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Volume 1 of *Advances in Photochemistry* appeared in 1963. The stated purpose of the series was to explore the frontiers of photochemistry through the medium of chapters written by pioneers who are experts. As editors we have solicited articles from scientists who have strong personal points of view, while encouraging critical discussions and evaluations of existing data. In no sense have the articles been simply literature surveys, although in some cases they may have also fulfilled that purpose.

In the introduction to Volume 1 of this series, the editors noted developments in a brief span of prior years that were important for progress in photochemistry: flash photolysis, nuclear magnetic resonance, and electron spin resonance. A quarter of a century later, in Volume 14 (1988), the editors noted that since then two developments had been of prime significance: the emergence of the laser from an esoteric possibility to an important light source; the evolution of computers to microcomputers in common laboratory use of data acquisition. These developments strongly influenced research on the dynamic behavior of excited state and other transients. We can look forward to significant developments to be included by the end of another quarter century.

With an increased sophistication in experiment and interpretation, photochemists have made substantial progress in achieving the fundamental objective of photochemistry: elucidation of the detailed history of a molecule that absorbs radiation. The scope of this objective is so broad and the systems to be studied are so many that there is little danger of exhausting
the subject. We hope that this series will reflect the frontiers of photochemistry as they develop in the future.

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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 found 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 at, for example, the active sites of enzymes. This new field of bioinorganic 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...
In the work of Lessen et al. [2], the vanadium ion ($V^+$) was created by laser vaporization and allowed to react with $\text{H}_2\text{O}$. The photodissociation of $\text{V}^+(\text{H}_2\text{O})$ 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 $\text{Mg}^+(\text{H}_2\text{O})$ [3] and $\text{Ca}^+(\text{H}_2\text{O})$ [4], while the Farrar group has looked at $\text{Sr}^+(\text{H}_2\text{O})$ and $\text{Sr}^+(\text{NH}_3)$ [5, 6]. These molecular ions are isoelectronic with the neutral molecules such as $\text{CaNH}_2$ and $\text{SrCH}_3$ that are discussed in this chapter.

Molecular ions such as $\text{Ca}^+(\text{H}_2\text{O})$ have relatively weak metal–ligand binding energies of about 25 kcal mol$^{-1}$ [7] compared to the stronger bond present in the isoelectronic $\text{CaNH}_2$ system. In $\text{Ca}^+(\text{H}_2\text{O})$, the $\text{H}_2\text{O}$ ligand perturbs the $\text{Ca}^+$ energy levels much less than the $\text{NH}_2^-$ ligand perturbs $\text{Ca}^+$ in the $\text{CaNH}_2$ molecule. The electrostatic interaction of $\text{NH}_2^-$ with $\text{Ca}^+$ is much stronger than the ion–dipole interaction of $\text{Ca}^+$ with $\text{H}_2\text{O}$, although the molecular symmetry ($C_{2v}$) is the same for $\text{CaNH}_2$ and $\text{Ca}^+(\text{OH}_2)$.

This chapter will cover the monovalent neutral polyatomic derivatives of the alkaline earth elements: $\text{Be}$, $\text{Mg}$, $\text{Ca}$, $\text{Sr}$, $\text{Ba}$, and $\text{Ra}$. 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 $\text{R-Mg-X}$ (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 $\text{Ca}$, $\text{Sr}$, and $\text{Ba}$ derivatives [8]. In contrast to this “normal” chemistry, the monovalent derivatives such as $\text{CaOH}$ are unstable in the solid state because they readily disproportionate:

$$2 \text{CaOH}(s) \rightarrow \text{Ca}(s) + \text{Ca(OH)}_2(s)$$

(1)

In fact, “proof” of the nonexistence of $\text{MgCl}(s)$ 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 $\text{CaOH}$ have strong bonds (dissociation energy, $D_{\text{Ca-O}} = 92$ kcal mol$^{-1}$) [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 $\text{Mg}$, $\text{Ca}$, $\text{Sr}$, and $\text{Ba}$. No monovalent polyatomic derivatives are known for the $\text{Be}$ or the $\text{Ra}$ members of the alkaline earth group, except for $\text{BeOH}$. There are two experimental reports on the $\text{BeOH}$ [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$^-\text{Ca}^{2+}\text{O}^-$. Perhaps the ultraviolet (UV) photochemical isomerization of CaOH in a rare gas matrix will yield HCaO.

