Figure 5. ESR powder patterns of AuO_2 simulated based on the **g** and Au hyperfine coupling tensors given in the text and increasingly larger quadrupole tensors symmetric about the z axis. The assumed P_z value (in MHz) is given at left.

tensor of AuC_2H_4 were redetermined corrected for the shift of the perpendicular signals by $3P_\parallel^2/(2A) \simeq 6.5$ G.

The electric field gradient eq at the nucleus due to an electron in a valence p_z orbital, for example, is given by $eq_{zz} = -2eq_{xx} =$

$-2eq_{yy} = (4/5)e\langle r^{-3}\rangle_p$, and if it is the only electron in the valence shell, the quadrupole coupling tensor in the form of eq 1 would be as follows.

$$P_z^0 = -2P_x^0 = -2P_y^0 = \frac{e^2Q}{2I(2I-1)} \frac{4}{5}\langle r^{-3}\rangle_p$$

Substituting the known quadrupole moment of the ^{197}Au nucleus $(0.59 \times 10^{-24} \text{ cm}^2)$ for Q and 5.19 au^{-3} for $\langle r^{-3}\rangle_{Au,6p}$ (the value estimated from the fine structure interval of Au atoms[15]) one obtains $P_z^0 = 96$ MHz.

Neglecting the shielding effect of the core electrons, the observed quadrupole tensors then indicate the electron population of ~1.0 in the Au p_x orbital of $AuC_2 H_4$ and ~0.5 in the Au p_z orbital in the case of AuO_2. Analysis of the hyperfine coupling tensor of AuC_2H_4 reported earlier showed the unpaired electron density of ~0.5 in the Au p_x orbital.[1] This is significantly less than that given from the analysis of the quadrupole tensor. The difference may be construed as an evidence for the dative interaction between the bonding π_x orbital and the vacant sp_x orbital of the Au atom.

In AuO_2 the unpaired electron is in the antibonding π_y* orbital and does not contribute to the electric field gradient at the Au nucleus. The dative interaction of the electrons in the bonding π_x orbital is more likely to involve the Au 6s orbital only as the latter is totally vacant in the $Au^+O_2^-$ situation. Back migration that would generate electric field gradient of consequence at the Au nucleus is that from the doubly occupied π_x* orbital of oxygen into the Au p_z orbital. The electron population of ~0.5 in the Au p_z orbital concluded in the anlysis of the quadrupole tensor indicates the extent of such migration.

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

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The calcium and strontium monocarboxylate free radicals were made by the gas-phase reaction of the metal vapors with carboxylic acids. Three electronic transitions, Ã–X̃, B̃–X̃, and C̃–X̃, were detected by laser-induced fluorescence. Metal–ligand stretching frequencies were derived from these low-resolution spectra. The carboxylate ligand binds in a bidentate manner to the metal.

Introduction

As part of a continuing study of gas-phase alkaline-earth-containing free radicals, we report here on the metal monocarboxylate derivatives. The laser-induced fluorescence spectra of calcium and strontium monoalkoxides,[1] monoalkylamides,[2,3] monoalkylthiolates,[4,5] monomethyl,[6] monoacetylide,[7,8] monoisocyanate,[9,10] monoazide,[11] monocyclopentadienide,[12] mono-

pyrrolate,[13] and monoformamidate[14] were all recorded in this laboratory. These new molecules were produced by the gas-phase

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reaction of calcium or strontium vapor with the corresponding organic oxidant (e.g., Ca + HN$_3$ → CaN$_3$ + H). In an earlier letter we reported our preliminary results on the observation of calcium and strontium monoformate and monoacetate.[15] Presented here are our complete results of this earlier study, plus our results for two larger metal monocarboxylates, calcium and strontium monopropanoate and monobutanoate.

