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Fourier transform emission spectroscopy and *ab initio* calculations on the visible spectrum of AlD^+

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Abstract

The spectrum of the AlD^+ isotopologue has been investigated at high resolution in the $27,000 - 29,000 \text{ cm}^{-1}$ region using a Fourier transform emission spectroscopy technique. The AlD^+ molecules were produced within a water-cooled aluminum hollow-cathode lamp in the presence of 1.5 Torr of Ne and 0.8 Torr of ND_3 . The (0,0) and (1,1) bands belonging to the $\text{A}^2\Pi - \text{X}^2\Sigma^+$ system were recorded with an instrumental resolution of 0.03 cm^{-1} . In total, almost 500 rotational frequencies were measured with an absolute accuracy of about 0.005 cm^{-1} . It improved the experimental accuracy of the determined frequencies by the factor 10 compared to the previous work [J Phys B: Mol Phys 1984;17:L861-L866]. The rotational analysis has shown irregularities in the Λ -doubling splitting of the $\text{A}^2\Pi$ $v = 0, 1$. Consequently, the $\text{A}^2\Pi$ state has been represented by the rotational term values, while the regular $\text{X}^2\Sigma^+$ state by the molecular constants. The causes of the irregulari-

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ties were identified in the interaction between the $A^2\Pi$ and the $B^2\Sigma^+$ states, which lies about 3720 cm^{-1} above. Supporting *ab initio* quantum chemical calculations, including spin–orbit effects, reproduce the observed spectroscopic constants including the small energy splittings due to spin–rotation interactions (for $^2\Sigma^+$ states) and Λ –doubling.

Key words: AlD^+ isotopologue, Visible spectrum, FT spectroscopy, Molecular parameters, Λ –doubling, *ab initio* calculations, spin–orbit coupling, excited state lifetimes, laser cooling
PACS: 33.20Kf, Visible spectra

1. Introduction

There has been a growing interest recently in the metal–bearing diatomic hydrides, and their ions, for the production of laser cooled molecules [1, 2]. From this perspective, the AlH^+ molecular ion is a very promising candidate, especially using the very diagonal $A^2\Pi - X^2\Sigma^+$ transition [3, 4, 5, 6]. In the latest reported experiments [6], broad–band laser cooling of AlH^+ cations in a linear Paul trap has achieved rotational temperatures around 3.8 K with 95.4% of the population in the ground $v = 0$, $N = 0$ state.

In this paper, we report the first Fourier transform (FT) spectroscopy of the $A^2\Pi - X^2\Sigma^+$ system of AlD^+ together with advanced *ab initio* calculations for this transition. The experimental part is a continuation of our recent work on the emission spectra of AlH [7, 8, 9, 10], AlH^+ [11] and AlD [12, 13]. The present high–quality FT data improves experimental information about $A^2\Pi$ and $X^2\Sigma^+$ states of AlD^+ significantly. It should be noted that, only one experimental study on the AlD^+ ion of Balfour and Lindgren [14] has been reported to date. In this classic emission experiment, a very wide spectrum of the $A - X$ (0, 0) and (1, 1) bands was registered with reciprocal dispersion of $0.5\text{ \AA/mm}$ and estimated absolute accuracy of the measured transition frequencies 0.03 cm^{-1} for the best lines. The former study provided the first estimated values for the main molecular constant of the $A^2\Pi$ $v = 0, 1$ and $X^2\Sigma^+$ $v = 0, 1$ levels of AlD^+ .

The first theoretical study on AlH^+ by Klein et al. [15] dealt with the first three electronic states and used the equivalent of a modern triple–zeta basis set (highest angular function $l = 3$) similar to cc–pVTZ [16], though with an additional rather diffuse p –function. Potential energy curves were computed at the Multi Configurational Self–Consistent Field (MCSCF)[17] level that

neglects dynamic electron correlation, along with permanent dipole moment functions (DMFs) and Transition Dipole Moments (TDMs) for the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states between $2 - 10 a_0$. Using this information the authors simulated the vibronic bands for both the $A^2\Pi - X^2\Sigma^+$ and $B^2\Sigma^+ - X^2\Sigma^+$ emission spectra and estimated the Einstein A-coefficient at the band head for the former transition as $3.8 \times 10^6 \text{ s}^{-1}$.

It would take 30 years before a complete electron-correlation treatment was conducted on the lowest electronic states in AlH^+ . A calculation of the spin-orbit splitting in the $A^2\Pi$ state was conducted by Gui-Xia [18] using perturbation theory on a limited configuration interaction wavefunction though the splitting was some 60% larger than the experimental value. As part of a study on laser cooling molecular ions, Nguyen et al. [3] conducted very detailed calculations on the lowest three doublet states of AlH^+ at the Multi-reference Configuration Interaction (MRCI) level (including spin-orbit coupling) and computed the lifetimes and branching ratios for decay of the $A^2\Pi$ state. The atomic orbitals were described using the larger cc-pCVQZ basis set of Peterson *et al.* [19] to include core-valence correlation effects. Spectroscopic constants for all three states were produced though the analysis essentially required neglecting the unpaired molecular spin. Later, the two-photon dissociation of the ion was studied by the same group [5], this time the lowest five AlH^+ doublet states calculated with the same basis set. They calculated the absorption cross-sections using their *ab initio* TDMs but did not present any new spectroscopic constants. No previous theoretical work has treated the rovibronic levels of the AlD^+ radical.

The major objectives of this work is to determine improved values for the transition frequencies (wavenumbers), refresh the molecular constants for the ground $X^2\Sigma^+$ state and obtain new rotational term values for the excited $A^2\Pi$ state of AlD^+ . Moreover, detailed analysis of the current data has shown anomalous Λ -doubling features in the $A^2\Pi v = 0, 1$ levels. Furthermore, theoretical potential energy curves are presented, based on MRCI calculations using the large AV5Z basis set. The lowest ro-vibrational levels for the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of the AlD^+ ion are determined and the spectroscopic constants found, including those describing the spin-rotation splitting. Spin-orbit coupling effects are also included (as are all the quartet states correlating the lowest excited dissociation limit for the first time) and calculations performed on the decay processes important for the low lying $A^2\Pi$ and $B^2\Sigma^+$ states, taking into account the presence of the molecular

spin. In addition, the present calculations simulate the Λ -doubling observed.

2. Experimental details

The emission spectrum of AlD^+ was produced in an aluminum water-cooled hollow-cathode lamp. The cathode was prepared by inserting a 20 mm long aluminum cylinder (with 3.5 mm diameter hole) into a brass cylinder in such a way that there was uniform contact between the aluminum and the brass walls. The outside diameter of the brass cylinder is about 2 mm smaller than the inside diameter of the glass flange. Thanks to this design, the discharge room is isolated from the joint between the cathode and the glass [20]. This type of hollow-cathode lamp can easily be run with high current value (up to 500 mA in the present tests) without any risk of arcing between the anode and the brass cylinder.

