

Laser Spectroscopy of Strontium and Calcium Monoalkylamides

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The reaction of strontium and calcium vapors with primary amines was studied in the gas phase. These reactions produce the metal monoalkylamides CaNHR and SrNHR. The $\tilde{C}^2A_1(^2A')-\tilde{X}^2A_1(^2A')$, $\tilde{B}^2B_1(^2A'')-\tilde{X}^2A_1(^2A')$, and $\tilde{A}^2B_2(^2A')-\tilde{X}^2A_1(^2A')$ electronic transitions were observed by laser excitation spectroscopy. Some Ca-N and Sr-N stretching frequencies were assigned from the electronic transitions.

Introduction

Recently, we have explored the reactivity of Ca, Sr, and Ba vapors with a variety of organic molecules including alcohols,^{1,2} aldehydes and ketones,² carboxylic acids,¹ thioethers,³ HNCO,⁴ and C₂H₆.⁵ The reaction products are a variety of novel gas-phase free radicals containing one metal atom and one ligand. In this paper we report our work on the reactions of Ca and Sr with alkylamines to produce the monoalkylamides MNHR (R = H, CH₃, CH₂CH₃, CH(CH₃)₂, C(CH₃)₃).

The only previous work on gas-phase metal amides was carried out by D. O. Harris and co-workers. They rotationally analyzed the $\tilde{C}^2A_1-\tilde{X}^2A_1$ transition of CaNH₂⁶ and observed chemiluminescent emission from SrNH₂ and CaNH₂.⁷ We have recently analyzed the $\tilde{B}^2B_1-\tilde{X}^2A_1$ and $\tilde{A}^2B_2-\tilde{X}^2A_1$ transitions of SrNH₂.⁸

Gas-phase metal amide molecules have been explored through quantum chemical calculations of the structure of LiNH₂.⁹ The production of LiNH₂ was suspected in the photoinduced reaction of Li with NH₃ in a rare gas matrix.¹⁰ Finally, the reactions of metal ions with amines were studied by Babinec and Allison by ion cyclotron resonance.¹¹

There is a well-developed inorganic chemistry of solid-state metal amides.¹² Crystals of compounds such as LiNH₂, Mg(NH₂)₂, and Ca(N-Bu₂)₂ have been synthesized.¹²

Experimental Section

The monoalkylamides were prepared in a Broida-type oven¹³ by the reaction of Sr and Ca metal vapor with the appropriate primary amine (ammonia, monomethylamine, monoethylamine, isopropylamine, and *tert*-butylamine). The metal was vaporized from an electrically heated alumina crucible and entrained in argon carrier gas. The total pressure was approximately 1.5 Torr, with a partial pressure of a few milli-Torr of the amine.

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TABLE I: Band Centers of the Strontium Monoalkylamides (in cm⁻¹)

molecule	$\tilde{A}^2B_2(^2A'')$	$\tilde{B}^2B_1(^2A')$	$\tilde{C}^2A_1(^2A')$
SrNH ₂	14 274	14 724	15 862
SrNHCH ₃	14 170	14 688	<i>a</i>
SrNHC ₂ H ₅	14 166	14 641	15 867
SrNHCH(CH ₃) ₂	14 135	~14 623	~15 885
SrNHC(CH ₃) ₃	~14 130	~14 600 ^b	~15 895

^a Obscured by SrNH₂. ^b ±100 cm⁻¹, very wide peak.

TABLE II: Band Centers of the Calcium Monoalkylamides (in cm⁻¹)

molecule	$\tilde{A}^2B_2(^2A'')$	$\tilde{B}^2B_1(^2A')$	$\tilde{C}^2A_1(^2A')$
CaNH ₂	15 605	15 802	17 364
CaNHCH ₃	15 338	~15 690 ^a	<i>b</i>
CaNHC ₂ H ₅	15 320	~15 625 ^a	<i>b</i>
CaNHCH(CH ₃) ₂	15 298	~15 590	~17 499
CaNHC(CH ₃) ₃	15 242	~15 550	~17 497

^a Obscured by CaH. ^b Obscured by CaNH₂.