The carboxylate ion, RCOO⁻, is a well-known ligand in transition-metal chemistry. It can bond in a monodentate (MOCOR), bidentate (MOOCR), or bridging (MOCROM) geometry.[16] The nature of the bonding is often determined by X-ray crystallography or by infrared spectroscopy of the two carbon–oxygen stretching vibrations. The metal–oxygen stretching vibrations are usually quite low in frequency (e.g., 100–480 cm⁻¹ for the rare-earth formates[17]), but scarcely any data are available for metal carboxylate compounds in the far-infrared region. Most previous infrared studies have focused on modes associated with the two carbon–oxygen bonds[18,19] to determine whether C=O double-bond character is present (relatively high vibrational frequency), which would indicate monodentate type bonding. Several far-infrared studies of metal formate crystals are available, but these are not isolated metal formates (e.g., anhydrous Ca(OOCH)$_2$ crystal has seven oxygen atoms less than 2.6 Å from a calcium atom[20]), and the metal–oxygen frequencies occur in the same spectral region as crystal lattice vibrations.[21]

Metal carboxylates are also well-known in surface chemistry, since formic and acetic acid strongly adsorb on many surfaces.[22] The surface metal atoms can cleave the O–H bond of the carboxylic acid, and the resulting carboxylate anion can bind to the surface in a monodentate, bidentate, or bridging structure.[23] In fact, the bonding geometry on a given surface can change depending on the surface temperature.[23] Electron energy loss spectroscopy (EELS) can be used to record the vibrational spectrum of the surface carboxylate, and the mode of bonding can usually be determined from the two C–O frequencies.[22] The metal–oxygen stretching frequencies of adsorbed formates on metal surfaces range from 280 cm⁻¹ for Ag(111) to 440 cm⁻¹ for Ni-(110).[24-29] The symmetric and asymmetric M–O frequencies were not resolved in these experiments.
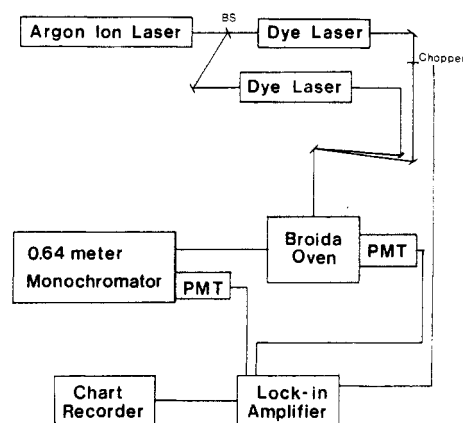

Figure 1. Experimental diagram for low-resolution laser spectroscopy.

Experimental Section

The alkaline-earth monocarboxylates were produced in a Broida-type oven[30] by the gas-phase reaction of the metal vapor (Ca or Sr) with the appropriate carboxylic acid. The metal was vaporized in a resistively heated alumina crucible, and the metal vapor was entrained in an argon flow. The acid vapor was added through an oxidant ring.

The laser beams are introduced into the oven through the top window and directed into the alumina crucible through the oxidant ring. The total pressure inside the Broida oven was typically 2 Torr, with a few milliTorr of oxidant. Since the vapor pressure of propionic and butanoic acid is quite low, a flow of argon was bubbled through the acid and injected into the Broida oven at the oxidant ring.

Two types of low-resolution (1-cm⁻¹) spectra were recorded: laser excitation spectra and resolved fluorescence spectra. Laser excitation spectra were normally recorded first to observe the molecular transitions. Resolved fluorescence spectra were then recorded to determine which transitions connect to the same excited state and to determine vibrational frequencies.

In some of our initial experiments on the reaction of strontium and acetone (in 1984), it was found that excitation of the strontium atoms greatly enhanced the production of the gas-phase product. This was discovered accidentally because a strontium atomic line was also coincident with a molecular transition. It was determined that excitation of the metal in this manner increased the molecular signal by as much as 3 orders of magnitude. Excitation of the $^3P_1$–$^1S_0$ alkaline-earth atomic transition was used in many of the recent experiments on the larger polyatomic free radicals.[1-14]

In our carboxylate experiment, two dye laser systems were usually used, one to drive the chemistry by providing excited metal atoms and a second to excite the molecular emission. The 5-W all-lines output of a Coherent Innova 90-4 argon ion laser was used to pump a Coherent 599-01 dye laser operated with DCM dye, which lases from 6150 to 7200 Å. The output from this dye laser was tuned to the $^3P_1$–$^1S_0$ Ca atomic transition at 6573 Å or to the corresponding Sr atomic transition at 6892 Å. A single thin etalon (from the intracavity assembly of a Coherent dye laser) was used inside the laser cavity for excitation of the Ca atomic line to narrow the line width and stabilize the excitation at 6573 Å.

