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The emission spectroscopy of AlD in the visible region: experimental and theoretical investigations

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ABSTRACT

The emission spectrum of the AlD isotopologue has been experimentally studied using Fourier transform spectroscopy in the 17, 700 – 28, 500 cm^{-1} spectral region. AlD molecules were produced within an aluminum hollow-cathode lamp with two anodes in the presence of 2.7 Torr of Ne and 0.2 Torr of ND_3. The observed bands have been assigned to the A $^1\Pi$– X $^1\Sigma^+$ (0 – 0, 1 and 1 – 0, 1, 2, 3 bands) and C $^1\Sigma^+$– A $^1\Pi$ (0 – 0 and 1 – 1 bands) transitions. In total, more than 450 rotational frequencies were measured with an absolute accuracy of about 0.002 cm^{-1}. The current data have been combined with available measurements of the pure rotational lines by Halfen and Ziurys [Astrophys J 2010; 713: 520-523] and with the ro-vibrational bands by White *et al.* [J Chem Phys 1993;99:8371-8378] to provide improved spectroscopic constants of the X $^1\Sigma^+$, A $^1\Pi$ and C $^1\Sigma^+$ states of AlD. These results match closely theoretical values obtained using a new set of *ab initio* potentials calculated with a spin-orbit Hamiltonian.

1. Introduction

The AlH molecule, along with its isotopologue AlD, is one of the most studied metal-bearing diatomic hydrides because of its importance in astrophysics [1–10] and chemistry [11–13]. In addition both the neutral AlH molecule [14] and AlH^+ ion [15–18] are very promising candidates for laser cooling [19].

The emission spectrum of AlD was first observed by Holst and Hulthén [20] in 1934. The study was focused on the rotational analysis of the eight bands (0 – 0, 1; 1 – 0, 1, 2, 3; 2 – 1, 2) of the prominent A $^1\Pi$– X $^1\Sigma^+$ system. The rotational term values for the observed vibrational levels, band origin values and estimated values of the main molecular constants for the A $^1\Pi$, $v = 0, 1, 2$ and X $^1\Sigma^+$, $v = 0, 1, 2, 3$ levels of AlD were obtained and reported. The authors have also observed a few rotational transitions beyond the predissociation limit in the A $^1\Pi$ state by using the arc-discharge technique in high deuterium pressure conditions. The predissociation data were used by Herzberg and Mundie [21] to estimate the dissociation energies of AlH and AlD. The predissociation phenomena in the A $^1\Pi$ state were also investigated by Olsson [22] at the low pressure discharge.

In 1948, Nilsson [23] supplemented previous measurement by recording many new lines, including lines beyond the predissociation limit in the A $^1\Pi$ state of the eight bands first observed by Holst and Hulthén [20]. He also discussed the pressure effect in the A $^1\Pi$– X $^1\Sigma^+$ system bands of AlH and AlD, observed in the arc-discharge.

The first rotational analysis of the C $^1\Sigma^+$– A $^1\Pi$ system of AlD includes the work of Balfour and Lindgren [24] in which they investigated the 0 – 0 and 1 – 1 bands. The bands were recorded up to the predissociation limit in the $A^1\Pi$ state, with the reciprocal dispersion of 0.5 Å/mm. The resulting set of molecular constants for the C $^1\Sigma^+$, $v = 0, 1$ levels confirms the very early results given by Grabe and Hulthén [25] and by Khan [26] from investigation of the C $^1\Sigma^+$– X $^1\Sigma^+$ system.

In the infrared, the ro-vibrational bands of the ground state of AlD were observed in absorption by Urban and Jones [27] using diode laser spectroscopy and in emission by White et al. [28] using Fourier transform (FT) spectroscopy. The experiments covered the same seven vibrational sequences, from 1 – 0 to 7 – 6, in the X $^1\Sigma^+$ state. The emission spectrum [28] was much richer, specifically

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with many high $-J$ value lines measured. Both studies resulted in the Dunham constants (Y_{ij}) for the X $^1\Sigma^+$ state of AlD as well as the mass-independent Dunham coefficient (U_{ij}) and mass scaling coefficients (Δ_{ij}) for the ground state of AlH. The former works show that the spectroscopy of the AlH and AlD isotopologues can efficiently support the investigation of the effects of breakdown in the Born-Oppenheimer approximation in diatomic molecules containing hydrogen.

Halfen and Ziurys [29,30] measured the pure rotational transitions of the AlD X $^1\Sigma^+$ state ($J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$) by submillimeter direct absorption method near the 393.6 and 590.3 GHz regions. The rotational, electric quadrupole and nuclear spin-rotation constants were determined for the AlD isotopologue.

Although widely studied experimentally, there have been relatively few theoretical studies of AlD. Calculations of the vibration-rotational line strengths for the X $^1\Sigma^+$ state have been carried out by Tipping et al. [31] in 1978. The hyperfine constants, rotational and vibration-rotation coupling constants as well as anharmonic vibrational frequencies for the ground state of AlH and AlD were recently calculated by Brown and Wasylishen [32]. The authors also widely compared present results with available previous theoretical and experimental data for the ground state of both isotopologues.

The present paper is a result of continuation of our recent spectroscopic studies on the emission spectra of AlH [33–36], AlH+ [37] and AlD [38] by high accuracy dispersive optical spectroscopy. The visible (VIS) spectra of the A $^1\Pi-$ X $^1\Sigma^+$ and C $^1\Sigma^+-$ A $^1\Pi$ systems of AlD are recorded by Fourier transform spectroscopy. The high-quality FT spectroscopic data provide significant improvement in wavenumber measurements for the observed bands of both systems under consideration. By including the most recent spectroscopic information on the ground X $^1\Sigma^+$ state obtained from submillimeter [30] and infrared [28] studies, an improved set of the spectroscopic constants of the X $^1\Sigma^+$, A $^1\Pi$ and C $^1\Sigma^+$ states of AlD was obtained. In addition, high quality *ab initio* techniques are used to produce potential energy curves of all the states recorded in the experimental study.