Two CW broad-band (1 cm⁻¹) dye lasers pumped by Coherent Innova 20 and Coherent Innova 90 argon ion lasers were used for the experiment. The dye lasers were operated with DCM and R6G dyes. One dye laser was used to excite the ³P₁-¹S₀ atomic transition of strontium (6892 Å) or calcium (6573 Å), while the wavelength of the second dye laser was scanned to record the laser excitation spectra of the metal monoalkylamides. For the excitation spectra, only the fluorescence to the red of both lasers was detected by a filter-photomultiplier combination. The laser resonant with the molecular electronic transition was chopped for lock-in detection.

The laser-induced fluorescence was also dispersed with a small monochromator, but these experiments were not very informative. Collisional and, possibly, intramolecular relaxation is sufficiently fast for these molecules that almost all of the fluorescence comes from the lowest excited state.

Results and Discussion

Portions of the laser excitation spectra of the SrNHR and CaNHR free radicals (R = H, CH₃, C₂H₅, *i*-C₃H₇, *t*-C₄H₉) are provided in Figures 1 and 2, respectively. Three electronic transitions were observed, $\tilde{A}^2B_2-\tilde{X}^2A_1$, $\tilde{B}^2B_1-\tilde{X}^2A_1$, and $\tilde{C}^2A_1-\tilde{X}^2A_1$, and the band centers are recorded in Tables I and II. The transitions are labeled with the irreducible representations of the C_{2v} point group, although the actual point group for the metal monoalkylamides is C_s. There is such a strong correspondence between the spectra of CaNH₂ (SrNH₂) and CaNHR (SrNHR) that this is useful. A similar correspondence was previously observed between the spectra of CaOH (SrOH) and CaOR (SrOR), so that the C_{∞v} point group was retained for the alkaline earth monoalkoxide molecules.²

The alkaline earth monoamide spectra resemble the corresponding monohydroxides. The $\tilde{B}^2\Sigma^+-\tilde{X}^2\Sigma^+$ transition of CaOH¹⁴ becomes the $\tilde{C}^2A_1-\tilde{X}^2A_1$ transition in CaNH₂, while the $\tilde{A}^2\Pi-$

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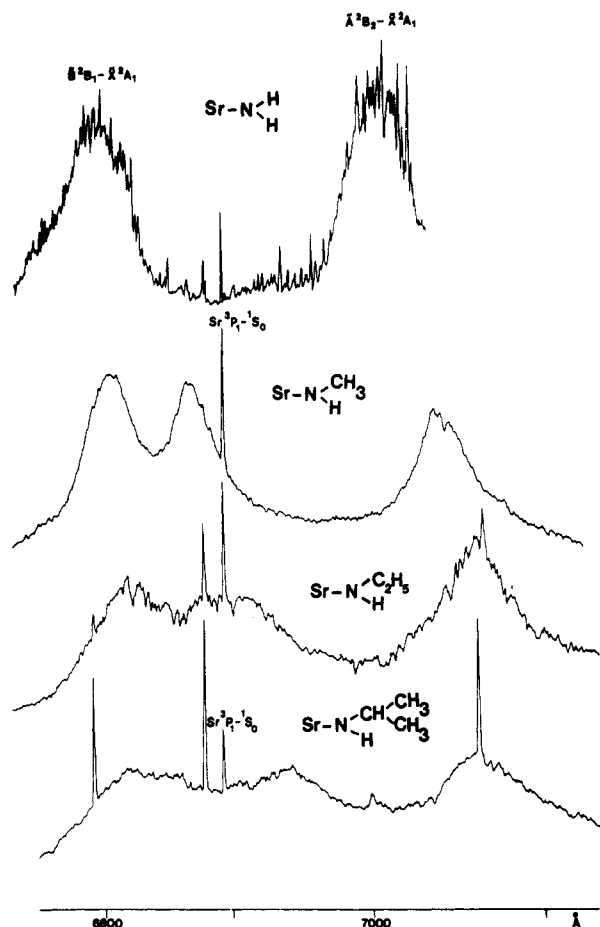


Figure 1. Excitation spectra of strontium monoalkylamides. The $\tilde{A}-\tilde{X}$ transition is on the right-hand side, and the $\tilde{B}-\tilde{X}$ is on the left-hand side. The strontium $^3P_1-^1S_0$ atomic transition (6892 Å) is marked. The central peak is assigned to the 1-0 vibronic band of the $\tilde{A}-\tilde{X}$ transition.

