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High-resolution laser spectroscopy of the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ transition of MgCCH

D.W. Tokaryk[a,*,1], A.G. Adam[b], W.S. Hopkins[b]

[a] *Physics Department, University of New Brunswick, P.O. Box 4400, Fredericton, NB, Canada E3B 5A3*
[b] *Chemistry Department, University of New Brunswick, Bag Service #45222, Fredericton, NB, Canada E3B 6E2*

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Abstract

The 0_0^0 and 3_0^1 bands of the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ electronic transition of the MgCCH radical have been recorded at low and high resolution using laser-induced fluorescence. The molecules were created in a laser ablation/molecular beam source through reaction of magnesium atoms ablated from a solid rod with methane gas entrained in helium. The rotationally resolved high-resolution data were fit to a $^2\Pi(a)$–$^2\Sigma^+(b)$ Hamiltonian, with standard deviations of 0.0025 cm^{-1} (0_0^0) and 0.0028 cm^{-1} (3_0^1). The Λ-type doubling constants p and q in the $\tilde{A}^2\Pi$ state are unexpectedly positive, indicating that interaction between $\tilde{A}^2\Pi$ and the next highest $^2\Sigma^+$ state is not the dominant cause of the doubling, as was assumed in the structurally similar molecules CaCCH, CaOH, and SrOH in which p and q are larger and negative.

Keywords: MgCCH; Magnesium-bearing molecule; High-resolution spectroscopy; Laser spectroscopy; Alkali earth metal bond

1. Introduction

Molecules made from an alkali earth metal atom bonded to a diatomic or polyatomic ligand have been studied extensively in the past 20 years. A recent review article [1] describes and inteprets the experimental and theoretical results obtained from 1990 to 2001, while another paper [2] examines work done prior to 1990. All of these molecules have a similar structure in that they resemble stable molecules (like H_2O, HCN, HCCH, and $HOCH_3$) in which the alkali earth metal M (=Be, Mg, Ca, Sr, Ba) replaces a terminal hydrogen atom to form radicals like M-OH, M-CCH, or M-OCH_3. In the ground state, one of the two valence *s* electrons from the metal replaces the electron previously provided by the hydrogen atom. This leaves the ligand L more negatively charged, and the metal atom more positively charged, forming a primarily ionic M–L bond. The other valence *s* electron is unpaired and is essentially nonbonding; its density concentrates mostly on the metal atom. This type of ionic bonding favors a linear molecular structure, and in cases where the molecule is bent (e.g., CaSH, SrSH [3], and excited states of MgOH [4]) the bonding is more covalent in character. M–L molecules also bear similarity to alkali metal halide diatomic molecules, since the halide atom like the ligands is monovalent.

The lowest electronic excitations of the alkali earth/ligand molecules primarily affect the unpaired electron, preserving the ionic nature of the bond. The resulting electronic spectra have distinct similarities for each alkali earth metal as the ligand is changed, since the negatively charged ligands act as ‘spectators’ that exert similar perturbations on the positive metal ion. For example, the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ electronic spectra of CaOH

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[*] Corresponding author. Fax: +1 506 453 4581.
E-mail address: dtokaryk@unb.ca (D.W. Tokaryk).

[1] Author is a member of the Canadian Institute for Photonic Innovations (CIPI).

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and CaCCH, the $\tilde{A}^2E$–$\tilde{X}^2A_1$ transition of $CaOCH_3$, and the $A^2\Pi$–$X^2\Sigma^+$ spectrum of CaCl lie in a narrow frequency window between about 15400 and 16200 cm^{-1}. In each of these cases, the nonbonding electron in the ground electronic state is promoted from a σ orbital to a low-lying π or π-like orbital in the excited state.

Compared to most other types of metal-bearing molecules, the structure of the alkali earth/ligand molecules is quite straightforward and their spectra are reasonably simple to interpret. This makes them attractive systems for detailed study, and the resulting body of work has significantly improved our understanding of the fundamental principles involved in metal–ligand bonds. The results are of potential significance in catalysis, biological processes, and in the synthesis of novel compounds. There are also important applications to astrophysics, since Be, Mg, and Ca are elements commonly found in the envelopes surrounding stars and in the interstellar medium, and both radicals like OH and CCH and stable precursor molecules like H_2O and HCCH are abundant in these environments. To date, it appears that only one alkali-earth-bearing molecule has been conclusively observed from an astrophysical source: the microwave spectrum of MgNC was detected in the atmosphere of the carbon star IRC +10216 in the early 1990s [5], and extensive laboratory work on both its microwave and optical spectra has been reported since then [6].

