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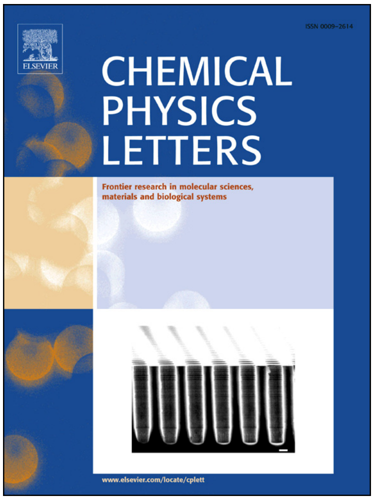

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Rotation-vibration motion of extremely flexible molecules - The molecular superrotor

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Abstract

This paper treats the low energy rotation-vibration problem in CH_5^+, an extremely flexible molecule lacking a well-defined structure. Using SO(5) symmetry it determines zeroth order energies, and complete nuclear permutation S_5 symmetries, using a five-dimensional model involving rotation and two vibrations (which one might imagine as two different "cooperative" HCH bends). These two vibrations are presumed to be unhindered by the molecular potential function and their analytical form is not determined. The other ten vibrational degrees of freedom are presumed to be "rigid" (or averaged over). The general energy expression for this "rigid superrotor" is obtained as $(B/2)[n_1(n_1+3)+n_2(n_2+1)]$ where B is the rotational constant and the non-negative integers n_1 and n_2 satisfy $n_2 \leq n_1$. The superrotor predictions agree favourably with the available experimental data. Applications of the superrotor model to extremely flexible molecules other than CH_5^+ are discussed.

1. Introduction

Customary molecular theory is based on the Born-Oppenheimer approximation (see, for example, Ref. [1] and references therein), where the observable molecular energies are obtained as the eigenvalues of a purely nuclear Hamiltonian. In this Hamiltonian, the energy contribution from the electrons is described by an effective potential energy function for the one electronic state under study. Conventionally, this potential energy function is assumed to have one minimum only, this minimum being situated in a deep potential well so that vibrational (nuclear) motion causes only minor distortions of the equilibrium structure. Consequently, in the initial approximation, the nuclear Hamiltonian is taken to be separable into three independent terms depending on different sets of coordinates, namely translational, vibrational, and rotational coordinates, respectively. It is well-known that the translational motion can be exactly separated from the other two types of motion and we can ignore it in the theoretical description of rotation-vibration spectra, but the near-separability of rotation and vibration is an essential prerequisite for employing the conventional methods for the dynamics and the symmetry classification of rotation-vibration states in the molecular symmetry (MS) group [2]. However, this separation becomes problematic if the amplitudes of the vibrational motions are comparable to the linear dimensions of the molecule. When *multiple* vibrations have such large amplitudes, we talk about an *extremely flexible*, or fluxional, molecule. Other authors have called such molecules "astructural" [3]. The currently most prominent member of this class is protonated methane CH_5^+, where the extra proton causes a three-center-two-electron bond, which makes the dynamics of CH_5^+ fundamentally different from that of the well-understood parent molecule, methane CH_4.

The problem of inseparable motions can, at least in principle, be circumvented by the use of complete basis sets for expressing the molecular wavefunctions. We can express the exact rotation-vibration wavefunction as a linear combination of the functions in a complete – and therefore infinitely large – basis set. The corresponding basis functions can be taken as products of vibrational and rotational wavefunctions combined such that all product functions in a given wavefunction expansion have the same symmetry – the symmetry of the exact wavefunction – in the MS group, and still each *basis function* is consistent with rotation and vibration being independent. As just mentioned, in order for the product basis functions to constitute a complete basis set we will generally have to take into account infinitely many of them. However, for many molecules accurate molecular energies and wavefunctions can be obtained by truncating the basis set, i.e., by approximating the infinitely large, complete basis set by a finite, incomplete one.

CH_5^+ is a prototypical example of an extremely flexible molecule, and so conventional rotation-vibration theory is not easily adaptable to it. With the results of Ref. [4], we can explain the failure of the well-established theoretical approach by the fact that for CH_5^+, the molecular symmetry (MS) group [2] is not isomorphic to any subgroup of SO(3) so that neither the SO(3) irreducible representations[1] themselves, nor by any finite linear combinations of them, can be used as starting point for determining the MS-group irreducible representations spanned by the molecular wavefunctions. The practical problem in this context is that the application of certain symmetry operations to the molecule-fixed axis system [2] changes the quantization axis. Hence, application of these symmetry operations to the

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[1] The irreducible representations are spanned by the rotational basis functions mentioned above.

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