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The emission spectrum of the $C^1\Sigma^+$–$X^1\Sigma^+$ system of AlH

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ABSTRACT

The ultraviolet spectrum of AlH has been investigated at high resolution between 42 000 and 45 000 cm^{-1} using a conventional spectroscopic technique. The AlH molecules were formed and excited in an aluminium hollow-cathode lamp with two anodes, filled with a mixture of Ne carried gas and a trace of NH_3. The emission from the discharge was observed with a plane grating spectrograph and recorded by a photomultiplier tube. The 0–0, 1–1 and 1–2 bands of the $C^1\Sigma^+$–$X^1\Sigma^+$ transition have been identified and rotationally analyzed. The new data were elaborated with help of recent $X^1\Sigma^+$ state parameters reported by White et al. [J. Chem. Phys. 99 (1993) 8371–8378] and by Szajna and Zachwieja [Eur. Phys. J. D. 55 (2009) 549–555]. Determined constants of the excited $C^1\Sigma^+$ state include: T_e = 44 675.3711(57) cm^{-1}, ω_e = 1575.3357(42) cm^{-1}, $\omega_e x_e$ = [125.5] cm^{-1}, B_e = 6.66804(32) cm^{-1}, α_e = 0.55839(56) cm^{-1}, D_e = 2.23 (13) × 10^{-4} cm^{-1}, β_e = 6.13(25) × 10^{-4} cm^{-1} and r_e = 1.613132(39) Å. The $C^1\Sigma^+$ state is found to be extensively perturbed in the v = 0 and 1 vibrational level at J = 20, 22 − 27 and J = 5 − 9, respectively. This was probably caused by the interaction with the vibrational levels of the outer minimum.

1. Introduction

Aluminium hydride has attracted the interest of theoretical and experimental spectroscopists for a long time. Physical and chemical properties make it important in nuclear engineering, in the purification of metals, and in the preparation of electronically pure metal films, used as chemical reducing agents, and high-energy propellants. Also, AlH is a molecule of a significante interest in astrophysics. It was found in the emission spectra of sunspots [1] and atmospheres of *M*-, *S*-, *Sp*-, and *C*-type stars [2–4].

Experimentally, the AlH molecule has been studied by electronic emission spectroscopy and many bands of visible and ultraviolet systems have been identified (for review see [5] and references therein). These studies have provided information on five singlet electronic states [1], viz., $X^1\Sigma^+$ (ground state), $A^1\Pi$, $C^1\Sigma^+$, $D^1\Sigma^+$, $E^1\Pi$, and on three triplet electronic states $a^3\Pi$, $b^3\Sigma^-$ and $c^3\Pi$. Known types of electronic transitions are singlet–singlet, triplet–triplet and inter-combination triplet–singlet. The $C^1\Sigma^+$–$X^1\Sigma^+$ band system was first reported by Bengtsson [6] in 1928, who studied 0–0 and 1–1 bands. Grabe and Hultén [7] reexamined the same bands and reported first molecular constants for the $C^1\Sigma^+(v = 0,1)$ state. The rotational structure of the off-diagonal 1–0 band of the *C*–*X* system was studied by Khan [8]. More recently, Zhu et al. [9] measured the absorption spectra of the $C^1\Sigma^+$–$X^1\Sigma^+$ (0–0) transition in AlH and AlD by laser-induced fluorescence. However, the line positions reproduced in this work differ from earlier [6] and present measurements by substantial amounts ranging from 3 to 5 cm^{-1}. Our measurements confirm wavenumbers values of the 0–0 band previously reported in work [6]. However, we found that J numbering of the observed lines of the *R*-branch lines near the head is incorrect. The $R(22)$ line was erroneously assigned probably due to the perturbation existing in the v = 0 vibrational level of the $C^1\Sigma^+$ state.

