SPECTROSCOPY AND PHOTOCHEMISTRY OF POLYATOMIC ALKALINE EARTH CONTAINING MOLECULES

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I. INTRODUCTION

The interaction of metals with organic molecules is one of the primary themes of modern chemistry [1]. This interest is based both on the possibility of important applications and on the fascinating variety of molecules that can be synthesized. Synthetic chemists working at the interface between organic and inorganic chemistry create new species and characterize them primarily by nuclear magnetic resonance (NMR) and X-ray crystallography. Many of their creations have great utility in, for example, the Ziegler–Natta polymerization of ethylene to make polyethylene [1]. Metal–ligand interactions are also important in the chemistry of life processes as, for example, the active sites of enzymes. This new field of biorganic chemistry continues to expand.

All of this chemistry occurs in either solution or the solid state and is often influenced by the presence of a solvent. Currently, the tools of modern chemical physics are used to try to understand metal–ligand chemistry in the gas phase, free from the effects of solvents. The focus has been on understanding the chemistry, photochemistry, and spectroscopy of relatively small systems. For reasons of sensitivity, the primary tool for these investigations is the mass spectrometer. Sometimes lasers are used to vaporize a metal or to excite and to ionize the species of interest. The experimental techniques range from traditional high-pressure mass spectrometry to Fourier transform ion cyclotron resonance.

The photochemistry and spectroscopy of simple metal–ligand ions has been studied, for example, by the Brucat, Duncan, and Farrar research groups. In the work of Lesen et al. [2], the vanadium ion (V^+\textsuperscript{+}) was created by laser vaporization and allowed to react with H\textsubscript{2}O. The photodissociation of V^+\textsuperscript{+}(H\textsubscript{2}O) was driven by a tunable dye laser. The spectra were recorded by monitoring the appearance of V^+ with a time-of-flight (TOF) mass spectrometer as the laser was scanned. Similar work in the Duncan group has provided spectra of Mg\textsuperscript{2+}(H\textsubscript{2}O)\textsuperscript{2}\textsuperscript{+} and Ca\textsuperscript{2+}(H\textsubscript{2}O)\textsuperscript{2}\textsuperscript{+} [4,5], while the Farrar group has looked at Sr\textsuperscript{2+}(H\textsubscript{2}O)\textsuperscript{2}\textsuperscript{+} and Ca\textsuperscript{2+}(NH\textsubscript{3})\textsuperscript{2}\textsuperscript{+} [5,6]. These molecular ions are isoelectronic with the neutral molecules such as CaNH\textsubscript{2} and SrCH\textsubscript{4}, that are discussed in this chapter.

Molecular ions such as Ca\textsuperscript{2+}(H\textsubscript{2}O)\textsuperscript{2}\textsuperscript{+} have relatively weak metal–ligand binding energies of about 25 kcal mol\textsuperscript{-1} [7] compared to the stronger bond present in the isoelectronic CaNH\textsubscript{2} system. In Ca\textsuperscript{2+}(H\textsubscript{2}O)\textsuperscript{2}\textsuperscript{+}, the H\textsubscript{2}O ligand perturbs the Ca\textsuperscript{2+} energy levels much less than the NH\textsubscript{3} ligand perturbs Ca\textsuperscript{2+} in the CaNH\textsubscript{2} molecule. The electrostatic interaction of NH\textsubscript{3} with Ca\textsuperscript{2+} is much stronger than the ion–dipole interaction of Ca\textsuperscript{2+} with H\textsubscript{2}O, although the molecular symmetry (C\textsubscript{2v}) is the same for CaNH\textsubscript{2} and Ca\textsuperscript{2+}(OH\textsubscript{2})\textsuperscript{2}\textsuperscript{+}.

This chapter will cover the monovalent neutral polyatomic derivatives of the alkaline earth elements: Be, Mg, Ca, Sr, Ba, and Ra. The alkaline earth metals are naturally divalent in the solid state. Well-known examples of alkaline earth compounds are the widely used Grignard reagents, which have an empirical formula R−Mg−X (R is an alkyl group and X is a halogen) [1]. More recently, the Hanusa group at Vanderbilt has explored the organometallic chemistry of divalent Ca, Sr, and Ba derivatives [8]. In contrast to this “normal” chemistry, the monovalent derivatives such as CaOH are unstable in the solid state because they readily disproportionate.

$$2\text{CaOH} (s) \rightarrow \text{Ca}^2+ (s) + \text{Ca(OH)}\textsubscript{2} (s)$$

In fact, “proof” of the nonexistence of MgCl\textsubscript{2}(s) is discussed in undergraduate chemistry textbooks as an exercise in calculating lattice energies using Madelung constants.

The monovalent derivatives of the alkaline earth metals are free radicals that are stable in the thermodynamic sense in the gas phase or when isolated in inert matrices. Molecules such as CaOH have strong bonds (dissociation energy, D\textsubscript{0} = 92 kcal mol\textsuperscript{-1}) [9,10] but are very reactive species because of the unpaired electron localized on the Ca atom. In spite of the transient nature of these monovalent derivatives, it has proved possible to develop an extensive gas-phase inorganic chemistry for Mg, Ca, Sr, and Ba. No monovalent polyatomic derivatives are known for the Be or the Ra members of the alkaline earth group, except for BeOH. There are two experimental reports on the BeOH [11,12] molecule in
the literature but one is apparently erroneous [12]. For technical reasons, the widest variety of molecules are known for Ca and Sr.

In addition to the usual divalent molecules and solids, for example, Ca(OH)$_2$ and the monovalent molecules, for example, CaOH, a third type of molecule has been predicted by Kong and Boyd [13]. They calculate that the H—Ca—O isomer of CaOH is a minimum on the potential energy surface. The H—Ca—O molecule is, in fact, a divalent derivative of Ca with an ionic electron distribution, H$^+$Ca$^{2+}$O$^-$ or, perhaps the tautomer (UV) photochemical isomerization of CaOH. This rare gas matrix will yield HCO$^+$(Ca).

The metal monohydrides CaH$_2$(CaOH) and SrOH are the simplest monovalent polyatomic derivatives of the alkaline earths. Both CaOH and SrOH have a surprisingly long history in view of their high chemical reactivity. While CaOH and SrOH can only be stored when isolated in rare gas matrices [14], substantial steady-state concentrations exist in a variety of energetic environments.

In 1823, Herschel [15] in the Transactions of the Royal Society of Edinburgh published his observations of the colors of flames produced by the introduction of alkaline earth salts. The green color obtained with barium salts is due to BaOH and the reddish color characteristic of strontium salts is due to SrOH. The red colors of fireworks can also be attributed to the emission from SrOH [16]. It was not until the 1950s that modern flame studies [17, 18] identified the molecules that are responsible for the alkaline earth flame color. In contrast to the alkaline earths, the flame colors of the alkali elements are produced by atomic emission. The formation of molecules such as CaOH and SrOH, in fact, greatly complicates the use of flame absorption and emission for the determination of the concentrations of alkaline earth elements in analytical chemistry.

The CaOH molecule is also predicted to be of importance in atmospheric chemistry and meteorology. It has been speculated that the ablation of metals from meteor results in the formation of CaOH [19]. In chemical equilibrium calcuations, Tsuchi [20] predicted that CaOH should form in the atmospheres of cool oxygen-rich stars. Peisch [21] identified the CaOH molecule through absorption in the $^{3}P_2$--$^{3}P_2$ transition near 550 nm. Pettersen and Hawley [22] confirmed this identification using the $^{1}P_1$--$^{1}S_0$ bands near 620 nm. The recent availability of microwave and millimeter wave spectra of MgOH [22] and CaOH [24] have resulted in successful searches by radioastronomers. While the high-temperature environment of a stellar atmosphere encourages the formation of CaOH, the molecule does not readily form in cold interstellar clouds.