A second low-resolution dye laser (Coherent 599-01) was used to obtain the laser-induced fluorescence spectra. This dye laser was operated with DCM or Pyridine 2 dyes. The two dye laser beams were spatially overlapped and focused into the Broida oven. Figure 1 is a block diagram of the experimental arrangement for the low-resolution laser spectra.

Low-resolution laser excitation spectra were recorded by scanning the broad-band laser (~1 cm⁻¹) while detecting the laser-induced fluorescence with the photomultiplier tube attached to the Broida oven. Laser excitation spectra are analogous to

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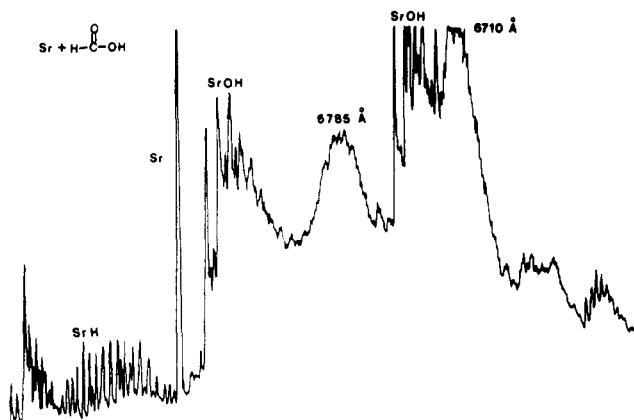
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Figure 2. Laser excitation spectrum of the strontium plus formic acid reaction products. SrH, SrOH, and SrOOCH are observed in this reaction.

classical absorption spectra. As the laser is scanned through a frequency resonant with a molecular transition, the molecule absorbs the radiation. The excited molecule fluoresces, and a signal is detected with the photomultiplier tube. A red pass filter (Schott glass filter RG9 for calcium carboxylates and RG780 for strontium carboxylates) was inserted before the photomultiplier tube to eliminate scattered laser light and the strong fluorescence of the alkaline-earth atomic line. The scanning laser was mechanically chopped, and lock-in detection was employed for recording the laser excitation spectra. This eliminates any chemiluminescent signal and cuts out the fluorescence from the atomic transitions (which is quite often coincident with a molecular metal carboxylate transition).

Low-resolution resolved fluorescence spectra were recorded by tuning the laser to a previously observed molecular transition and focusing the emission onto the slits of a 0.64-m monochromator. The intensity of the laser-induced fluorescence was recorded as a function of wavelength by scanning the monochromator. The emission was detected by a cooled photomultiplier tube (RCA C31034) operated in photon counting mode. Resolved fluorescence spectra yield information about vibrational levels in the ground state. The laser excites molecules to a particular vibrational level of an excited electronic state, and the excited molecules emit to a variety of ground-state vibrational levels depending on the selection rules and the Franck–Condon factors. Unfortunately, there is usually collisional relaxation in the excited states so considerable nonresonant emission is also present in the spectrum.

Results

The alkaline-earth monocarboxylates were produced by the gas-phase reaction of the metal vapor with formic, acetic, propionic, and butanoic acids. Three electronic transitions ($\tilde{A}$–$\tilde{X}$, $\tilde{B}$–$\tilde{X}$, and $\tilde{C}$–$\tilde{X}$) were found for these new molecules. This reaction produces the alkaline-earth monohydride and monohydroxide molecules as well as the alkaline-earth monocarboxylate, so the spectra were very congested.[15] Figure 2 shows a portion of the laser excitation spectrum of the strontium plus formic acid reaction. No filter or modulation was used to record this spectrum. The features due to SrH and SrOH are labeled, but three new peaks at 6785, 6710, and 7285 Å (not shown in Figure 2) were observed and assigned to the strontium monoformate radical, SrOOCH.

