper and lower state as derived from the spectrum. In the lower state ($^2B_1$) the molecule has nearly the same angle as H$_2$O in its ground state: NH$_2$ has one electron less than H$_2$O, but this is taken from a lone pair ($b_1$) orbital, which does not affect the bonding. In the excited state the molecule is slightly bent. Both electronic states arise from a $^2\Pi$ state of the linear conformation.

The radical CH$_2$, with one electron less than NH$_2$ (i.e., with no electrons in the lone pair orbital $b_1$), might be expected to have ground and first excited states similar to NH$_2$. Indeed, by using the flash photolysis of diazomethane (CH$_2$N$_2$), an absorption spectrum in the red region of the spectrum very similar to that of NH$_2$ has been found. The observation of isotope shifts on substituting $^{13}$C or D, the presence of an intensity alternation, and the detailed analysis of the
TRIATOMIC FREE RADICALS

Spectrum show that CH₂ is the molecule responsible for this spectrum. In the lower state the angle is very nearly the same as in the ground states of NH₂ and H₂O, while in the upper state the angle is close to 140°. In the latter state there is only a very small potential hump in the linear conformation, and all observed bands correspond to vibrational levels in which the molecule is effectively linear. In agreement with expectation for a molecule with an even number of electrons, no spin doubling has been observed in the red CH₂ bands; that is, the two states involved are singlet states.

Even before the red absorption spectrum was discovered, another spectrum of CH₂ had been observed in the vacuum ultraviolet, also by the flash photolysis of CH₂N₂, but at a delay time somewhat longer than for the red bands.¹⁰ Unlike the red spectrum, the vacuum ultraviolet spectrum is extremely simple. While this was, at first, not obvious for CH₂, it is very clear for CHD and CD₂ whose spectra are not broadened by predissociation. The analysis of these spectra is quite straightforward and shows that in both upper and lower states, the molecule is linear. A simple molecular orbital consideration predicts for linear CH₂ a \(^3\Sigma^–\) ground state. The observed intensity alternation in the vacuum ultraviolet CD₂ (and CH₂) bands is in agreement with the assumption that the lower state is the predicted \(^3\Sigma^–\) state. Although the triplet splitting has not yet been resolved, we must conclude that the vacuum ultraviolet spectrum corresponds to triplet CH₂ and the red spectrum to singlet CH₂; in other words, two kinds of CH₂ are produced in the flash photolysis of CH₂N₂, but the singlet form occurring first is transformed by collisions into the triplet form, and the lower state of the triplet bands in the ultraviolet is the ground state of CH₂.

In Figure 2 the structures of CH₂ in the four states discussed here
are shown. Several other states have been observed but have not been analyzed in detail.

For the BH$_2$ radical, with one further electron removed, we can no longer expect the same valence angle as in H$_2$O. Indeed, from valence bond calculations Jordan and Longuet-Higgins$^{11}$ predicted a linear ground state of type $^2\Pi$. However, in the flash photolysis of H$_3$BCO, Johns and I$^{12}$ have observed an absorption spectrum in the red and photographic infrared similar to that of NH$_2$. The analysis (including isotope effects, doublet splitting, and intensity alternation) leaves no doubt that this spectrum is due to the BH$_2$ radical, and that in the lower (ground) state the molecule is bent, while in the upper state it is linear. The angle in the ground state is 131°. Because of this larger angle, the molecule is much closer to a symmetric top than NH$_2$ and CH$_2$, and the band structure is correspondingly simpler. As in NH$_2$, both observed states are derived from the $^2\Pi$ state of the linear conformation. Figure 3 shows the geometrical structures.

