are not related. We do believe, however, that these two new transitions are to the 4d-5p strontium atomic orbitals, now of b_1 and b_2 symmetry, which correlate to the $\tilde{A}^2\Pi$ state of the metal monoalkoxides. The assignment of the symmetry of the $\tilde{B}$ and $\tilde{C}$ states is somewhat dubious, although we prefer $\tilde{B}^2B_1$ and $\tilde{C}^2B_2$ (rather than $\tilde{B}^2B_2$ and $\tilde{C}^2B_1$). From crystal field arguments, the p orbital in-plane (b_2) should be higher in energy than the p orbital out-of-plane (b_1) due to the repulsion of the negative charge on the oxygen atoms. The observed splitting between the $\tilde{B}$ and $\tilde{C}$ states is, however, so small (<200 cm^{-1} from the strontium carboxylates) that other interactions may be more important. The corresponding splitting between the $\tilde{B}$ and $\tilde{C}$ states is unresolved for the calcium monocarboxylates.

This ordering of the in-plane and out-of-plane excited p orbitals of the alkaline-earth carboxylates ($\tilde{B}^2B_1$ and $\tilde{C}^2B_2$) is in contrast with that observed for the corresponding states of $SrNH_2$ ($\tilde{A}^2B_2$ and $\tilde{B}^2B_1$) where the symmetry is known from a high-resolution rotational analysis of the $\tilde{A}$-$\tilde{X}$ and $\tilde{B}$-$\tilde{X}$ transitions.[3] 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 carboxylate states. 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 assignments are based more on supposition than fact. Perhaps some ab initio calculations would help to clarify the problem.

Gas-Phase Chemistry of Alkaline-Earth Compounds

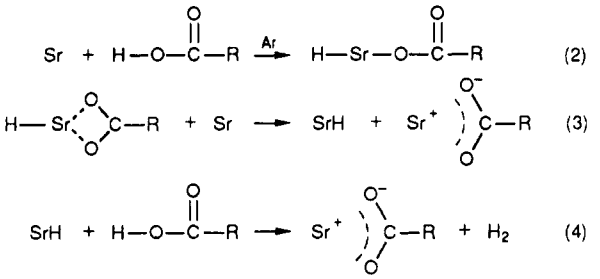
Little is known about the gas-phase chemistry of the larger polyatomic free radicals. Several studies performed by matrix isolation techniques provide some insight into the gas-phase reactions of these molecules. For example, in an argon matrix the reaction of an alkaline-earth atom with a water atom first produces the $M-OH_2$ complex.[36] 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:

$$Sr^* + HOOCR \rightarrow SrOOCR + H \quad (1)$$

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



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 not 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

A. M. R. P. Bopegedera,† W. T. M. L. Fernando, and P. F. Bernath*,‡

Department of Chemistry, University of Arizona, Tucson, Arizona 85721 *(Received: October 10, 1989)*

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, MNHCOH. 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 metal borohydrides and carboxylates. The borohydride ligand bonds to the metal in a tridentate fashion[10] while the carboxylate ligand bonds in a bidentate fashion.[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, $Rh_2(ONH-$

† Current address: NOAA, ERL, R/E/AL2, 325 Broadway, Boulder, CO 80303.
‡ Alfred P. Sloan Fellow; Camille and Henry Dreyfus Teacher-Scholar.
* To whom correspondence should be addressed.

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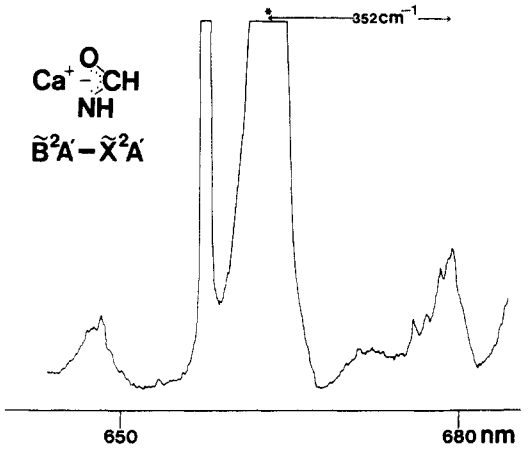


Figure 1. Resolved fluorescence spectrum of the $\tilde{B}^2A'-\tilde{X}^2A'$ transition of calcium monoformamidate. The asterisk marks the position of the laser, which is tuned to the 0–0 band. The strong feature to the blue of the asterisk is the $^3P_1-^1S_0$ atomic transition of Ca. Features at ≈680 and ≈645 nm are assigned to the 0–1 and 1–0 bands, respectively. Although not shown here, strong $\tilde{A}^2A'-\tilde{X}^2A'$ emission was observed in this spectrum at ≈706 nm (see text).

