Experimental and theoretical investigations on the visible spectrum of AlD^+

W. Szajna[1], **R. Hakalla**[1], K. Moore[2], I.C. Lane[2], M. Ostrowska-Kopeć[1], I. Piotrowska[1], P. Kolek[1], M. Zachwieja[1] and R. Kepa[1]

[1]Materials Spectroscopy Laboratory, Departament of Experimental Physics, Faculty of Mathematics and Natural Science, University of Rzeszów, Pigonia 1 Street, 35-959 Rzeszów, Poland.

[2]School of Chemistry and Chemical Enginereeng, Queen's University Belfast, Stranmillis Road, Belfast Bt9 5AG, UK.

Abstract

The emission spectrum of the AlD^+ ion has been studied by Fourier transform spectroscopy technique, as a further step of our investigation of the AlD neutral molecule [1]. The 0-0 and 1-1 bands of the $A^2\Pi$-$X^2\Sigma^+$ system have been recorded in the 27000-29000 cm^{-1} region. In total, almost 500 rotational frequencies were measured with an absolute accuracy of about 0.005 cm^{-1}.

The rotational analysis has shown irregularities in the Λ-doubling splitting of the $A^2\Pi$, v =0;1. Consequently, the $A^2\Pi$ state has been represented by the rotational term values, while the regular $X^2\Sigma^+$ state by the molecular constants. The causes of the irregularities were identified in the interaction between the $A^2\Pi$ state the lying higher the $B^2\Sigma^+$ state.

Ab initio calculations were performed using a parallel version of the MOLPRO [2] 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 $Al^+(^1S)+D(^2S)$. The static electron correlation was calculated using the State-Averaged Complete Active Space Self-Consistent Field method [3]. The active space consisted of all the occupied valence orbitals of the aluminium 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. In addition, SA-CASSCF can be used to calculate the excited electronic states corresponding to the $Al^+(^3P)+D(^2S)$ asymptote so a total of five electronic states are included (2 x $^2\Sigma^+$, $^2\Pi$, $^4\Sigma^+$, ^4P). The accuracy of the potentials can be improved by including dynamic electron correlation, that was handled here by using the Multi-reference Configuration Interaction (MRCI) method [4].

References

[1] W. Szajna, K. Moore, I.C. Lane. J. Quant. Spectrosc. Radiat Transf. **196** , 103-111 (2017).

[2] H.J. Werner, P.J. Knowles, G. Knizia, F.R. Manby et al., MOLPRO 2010, http://www.molpro.net.

[3] P. Siegbahn, A. Heiberg, B. Roos, B. Levy . Phys. Scr. **21**, 323-330 (1980).

[4] H.J. Werner, P.J. Knowles P.J. J. Chem. Phys. **89**, 5803-5808 (1988).

[5] W.J. Balfour, B. Lindgren. J. Phys. B: At. Mol. Phys. **17**, L861-866 (1984).

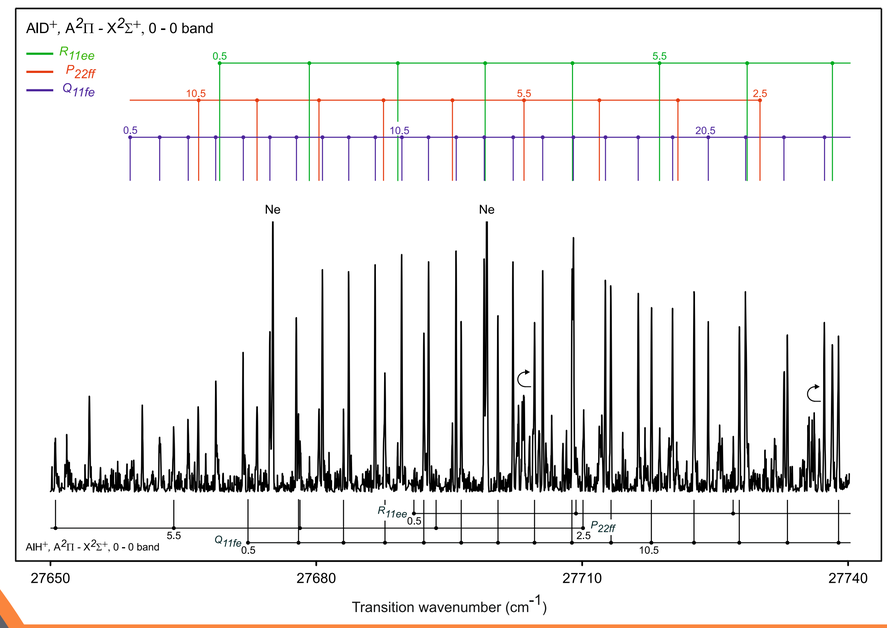
[6] S.N. Yurchenko, L. Lodi, J. Tennyson, A.V. Stolyarov. Comp. Phys. Comm. **202**, 262-275 (2016).

