High-resolution Fourier transform emission spectroscopy of the $A^2\Pi_i$ - $X^2\Pi_i$ band of the OCS^+ ion

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High resolution Fourier transform (FT) emission spectroscopy of the $A^2\Pi_i$ - $X^2\Pi_i$ band of OCS^+ generated by Penning ionization with metastable He* atom was performed in the 370 - 490 nm UV region at a resolution of 0.03 cm^{-1}. The ν_1 (CO stretching) progression bands from the ground vibrational state of $A^2\Pi_i$ to the ν_1 excited states of $X^2\Pi_i$ were observed for the $v_1 = 0 \leftarrow 2$ - 5 bands of the $\Omega = 3/2$ and 1/2 components. The parity doubling were resolved for the *P*- and *R*-branch lines for $\Omega = 1/2$.

Observed ν_1 progression bands were analyzed together with the origin bands reported by LIF study to give the accurate molecular constants of OCS^+. The spin-orbit interaction constants A_0 determined are -381.0(56) and -126.5(56) cm^{-1}, respectively, for the $X^2\Pi_i$ and $A^2\Pi_i$ states to agree with the previously reported ones. The CO bond length for the $A^2\Pi_i$ state is longer by 0.1756 Å than that for the $X^2\Pi_i$ state, while the CS bond length shorter by 0.0905 Å, as determined by the observed rotational constants B_0 and Franck-Condon factors, implying the excited state has much weaker CO bond than that of the ground state. The large change in the molecular structure between $A^2\Pi_i$ and $X^2\Pi_i$ causes the prominent ν_1 progression bands observed in the present FT emission spectrum.

＜Introduction＞ For the OCS^+ ion, observation of the $A^2\Pi_i$ - $X^2\Pi_i$ emission band is limited only from the vibrational ground state of $A^2\Pi_i$ to the ν_1 (CO stretch) vibrational excited states of the $X^2\Pi_i$ state (**Fig. 1**). It is because the internal conversion (IC) occurs from the $A^2\Pi_i$ state to the highly excited vibrational levels of $X^2\Pi_i$ state and the OCS^+ ion rapidly predissociates to $S^+(^4S_u)$ + $CO(X^1\Sigma^+)$ due to the crossing of a repulsive $^4\Sigma^-$ state. In the present study[1)], we report a Fourier transform (FT) emission spectroscopy of the $A^2\Pi_i$ - $X^2\Pi_i$ band of OCS^+ for both the Ω=3/2 and 1/2 spin components to give the accurate molecular constants in the $X^2\Pi_i$ state.

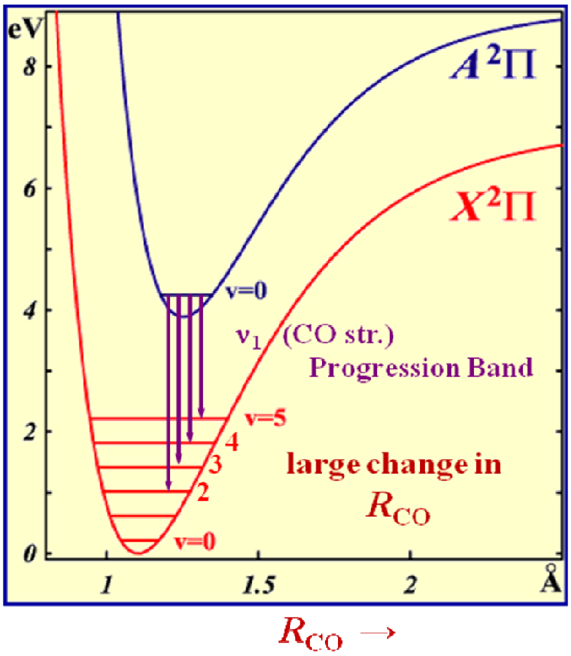

Fig.1 A-X Emission Bands of OCS^+

＜Experiment＞ The OCS^+ ion was generated by Penning ionization of OCS with metastable helium atoms, He*+OCS → He+ $(OCS^+)^*$. Emitted UV light was introduced to a FT spectrometer (Brucker IFS-120 HR) to be recorded with a resolution of 0.03 cm^{-1} accumulating for 60 hours in total. Four CO-stretch progression bands (v_1= 0→2-5) were observed in the frequency range of 21,000-27,000 cm^{-1}

which were split into two spin components (Ω = 3/2 and 1/2). The $v_1 = 0 \rightarrow 3$ band (Ω = 3/2) has a strong *R*-branch head together with the well resolved *P*- and *R*-branch lines and a weak *Q*-branch in the *R* and *P* branch gap (**Fig. 2**). The *R* and *P*-branch lines for Ω = 1/2 split into the Λ-type doubling, but no *Q*-branch lines were recorded. Accuracy of the line position is estimated to be 0.005 cm^{-1}.

