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According theory and experiment in CaH: Laser-induced fluorescence study of new B/B′–X bands in the UV region

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ABSTRACT

Despite the astrophysical importance of calcium monohydride (CaH), a long-standing discrepancy exists between the experimental and theoretical analysis of its first two excited $^2\Sigma^+$ states. In a bid to resolve this discrepancy, we observed the rotationally-resolved laser-induced fluorescence spectrum of CaH in the 23,300–27,800 cm^{-1} region. We assigned all newly observed vibrational levels, and five levels previously assigned to the D state, to the B/B′ state. The level properties alternate strongly with vibrational excitation and this new assignment brings the experimental vibronic structure into remarkably good agreement with the predictions of Carlsund-Levin et al. (2002).

1. Introduction

Calcium monohydride (CaH) is an abundant molecule in the stellar environment [1]. The first spectroscopic study on CaH was by Mulliken in 1925 [2] and many electronic states have now been identified [3]. The $^2\Sigma^+$ manifold exhibits a long series of avoided crossings which gives rise to the individual $^2\Sigma^+$ electronic states, included the three lowest, the X, B/B′ and D states. Despite the long history of study of this molecule the analysis of the first two excited $^2\Sigma^+$ states has continued to pose challenges for experiment and theory. Various observed vibronic levels have been assigned to different states (B/B′ or D) by different authors, different vibrational numberings have been proposed, and, in certain cases, theory and experiment have not been in good accord. In the present work we propose a resolution for some of these difficulties by a combination of re-appraisal of the previous work and by observing the rotationally-resolved laser-induced fluorescence spectrum of CaH in the range 23,300–27,800 cm^{-1} which is at the heart of the region of confusion.

One of the two states of principal concern is the B/B′ state, formed by avoided crossings between two diabatic bonding states crossed by a non-bonding diabatic state and leading to the B/B′ state having a double minimum potential energy function. This state is shown by the lower curve in Fig. 1. “B” is used to denote the inner well while the shallow outer well is denoted “B′”. The first experimental evidence for the B′ state was obtained through a local perturbation seen in a laser spectroscopic study of the B/B′ state by Martin [4]. Bernath and his coworkers published several papers on transitions between the ground state and the A $^2\Pi$, B $^2\Sigma^+$, and E $^2\Pi$ states [5–7]. The first report of the other state of principal concern, the D state, was by Grundström when he reported on the D–X band [8,9]. Later, Bell et al. presented an extensive assignment of the vibrationally excited levels of the D state [10] and proposed a change in the vibrational numbering from that used in previous studies. Based on their assignments those authors noticed very irregular vibrational spacings of the D state and an alternation of the rotational constants with vibrational excitation. They explained this behavior as due to a homogenous interaction with the vibrational excited states of the B state. Kaving and Lindgren reported a very high lying vibrationally excited level of the D state in addition to two low lying vibrational levels of the C $^2\Sigma^+$ state [11].

Later, Martin modeled the $^2\Sigma^+$ manifold with four diabatic (crossing) potential energy functions mutually coupled by R-dependent non-adiabatic (non-Born–Oppenheimer) interactions, where R is the internuclear distance. This model produces adiabatic (non-crossing) potential energy functions. By calculating energy levels in the Born–Oppenheimer approximation (*i.e.* separately for each adiabatic potential) he was able to perform a least-squares fitting of this model to the available rovibronic data. The result was a set of empirically generated but physically-constrained potential energy curves for the X, B/B′, and D states [12]. Carlsund-Levin et al. used updated versions of Martin’s potentials but also

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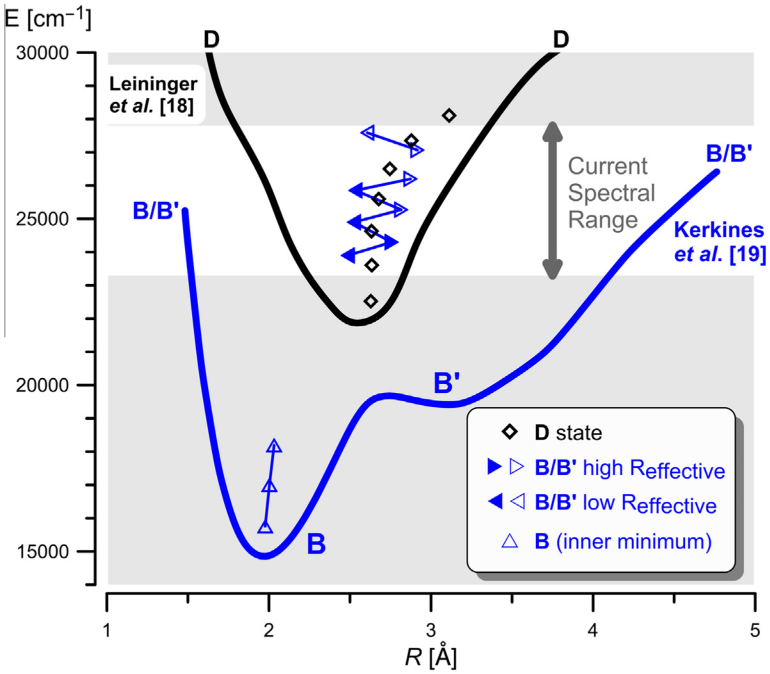

