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Rotational analysis and deperturbation of the $A\ ^2\Pi \rightarrow X\ ^2\Sigma^+$ and $B'\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$ emission spectra of MgD

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ABSTRACT

High resolution Fourier transform emission spectra of MgD radical were analyzed, and the $A\ ^2\Pi \rightarrow X\ ^2\Sigma^+$ bands with $v'=2$ and $v'=3$ were rotationally assigned. Several local perturbations were observed in the $A\ ^2\Pi$ and $B'\ ^2\Sigma^+$ excited states of ^{24}MgD, and a deperturbation analysis was carried out using an appropriate Hamiltonian matrix containing off-diagonal terms connecting the vibrational levels of the two states. Dunham coefficients and band constants were determined for the $A\ ^2\Pi$ and $B'\ ^2\Sigma^+$ states, along with off-diagonal parameters. The equilibrium vibrational constants ω_e and $\omega_e x_e$ have been determined to be 1155.040(6) and 16.764(4) cm^{-1}, respectively, for the $A\ ^2\Pi$ state, and 598.108(11) and 6.394(8) cm^{-1}, for the $B'\ ^2\Sigma^+$ state. The equilibrium Mg–D distances were found to be 1.67819(3) Å and 2.59355(2) Å for the $A\ ^2\Pi$ and $B'\ ^2\Sigma^+$ states, respectively. RKR potential curves were constructed for the $A\ ^2\Pi$ and $B'\ ^2\Sigma^+$ states, and vibrational radial overlap integrals were computed for the perturbed levels. The off-diagonal matrix elements coupling the electronic wavefunctions of the $A\ ^2\Pi$ and $B'\ ^2\Sigma^+$ states were determined independently for MgD to be $a^+ = 18.9 \pm 0.2\ cm^{-1}$ and $b = 0.694 \pm 0.005$, in excellent agreement with those for the MgH isotopologue.

1. Introduction

Magnesium monohydride is an important molecule in astrophysics, and its electronic spectra have been studied extensively. Fowler [1,2] reported the first spectrum of MgH and identified its bands in the solar spectrum more than a century ago. Lines from the $A\ ^2\Pi - X\ ^2\Sigma^+$ and $B'\ ^2\Sigma^+ - X\ ^2\Sigma^+$ transitions of MgH are used routinely to determine the magnesium isotope ratio in stellar atmospheres [3–5]. A series of studies on these electronic transitions were conducted in the 1920s and 1930s [6–9], and continued by Balfour in the 1970s. Balfour and co-workers recorded the $A\ ^2\Pi - X\ ^2\Sigma^+$and $B'\ ^2\Sigma^+ - X\ ^2\Sigma^+$ spectra for both MgH and MgD isotopologues using low resolution spectrographs, and performed rotational and vibrational analyses to determine spectroscopic constants and to estimate the ground state dissociation energy [10–16].

Accurate data for the $X\ ^2\Sigma^+$ ground state of MgH and MgD have been obtained by diode laser infrared, far infrared and millimeter-wave spectroscopy [17–20]. High resolution infrared emission spectra of MgH and MgD were recorded with a Fourier transform spectrometer, and Dunham coefficients were determined for the $X\ ^2\Sigma^+$ ground state from a multi-isotoplogue fit [21]. Shayesteh et al. reported high resolution emission spectra of the $A\ ^2\Pi - X\ ^2\Sigma^+$ and $B'\ ^2\Sigma^+ - X\ ^2\Sigma^+$ band systems of MgH [22], and were able to find the highest bound vibrational level of the ground state ($v''=11$) in the $B'\ ^2\Sigma^+ - X\ ^2\Sigma^+$ spectrum. They added all available high resolution data of the $X\ ^2\Sigma^+$, $A\ ^2\Pi$ and $B'\ ^2\Sigma^+$ states of MgH [17–21,23] to their data set, and performed a direct-potential-fit analysis, determining an accurate value for the dissociation energy of the ground state [22]. Local perturbations were observed in both $A\ ^2\Pi$ and $B'\ ^2\Sigma^+$ excited states of MgH, and a deperturbation analysis was carried out by Shayesteh and Bernath [24], who used a 15×15 Hamiltonian matrix to fit simultaneously the $v=0$ to 3 levels of the $A\ ^2\Pi$ state and the $v=0$ to 4 levels of the $B'\ ^2\Sigma^+$ state.