< Results > The progression bands (v_1=0→2-5) for both Ω = 3/2 and 1/2 were analyzed together with the origin band (v_1=0→0) observed by LIF study2) accounting for the spin-orbit interaction explicitly. Eighteen molecular constants were fitted as listed in **Table 1** including the spin-orbit interaction constants A_0 and A_{D0} and the Λ-type doubling constant $(q+p/2)_0$. The standard deviation of the fit was 0.0034cm^{-1} consistent with the estimated accuracy of 0.005cm^{-1}.

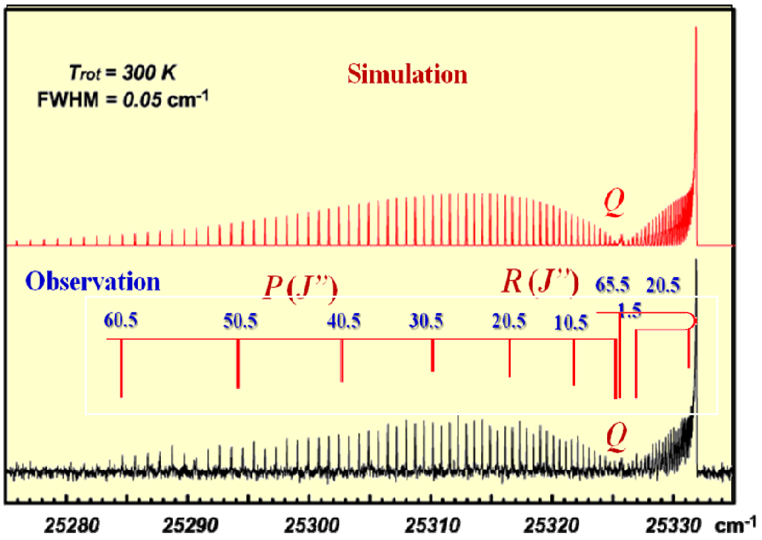

Fig. 2 $A^2\Pi_i$-$X^2\Pi_i$ v=0→3 (Ω=3/2) band of OCS^+

The rotational constants B_0 determined for the ground $X^2\Pi_i$ state is by 0.007659(18) cm^{-1} (~4%) larger than that for the excited $A^2\Pi_i$ state. The spin-orbit interaction constant A_0 = -381.0(56) cm^{-1} for the $X^2\Pi_i$ state is three times larger in magnitude than that -126.5 (56) cm^{-1} for the $A^2\Pi$ state, which are consistent with those (-367.2 and -111.8 cm^{-1}) reported by laser induced fragmentation study3).

The CO bond length for the $X^2\Pi_i$ state was determined to be 1.10543 Å from the rotational constant B_0 assuming that for CS to be 1.6570 Å as given by the MRSD-CI calculation4). The CO and CS bond lengths for the $A^2\Pi_i$ state were determined to be 1.2810 and 1.5665 Å, respectively, from Franck-Condon factors given by emission band intensities and the observed rotational constant B_0. The CO bond length for the $A^2\Pi_i$ sate is longer by 0.1756 Å than that for the $X^2\Pi_i$ state, but the CS bond length is shorter by 0.0905 Å to accord with the prominent ν_1 progression bands observed in the wide range of UV region.

Excitation of one electron from the 2π orbital to the 3π orbital gives the $A^2\Pi_i$ excited state with the electronic configuration of

$(8\sigma)^2\ (9\sigma)^2\ (2\pi)^3\ (3\pi)^4$,

where the 2π orbital consists of the π_{CO} bonding orbital and the 3π orbital mainly of a π bonding orbital between C and S to weaken the CO bond and to strengthen CS bond for $A^2\Pi_i$ than those for $X^2\Pi_i$.

Table 1. Molecular Constants of OCS+

	$X^2\Pi$		$A^2\Pi$	cm^{-1}
T_0	0.0		31276.826	Term Value
A_0	-381.0	>	-126.5	S-O Int.
ω_1	2088.97		(2039.50)	Vib. Freq.
$\omega_1 x$	19.975		(9.78)	
B_0	0.19477	>	0.18711	Rot. Con.
$\alpha_1 * 10^4$	6.435		---	
$D_0 * 10^8$	6.43		4.23	Cent. Dist.

<文献>

1) *JCP* **146**, 144302 (2017). 2) *CPL* **115**, 373 (1987). 3) *CPL* **119**, 467 (1985). 4) *TCA* **107**, 33 (2001).