Fig. 1. The B/B′ [19] and D [18] potential energy functions, showing the double minimum of the B/B′ state and the spectral region explored in the current work. The effective bond lengths, $R_{effective}$, for each vibronic level are shown by triangles (B/B′ state) and diamonds (D state), with points for contiguous levels of the B/B′ state connected by a thin line. Solid triangles indicate results from the present work while open triangles indicate previous work. The open left and right facing triangles were assigned as D levels by Bell et al. [10] but have here been re-assigned to the B/B′ state.

accounted for Martin's *R*-dependent interaction terms in a coupled channel calculation of the rovibronic energies [13]. Born–Oppenheimer type calculations on *ab initio* potential energy functions have also been done, in particular by Weck et al. [14].

Here we report laser-induced fluorescence (LIF) spectroscopy of CaH in the energy range where the vibrational levels of the B/B′ and D states intermingle and are presumed to engage in strong interaction. We observed four new rovibronic levels and attribute them to vibrational levels of the B/B′ electronic state lying above the double-minimum potential energy barrier. The observation of these levels allows us to make a firm assignment of the vibronic character of all known vibrational levels in this range to either the B/B′ or D electronic states, bringing the experimental results into much better agreement with the coupled-channel calculations of Carlsund-Levin et al. [13]. We are also then in a position to present a simple conceptual explanation of the unusual alternation of vibrational spacing in this molecule.

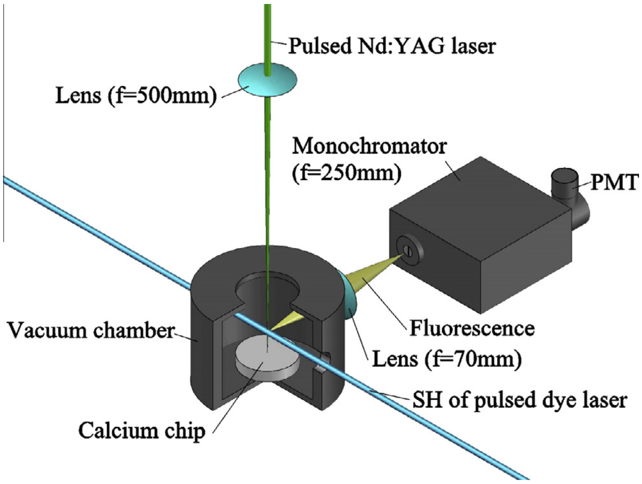

Fig. 2. The experimental setup.

2. Experiment

Our LIF setup is shown in Fig. 2. We prepared CaH by laser ablation of calcium metal chip under a hydrogen atmosphere in a vacuum chamber. The second harmonic pulses of Nd:YAG laser (532 nm) with a pulse width of 5 ns, pulse energy of 1 mJ, and a pulse rate of 10 Hz are focused on the Ca metal chip, which is placed on a stage rotating at a rate of about 1 Hz to avoid laser ablating the same spot on the chip. The vacuum chamber is filled with hydrogen gas at a pressure of about 400 Pa. Calcium monohydride molecules are then produced due to collisions of Ca or Ca$^+$ with H_2 molecules in the ablation plume. These molecules are then excited by a second harmonic pulse of a dye laser. Using LDS765, LDS798, LDS821 and LDS867 dyes allows us to cover the excitation range 23,300–27,800 cm^{-1}. Photons emitted from the molecules are focused on to the monochromator (f = 25 cm) and outputs at either 678 nm or 630 nm are detected by a photo-multiplier tube. These output signals are accumulated by a boxcar integrator and are recorded by PC. A part of the dye laser fundamental wave is monitored by a wavemeter. Over 800 rotational resolved transitions were observed. In our experiment the accuracy of the laser frequency is 0.03 cm^{-1}. Dispersed fluorescence was also recorded for selected transitions to help in assigning the observed spectrum.

3. Results and analysis

We first observed the spectrum of CaH around 27,000–27,500 cm^{-1}. The spectrum in this region had previously been attributed to the D $^2\Sigma^+$ ($\upsilon = 5$)–X $^2\Sigma^+$ ($\upsilon = 0$) transition [10]. Our observation of these transitions confirmed the production of CaH molecules and the intensity distribution of the rotational transitions allowed us to estimate the rotational temperature to be around 300–600 K. No prominent features from the excited X $^2\Sigma^+$ ($\upsilon = 1$) level were noted.