The lamp, filled with a static mixture of helium (~ 1.5 Torr) and deuterated ammonia, was operated at 600 V with 250 mA current. The AlH^+ bands are a permanent feature of the spectrum, with or without any additional hydrogen source inside the lamp. Consequently, in the preliminary experiments, we were able to record good quality AlH^+ A – X (0,0) and (1,1) bands with the best signal-to-noise ratio (SNR) of $\sim 70 : 1$. The constant electric discharge (of about 20 hours) as well as a gradual addition of ND_3 (up to the effective pressure of ~ 0.8 Torr) caused the decreasing of the intensity of the AlH^+ spectrum. Finally, we obtained the satisfied intensity ratio of the $\text{AlD}^+:\text{AlH}^+$ lines of $\sim 1 : 0.75$ (see Fig. 1).

A 1.71-m FT spectrometer operated under vacuum conditions (pressure below 0.003 mbar) was used to record the visible (VIS) spectrum of AlD^+ . A VIS-wavelength quartz beamsplitter and a photomultiplier tube running in integration mode were used to record the spectrum in the 11,000 – 32,000 cm^{-1} spectral region. The spectra bandpass was limited to 17,700 – 32,000 cm^{-1} by a 575 nm shortpass filter in order to block out the strong Ne lines. In total, 128 scans were co-added in ~ 2.5 h of integration at an instrumental resolution of 0.03 cm^{-1} .

The program included in the OpusTM software package [21] was used for the line measurement. The Voigt lineshape function was fitted to the spectral line profiles. The spectrum was calibrated using the Ne atomic lines [22]. The absolute accuracy of the wavenumber scale is expected to be better than 0.002 cm^{-1} . The strong, isolated lines of the Q_{11} branch of the (0,0) band appear with maximum SNR of $\sim 50 : 1$ and the typical width of ~ 0.11

cm^{-1} . At the same time, the SNR for the strongest Q_{11} lines of the prominent $A^1\Pi - X^1\Sigma^+$ (0,0) band of AlD [13] is about 3000 : 1.

The estimated absolute accuracy of our measurements of the AlD^+ transitions is 0.005 cm^{-1} for the strong and unblended lines. For weaker lines, the poor SNR and blending caused by overlapping lines limited the accuracy of measurement to 0.01 cm^{-1} (see Table 1 and 2). Currently determined transition frequencies are blue-shifted, by about 0.4 cm^{-1} , relative to those reported by Balfour and Lindgren [14] obtained from a non-FT spectrometer in which the AlD^+ spectrum has been calibrated using Fe atomic lines.

Table 1: Transition frequencies (in cm^{-1}) of the $\text{A}^2\Pi - \text{X}^2\Sigma^+$ (0,0) band of AlD^+ .^a

J	R_{11ee}	R_{22ff}	Q_{11fe}	Q_{22ef}	P_{11ee}	P_{22ff}
0.5		27,764.25 ^{b,w}	27,659.03 ^{b,w}			
1.5	27,679.23 ^w		27,662.31 ^{b,w}	27,750.57 ^w	27,652.12 ^{b,w}	
2.5	27,689.19 ^w	27,773.50 ^b	27,665.534	27,748.18 ^{b,w}	27,648.59 ^{b,w}	27,730.01 ^w
3.5	27,699.12 ^{b,w}	27,778.655	27,668.662	27,746.16 ^b	27,644.95 ^b	27,720.78 ^{b,w}
4.5	27,708.97 ^b	27,784.20 ^b	27,671.731	27,744.44 ^b	27,641.21 ^b	27,711.92 ^b
5.5	27,718.743	27,790.073	27,674.748	27,743.19 ^b	27,637.47 ^b	27,703.420
6.5	27,728.51 ^b	27,796.258	27,677.735	27,742.251	27,633.66 ^b	27,695.361
7.5	27,738.225	27,802.746	27,680.690	27,741.641	27,629.861	27,687.64 ^b
8.5	27,747.94 ^b	27,809.549	27,683.656	27,741.37 ^b	27,626.014	27,680.305
9.5	27,757.69 ^b	27,816.588	27,686.624	27,741.42 ^b	27,622.244	27,673.310
10.5	27,767.412	27,823.919	27,689.622	27,741.799	27,618.461	27,666.667
11.5	27,777.172	27,831.469	27,692.666	27,742.421	27,614.77 ^b	27,660.370
12.5	27,786.987	27,839.26 ^b	27,695.764	27,743.354	27,611.135	27,654.394
13.5	27,796.834	27,847.32 ^b	27,698.938	27,744.57 ^b	27,607.615	27,648.75 ^b
14.5	27,806.761	27,855.579	27,702.191	27,746.04 ^b	27,604.219	27,643.397
15.5	27,816.738	27,864.042	27,705.551	27,747.771	27,600.911	27,638.371
16.5	27,826.800	27,872.729	27,709.01 ^b	27,749.76 ^b	27,597.766	27,633.66 ^b
17.5	27,836.92 ^b	27,881.599	27,712.624	27,752.036	27,594.778	27,629.263
18.5	27,847.14 ^b	27,890.681	27,716.332	27,754.556	27,591.92 ^b	27,625.164
19.5	27,857.505	27,899.96 ^b	27,720.194	27,757.332	27,589.331	27,621.407
20.5	27,867.94 ^b	27,909.462	27,724.218	27,760.371	27,586.893	27,617.93 ^b
21.5	27,878.485	27,919.178	27,728.41 ^b	27,763.663	27,584.705	27,614.83 ^b
22.5	27,889.137	27,929.063	27,732.775	27,767.227	27,582.69 ^b	27,611.991
23.5	27,899.96 ^b	27,939.14 ^w	27,737.313	27,771.05 ^b	27,580.953	27,609.578
24.5	27,910.940	27,949.51 ^w	27,742.08 ^b	27,775.18 ^b	27,579.492	
25.5	27,922.041	27,959.99 ^w	27,747.042	27,779.569	27,578.286	
26.5	27,933.290	27,970.78 ^w	27,752.247	27,784.29 ^b	27,577.39 ^b	
27.5	27,944.73 ^b		27,757.69 ^b	27,789.251	27,576.77 ^b	
28.5	27,956.386		27,763.406	27,794.56 ^b	27,576.49 ^b	
29.5	27,968.215		27,769.367	27,800.26 ^b	27,576.57 ^b	
30.5	27,980.221		27,775.604	27,806.23 ^b	27,577.00 ^b	
31.5	27,992.55 ^w		27,782.21 ^b	27,812.56 ^b	27,577.78 ^b	
32.5	28,005.04 ^w		27,789.11 ^{b,w}	27,819.26 ^b	27,578.99 ^b	
33.5	28,017.80 ^w		27,796.31 ^{b,w}	27,826.418	27,580.64 ^b	
34.5			27,803.93 ^{b,w}	27,833.981	27,582.76 ^{b,w}	
35.5					27,585.30 ^w	
J	R_{12ff}	R_{21ee}	Q_{12ef}	Q_{21fe}	P_{12ff}	P_{21ee}
0.5	27,662.42		27,652.22			
1.5	27,665.60	27,782.31	27,648.68	27,764.22	27,638.52	
2.5	27,668.77	27,793.98	27,645.03		27,628.18	27,750.46
3.5	27,671.86	27,805.93	27,641.36	27,773.42	27,617.64	27,748.05
4.5	27,674.94	27,818.31	27,637.63	27,778.52	27,607.18	27,746.00
5.5	27,677.92	27,830.95	27,633.86	27,784.03	27,596.61	27,744.32
6.5	27,680.89	27,843.84	27,630.07	27,789.87	27,586.09	27,742.97
7.5	27,683.93	27,857.08	27,626.28	27,796.03	27,575.48	27,742.01
8.5	27,686.94		27,622.51	27,802.50	27,565.01	27,741.37
9.5	27,689.97	27,884.37	27,618.76	27,809.25	27,554.46	27,741.12
10.5	27,693.01		27,615.07	27,816.25	27,544.03	27,741.12
11.5	27,696.13	27,912.56	27,611.52	27,823.55	27,533.68	27,741.46
12.5			27,607.99	27,831.10		27,742.08
13.5		27,941.55	27,604.64	27,838.84		27,742.97
14.5		27,956.30	27,601.34	27,846.89		27,744.12
15.5			27,598.21			
16.5			27,595.25			
17.5			27,592.51			
18.5			27,589.92			
19.5			27,587.45			
20.5			27,585.30			