Interstellar molecular clouds are the sites of star formation and so are of great astronomical interest. In general, metal-containing molecules are not very abundant in dark molecular clouds because they are depleted onto grains. It was, therefore, with some surprise that the MgNC molecule [25, 26] and its isomer MgCN [27] were identified by radioastronomers in the circumstellar envelope of a carbon star. This finding has inspired the Zurey [28] group to record the laboratory spectra of a large number of simple derivatives of Mg and Ca such as MgCH$_3$ and CaCH$_3$.

A review on the calcium- and strontium-containing polyatomic free radicals appeared in 1991 [29], but there has been significant progress since then. In addition to the radio astronomical and laboratory measurements of pure rotation spectra already mentioned, modern molecular beam technology has been used extensively in recent years. Molecular beam spectroscopy has led to an improved understanding of the electronic and vibrionic structure of the large free radicals such as CaC$_2$H$_2$ and CaC$_2$H$_4$N. It is time to cover the field again with a comprehensive review, emphasizing the recent advances.

II. EXPERIMENTAL METHODS

A. Flames

The alkaline earth hydroxides molecules were first made in flames and studied by emission spectroscopy [15]. Metal salt solutions are aspirated into atmospheric pressure flames or the salts are placed on a loop of wire in the flame. The MOH (M is an alkaline earth metal) molecules form through a complicated set of flame reactions [18]. More recent flame work has included laser-induced fluorescence studies of CaOH [29] and SrOH [30]. Some of this work is motivated by the observation that soot formation is suppressed in flames when alkaline earth salts are added [31].

Although flames are convenient sources of MOH molecules, they suffer from serious drawbacks for spectroscopic and dynamical studies. The high-temperature ($\sim 2000$K) of flames causes numerous vibrational and rotational levels to be populated resulting in very dense spectra. The high pressure (1 atm) broadens the rotational lines ($>0.1$ cm$^{-1}$) and increases the overlap of the lines. In addition, resonant laser-induced fluorescence is difficult to detect because of quenching and the overwhelming presence of nonresonant fluorescence caused by rapid collisional energy transfer. The luminescence of the flame itself also interferes with measurements.
B. Broida Oven

The key discovery that opened up the field was made by Harris and co-workers [32-35] in the early 1980s. They found that alkaline earth monohydrides and monoamides could be made readily in a flow reactor called a Broida oven [36]. The Broida oven is a relatively cool (~500K), low-pressure (~5 Torr) source of high-temperature molecules that is suitable for spectroscopic studies. The work of Harris and our own work owes a great debt to the pioneering efforts of Broida in developing the source and demonstrating its potential.

The Broida oven is a remarkable source of molecules. It offers a large concentration of free radicals (~10^13 molecules cm⁻³) isolated in a flow of inert carrier gas such as argon. In contrast to a molecular beam, a Broida oven also offers a large flux of molecules (~1 g h⁻¹) that could be used for preparative chemistry, although this aspect of the technology has never been exploited. The continuous injection of a room temperature carrier gas is responsible for both the large flux and the relatively low temperature of the source. Molecules produced in a furnace are sometimes called high-temperature molecules and the Broida oven offers the possibility of studying them near room temperature.

The molecular species in a Broida oven can often be detected through their chemiluminescent emission [32]. It is particularly convenient to monitor this emission in the early stages of a low-resolution analysis. The information that can be extracted from a chemiluminescent spectrum recorded with a monochromator is, however, limited. More typically, the molecules are detected by laser-induced fluorescence using either pulsed or continuous wave (CW) dye lasers.

The molecules in a Broida oven are produced by the reaction of a metal vapor with an appropriate oxidant (Fig. 1). The metal (Mg, Ca, Sr, or Ba) is vaporized in a resistively heated crucible and entrained in a flow of Ar gas. The oxidant is added at the top through an oxidant ring. The reaction of the metal with an oxidizer, for example,

\[ \text{Ca} + \text{H}_2\text{O} \rightarrow \text{CaOH} + \text{H} \]  

(2)

often produces a low-pressure chemiluminescent flame above the oxidant injection ring (Fig. 1). The mechanism for this chemical reaction (2) is discussed below. Typical pressures are 5 Torr of Ar carrier gas, 1 mtorr of metal vapor (Ca), and 10 mtorr of oxidant (H₂O). The resulting product (CaOH) has a concentration of less than 1 mtorr, perhaps as high as 10^13 molecules cm⁻³ in the most favorable cases.

During the course of our investigations, we found that if the metal atoms are excited by a laser to the metastable 3Pᵢ electronic state, then the concentration of product molecules is dramatically increased.

\[ \text{Ca}^*\left(3P_i\right) + \text{H}_2\text{O} \rightarrow \text{CaOH} + \text{H}, \]  

(3)

where the asterisk denotes electronic excitation. Reaction 2 is endothermic.
as written but Reaction 3 can occur directly because the additional energy stored in Ca* makes Reaction 3 exothermic. The use of excited Ca atoms is particularly important for the formation of organometallic molecules such as CaC2H4 since ground-state Ca atoms will not react with the C2H4 precursor. Almost all of the molecules discussed in this chapter are produced through photochemistry.

Exploiting the enhanced reactivity of Ca* often requires the use of two tunable dye lasers (Fig. 2); one to excite the metal atoms to the metastable 1P1 state and the second to detect the product molecules. (Excited metal atoms can also be produced in an electrical discharge or in a laser-vaporized plume.) The two laser beams are introduced into the Broida oven chamber through Brewster angle windows on the top or the side. The first laser (dye laser 1) is tuned to the 2P1-1S0 atomic transition at 471.1, 657.3, 689.2, and 791.1 nm for Mg, Ca, Sr, and Ba, respectively. The second laser (dye laser 2) can be operated broadband for survey work or in a single longitudinal mode (~ 1 MHz bandwidth) for high-resolution work. In our laboratory, the lasers we use are the Coherent model 599, 699-29, and 899-29 dye lasers and a titanium-sapphire laser, all pumped by Ar ion lasers. The typical laser powers are 0.5 W at the Broida oven. The two dye laser beams are spatially overlapped and focused into the Broida oven.

The first laser beam can be amplitude modulated (~ 1 kHz) with an optical chopper (Fig. 2), which modulates the concentration of the excited metal atoms, M*. Because the excited metal atoms have a much higher reactivity, the concentration of product molecules is also modulated. The modulated fluorescence excited by the second laser is then detected by a PMT and a lock-in amplifier. A monochromator or an optical filter is used to analyze the emission and to control the optical bandwidth detected by the PMT. This photochemical modulation and synchronous detection of the fluorescent signal is a very powerful technique for increasing the signal-to-noise (S/N) ratio.

There are two typical experimental setups. In the first, both lasers are in resonance with a molecular laser 1 and molecular laser 2) transitions and the monochromator (Fig. 2) is scanned to record the laser-induced fluorescence. In the second type of experiment, the monochromator is used as a filter and is not scanned while the second laser wavelength is changed. This second type of experiment is called a laser excitation scan since a fluorescent signal is detected by the PMT only when laser 2 is in resonance with a molecular transition. In this case, the scanning laser can be broadband for survey work or a single mode for high-resolution experiments.

The high-resolution spectra recorded with a Broida oven are limited by the effects of Doppler and collisional broadening. For example, in the visible region with a pressure of 10 Torr, Doppler broadening dominates and a typical line width for a molecule like CaC2H4 is about 0.03 cm~1. Nonlinear techniques such as intermodulated fluorescence are feasible in a Broida oven in order to remove the effects of Doppler broadening. The technique of laser excitation spectroscopy with selective fluorescence detection is often necessary to simplify the complex rotational structure of a molecule such as CaC2H4. Ultimately, the collisional redistribution of the excited state population in a Broida oven limits the size of molecule for which a rotational analysis is possible. For example, the rovibronic lines of CaC2H4 cannot be resolved in a Broida oven and a molecular beam experiment is necessary.
One of the recent developments has been the use of Broida oven technology in recording millimeter wave pure rotational spectra (Fig. 3). The pure rotational transitions are recorded in absorption using a free space cell. There are two main groups working in this area, the Zirits group at Arizona State University [37] and the Saito group [25] at the Institute for Molecular Science in Japan.

