Phonon-mediated nuclear spin relaxation of H_2O trapped in Ar matrix

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Water molecules are classified into two kinds of nuclear spin isomers, i.e., ortho and para, just like hydrogen molecules. The abundance ratio of ortho to para, so called ortho-to-para ratio (OPR), has attracted much attention in the fields of astronomy and interstellar physics [1,2]. Since the nuclear spin conversion (NSC) of gaseous H_2O through radiation is extremely slow [3], one assumed that OPR provides information of the temperature where an interstellar medium was formed [1]. However, recent investigations have revealed that NSC of H_2O proceeds much faster in condensed systems [4,5]. Thus, interest in the NSC mechanism and channels is getting greater. In the present work, we devised a theoretical model of the phonon-mediated nuclear spin relaxation of H_2O trapped in cryomatrices to correctly describe the temperature dependence of the NSC rate [6]. For the purpose of testing the validity of this model, we also monitored the rotational relaxation of H_2O in solid Ar associated with the nuclear spin flip to experimentally obtain the NSC rates in the temperature range of 5-15 K.

After baking at 373 K for 24 hours, the interior of a vacuum chamber went below 1×10^{-8} Pa. An oxygen-free copper block was screwed in the bottom of a helium continuous-flow cryostat, which was mounted on the vacuum chamber. A $15 \times 15 \times 5$ mm^3 gold plate mechanically fixed on the copper block was used for the substrate. Temperature of the substrate was measured with a silicon diode sensor and was raised with a heater wrapped around the bottom part of the cryostat. The substrate and block were covered with a radiation shield attached to the cryostat, so that the helium flow made the substrate temperature as low as 5.2 K. The gases of H_2O and Ar were mixed in the gas handling system equipped with a quartz oscillator gage; distilled water was preliminarily degassed by multiple freeze-pump-thaw cycles whereas the Ar gas (99.9999% purity) was used without further purification. The molar ratio of Ar to H_2O was set to be 1.0×10^4 using the standard manometric technique. The mixed gas was dosed through a variable leak valve onto the substrate kept at 13 K. Infrared spectra were recorded with a Fourier transform infrared spectrometer and a HgCdTe detector at the resolution of 2 cm^{-1}. We used the reflection configuration, where the incident angle of infrared light was 80 degrees. The whole optical path was evacuated in order to eliminate infrared absorption by atmospheric CO_2 and H_2O.

In Fig. 1, time evolution of the infrared spectrum of H_2O in solid Ar is shown. The time when the substrate temperature settled at 7.0 K was set to be 0 s. Sharp absorption peaks at 1608 (O1), 1624 (P1), and 1636 cm^{-1} (O2) are assigned to the $1_{10} \leftarrow 1_{01}$, $1_{11} \leftarrow 0_{00}$, and $2_{12} \leftarrow 1_{01}$ rovibrational transitions of H_2O, respectively [7,8]. In the notation of $J_{kk'}$, the quantum number of the rotational angular momentum is denoted by J, and that of its projection on the a (c) axis of H_2O is expressed by k (k'). While P1 corresponds to the transition of para H_2O, O1 and O2 originate from the ortho species. P1 grew with increasing time whereas O1 and O2 decayed. This time evolution

means NSC of H_2O. We obtained the integrated intensity of P, which is proportional to the number of para H_2O, by Gaussian fitting. The time dependence of the integrated intensity was well-described by an exponential function with the relaxation rate of 0.36 h^{-1}. We also measured the rate at other temperatures in the range of 5-15 K. Figure 2 shows the temperature dependence of the measured relaxation rate. The solid line, which was derived from the phonon-mediated relaxation model we devised, is found to reproduce the experimental data well. This result supports the validity of our model and suggests that the rotational relaxation from 1_{01} to 0_{00} associated with the nuclear spin flip proceeds not only directly but also indirectly, i.e., via 1_{11} [6].

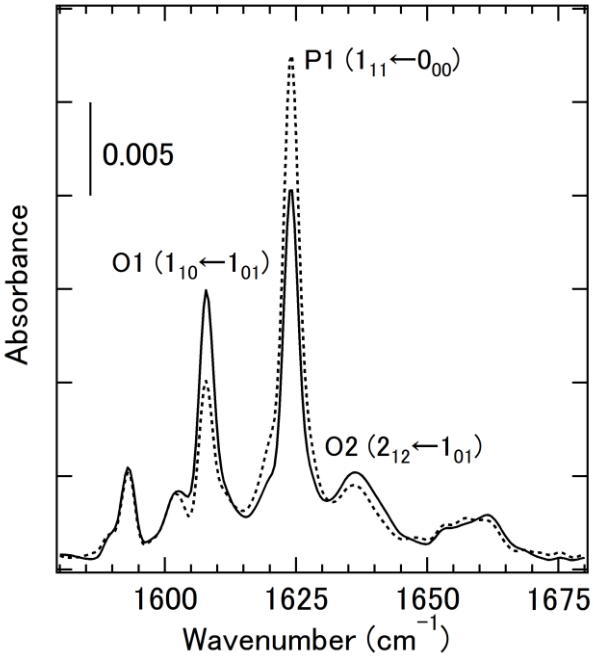

Fig. 2 Infrared spectra of H_2O in solid Ar at 50 (solid line) and 11730 (dotted line) s. The substrate temperature was 7.0 K.

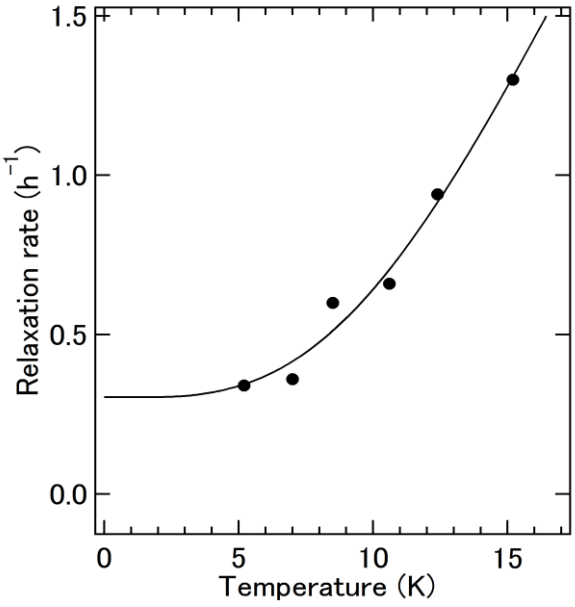

Fig. 1 Temperature dependence of the NSC rate of H_2O in solid Ar. The solid curve was derived from the phonon-mediated relaxation model.

References

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