Spectra very similar to those of NH$_2$, CH$_2$, and BH$_2$ have been observed in the red region of the spectrum for PH$_2$,$^{13}$ SiH$_2$,$^{14}$ and AlH$_2$.$^{15}$ One of the bands of PH$_2$ has recently been analyzed by Dixon, Duxbury, and Ramsay,$^{16}$ and one of the bands of AlH$_2$ by Johns and myself.$^{15}$ The geometrical data derived from these analyses are represented in Figures 4 and 5. Our recent analysis$^{14}$ of several bands of SiH$_2$ in the visible region has shown them to be singlet bands similar to the singlet bands of CH$_2$. We find an HSiH angle of 92° and an SiH distance of 1.52 Å in the lower state. In spite of much effort, a spectrum corresponding to the vacuum ultraviolet spectrum of CH$_2$ has

![Fig. 3. BH2.](image)
The question of whether the ground state of SiH₂ is triplet or singlet must therefore remain open. Recent theoretical work by Jordan¹⁷ predicts that the lowest triplet state of SiH₂, unlike that of CH₂, lies fairly high above the lowest singlet state.

In Table I the electron configurations of the lowest states of BH₂, CH₂, and NH₂ are given. The low-lying states predicted on the basis of these electron configurations agree very well with those

\[ ^2B_1(\Pi_u) \]

Fig. 4. PH₂.

Fig. 5. AlH₂.
observed. The electron configurations for AlH₂, SiH₂, and PH₂ are entirely analogous.

### TABLE I

Electron Configurations of Triatomic Dihydride Radicals

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Point group</th>
<th>Electron configurations</th>
<th>Resulting states</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH₂</td>
<td>C₂ᵥ</td>
<td>(1a₁)² (2a₁)² (1b₁)² (1b₁)</td>
<td>²B₁(Πᵤ)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1a₁)² (2a₁)² (1b₂)² (3a₁)</td>
<td>²A₁</td>
</tr>
<tr>
<td>CH₂</td>
<td>C₂ᵥ</td>
<td>(1a₁)² (2a₁)² (1b₁)² (3a₁) (1b₁)</td>
<td>¹B₁(Δ₅)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1a₁)² (2a₁)² (1b₂)² (3a₁)²</td>
<td>¹A₁</td>
</tr>
<tr>
<td></td>
<td>Dₘₘ</td>
<td>(1a₁)² (2a₂)² (1a₁)² (1πₚ) (3dπₚ)</td>
<td>³Σ⁻ᵤ, ¹Σ⁺ₚ, ³Σ⁺ₚ, ¹Σ⁺ₚ</td>
</tr>
<tr>
<td>NH₂</td>
<td>C₂ᵥ</td>
<td>(1a₁)² (2a₁)² (1b₁)² (3a₁) (1b₁)²</td>
<td>²A₁(Πᵤ)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1a₁)² (2a₁)² (1b₂)² (3a₁)² (1b₁)</td>
<td>²B₁</td>
</tr>
</tbody>
</table>

### IV. MONOHYDRIDES

Flames of most hydrocarbons show a fairly extensive system of emission bands, which were assigned by Vaidya to the HCO radical more than thirty years ago. Yet, even today an unambiguous analysis of this spectrum has not been accomplished. On the other hand, in 1956 a progression of discrete simple absorption bands was found in the flash photolysis of CH₃HCO and other aldehydes by Ramsay and fully analyzed by Herzberg and Ramsay. (See also the more recent work of Johns, Priddle, and Ramsay.) Although only H—D isotope substitutions have been made, there can be no doubt from the structure of the spectrum that the molecule responsible is the free HCO radical. Figure 6 shows the geometry of the molecule in the upper and lower states. In all probability, the lower state, in which the molecule is bent, is the ground state. The observed absorption spectrum shows clear evidence of predissociation (alternate bands of the progression are quite diffuse), confirming what had already been suggested by a good deal of indirect evidence, namely, that the dissociation energy $D$(H—CO) is quite small ($<1.54$ eV). It is very probable that both observed states are derived from the $^2Π$ state of the linear conformation, as for NH₂ and BH₂.
It is possible, but has by no means been proved, that the lower state of the hydrocarbon flame bands is the same as that of the absorption bands just described. If the two systems do have a common lower state, the upper state of the flame bands would represent a third, more highly excited, electronic state of HCO.

