



High-resolution emission spectroscopy of the $A^2\Pi-X^2\Sigma^+$ system of AlH^+

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ABSTRACT

The emission spectrum of the $A^2\Pi-X^2\Sigma^+$ system of the AlH^+ ion was investigated in the range of 27 000–29 000 cm^{-1} by 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 full rotational structure of the 0-0 and 1-1 bands has been observed for the first time (12 branches up to $J'' = 36.5$) and many new constants of the $X^2\Sigma^+$ state have been derived from the analysis. For the $A^2\Pi$, $v = 0$ and 1 state a considerable irregularities of the Λ -doubling have been observed. The most reasonable explanation for this anomaly is an interaction with unstableness rotational levels of $X^2\Sigma^+$ state and perturbing of the $A^2\Pi$ state by the nearly lying $B^2\Sigma^+$ state.

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1. Introduction

It is true to say that the neutral AlH molecule and its ion AlH^+ take a fundamental place in laboratory spectroscopy of metal hydrides diatomic molecules. What is more its importance in several areas of science, including astrophysics and chemistry, is generally known. In contrast to the spectrum of the AlH molecule, where many electronic transitions have been experimentally studied, only one $A^2\Pi-X^2\Sigma^+$ bands system of AlH^+ has been reported from conventional emission spectroscopy.¹ The first information about new band system at 3600 Å has been developed by Holst [1,2], who suggested that this must be a $^2\Pi-^2\Sigma^+$ transition, where $^2\Pi$ is an inverted state. The Holst hypothesis was refuted by Almy and Watson [3] and by Rafi et al. [4] who studied the 0-0 and 1-1 bands and confirmed, from initial $Q_1(\frac{1}{2})$ and $P_1(\frac{3}{2})$ lines presence, that the $^2\Pi$ state is regular.

Almy and Watson [3] experimental data have been refitted by Balfour and Lindgren [5] incidentally when they studied the $A^2\Pi-X^2\Sigma^+$ system of AlD^+ . Müller and Ottinger [6] have recently reported briefly the results of reanalyzing the previous experimental data [3,4] and published new values of equilibrium constants of the $A^2\Pi$ and $X^2\Sigma^+$ states of AlH^+ .

The electronic structure of low lying states of AlH^+ has been the subject of some theoretical studies. Rosmus and Meyer [8] made extended CI calculations on the ground states of BH^+ and AlH^+

and derived new spectroscopic constants for both ions. Sabelli et al. [9] performed SCF calculations of the PEF's for the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of AlH^+ . Guest and Hirst [10], using the *ab initio* CI calculations, mapped out the $^2\Pi$ and $^2\Sigma^+$ states potential energy curves. Klein et al. [11] calculated many spectroscopic properties for the X , A and B states and also absolute emission intensities of the $A-X$ and $B-X$ transitions of AlH^+ using the PNO-CEPA and MC-SCF methods.

The present work re-examines the 0-0 and 1-1 bands of the $A^2\Pi-X^2\Sigma^+$ transition of AlH^+ between 27 000–29 000 cm^{-1} at a high-resolution of about 0.060 nm/mm. Our measurements of AlH^+ rotational lines are in good agreement with the measurements of Holst [2] and Almy and Watson [3] where they overlap. However, full rotational structure of the bands (12 clearly resolved branches) has been observed for the first time. The major objective of this work is to determine precise values of the wavenumbers of lines, improved molecular constants for the ground $X^2\Sigma^+$ state and obtained new rotational terms values of the exciting $A^2\Pi$ state of AlH^+ . Also an anomalous Λ -doubling of the $A^2\Pi$, $v = 0$ and 1 state has been observed.

2. Experimental details

As a source of the emission spectrum of the $A^2\Pi-X^2\Sigma^+$ bands, just as in our earlier investigation of AlH spectra, a water-cooled aluminium hollow-cathode lamp with two anodes [12] was used. The anodes were operated at 2×490 V, 2×80 mA dc and extra electric field was added between anodes in order to convert one of them into a hollow-cathode (300 V, 140 mA dc). A non-flowing mixture of 2.5 Torr of Ne carried gas and a trace amount of NH_3

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¹ The chemiluminescence spectra of AlH^+ have been observed by Müller and Ottinger [7] and the $A^2\Pi-X^2\Sigma^+$ and a new one $B^2\Sigma^+-X^2\Sigma^+$ systems have been identified and vibrationally analyzed.

(~ 0.2 Torr) was found as optimal for production of strong AlH^+ spectrum.

The emission from the discharge was observed with the 2-m Ebert plane grating PGS-2 spectrograph in the 7th order. The reciprocal linear dispersion was about 0.060 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 ms. 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 $^\circ\text{C}$ accuracy. Repeatability of the line position measurements was tested to be 0.2 – 0.5 μm according to the variations of the atmospheric pressure.

Simultaneously recorded Th lines [13], 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 seventh-order interpolation polynomials were used. The standard deviation of the least-squares fit for the 80 calibration lines was 0.0016 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 $100:1$ for the strongest 0 – 0 band. Consequently, the positions for strong and isolated lines were determined with an accuracy of better than ± 0.003 cm^{-1} . However, some weaker and blended lines were measured with lesser precision of ± 0.006 cm^{-1} . In total, 450 lines belonging to 0 – 0 and 1 – 1 bands of the $A^2\Pi$ – $X^2\Sigma^+$ system of AlH^+ have been measured and their wavenumbers are provided in Supplementary material.

