Fourier transform emission spectra of the $\text{A}^2\Pi \rightarrow \text{X}^2\Sigma^+$ and $\text{B}^2\Sigma^+ \rightarrow \text{X}^2\Sigma^+$ transitions of CaD

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A R T I C L E   I N F O
Article history:
Received 26 August 2012
Available online 11 October 2012

Keywords:
CaD
Fourier transform spectroscopy
Emission spectra
Electronic transitions

A B S T R A C T
Emission spectra of the $\text{A}^2\Pi \rightarrow \text{X}^2\Sigma^+$ and $\text{B}^2\Sigma^+ \rightarrow \text{X}^2\Sigma^+$ transitions of CaD were produced in a discharge-furnace emission source and recorded with a high resolution Fourier transform spectrometer. The $\Delta v = 0$ and $\Delta v = -1$ sequences up to $v = 3$ of the $\text{A}^2\Pi$ state and $v = 2$ of the $\text{B}^2\Sigma^+$ state have been observed and rotationally analyzed. Empirical band constants and Dunham-type constants were determined for all electronic states using $\mathbf{N}$ Hamiltonians. The equilibrium constants $T_e$, $\omega_e$ and $\omega_b$ were determined to be 14407.604(2), 957.330(4) and 10.415(2) cm$^{-1}$ for the $\text{A}^2\Pi$ state, and 15751.570(2), 925.840(4) and 12.417(2) cm$^{-1}$ for the $\text{B}^2\Sigma^+$ state, respectively. The equilibrium bond lengths ($r_e$) of the $\text{A}^2\Pi$ and $\text{B}^2\Sigma^+$ states are 1.977495(3) and 1.963467(6) Å, respectively.

1. Introduction

The $\text{A}^2\Pi$-$\text{X}^2\Sigma^+$ and $\text{B}^2\Sigma^+$-$\text{X}^2\Sigma^+$ transitions of CaH were studied early in the 20th century [1–4]. CaH has been detected in sunspot spectra by its band heads in the orange and red [5,6], and quantitative measurements of CaH in M-dwarfs and M-subdwarfs are used to determine metallicities of stars [7]. Parallel to the early studies on CaH, the $\text{B}^2\Sigma^+$-$\text{X}^2\Sigma^+$ spectrum of CaD was photographed by Watson in 1935, and the 0–0 and 1–1 bands were rotationally analyzed [8]. Electronic transitions of CaH involving the $X^2\Sigma^+$ ground state and several low-lying excited states, i.e., $\text{A}^2\Pi$, $\text{B}^2\Sigma^+$, $\text{C}^2\Sigma^+$, $\text{D}^2\Sigma^+$ and $\text{E}^2\Pi$ states were studied in the 1970s [9–18], while only the $\text{D}^2\Sigma^+$-$\text{X}^2\Sigma^+$ spectrum was recorded for CaD [19]. Martin used spectroscopic data from both CaH and CaD to generate a set of empirical potential energy curves for the three lowest $^2\Sigma^+$ states of CaH [20].

The low-lying electronic states of CaH have been subject of several ab initio calculations [21–30]. Electronic states of CaH have been studied with multi-reference configuration interaction and coupled cluster methods, and spectroscopic constants ($r_e$, $\omega_e$, $D_e$, $T_e$), oscillator strengths, dipole moments and transition dipole moments have been calculated [28–30].

The millimeter-wave and microwave spectra of CaD have been recorded containing the $N = 1 \rightarrow 0$ to $4 \rightarrow 3$ transitions [31,32]. Vibration–rotation bands of CaH and CaD including hot bands up to $v = 4 \rightarrow 3$ were observed near 10 μm using a diode laser spectrometer [33]. Shayesteh et al. [34] combined their FT-IR data on CaH with all previous infrared and microwave data on CaH and CaD, and preformed a multi-isotopologue Dunham fit for the $X^2\Sigma^+$ ground state.

A few studies on electronic spectra of CaD have been carried out more recently. Balfour assigned the 0–0, 1–1 and 2–2 bands of the $\text{A}^2\Pi$-$\text{X}^2\Sigma^+$ spectrum of CaD recorded by a spectrograph, but no spectroscopic constants were reported [35]. Using sub-Doppler laser induced fluorescence, the permanent electric dipole moments of CaD have been measured for the $\text{X}^2\Sigma^+$ and $\text{B}^2\Sigma^+$ states [36]. Emission spectra of CaH and CaD including the 0–0 and 1–1 bands of the $\text{E}^2\Pi$-$\text{X}^2\Sigma^+$ system have been recorded at high resolution using a Fourier transform spectrometer [37].

In this paper, we report high resolution Fourier transform emission spectra of CaD in the 12000–17000 cm$^{-1}$ region. The $\Delta v = 0$ and $\Delta v = -1$ sequences of the $\text{A}^2\Pi$-$\text{X}^2\Sigma^+$ and $\text{B}^2\Sigma^+$-$\text{X}^2\Sigma^+$ band systems have been observed and rotationally analyzed.