Dalbý in this laboratory was the first to observe a fairly extensive absorption spectrum of HNO in the flash photolysis of CH₃NO and similar compounds, as well as of mixtures of NH₃ and NO. The same spectrum has been observed by Cashion and Polanyi and Clement and Ramsay in emission in the flame formed when H atoms enter a stream of NO, thus indicating the formation of HNO directly from H + NO. The molecule HNO is found to have a lifetime of the order of 10-100 msec, which is much longer than that of the radicals considered earlier, but still short enough to justify the designation of free radical.

The observed spectrum of HNO is that of a nearly symmetric top, and shows that the molecule is bent in both the upper and lower states. Figure 7 shows the geometrical data. Both states are unquestionably singlet states which, in all probability, are derived from the ¹Δ state of the linear conformation. Since HNO is isoelectronic with O₂, its lowest electron configuration for the linear conformation must be \ldots \pi² which, as in O₂, must give rise, in addition to ¹Δ, to a ³Σ⁻ and a ¹Σ⁺ state. As for O₂, the ³Σ⁻ is expected to be the ground state as long as the HNO molecule is linear. But it is difficult to predict whether the
triplet state would also lie below the singlet states when the molecule is bent. No evidence for the triplet state, which must surely exist, has yet been found.

A breaking off of the branches has been observed in the emission spectrum of HNO by Clement and Ramsay and, correspondingly, higher rotational lines have been found to be diffuse in absorption. These observations lead to an upper limit of 2.11 eV for $D(\text{H—NO})$.

The spectrum of the corresponding radical in the next period, HPO, was first observed, without being recognized as such, by Ludlam 30 years ago in the flame of phosphorus burning in hydrogen. It was recently studied and analyzed in detail by Lam Thanh and Peyron. The spectrum is very similar to that of HNO. Just as in HNO, the transition moment is perpendicular to the plane of the molecule: the transition is $^1A''-^1A'$. Since the corresponding spectrum of DPO has not yet been analyzed in detail, unambiguous values for the geometrical parameters cannot be given, but there is no question that the molecule is bent in both upper and lower states.

Another interesting radical, isoelectronic with HNO, is HCF. Its spectrum has recently been obtained by Merer and Travis in the flash photolysis of HCFBr. It occurs at somewhat shorter wavelengths than the HNO spectrum, but otherwise is of very similar structure. Preliminary values for the geometrical parameters are shown in Figure 8. Again the observed spectrum is a singlet spectrum. The
possibility that a triplet state is the ground state cannot be eliminated and indeed in CH₂, of which HCF may be considered a derivative, it is the ground state.

Merer and Travis⁵⁰ have also observed an analogous spectrum of HCCl in the flash photolysis of HCClBr₂. Figure 9 shows the structure.
In the upper state the angle is larger than for the other molecules of this group (12 valence electrons). Earlier, Verma and I had found absorption spectra of the related radicals, HSiCl and HSiBr, both in absorption and emission, in the flash photolysis of SiH$_3$Cl and SiH$_3$Br. These spectra were originally assigned to a triplet–singlet transition, but may also be the exact analogs of the HCF and HCCl spectra which represent $^1A^→^1A^′$ transitions (see note added in proof to ref. 31). The shift to shorter wavelengths in HSiCl and HSiBr is, however, puzzling.

V. NONHYDRIDES

The spectra of a considerable number of triatomic nonhydride radicals, consisting of atoms of the first period of the periodic table, are now known. One of the oldest spectra is that now established to be due to the C$_3$ radical. It was first observed in emission in the spectra of comets and much later in the laboratory in discharges through methane and other hydrocarbons. The spectrum was first analyzed and identified as that of C$_3$ (on the basis of isotope studies) by Douglas. Up to that time, the free radical C$_3$ had not even been postulated in chemical reactions or equilibria, but since then it has been shown to be one of the most important constituents of carbon vapor and to be present in a number of photochemical reactions. Indeed, its occurrence in the flash photolysis of diazomethane has made possible a very detailed analysis of the spectrum, which has only recently been completed. This analysis has shown that the molecule is linear in both the upper and lower states and that the transition is $^1Π_u→^3Σ^+_g$. Two features make the spectrum much more complicated than one might have expected for a $^1Π→^3Σ$ transition of a linear molecule in absorption: (1) the bending frequency in the ground state has the surprisingly low value 63 cm$^{-1}$ (only one-tenth of that of CO$_2$), and therefore absorption bands originating from vibrating molecules occur strongly even at room temperature; (2) in the excited state the Renner-Teller splitting is larger than in any other linear molecule and produces apparent irregularities in the vibrational structure. The results of the analysis are given in Table II.