In Figure 3 the $\tilde{B}$–$\tilde{X}$ and $\tilde{C}$–$\tilde{X}$ laser excitation spectra of the strontium monocarboxylates are illustrated for comparison purposes. The spectra appear clearer compared with Figure 2, because a red pass filter (Schott glass RG 780) was used in recording these spectra. The red pass filter discriminates against fluorescence from SrH and SrOH because only fluorescence from the lower lying $\tilde{A}$ state in the metal carboxylates is observed. This happens because the lower lying $\tilde{A}$ state in the metal carboxylates is populated by collisional transfer from the $\tilde{B}$–$\tilde{X}$ and $\tilde{C}$–$\tilde{X}$ states. As the alkyl group lengthens, the $\tilde{B}$–$\tilde{X}$ and $\tilde{C}$–$\tilde{X}$ electronic
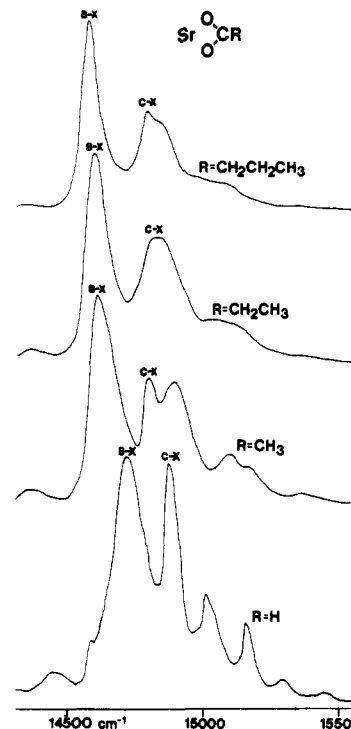
Figure 3. Laser excitation spectra of the $\tilde{B}$–$\tilde{X}$ and $\tilde{C}$–$\tilde{X}$ transitions of strontium monocarboxylates. From bottom to the top, the spectra are of strontium monoformate, strontium monoacetate, strontium monopropanoate, and strontium monobutanoate.

TABLE I: Observed Positions of the $\tilde{A}$–$\tilde{X}$, $\tilde{B}$–$\tilde{X}$, and $\tilde{C}$–$\tilde{X}$ Electronic Transitions of the Calcium and Strontium Monocarboxylates (in cm^{-1})[a]

molecule	$\tilde{A}^2A_1$–$\tilde{X}^2A_1$	$\tilde{B}^2B_2$–$\tilde{X}^2A_1$	$\tilde{C}^2B_1$–$\tilde{X}^2A_1$
CaOOCH	14 715	15 913[b]	15 913[b]
CaOOCCH$_3$	14 573	15 850[b]	15 850[b]
CaOOCCH$_2$CH$_3$	14 545	15 835[b]	15 835[b]
CaOOCCH$_2$CH$_2$CH$_3$	14 524	15 795[b]	15 795[b]
SrOOCH	13 624	14 749	14 903
SrOOCCH$_3$	13 500	14 643	14 832
SrOOCCH$_2$CH$_3$	13 500	14 620	14 857
SrOOCCH$_2$CH$_2$CH$_3$	13 459	14 609	14 841

[a]Uncertainty ~20 cm^{-1}. [b]$\tilde{B}$–$\tilde{X}$ and $\tilde{C}$–$\tilde{X}$ peaks were unresolved.

transition energies are slightly shifted to lower energy. The apparent relative intensity of the $\tilde{C}$–$\tilde{X}$ transition decreases as the alkyl group increases, perhaps because the rate of nonradiative processes is increasing. This effect has been observed in the alkaline-earth alkoxides,[1] alkylamides,[2] and alkylthiolates.[4] The electronic band origins of the $\tilde{A}$–$\tilde{X}$, $\tilde{B}$–$\tilde{X}$, and $\tilde{C}$–$\tilde{X}$ transitions of the calcium and strontium monocarboxylates are given in Table I.

The smaller peaks to higher energy shown in Figure 3 are vibronic transitions involving one or two quanta of the symmetric metal–ligand stretching vibration in the excited state. Since the electronic transition is metal-centered, only vibrations involving the metal atom have significant vibronic intensity. The metal–oxygen bending modes are probably so low in frequency (50–100 cm^{-1}) that they are hidden by the broad peaks in the spectra. As expected, the metal–ligand stretching frequency decreases as the alkyl group increases. Low-resolution resolved fluorescence spectra were recorded for these molecules by exciting an electronic transition and dispersing the emission with the monochromator (see Figures 1 and 4). Vibrational frequencies of the ground and excited states were obtained in this manner and are provided in Table II.