e-mail: szajna@ur.edu.pl

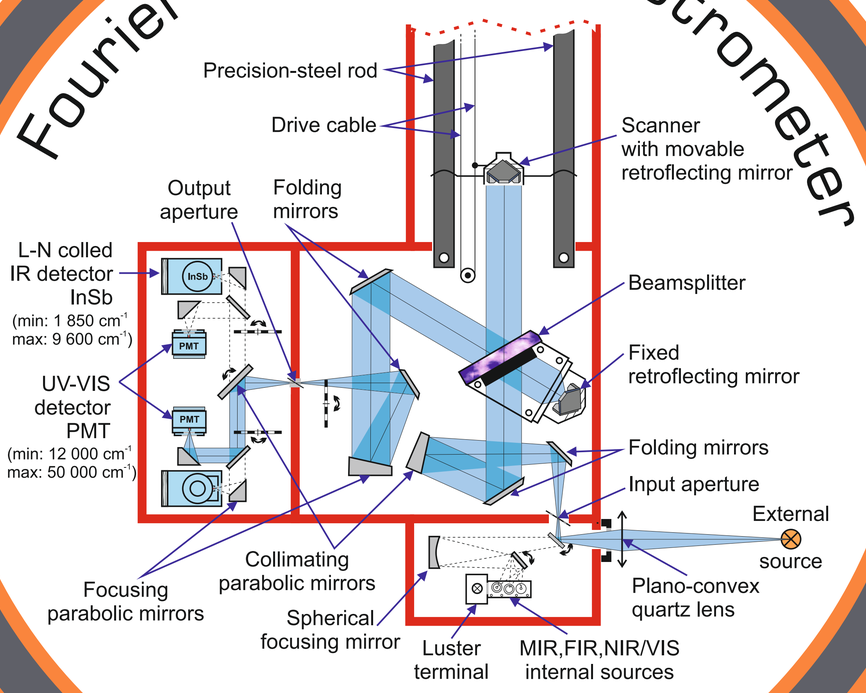
Spectrum

High-resolution VIS-FTS emission spectrum of the AlD^+ $A^2\Pi$-$X^2\Sigma^+$ system.

- **instrumental resolution:** 0.03 cm^{-1},
- **signal-to-noise ratio:** 50 : 1
- **FWHM of AlD+ lines:** 0.11 cm^{-1}
- **spectrum source:** water-cooled hollow-cathode lamp



Fourier Transform Spectrometer



Spectral range: 1850 - 50000 cm^{-1} (5400- 200 nm)
Maximum Optical Path Diffeerence: $(OPD)_{max}$ = 258 cm
Maximum spectral resolution: $(\Delta\upsilon)_{max}$ = 0.0035 cm
Resolving power: $> 10^6$
Vacuum conditions: p ≈ 0.002 hPa
Aperture: 0.5 - 12.5 mm
Detector: PMT in integration pulse mode
Interferometer: modified Michelson's system
Control the scanner position: 1.2 mW single mode He-Ne laser

Results

Experimental molecular constants for the X state of AlD^+

State	v	B_v	$10^4 D_v$	$10^8 H_v$	$10^2\gamma_v$
$X^2\Sigma^+$	0	3.42867(11)	1.1994(20)	−0.211(10)	2.910(29)
		3.4299(2)	1.237(2)		2.91(6)
	1	3.29470(19)	1.2789(58)	−0.698(55)	2.735(32)
		3.2957(3)	1.342(3)		2.64(6)

All values in cm^{-1}, 1σ in parentheses. The second line contains the values of Balfour and Lindgren [5].

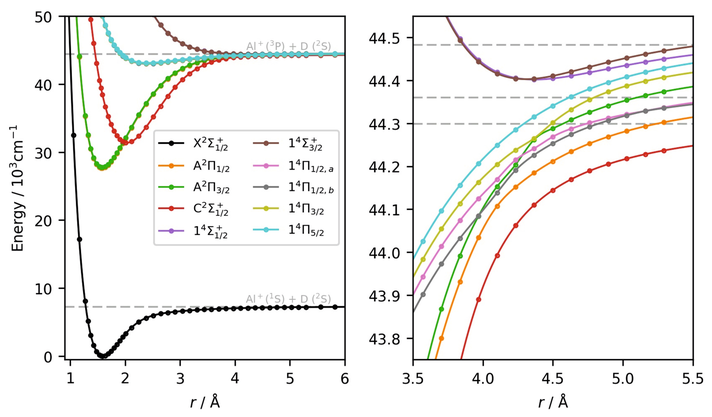
Ab initio molecular constants of the X, A and B states of AlD^+

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	–
$A^2\Pi$	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	–

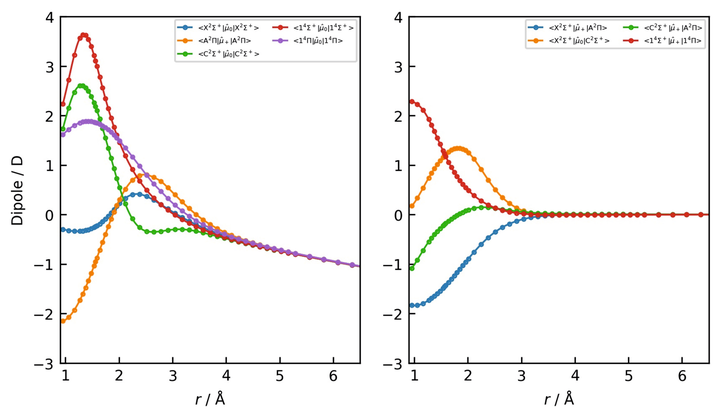
All values in cm^{-1}. Constants obtained from $^2\Pi$ and $^2\Sigma^+$ states model [5] fit to DUO [6] generated term values.

Ab initio MRCI results for AlD+

(a) potential energy curves



(b) dipol moments



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

(a) experimental results **(b) theoretical results**

Equilibrium parameters of the X, A and B states of AlD^+

	$X^2\Sigma^+$	$A^2\Pi$	$B^2\Sigma^+$
T_e	0.00	27681.21	31403.91
ω_e	1233.22	1287.26	954.89
A_e	–	111.41	–
B_e	3.5140	3.5855	2.1753
$10^4\ D_e$	1.0705	1.3246	0.3667
$10^2\ \gamma_e$	1.6429	–	-4.3898
$10^2\ p$	–	-1.9889	–

All values in cm^{-1}.