For the MgD isotopologue, high resolution emission spectra of the $A\ ^2\Pi \rightarrow X\ ^2\Sigma^+$ and $B'\ ^2\Sigma^+ - X\ ^2\Sigma^+$ transitions were reported by Henderson et al. [25]. They assigned some bands from the $v'=0$ and 1 levels of the $A\ ^2\Pi$ state and the $v'=0$ to 4 levels of the $B'\ ^2\Sigma^+$ state, and found the $v''=15$ of MgD near the asymptote of the $X\ ^2\Sigma^+$ ground state. They also assigned some $B'\ ^2\Sigma^+ - X\ ^2\Sigma^+$ bands from the ^{25}MgD, ^{26}MgD, ^{25}MgH and ^{26}MgH minor isotopologues [25] and added all previous ^{24}MgH data [21,22], in order to perform a multi-isotopologue direct-potential fit analysis for the $X\ ^2\Sigma^+$ ground state. They determined an analytical potential energy function for the ground state of ^{24}MgH, and radial Born-Oppenheimer breakdown correction functions for the other isotopologues [25]; the potential energy well of ^{24}MgD was found

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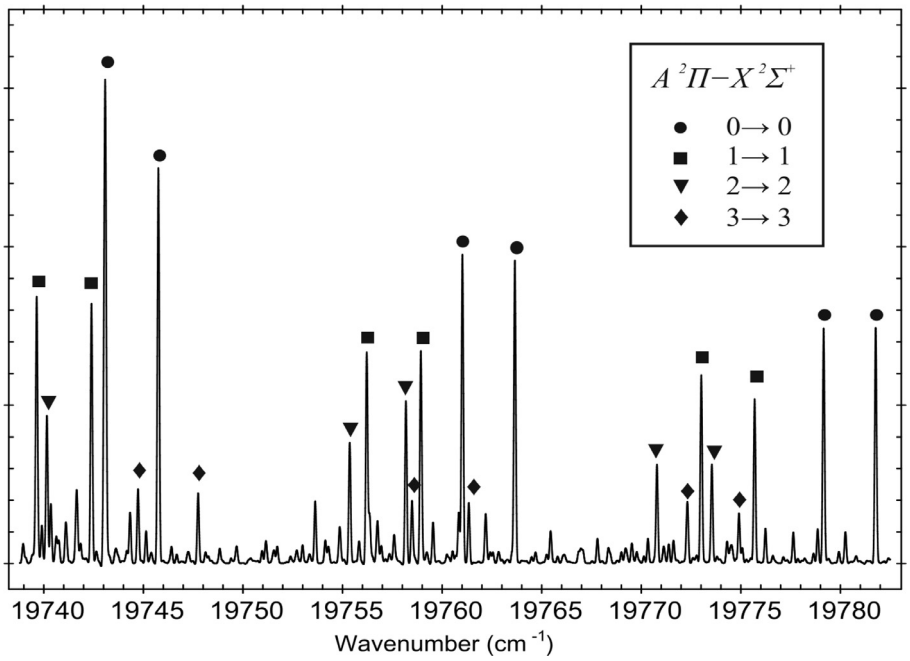

Fig. 1. An expanded view of the $A\ ^2\Pi \rightarrow X\ ^2\Sigma^+$ spectrum of MgD near 19,760 cm^{-1}, showing a few R branch lines in the $\Delta v = 0$ sequence.