In the Arizona State University design, the radiation is collimated with Teflon lenses and passes twice through the Broida oven. This double passing is achieved (Fig. 3) by sending the radiation through a wire grid polarizer, then reflecting the radiation with a rooftop prism oriented in such a way to rotate the plane of linear polarization by 90°. The return beam through the cell is now totally reflected by the polarizer and focused onto an InSb hot electron bolometer detector.

The source of microwave radiation at Arizona State University is a set of three phase-locked Gunn oscillators (Fig. 3), which operate in the 65-140-GHz region at power levels of about 50 mW. Higher frequencies are obtained by doubling, tripling, or quadrupling the fundamental frequency in a nonlinear Schottky diode multiplier. The millimeter wave radiation is frequency modulated at 25 kHz by adjusting the reference frequency used in the lock circuit.

The main difficulty in adapting the Broida oven to "low"-frequency millimeter wave measurements is the problem of pressure broadening [38]. Since the Doppler broadening of molecular lines is linearly proportional to the transition frequency, the Doppler effect is negligible in the millimeter wave region. The molecular line widths are dominated by pressure broadening. The effect of pressure broadening depends linearly on the pressure with a typical magnitude of 10 MHz/mTorr of gas. This result means that the total pressure in the Broida oven chamber (mainly argon carrier gas) has to be reduced to below 100 mTorr in order to obtain narrow lines and strong peak absorption coefficients. The solution to this problem is to increase the pumping speed by replacing the usual mechanical vacuum pump on the Broida oven with a Roots blower.

C. Molecular Beams

The Broida oven is a nearly ideal source for the spectroscopy of diatomic molecules and small polyatomic molecules such as CO₂. For larger species, however, the spectral congestion is too severe and the collisional relaxation rates are too high to record resonant, rotationally resolved spectra. The solution to this problem is to lower the temperature to eliminate the spectral congestion and to lower the pressure to eliminate the
collision-induced redistribution of the excited-state population. A molecular beam source has these desirable properties.

The breakthrough experiment was carried out by Whitham et al. [39, 40] in France. They used a "Smalley-type" laser vaporization source (Fig. 4) to provide a molecular beam of Ca atoms entrained in He or Ar gas. The second harmonic (332 nm) from a pulsed Nd:YAG laser was focused (Fig. 4) on a rotating calcium rod. About 500 μs prior to this, a pulsed valve (left side of Fig. 4) is opened and the plume of vaporized metal is entrained in Ar or He gas. The carrier gas is seeded with a few percent of the oxidant such as H₂O. The plume of excited- and ground-state metal atoms are carried down a short channel and react with the oxidant. At the end of the channel, the product molecules such as CaOH expand into the vacuum chamber and cool. After a short expansion, the pressure has dropped so low that the molecules are effectively in a collisionless, ultracold (<10 K) environment.

The molecular jet of molecules is crossed with a tunable dye laser and the laser-induced fluorescence is collected with a lens and focused on a PMT detector (Fig. 5). In the original experiments, a standard pulsed dye laser was used to match the 10-Hz duty cycle of the pulsed valve and the pulsed Nd:YAG vaporization laser. Although this approach provides a high S/N ratio and wide spectral coverage, the resolution is limited by the laser line width of typically 0.5 cm⁻¹ (no étalon) to 0.05 cm⁻¹ with an étalon.

The simplest method to obtain high-resolution spectra is to replace the pulsed dye laser with a CW single-mode dye laser. As Steinle and co-workers have demonstrated in a series of beautiful experiments, this
III. CHEMISTRY AND PHOTOCHEMISTRY

One of the surprising aspects of the chemistry of alkaline earth atoms is that ground-state atoms can react readily in the gas phase with molecules such as H₂O and CH₃(Oh). In solution, the overall reaction:

\[ \text{Ca(s) + 2H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2(s) + \text{H}_2(g) \]  

is vigorous. In the gas phase, however, the elementary reaction:

\[ \text{Ca(g) + H}_2\text{O(g)} \rightarrow \text{CaOH(g) + H}_2(g) \]  

does not occur because it is endothermic by 27 kcal mol⁻¹. The CaOH molecule obviously does form in a Broida oven and even chemiluminescence from the B²Σ⁺ and A¹Σ⁺ states can be seen. What is the source of this extra energy?

The laser excitation of Ca atoms to the \(^{3}P_1\) state can provide an additional 44 kcal mol⁻¹ of energy and the direct reaction

\[ \text{Ca}^{(3P_1)} + \text{H}_2\text{O(g)} \rightarrow \text{CaOH(g) + H}_2(g) \]  

is now exothermic by 17 kcal mol⁻¹. Thus, the increased production of CaOH when \(\text{Ca}^{*}\) is available is explained by the opening of the direct reaction channel (6). In a high-pressure CH₃OH flame, there is also considerable energy available and many free radicals such as OH can react with Ca.

\[ \text{Ca}^{*} + \text{OH(g)} \rightarrow \text{CaOH(g)} \]  

in the presence of a third body. In a laser vaporization source, the plume of Ca atoms contains a large fraction of \(\text{Ca}^{*}\) and \(\text{Ca}^{+}\), which readily react to give CaOH in the molecular beam. Thus in many cases the deliberate or inadvertent presence of \(\text{Ca}^{*}\) or OH accounts for the synthesis of CaOH. In a normal Broida oven, however, the thermal vaporization of Ca at about 1000°C yields a very low concentration of \(\text{Ca}^{*}\). It is found that the production of CaOH can be dramatically increased by simply increasing the total pressure in the chamber from 1 to 10 torr by decreasing the pumping speed. This fact points to a mechanism that needs a third body in a rate-controlling step.

Two possible mechanisms [41] are

Mechanism A

\[ \text{Ca} + \text{H}_2\text{O} \rightarrow \text{HCAOH} \]  

\[ \text{HCAOH} + \text{H} \rightarrow \text{CaH + CaOH} \]  

\[ \text{CaH} + \text{H}_2 \rightarrow \text{CaOH} + \text{H}_2 \]  

\[ 2\text{Ca} + 2\text{H}_2\text{O} \rightarrow 2\text{CaOH} + \text{H}_2 \]  

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Mechanism B

\[
\begin{align*}
\text{Ca} + \text{H}_2\text{O} & \rightarrow \text{HCaOH} \\
\text{HCOH} + \text{H}_2\text{O} & \rightarrow \text{CaH}_2\text{O} + \text{H}_2 \\
\text{Ca}(\text{OH})_2 + \text{Ca} & \rightarrow 2\text{CaOH} \\
2\text{Ca} + 2\text{H}_2\text{O} & \rightarrow 2\text{CaOH} + \text{H}_2
\end{align*}
\]

In these reactions, other alkaline earths can be substituted for Ca and other oxidants such as CH\textsubscript{2}OH or HCOOH, which contain the OH group, can be substituted for H\textsubscript{2}O.

Both mechanisms have as their first, and rate-controlling step, the insertion of a Ca atom into one of the O–H bonds of water. Additional support for the existence of an HCaOH intermediate comes from the matrix isolation experiments of Margrave and co-workers [14]. When Ca and H\textsubscript{2}O were cocondensed in an argon matrix, a Ca(\textsubscript{2}H\textsubscript{2}O) complex formed. Upon irradiation of the matrix with light near the metal resonance lines, the Ca atom inserted into H\textsubscript{2}O and the infrared (IR) absorption of the HCaOH molecules was detected. Irradiation with UV light then gave the CaOH molecule.

