are not related. We do believe, however, that these two new transitions are to the 4d–5p strontium atomic orbitals, now of \( b_2 \) and \( b_3 \) symmetry, which correlate to the \( A_2 \) state of the metal monoalkoxides. The assignment of the symmetry of the \( b_2 \) and \( b_3 \) states is somewhat dubious, although we prefer \( B_2 \) and \( C_2 \) (rather than \( B_2 \) and \( C_2 \)). From crystal field arguments, the \( p \) orbital in-plane (\( b_3 \)) should be higher in energy than the \( p \) orbital out-of-plane (\( b_2 \)) due to the repulsion of the negative charge on the oxygen atoms. The observed splitting between the \( b_2 \) and \( b_3 \) states is, however, so small (<200 cm\(^{-1}\) from the strontium monoalkoxides) that other interactions may be more important. The corresponding splitting between the \( b_2 \) and \( b_3 \) states is unresolved for the calcium monoalkoxides.

This ordering of the in-plane and out-of-plane excited \( p \) orbitals of the alkaline-earth carboxylates (\( B_2 \) and \( C_2 \)) in contrast with that observed for the corresponding states of \( Sr\) and \( Ca\) (\( A_2 \) and \( B_2 \)) where the symmetry is known from a high-resolution rotational analysis of the \( A-X \) and \( B-X \) transitions.\(^1\) Note that for the carboxylates the negatively charged oxygen atoms point directly at the metal, while the partially positive hydrogens in the amides point away from the metal.

A definitive high-resolution analysis was attempted to determine the symmetry and molecular geometry of the metal carboxylates. However, the molecules proved to be too relaxed for any resonant laser-induced fluorescence to be observed, so a high-resolution analysis was impossible. This means that our assignment is based more on supposition than fact. Perhaps some ab initio calculations would help to clarify the problem.

Gas-Phase Chemistry of Alkaline-Earth Compounds

Little is known about the gas-phase chemistry of the larger polyatomic free radicals. Several studies performed by matrix isolation techniques provide some insight into the gas-phase reactions of these molecules. For example, in an argon matrix the reaction of an alkaline-earth atom with a water atom first produces the M–OH complex.\(^{35}\) Upon photolysis, the metal atom inserts between an oxygen–hydrogen bond to form \( H-M-OH \). On UV irradiation, \( H-M-OH \) dissociates to form \( MOH \).\(^{36}\)

The reaction between excited strontium (or calcium) can probably proceed directly in a single step:

\[ Sr^+ + HOOCR \rightarrow SrOOOCR + H \]  \hspace{1cm} (1)

However, ground-state \( Sr \) (or \( Ca \)) atoms are also found to react, although reaction 1 is probably endothermic in this case.

Another possible mechanism for the formation of alkaline-earth monocarboxylates is

\[ Sr + H-O-C--R \rightarrow SrH + H_2 \]  \hspace{1cm} (2)

This mechanism accounts for our observation of substantial amounts of \( SrH \) in the oven. Surface and metal cluster reactions are also possible. It is also clear whether the observed \( SrOH \) (and \( CaOH \)) comes from \( H_2O \) impurity or from a chemical reaction with the carboxylic acid. The study of the reactions of alkaline-earth vapors with carboxylic acids under molecular beam conditions would be very fruitful.

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Gas-Phase Inorganic Chemistry: Laser Spectroscopy of Calcium and Strontium Monoformamidates

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The reaction products of calcium and strontium metal vapors with formamide were studied by using laser spectroscopic techniques. Three electronic transitions were observed for the resulting metal monoformamidates, \( MNHCO \). The formamidate ligand is probably bonding to the metal in a bidentate manner. The metal–ligand stretching vibrational frequencies were assigned from the low-resolution spectra.

Introduction

In our laboratory, we have investigated the spectra of alkaline earth metal containing free radicals including metal monoalkoxides,\(^1\)\(^{2}\) monothiolates,\(^3\) isocyanates,\(^4\) cyclopentadienides,\(^5\) monoalkylamides,\(^6\) monomethides,\(^7\) acetylides,\(^8\) azides,\(^9\) borohydrides,\(^10\) and carboxylates.\(^11,12\) All these free radicals have a single metal–ligand bond (monodentate bonding) except for the carboxylates which are forming bidentate bonds.\(^12\)

Although the formate anion (\( HCOO^- \)) is a commonly encountered ligand in transition-metal chemistry, the chemistry of the isoelectronic formamidate anion (\( HCONH^- \)) has hardly been explored.\(^13\) A few workers have explored the substitution of formate ligands by amidato ligands in, for example, \( R_2(ONH)\)
carrier gas. The pressure of formamide vapor inside the oven, argon gas was used for our experiments. Since analytical grade formamide contains undesirable impurities such as NH₃, spectrometric grade (99+%) formamide (Aldrich) was bubbled through the glass cell containing formamide. The metal was resistively heated in an alumina crucible and the vapor entrained in 1.5 Torr of argon carrier gas.

Formamide has a very low vapor pressure at room temperature (1 Torr at 70 °C). Therefore, to provide a sufficient partial pressure of formamide vapor inside the oven, argon gas was bubbled through the glass cell containing formamide. The total pressure inside the oven was maintained at approximately 3 Torr. Since analytical grade formamide contains undesirable impurities such as NH₃, spectrometric grade (99+%) formamide (Aldrich) was used for our experiments.