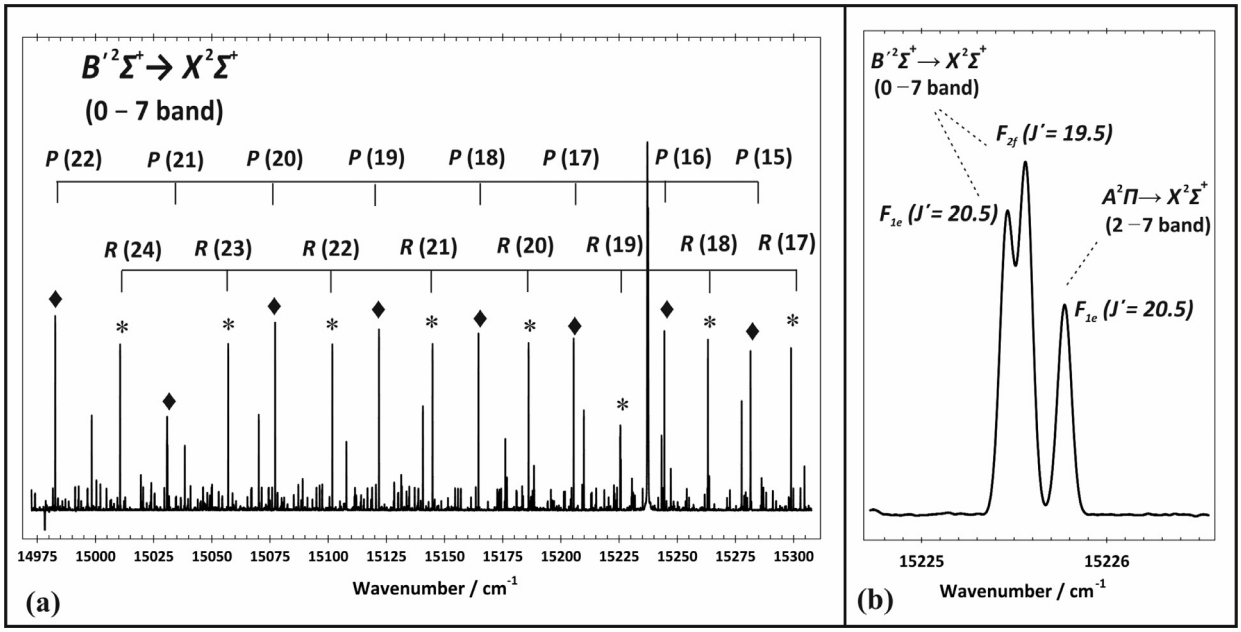

Fig. 2. An expanded view of the MgD spectrum near 15,200 cm^{-1}. (*a*) The P and R branch lines of the 0–7 band of the $B'\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$ transition, showing perturbations at $N' = 20$. (*b*) splitting of the $R(19)$ line in the 0–7 band of the $B'\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$ transition, and the existence of a third line from the perturbing state.

to be deeper than that of ^{24}MgH by 7.58 ± 0.10 cm^{-1}. Similar to Ref. [22], only term values were reported by Henderson et al. [25] for the $A\ ^2\Pi$ and $B'\ ^2\Sigma^+$ excited states. Recently, the $A\ ^2\Pi$ – $X\ ^2\Sigma^+$ spectra of cold molecular beams of MgH and MgD were recorded in the presence of electric and magnetic fields, and low J lines of the 0–0 band were measured [26,27].

In this paper we report assignment of the $v' = 2$ and 3 progressions of the $A\ ^2\Pi \rightarrow X\ ^2\Sigma^+$ band system of ^{24}MgD, and extension of the heavily perturbed $v' = 3$ bands of the $B'\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$ transition to significantly higher J values. Rotational analysis and deperturbation are reported for all the observed vibrational levels of the $A\ ^2\Pi$ and $B'\ ^2\Sigma^+$ excited states of ^{24}MgD.

2. Experimental details

The spectra of MgD were obtained using a high temperature furnace-discharge emission source and recorded by a Bruker IFS 120 HR Fourier transform spectrometer at the University of Waterloo, as described in details previously [22,25]. A silicon photodiode detector was used with appropriate optical filters; the $B'\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$ spectrum was recorded in the 9000–18,000 cm^{-1} spectral range with an instrumental resolution of 0.0375 cm^{-1}, and the $A\ ^2\Pi \rightarrow X\ ^2\Sigma^+$ spectrum was recorded in the 16,000–23,000 cm^{-1} spectral range with 0.065 cm^{-1} resolution. Line positions were measured using the program WSPECTRA, and calibrated using argon atomic lines, as described in our previous pa-