Although we cannot directly detect H\textsubscript{2}CaOH because it probably has a dissociative UV spectrum [14], we can detect another predicted reaction intermediate in some of our experiments. Mechanism A predicts that the CaH molecule will be present in the Bridgman oven, and with some oxidants we have detected it by laser-induced fluorescence. The CaH molecule is seen when carboxylic acids such as formic acid are used to make the monocarboxylates such as SrO\textsubscript{2}CH\textsubscript{2}OH [42]. Curiously, CaOH is not detected [41] when water or alcohols such as CH\textsubscript{3}OH are used to make alkoxides such as CaOCH\textsubscript{3}. More experimental and theoretical work is necessary to establish the chemical mechanisms involved in the reactivity of the alkaline earth atoms.

There have been several studies of the reaction dynamics of the ground and excited states of the alkaline earth atoms with various oxygen-containing molecules under single collision conditions. Although these studies are not directly applicable to the multiple collision regime in the Bridgman oven, they clarify the dynamics of a single encounter between a metal atom and an oxidant molecule. Oberlander and Parson [43] looked at the reactions of Ca and Sr with water, alcohols, and peroxides. Similar studies of the reactivity of Ba were made by Davis et al. [44] as well as by de Pujo and co-workers [45–47]. The basic conclusions are illustrated in Figure 6.

The ground state of the Ba atom reacts with water by two different mechanisms [44] (Fig. 6). The main channel is the direct exothermic reaction that results in the products BaO and H\textsubscript{2}. The minor channel (dotted lines) is the insertion of Ba into the OH bond (H migration) that results in the endothermic BaOH + H\textsubscript{2} products. More than simple energetics is involved, however, because even when the Ba atom is given enough energy to overcome the insertion barrier, the reaction strongly favors the direct BaO product. The reactivity of excited 1D atoms with water is very different than the reactivity of the ground state Ba atoms (Fig. 6). The "diagonal" character of the excited state strongly favors insertion to give the BaOH product.
exclusively. Even though the BaO product is favored on energetic grounds, none is produced. The BaSO product angular distributions are consistent with an HSOOH intermediate. The reactions of Ca and Sr with H₂O and H₂O₂ follow a similar pattern, although the dynamics are postulated by Parson and co-workers [48, 49] to be slightly different.

The reactions of Ca, Sr, and Ba with alcohols [41-45] are also different in that only the insertion channel is seen for both ground- and excited-metal atoms. The reaction intermediate is HMO or in all cases and the H atom leaves to give the MOR product. Very recently, the production of a small amount of CaOH was reported in the reaction of Ca with alcohols [50, 51]. The bulky R group suppresses the production of the energetically favored MO + HR products. Under both single collision and multiple collision conditions the most important dynamical event is the insertion of an alkaline earth metal atom in an H—OR bond.

It is presumed that the production of other monovalent derivatives such as CaNH₂, CaC₂H₅ from NH₃ and CH₃H₂ may involve similar excited metal atom insertions into N—H or O—H bonds. Unlike the reactions with H₂O and alcohols, however, no studies of the dynamics have been carried out and even the thermochemistry is very uncertain. Clearly, more experimental and theoretical work is necessary before any firm conclusions can be drawn about mechanisms.

IV. ELECTRONIC STRUCTURE

One of the most appealing aspects of the spectroscopy of the monovalent alkaline earth derivatives is that a simple, one-electron, hydrogenic model provides a reasonable picture of the electronic structure. This simple model is not usually applicable to the derivatives of the other elements of the periodic table. In fact, the major impediment to extending the work to the more chemically interesting transition elements is that the spectra will be difficult to interpret because of the presence of many states with large spin and orbital angular momenta.

The electronic structure can best be explained with a correlation diagram for Ca⁺, CaF, and CaNH₂ as shown in Figure 7. The CaNH₂ molecule is ionic like Ca⁺F⁻, so the electronic distribution can be approximated as Ca⁺NH₂-. The CaNH₂ molecule is planar with C₂₃ symmetry, not pyramidal like NH₂-. The Ca⁺ ion is isoelectronic with N⁺ and has a 'S ground state with lowlying 'D and 'P states. The approach of an F⁻ ligand changes the atomic ground state into a 4σ(π)² molecular state in CaF.

The effect of the F⁻ ligand on the Ca⁺ excited states is more complicated. The threefold orbital degeneracy of the 'P state is partly lifted to give 4p and 4p₁ orbitals that correlate mainly with the B⁺2 and A⁺2 states of CaF, respectively. For a 'D atomic state, one obtains 3d₄, 3d₅, and 3d₆ orbitals and Σ⁺, Σ⁻, 'H, and 'A molecular states. In addition to lifting the degeneracy, the F⁻ ligand shifts the location of the states, stabilizing the Ca⁺ 'P states more than the 'D states. Since the atomic L quantum number is no longer good in a molecule, some mixing of atomic orbitals also occurs.
In particular, the $A^\Pi$ state in CaF is about 70% $4\pi$ and 30% $3\sigma$, while the $B^2\Sigma^+$ state is nearly a 50:50 mixture of $4\pi$ and $3\sigma$ atomic orbitals [52]. This orbital mixing distorts the molecular orbitals in such a way as to keep the unpaired electron as far away as possible from the F$^-$ ligand.

For simplicity, the $A^\Pi$ state and $B^2\Sigma^+$ state of CaF can be considered to be three pure $\pi$ orbitals, $\pi_x$, $\pi_y$, $\pi_z$, for the $A^\Pi$ state and $\pi_x$, $\pi_y$, $\pi_z$, for the $B^2\Sigma^+$ state. If the F$^-$ ligand is changed to NH$_2$, then the degeneracy of the $\pi_x$, $\pi_y$, and $\pi_z$ orbitals is lifted. From a high-resolution rotational analysis of the $A^\Pi - \tilde{X}$ transition, the first excited state is the in-plane $\pi$ orbital of $b_1$ symmetry. In Figure 7, the CaNH$_2$ is considered to lie in the plane of the paper so the $B^2\Pi$ state is the $\pi$ orbital out of the plane of the molecule.
V. SURVEY OF MOLECULES

A. Monohydroxides, MOH

The alkaline earth monohydroxides are the most studied of all of the molecules discussed in this chapter because they are easy to make and are relatively simple to study. Since the early literature has already been reviewed [28], mainly the more recent (since ~1990) work will be discussed.

The Ziurys laboratory has recorded the millimeter wave pure rotational spectra for MgOH [23, 58-60], MgOD [60, 61], CaOH [58, 59, 62], CaOD [61], SrOH [58, 59, 63], SrOD [63], BaOH [58, 59, 64], and BaOD [64]. The spectra are simple and show the spin-rotation doublets in the \( \Sigma^+ \) ground state (Fig. 11) as well as numerous vibrational satellites. A typical spin doublet is shown for the MgOH \( N = 12 \rightarrow 13 \) transition [23].

The alkaline hydroxides have low-lying vibrational states (Fig. 12) that are populated in the Broida oven and give rise to numerous vibrational satellites as shown in a stick diagram in Figure 13.

\[
\text{MgOH} \ (\Sigma^+): \ N = 12 \rightarrow 13
\]

\[
\begin{align*}
\text{FREQUENCY (MHz)} & \quad \text{385,105.0} & \quad \text{385,155.0} & \quad \text{385,205.0} \\
J = \frac{23}{2} - \frac{23}{2} & \\
J = \frac{23}{2} - \frac{23}{2} &
\end{align*}
\]
The high-quality pure rotational data, combined with the earlier measurements of the vibrational intervals by laser spectroscopy, allows an improved molecular geometry to be determined. For MgOH, CaOH, SrOH, and BaOH, the geometries are linear in the ground state although the bonding potentials [60] are very flat (Fig. 14). Although quasilinear behavior has been ruled out for the heavier members of the family, the situation is more ambiguous for BeOH. The latest ab initio calculations [65] do not predict a barrier to linearity for BeOH in the ground state, in agreement with a linear structure proposed on the basis of electron spin resonance (ESR) experiments by Brom and Wellner [11]. Table 1 gives the \( r_0 \) bond lengths for the alkaline earth monohydrides. The values for BeOH are the \( r_0 \) predictions of an ab initio calculation by Fernandez [65]. Note that the first excited electronic state of MgOH [66] and the \( F \) state of CaOH [67] have bent geometries.