2. Experimental details

A discharge-furnace emission source was used to generate the electronic spectra of CaD at the University of Waterloo. About 50 g of calcium was placed inside an alumina tube (120 cm long and 5 cm in diameter), and heated to about 780 °C. The tube was sealed with CaF$_2$ windows and evacuated by a rotary pump. A mixture of argon and deuterium (∼1.5 Torr) flowed slowly through the cell, and a dc discharge was struck between stainless-steel electrodes located at each end of the tube. A CaF$_2$ lens was used to focus emission of the source onto the entrance aperture of a Bruker
IFS 120 HR Fourier transform spectrometer with a silicon photodiode detector.

Two emission spectra of CaD were recorded: the first one was recorded at an instrumental resolution of 0.04 cm\(^{-1}\), and the spectral range was limited to 8000–15798 cm\(^{-1}\) using an appropriate long-wave-pass filter. The second spectrum covered the 8000–31596 cm\(^{-1}\) range with an instrumental resolution of 0.07 cm\(^{-1}\).

About 200 scans were co-added to improve the signal-to-noise (S/N) ratios, and S/N values of ~500 and ~100 were obtained for the strongest emission lines of CaD in the first and second spectra, respectively. The first CaD spectrum, 8000–15798 cm\(^{-1}\) with 0.04 cm\(^{-1}\) resolution, contained all the A\(^2\)P\(^\rightarrow\)X\(^2\)Σ\(^+\) bands and the P-branch lines of the B\(^2\)Σ\(^+\) → X\(^2\)Σ\(^+\) system. The second spectrum, 0.07 cm\(^{-1}\) resolution, was used only for the B\(^2\)Σ\(^+\) → X\(^2\)Σ\(^+\) lines of CaD that appear above 15798 cm\(^{-1}\). In addition to CaD, several bands of CaH were present in our spectra.

Using the program WSPECTRA written by Carleer, line positions in the spectra were measured. Since the spectrometer was not operated under vacuum, an air-vacuum correction was performed by the formula given by Hirao et al. [38] and also the absolute wavenumber scales of both spectra were calibrated using argon atomic lines reported by Norlén [39]. According to a more recent report on argon atomic emission lines in a hallow-cathode discharge lamp [40], the line positions of Norlén [39] should be multiplied by the factor \[1 \pm 6.7 \times 10^{-9}\]. To make them consistent with the most accurate measurement of argon atomic lines [40], we also multiplied our line positions by this factor. The absolute accuracy of our calibrated line positions is better than 0.005 cm\(^{-1}\) for unblended lines.

3. Results and analysis

An overview of the A\(^2\)Π → X\(^2\)Σ\(^+\) spectrum of CaD is presented in Fig. 1. We assigned the \(\Delta v = 0\) and \(\Delta v = -1\) sequences up to \(v = 3\) for the A\(^2\)Π → X\(^2\)Σ\(^+\) system, i.e., the 0–0, 1–1, 2–2, 3–3, 0–1, 1–2, 2–3 and 3–4 bands. For the B\(^2\)Σ\(^+\) → X\(^2\)Σ\(^+\) system, the \(\Delta v = 0\) bands (0–0, 1–1 and 2–2), and a very weak 0–1 band were assigned. Compared to previous studies, our data span a larger range of \(v\) and \(J\) values, and have much higher accuracy. Expanded views of the A\(^2\)Π → X\(^2\)Σ\(^+\) and B\(^2\)Σ\(^+\) → X\(^2\)Σ\(^+\) spectra showing the rotational structure are presented in Figs. 2–4.

The A\(^2\)Π state of CaD is an intermediate between Hund’s cases (a) and (b). In the A\(^2\)Π → X\(^2\)Σ\(^+\) system, all the observed bands have
six strong branches: P11, P22, Q11, Q22, R11 and R22. For most bands 3 – 4 bands of the A–X system were given an uncertainty of 0.015 cm⁻¹. For the blended lines we used uncertainties of 0.015 cm⁻¹ or higher. A complete line list and outputs of the least-squares fitting program are presented in the Supplementary files.

Energy levels of the X2Σ⁺, A2Π and B2Σ⁺ states were also fitted to Dunham-type energy level expressions in which vibrational dependences of A, γ, p and q are accounted for by the following equations [41]:

\[ A_v = A_e + \sum_{k=1}^{4} a_k(v + 1/2)^k, \]

\[ \gamma_v = \gamma_e + \sum_{k=1}^{4} \gamma_k(v + 1/2)^k, \]

\[ p_v = p_e + \sum_{k=1}^{4} p_k(v + 1/2)^k, \]

\[ q_v = q_e + \sum_{k=1}^{4} q_k(v + 1/2)^k. \]
The numbers in parentheses are 1σ uncertainties in the last quoted digits.