The electronic structure of the ground state and the first, low lying excited states has been the subject of numerous theoretical studies [10–15]. The most accurate description of the $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^+$ states from the CASSCF calculations have been reported by Matos et al. [14]. The *ab initio* studies of the *C* state predicted that the potential curve has two minima, the inner one of Rydberg character and the outer one, ionic. The inner minimum of the $C^1\Sigma^+$ state contains only two bound vibrational levels (v' = 0, 1).

No sufficient information about the $C^1\Sigma^+$ state molecular constants and low precision of assignation of wavenumbers of the *C*–*X* transition still motivate to carry on further investigation. In the present study we have recorded the emission spectrum of AlH in the 42 000–45 000 cm^{-1} region, and observed two previously analysed bands (0–0, 1–1) and a new 1–2 band belonging to the $C^1\Sigma^+$–$X^1\Sigma^+$ transition. The major objective of this work is to determine precise values of the wavenumbers of lines, rotational terms values and improved molecular constants for the exciting state. Also, not observed earlier (but predicted theoretically) rota-

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[1] In our previous paper [5], due to our oversight, six observed singlet electronic states were mentioned. Hypothesis of the $B^1\Sigma^-$ state existence, suggested by Holst [Z. Phys. 90 (1934) 735–741], was refuted by Zeeman and Ritter [Can. J. Phys. 32 (1954) 555–561].

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tional perturbations in the $v = 0$ and $v = 1$ of the $C^1\Sigma^+$ state have been identified.

2. Experimental details

The experimental details were almost the same as described in our previous paper [5]. The spectrum of the $C^1\Sigma^+$–$X^1\Sigma^+$ transition of AlH was excited in a water-cooled aluminium hollow-cathode lamp with two anodes [16]. The anodes were operated at 2×490 V, 2×90 mA dc and extra electric field was added between anodes in order to convert one of them into a hollow-cathode (300 V, 160 mA dc). A non-flowing mixture of 2.5 Torr of Ne carried gas and a trace amount of NH_3 (~0.2 Torr) was found as optimal for production of strong spectrum.

The emission from the discharge was observed with the 2-m Ebert plane grating PGS-2 spectrograph in the 10th order. The reciprocal linear dispersion was about 0.050 nm/mm. The spectrum of AlH was recorded by translating on a linear stage an exit slit and photomultiplier tube (HAMAMATSU R943-02) along the focal curve of the spectrograph. The entrance and exit slit widths were 0.035 mm. The line intensities were measured by a single photon counting with a counter gate time of 200–500 ms depending on spectrum intensity. Positions of the exit slit were measured using He–Ne laser interferometer synchronized with the photon counting board. The total number of the measurement points was about 73 000, for one 21-cm long scan with the sample step of 3 μm. In order to reduce the fluctuations of the line positions, the apparatus is thermally insulated and mounted on the main wall with channel iron and a 6-cm thick granite plate, whereas the temperature in the laboratory room is stabilized with an air conditioner and 0.2 degree centigrade accuracy. Repeatability of the line position measurements was tested to be 0.2 – 0.5 μm according to the variations of the atmospheric pressure. The clear diagram of the experimental setup has been presented in Fig. 3 of paper [5].

Simultaneously recorded Th lines [17], obtained from several overlapped orders of the spectrum from a water-cooled hollow-cathode tube were used for absolute wavenumber calibration. Peak positions of the spectral lines were calculated by using the least-squares procedure and assuming Gaussian line-shape to each spectral contour. For the wavenumber calculations fourth-order interpolation polynomials were used. The typical standard deviation of the least-squares fit for the 20–30 calibration lines was about 0.0020–0.0023 cm^{-1}. The AlH lines have spectral widths of about 0.15–0.20 cm^{-1} and appear with a maximum signal-to-noise ratio of about 50:1 for the strongest 0–0 band. Consequently, the positions for strong and isolated lines were determined with an accuracy of better than ±0.004 cm^{-1}. However, some weaker and blended lines were measured with a lesser precision of ±0.008 cm^{-1}. In total, 95 lines belonging to 0–0, 1–1 and 1–2 bands of the $C^1\Sigma^+$–$X^1\Sigma^+$ system of AlH have been measured and their wavenumbers are provided in Supplementary material.