$\tilde{X}^2\Sigma^+$ ¹⁵ correlates to the $\tilde{A}^2B_2-\tilde{X}^2A_1$ and $\tilde{B}^2B_1-\tilde{X}^2A_1$ transitions of CaNH_2 (Figure 3).

The observed electronic states for the alkaline earth monoamides can be explained with the aid of the correlation diagrams in Figures 3 and 4. The alkaline earth monoalkylamides are ionic molecules well represented by the charge distributions Ca^+NHR^- and Sr^+NHR^- .

The valence ns , $(n-1)d$, and np atomic orbitals of the M^+ ion give rise to the electronic states shown in Figure 3 for the $C_{\infty v}$ point group (when the ligand is OH^-). The ligand also mixes the parent atomic orbitals of the states so that for the hydroxides the $\tilde{B}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states are $p\sigma-d\sigma$ and $p\pi-d\pi$ mixtures.¹⁶ The exact location of the $^2\Delta$ state and the higher lying $^2\Sigma^+$ and $^2\Pi$ states is unknown. When the symmetry is lowered to C_{2v} (ligand is NH_2^-), the in-plane p/d orbitals and the out-of-plane p/d orbitals are no longer degenerate. Therefore, the $\tilde{A}^2\Pi$ state splits into the \tilde{B}^2B_1 (out-of-plane) and \tilde{A}^2B_2 (in-plane) states. In addition, one component of the forbidden $^2\Delta-^2\Sigma^+$ ($C_{\infty v}$ point group) transition becomes allowed ($^2A_1-^2A_1$ in the C_{2v} point group) but was not experimentally observed. When the symmetry is lowered further from C_{2v} ($-\text{NH}_2$) to C_s ($-\text{NHR}$), the number of states remains unchanged but now all the states can be connected by electric dipole allowed transitions (Figure 4).

Experimentally, only three electronic transitions are known for CaNH_2 and SrNH_2 . The planarity of SrNH_2 and the $\tilde{B}^2B_1-\tilde{X}^2A_1$ and $\tilde{A}^2B_2-\tilde{X}^2A_1$ assignments were proven by a high-resolution rotational analysis.⁸ The $\tilde{C}^2A_1-\tilde{X}^2A_1$ assignment for CaNH_2 was