$CCF_3)_4$.[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[15] by the reaction of the metal (Ca, Sr) vapor with formamide ($HCONH_2$). 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).[16] 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 NH_3, 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 $^3P_1-^1S_0$ atomic transition of the metal (6573 Å for Ca and 6892 Å for Sr). The second dye laser was used to excite the molecular transitions of the calcium and strontium monoformamidates. Several laser dyes (DCM, Pyridine 2, and Rhodamine 6G) were required to cover the desired spectral region.

Two types of spectra were recorded. Laser excitation spectra were recorded by scanning the wavelength of the laser that was exciting the molecular transition. The beam from this laser was chopped and the signal demodulated with a lock-in amplifier. Red pass filters (Schott RG9, RG780, and RG830), were used to block the scattered laser light. A photomultiplier–filter combination was used to detect the total fluorescence from the excited electronic states.

Resolved fluorescence spectra were recorded by tuning the wavelength of the second dye laser to a molecular transition and dispersing the fluorescence through a small monochromator equipped with photon counting detection electronics.

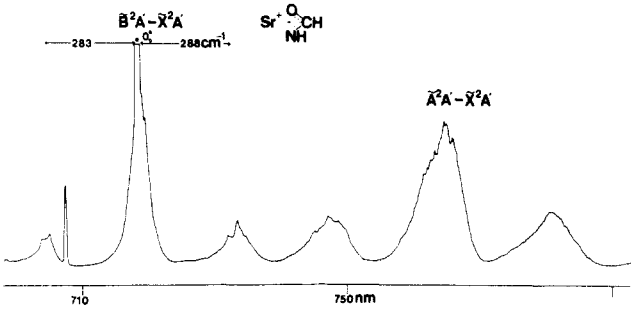


Figure 2. Resolved fluorescence spectrum of the $\tilde{B}^2A'-\tilde{X}^2A'$ transition of strontium monoformamide. The asterisk marks the position of the laser, which is tuned to the 0–0 band. Strong $\tilde{A}^2A'-\tilde{X}^2A'$ emission can also be seen to the red (see text). The features at ≈705, ≈735, and ≈745 nm are assigned to the 1–0, 0–1, and 0–2 vibronic bands, respectively. The feature at ≈780 nm is the 0–1 band of the $\tilde{A}^2A'-\tilde{X}^2A'$ transition.

TABLE I: Band Origins of the Calcium and Strontium Monoformamidate Vibronic Transitions (in cm^{-1})

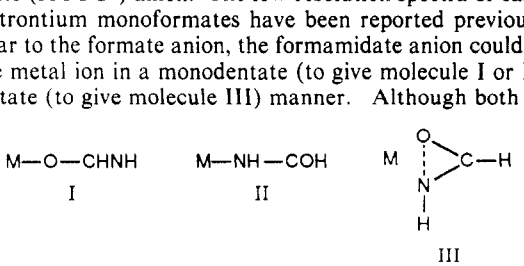
band	CaNHCOH	SrNHCOH
	$\tilde{A}^2A'-\tilde{X}^2A'$	
2–0	14859	13624
1–0	14509	13351
0–0	14154	13077
0–1	13803	12789
0–2	13457	12501
0–3	13108	12222
	$\tilde{B}^2A'-\tilde{X}^2A'$	
1–0	15440	14201
0–0	15083	13917
0–1	14727	13630
0–2		13389
	$\tilde{C}^2A''-\tilde{X}^2A'$	
2–0		15205
1–0	16601	14895
0–0	16248	14580
0–1	15896	14296