^a Absolute accuracy of the line frequency measurement amounts 0.005 cm^{-1} for the strongest lines and 0.01 cm^{-1} for the blended ("b") and/or weak ("w") ones as well as for all satellite branch lines.

Table 2: Transition frequencies (in cm^{-1}) of the $\text{A}^2\Pi - \text{X}^2\Sigma^+$ (1, 1) band of AlD^+ .^a

J	R_{11ee}	R_{22ff}	Q_{11fe}	Q_{22ef}	P_{11ee}	P_{22ff}
0.5	27,761.15 ^{b,w}	27,856.22 ^{b,w}				
1.5		27,860.74 ^{b,w}				
2.5	27,780.97 ^{b,w}	27,865.63 ^b	27,757.81 ^{b,w}	27,840.99 ^w		27,823.33 ^w
3.5	27,790.91 ^w		27,761.15 ^b	27,839.33 ^{b,w}	27,738.08 ^{b,w}	27,814.69 ^w
4.5	27,800.892	27,876.855	27,764.60 ^b	27,838.177	27,734.90 ^b	27,806.485
5.5	27,810.913	27,883.039	27,767.963	27,837.426	27,731.70 ^b	
6.5	27,821.034	27,889.686	27,771.436	27,837.13 ^b	27,728.55 ^b	27,791.499
7.5	27,831.17 ^b	27,896.710	27,774.989	27,837.29 ^b	27,725.510	27,784.701
8.5	27,841.439	27,904.112	27,778.655	27,837.804		27,778.33 ^b
9.5	27,851.788	27,911.871	27,782.414	27,838.75 ^b	27,719.773	27,772.392
10.5	27,862.275	27,920.007	27,786.300	27,840.139	27,717.083	27,766.945
11.5	27,872.86 ^b	27,928.478	27,790.346	27,841.870	27,714.563	27,761.928
12.5	27,883.605	27,937.290	27,794.558	27,844.030	27,712.307	27,757.33 ^b
13.5	27,894.497	27,946.446	27,798.947	27,846.554	27,710.17 ^b	27,753.14 ^b
14.5	27,905.560	27,955.896	27,803.536	27,849.46 ^b	27,708.225	27,749.389
15.5	27,916.796	27,965.747	27,808.327	27,852.732	27,706.564	
16.5	27,928.26 ^b	27,975.882	27,813.364	27,856.42 ^b	27,705.196	
17.5	27,939.874	27,986.373	27,818.656	27,860.50 ^b	27,704.034	27,740.790
18.5	27,951.746	27,997.189	27,824.191	27,864.968	27,703.22 ^b	27,738.79 ^b
19.5	27,963.847	28,008.380	27,830.00 ^b		27,702.75 ^b	27,737.27 ^b
20.5	27,976.224	28,019.841	27,836.153	27,875.094	27,702.56 ^b	27,736.18 ^b
21.5	27,988.84 ^{b,w}	28,031.714	27,842.575	27,880.800	27,702.82 ^b	27,735.61 ^b
22.5	28,001.74 ^w	28,043.95 ^{b,w}	27,849.39 ^b	27,886.926	27,703.38 ^b	27,735.55 ^b
23.5		28,056.56 ^b	27,856.50 ^b	27,893.512	27,704.42 ^b	27,735.95 ^b
24.5			27,864.04 ^b	27,900.560	27,705.911	27,736.890
25.5			27,871.928	27,908.10 ^b		27,738.433
26.5			27,880.288	27,916.139		
27.5			27,889.137	27,924.719		
28.5			27,898.38 ^b	27,933.854		
29.5			27,908.20 ^b	27,943.574		
30.5			27,918.558	27,953.922		
31.5			27,929.475	27,964.934		
32.5			27,941.11 ^w	27,976.56 ^b		
33.5			27,953.38 ^w	27,988.93 ^{b,w}		
J	R_{12ff}	R_{21ee}	Q_{12ef}	Q_{21fe}	P_{12ff}	P_{21ee}
1.5				27,856.20		
2.5			27,738.13	27,860.68	27,721.66	
3.5		27,897.24	27,735.02	27,865.52	27,711.85	27,840.89
4.5	27,768.10		27,731.85			
5.5		27,922.32	27,728.76	27,876.68	27,692.34	27,838.03
6.5		27,935.49	27,725.71	27,882.90	27,682.72	27,837.25
7.5		27,948.96	27,722.84	27,889.50	27,673.26	27,836.92
8.5	27,782.71	27,962.81		27,896.50	27,663.82	27,837.04
9.5	27,786.58	27,977.01	27,717.41	27,903.85	27,654.57	27,837.53
10.5	27,790.65		27,714.87	27,911.56	27,645.54	27,838.46
11.5	27,794.90	28,006.39		27,919.68	27,636.66	27,839.80
12.5	27,799.31	28,021.48	27,710.52	27,928.12	27,627.97	
13.5		28,036.96	27,708.61	27,936.93	27,619.62	
14.5		28,052.69		27,946.01	27,611.41	
15.5				27,955.47	27,603.55	
16.5				27,965.29	27,596.04	
17.5			27,703.73	27,975.41	27,588.86	
18.5					27,582.03	
19.5					27,575.56	

^a Absolute accuracy of the line frequency measurement amounts 0.005 cm^{-1} for the strongest lines and 0.01 cm^{-1} for the blended ("b") and/or weak ("w") ones as well as for all satellite branch lines.

3. Description of the spectra

Two vibrational bands of the AlD^+ were observed in the $27,000 - 29,000 \text{ cm}^{-1}$ region. The bands with the strong heads at $27,713 \text{ cm}^{-1}$ and $27,864 \text{ cm}^{-1}$ have been recognized as $(0,0)$ and $(1,1)$ bands of the $\text{A}^2\Pi - \text{X}^2\Sigma^+$ system. We have no identified further $\Delta v = 0$ bands, as in the expected region many lines with the low signal-to-noise ratio ($\text{SNR} \approx 5$) have been observed. Most of them belong to the $(0,0)$ and $(1,1)$ bands of AlD^+ and AlH^+ and other lines cannot be assigned to the desired $(2,2)$ and $(3,3)$ bands unambiguously.