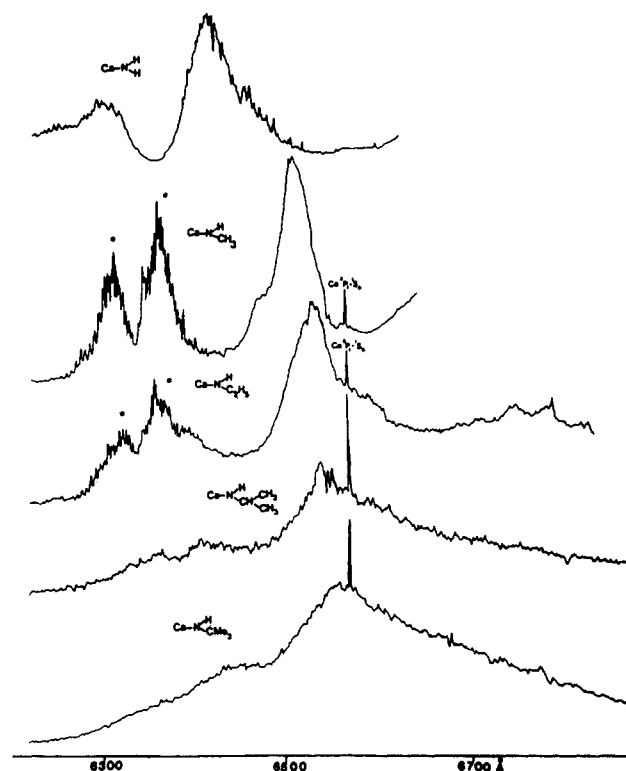


Figure 2. Excitation spectra of calcium monoalkylamides. The asterisks mark the $\tilde{B}^2\Sigma^+-\tilde{X}^2\Sigma^+$ transition of the CaH molecule. Note that for CaNH_2 , $\text{CaNHCH}_2\text{CH}_3$, and $\text{CaNHC}(\text{CH}_3)_3$ CaH is not observed. The calcium $^3P_1-^1S_0$ atomic transition (6573 Å) is marked.

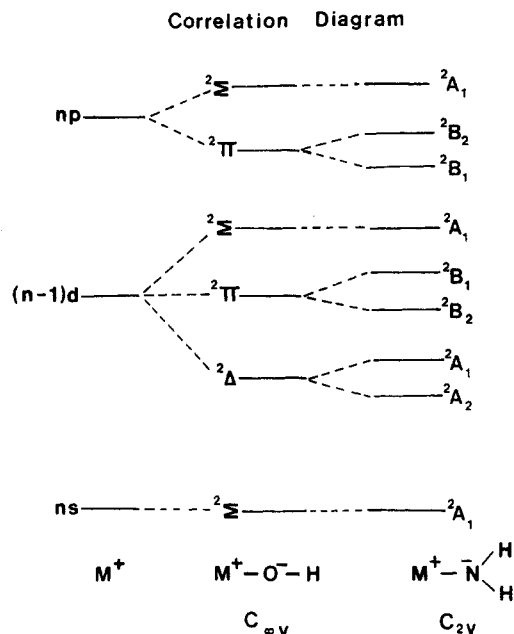


Figure 3. Correlation diagram for the M^+ ion ($M = \text{Sr}, \text{Ca}$) perturbed by a linear OH^- ligand ($C_{\infty v}$ symmetry) and NH_2^- ligand (C_{2v} symmetry).

made by Wormsbecher, Penn, and Harris⁶ from their rotational analysis. All other assignments are made by analogy. The 2A_1 and 2A_2 ($^2A'$ and $^2A''$) states which correlate to the $^2\Delta$ state of the MOH molecule were not observed.

As the alkyl group becomes larger, the $\tilde{A}-\tilde{X}$ and $\tilde{B}-\tilde{X}$ transitions shift to the red (Figures 1 and 2), while the $\tilde{C}-\tilde{X}$ transitions shift slightly to the blue (Tables I and II). The signal-to-noise ratio also decreases as the vapor pressure of the parent amine decreases and the product molecules become more difficult to make. The sharp features in the SrNH_2 and CaNH_2 spectra are sub-band heads. For the heavier Sr-containing compounds, the Sr atomic lines become prominent. When CH_3NH_2 and $\text{CH}_3\text{CH}_2\text{NH}_2$ were

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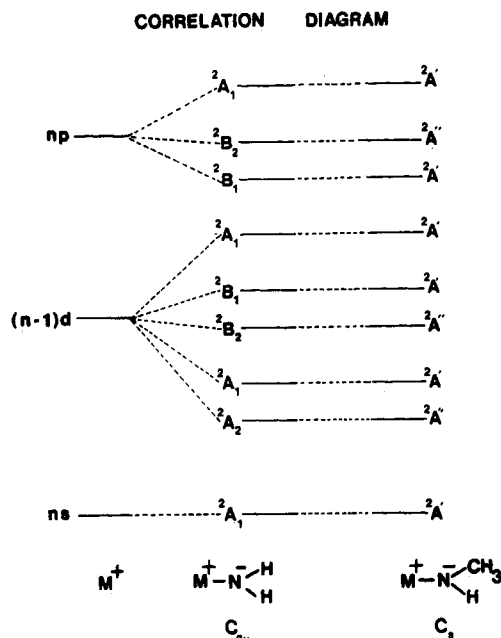


Figure 4. Correlation diagram for Ca^+ and Sr^+ with NH_2^- and NHR^- (C_s symmetry) ligands.

used as oxidants with Ca, very strong spectra of CaH ($B^2\Sigma^+-X^2\Sigma^+$) appeared (Figure 2, marked with asterisks). Many of the alkylamine oxidants also produced some $CaNH_2$ and $SrNH_2$. The $SrOC(CH_3)_3$ molecule appeared in the $SrNHC(CH_3)_3$ spectra, possibly from a *tert*-butyl alcohol impurity in the *tert*-butylamine oxidant.