Millimeter wave spectroscopy with a free space cell such as a Broida oven is more sensitive than lower frequency microwave spectroscopy. However, the higher \( J \) transitions monitored by millimeter wave spectroscopy often do not show the effects of hyperfine structure. In the case of CaOH and SrOH, the proton hyperfine structure was measured in beautiful pump-probe microwave optical double resonance experiments in the Steinle group [24,68]. They adapted the classic atomic beam magnetic resonance experiments to work with a pulsed laser vaporization source and replaced the microwave fields in the \( A \) and \( C \) regions by optical fields (Fig. 15). These sensitive, high-precision measurements yielded a very small value for the proton Fermi contact parameter \( \alpha_p \), consistent with ionic bonding and a
<table>
<thead>
<tr>
<th>Molecule</th>
<th>( r_{\text{MO}} ) (Å)</th>
<th>( r_{\text{OH}} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeOH(^\ast)</td>
<td>1.378</td>
<td>0.944</td>
</tr>
<tr>
<td>MgOH(^\ast)</td>
<td>1.780</td>
<td>0.871</td>
</tr>
<tr>
<td>CaOH(^\ast)</td>
<td>1.985</td>
<td>0.922</td>
</tr>
<tr>
<td>SrOH(^\ast)</td>
<td>2.111</td>
<td>0.922</td>
</tr>
<tr>
<td>BaOH(^\ast)</td>
<td>2.200</td>
<td>0.927</td>
</tr>
</tbody>
</table>

\(^{\ast}\) Ab initio \( r \) values in [65].

\(^{\dagger}\) Reference 61.
closed-shell OH ligand. In general, hyperfine structure is very valuable because the hyperfine parameters are determined by the electron distribution.

The Stemple group also measured the dipole moments of CaOH and SrOH in a molecular beam Stark experiment [69]. The surprisingly low values of 1.46 D and 1.90 D in the ground $3P^0$ state for CaOH and SrOH, respectively, were found in moderate agreement with the ab initio calculation of 0.98 D for CaOH [70]. The semiempirical predictions of Mestdagh and Vistocco [71] are in good agreement with experiment and explain the small values. The semiempirical scheme is a modified electrostatic Ritter model that allows for the effect of the unpaired electron on the opposite side of the metal away from the OH ligand (cf. Fig. 8). In other words, the large Ca$^{15}$OH$^\cdot$ dipole is nearly canceled by the dipole created by the unpaired electron on the opposite side of the Ca$^{15}$ atom. A ligand field treatment of the bonding is also available [72].

In recent years, the optical spectroscopy of the metal hydrides has also bloomed with new analyses of the 0–0 bands of the $\Sigma^+$ transitions of CaSOH [73], SrSOH [74], and BaSOH [47]. The use of a cold molecular beam source results in a simple spectrum and in narrower lines as illustrated in Figure 16 for SrSOH [74].

**TABLE 2 Vibrational Frequencies for MOH and MO$^+$ Molecules (cm$^{-1}$)**

<table>
<thead>
<tr>
<th>Molecules</th>
<th>$v_1$ ($\text{O–H stretch}$)</th>
<th>$v_2$ ($\text{M–O–H bond}$)</th>
<th>$v_3$ ($\text{M–O stretch}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgOH</td>
<td>160$^\circ$</td>
<td></td>
<td>750$^\circ$</td>
</tr>
<tr>
<td>MgOB</td>
<td>118$^\circ$</td>
<td>50$^\circ$</td>
<td>603$^\circ$</td>
</tr>
<tr>
<td>CaOH</td>
<td>379$^\circ$</td>
<td>55$^\circ$</td>
<td>609$^\circ$</td>
</tr>
<tr>
<td>CaOD</td>
<td>379$^\circ$</td>
<td>55$^\circ$</td>
<td>609$^\circ$</td>
</tr>
<tr>
<td>SrOH</td>
<td>242$^\circ$</td>
<td>52$^\circ$</td>
<td>517$^\circ$</td>
</tr>
<tr>
<td>SrOD</td>
<td>242$^\circ$</td>
<td>52$^\circ$</td>
<td>517$^\circ$</td>
</tr>
<tr>
<td>BaOH</td>
<td>342$^\circ$</td>
<td>492$^\circ$</td>
<td>482$^\circ$</td>
</tr>
<tr>
<td>BaOD</td>
<td>258$^\circ$</td>
<td></td>
<td>482$^\circ$</td>
</tr>
</tbody>
</table>

References:
- Reference 60
- Reference 67
- Reference 55
- Reference 51
- Reference 81
- Reference 83
- Reference 77
- Reference 77
- Reference 53
- Reference 74
- Reference 16
Figure 17. Laser excitation spectra (top arrows) and dispersed laser-induced fluorescence spectra (down arrows) of the \( \tilde{b}^2 \Sigma^+ \rightarrow \tilde{a}^2 \Sigma^+ \) transition of SiOH. [Reprinted with permission from ref. 77. Copyright 1993 NRC Research Press.]

The majority of the work, however, has been carried out in a Breoda oven by Coxon and co-workers [75–84]. They concentrated on the study of the vibrational intervals in the ground \( \tilde{a}^2 \Sigma^+ \) states (Table 2) and in understanding the vibronic interactions in the \( \tilde{A}^2 \Pi \) states. As illustrated in Figure 17, the combination of laser excitation spectroscopy and dispersed laser-induced fluorescence allows the vibronic levels to be mapped out. The \( \tilde{A}^2 \Pi \) states suffer from the combined influence of the Renner–Teller effect, Fermi resonance and spin– orbit coupling. The Coxon group recorded a large number of bands in the \( \tilde{b}^2 \tilde{X} \) and \( \tilde{A}^\prime \tilde{X} \) transitions of SiOH [75–77], CaOH, and CaOD [78–84].

The Herzberg–Teller effect is another name for the vibronic coupling of electronic and vibrational motion. This effect was used by Jarman and Bernath [83] to locate the missing \( \tilde{C}^2 \Delta \) state in CaOH via the forbidden \( \tilde{C}^2 \Delta \rightarrow \tilde{X}^2 \Sigma^+ \) transition. In this case, the 0–0 band remains forbidden but the interaction between the bending motion and the electronic motion in the \( \tilde{C}^2 \Delta \) state make bands such as 000–000 weakly allowed (Fig. 18). The \( \tilde{C}^2 \Delta \) state also displays the Renner-Teller effect, which is the interaction of vibrational angular momentum with orbital angular momentum in a linear molecule. There is some evidence for a low-lying \( \tilde{C}^2 \Delta \) state in the spectrum of BaOH, again through the effects of vibronic coupling [86].

Spectroscopic efforts have concentrated on the \( \tilde{A}^2 \Pi \rightarrow \tilde{X}^2 \Sigma^+ \) and \( \tilde{B}^2 \Sigma^+ \rightarrow \tilde{X}^2 \Sigma^+ \) transitions of the MOH molecules although these transitions for
C. Monooxalides, MOOR

The low-resolution spectra of C₂ and S₂ monooxalides and the monooxalyl radical, CaO₂⁺, of the corresponding sulfur systems have been recorded. Calcium monooxalyl radical is believed to have a C₂v symmetry with both electronic transitions similar to CaO₂⁺.

