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## Full-dimensional MCTDH/MGPF study of the ground and lowest lying vibrational states of the bihydroxide $\text{H}_3\text{O}_2^-$ complex



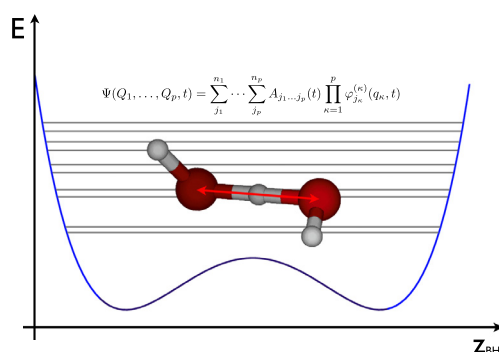
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### HIGHLIGHTS

- Proton transfer in  $\text{H}_3\text{O}_2^-$  characterized in agreement with experiment.
- We have combined MCTDH with numerical KEO and newly developed MGPF.
- Full (9D) and reduced (7D) dimensionality models are consistent.

### GRAPHICAL ABSTRACT



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### ABSTRACT

In this study, we present a full-dimensional (9D) quantum dynamical analysis of the lowest vibrational eigenstates of  $\text{H}_3\text{O}_2^-$ . We have made use of the Multiconfiguration Time-Dependent Hartree method in conjunction with both an analytical and a numerical representation of the Kinetic Energy Operator and the newly developed Multigrid POTFIT [D. Peláez, H.-D. Meyer, J. Chem. Phys. 138 (2013) 014108], an algorithm which performs the transformation of a high-dimensional (up to  $\sim 12\text{D}$ ) Potential Energy tensor into product form. Many sets of top-down Multigrid POTFIT expansions, differing in the system coordinate definition (valence and Jacobi), as well as in the number of terms in the expansion, have been analyzed. Relaxations for the computation of the ground states energies have been carried out on these potentials, obtaining an excellent overall agreement with accurate previous Diffusion Monte Carlo (DMC) calculations, irrespective of the coordinate choice. The 24 lowest excited vibrational states of  $\text{H}_3\text{O}_2^-$  have been computed by Block Relaxation and assigned for the first time. This has been carried out in two different pictures, namely: a 7D reduced dimensional one, in which the OH distances have been frozen at the Potential Energy Surface minimum, and a 9D full-dimensional one. The agreement between both descriptions is remarkable. The following fundamental modes have been characterized: OH torsion, OO stretching, OH wagging, OH rocking, and the elusive bridging H stretching. In particular, we provide a very accurate description of the latter in perfect agreement with experiment.

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### Introduction

Small molecular systems are excellent benchmarks for the development of new theories and methodologies. However, de-

spite their delusive simplicity, they keep posing challenges both from an experimental and a theoretical point of view. A relevant example of this is the hydrogen exchange reaction, which, though having been studied for more than 40 years now, still provides us with surprising results [1].

Proton transfer in water and related species constitutes another formidable problem which has drawn attention for an even longer time [2]. The appeal of this reaction not only comes from its

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relevant implications in basic biological processes [3] but also from the need of techniques which provide a correct and fundamental description of this highly quantum motion [4–7].

The species involved in the proton transfer in water can be categorized in two groups: cationic and anionic ones. The former, collectively represented as  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ , the smallest family member being the Zundel cation,  $\text{H}_5\text{O}_2^+$ , has received much attention (see Ref. [8] and references therein). Of particular relevance is the full dimensional (15D) quantum description of its infrared spectrum [8,9]. However, it is often recognized that the anionic counterparts,  $\text{HO}^-(\text{H}_2\text{O})_n$ , of which  $\text{H}_3\text{O}_2^-$  is the simplest member, have received much less attention.

This study focuses on the theoretical characterization of the gas-phase proton transfer in the  $\text{H}_3\text{O}_2^-$  (bihydroxide) complex. It has been observed spectroscopically and characterized in the gas phase [10,11] and in solution [12]. With respect to proton transfer in this species, Diken et al. [11] observed a very intense and narrow feature at  $697\text{ cm}^{-1}$  by argon predissociation spectroscopy in the  $600\text{--}1900\text{ cm}^{-1}$  region. Consistent with previous Diffusion Monte Carlo (DMC) calculations [13], they assigned this band to the fundamental transition of the bridging hydrogen motion parallel to the H-bond axis. Theoretical characterization of the ground state and vibrationally excited states of  $\text{H}_3\text{O}_2^-$  has been carried out by several groups [6,14,15]. However, there still exist some discrepancies among these results and the agreement with experiment is not fully satisfactory. For instance, the aforementioned fundamental transition occurs at  $759.9\text{ cm}^{-1}$  according to the full-dimensionality calculations by Yu [15] and at  $741(644)\text{ cm}^{-1}$  according to the VSCF/CI (DMC) calculations of McCoy et al. The difference in the results evidences the complexity in the full-dimensional treatment of this highly quantum system.

The goal of the present work is twofold. Firstly, we aim to provide a more accurate description of the vibrational levels of the  $\text{H}_3\text{O}_2^-$  system, particularly concerning the bridging hydrogen (BH) motion parallel to the H-bond axis. Secondly, to achieve this, we introduce and benchmark some quantum dynamical methodologies. We solve the  $\text{H}_3\text{O}_2^-$  vibrational eigenproblem in its full (9D) dimensionality with the Multiconfiguration Time-Dependent Hartree (MCTDH) method using an exact analytic Kinetic Energy Operator (KEO) and the newly developed Multigrid POTFIT (MGPF) [16], a variational potential re-fitting algorithm which allows the treatment of large systems (up to  $\sim 12\text{D}$ ). We also studied  $\text{H}_3\text{O}_2^-$  in reduced dimensionality (7D) by freezing the two outer OH distances and adopting a numerical KEO [17]. The quite satisfying 7D results show that both freezing the OH distances and the use of an approximate numerical KEO are valid approximations.