The observed bands show a typical structure for the $^2\Pi - ^2\Sigma^+$ transition, when the upper state belongs to Hund's case (a) and the lower state to case (b). Twelve branches are expected, six each in the $\text{A}^2\Pi_{1/2} - \text{X}^2\Sigma^+$ and $\text{A}^2\Pi_{3/2} - \text{X}^2\Sigma^+$ subbands [23].

A part of the $\text{AlD}^+ \text{ A} - \text{X}$ system spectrum, found between $27,650$ and $29,740 \text{ cm}^{-1}$, is shown in Fig. 1. In the same spectral region the bands of the $\text{A} - \text{X}$ system of AlH^+ occur with intensity of about 75% of the AlD^+ bands. The identification of the AlD^+ lines was carried out by means of the information reported by us in our recent work [11] as well as on the basis current observations of the AlH^+ spectrum in the initial experiments (see Section 2). It should be stressed, that the AlH^+ transition frequencies for the good quality lines of the main branches obtained in two former observations are in agreement to within $\pm 0.002 \text{ cm}^{-1}$.

The observed intensity of the $\text{AlD}^+ (1,1)$ band is about 50% of the intensity of the strongest $(0,0)$ band. We recognized rotational lines up to $J' = 36.5$ and $J' = 33.5$ in main branches of the $(0,0)$ and $(1,1)$ bands, respectively. The satellite branches were significantly weaker and can be followed up to the $J' = 20.5$ level in both the considered bands. The major impediment to the identification and measurements of any further lines was the presence of an analogous spectrum of the $\text{A}^2\Pi - \text{X}^2\Sigma^+$ system in the studied region, deriving from the AlH^+ isotopologue.

Figure 1: High-resolution VIS-FT emission spectrum of the $\text{AlD}^+ \text{A}^2\Pi - \text{X}^2\Sigma^+ (0, 0)$ band recorded with an instrumental resolution of 0.03 cm^{-1} . The SNR was ca. 50 : 1. Only main R_{11} , Q_{11} , P_{11} branch lines are interpreted. Lines of the $\text{AlH}^+ \text{A}^2\Pi - \text{X}^2\Sigma^+ (0, 0)$ band, occurring in the same spectral region, are marked at the bottom. Two characteristic features distinguished by turning back arrows are the P_{11} and P_{22} branch heads of the $\text{AlD}^+ \text{A}^2\Pi - \text{X}^2\Sigma^+ (1, 1)$ band at the $27,703 \text{ cm}^{-1}$ and $27,735 \text{ cm}^{-1}$, respectively.

4. Computational method

Ab initio calculations on the ion were performed using a parallel version of the MOLPRO [24] (version 2010.1) suite of quantum chemistry codes. The calculations are based on a Hartree–Fock treatment of the ground electronic wavefunction ($^2\Sigma^+$), the only molecular state that correlates to the lowest dissociation limit $\text{Al}^+(^1\text{S}) + \text{D}(^2\text{S})$. As is normal for treating molecules with $\text{C}_{\infty v}$ symmetry the Abelian point group C_{2v} is used to describe the diatomic orbitals and molecular symmetry labels. To describe the atomic orbitals, one–electron Gaussian functions from the correlation consistent aug–cc–pV5Z basis set [16, 19] was used for both atoms.

The static electron correlation was calculated using the State–Averaged Complete Active Space Self–Consistent Field (SA–CASSCF) method [17]. The active space consisted of all the occupied valence orbitals of the aluminum atom plus the $1s$ orbital from the deuterium atom. The $1s$ orbital on the Al^+ atom is kept frozen while the $2s2p$ orbitals are closed (kept doubly occupied in all configurations). In addition, SA–CASSCF can be used to calculate the excited electronic states corresponding to the $\text{Al}^+(^3\text{P}) + \text{D}(^2\text{S})$ asymptote so a total of five electronic states are included ($2 \times ^2\Sigma^+$, $^2\Pi$, $^4\Sigma^+$, $^4\Pi$). The accuracy of the potentials can be improved by including dynamic electron correlation, that was handled here by using the MRCI method [25]. This makes one and two electron excitations of all the configurations that make up the SA–CASSCF wavefunction. As the MOLPRO MRCI code is restricted to excitations of single or double electrons it is necessary to use the Davidson correction [26] to estimate the higher order contributions to the electronic energy.

The MOLPRO spin–orbit code [27] is used to compute the spin–orbit coupling matrix elements (including the relevant ladder operators) as well as the TDMs based on the MRCI wavefunctions.

5. Experimental results and discussion

The results of Balfour and Lindgren [14], especially the reported negative values of the $p_{0,1}$ constants of the $A^2\Pi$ state, have suggested some irregularities in the Λ -doubling of the first excited state of AlD^+ . Our preliminary analysis have confirmed these previous observations. Consequently, the observed levels of the $A^2\Pi$ state has been represented by the rotational term values while for the more regular $X^2\Sigma^+$ state the usual molecular constants are used. **However, we decided to provide effective values of the molecular constants for the $A^2\Pi$ $v = 0, 1$ level by fitting the current (0, 0) and (1, 1) bands data to a regular Hamiltonian (see Section 5.3).**

5.1. Molecular constants of the $X^2\Sigma^+$ $v = 0, 1$ levels

For the ground state constants determination we used the least-squares method proposed by Curl and Dane [28] and Watson [29]. This type of approach is an efficient means to separate molecular information concerning the lower $X^2\Sigma^+$ $v = 0, 1$, which are considered to be regular, from that which concerns the perturbed $A^2\Pi$ $v = 0, 1$ upper state. The $X^2\Sigma^+$ state was represented by the effective Hamiltonian proposed by Brown et al. [30] while the rotational terms of the $v = 0, 1$ levels of the $A^2\Pi$ state were treated as independent parameters in the fit [28, 29]. Direct matrix elements of the Hamiltonian for a $^2\Sigma^+$ state were given by Amiot et al. [31] and Douay et al. [32].

The fit of the $A - X$ (0, 0) and (1, 1) bands has given satisfactory results with the acceptably low standard deviations of 0.012 cm^{-1} and 0.014 cm^{-1} , respectively. It shows that there was no evidence of systematic trends in the residuals, indicating that all lines were adequately fitted.

Currently obtained $B_{0,1}$ and $\gamma_{0,1}$ constants (see Table 3) of the ground state confirm the previous results derived by Balfour and Lindgren [14]. A slight differences in the $D_{0,1}$ values arise from the influence of the $H_{0,1}$ constants which were included in our fit.

