

Discrimination of nuclear spin isomers exploiting the excited state dynamics of a quinodimethane derivative

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Despite the concept of nuclear spin isomers (NSIs) exists since the early days of quantum mechanics, only few approaches have been suggested to separate different NSIs. Here, a method is proposed to discriminate different NSIs of a quinodimethane derivative using its electronic excited state dynamics. After electronic excitation by a laser field with femtosecond time duration, a difference in the behavior of several quantum mechanical operators can be observed. A pump-probe experimental approach for separating these different NSIs is then proposed. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4899178>]

I. INTRODUCTION

The concept and the existence of nuclear spin isomers (NSIs) was already shown in the early days of quantum mechanics, independently by Heisenberg¹ and Hund.² This discovery immediately allowed for understanding phenomena like the anomalous specific heat capacity of molecular hydrogen, already measured 1912 by Eucken,³ or the intensity alternations found in rotational spectra of several diatomic molecules – first reported by Mecke 1925.⁴ Both phenomena were explained on a theoretical basis by Bonhoeffer and Harteck in 1929,⁵ introducing the concept of ortho- and parahydrogen – see also the work of Farkas.⁶ The fact that some lines were “missing” in rotational spectra was later also observed for a number of small, rigid polyatomic molecules, such as H₂O, CO₂ and even non-rigid molecules like NH₃; for an overview see Ref. 7.

Today, the existence of NSIs has implications all over Chemistry and Physics, affecting spectroscopy, boiling/melting points, and heats of vaporization,^{7,8} nuclear magnetic resonance (NMR) spectra, see, e.g., the work of Buntkowsky and Limbach,⁹ the area of selective reaction rates,¹⁰ and many other fields. Interestingly, and despite the fact that the occurrence of NSI is well understood from a theoretical point of view, only few experimental approaches exploit the concept of NSIs. The separation of o- and p-H₂ has been technically feasible for quite some time,^{11,12} but almost no other ensemble of molecule with a NSI ratio different from its high temperature equilibrium value has been produced ever since.¹³ Several separation methods are under development.⁸ The most promising one uses the concept of a light-induced drift¹⁴ to separate NSIs of CH₃F.^{15–18}

The present paper suggests a novel method to discriminate NSIs making use of ultrashort laser pulses and concepts from time-resolved pump-probe spectroscopy.^{19,20} The work presented here is inspired by other quantum dynamical simu-

lations on the torsional motion of several types of molecules, including enantiomers and spin isomers, all of them showing the usability and applicability of laser driven ultra fast dynamics for selective chemical processes.^{21–32} It is an extension to previous studies on molecules containing only one torsional angle,^{31,32} which showed the dependency of molecular alignment by ultra short, non-resonant laser pulses on the nuclear spin³¹ and explored the possibility of a nuclear spin selective control of the rotational and torsional dynamics of non-rigid molecules.³²

The discrimination of NSIs will be demonstrated for a model system, a quinodimethane derivative (2-[4-(cyclopenta-2,4-dien-1-ylidene)cyclohexa-2,5-dien-1-ylidene]-2H-1,3-dioxole), which we abbreviate henceforth as CCD (see Fig. 1). In Ref. 33, it is shown that for CCD four different NSIs are populated at very low temperatures. The discrimination among the four NSIs will be achieved exciting the molecule electronically and exploiting the relative torsional motion of the three different rings A, B, and C that conform the molecule, see Fig. 1.

II. THEORY

A. Symmetry properties of the wavefunction

The total wavefunction of a free molecule ψ_{tot} can be written as a product of the translational wave function, ψ_{trans} , and the wavefunction that takes into account all the internal degrees of freedom (rotational, vibrational, electronic, as well as everything related to the spins of nuclei composing the molecule), ψ_{int} ,

$$\psi_{tot} = \psi_{trans} \cdot \psi_{int}. \quad (1)$$

The total wavefunction ψ_{tot} must follow the symmetrization postulate.^{7,34} Since permutations of identical nuclei do not change the translational motion (i.e., ψ_{trans}), only ψ_{int} is subjected to the symmetrization postulate. The latter wavefunction can be written as the product of its individual contribu-

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