Discussion

The geometry of the calcium and strontium carboxylates is not immediately obvious from the low-resolution spectra. The car-
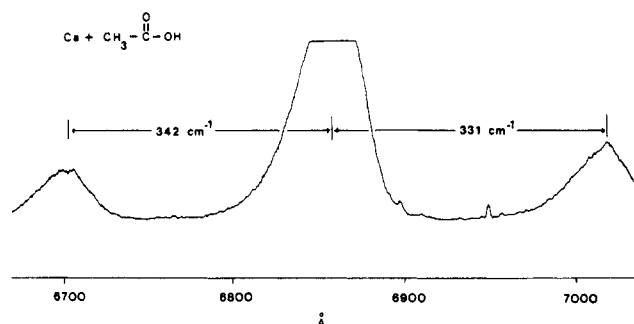
Figure 4. Resolved fluorescence spectrum of the $\tilde{A}$-$\tilde{X}$ transition of calcium monoacetate. The laser is exciting the $\tilde{A}$-$\tilde{X}$ 0-0 transition.

TABLE II: Vibrational Frequencies of the Symmetric Metal–Oxygen Stretching Vibrations of the Calcium and Strontium Monocarboxylates (in cm^{-1})^a

molecule	$\tilde{X}^2A_1$	$\tilde{A}^2A_1$	$\tilde{B}^2B_2$	$\tilde{C}^2B_1$
CaOOCH	349	356	354	354
CaOOCCH$_3$	332	347	341	341
CaOOCCH$_2$CH$_3$	315	360		
CaOOCCH$_2$CH$_2$CH$_3$	279	308		
SrOOCH	275	307	291	285
SrOOCCH$_3$	253	284	282	292
SrOOCCH$_2$CH$_3$	247	269	258	
SrOOCCH$_2$CH$_2$CH$_3$	219	251	271	

^{a} Uncertainty $\sim$10 cm^{-1}.

boxylate ligand can bind either in a bidentate fashion through both oxygen atoms equally or in a monodentate fashion where the bonding occurs through one oxygen. The alkaline-earth monoformate would thus have C_{2v} symmetry for a bidentate ligand and would have C_s symmetry if the ligand was binding in a monodentate fashion, similar to the calcium and strontium monoalkoxides studied earlier. Because of the many differences in the spectra of the alkaline-earth monocarboxylates and the alkaline-earth monoalkoxides, we believe the carboxylates are bonding in a bidentate fashion. Although there are no direct ab initio calculations to support this geometry, the simplest ionic monocarboxylate, LiOOCH, is predicted[31] to have C_{2v} symmetry.

Since high-resolution spectra are unavailable, the symmetries of the four observed electronic states $\tilde{X}$, $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ are unconfirmed. The bonding in these molecules is very ionic, and the one unpaired valence electron is localized in a metal-centered orbital.
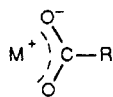
The electronic transitions arise from one-electron excitations to excited metal-centered orbitals. The presence of the carboxylate ligand lowers the symmetry of the atomic Ca$^+$ and Sr$^+$ orbitals. The metal–ligand interactions are well-characterized for the alkaline-earth monohalides and monohydroxides and other ligands with axial symmetry (Figure 5).

The energy level pattern for Ca$^+$ and Sr$^+$ perturbed by a low-symmetry ligand such as a carboxylate is more difficult to predict. The strong similarity between the MOOCR (M = Ca, Sr; R = H, CH$_3$, CH$_2$CH$_3$, CH$_2$CH$_2$CH$_3$) spectra (Figure 2) implies that the effective electronic symmetry is the same (C_{2v}) for the entire family. The alkyl side chains are distant from the unpaired electron on the metal so that although all of the carboxylates other than the formates have C_s symmetry, the "local" symmetry experienced by the metal orbitals is always approximately C_{2v}. A similar effect was found for the alkaline-earth monoalkoxides where the "local" symmetry at the metal center[1] was always approximately $C_{\infty v}$. The C_{2v} point group symbols will, therefore,

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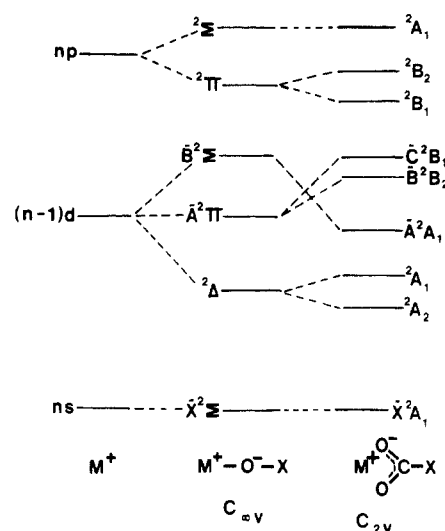
Figure 5. Correlation diagram of the valence orbitals of the alkaline-earth cations, M$^+$, the alkaline-earth monoalkoxides, and the alkaline-earth monocarboxylates.

be used to discuss the electronic states of the entire carboxylate family.