5.2. Rotational term values of the $A^2\Pi$ $v = 0, 1$ levels

The experimental $A^2\Pi$ $v = 0, 1$ term values were derived by adding the measured line frequencies (see Table 1 and 2) to the appropriate $X^2\Sigma^+$ $v = 0, 1$ term values calculated from the X state constants determined above and collected in Table 3. For the $A^2\Pi$ F_{1e} , F_{1f} , F_{2e} and F_{2f} levels, at most three individual values for each J number were calculated; the exact value

Table 3: Experimental molecular constants (in cm^{-1}) of the $\text{X}^2\Sigma^+$ state of AlD^+ .^a

Constant	$\text{X}^2\Sigma^+ v = 0$		$\text{X}^2\Sigma^+ v = 1$	
	This work	Balfour and Lindgren [14]	This work	Balfour and Lindgren [14]
B_v	3.42867(11)	3.4299(2)	3.29470(19)	3.2957(3)
$D_v \times 10^4$	1.1994(20)	1.237(2)	1.2789(58)	1.342(3)
$H_v \times 10^8$	-0.211(10)		-0.698(55)	
$\gamma_v \times 10^2$	2.910(29)	2.91(6)	2.735(32)	2.64(6)

^a Numbers in parentheses represent a 1σ error estimate.

depended on the number of the main and/or satellite branches observed in the $\text{A} - \text{X}$ (0,0) and (1,1) bands. Next, the single weighted average values were calculated. The individual values were weighted on the basis the estimated accuracy of the measured transition frequencies of the rotational lines (see Section 5.3). The estimated global accuracy of the term values determined in this way is about 0.03 cm^{-1} . The final results are collected in Table 4.

Our program returns rotational term values for the upper $\text{A}^2\Pi$ state, relative to the lowest term of the appropriate vibrational level of the lower $\text{X}^2\Sigma^+$ state. The absolute position of the $\text{A}^2\Pi v = 1$ terms, relative to the $\text{X}^2\Sigma^+ v = 0 J = 0.5 F_{1e}$, can be calculated by adding the $G(1) - G(0)$ difference for the ground state. Currently, only *ab initio* value for this is known and equals 1664.84 cm^{-1} (see Table 6). The former value can be verified by the future theoretical results or by the experimental investigations when the (1,0) band of the $\text{A} - \text{X}$ system will be observed.

The rotational term values of Table 4, have been used to the graphical presentation of the Λ -doubling observed in the $\text{A}^2\Pi v = 0, 1$ levels (see Fig. 5(a) in Section 7).

Table 4: Experimental values of the rotational term (in cm^{-1}) of the $\text{A}^2\Pi$ $v = 0, 1$ levels of AlD^+ .^a

J	$\text{A}^2\Pi$ $v = 0^b$				$\text{A}^2\Pi$ $v = 1^c$			
	F_{1e}	F_{1f}	F_{2e}	F_{2f}	F_{1e}	F_{1f}	F_{2e}	F_{2f}
0.5	27,659.03	27,659.04						
1.5	27,669.19	27,669.22	27,771.08	27,771.08		27,761.12		27,862.79
2.5	27,686.11	27,686.12	27,789.22	27,789.23	27,777.62	27,777.61	27,880.45	27,880.47
3.5	27,709.80	27,709.84	27,814.59	27,814.58	27,800.78	27,800.77	27,905.10	27,905.11
4.5	27,740.29	27,740.31	27,847.11	27,847.11	27,830.48	27,830.46	27,936.82	
5.5	27,777.55	27,777.58	27,886.88	27,886.87	27,866.80	27,866.75	27,975.48	27,975.49
6.5	27,821.58	27,821.61	27,933.76	27,933.76	27,909.71	27,909.67	28,021.12	28,021.12
7.5	27,872.38	27,872.43	27,987.74	27,987.77	27,959.27	27,959.18	28,073.72	28,073.68
8.5	27,929.97	27,930.02	28,048.83	28,048.85	28,015.37	28,015.31	28,133.15	28,133.13
9.5	27,994.30	27,994.37	28,116.96	28,116.99	28,078.10	28,078.03	28,199.47	28,199.45
10.5	28,065.41	28,065.47	28,192.11	28,192.12	28,147.38	28,147.30	28,272.62	28,272.58
11.5	28,143.26	28,143.32	28,274.18	28,274.22	28,223.28	28,223.15	28,352.53	28,352.50
12.5	28,227.83	28,227.88	28,363.19	28,363.23	28,305.70	28,305.56	28,439.20	28,439.13
13.5	28,319.12	28,319.16	28,459.06	28,459.10	28,394.60	28,394.49	28,532.53	28,532.45
14.5	28,417.06	28,417.11	28,561.76	28,561.81	28,490.04	28,489.91	28,632.51	28,632.42
15.5	28,521.68	28,521.71	28,671.21	28,671.28	28,591.95	28,591.80	28,739.06	28,738.95
16.5	28,632.90	28,632.92	28,787.38	28,787.48	28,700.27	28,700.14	28,852.18	28,852.08
17.5	28,750.71	28,750.75	28,910.25	28,910.34	28,815.03	28,814.90	28,971.79	28,971.65
18.5	28,875.07	28,875.09	29,039.72	29,039.82	28,936.13	28,935.99	29,097.84	29,097.67
19.5	29,005.90	29,005.93	29,175.75	29,175.85	29,063.54	29,063.41		29,230.05
20.5	29,143.24	29,143.24	29,318.29	29,318.41	29,197.26	29,197.13	29,368.96	29,368.78
21.5	29,286.94	29,286.95	29,467.25	29,467.37	29,337.19	29,337.04	29,513.96	29,513.74
22.5	29,437.02	29,437.02	29,622.60	29,622.77	29,483.29	29,483.16	29,665.14	29,664.88
23.5	29,593.40	29,593.37	29,784.25	29,784.44	29,635.52	29,635.36	29,822.45	29,822.16
24.5	29,756.03	29,755.99	29,952.19	29,952.34		29,793.65	29,985.82	29,985.50
25.5	29,924.85	29,924.79	30,126.26	30,126.51		29,957.88	30,155.18	
26.5	30,099.78	30,099.71	30,306.49	30,306.69		30,128.09	30,330.45	
27.5	30,280.76	30,280.69	30,492.70	30,492.99		30,304.20	30,511.56	
28.5	30,467.75	30,467.68	30,684.89			30,486.01	30,698.44	
29.5	30,660.66	30,660.56	30,883.04			30,673.60	30,891.00	
30.5	30,859.38	30,859.27	31,086.91			30,866.82	31,089.17	
31.5	31,063.89	31,063.80	31,296.52			31,065.58	31,292.86	
32.5	31,274.12	31,274.01	31,511.75			31,269.93	31,501.90	
33.5	31,489.95	31,489.78	31,732.62			31,479.64	31,716.28	
34.5	31,711.28	31,711.13	31,958.93					

^a The estimated global accuracy of the term values is about 0.03 cm^{-1} .

^b Related to the $\text{X}^2\Sigma^+$ $v = 0$, $J = 0.5$, F_{1e} level.

^c Related to the $\text{X}^2\Sigma^+$ $v = 1$, $J = 0.5$, F_{1e} level. To obtain the absolute position of the terms the present *ab initio* ground state $G(1) - G(0)$ distance, equals 1664.84 cm^{-1} , should be added.