D. Monoformanilides, MONOFH

The electronic transitions of the monoformanilide radical, C₆H₅–NO₂, have been studied. The electronic structure of the monoformanilide radical is similar to that of the monooxalyl radical. The electronic transitions are assigned in terms of the electronic configuration of the radical.
vibrational frequencies of 351 and 288 cm$^{-1}$ in the ground state for the calcium and strontium monoformamidates [93] are similar to the values (349 and 275 cm$^{-1}$, respectively) for the corresponding monoformates [92]. Again high-resolution spectra and theoretical calculations would be very helpful in confirming the assignments of the low-resolution spectra. Interestingly, while formamidate salts are unknown in normal inorganic chemistry (formates are common), they form readily in the gas phase.

**E. Monoisocyanates, MNCO**

The spectra of CaNCO and SrNCO were first reported in 1986 based on a low-resolution analysis of the products of the reaction of Ca and Sr with HNCO [94]. The $^{4}I_{3/2}$, $^{4}I_{5/2}$, and $^{4}I_{3/2}$ transitions were clearly due to a linear molecule (cf. CaF in Fig. 7). For NCO derivatives, there is the possibility of linkage isomers. In the initial paper [94], we guessed that the oxygen-bonding structures, MOCN, were lowest in energy (cyanates), but this proved to be erroneous. The NCO ligand binds to Ca and Sr through the N atom to give metal isocyanates.

To determine the structure of CaNCO and SrNCO, a rotational analysis of the $^{2}I_{11/2}$ transition of the SrNCO molecule was carried out [95].
By fixing the N—C bond length to 1.19 Å and the CO bond length to 1.23 Å, the Sr—N bond length of 2.26 Å was determined from the rotational constant (0.00258 cm⁻¹) in the $^3\Sigma^+$ state. A rotational analysis [96] of the corresponding $^2\Pi$--$^2\Sigma^+$ transition of SrN₂ gave an identical Sr—N bond length when the N—N bond lengths in the N₂ ligand were fixed to 1.18 Å. 

For SrNCO and SrN₂, to have identical metal-ligand bond lengths is consistent only with an isocytosinate structure for SrNCO.

The corresponding rotational analyses have not yet been carried out for CaNCO and CaN₂, but some ab initio predictions [97] have been made by Chan and Hamilton (Tables 3 and 4). These calculations used the same 6–31 + G* basis set used by Ortiz [54] and are at the MP2 level. There is good agreement between the calculated vibrational frequencies and the experimental values (Table 4). The vibrational frequencies of NCO in the solid state are 2182, 1211, and 631 cm⁻¹ to be compared with the calculated values of 2191, 1327, and 826 cm⁻¹ for $\nu_1$, $\nu_2$, and $\nu_3$, respectively (Table 4).

No laboratory spectra are available for CaNCS.

F. Monoazides, MN₃⁻

The isoelectronic NCO and N₃⁻ anions are often called pseudohalides because they have a chemistry similar to that of F⁻, Cl⁻, Br⁻, and I⁻. In a similar fashion, we find that CaN₃, SrN₃, CaNCO, and SrNCO all have similar spectra and that the electronic structure is that of CaF (Fig. 7). As in "regular" chemistry, chemical and isoelectronic analogies are a powerful tool for interpreting our gas-phase inorganic chemistry.

The CaN₃ and SrN₃ molecules were made in a Broida oven by the reaction of Ca and Sr vapors with hydrazine and HN₃ [96]. The reaction is relatively vigorous and, in contrast to the other Ca and Sr reactions, exciting the atomic $^1P_1$ state of the metal increases the reactivity only slightly. The $^3\Sigma^+ - ^3\Pi$ and $^2\Pi - ^2\Sigma^+$ transitions could be identified...
Figure 21. The chemiluminescence spectrum of the Ca + HN$_2$ reaction. [Reprinted with permission from ref. 96. Copyright 1988 American Institute of Physics.]

Figure 22. The dispersed fluorescence spectrum of CaN$_2$ [96]. The laser is exciting the 0-0 band of the $^2$II$^2$S$^-$ transition of CaN$_2$. The $^2$II state has a spin-orbit splitting of 76 cm$^{-1}$. [Reprinted with permission from ref. 96. Copyright 1988 American Institute of Physics.]

Figure 23. The high-resolution laser excitation spectrum of the $^4$II$_{13/2} - ^2$II$^2S^-$ transition of SrN$_2$ recorded using a monochromator as a narrow band filter. [Reprinted with permission from ref. 96. Copyright 1988 American Institute of Physics.]

by chemiluminescence (Fig. 21) and by low-resolution laser-induced fluorescence (Fig. 22). A rotational analysis of the $^4$II$^2$II$^2S^-$ transition (Fig. 23) of SrN$_2$ was carried out and confirmed the linear geometry [96].

The vibrational frequencies of CaN$_2$ were measured by fixing the laser on an electronic transition and dispersing the fluorescence with a small monochromator [96]. In this way, it was possible to measure four out of the five expected vibrational frequencies (Table 4). In general, the agreement with the ab initio predictions of Chan and Hamilton [97] is excellent except for the low-frequency metal–ligand bending mode. In this case, the interval of 86 cm$^{-1}$ was measured by laser-induced fluorescence and interpreted as 2$v_b$ since the selection rules forbid $(\Delta \Gamma = \pm 1)$ transitions for non totally symmetric vibrational modes like $v_b$. It would be expected that the ab initio calculations would have difficulty in predicting such a low frequency in an ionic molecule.

G. Monoisocyanoanides, MNC and Monocyanides, MCN

In many ways, the alkaline earth monoisocyanoanides have generated the most widespread interest and still remain the most mysterious of the molecules discussed in this chapter. The CaNC, SrNC, and BaNC molecules were
H. Monoxydihalides, MSI

The electronic spectra of the CASH and SASH are very similar to the three-electron spectra of the CASH and SASH. The electronic spectra of the CASH and SASH are very similar to the three-electron spectra of the CASH and SASH. The electronic spectra of the CASH and SASH are very similar to the three-electron spectra of the CASH and SASH.

The electronic spectra of the CASH and SASH are very similar to the three-electron spectra of the CASH and SASH. The electronic spectra of the CASH and SASH are very similar to the three-electron spectra of the CASH and SASH. The electronic spectra of the CASH and SASH are very similar to the three-electron spectra of the CASH and SASH. The electronic spectra of the CASH and SASH are very similar to the three-electron spectra of the CASH and SASH. The electronic spectra of the CASH and SASH are very similar to the three-electron spectra of the CASH and SASH.

The electronic spectra of the CASH and SASH are very similar to the three-electron spectra of the CASH and SASH. The electronic spectra of the CASH and SASH are very similar to the three-electron spectra of the CASH and SASH. The electronic spectra of the CASH and SASH are very similar to the three-electron spectra of the CASH and SASH. The electronic spectra of the CASH and SASH are very similar to the three-electron spectra of the CASH and SASH.
I. Monothiolates, MSR

The sulfur analogues of the alkaline earth monoalkoxides have also been made in a Broida oven by the reactions of Ca* and Sr* with thiols [111].

Figure 26. The laser excitation spectrum of the $\lambda^2 A^g \rightarrow \tilde{X}^2 A^g$ and $\tilde{C}^2 A^g \rightarrow \tilde{X}^2 A^g$ transitions of CaSH [112]. The asterisks in this case mark CaOH impurity bands. [Reprinted with permission from ref. 112. Copyright 1993 American Institute of Physics.]

The two spin components linearly with increasing $K_a$ (Fig. 27) so that only $K_a = 0$ obeys Hund's case (i) coupling and the higher $|K_a|$ values obey Hund's case (ii) coupling. $K_a$ is the projection of the total angular momentum $\mathbf{N}$ (exclusive of electron spin) onto the $\mathbf{e}_z$ inertial axis.

The $\tilde{B}^2 A^g \rightarrow \tilde{X}^2 A^g$ electronic transition of CaSCH was rotationally analyzed in a pulsed molecular beam source by Scurlock et al. [113]. The $a$ axis of this asymmetric rotor lies very close to the Ca–S bond and there is a large dipole moment of 5.36 D projected along it in the $\tilde{X}^2 A^g$ state.

