NUCLEAR SPIN MODIFICATION OF METHANE IN PARAHYDROGEN CRYSTALS

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Solid parahydrogen is an excellent matrix for matrix-isolation spectroscopy because of its high spectral resolution. Here, we report the nuclear spin symmetry selection rule of a chemical reaction $\mathrm{CH_2} + \mathrm{H_2} \rightarrow \mathrm{CH_4}$ and the nuclear spin conversion of CH_4 embedded in parahydrogen crystals studied by infrared absorption spectroscopy. Due to the nuclear spin modification, not only the J=0 rotational level but also the J=1 level of CH_4 is populated even if the temperature is lowered sufficiently. Since conversion among different nuclear spin states is very slow, population ratio between the J=1 and J=0 levels observed just after the crystal growth reflects the ratio of A and F nuclear spin states before the cooling. The vibration-rotation absorption of CH_4 in parahydrogen crystal grown from a premixed gas of methane and hydrogen molecules shows the population ratio of approximately (J=1):(J=0)=2:1. On the other hand, CH_4 produced by the photochemical reaction of $\mathrm{CH_3} + \mathrm{H_2} + 193nm \rightarrow \mathrm{CH_2} + \mathrm{H} + \mathrm{H_2} \rightarrow \mathrm{CH_4} + \mathrm{H}$ was found to have four times larger population in the J=1 rotational level than in the J=0 level just after the reaction. The former reflects the ratio of the A and F nuclear spin states being 5:9 at room temperature, while the latter is due to a nuclear spin selection rule of the reaction.
In addition, the vibration-rotation absorptions of CH_4 exhibit time-dependent intensity changes at 4.8K. These changes are interpreted to be a result of the $I = 1(F) \rightarrow I = 2(A)$ nuclear spin conversion which accompanies the $J = 1 \rightarrow J = 0$ rotational relaxation. The half-lifetime of the upper $J = 1$ rotational state is unchanged by the addition of up to 2% orthohydrogen molecules, but decreases with more than 10% orthohydrogen molecules. The increase of the decay rate at higher orthohydrogen concentration indicates that the magnetic field gradient across CH_4 caused by orthohydrogen molecules mixes the nuclear spin states which accelerate the conversion.