5.3. Molecular constants of the $\text{A}^2\Pi$ $v = 0, 1$ levels

As the observed J -dependence of the Λ -doubling of the $\text{A}^2\Pi$ state is smooth (see Fig. 5(a)), we decided to fit the observed data to a regular Hamiltonian to get an effective parameters of the $\text{A}^2\Pi$ state. We used the PGOPHER software [33] with a $\text{A}^2\Pi$ state matrix elements defined by Amiot et al. [31] and Douay et al. [32]. The rotational structure of the ground state was fixed to the constants obtained in first step and collected in Table 3 (see Section 5.1).

The input set of the data contains 484 transition frequencies for both (0, 0) and (1, 1) bands of the $\text{A}^2\Pi - \text{X}^2\Sigma^+$ transition of AlD^+ . Each line-frequency have been individually weighted, according its accuracy: 1 is assigned to strong, isolated lines and 0.5, 0.25, 0.15 to weak and/or blended transitions.

The root-mean-square error (rmse) of unweighted transition-frequency residuals is 0.015 cm^{-1} and is dominated by the uncertainties of the weak and blended satellite lines.

The final set of $A^2\Pi$ $v = 0, 1$ molecular constants is listed in Table 5 while the obtained band origin values are $27,706.1142(20) \text{ cm}^{-1}$ and $27,798.3084(31) \text{ cm}^{-1}$ for the $(0, 0)$ and $(1, 1)$ band, respectively. To reduce the correlation between $A_{D,v}$ and γ_v parameters of the $A^2\Pi$ state [35] the $A_{D,v=0,1}$ constants were fixed to the same value calculated from the formula provided by Veseth [34]:

$$A_D = \frac{2(A_{v+1} - A_v)D_{v=0}}{B_v - B_{v+1} + 6B_e^2/\omega_e}.$$

It gives $A_{D,0} = -0.663 \times 10^{-3} \text{ cm}^{-1}$, on the basis $B_{0,1}$, D_0 , $A_{0,1}$ constants from [14] and B_e , ω_e equilibrium parameters recalculated from AlH^+ data [36]. The above $A_{D,v=0,1}$ values can be compared with the experimental results of Balfour and Lindgren [14] $A_{D,0} = -9.3(5) \times 10^{-3} \text{ cm}^{-1}$ and $A_{D,1} = -12(1) \times 10^{-3} \text{ cm}^{-1}$, obtained by authors from the fit with $\gamma_{0,1}$ equal zero. The analogous fit of current data results in $A_{D,v}$ constant values as follows: $A_{D,0} = -0.647(11) \times 10^{-3} \text{ cm}^{-1}$ and $A_{D,1} = -1.636(19) \times 10^{-3} \text{ cm}^{-1}$.

The present excited state constants are compatible but more accurate than results of the previous study [14]. In addition, we obtained a more complete set of band constants for the $A^2\Pi$ $v = 0, 1$ levels, including new values of the $p_{0,1}$ and $q_{0,1}$ Λ -doubling parameters. The former values have to be treated with a great care as they are only effective fitting parameters and cannot be used to understand the sources of the observed anomalous Λ -doubling in the $A^2\Pi$ state.

Both p_0 and p_1 constants, but especially p_0 , are quite different from those reported by Balfour and Lindgren [14]. From the pure precession theory [37, 38] we can estimate the sign and approximate value of the Λ -doubling constants for the $A^2\Pi$ state of AlD^+ . We have assumed the separate interaction between the $A^2\Pi$ state and a nearby $^2\Sigma^+$ states (see Fig. 2): $X^2\Sigma^+$ (ground state) and $B^2\Sigma^+$ (at $31,400 \text{ cm}^{-1}$). For estimation we used $l = 0$ with present experimental A_0 , B_0 constants and $E^\Pi - E^{\Sigma^+}$ distances calculated from theoretical T_0^A and T_0^B values of Table 6.

In the first case, the p_v and q_v should both be positive with values about of $+0.03 \text{ cm}^{-1}$ and $+0.0009 \text{ cm}^{-1}$. In the second case, both are expected to be negative and equal ca. -0.2 cm^{-1} and -0.007 cm^{-1} , respectively. However, the p_v and q_v constants are actually observed to be positive for

Table 5: Effective molecular constants (in cm^{-1}) of the $\text{A}^2\Pi$ state of AlD^+ .^a

Constant	$\text{A}^2\Pi \ v = 0$		$\text{A}^2\Pi \ v = 1$	
	This work	Balfour and Lindgren [14]	This work	Balfour and Lindgren [14]
B_v	3.506760(19)	3.50507(5)	3.415792(32)	3.4155(2)
$D_v \times 10^4$	1.12375(46)	1.1035(4)	1.10772(81)	1.120(2)
$H_v \times 10^8$	0.1103(29)		-0.0614(54)	
A_v	108.1884(33)	108.21(2)	107.8042(55)	107.76(3)
$A_{D,v} \times 10^3$	-0.667 ^b	-9.3(5)	-0.667 ^b	-12(1)
$\gamma_v \times 10^3$	-1.62(40)		8.63(72)	
$\gamma_{D,v} \times 10^6$	2.03(56)		10.4(11)	
$p_v \times 10^3$	6.88(25)	-1.1(9)	-10.48(49)	-5(2)
$p_{D,v} \times 10^5$	-0.220(54)		-1.22(13)	
$q_v \times 10^4$	2.715(75)		-3.585(93)	

^a Numbers in parentheses represent a 1σ error estimate.

^b Fixed at computed value (see text).

the $v = 0$ and negative for $v = 1$ (see Table 5). This discrepancy reveals that the pure precession model that we assumed, between $\text{A}\sim\text{X}$ or $\text{A}\sim\text{B}$ states, does not describe the observed Λ -doubling in the $\text{A}^2\Pi$ state correctly. Presumably, the $\text{A}^2\Pi$ state interacts with the $\text{X}^2\Sigma^+$ and $\text{B}^2\Sigma^+$ states in more complicated way and/or the other $^2\Sigma^{+/-}$ states can substantially contribute to the observed phenomenon.

6. *Ab initio* results and discussion

The calculated electronic states correlating to the lowest atomic asymptotes of the aluminum ion are presented in Fig 2. The ground state potential is quite shallow with a dissociation energy D_e of 7275 cm^{-1} . As the zero-point energy is large on account of being a deuteride (608 cm^{-1}), the D_0 dissociation energy is significantly smaller (6667 cm^{-1}). The calculations suggest that even the $^4\Sigma^+$ state, though essentially a repulsive electronic potential, possesses an equilibrium bond length ($r_e = 4.337 \text{ \AA}$, $D_e = 120 \text{ cm}^{-1}$) though it does not support a bound level.

Figure 2: *Ab initio* MRCI+Q (with Davidson correction) results for AlD^+ calculated using the AV5Z basis set: (a) the potential energy curves out to $6 \text{ \AA}$, where the spin-orbit separation begins to match the values of the $\text{Al}^+(^3\text{P})$ ion, (b) a close up of the long-range region close to the excited Al^+ asymptote to reveal the interaction between the individual molecular spin-orbit states. Note all potentials are bound though neither $^4\Sigma^+$ spin-orbit component can support a rovibrational level.

