

Calculation of the ortho-para conversion rate of gaseous methanol by the internal axis method

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In astrophysics and astrochemistry, the ortho-para conversion rate is an important parameter which is related to the ortho-to-para population ratio (OPR) and the nuclear-spin temperature of nuclear-spin isomers of molecules in the interstellar medium (ISM) [1]. The methanol (CH_3OH) molecule is a major source of interstellar organic species due to its abundance in the ISM. Although conversion rate of nuclear-spin isomers in gaseous methanol has been experimentally measured recently [2], the quantum calculation of the ortho-para conversion rate of methanol molecules in the gas phase, the conversion mechanism in the nuclear-spin isomers conversion of methanol, and the most probable gateways of spin conversion in methanol have not yet theoretically studied by the internal axis method (IAM) that is a classical method commonly used by many researchers.

In molecular physics, methanol is one of the simplest asymmetric-top molecules with hindered internal rotation (*i.e.* torsion) [3]. Methanol does not rotate around the overall rotational symmetry axis but the methyl (CH_3) group axis. In the IAM, the CH_3 -group and the OH-group in methanol relatively rotate in the opposite directions with each other, and the coupling of the angular momenta between torsion and overall rotation in the Hamiltonian of methanol can therefore be completely separated from each other. In accordance with Pauli's principle in quantum mechanics, the identical nuclei in the methyl group produce a specific type of nuclear spin isomers of the ortho- CH_3OH and para- CH_3OH in methanol. In this study, we have developed a theoretical model by the IAM for the description of isomer conversions by molecular collisions in gaseous methanol. The model is based on the quantum-relaxation theory confirmed to be valid for the standard nuclear-spin isomers based on the molecular rotational states [4]. The expressions of the ortho-para state-mixing strengths induced by intramolecular nuclear-spin–nuclear-spin and nuclear-spin–rotation interactions in methanol have been analytically deduced and numerically calculated. We found that the ortho-para states-mixings and ortho-para conversion can be induced by both of these two intramolecular hyperfine interactions whereas the nuclear-spin–rotation interaction plays a major role. The conversion rates at room temperature low pressures over eight ortho-para level pairs have been calculated to be closely to the measured values and the most probable gateways of spin conversion in methanol by collision-induced population transfers are found.

Acknowledgements

We express sincere thanks to P. L. Chapovsky for valuable guidance and discussions with us when he visited our laboratory. This work was jointly supported by the National Natural Science Foundation of China (Grants No. 91536105, No. 11174186, and No. 11074147) and the Tianshan Scholar Program and the FY2021 JSPS Invitational Fellowship for Research in Japan in a short-term program (S21002).

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