Two CW broad-band (1-cm⁻¹) dye lasers pumped by a 5.5-W all-lines output of a Coherent Innova 70 argon ion laser were used in this experiment. One dye laser was tuned to excite the ⁵P₂ -S₀ atomic transition of Ca. Features at ~680 and ~645 nm are assigned to the 0-1 and 1-0 bands, respectively. Although not shown here, strong A₂A' -X₂A' emission was observed in this spectrum at ~706 nm (see text).

CCF₃₃₄.₁₄ We report here on the gas-phase calcium and strontium monoformamidates synthesized by the direct reaction between the metal vapor and formamide.

Experimental Section

The gas-phase alkaline-earth monoformamidates were prepared in a Broida type oven by the reaction of the metal (Ca, Sr) vapor with formamide (HCONH₂). The metal was resistively heated in an alumina crucible and the vapor entrained in 1.5 Torr of argon carrier gas.

Formamide has a very low vapor pressure at room temperature (1 Torr at 70 °C). Therefore, to provide a sufficient partial pressure of formamide vapor inside the oven, argon gas was bubbled through the glass cell containing formamide. The total pressure inside the oven was maintained at approximately 3 Torr. Since analytical grade formamide contains undesirable impurities such as NH₃, spectrometric grade (99+%) formamide (Aldrich) was used for our experiments.

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Table I: Band Origins of the Calcium and Strontium Monoformamidate Vibronic Transitions (in cm⁻¹)

<table>
<thead>
<tr>
<th>Band</th>
<th>CaNHCOH</th>
<th>SrNHCOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-0</td>
<td>14 859</td>
<td>13 624</td>
</tr>
<tr>
<td>1-0</td>
<td>14 509</td>
<td>13 351</td>
</tr>
<tr>
<td>0-0</td>
<td>14 154</td>
<td>13 077</td>
</tr>
<tr>
<td>0-1</td>
<td>13 803</td>
<td>12 789</td>
</tr>
<tr>
<td>0-2</td>
<td>13 457</td>
<td>12 501</td>
</tr>
<tr>
<td>0-3</td>
<td>13 108</td>
<td>12 222</td>
</tr>
</tbody>
</table>

results and Discussion

Three electronic transitions A₂A' -X₂A', B₂A' -X₂A' and Ĉ₂A' -X₂A' were observed in the excitation spectra of the metal monoformamidates. Figures 1 and 2 show parts of the resolved fluorescence spectra of the B₂A' -X₂A' transition of calcium and strontium monoformamidate molecules, respectively. To obtain these spectra, the dye laser exciting the molecular transition was tuned to the 0-0 band of the B₂A' -X₂A' transition, and the fluorescence dispersed with the monochromator. Emission from the excited electronic state to higher vibrational levels of the ground electronic state was observed in all of the resolved fluorescence spectra. The band origins of these vibronic transitions are given in Table I.

When the B₂A' -X₂A' transition of the metal monoformamidates was excited by the laser, relaxation to the Ĉ₂A' state was observed (Figure 2). In fact, strong A₂A' -X₂A' emission was observed in the spectra of both molecules when either the B₂A' -X₂A' or the Ĉ₂A' -X₂A' transition was excited by the laser. The formamidate anion (HCONH⁻) is isoelectronic with the formate (HCOO⁻) anion. The low-resolution spectra of calcium and strontium monoformates have been reported previously.₁₂

Similar to the formate anion, the formamidate anion could bond to the metal ion in a monodentate (to give molecule I or II) or bidentate (to give molecule III) manner. Although both types

\[
\begin{align*}
M - O - CHNH & \quad M - NH - COH \\
\text{I} & \quad \text{II} \\
& \quad \text{III}
\end{align*}
\]
of bonding result in a molecule in the C₃ point group, the nature of bonding will have a strong effect on the electronic spectra of the metal monoformamidates. If the bonding is monodentate, then the spectra of the M–NH–COH or M–O–CHNH (M = Ca, Sr) molecules will resemble those of the monoalkylamides⁶ or the monoalkoxides.² If the bonding is bidentate, the spectra of the metal monoformamidates correlates with the A state of the metal monoformates (Figure 3). Therefore, the three observed electronic transitions of the metal monoformamidates are assigned as A₁, A₂, and C₂. We have observed a similar switching of states in two other families of molecules we have studied previously: the metal borohydrides⁹ and the metal monoborohydrides. This was necessary because definitive high-resolution spectra are not available.

Boidyrev and co-workers¹⁸ have carried out ab initio calculations of the electronic transitions, any vibrational activity that is observed is also associated with the metal atom. We therefore assign the single observed Franck–Condon-active mode as a metal–ligand stretching vibration. The observation of progressions in the metal–ligand stretching mode suggests that there are significant changes in the metal–ligand bond lengths in the excited electronic states.

The electronic assignments of the metal monoformamidate spectra were based on qualitative arguments made by comparing the spectra of metal monoformamidates, monoformates, and monoborohydrides. This was necessary because definitive high-resolution spectra are not available.

Boidyrev and co-workers have carried out ab initio calculations of the molecular properties of LiBH₄. They find that the C₃₄ tridecane structure has the lowest energy on the potential surface. Similar ab initio calculations on metal monoformamidates and monoborohydrides would provide some additional insight into the structures of these molecules.

**Conclusion**

The gas-phase reaction between alkaline-earth metals and formamide produces the alkaline-earth monoformamidate free radicals. Three electronic transitions (A₁, A₂, C₂) were observed at low resolution. Comparison of the spectra with those of the alkaline-earth monoborohydrides and monofomates enables us to conclude that the formamide ligand bonds to the metal in a bidentate fashion.

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