Experimental and Theoretical Investigations on the Visible Spectrum of AlD^+

W. Szajna,[1], R. Hakalla, University of Rzeszów; K. Moore, I. C. Lane, Queen's University Belfast; M. Ostrowska−Kopeć, I. Piotrowska, P. Kolek, M. Zachwieja, University of Rzeszów, R. Kępa, University of Rzeszów

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.[2] The $0-0$ and $1-1$ bands of the $A\,^1\Pi - X\,^1\Sigma^+$ system have been recorded in the $27,000 - 29,000$ cm^{-1} region 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.[3] The rotational analysis has shown irregularities in the $\Lambda-$ doubling splitting of the $A\,^1\Pi$ $v = 0, 1$. Consequently, the $A\,^1\Pi$ state has been represented by the rotational term values, while the regular $X\,^1\Sigma^+$ state by the molecular constants. The causes of the irregularities were identified in the interaction between the $A\,^1\Pi$ state the lying higher the $B\,^1\Pi$ state.

Ab initio calculations on the ion were performed using a parallel version of the MOLPRO[4] (version 2010.1) suite of quantum chemistry codes. The static electron correlation was calculated using SA−CASSCF method.[5] 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 of 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 $\mathrm{Al}^+(^3\mathrm{P}) + \mathrm{D}(^2\mathrm{S})$ asymptote so a total of five 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 MRCI method.[6]

[1]szajna@ur.edu.pl

[2]W. Szajna, K. Moore, I.C. Lane. J. Quant. Spectrosc. Radiat. Transf. **196**, 103 – 11 (2017).
[3]W.J. Balfour, B. Lindgren. J. Phys. B: At. Mol. Phys. **17**, L861−6 (1984).
[4]H.J. Werner,P.J. Knowles, R. Lindh,F.R. Manby et.al. MOLPRO (2010), http://www. molpro.net.
[5]P. Siegbahn ,A. Heiberg, B. Roos, B. Levy. Phys. Scr. **21**, 323 – 30 (1980).
[6]H.J. Werner, P.J. Knowles. J. Chem. Phys. **89**, 5803 – 8 (1988).