Results and Discussion

Three electronic transitions $\tilde{A}^2A'-\tilde{X}^2A'$, $\tilde{B}^2A'-\tilde{X}^2A'$ and $\tilde{C}^2A''-\tilde{X}^2A'$ were observed in the excitation spectra of the metal monoformamidates. Figures 1 and 2 show parts of the resolved fluorescence spectra of the $\tilde{B}^2A'-\tilde{X}^2A'$ 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 $\tilde{B}^2A'-\tilde{X}^2A'$ 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 $\tilde{B}^2A'-\tilde{X}^2A'$ transition of the metal monoformamidates was excited by the laser, relaxation to the $\tilde{A}^2A'$ state was observed (Figure 2). In fact, strong $\tilde{A}^2A'-\tilde{X}^2A'$ emission was observed in the spectra of both molecules when either the $\tilde{B}^2A'-\tilde{X}^2A'$ or the $\tilde{C}^2A''-\tilde{X}^2A'$ 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



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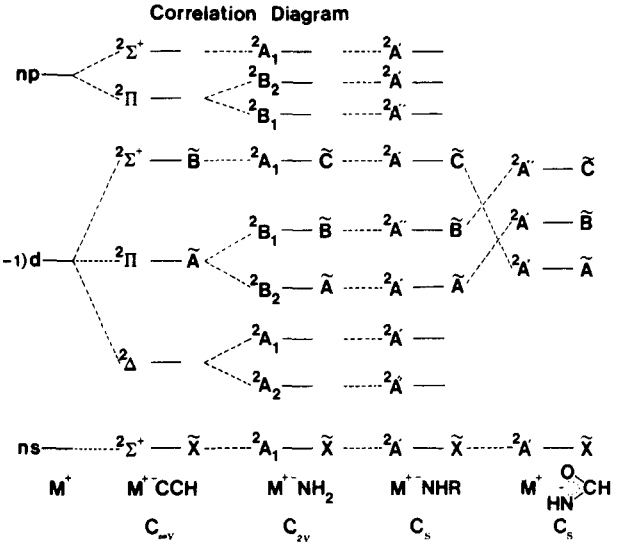

Figure 3. Correlation diagram for Ca^+ and Sr^+ with CCH^- ($C_{\infty v}$), NH_2^- (C_{2v}), NHR^- (C_s, monodentate) and $HCONH^-$ (C_s, bidentate) ligands. Note that in our previous paper on calcium and strontium monoalkylamides (ref 6) the corresponding figure (Figure 4) is in error. The out-of-plane B_1 states correlate with A″ states while the in-plane B_2 states correlate with A′.

of bonding result in a molecule in the C_s 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 monoalkylamides[6] or the monoalkoxides.[2] If the bonding is bidentate, the spectra of molecule III will resemble those of the isoelectronic metal monoformates.[12] A close look at the spectra of the metal monoformamidates reveals considerable similarity with those of the metal monoformates, suggesting that the formamidate anion is a bidentate ligand.

The metal monoformamidates are ionic molecules represented by the structure M^+HNCOH^-, where the $HCONH^-$ ligand is closed shell. Therefore, the molecular orbitals of the metal monoformamides can be described as the orbitals of the M^+ ion perturbed by the $HCONH^-$ ligand in the C_s point group. The correlation diagram in Figure 3 is helpful to describe these molecular orbitals and the electronic structure of CaNHCOH and SrNHCOH.

The valence ns (n = 4 for Ca, n = 5 for Sr) orbital of the M^+ ion contains one unpaired electron. This results in a $^2\Sigma^+$ ground state for the linear ($C_{\infty v}$) MCCH molecule. In the C_s point group, this transforms to a $^2A'$ state (Figure 3). The 5-fold degeneracy of the $(n-1)$d orbitals is lifted in the $C_{\infty v}$ point group, giving rise to δ ($d_{x^2-y^2}$, d_{xy}), π (d_{xz}, d_{yz}), and σ (d_{z^2}) orbitals. Similarly, the 3-fold degenerate np orbitals split into π (p_x, p_y) and σ (p_z) orbitals in the $C_{\infty v}$ point group. In addition, the presence of the linear ligand mixes $d\pi$ with $p\pi$ and $d\sigma$ with $p\sigma$ so that these orbitals are now $d\pi$–$p\pi$ and $d\sigma$–$p\sigma$ mixtures. Transition to the $^2\Delta$ state ($d_{x^2-y^2}$, d_{xy} orbitals) from the $^2\Sigma^+$ ground state is forbidden. Consequently, in the $C_{\infty v}$ point group the first allowed electronic transition is from the $\tilde{X}^2\Sigma^+$ ground state to the $\tilde{A}^2\Pi$ state.