The calculated dipoles, both permanent and transition varieties, are shown in Fig. 3, while the spin-orbit coupling matrix (SO-matrix) elements are presented in Fig. 4. The latter are consistent at long range with the results of Nguyen et al. [3] though at shorter range they are generally greater in magnitude.

Figure 3: *Ab initio* dipole moments calculated using the AV5Z basis set and based on the MRCI wavefunctions (using the spin-orbit routine [27] in MOLPRO.) In (a) are the DMFs and (b) the TDMs, the latter are all zero at long range because of the $\Delta S = 0$ and Laporte selection rules.

The molecular rovibrational levels in each electronic state can be calculated using the DUO code [39]. MOLPRO conducts *ab initio* calculations in the C_{2v} point group symmetry, while DUO handles explicitly $C_{\infty v}$ symmetry states. Therefore, a series of conversions [40] are necessary to prepare the MOLPRO output prior to use:

Figure 4: The spin-orbit matrix elements as a function of internuclear separation calculated at the MRCI level [27] using the AV5Z basis set. $\langle X|H_{SO}|A\rangle \equiv \langle X^2\Sigma^+, 0, -\frac{1}{2}|\hat{H}_{SO}|A^2\Pi, -1, +\frac{1}{2}\rangle$ etc (see text).

$$\begin{aligned}
^2\Sigma^+ \text{ states} \quad & |n\Sigma, 0, \pm\frac{1}{2}\rangle = |nA_1, \pm\frac{1}{2}\rangle \\
^2\Pi \text{ states} \quad & |n\Pi, \pm 1, \pm\frac{1}{2}\rangle = \mp |nB_1, \pm\frac{1}{2}\rangle - i |nB_2, \pm\frac{1}{2}\rangle \\
\text{Dipole} \quad & \hat{\mu}_0 = \hat{\mu}_z \\
& \hat{\mu}_{\pm} = \mp \frac{1}{\sqrt{2}} (\hat{\mu}_x \pm i\hat{\mu}_y) \\
\text{Ladder} \quad & \hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y \\
\text{Spin-Orbit} \quad & \hat{H}_{SO} = \hat{H}_{SO,x} + \hat{H}_{SO,y} + \hat{H}_{SO,z} \\
SO_{\Sigma-\Pi} \quad & \langle ^2\Sigma^+, 0, -\frac{1}{2}|\hat{H}_{SO}|^2\Pi, -1, +\frac{1}{2}\rangle = \\
& \frac{1}{\sqrt{2}} \left(\langle A_1, -\frac{1}{2}|\hat{H}_{SO,y}|B_1, +\frac{1}{2}\rangle - i \langle A_1, -\frac{1}{2}|\hat{H}_{SO,x}|B_2, +\frac{1}{2}\rangle \right) \\
SO_{\Pi-\Pi} \quad & \langle ^2\Pi, +1, +\frac{1}{2}|\hat{H}_{SO}|^2\Pi, +1, +\frac{1}{2}\rangle = i \langle B_1, +\frac{1}{2}|\hat{H}_{SO,z}|B_2, +\frac{1}{2}\rangle
\end{aligned}$$

where $|state, \Lambda, \Sigma\rangle$ are the $C_{\infty v}$ electronic wavefunctions [39, 40]. All the cal-

culated SO–matrix elements and ladder operators are included to correctly simulate the complicated level structure due to the unpaired electronic spin in all the electronic states. The computed spin–orbit splitting for $A^2\Pi$ $v = 0$ ($N = 0$) is 111 cm^{-1} which is within 2% of the **current experimental value equals $108.1884(33) \text{ cm}^{-1}$** . The spin–orbit couplings also have a strong effect on the $^4\Sigma^+$ state, which splits into two rather different potential curves with relatively large differences in dissociation energy ($D_e = 109 \text{ cm}^{-1}$ for $^4\Sigma_{1/2}^+$, $D_e = 131 \text{ cm}^{-1}$ for $^4\Sigma_{3/2}^+$).

Table 6: Ro–vibrational constants (in cm^{-1}) of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of AlD^+ .
^a

State	v	T_v	A_v	$A_{D,v}$	B_v	$10^4 D_v$	$10^2 \gamma_v$	$10^2 p_v$
$X^2\Sigma^+$	0	0.00			3.473406	1.1788	1.6048	
	1	1164.84			3.343229	1.2801	1.4882	
	2	2242.86			3.195912	1.4379	1.3522	
	3	3222.29			3.024578	1.7031	1.2057	
	4	4087.35			2.825036	2.1934	1.1404	
$A^2\Pi^b$	0	27710.29	111.1990	0.3332	3.539210	1.3202		−0.5577
	1	28950.05	110.4661	0.3197	3.445932	1.3193		0.0823
	2	30143.91	109.8179	0.3054	3.352814	1.3338		1.4970
	3	31288.30	112.4429	0.2647	3.377430	4.9506		−18.4957
	4	32397.10	107.6012	0.2829	3.172055	1.3978		−1.9759
$B^2\Sigma^+$	0	31271.06			1.908245	−8.2751	39.570	
	1	32209.06			2.142094	0.40465	−2.7196	
	2	33131.25			2.119465	0.35930	5.1767	
	3	34030.64			2.095616	0.50149	−1.5383	
	4	34905.07			2.068223	0.53319	−1.2264	

^a Determined by [14] model fit to DUO [39] generated term values.

^b For the $A^2\Pi$ state: A_v is the vibrational level dependent spin–orbit splitting, $A_{D,v}$ determines the rotational dependence, γ_v is the spin–rotation constant, p_v is the vibrational state dependent Λ –doublet parameter [14] that determines $\Delta F_{1,2}(J)$.

The rovibrational terms of a $^2\Sigma^+$ state in AlD^+ may be described by [14]

$$\begin{aligned} F_{1,v}(N) &= B_v N(N+1) - D_v N^2(N+1)^2 + \gamma_v N & \text{where } N = J - \frac{1}{2} \\ F_{2,v}(N) &= B_v N(N+1) - D_v N^2(N+1)^2 - \gamma_v(N+1) & \text{where } N = J + \frac{1}{2} \end{aligned}$$

The corresponding spectroscopic constants for the $\text{X}^2\Sigma^+$ and $\text{B}^2\Sigma^+$ states are presented in Table 6. Those for vibrational levels $v = 0$ and $v = 1$ match the present experimental results very well although the computed spin–rotation constant is around a third smaller than the experimental value for the levels of $\text{X}^2\Sigma^+$. The rovibrational terms of the $\text{A}^2\Pi$ state in AlD^+ require a more involved analysis, again following the method from [14]:

$$T_{1,2}(N) = T_v + B_v x - D_v x^2 \mp Z(\pm) \Delta F_{1,2}(J)$$

where,

$$\begin{aligned} Z &= \left\{ \frac{(A_v^* - 2B_v^*)^2}{4} - B_v^* x \right\}^{1/2} \\ \Delta F_{1,2}(J) &= \frac{1}{2} p_v \left(J + \frac{1}{2} \right) \left\{ 1 \pm \left(\frac{A_v^* - 2B_v^*}{2Z} \right) \right\} \\ x &= (J + \frac{1}{2})^2 - 1 \\ B_v^* &= B_v - 2D_v x \\ A_v^* &= A_v + A_{D,v} J(J+1) \end{aligned}$$

The ro–vibrational constants for $\text{A}^2\Pi_{1/2}$ $v = 3$ clearly reveal there is substantial interaction predicted between this level and the lowest $\text{B}^2\Sigma_{1/2}^+$ $v = 0$ vibronic level. This is unlikely to be a precise reflection of experiments because such interactions are typically sensitive at the sub–wavenumber level to the relative energies of the interacting ro–vibrational states. While a fitting can be made using the present *ab initio* and spectroscopic data to refine the $\text{A}^2\Pi_{1/2}$ potential this cannot be done for the $\text{B}^2\Sigma_{1/2}^+$ state as there is presently no spectroscopic information. The most significant omission is the energy minimum of the $\text{B}^2\Sigma_{1/2}^+$ potential and that is difficult to calculate to an accuracy better than 100 cm^{-1} .

