LASER SPECTROSCOPY OF CALCIUM AND STRONTIUM MONOACETYLIDES

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The gas-phase free radicals CaCCH and SrCCH were synthesized by the reaction of Ca or Sr vapor with HCCH. The electronic and vibrational structure of these molecules were investigated by laser excitation spectroscopy and laser-induced fluorescence. These ionic metal acetylides proved to be linear in geometry.

1. Introduction

In our laboratory we are studying the reactions of metal vapors (particularly calcium and strontium) with organic molecules. To date we have detected polyatomic free radicals containing calcium and strontium bonded to oxygen, sulfur, nitrogen and carbon. The metal–oxygen derivatives include hydroxides [1], alkoxides [2] and carboxylates [3] while some of the corresponding metal–sulfur radicals MSH, MSR and MSCN have also been found [4].

The metal–nitrogen containing compounds are metal amides [5], alkylamides [6], azides [7] and probably, isocyanates [8] ‡. The first free radicals with a metal–carbon bond that we have discovered are the "open-faced sandwich" molecules CaC_5H_5 and SrC_5H_5 [9]. More recently we have found the metal alkyls $CaCH_3$ and $SrCH_3$ [10]. In this paper we report on the CaCCH and SrCCH free radicals.

Solid state calcium, strontium and barium diacetylides have been previously synthesized. The direct reaction of the metal with alkynes in liquid ammonia produces these dialkynyl compounds [11].

$$2\,RC\equiv CH + M \xrightarrow[\text{liq NH}_3]{} (RC\equiv C)_2 M + H_2 ,$$
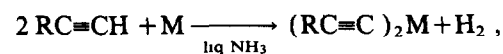
M = Ca, Sr, Ba, R = H [12], Ph [13].

Since the time ref. [8] was published, we have decided that CaNCO and SrNCO are the correct structures rather than CaOCN and SrOCN. The comparison with the CaNNN and SrNNN spectra is very suggestive of M–N rather than M–O bonding.

The $M(C\equiv CH)_2$ compounds are quite unstable and decompose to provide the metal carbides, MC_2. Alkynylcalcium iodides RCCCaI were synthesized by the reaction of alkynes with PhCaI [14]. The coordination chemistry of metal acetylides was reviewed by Nast [15].

Veillard [16] and Streitweiser et al. [17] carried out ab initio calculations to determine the structure of lithium acetylide. A linear geometry was assumed in these calculations. They concluded that the lithium acetylide molecule is highly ionic in character. The molecule is described as an ionic association between the Li^+ ion and the $^-(CCH)$ ligand, with the first carbon atom bearing most of the negative charge. A neutron powder-diffraction study of monosodium acetylide by Atoji [18] also concludes that the molecule is ionic in nature and has a linear geometry.

Acetylides can form on metal surfaces. For example Madix [19] has applied a battery of surface techniques (UPS, XPS, LEED and EELS) to the characterization of the CCH fragment bonded to the Ag(110) surface.

Our work on CaCCH and SrCCH represents the first gas-phase spectroscopic observation of a metal monoacetylide. These radicals were synthesized by reacting the metal vapors with HCCH. Their electronic and vibrational structures were detected by laser-induced fluorescence. The assignments were made by analogy to the corresponding CaOH and SrOH spectra. A high-resolution rotational analysis of the $\tilde{A}\,^2\Pi$–$\tilde{X}\,^2\Sigma^+$ transition of CaCCH is currently in progress.

2. Experimental

The metal acetylides were generated in a Broida-type oven [20] by the reaction of metal vapor with acetylene. The metal was vaporized by resistive heating in an alumina crucible and entrained in argon carrier gas. The total pressure was approximately 1.5 Torr with about 10 mTorr of purified acetylene. The signal-to-noise ratio increased when the pressure in the reaction chamber was increased from 1.5 to 10 Torr by partially closing the valve to the vacuum pump.

Two years ago in our initial acetylene experiments unpurified acetylene was used. Welding-grade acetylene contains acetone, which reacts with calcium or strontium to produce mainly the $CaOCH(CH_3)_2$ or $SrOCH(CH_3)_2$ molecules [2]. The alkaline earth vapors react more easily with water and acetone than with acetylene so a purification step is vital. In the current experiments, welding-grade acetylene was passed through a trap cooled by a mixture of dry ice and acetone, bubbled through concentrated sulfuric acid and then cleaned with solid NaOH and anhydrous $CaCl_2$.

Two cw broad band (1 cm^{-1}) dye lasers, pumped by two argon ion lasers (Coherent Innova 20 and Coherent Innova 90), were used for the experiments. One dye laser excited the $^3P_1-^1S_0$ atomic transition (6573 Å for calcium and 6892 Å for strontium) while the second laser was resonant with the product molecule (CaCCH or SrCCH) $\tilde{A}\,^2\Pi-\tilde{X}\,^2\Sigma^+$ electronic transition. Unexcited metal atoms do not react with HCCH. The chemical mechanism responsible for the production of CaCCH and SrCCH is unclear because of the unknown M–C bond energies and the relatively high pressure in the Broida oven.