The millimeter wave spectra of CaSCH, CaSCH$_2$, and MgSCH were recorded in Ottawa by Taleb-Bendiab et al. [114]. The pure rotational spectra of CaSCH and CaSCH$_2$ allow an improved molecular geometry to be determined for the $\tilde{X}^2 A^g$ state. They found a $r_e$ Ca–S bond length of 2.564 Å, a S–H bond length of 1.357 Å, and a bond angle of 91°.

Figure 27. The spin splitting of the $\tilde{X}^2 A^g \rightarrow \tilde{X}^2 A^g$ transition of CaSCH as a function of $K_a$. The large value of $r_e$ in the $\tilde{A}$ state causes the $F_{1/2}$ and $F_{3/2}$ components to split linearly with $K_a$. [Revised with permission from ref. 112. Copyright 1993 American Institute of Physics.]

The low-resolution laser excitation and fluorescence spectra of the $\lambda^2 A^g \rightarrow \tilde{X}^2 A^g$, $B^2 X^g \rightarrow \tilde{X}^2 A^g$, and $C^2 X^g \rightarrow \tilde{X}^2 A^g$ transitions of CaSCH$_2$, SrSCH$_2$, CaSCH$_3$CH$_2$, and so on, were recorded. The strong resemblance between the CaSCH and CaSCH$_2$ spectra suggest that the monothiolates and monohydroxylates have a similar electronic structure and that the Ca–S–C molecular backbone is bent.
J. Monoozimzides, MNH₂

The CaNH₂, SrNH₂, and BaNH₂ molecules were discovered by Wörnsbecher et al. [32, 34] in Santa Barbara using a Broda oven. This work in the Harris group on amides and hydroxides was the crucial first step in the production of the now numerous monovalent derivatives of the alkaline earth metals. The electronic structure of CaNH₂ has already been discussed (Fig. 7) and Wörnsbecher et al. [34] attempted a rotational analysis of the C₂v Å • Å transition.

The CaNH₂ and SrNH₂ molecules, like CaSH, display three visible electronic transitions C₂v Å • Å, B₂g • Å, and B₂g • Å. The Å • Å and B • Å transitions of SrNH₂ are perpendicular transitions with Å subband structure that spreads out while the Å • Å transition has a transition dipole moment that lies along the Å • Å axis and Å subbands that overlap (Fig. 28). A rotational analysis of the Å • Å and B • Å transitions of SrNH₂ by Bazzari and Bernath [112] confirmed the symmetries of the Å and B states and they found an Å • Å bond length of 2.25 Å and an Å • Å bond angle of 104° in the Å state.

The molecular beam measurements of the Å • Å, Å • Å, and B • Å transitions of CaNH₂ by Whitham et al. [40] were pioneering experiments. Marr et al. [116] used the improved resolution of a CW dye laser to make a complete analysis of the Å • Å transition. Like CaOH, CaNH₂ has a small dipole moment of 1.74 D in the ground Å • Å state. Marr et al. [116] also measured a large ϵ Å spin–rotation constant in the Å • Å state.

The B • Å, Å • Å, and C • Å transitions have also been analyzed at Waterloo with a molecular beam spectrometer [117]. All three known electronic transitions have been fitted together to improve the molecular constants. The molecular geometry (Table 5) in the Å • Å state was found by fixing the Å • Å bond length to 1.04 Å (from NH₃) or 1.025 Å (from NH₄). Vibrational frequencies were measured by laser-induced fluorescence.

For comparison (Table 5), Chan and Finamore [97] calculated the molecular geometry and vibrational frequencies using density functional theory. The most interesting aspect of the rotational analysis of the Å, Å, and Å transitions are the values for the complete set of nine spin–rotation parameters of the Å, Å, and Å states (ϵ Å, ϵ Å, and ϵ Å, ϵ Å, for each state). If the orbitals containing the unpaired electron in these three states (Fig. 7) are approximate by a set of p orbitals (p, p, p) then all nine spin–rotation constants can be easily estimated by pure predissociation relationships. Van Vleck introduced the pure predissociation approximation for diatomic molecules. The basic idea is that if the one-electron, atomic orbital angular momentum is preserved in a diatomic molecule then the A-doubling and spin–rotation constants can be predicted, for example, in a 4p(3/2) and a 4p(1/2) state. This pure predissociation picture can easily be generalized to
polyatomic molecules and used to predict the spin–rotation parameters $\tau_{\perp}$, $\kappa_{\perp}$, and $\kappa_{\parallel}$ of the interacting electronic states [117]. The results of this model are presented in Table 6. On the whole, the agreement is between experiment and prediction is reasonable with the greatest discrepancies occurring because of vibronic interactions in the $B$ state.

### K. Monoalkylamides, MNHR

The preparation and low-resolution spectra of a few calcium and strontium alkylamines were reported in 1987 [118]. By replacing NH$_3$ with monoalkylamines, NH$_3$R (R = CH$_3$, C$_2$H$_5$, CH(CH$_3$)$_2$, or C(CH$_3$)$_3$) in a vacuum oven, the laser-induced fluorescence spectra of the $A^2 \Sigma^+ - X^2 \Pi$ transitions were recorded. There was a strong similarity with the spectra of CaNH$_3$ [117], although the symmetry is lower than $C_s$ for the monoalkylamide derivatives.

![Figure 29. Laser excitation spectra of the $A^2 \Sigma^+ - X^2 \Pi$ transitions of the strontium monoalkylamides. (Reprinted with permission from ref 118. Copyright 1987 American Chemical Society.)](image-url)
L. Monomethylhy, MCH$_3$

The monomethyl derivatives are prototypical metal alkyl molecules, which can be made by the reactions of various methylating agents such as CH$_3$—Li, CH$_3$Hg, CH$_3$Sn, and CH$_3$CN with excited Mg, Ca, or Sr atoms. The low-resolution spectra of the $2\pi^*\rightarrow\pi^*$ and $1\pi^*\rightarrow\pi^*$ transitions of CaCH$_3$ and SrCH$_3$ were published by Brixner and Bernath [119] in 1967. These molecules have $C_3$ symmetry so that the electronic structure is similar to CaF (Fig. 7) but because of the reduction in symmetry the states are renamed $^1\Pi\rightarrow^1\Sigma^+$ and $^1\Sigma^+\rightarrow^1\Sigma^+$. In this early work, upper limits for the metal–ligand dissociation energies of 46 and 43 kcal mol$^{-1}$ for CaCH$_3$, and SrCH$_3$, respectively, were estimated from the offset of predissociation [119].

In view of the relatively weak metal–methyl bond, a measurement of the bond length would be useful. The $^2\Pi\rightarrow^2\Sigma^*$ transition of CaCH$_3$ was rotationally analyzed and the ground-state $r_g$ Ca–C bond length of 2.349 Å and $\theta$ C–H–C angle of 105.6° (with $r_c$, $r_e$ fixed to 1.10 Å) were extracted [120]. The calculations of Ortiz [54] gave $r_{e}$, $r_{c}$ = 2.388 Å, $\theta_{	ext{CHC}}$ = 105.9°, and $\theta_{C\text{CH}}$ = 107.0 Å. In Table 7, the experimental and predicted ground-state vibrational frequencies of CaCH$_3$ are compared. Tjerman et al. [112] calculated the ground-state properties of MCH, MCH$_3$, and MCH$_4$, for the lighter alkali and alkaline earth metals. The Arizona State University group recorded the millimeter wave spectra of MgCH$_3$, [122], CaCH$_3$, [123], SrCH$_3$, [124], and BaCH$_3$.