3. Description of the spectra

Three bands, belonging to the $C^1\Sigma^+$–$X^1\Sigma^+$ transition, with open rotational structure have been observed in the 42 000–45 000 cm^{-1} region. The bands with the origins at 44 597.7084(36) and 44 296.9738(21) cm^{-1} have been assigned as previously analysed the 0–0 and 1–1 [7] bands, respectively. Whereas, the 1–2 band, which lies in the 42 727.8359 (68) cm^{-1} spectral region, has been recorded experimentally for the first time. Despite conducted experiments we did not observe 1–0 band (recorded by Khan [8]) and other off-diagonal bands in our spectra because of their weak intensity. The C–X band system of the AlH molecule originates as a result of transition between two $^1\Sigma^+$ states, which belong to Hunds case (b). The rotational structure of each band consists of two main branches: a single R and a single P branch without any doubling. A high quality spectrum of the 0–0 and 1–1 bands of the C–X system is shown in Fig. 1, where clearly resolved lines of the R and P branches are rotationally interpreted. The 1–1 and 1–2 bands have about 30% and 6% of intensity of the 0–0 band, respectively. All observed bands are affected by local rotational perturbations and this problem will be discussed in detail in Section 5.

4. Analysis and results

Initially, band-by-band fits were made via a linear least-squares procedure and using the observed line positions showed in Table 5 see Supplementary material. The following customary term value expression, for both combining $^1\Sigma^+$ states, was used:

$$T_{vJ} = T_v + B_v J(J+1) - D_v[J(J+1)]^2 + H_v[J(J+1)]^3 + L_v[J(J+1)]^4 + \ldots. \quad (1)$$

The 0–0, 1–1 and 1–2 bands were analysed with lower $X^1\Sigma^+$, $v = 0$, 1, 2 state molecular parameters constrained to the values reported in work [5]. It should be noted that wavenumbers of the perturbed lines which deviated from the model were not included in the fit. For the 1–1 and 1–2 bands about 50% of lines were affected by perturbation and only a band origin $\sigma_{v'-v''}$ and B_v, D_v rotational constants of the $C^1\Sigma^+$ were determined. Whereas, for the 0–0 band a H_v and L_v constants had to be added to get a satisfactory fit. The molecular constants obtained from an individual fits of the 1–1 and 1–2 bands were subsequently used as an input data for the merge calculations described by Albritton et al. [18] and Coxon [19]. In this method, the output molecular constants and accompanying variance–covariance matrices from each of the individual fits of the bands are taken together as input to a correlated least-squares fit, which then yields the desired merged single values. Such merging is equivalent to a global fit of all data parameters sets for both states but it is more careful and makes it possible to find prospective strong correlations between molecular parameters or systematic errors of wavenumbers measurements. In this way, final molecular parameters for the $C^1\Sigma^+$, $v = 1$ state were derived. As the

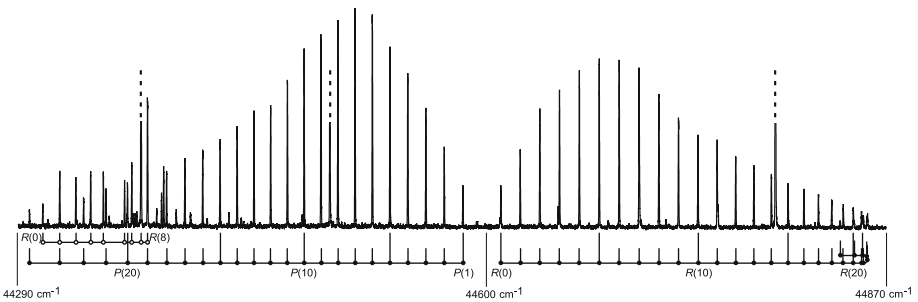

Fig. 1. Rotational structure of the 0–0 (•) and 1–1 (○) bands of the $C^1\Sigma^+$–$X^1\Sigma^+$ system of AlH. Three strongest atomic lines are marked with a broken line.