HIGH RESOLUTION FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $\tilde{A}^2\Pi - \tilde{X}^2\Pi$ TRANSITION OF THE OCS^+ ION

YOSHIHIRO NAKASHIMA, KEIICHI TANAKA, and TAKEHIKO TANAKA, *Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812-8581, Japan..*

The OCS^+ ion was produced by Penning ionization of OCS with metastable He^*, and UV emission in the $370 - 500$ nm region was measured by Fourier transform spectrometer. The $\tilde{A}^2\Pi - \tilde{X}^2\Pi$ electronic transition has been reported in the $300 - 500$ nm region, but only the emission bands from the vibrational ground state of the $\tilde{A}^2\Pi$ state were observed because of the predissociation in the $\tilde{A}^2\Pi$ state [a]. High resolution study of the 0-0 band has been reported for both the $\Omega = 3/2$ and $\Omega = 1/2$ spin states [b, c].

In the present study, seven rotationally resolved bands were observed in the $370 - 500$ nm region and assigned to the CO stretch (ν_3'') progression : $\tilde{A}^2\Pi_{3/2}(000) - \tilde{X}^2\Pi_{3/2}(00v)$ $(v = 2 - 5)$ and $\tilde{A}^2\Pi_{1/2}(000) - \tilde{X}^2\Pi_{1/2}(00v)$ $(v = 3 - 4)$. The observed lines of the $\Omega = 1/2$ substate were split into the two components due to the Λ-type doubling. The spectra for $\Omega = 3/2$ and $\Omega = 1/2$ were analysed separately to obtain molecular constants for each spin state.

Band origins, vibrational frequencies, rotational constants, vibrational-rotational constants for both spin substates and Λ-type doubling constant for the $\Omega = 1/2$ substate were determined by a least squares fitting. Rotational constants in the vibrational ground state were determined for both spin states. The spin-orbit interaction constants derived from these rotational constants, $A' = -125.0$ cm^{-1} and $A'' = -383.8$ cm^{-1}, are consistent with those derived from the photodissociation study [d].

---

[a] D. L. Judge and L. C. Lee, Int. J. Mass Spectrom. Ion Phys., **17**, 329, (1975)
[b] M. Oschner, M. Tsuji, and J. P. Maier, Chem. Phys. Lett., **115**, 373, (1985)
[c] R. Weinkauf and U. Boesl, J. Chem. Phys., **101**, 8482, (1994)
[d] R. Kakoschke, U. Boesl, J. Hermann and E. W. Schlag, Chem. Phys. Lett., **119**, 467, (1985)