Two types of spectra were recorded. Laser excitation spectra were obtained by scanning the frequency of the second dye laser while detecting the fluorescence with a photomultiplier–filter combination. Schott RG 9 and RG 780 red pass filters blocked the scattered laser light. Lock-in detection was made possible by chopping the laser resonant with the molecular transition.

Laser-induced fluorescence spectra were obtained by fixing the second laser on a molecular absorption and then dispersing the fluorescence with a mono-chromator. In order to improve the signal-to-noise ratio the laser exciting the molecular transition was chopped and lock-in detection utilized. DCM and/or pyridine 2 dyes were used in the dye lasers.

Strontium vapor was also allowed to react with perdeuteroacetylene, which was synthesized by the reaction of calcium carbide with deuterium oxide. A resolved fluorescence spectrum of SrCCD was recorded with the same experimental parameters (pressures and laser wavelengths) as SrCCH. The SrCCD and SrCCH spectra were different confirming that the product molecule contained hydrogen.

An attempt was made to study the spectra of calcium and strontium monomethylacetylide $MCCCH_3$ by using monomethylacetylene as an oxidant. Calcium vapor produced only calcium monoacetylide in this reaction. However, there was some evidence from the excitation and resolved fluorescence spectra that $SrCCCH_3$ was formed. These spectra were very poor and obscured by the presence of strontium hydroxide (which is an impurity) so that no spectroscopic measurements were made.

3. Results and discussion

The laser excitation spectrum of the $\tilde{A}\,^2\Pi-\tilde{X}\,^2\Sigma^+$ transition of strontium acetylide is given in fig. 1. The two main features in fig. 1 are separated by about 260 cm^{-1}, which is a characteristic $\tilde{A}\,^2\Pi$ spin–orbit splitting when Sr$^+$ is perturbed by a linear ligand. The laser-induced fluorescence spectra of CaCCH and SrCCH (figs. 2 and 3) provide more accurate data on the electronic transition

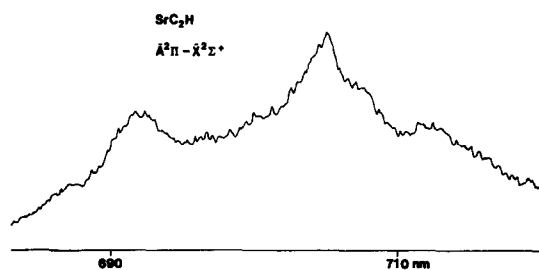Fig. 1. Laser excitation spectrum of SrCCH. The features near 692 and 705 nm are the two spin–orbit components of the $\tilde{A}\,^2\Pi-\tilde{X}\,^2\Sigma^+$ electronic transition.
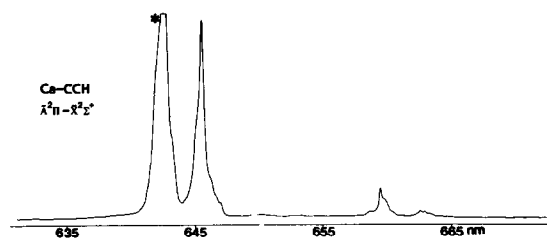
Fig. 2. Laser-induced fluorescence spectrum from the $\tilde{A}$–$\tilde{X}$ transition of CaCCH. The asterisk marks the position of the laser exciting the $\tilde{A}\,^2\Pi_{3/2}$–$\tilde{X}\,^2\Sigma^+$ transition. The peak just to the red of the laser is the $\tilde{A}\,^2\Pi_{1/2}$–$\tilde{X}\,^2\Sigma^+$ transition. Collisions have populated the $\tilde{A}\,^2\Pi_{1/2}$ spin component from the directly excited $\tilde{A}\,^2\Pi_{3/2}$ component. The two peaks near 660 nm are assigned to the 3^0_1 vibrational band of the $\tilde{A}$–$\tilde{X}$ transition.

frequencies. In both these figures an asterisk marks the laser wavelength. In fig. 2 the laser excites the $\tilde{A}\,^2\Pi_{3/2}$–$\tilde{X}\,^2\Sigma^+$ of CaCCH while in fig. 3 the $\tilde{A}\,^2\Pi_{1/2}$–$\tilde{X}\,^2\Sigma^+$ spin component of SrCCH is excited. Collisions connect the $\tilde{A}\,^2\Pi_{1/2}$ and $\tilde{A}\,^2\Pi_{3/2}$ spin components so both components are observed in fig. 2 although only one component is directly excited. The band origins and spin–orbit coupling constants (A) of the $\tilde{A}\,^2\Pi$–$\tilde{X}\,^2\Sigma^+$ transitions of CaCCH and SrCCH are reported in table 1, with an estimated uncertainty of ± 10 cm^{-1}.
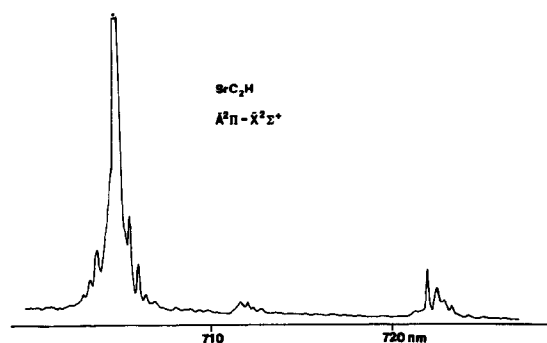