3. Description of the spectra

Two vibrational bands of the $A^2\Pi$ – $X^2\Sigma^+$ transitions were observed in the $27\,000$ – $29\,000$ cm^{-1} region. The bands with the origins at $27\,713$ cm^{-1} and $27\,864$ cm^{-1} have been recognized as 0 – 0 and 1 – 1 bands, respectively. For the A – X system of the AlH^+ molecule the upper, $A^2\Pi$, state belongs to Hund's case (a) and the lower, $X^2\Sigma^+$, state to case (b). Twelve branches are expected, six each in the $A^2\Pi_{1/2}$ – $X^2\Sigma^+$ and $A^2\Pi_{3/2}$ – $X^2\Sigma^+$ sub-bands. The

branches of the first sub-band (with F_1 upper level) are designated P_1, Q_1, R_1 (or P_{11}, Q_{11}, R_{11}) and P_{12}, Q_{12}, R_{12} depending on whether the lower levels are F_1 or F_2 , and similar for the second sub-band. Because the spin-rotation interaction constants, γ_v , for the vibrational levels of the lower state are relatively big (of the order of 10^{-2}) the spin splitting is well resolved. The complete rotational structure (described above) has been observed in all recorded bands for the first time. A high quality spectrum of the 0 – 0 band of the A – X system is shown in Fig. 1, where clearly resolved lines of the Q_{11} and Q_{22} branches are rotationally interpreted (the presence of the other branches lines can also be noticed in this figure as the unmarked lines). We have attempted to excite other bands (2 – 2 , 3 – 3 , and 3 – 4) of the A – X system, but with no success. No emission attributable to the desired bands spectra could be identified. Theoretical predictions regarding the occurrence of these bands have been made by Klein et al. [11] and they have been observed from chemiluminescence spectra by Müller and Ottinger [7]. We found many lines in the spectral region of 3576 \AA , 3522 \AA and 3685 \AA , where 2 – 2 [11], 3 – 3 and 3 – 4 [7] bands, respectively, should be observed. However, we can not assign them explicitly to the wanted bands. Most of them belong probably to the “new” 1 – 0 band of the $b^3\Sigma^-$ – $a^3\Pi$ transition of AlH , which should lie at the 3530 \AA region.

In the earliest experimental work Holst [1,2] provided a hypothesis of the predissociation in AlH^+ in $A^2\Pi, v=0$ state. It was summarized by Huber and Herzberg [14] as a “breaking-off in P and R at $N=28$ ”. Rafi et al. [4], in their study of the 0 – 0 and 1 – 1 band, found many rotational lines far over predicted by Holst predissociation limit, up to $N=54$ for the strongest Q branch in the 0 – 0 band. However, we found out that many lines (especially beyond the $N=35$) have been incorrectly assigned.

In our 0 – 0 band spectrum we observed rotational lines up to $J''=36.5$ in main P_{11} branch. The next lines of the 0 – 0 band disappear rapidly, but any diffuse of the last observed lines does not occur. Our observations are consistent with the description of the dissociation phenomena in the ground state of HgH as given in Herzberg's book [15]. For that reason we concluded that breaking-off in the intensity of rotational lines of the 0 – 0 band at $J''=36.5$ is due to the dissociation in the ground $X^2\Sigma^+$ state of AlH^+ . The rotational lines of the 1 – 1 band can be followed up to $J''=25.5$ in main P_{11} branch.

4. Analysis and results

The preliminary rotational analysis of the observed bands were made via a non-linear least-squares fitting procedure, by using the customary effective Hamiltonian proposed by Brown et al. [18].

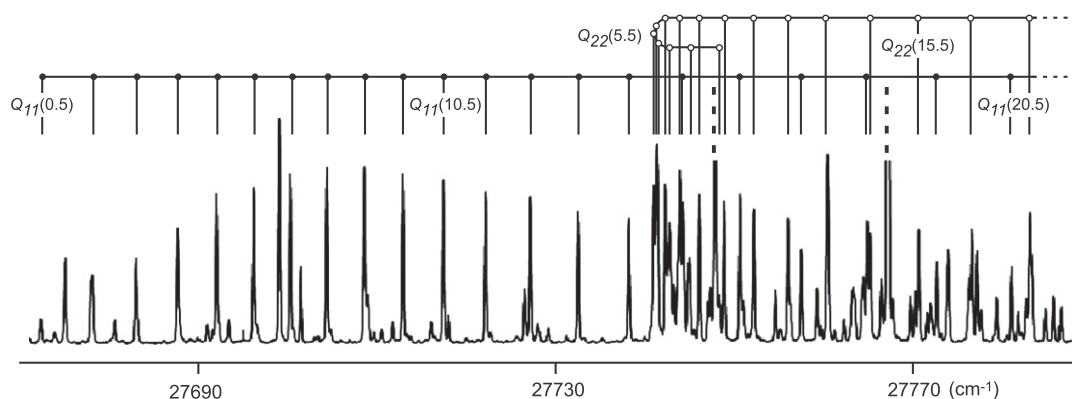


Fig. 1. Part of the rotational structure of the 0 – 0 band of the $A^2\Pi$ – $X^2\Sigma^+$ transition of AlH^+ . Only two strongest branches Q_{11} (●) and Q_{22} (○) have been rotationally interpreted (the other lines can also be noticed as the unmarked lines). Two strongest atomic lines are marked with a broken line.

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