This article is structured as follows. Section ‘Calculation of vibrational states with MCTDH’ introduces the fundamentals of the theory behind the methods we utilize. Section ‘Computational and numerical details’ presents the numerical details of the calculations. In Section ‘Results and discussion’, we discuss the obtained results. Section ‘Conclusions’ concludes the paper.

### Calculation of vibrational states with MCTDH

We have computed the lowest vibrational energy levels of the  $\text{H}_3\text{O}_2^-$  complex in full dimensionality (9D). For this, we have made use of the Multiconfiguration Time-Dependent Hartree method [18] in combination with the newly developed Multigrid POTFIT algorithm [16] for the re-fitting of the PES in product form. The Kinetic Energy Operators have been obtained by means of the TNUM [17,19] and TANA software packages [20]. The vibrational energy levels have been obtained using the Improved Relaxation algorithm [21,22] as implemented in the Heidelberg MCTDH software package [23]. In the following subsections, a concise description of the methodology is given.

### Multiconfiguration Time-Dependent Hartree

Multiconfiguration Time-Dependent Hartree (MCTDH) is a general algorithm for the solution of the time-dependent Schrödinger equation [18,24–26]. The MCTDH wavefunction *ansatz*, which consists in a sum of products of time-dependent basis functions, reads:

$$\Psi(q_1, \dots, q_f, t) \equiv \Psi(Q_1, \dots, Q_p, t) \\ = \sum_{j_1=1}^{n_1} \dots \sum_{j_p=1}^{n_p} A_{j_1 \dots j_p}(t) \prod_{\kappa=1}^p \varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) = \sum_J A_J \Phi_J, \quad (1)$$

where  $f$  is the number of degrees of freedom (DOF) and  $p$  the number of particles, also known as combined modes, defined as a set of one or more DOFs ( $Q_\kappa \equiv q_{\kappa,1}, \dots, q_{\kappa,d}$ ).  $A_J \equiv A_{j_1 \dots j_p}$  are the expansion coefficients, and  $\Phi_J \equiv \prod_{\kappa=1}^p \varphi_{j_\kappa}^{(\kappa)}$  are the Hartree products, that is, products of single-particle functions (SPF). Although similar to the expression of the wavefunction (WF) in the standard method, in MCTDH the time-dependence not only resides in the expansion coefficients, but also in the SPFs. Therefore, the latter adjust their values at every time-step. The flexibility of the MCTDH theory is reflected in the fact that both the time-dependent Hartree and the standard method can be viewed as limiting cases of the MCTDH *ansatz* [18]. The former is obtained by setting all the expansion orders  $n_\kappa = 1$  and the latter is achieved by setting  $n_\kappa = N_\kappa$ , that is, the expansion orders equal to the number of grid points.

From the MCTDH *ansatz*, two sets of equations of motion (EOM) can be derived. Using the Dirac–Frenkel variational principle (see Ref. [18]), one obtains:

$$i\dot{A}_J = \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L, \quad (2)$$

$$i\dot{\varphi}_j^{(\kappa)} = (1 - P^{(\kappa)}) \sum_{k,l=1}^{n_\kappa} (\rho^{(\kappa-1)})_{jl} \langle H \rangle_{lk}^{(\kappa)} \varphi_k^{(\kappa)}. \quad (3)$$

A detailed explanation of the mean-fields  $\langle H \rangle^{(\kappa)}$ , the projector  $P^{(\kappa)}$ , and the one-particle densities  $\rho^{(\kappa)}$ , can be found elsewhere [18,24].

It is well-established that the ground state energy can be obtained by propagation of the WF in imaginary time [27]. In the Heidelberg MCTDH software package, a modified version of this idea, the so-called Improved Relaxation method [21,28], is applied. The difference lies on the fact that the  $A$ -(coefficient) vector is obtained as an eigenvector of the Hamiltonian in the basis of the configurations:

$$\sum_L \langle \Phi_J | H | \Phi_L \rangle A_L = E A_J, \quad (4)$$

by (Davidson) diagonalization. Selecting an appropriate eigenvector when solving Eq. (4), excited states can be computed as well. On the other hand, the SPFs are propagated in imaginary time according to the same EOM (3). This procedure is repeated until convergence in the energy is achieved. Additionally, a block version of the Improved Relaxation algorithm is also available. In this case, a certain block of eigenstates is calculated by a block-Davidson routine while using state-averaged mean-fields for relaxing a common set of SPFs.

Solving the MCTDH EOMs requires, at every time step, the efficient computation of multidimensional integrals  $\langle \Phi_J | H | \Phi_L \rangle$  and mean-fields  $\langle H \rangle^{(\kappa)}$ . For this, the Heidelberg MCTDH profits from product form approximations [29–31]. The idea is to represent multidimensional quantities in terms of products of one-dimensional functions. In this way, it is possible to turn cumbersome multidimensional integrals into products of one-dimensional ones. If the Hamiltonian is written in product form:

$$\hat{H} = \sum_{r=1}^s c_r \prod_{\kappa=1}^p \hat{h}_r^{(\kappa)}, \quad (5)$$

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