The C$_3$ molecule has 12 valence electrons which, in the ground state, just fill the $1\pi_u$ and $3\sigma_g$ shells. The next electron must go into the $1\pi_g$ shell. Thus, we expect a $^2Π$ ground state for a linear molecule with 13 valence electrons. Merer and Travis in our laboratory have recently discovered, in the flash photolysis of diazoacetonitrile, a number
of extensive and well-resolved band systems whose analysis shows that there are two lower $^2\Pi$ states. Isotope investigations with C$^{13}$ and N$^{15}$ have shown that both groups of band systems belong to a molecule with two C atoms and one N atom, but in one group alternate lines are missing, showing that the carrier is a symmetrical molecule CNC, while in the other group all lines are present (without intensity alternation).

### TABLE II

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>$T_0$, cm$^{-1}$</th>
<th>$B_0$, cm$^{-1}$</th>
<th>$r_0$, Å</th>
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<tr>
<td>C$_3$</td>
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<td>24675.5</td>
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<td>$\tilde{B}^2\Sigma^-_g$</td>
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<td></td>
<td>$A^2\Delta_u$</td>
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<td>NCN</td>
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<td>$A^2\Sigma^+_g$</td>
<td>22754.0</td>
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<td>(≤ 2.408)$^b$</td>
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<td>N$_2$</td>
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<td>0</td>
<td>0.3292</td>
<td>1.265</td>
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</table>

$^a$ This value refers to the 100 vibrational level.

$^b$ These values refer to the sum $r$(NC) + $r$(CO); the individual distance cannot be given, since only one isotopic species has as yet been studied in detail.

showing that the carrier is CCN. We have here an interesting example of isomerism in triatomic systems. Both molecules are linear in their ground states, as well as in all their observed excited states. In Table II some of the results of the analysis of the spectra of these two molecules are included.

A radical with 14 valence electrons is NCN. Its ground state, if it is linear, should be a $^3\Sigma^-_g$ state since there are two electrons in the
1ε orbital. A strong group of bands near 3285 Å was observed both in absorption and fluorescence in the flash photolysis of diazomethane mixed with C₂N₂. On the basis of isotope substitutions, as well as of the observed intensity alternation in the rotational structure, it could unambiguously be assigned to NCN. The lower state is indeed the predicted 3Σ⁻ state, while the upper state is 5Π_u. The same spectrum had previously been observed in emission in the reaction of active nitrogen with hydrocarbons by Jennings and Linnett. More recently, Pontrelli and Anastassiou have obtained much stronger spectra by the flash photolysis of cyanogen azide. Using the same method, Kroto in this laboratory, has obtained a 1Π-1Δ transition of NCN. The lower 1Δ state belongs to the same electron configuration as the 3Σ⁻ state. Even though no intercombination has been observed, there can be little question that the 5Π_u state is the ground state. The geometrical data on NCN are included in Table II.

The spectra of a number of triatomic radicals with 15 valence electrons are now known; for elements of the first period they are BO₂, N₃, and NCO. In addition, the isoelectronic ions CO₂⁺ and N₂O⁺ have been investigated. The spectrum of BO₂ was observed by Johns in the flash photolysis of a mixture of BCl₃ and O₂, but later was found to be identical to the green bands observed in most flames and arcs containing boron. Isotope shifts (B¹¹-B¹⁰) and alternate missing lines in the spectrum immediately identify the carrier as BO₂.

The spectrum of N₃, first observed by Thrush under low resolution in the flash photolysis of HN₃, has recently been studied under high resolution by Douglas and Jones in our laboratory. Again the observed intensity alternation identifies the carrier as NXN and the observed rotational constant show that X must be N.