Another sensitive test of the potentials is a calculation of the Λ –doubling observed for the lowest excited ro–vibrational levels of the $\text{A}^2\Pi_{1/2}$ and $\text{A}^2\Pi_{3/2}$ states. This is achieved by including all *ab initio* electronic states calculated

and the relevant interaction matrix elements (spin–orbit coupling and the rotational–electronic Coriolis term.) This phenomenon is additionally very sensitive to the relative energies of the nearest $^2\Sigma^+$ and $^2\Pi$ states. The resulting Λ –doubling predicted for both $v = 0$ and $v = 1$ vibrational levels of $A^2\Pi$ is presented as a function of the rotational quantum number in Fig. 5(b).

Finally, the ro–vibrational constants in Table 6 are fit to simple polynomial expansions in $(v + \frac{1}{2})^n$ and reported in Table 7.

Table 7: Equilibrium constants (in cm^{-1}) of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of AlD^+ .^a

State	T_e	ω_e	A_e	B_e	$10^4 D_e$	$10^2 \gamma_e$	$10^2 p_e$
$X^2\Sigma^+$	0.00	1233.22		3.5140	1.0705	1.6429	
$A^2\Pi$	27681.21	1287.26	111.41	3.5855	1.3246		−1.9889
$B^2\Sigma^+$	31403.91	954.89		2.1753	0.3667	−4.389	

^a Determined by $(v + \frac{1}{2})^n$ polynomial fit to ro–vibrational constants of Table 6.

Using the calculated TDMs (Fig. 3) the lifetime of the $v = 0$ level in the $A^2\Pi_{1/2}$ and $B^2\Sigma_{1/2}^+$ states was found to be 76 ns and 97 ns, respectively. In addition, the decay from $A^2\Pi_{1/2} v = 0$ was 97.9% to the corresponding $v = 0$ level of the ground state, confirming that this transition is highly diagonal [3]. By contrast, the majority of the decay from $B^2\Sigma_{1/2}^+ v = 0$ is to three vibrational levels, namely $v = 2$ (19%), $v = 3$ (49%) and $v = 4$ (23%) and some 7.8% to other vibrational levels. Although some decay was found to the $A^2\Pi_{1/2}$ state, this did not exceed 0.001%. However, the present simulations only consider radiative decay and as the $A^2\Pi_{1/2} v = 0$ level lies over twenty thousand wavenumbers above the first dissociation limit, it could be adversely affected by predissociation [3], unlike the corresponding $\Pi \leftarrow \Sigma^+$ transition in AlD [2]. A calculation of Nguyen et al. [3] for AlH^+ suggests that this rate is indeed negligible, around $0.2 \pm 0.1 \text{ s}^{-1}$.

7. Λ -doubling of the $A^2\Pi v = 0, 1$ levels

The $^2\Pi \sim ^2\Sigma^+$ interaction, which is different for the e and f levels, gives rise to Λ –doubling in the $^2\Pi$ and spin–doubling of the $^2\Sigma^+$ state [38]. Moreover, the different kinds of $^2\Pi_{1/2} \sim ^2\Sigma^+$ and $^2\Pi_{3/2} \sim ^2\Sigma^+$ interactions cause that the value of the Λ –doubling splitting is different for the two

substates of the $^2\Pi$ state [38]. For the $^2\Pi_{1/2}$ the ΔF_{fe} value should be zero at the origin, then negative with increasing J , and finally rise to positive values. For the $^2\Pi_{3/2}$ substate the ΔF_{fe} should rise slowly from zero at small J [41]. Thus for large enough J it has the same sign (and similar value) for the F_1 and F_2 terms [37].

For the AlD^+ $\text{A}^2\Pi$ state Λ -doubling should arise mainly from the interaction with the nearby $\text{B}^2\Sigma^+$ state. The present *ab initio* calculations locate the $\text{B}^2\Sigma^+$ state about 3720 cm^{-1} above from the $\text{A}^2\Pi$ state (see Table 7). However, the simple pure precession estimation in Section 5.3 and present *ab initio* results do not give a full understanding of this interaction. The observed Λ -doubling of the $\text{A}^2\Pi$ $v = 0, 1$ levels is presented in Fig. 5(a) and compared with theoretical prediction in Fig 5(b).

Figure 5: The Λ -doubling of the $\text{A}^2\Pi$ $v = 0, 1$ levels of AlD^+ : (a) observed on the basis of the term values from Table 4, (b) calculated using the potentials from Fig. 2.

The calculated J -dependence is in excellent agreement with the experimental values in Fig. 5(a) for $v = 0$, both in general trends and absolute value. However, the calculated splitting for $v = 1$, while still in reasonable agreement, clearly does not reproduce the observed J -dependence as ac-

curately. Moving the $B^2\Sigma^+$ state potential relative to the $A^2\Pi$ state by as much as $\pm 200\text{ cm}^{-1}$ did not strongly improve this result. Shifting the potential up improves slightly the agreement for $A^2\Pi_{1/2}\ v = 1$, while shifting down strongly improves $A^2\Pi_{3/2}\ v = 1$ at the expense of $A^2\Pi_{1/2}\ (v = 0\text{ is not really changed})$. It looks like a simple shift won't solve this and the potential would have to be more accurate - a very long project. - I took this sentences from your "Notes...". Please improve this, it may be some kind of summary. What do you think?

8. Conclusions

The emission VIS spectrum of the AlD^+ isotopologue was recorded with a Fourier transform spectrometer for the first time. The $(0,0)$ and $(1,1)$ bands belonging to the $A^2\Pi - X^2\Sigma^+$ electronic transitions were identified and analyzed. The Λ -doubling of the $A^2\Pi\ v = 0, 1$ levels has been studied on the basis of the experimental rotational term values. Molecular constants of the $X^2\Sigma^+$ state have been obtained by method based on the Curl and Dane [28] and Watson [29] approach. *Ab initio* calculations reproduce these results very well including the Λ -doubling observed for the lowest vibrational level of the excited $A^2\Pi$ state. The highly diagonal nature of the $A^2\Pi - X^2\Sigma^+$ transition coupled with its relatively short lifetime suggests AlD^+ is a good laser cooling prospect, though it is critical that any predissociation loss is below 0.01% or the cooling will be terminated within 10^4 cycles.

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