ROTATIONAL PERTURBATION IN THE EXCITED $^1\Pi_u$ ELECTRONIC STATE OF SiOSi

MASARU FUKUSHIMA and TAKASHI ISHIWATA, Faculty of Information Sciences, Hiroshima City University, Asa-Minami, Hiroshima 731-3194, Japan

In our past SiCN investigation$^1$, we found unassigned bands with $^1\Pi - ^1\Sigma$ rotational structure in the laser induced fluorescence (LIF) excitation spectrum of SiCN. Dispersed fluorescence (DF) spectra from single vibronic levels have fairly long progressions with very harmonic structure, but no hot-band structure. From the rotational constants, the spectral species may possibly be attributed to SiOSi. The most stable geometry of the ground electronic state is reported to be cyclic by CCSD(T)/cc-pVTZ level calculation$^2$. Our CCSD(T) calculation with arg-cc-pCVTZ indicates a linear geometry, $^1\Sigma^+_g$, lying $\sim 6,000$ cm$^{-1}$ above this lowest cyclic structure. More advanced calculations by CAS-SCF and MR-CI indicate that the most stable cyclic geometry correlates to $^1\Delta_g$, which is the ground electronic state, and the $^1\Sigma^+_g$ state is the lowest excited state, lying $\sim 740$ cm$^{-1}$ above the $^1\Delta_g$ state. For the ground electronic state consisting of the cyclic and $^1\Delta_g$ linear geometries as the two minima, our calculation predicts a strange potential energy surface: the state has a 1,400 cm$^{-1}$ barrier from the cyclic structure to the linear geometry. In contrast, the $^1\Sigma^+_g$ state is predicted to have a linear structure as a single minimum. At present, we postulate that our unknown spectrum may be attributed an electronic transition from the low-lying $^1\Sigma^+_g$ state to a $^1\Pi_u$ state of SiOSi.

Due to the red-shaded structure of the spectrum, the R-branch makes a band head, and a rotational analysis adopting $P$- and $Q$-branches had not been satisfactory. Since ab initio calculations suggest the lower electronic state of the spectrum is $^1\Sigma^+_u$, we have tried more precise analysis applying combination difference procedure also, and we found there is heavy irregularity in only the upper levels of the $Q$-branch. Our calculation predicts that there are several electronic states in the vicinity of this state; such as $^1\Delta_u$, $^1\Sigma_u^+$, $^2\Sigma^+_g$, $^2\Sigma^+_u$, and $^1\Sigma^+_u$, in order of energy, besides low-lying three states, $^1\Delta_g$, $^1\Sigma_g^+$, and $^1\Sigma_g^-$, and that, for most of all states, their linear geometries do not give local minima, but have saddle points or local maxima, except $^1\Pi_u$ and $^1\Sigma_u^-$. Considering parities of the rotational levels, it is realized that $L$-uncoupling interaction between the $^1\Pi_u$ and $^1\Sigma_u^-$ states is only effective for the upper rotational levels of the $Q$-branch in the observed spectrum, and the electronic states, such as $^1\Sigma_u^+$, effective for those of the $P$- and $R$-branches do not exist as linear electronic states. At present, we think that $L$-uncoupling with the linear $^1\Sigma_u^-$ state causes the irregularity of the $^1\Pi_u$ state. More precise computational studies are currently underway.