The $Sr-NH_2$ vibrational frequency (459 cm^{-1}) matches the 450-cm^{-1} splitting between the \tilde{B}^2B_1 and \tilde{A}^2B_2 electronic states, so the $v = 0$ of the \tilde{B}^2B_1 state is extensively perturbed by $v = 1$ of \tilde{A}^2B_2 . As the ligand becomes heavier, the $Sr-N$ stretching frequency decreases but the $\tilde{B}-\tilde{A}$ electronic separation remains the same. Therefore, we assign the central peak in the scans of Figure 1 to the $1-0$ vibronic band of the $\tilde{A}-\tilde{X}$ transition. This central feature could also be assigned to an additional electronic transition (for example ${}^2A_1-{}^2A_1$, Figures 3 and 4), but we do not favor this assignment. Note that relative intensities of the features in Figures 1 and 2 may not be reliable because the red pass filter enhances some features (and molecules) in the excitation spectrum. The intensity of the $1-0$ $\tilde{A}-\tilde{X}$ vibronic transition may also be

TABLE III: Metal-Nitrogen Stretching Frequencies of Strontium and Calcium Monoalkylamides (in cm^{-1})

molecule	M = Sr			M = Ca	
	\tilde{X}	\tilde{A}	\tilde{B}	\tilde{X}	\tilde{A}
MNH_2	459		~ 450	524	520
$MNHCH_3$	393	387		480	467
$MNHC_2H_5$	~ 331	~ 337	~ 315		
$MNHC(CH_3)_3$		~ 292			

enhanced by the $\tilde{B}(v=0)-\tilde{A}(v=1)$ interaction.

For the $CaNHR$ molecules, the $\tilde{B}^2B_1-\tilde{X}^2A_1$ transition is never as clear as for the corresponding $SrNHR$ molecules. The $\tilde{B}-\tilde{A}$ interval for $CaNHR$ is about 300 cm^{-1} , compared to the $\sim 500\text{-cm}^{-1}$ interval for $SrNHR$.

The $Ca-N$ and $Sr-N$ stretching frequencies, which were mainly obtained from the laser excitation spectra, were difficult to measure for the larger molecules (Table III). The laser-induced fluorescence was very relaxed, and vibrational bands were not clear. This is in contrast to the corresponding alkoxides,² where even for the $SrOC(CH_3)_3$ radical the $Sr-O$ stretch appeared clearly in the spectra. The $Sr-N$ and $Ca-N$ frequencies of the metal monoalkylamides are all less than the corresponding $Sr-O$ and $Ca-O$ stretching frequencies of the metal alkoxides, indicating that the force constants are smaller. The weaker force constants for the metal alkylamides suggest that the $M-NHR$ bond dissociation energies are smaller than the corresponding $M-OR$ dissociation energies.

An attempt was made to detect the $CaN(CH_3)_2$ and $SrN(CH_3)_2$ free radicals with the $HN(CH_3)_2$ oxidant. The reaction was very sluggish, and no alkylamide product was formed. The main reaction products were the $SrOCH_3$ and $CaOCH_3$ impurity molecules, not the desired dialkylamides.

Conclusion

The $CaNHR$ and $SrNHR$ free radicals were produced by vapor-phase chemical reactions. The laser excitation spectra of the $\tilde{C}^2A_1-\tilde{X}^2A_1$, $\tilde{B}^2B_1-\tilde{X}^2A_1$, and $\tilde{A}^2B_2-\tilde{X}^2A_1$ electronic transitions were observed. The spectra of other metal alkylamides can be observed with our experimental methods.

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