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A high-resolution laser ablation study of the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ transition of SrCCH

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Abstract

The laser-induced excitation spectrum of the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ transition of SrCCH has been recorded at high resolution. A rotational analysis has been performed yielding rotational and fine structure parameters for the $\tilde{A}$ state. In addition, a vibrational frequency for the Sr–C stretch (ν_3) in the $\tilde{A}^2\Pi$ state has been determined. Using the rotational constant of the $\tilde{A}$ state, the Sr–C bond length was determined to be 2.43 Å, which is ~0.03 Å shorter than in the ground state. A comparison of the Λ-doubling constant p, to those of the other alkaline-earth acetylides suggests that SrCCH and CaCCH appear to follow the pure precession model unlike MgCCH. Finally, a search for the $\tilde{B}^2\Sigma^+$–$\tilde{X}^2\Sigma^+$ transition was negative, as with CaCCH, suggesting that the $\tilde{B}$ state may be predissociative.
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1. Introduction

Unlike their diatomic counterparts, metal containing polyatomic molecules have been the focus of a limited number of gas phase spectroscopic studies. However, for one such class of molecule, the metal monoacetylides, work has progressed steadily over the past 20 years. These investigations, which include both theory and experiment, have focused mainly on the alkali and alkaline-earth metals with only a few notable exceptions, Cr and Yb [1,2], having been completed. A brief summary of this work follows.

Experimentally, the alkali metal monoacetylides have been studied in their ground states by millimeter wave spectroscopy. From the pure rotational spectra of LiCCH, NaCCH, and KCCH [3–6], each species has been shown to be linear in its $^1\Sigma^+$ ground state. This work is in agreement with Scalmani et al. [7] who have investigated the electronic properties of these molecules using ab initio methods. Unfortunately, no information is available for the excited electronic states of these species perhaps because these excited states are not bound.

The alkaline-earth monoacetylides have been the subject of more extensive investigations than their alkali counterparts. The ground electronic states of MgCCH, CaCCH, and SrCCH ($^2\Sigma^+$) have been studied by several experimental techniques [5,8–11] as well as by ab initio calculations [12–14]. In addition, experimental data exist for the excited states of these molecules. For CaCCH, the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ transition has been observed experimentally both at low [15,16] and high resolution [17–21], including a determination of the dipole moments for the $\tilde{A}$ and $\tilde{X}$ states of CaCCH using Stark spectroscopy [22]. In addition, the $\tilde{C}^2\Delta$–$\tilde{X}^2\Sigma^+$ transition [23] of CaCCH has been observed at low resolution. The $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ transition of MgCCH has also been

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examined both at low [24,25] and recently at high resolution [26]. The $\tilde{A}$–$\tilde{X}$ transition of SrCCH was first observed by Bernath and co-workers [15] at low resolution, while Ellis and co-worker [27] have reported measurements of the $\tilde{B}'^2\Delta$–$\tilde{X}^2\Sigma^+$ transition at low resolution.

In this work, we report the first high-resolution spectroscopic analysis of the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ transition of SrCCH. For the $\tilde{A}^2\Pi$ state rotational and fine structure constants have been determined. Trends in the geometries and Λ-doubling constants for the alkaline-earth monoacetylides will be discussed.

2. Experimental

The $\tilde{A}$–$\tilde{X}$ transition of SrCCH was observed using the laser ablation source of the Bernath group at the University of Waterloo. This instrument has been described in detail previously [28] and, therefore, only minor modifications made for this study will be discussed. In our work, the third harmonic (355 nm) of a pulsed (10 Hz) Nd/YAG laser (10 mJ/pulse) was used to vaporize a strontium target rod. (The first and second harmonics were found to produce a weaker SrCCH signal). The molecular jet was formed by the expansion of a 7% gas mixture of HCCH in Ar at a backing pressure of 100 psi, resulting in a rotational temperature of only 4–6 K. Following the recent work on MgCCH [26] a 10% mixture of CH_4 in Ar was tested as the reactant gas mixture, but HCCH was found to yield stronger SrCCH signals. Finally, the molecular expansion was not skimmed; instead the probe laser interrogated a free jet expansion ~15 cm downstream. As before, band pass filters (±20 nm) were used to attenuate most of the plasma radiation from the ablation source.

Low-resolution spectra were obtained using an Ar^+-pumped linear dye laser operating with DCM laser dye. This laser has a linewidth of 30 GHz and a maximum power of 800 mW when the pump power is 5 W. A typical scan rate of ~1000 cm^{-1} in 20 min was employed. Signals from the boxcar integrator and frequency readings from a wavemeter (Burleigh WA—2500 Wavemeter Jr) were processed using a data acquisition program written in Labview.