The metal monohydroxides 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 caused by SrOH. The red colors of fireworks can also be attributed to 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 colors. 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 in astronomy. It has been speculated that the ablation of metals from meteors results in the formation of CaOH [19]. In chemical equilibrium calculations, Tsuji [20] predicted that CaOH should form in the atmospheres of cool oxygen-rich stars. Pesch [21] identified the CaOH molecule through absorption of the $\tilde{B}^{2}\Sigma^+-\tilde{X}^{2}\Sigma^+$ transition near 550 nm. Pettersen and Hawley [22] confirmed this identification using the $\tilde{A}^{2}\Pi-\tilde{X}^{2}\Sigma^+$ bands near 620 nm. The recent availability of microwave and millimeter wave spectra of MgOH [23] and CaOH [24] have resulted in unsuccessful 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 Ziurys [27] group to record the laboratory millimeter wave spectra of a large number of simple derivatives of Mg and Ca such as MgCCH and CaCH$_3$.

A review on the calcium- and strontium-containing polyatomic free radicals appeared in 1991 [28], 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 vibronic structure of the larger free radicals such as CaC$_2$H$_5$ and CaC$_4$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 hydroxide 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 earths 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.
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 monohydroxides and monoamides could be made readily in a flow reactor called a Broida oven [36]. The Broida oven is a relatively cool (~500 K), 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,

$$Ca + H_2O \rightarrow CaOH + H$$

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 $^3P_1$ electronic state, then the concentration of product molecules is dramatically increased,

$$\text{Ca}^* (^3P_1) + \text{H}_2\text{O} \rightarrow \text{CaOH} + \text{H},$$  \hspace{1cm} (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 CaC₂H₅ since ground-state Ca atoms will not react with the C₄H₆ 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 3P₁ 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

Figure 2. Experimental block diagram for Broida oven experiments in the Bernath laboratory. Two Ar ion lasers pump dye lasers that are used to make and to detect the free radicals in the oven. The laser-induced fluorescence is monitored with photomultiplier tubes (PMTs) mounted either directly on the oven or on the exit port of a monochromator (MONO). [Reprinted with permission from ref. 28. Copyright 1991 American Association for the Advancement of Science.]
through Brewster angle windows on the top or the side. The first laser (dye laser 1) is tuned to the $3P_1 - 1S_0$ atomic transition at 457.1, 657.3, 689.2 and, 791.1 nm for Mg, Ca, Sr, and Ba, respectively. This first laser is a typically operated broadband ($\sim 1$ cm$^{-1}$ line width) although an étalon is sometimes used to increase the spectral power density and the stability. The second laser (dye laser 2) can be operated broadband for survey work or in single longitudinal mode ($\sim 1$-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 ($\sim 1$ 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 spectroscopic experiments. In the first, both lasers are in resonance with atomic (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 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 CaCCH 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 CaCH$_3$. 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 CaC$_5$H$_5$ 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 Ziurys 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 torr⁻¹ 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 CaOH. 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
Figure 3. Block diagram of the millimeter wave spectrometer used by the Ziurys group. The instrument uses a phase locked Gunn oscillator as a source of radiation and an InSb detector. [Reprinted with permission from ref. 37. Copyright 1994 American Institute of Physics.]
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 (532 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 Steimle and co-workers have demonstrated in a series of beautiful experiments, this
Figure 5. A block diagram of the laser ablation, molecular beam spectrometer at the University of Waterloo. [Reprinted with permission from ref. 74. Copyright 1996 Academic Press.]
technique is very effective. The main drawback is that most of the laser photons are wasted because of the duty cycle mismatch between the pulsed molecular beam source and the CW laser.