When the symmetry is reduced to C_{2v} (as in metal monoamides), the degeneracy of the δ and π orbitals is lifted, giving rise to a_1, a_2 ($d_{x^2-y^2}$, d_{xy}) and b_2, b_1 (mixture of d_{yz} and p_y, d_{xz} and p_x) orbitals, respectively. The corresponding electronic states are given in Figure 3. Note that the x-axis is out of plane. The relative ordering of the $\tilde{A}^2B_2$ and $\tilde{B}^2B_1$ states was determined experimentally[17] for $SrNH_2$. Although transitions are allowed from the ground $^2A_1$ state to all the other states in the C_{2v} point group, except to the $^2A_2$ state, a transition was not observed to the low-lying $^2A_1$ state in any of the Ca- and Sr-containing molecules that we studied. When a H atom of a metal monoamide is replaced by an alkyl group to obtain the metal monoalkylamides, the symmetry is reduced from C_{2v} to C_s. The relative ordering of the $\tilde{A}^2A'$, $\tilde{B}^2A''$, and $\tilde{C}^2A'$ states of the metal monoalkylamides is obtained by correlating to the C_{2v} point group.

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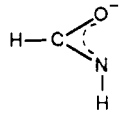
TABLE II: Vibrational Frequencies of Calcium and Strontium Monoformamidates (in cm^{-1})

state	CaNHCOH	SrNHCOH
$\tilde{X}^2A'$	351	288
$\tilde{A}^2A'$	355	278
$\tilde{B}^2A'$	357	284
$\tilde{C}^2A''$	353	315

Since the formamidate ligand bonds to the metal in a bidentate fashion, the nitrogen and the oxygen atoms on the anion



are partially negatively charged. We believe that these off-axis negative charges destabilize the metal orbitals that are perpendicular to the z axis (π orbitals) relative to the metal orbitals that are parallel to the z axis (σ orbitals). This has pronounced effects on the relative ordering of the electronic states in the metal monoformamidate. As a result of this, the $\tilde{A}$ and $\tilde{B}$ electronic states of the metal monoalkylamides correlate with the $\tilde{B}$ and $\tilde{C}$ states of the metal monoformamidates while the $\tilde{C}$ state of the monoalkylamides correlates with the $\tilde{A}$ state of the monoformamidates (Figure 3). Therefore, the three observed electronic transitions of the metal monoformamidates are assigned as $\tilde{A}^2A'$–$\tilde{X}^2A'$, $\tilde{B}^2A'$–$\tilde{X}^2A'$, and $\tilde{C}^2A''$–$\tilde{X}^2A'$. We have observed a similar switching of states in two other families of molecules we have studied previously: the metal borohydrides[10] and the metal monoformates.[12] The borohydride (BH_4^-) anion bonds in a tridentate fashion. In both these cases off-axis negative charges are present on the ligands.

The low-resolution electronic spectra enabled us to obtain vibrational frequencies for the metal monoformamidates which are reported in Table II. Since only metal-centered orbitals are involved in 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.

Boldyrev and co-workers[18] have carried out ab initio calculations of the molecular properties of $LiBH_4$. They find that the C_{3v} tridendate structure has the lowest energy on the potential surface. Similar ab initio calculations on metal monoformates and monoformamidates 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 ($\tilde{A}^2A'$–$\tilde{X}^2A'$, $\tilde{B}^2A'$–$\tilde{X}^2A'$, and $\tilde{C}^2A''$–$\tilde{X}^2A'$) were observed at low resolution. Comparison of the spectra with those of the alkaline-earth monoborohydrides and monoformates enables us to conclude that the formamide ligand bonds to the metal in a bidentate manner.

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