A correlation diagram (Figure 5) is helpful in interpreting the observed spectra. A linear or axial ligand only partially lifts the degeneracy of the M$^+$ (M = Ca or Sr) atomic orbitals while a low-symmetry ligand completely lifts this degeneracy. For example, in CaOH the 3d Ca$^+$ orbital gives the rise to $^2\Sigma$, $^2\Pi$, and $^2\Delta$ states, while in CaOOCH the $^2\Pi$ and $^2\Delta$ states are further split ("in-plane" and "out-of-plane" components) into $^2B_1$, $^2B_2$ and $^2A_1$, $^2A_2$ states. In addition, the ligand induces mixing among the atomic basis orbitals of the same symmetry so, for example, the $\tilde{A}^2\Pi$ state of CaOH is primarily a $p\pi$–$d\pi$ mixture of Ca$^+$ orbitals.

For the Ca and Sr derivatives, the location of the $^2\Delta$ state and the correcesponding $^2A_1$ and $^2A_2$ states is unknown. Although we previously assigned[15] the $\tilde{A}$ state as the $^2A_1$ component of the $^2\Delta$ state, we have reinterpreted our spectra and no longer believe this to be true. Only for BaH,[32] BaF,[33] BaCl,[34] and, presumably, other barium derivatives is the simple d-complex (B$^2\Sigma^+$, A$^2\Pi$, and A$'^2\Delta$) pattern of Figure 5 known to be valid.

Notice that we believe the ordering of the $\tilde{A}$ and $\tilde{B}$ states of the alkaline-earth monoalkoxides is "reversed" for the alkaline-earth monocarboxylates, so that the $\tilde{B}^2\Sigma^+$ state of the alkoxides correlates to the lowest excited $\tilde{A}^2A_1$ state of the carboxylates. This particular ordering of the states was quite unexpected, but it is also observed for the calcium and strontium formamidates (see following paper[14]) and the calcium and strontium borohydrides, CaBH$_4$ and SrBH$_4$.[35]

This unusual ordering of the excited $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ state energy levels is probably characteristic of ligands with charge distributed off the z axis. This off-axis charge destabilizes the nonbonding π-orbitals relative to the σ orbitals. In the linear case, the excited σ orbital is higher in energy than the π orbital since an electron in the σ orbital would be pointing directly toward the negatively charged ligand. For the carboxylate ligand, the negative charge is primarily located on the two off-axis oxygen atoms, thus stabilizing the excited a_1 orbital relative to the b_1 and b_2 pair of orbitals.

The splitting between the peaks at 6785 Å ($\tilde{B}$-$\tilde{X}$) and 6710 Å ($\tilde{C}$-$\tilde{X}$) in SrOOCH is 165 cm^{-1}. Although this splitting is reminiscent of the strontium spin–orbit splitting in the $\tilde{A}^2\Pi$ states of the strontium monoalkoxides ($\sim$260 cm^{-1}), these two splittings

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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:

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

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
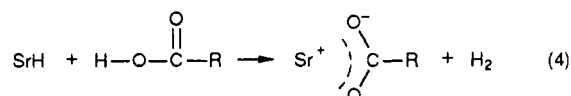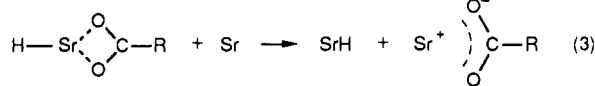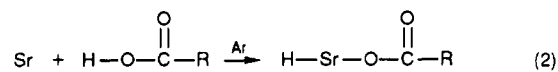
This mechanism accounts for our observation of substantial amounts of SrH in the oven. Surface and metal cluster reactions are also possible. It is also not clear whether the observed SrOH (and CaOH) comes from H$_2$O impurity or from a chemical reaction with the carboxylic acid. The study of the reactions 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, 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-

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