Fig. 3. Laser-induced fluorescence spectrum of the $\tilde{A}$–$\tilde{X}$ transition of SrCCH. The asterisk marks the position of the laser exciting the $\tilde{A}\,^2\Pi_{1/2}$–$\tilde{X}\,^2\Sigma^+$ transition. No emission from the $\tilde{A}\,^2\Pi_{3/2}$ spin component appears in this spectrum. The weak feature near 710 nm is assigned to the 5^0_2 band of the $\tilde{A}$–$\tilde{X}$ transition while the feature near 720 nm is the 3^0_1 band of the $\tilde{A}$–$\tilde{X}$ transition.

Table 1
Band origins of the $\tilde{A}\,^2\Pi$–$\tilde{X}\,^2\Sigma^+$ calcium and strontium monoacetylide (in cm^{-1})

Molecule	$\tilde{A}\,^2\Pi_{1/2}$–$\tilde{X}\,^2\Sigma^+$	$\tilde{A}\,^2\Pi_{3/2}$–$\tilde{X}\,^2\Sigma^+$	A [a]
CaCCH	15487	15560	73
SrCCH	14176	14451	275

[a] Spin–orbit constant.

The $\tilde{B}\,^2\Sigma^+$–$\tilde{X}\,^2\Sigma^+$ transitions of calcium and strontium acetylide were not found in the low-resolution scans despite an extensive search in the expected region. It is possible that the $\tilde{B}\,^2\Sigma^+$–$\tilde{X}\,^2\Sigma^+$ transition was obscured by the strong CaOH or SrOH spectra. However, a preliminary analysis of the high-resolution spectrum of calcium acetylide is consistent with a distant or dissociative $\tilde{B}\,^2\Sigma^+$ state. The Λ doubling constant p of the $\tilde{A}\,^2\Pi$ state is very small and positive rather than large and negative as expected from the $\tilde{B}\,^2\Sigma^+$–$\tilde{A}\,^2\Pi$ interaction.

Resonant emission to excited vibrational levels of the ground electronic state was observed in the $\tilde{A}$–$\tilde{X}$ laser-induced fluorescence spectra. The MCCH molecule has five vibrational modes ν_1 (C–H stretch), ν_2 (C≡C stretch), ν_3 (M–C stretch), ν_4 (C–C–H bend) and ν_5 (M–C–C bend) with the stretches and bends having σ and π symmetry, respectively. The M–C stretch (ν_3) had the largest Franck–Condon factor so ν_3 and $2\nu_3$ for the $\tilde{X}\,^2\Sigma^+$ state were observed (table 2). An additional mode at 181 cm^{-1} for CaCCH and 139 cm^{-1} for SrCCH was also found. The most likely assignment is $2\nu_5$ in the $\tilde{X}\,^2\Sigma^+$ state since the observation of ν_5 is forbidden [21]. An attempt was made to detect ν_2 (C≡C stretch) but without success. The vibrational frequencies in the $\tilde{A}$ and $\tilde{X}$ states are similar so that no sequence structure was resolved.

Table 2
Vibrational frequencies of the calcium and strontium acetylides (in cm^{-1}) in the $\tilde{X}\,^2\Sigma^+$ state

Mode	M = Ca	M = Sr
ν_3 (M–C stretch)	399	343 [a]
$2\nu_3$	788	684
$2\nu_5$ (M–C≡C bend)	181	139
$\nu_3 + 2\nu_5$	–	500

[a] 354 cm^{-1} for the $\tilde{A}\,^2\Pi$ state.

The attribution of our spectra to CaCCH and SrCCH rests largely on similarities to the corresponding CaOH and SrOH spectra [1]. The spin–orbit coupling constant of the $\tilde{A}\,^2\Pi$ state of SrCCH (CaCCH) is 275 cm^{-1} (73 cm^{-1}) compared to 264 cm^{-1} (66 cm^{-1}) for SrOH (CaOH). The M–C bond, compared to the M–O bond, shifts the $\tilde{A}$–$\tilde{X}$ band origins to the red and increases the spin–orbit constant of the $\tilde{A}\,^2\Pi$ state slightly. The SrCH$_3$ (CaCH$_3$) molecule shows similar changes with, for example, $A = 273$ cm^{-1} (79 cm^{-1}) for the corresponding $\tilde{A}\,^2E$ states [10]. The observation of spin–orbit splittings for the $\tilde{A}$ states means that the new molecules have high symmetry, probably linear. The reactions of Ca and Sr with DCCD show that the new species contain hydrogen. The chemical evidence also strongly suggests that we have discovered the linear, CaCCH and SrCCH free radicals.

Acknowledgement

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