An alternate approach used by the Miller group is to pulse amplify a CW dye laser. This approach degrades the laser resolution from about 1 MHz to about 200 MHz but results in a high-power pulsed laser beam with excellent mode quality. This high peak power and high spectral resolution results in excellent spectra with an improved S/N ratio. The only serious drawback of this scheme is the increased complexity and cost of the laser systems.

There is one additional choice that needs to be made in setting up a pulsed molecular beam spectrometer. The laser beam can cross the molecular jet close (~1 cm) to the pulsed valve, as implemented by the Miller group. This technique gives a relatively large signal, but there is often a fluorescent background from the laser-vaporized plume of metal atoms (high signal/high noise). In this case, it is useful to use filters or a monochromator to isolate the laser-induced fluorescence signal. The alternative approach is to skim the jet (with either a true skimmer or a large hole) in order to form a molecular beam and to cross the laser and molecular beams at some distance (~10 cm) from the pulsed valve (Fig. 5). This arrangement gives a much reduced signal since the molecular concentration is dropping rapidly during the expansion but the fluorescent background is nearly eliminated (low signal/low noise). This latter approach is advocated by the Steimle group.

The application of molecular beam technology has resulted in the detailed rotational analysis of numerous larger alkaline earth derivatives such as CaC$_5$H$_5$. From the rotational analysis (and the improved vibrational analysis), one can infer molecular structure. In addition, large electric fields can be easily applied to molecular beams in order to measure dipole moments through the Stark effect. Dipole moments provide information about charge distributions. The alkaline earth derivatives are a unique family of molecules because so much detailed information is available for them. These simple one metal—one ligand molecules are useful as models for more complex species found in inorganic chemistry and surface science.

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 H$_2$O and CH$_3$OH. In solution, the overall reaction

$$\text{Ca(s)} + 2\text{H}_2\text{O(\ell)} \rightarrow \text{Ca(OH)}_2(\text{s}) + \text{H}_2(\text{g})$$

(4)
is vigorous. In the gas phase, however, the elementary reaction

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

(5)

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 \( \tilde{B}^2\Sigma^+ \) and \( \tilde{A}^2\Pi \) states can be seen. What is the source of this extra energy?

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

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

(6)

is now exothermic by 17 kcal mol\(^{-1}\). Thus, the increased production of CaOH when Ca* is available is explained by the opening of the direct reaction channel (6). In a high-pressure CH\(_4\)/O\(_2\) flame, there is also considerable energy available and many free radicals such as OH can react with Ca,

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

(7)

in the presence of a third body. In a laser vaporization source, the plume of Ca atoms contains a large fraction of Ca* and Ca\(^+\), which readily react to give CaOH in the molecular beam. Thus in many cases the deliberate or inadvertent presence of 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 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**

\[ \text{Ca} + \text{H}_2\text{O} \overset{A^+}{\rightarrow} \text{HCaOH} \]  

(8)

\[ \text{HCaOH} + \text{Ca} \rightarrow \text{CaH} + \text{CaOH} \]  

(9)

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

(10)

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

(11)
Mechanism B

\[
\text{Ca} + \text{H}_2\text{O} \rightarrow \text{HCaOH} \quad (8)
\]

\[
\text{HCaOH} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{H}_2 \quad (12)
\]

\[
\text{Ca(OH)}_2 + \text{Ca} \rightarrow 2\text{CaOH} \quad (13)
\]

\[
2\text{Ca} + 2\text{H}_2\text{O} \rightarrow 2\text{CaOH} + \text{H}_2 \quad (11)
\]

In these reactions, other alkaline earths can be substituted for Ca and other oxidants such as CH$_3$OH or HC(O)OH, which contain the OH group, can be substituted for H$_2$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$_2$O were cocondensed in an argon matrix, a Ca(H$_2$O) complex formed. Upon irradiation of the matrix with light near the metal resonance lines, the Ca atom inserted into H$_2$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 HCaOH 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 Broida 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$_2$CH \[42\]. Curiously, CaH is not detected \[41\] when water or alcohols such as CH$_3$OH are used to make alkoxides such as CaOCH$_3$. 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 Broida 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