High-resolution spectra were obtained using a Coherent Autoscan 699-29 ring dye laser system. This laser has a linewidth of 10 MHz. The spectra were calibrated using I_2 lines, [29] which were recorded at the same time as the experimental data. A typical spectrum was taken in 5 cm^{-1} segments at a scan speed of 60 s per wavenumber with a data sampling rate of 10 MHz. Several of these scans (4–6) were then averaged together to further increase the signal-to-noise ratio. Typical experimental linewidths were 350 MHz as a result of residual Doppler broadening of the molecular jet as it passes through the detection region.

3. Results and analysis

Initially, a broadband survey spectrum was measured for SrCCH over the range 14000–16000 cm^{-1}. A portion of this spectrum is shown in Fig. 1. The spin–orbit components of the $\tilde{A}$–$\tilde{X}$ (0_0^0) transition of SrCCH are clearly visible on the red side of the spectrum. The location of these features at 14182 cm^{-1} ($^2\Pi_{1/2}$–$^2\Sigma^+$) and 14454 cm^{-1} ($^2\Pi_{3/2}$–$^2\Sigma^+$) is consistent with previous observations [15]. Also visible is the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ (0_0^0) transition of SrOH, which is present as a result of impurities, and the $^3P_1$–$^1S_0$ atomic transition of Sr. Two additional small features can be attributed to the (ν_3) Sr–C stretch of SrCCH; the $^2\Pi_{1/2}$–$^2\Sigma^+$ (3_0^1) transition is located at 14527 cm^{-1} and the $^2\Pi_{3/2}$–$^2\Sigma^+$ (3_0^1) transition is found at 14800 cm^{-1}. Unfortunately, the $^2\Pi_{3/2}$–$^2\Sigma^+$ (3_0^1) transition is overlapped with the $\tilde{A}^2\Pi_{3/2}$–$\tilde{X}^2\Sigma^+$ (0_0^0) transition of SrOH.

Using the frequency positions determined from the low-resolution study, high-resolution spectra of the $^2\Pi_{1/2}$–$^2\Sigma^+$ and $^2\Pi_{3/2}$–$^2\Sigma^+$ (0_0^0) bands of SrCCH were obtained. In Fig. 2, spectra of these two spin–orbit components are shown, one above the other for comparison. These spectra exhibit a typical Hund's case (a) $^2\Pi$—Hund's case (b) $^2\Sigma^+$ structure for a linear molecule with ~1B and ~3B spaced branches present. The structure of the $^2\Pi_{1/2}$–$^2\Sigma^+$ and $^2\Pi_{3/2}$–$^2\Sigma^+$ spin components differ as expected, with the $^2\Pi_{3/2}$–$^2\Sigma^+$ transition exhibiting a larger origin gap, as well as the ~1B spaced branches of the $^2\Pi_{1/2}$–$^2\Sigma^+$ band being more compressed.

High-resolution spectra were also obtained for the (3_0^1) bands of the $^2\Pi_{1/2}$–$^2\Sigma^+$ and $^2\Pi_{3/2}$–$^2\Sigma^+$ transitions.

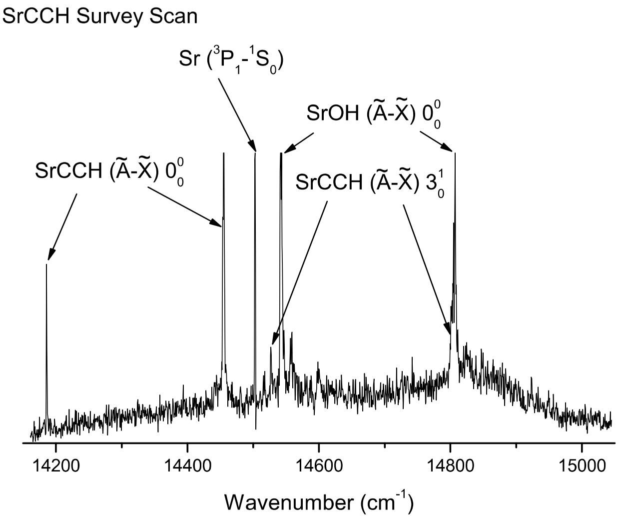

Fig. 1. A section of the low-resolution survey scan over the range ~14000–15000 cm^{-1}. The spin–orbit components of the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ transition of SrCCH are located at 14182 and 14454 cm^{-1}. In addition the $^3P_1$–$^1S_0$ atomic transition of the Sr atom and the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ transition of SrOH (a result of impurities) are present in this spectrum. Also present are the $\tilde{A}$–$\tilde{X}(3_0^1)$ bands as weak features. The uneven baseline is a result of varying laser power.