Another molecule of potential interest in astrophysics is MgCCH. The microwave spectra in both its ground vibrational state [7] and its v_5 vibrational mode (the Mg–C–C bend) [8] have been reported, and the optical spectrum of the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ electronic transition has been studied at low resolution with laser-induced fluorescence [9,10]. Some ab initio calculations on MgCCH have been performed as well [11], including a study of the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ transition [12]. In this paper, we report on high-resolution spectra of the $\tilde{A}^2\Pi$–$\tilde{X}^2\Sigma^+$ system, which we observed during a search for the MgC radical. We have been able to rotationally resolve and analyze spectra of the 0_0^0 and 3_0^1 bands. These data supplement and extend the existing information on MgCCH, and provide a detailed picture of its properties, particularly in the excited electronic state.

2. Experiment

MgCCH was produced and studied in the laser ablation molecular beam source at the University of New Brunswick. Magnesium atoms were ablated under vacuum from a continuously rotating and translating rod (99.99% pure, purchased from Electronic Space Products International) with 12 mJ pulses of 355 nm laser light generated by a Lumonics HY-400 Nd:YAG laser. The atoms reacted with a gas mixture of 90% helium and 10% methane admitted through a pulsed valve opened at a fixed time interval after firing of the ablation laser. While MgCCH could be produced with other gases, notably acetylene and methanol, signal strength with methane was considerably greater in our source. The pressure of the helium/methane mixture behind the valve was regulated to 40 psi. The jet containing magnesium and the reactant gases passed through a short expansion channel into a region about 5 cm below, where the resulting molecules were probed with a beam from either a pulsed (Lumonics HD-500, pumped with a YM-600 Nd:YAG laser) or continuous (Coherent 699-29) dye laser. Stilbene 420 laser dye was used to cover the spectral regions of interest. Laser-induced fluorescence was focused into a Jarrel-Ash 0.25 m grating spectrometer equipped with a thermoelectrically cooled Hamamatsu 943-02 photomultiplier tube. Current signals from the photomultiplier tube were processed with a boxcar integrator, and recorded on a microcomputer.

Two aspects of this experiment were unusual—the high-ablation laser power required to get a strong signal, and the rich concentration of methane entrained in the helium carrier gas. In similar experiments with this apparatus, the ablation laser was usually set to 3–5 mJ per pulse, and 1–3% gas mixtures were used most frequently. However, in experiments by another group, 8–10% methane mixtures were used in the production of YbCCH [13].

The bandwidth of the pulsed laser light was about 0.04 cm^{-1} (1200 MHz), while that of the continuous wave laser was about 1 MHz. Line widths of about 400 MHz were observed due to a small amount of Doppler broadening resulting from divergence of the molecular jet as it passed through the detection region. The frequency of the beam from the ring dye laser was calibrated to within about 0.002 cm^{-1} with optogalvanic spectra obtained from a U/Ar hollow cathode lamp.

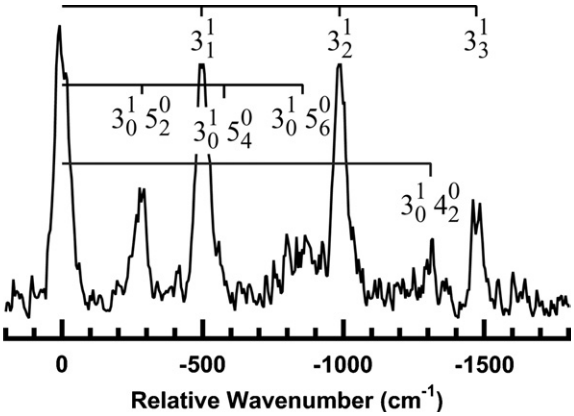

Fig. 1. A spectrum of the dispersed fluorescence of MgCCH arising from excitation of the $\tilde{A}^2\Pi_{3/2}$–$\tilde{X}^2\Sigma^+$ component of the 3_0^1 band with a pulsed dye laser. The indicated transition wavenumbers are given relative to the frequency of the exciting laser, which was set to 23378 cm^{-1} for this scan.