The spectrum of the NCO radical was first observed in emission in discharges through ethyl isocyanate and in absorption in the flash photolysis of the same compound as well as of HNCO and other compounds. The spectrum was fully analyzed by Dixon; its assignment to NCO is based mainly on chemical evidence, the doublet structure, and the observed rotational constant.

All three radicals, BO₂, N₃, and NCO, are linear in both their ground states and their excited states. The ground states of all three molecules are 2Π states, as predicted, since there are now three electrons in the 1ε orbital. The structural data are included in Table II.
It is interesting to consider the variation of the bending frequency $\nu_2$ in the series of linear molecules with 12, 13, 14, 15, and 16 valence electrons. In Figure 10 this variation is plotted as a function of the number of electrons in the $1\pi_g$ orbital. It is seen that, with increasing number of $\pi_g$ electrons the frequency $\nu_2$, that is, the rigidity of the linear conformation, increases very rapidly; it is very small when no electrons are present in the $\pi_g$ orbital, as in $C_3$.

Molecules with 16 valence electrons, like $CO_2$, are, of course, stable molecules and do not belong in this discussion. Spectra of three triatomic free radicals with more than 16 valence electrons, but containing only atoms of the first period, have been found: $FCO$, $CF_2$ and $NF_2$. The spectrum of $CF_2$ in the ultraviolet was one of the first free-radical spectra to be recognized as such (Venkateswarlu$^{48}$) and the first to be observed in absorption (Laird, Andrews, and Barrow$^{49}$). Later, the same spectrum was observed by Mann and Thrush$^{50}$ in the flash photolysis of various compounds, but a detailed rotational analysis has only recently been accomplished in our laboratory by Mathews$^{51}$ from high resolution spectra obtained in the absorption of the gases emerging from a high frequency discharge through

Fig. 10. Frequency of bending vibration as a function of the number of $\pi_g$ electrons.
fast-streaming $\text{C}_2\text{F}_3\text{Cl}$. It is a $^1\text{B}_1-^1\text{A}_1$ transition. The structures of the molecule in upper and lower states are shown in Figure 11. The FCF angle in the ground state, recently confirmed by microwave studies of Powell and Lide, is surprisingly close to the HOH and HNH angles in the ground states of $\text{H}_2\text{O}$ and $\text{NH}_2$, as well as the HCH angle in the lowest singlet state of $\text{CH}_2$. In spite of considerable searching, the expected low-lying triplet state has not yet been found.

$\text{FCO}$ has only been observed in CO and Ar matrices at low temperature. $\text{NF}_2$ can be produced by thermal dissociation from $\text{N}_2\text{F}_4$ at moderate temperatures. Its infrared and ultraviolet absorption spectra have been studied. The ultraviolet bands are rather indistinct, and no high resolution studies of the infrared bands have been carried out. The FNF angle is estimated to be 104.2°.

Three triatomic nonhydride radicals with atoms from the second period have been identified: $\text{SiC}_2$, $\text{NCS}$, and $\text{SiF}_2$, in addition to the molecular ion $\text{CS}_2^+$. The unsymmetrical SiCC radical was first observed in thermal emission and absorption at high temperature by Kleman, and more recently at low temperature in the flash photolysis of phenyl silane. NCS occurs under conditions similar to NCO. The SiF$_2$ radical has been observed in discharges through silicon tetrafluoride. Only vibrational analyses of these spectra have as yet been made, but it is fairly certain from the appearance of the band structure that SiC$_2$ and NCS are linear, just as their analogs C$_3$ and NCO, while SiF$_2$ is nonlinear, just as CF$_2$.

![Fig. 11. CF$_2$.](image-url)
VI. CONCLUSION

The preceding review shows that the number of triatomic radicals for which ultraviolet spectra have been observed and analyzed during the past 15 years is quite considerable. Some of these radicals were long known to chemists, but others, like $C_3$, CNC, NCN, and $BO_2$, had not previously been assumed to exist in chemical reactions. In addition, in several instances, particularly in the case of $CH_2$, the importance of both low-lying singlet and triplet states has been established. In this way, even apart from the determinations of the structures of the radical, the spectroscopic studies have advanced the understanding of the chemistry of free radicals.

References