The MgCH$_3$ $^2\Pi\rightarrow^2\Sigma^*$ spectrum was analyzed in a laser ablation molecular beam spectrometer [125]. It was noted in this article that the $\omega_{\text{H}}$ spin–rotation parameter in the $^4\Sigma^+$ state for CaCH$_3$ [120] seemed to have an anomalous sign when compared to the values obtained for MgCH$_3$, ZnCH$_3$, and CaCH$_3$. In fact, the original assignment of the excited state $\lambda$ values by Brixner and Bernath [120] was not correct because they did not see the first rotational lines of the branches. A reassessment of the $^2\Pi\rightarrow^2\Sigma^*$ transition of CaCH$_3$ by Marr et al. [126] using data from a molecular beam spectrometer corrected this problem and yielded a dipole moment of 2.62 D in the ground state. The power of the molecular beam method is illustrated clearly by this example.

TABLE 7  Experimental and Calculated Frequencies of CaCH$_3$ (in cm$^{-1}$)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Observed Value*</th>
<th>Calculated Value$^a$</th>
<th>Calculated Value$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$ (a$_1$) sym C–H str</td>
<td>1085</td>
<td>3023</td>
<td>3020</td>
</tr>
<tr>
<td>$v_2$ (a$_2$) sym C–H bend</td>
<td>1203</td>
<td>425</td>
<td>417</td>
</tr>
<tr>
<td>$v_3$ (a$_3$) C–C–C str</td>
<td>1483</td>
<td>385</td>
<td>366</td>
</tr>
<tr>
<td>$v_8$ (a$_8$) C–C–H str</td>
<td>1445</td>
<td>385</td>
<td>366</td>
</tr>
</tbody>
</table>

$^a$Reference 119.

$^b$Reference 97.

$^c$Reference 121.

TABLE 8  Ground-State Vibrational Frequencies of the CaCCH$_3$ Molecule (in cm$^{-1}$)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Experimental$^*$</th>
<th>Calculated$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$ (e) C–H str</td>
<td>3007</td>
<td>3007</td>
</tr>
<tr>
<td>$v_1$ (e) C–C–C str</td>
<td>2466</td>
<td>2466</td>
</tr>
<tr>
<td>$v_2$ (e) C–C–C str</td>
<td>385</td>
<td>385</td>
</tr>
<tr>
<td>$v_3$ (e) C–C–H str</td>
<td>701</td>
<td>701</td>
</tr>
</tbody>
</table>

$^a$Reference 127.

$^b$Reference 97.
The sandwich complexes are among the most celebrated molecules in organometallic chemistry. The discovery of the structure of the ferrocene molecule, Fe(C₅H₅)₂, by Wilkinson was rewarded with a Nobel prize. The possibility of making half-sandwich complexes in the gas phase was very enticing and, inspired by a report of a metal vapor synthesis of magnesium, Mg(C₅H₅)₂, we looked for CaC₅H₅ and SrC₅H₅ in a Brosda oven [116]. The reaction of laser excited metal atoms with the cyclopentadienide precursor C₅H₅ resulted in the low-resolution spectra of the A′1E1−X′1A₁ and B′2A₁−X′1A₁ transitions of CaC₅H₅ and SrC₅H₅.

The half-sandwich complexes have C₅ᵥ symmetry and the states are labeled in a similar way as for the metal monomethylenes of C₅H₅. The spectra recorded by the Miller group [117, 118] for jet-cooled CaC₅H₅ allow a much improved vibrational analysis. Ultimately, in a spectroscopic tour-de-force, the A′1E1−X′1A₁ transition of CaC₅H₅ (Fig. 30) was rotationally analyzed and the Ca−ring distance of 2.333 Å was determined [119]. The metal−ring distance is very close to the Ca−C bond distance in the CaCH₃ and CaCCH molecules.

O. Monomethylcyclopentadienides, C₅H₅CH₃

The first detection of a derivative of the monomethyuesubstituted ligand C₅H₅CH₃ was carried out by Robben et al. [138] at Ohio State University. The substitution of a methyl group for an H atom on the ring lowers the symmetry to C₅v from C₅ᵥ and lifts the double degeneracy in the 1E state (cf. Fig. 7). The A’ and A” components that correlate to the 1E state of CaC₅H₅ are split by 100 cm⁻¹. The torsional splittings of the CH₃ group were also analyzed in the molecular beam experiment.
P. Monopyrrolates, MC₅H₅N

The isoelectronic analogy again proves to be very useful when the CH group of the C₅H₅ ligand is replaced by N to give the C₅H₅N⁻ ligand. Laser excited Ca and Sr atoms reacted with the pyrrole C₅H₅N precursor in a Broida oven to give CaC₅H₅N and SrC₅H₅N [140]. The strong similarity between the monopyrrolates and monocyclopentadienides led us to conclude that CaC₅H₅N and SrC₅H₅N were both half-sandwich complexes.

Figure 31. The laser excitation spectrum of the A, B, C, and D transitions of jet-cooled CaC₅H₅N. [Reprinted with permission from ref. 138. Copyright 1992 American Chemical Society]

Although this geometric structure turned out to be correct, there were problems with interpretation of the electronic structure in this early work. Once again, it was jet cooling of CaC₅H₅N that clarified the problem [138]. The higher resolution spectra recorded in the Miller group did show that the ligand had π binding but that the lower C₅ symmetry of CaC₅H₅N split the degenerate A²E state of CaC₅H₅ into two states. The 68 cm⁻¹ splitting (Fig. 31) between these two electronic states of CaC₅H₅N was accidentally close to the expected spin–orbit splitting in a A²E state and caused the confusion in the early work. A thorough vibrational analysis, made possible by the sharp bands in the cold spectrum, proved that the observed 68 cm⁻¹ splitting was not a spin–orbit interval in the CaC₅H₅N molecule.

The MgC₅H₅, Mg₂C₅H₅, and Mg₂C₅H₅N molecules have also been synthesized in a pulsed jet source and their spectra analyzed [141]. The A²E₁ state in MgC₅H₅ is very peculiar since it has no observable spin–orbit splitting. Unlike the metal-centered A²E states of the other molecules (e.g., CaC₅H₅ [56]) in MgC₅H₅, the unpaired electron is located on the C₅H₅ ring. In this case, the A²E₁ → A²E₂ transition is a transition metal-to-ligand charge-transfer transition.

Q. Monoborohydrides, MBH₄

The CaBH₄ molecule completes the isoelectronic CaF, CaOH, CaNH₂, and CaCH3 series of molecules. The Ca and Sr vapors react spontaneously with

CaBH₄ Configurations

Figure 32. Three possible structures for the CaBH₄ molecule. The tridentate structure has the lowest energy. [Reprinted with permission from ref. 142. Copyright 1990 American Chemical Society]
diborate, $\text{B}_2\text{H}_6$, to give $\text{CaBH}_4$ and $\text{SrBH}_4$. So far, there has been only one experimental paper written about these molecules [14]. The low-resolution laser-induced fluorescence spectra suggest that $\text{CaBH}_4$ and $\text{SrBH}_4$ have $\text{C}_3\text{v}$ symmetry with the metal atom bonding to the face of the $\text{BH}_4^{-}$ tetrahedron (Fig. 32). In addition, the $E$ and $A_1$ states seem to be switched compared to $\text{CaF}$ (Fig. 7) so that one detects $\Delta \Delta E$, $\Delta A_1$, and $\Delta E$-$\Delta E$ electronic transitions. The ab initio calculations of Orrit [35] are in general agreement with our observations (although not in the ordering of the states) but more experimental work is necessary.

VI. CONCLUSIONS

The alkaline earth metals form a host of unique monovalent free radicals. Most of these molecules can be formed by the laser-driven chemical reactions of metal vapors with a wide variety of organic and inorganic molecules. This photochemical production of new molecules has led to an extensive gas-phase inorganic chemistry and spectroscopy of alkaline earth derivatives. In recent years, the Iodine source has been displaced by the pulsed molecular beam spectrometer. The chemical dynamics and photochemistry of these new molecules are still at a very early stage of investigation.

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