FIRST OBSERVATION OF THE SPIN-ORBIT INTERACTION BETWEEN THE $\tilde{X}\ ^1A_1$ AND THE $\tilde{a}\ ^3B_1$ STATES of SiH_2 BY STIMULATED EMISSION PUMPING SPECTROSCOPY

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The energy separation and order between the triplet and the singlet electronic states have been one of the central issues of SiH_2 radical from both chemical and spectroscopic points of view. However, any rotationally and/or vibrationally resolved observation of the triplet ($\tilde{a}\ ^3B_1$) state has not yet been reported. Since the $\tilde{a}$ state is considered to be located $\sim$7000 cm^{-1} above the singlet ($\tilde{X}\ ^1A_1$) state, it is expected that an effect of the singlet-triplet interaction appears among highly excited vibrational levels of the $\tilde{X}$ state. Thus, we have carried out the stimulated emission pumping (SEP) spectroscopy of SiH_2 in the vibrational energy region up to 10000 cm^{-1}. In this paper, we will report an observation of a small but a definitive perturbation due to the singlet-triplet interaction in the SEP spectrum.

We have observed fifty-one vibrational levels in the vibrational energy region of 4800–10000 cm^{-1}. Due to strong $1\nu_1$:$2\nu_2$ Fermi and $2\nu_1$:$2\nu_3$ Darling-Dennison resonances, vibrational levels having the same polyad quantum number, $P = 2v_1 + v_2 + 2v_3$, construct polyad structures. The vibrational levels observed belong to polyads of $P = 5 - 10$. In the case of $P \leq 9$, all the vibrational energies observed were fitted very well by the effective Hamiltonian model in which the above resonances were considered. In the case of the $P = 10$ polyad, however, an unexpected splitting of the band was observed. It was confirmed that this splitting is due to the spin-orbit interaction between the $\tilde{X}$ and the $\tilde{a}$ states based on the rotational dependence of this perturbation. The internal energy of the triplet state observed was about 9645 cm^{-1} measured from the (000) level of the $\tilde{X}$ state. This level is tentatively assigned as (030), based on the theoretical calculation[a]. Details of the analysis will be discussed at the presentation.

[a] W. GABRIEL *et al.*, Chem. Phys. **174**, 45 (1993).