2. Experimental details and observations

The AlD molecule was produced and excited by an electric discharge in a water-cooled hollow-cathode aluminum lamp with two anodes [39]. The anodes were operated at 2×400 V, 2×60 mA dc and an additional electric field was added between anodes in order to convert one of them into a cathode (400 V, 120 mA dc). A static mixture of the Ne buffer gas (~2.7 Torr) and a trace amount of ND_3 (~0.2 Torr, 99% of D_3) was let into the lamp.

In the preliminary experiment we observed that AlH bands occur in the spectrum, without any additional hydrogen source in the lamp. Evidently there were enough H-containing impurities to provide a significant AlH spectrum. The still electric discharge (of about 10 hours) causes a gradual decrease of the intensity of the AlH spectrum. When the AlH bands were approximately half their initial intensity we decided to let deuterated ammonia into the lamp. Consequently, a very satisfying intensity ratio of the AlD:AlH spectra was obtained (ca. 3:1).

A Fourier transform spectrometer (Bruker IFS 125HR), operated under vacuum conditions, was used to record the VIS spectrum of AlD. The photomultiplier tube was used as an internal detector to cover the $11,000 - 32,000$ cm^{-1} spectral region. The low frequency region of observation was rejected (up to 17,700 cm^{-1}) by using a 575 nm shortpass filter (Edmund optics) in order to block out the strong Ne lines: none of the desired bands are found in the excluded region. The use of a filter led to an approximately sixfold improvement of the signal-to-noise ratio. Therefore, the weakest A $^1\Pi-$ X $^1\Sigma^+$, 0 – 1 and C $^1\Sigma^+-$ A $^1\Pi$, 1 – 1 bands could be registered. In total, 128 scans were co-added in ~2.5 h of integration at a resolution of 0.03 cm^{-1}.

The spectral line positions were extracted from the observed spectrum using a data reduction program included in the Opus™ software package [40]. The peak positions were determined by fitting a Voigt lineshape function to each spectral contour. The spectrum was calibrated with the measurements of the Ne atomic lines [41]. The AlD lines have width of ~0.08 cm^{-1} and appear with a maximum signal-to-noise ratio of ~1400: 1 for the strongest A $^1\Pi-$ X $^1\Sigma^+$, 0 – 0 band. It limits the absolute accuracy of our measurements of the strong and unblended molecular transitions to ±0.002 cm^{-1}. However, the blended and/or weaker lines and the lines belonging to the weakest bands were measured with lower accuracy, which amounted to ±0.01 cm^{-1}.

The observed line positions of A $^1\Pi-$ X $^1\Sigma^+$ and C $^1\Sigma^+-$ A $^1\Pi$ systems are collected in Tables 1 and 2.

2.1. The A $^1\Pi-$ X $^1\Sigma^+$ transition

The six bands, 0 – 0, 1 and 1 – 0, 1, 2, 3 progressions, of the A $^1\Pi-$ X $^1\Sigma^+$ system of AlD were observed. A search for the $2 - v''$ progression bands [20,23] was unsuccessful, probably due to the too low discharge temperature in the lamp we used. The low-pressure discharge did not populate higher excited vibrational levels of the $A^1\Pi$ states. The 0 – 0 band is the strongest in intensity, while the 1 – 1 band has about 40% of the intensity of the 0 – 0 band. The other off-diagonal bands are much weaker in intensity (for details see Table 3).

The rotational structure of each band of the A-X transition consists of only three branches which are degraded to the red: a single $R-$, a single $Q-$, and a single $P-$ branch. The lines of the $Q-$ branch have approximately twice the intensity of the corresponding lines of the $P-$ branch and $R-$ branch. The lines of the $R-$ branch form a characteristic band-head. An example of the high quality spectrum of the A $^1\Pi-$ X $^1\Sigma^+$, 1 – 0 band of AlD is illustrated in Fig. 1.

The A $^1\Pi$ state is predissociated by rotation [20–23]. The low-pressure discharge experiments [22,38] report the last observed rotational levels as A $^1\Pi$, $v = 0$, $J = 29$ and A $^1\Pi$, $v = 1$, $J = 19$. The same phenomenon was observed in our strongest 0 – 0 and 1 – 1 bands of the A $^1\Pi-$ X $^1\Sigma^+$ system. In the 0 – 0 band the last observed line is $Q(29)$ and the $Q(30)$ line is absent. For the 1 – 1 band the $R(18)$, $P(20)$ and $Q(19)$ lines were recognized as the last ones. The other bands of the A $^1\Pi-$ X $^1\Sigma^+$ system are definitely weaker and are not visible when the upper level lies close to the predissociation limit.

2.2. The C $^1\Sigma^+-$ A $^1\Pi$ transition

The C $^1\Sigma^+-$ A $^1\Pi$ system bands are very similar in structure to the A-X system bands, but they are violet degraded and formed the band-head in the $P-$ branch (see Fig. 2). The C-A system bands were recognized as much weaker (see Table 3) and the last observed lines correspond to the A $^1\Pi$, $v = 0$, $J = 21$ and A $^1\Pi$, $v = 1$, $J = 15$ levels. This is considerably lower than in the work of Balfour and Lindgren [24]. The authors recorded the 0 – 0 and 1 – 1 bands of the C-A system up to predissociation limits of the A $^1\Pi$ state.

3. Computational method

Ab initio calculations of the potential energy curves were performed at a post Hartree-Fock level using a parallel version of the