



Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

First-principles simulations of vibrational states and spectra for H_5^+ and D_5^+ clusters using multiconfiguration time-dependent Hartree approach



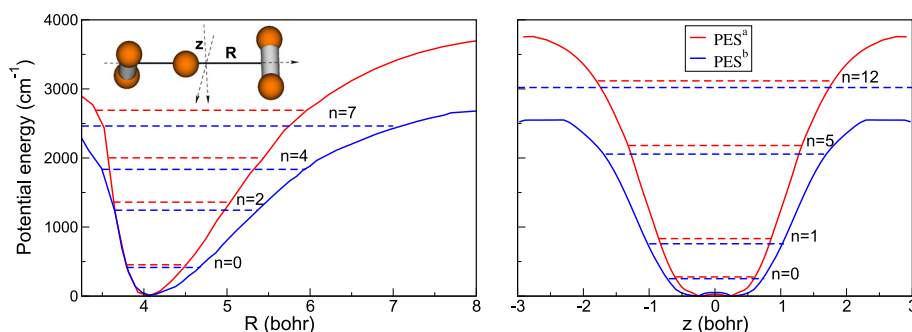
Álvaro Valdés, Rita Prosimiti*

Instituto de Física Fundamental, IFF-CSIC, Serrano 123, 28006 Madrid, Spain

HIGHLIGHTS

- Theoretical simulations of the infrared spectra of the H_5^+ and D_5^+ cations.
- The results obtained from first-principles & reduced dimensional MCTDH computations.
- Comparison with the experiment provides information on the PESs' uncertainties.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Available online 29 May 2013

Keywords:
Vibrational quantum dynamics
Potential energy surfaces
Electronic structure calculations

ABSTRACT

Simulations of the infrared (IR) spectra of the H_5^+ and D_5^+ clusters are carried out in the whole energy range, using a recent, reliable “on the fly” DFT-based potential energy surface, and its corresponding dipole moment surface. For the present study we adopted a recently proposed four-dimensional quantum model to describe the proton transfer motion between the two vibrating H_2 or D_2 units. Time-dependent and time-independent approaches within the multiconfiguration time-dependent Hartree method are employed for investigating the vibrational dynamics of the complexes. The obtained spectra are compared with recent experimental data available for energies up to 4500 and 3500 cm^{-1} for the H_5^+ and D_5^+ , respectively. Even though the present results are based on a reduced dimensional model, the infrared spectra are shown to be in good qualitative accord with those observed experimentally. Also as the reported data are subject to the potential energy surface, comparisons with previous theoretical calculations based on an analytical *ab initio* parameterized surface are also presented. The differences on the topology of the potentials are discussed in connection with their effect on the spectral features. We found that the main characteristics of the experimentally observed spectra are reproduced by both surfaces, evaluating in this way the sensitivity of such computations on the quality of the underlying potential. This finding serves to connect aspects of the potential surface of these systems to their spectral complexity, and could be indicative to calibrate intrinsic errors in their calculation for future studies.

© 2013 Elsevier B.V. All rights reserved.

Introduction

Molecular spectroscopy is the most powerful way to gain information about the molecular world, such as molecular structure and

properties, molecular dynamics and chemical reactivity. However, the desired information is not provided directly, and it is coded in the spectra in a rather complicated way. Thus, computational modeling of the spectra helps to uncode the information allowing in this way their interpretation. Here, we are interested on computations of molecular vibrations. Developments during the last decade in theory and computational techniques allow nowadays applica-

* Corresponding author. Tel.: +34 915616800.
E-mail address: rita@iff.csic.es (R. Prosimiti).

tions to polyatomic molecules, with more than four atoms, demonstrating the power and the increased accessibility of these methods [1–6]. A computer model is defined by concepts and assumptions, and ideally could be applied to any molecular system. For the vibrational spectra computation we should first calculate the relevant molecular properties, *e.g.* force constants and electric dipole moments, and then use them to calculate transition frequencies and intensities to compare with the experiment.

In other words, within the quantum mechanical based approaches the molecular Hamiltonian operator (the sum of kinetic and potential energy) is required to extract the vibrational information. This involves joint efforts in quantum nuclear motion theory together with the electronic structure calculations to provide an accurate description of interaction energy, and efficient representation of the potential energy surface (PES) for multidimensional systems [7]. The concept of a PES is fundamental for understanding most of the molecular processes, and its representation essential in the spectral computations. Any comparison between theoretical results and experimental data is subject to the errors coming, in general, from the representation of the underlying potential, and for polyatomic systems, as the number of degrees of freedom increases, the route to obtain improved PESs is getting hard.

In this study will focus exclusively on the computation of the H_5^+ and D_5^+ spectra from *ab initio*-based surfaces. These ions have been proposed to play a key role in interstellar chemistry [8–10], and thus, have been the subject of spectroscopic and theoretical investigations [11–21]. The present work is simulated by the recent experimental observations in the mid- and far-IR region [16,17], as well as by theoretical studies employing state-of-the-art methodology to assign the observed transitions. In particular, recently diffusion Monte Carlo (DMC), vibrational configuration interaction, using the reaction path version of the MULTIMODE method (MM-RPH), and multiconfiguration time-dependent Hartree (MCTDH) calculations have been performed to deal with the vibrational dynamics of the H_5^+ and D_5^+ [16,17,22–24]. However, full-dimensional treatments such as fixed-node DMC calculations are limited to just the first three vibrational excited levels, the MULTIMODE ones are based on normal mode basis sets, and MCTDH data are only available for energies up to half-way to the dissociation of these clusters. In this vein, several reduced dimensional models, from 2° to 5° of freedom, have been also proposed [25–27,23,28], aiming to describe the spectroscopic features of the H_5^+ and D_5^+ cations.

Just recently we proposed a four-dimensional model Hamiltonian that includes two coordinates to describe the proton stretching motion, while the other two correspond to the H_2 vibrations, with H_5^+ fixed at its C_{2v} orientation [28]. By carrying out quantum dynamics simulations the IR-spectra for both H_5^+ and D_5^+ cations in the whole spectral range have been obtained. It has been found that in the low energy regime, a transition from normal-mode to local-mode states takes place, and manifests its presence in the spectra [23,28]. Such type of transition is well-studied in the literature, by examining the role of the potential and kinetic coupling terms, and has been found to play a crucial role in the spectra assignment [29–32]. Usually a transition from normal to local modes occurs at higher excitation energies, and is related with bifurcation phenomena [30,32]. Although given the topology of the potential surface of the H_5^+ with very low-lying stationary points, such nonlinear mechanical behavior should be expected. Thus, H_5^+ and D_5^+ are very good candidates for investigating if and how the dynamics changes by modifying the potential energy surface.

Despite the fact that the H_5^+ cluster has been of interest to theoreticians since long time ago [18], only recently reliable potential surfaces have been reported in the literature [33–35]. Two of

them, by Xie et al. [33] and Aguado et al. [34], are analytical representations of the PES fitted to roughly 10^5 CCSD(T) data using generalized many-body expansion and permutationally invariant functional forms and triatomics-in-molecules method for the parameterization of the surface, respectively. The third one, is an “on the fly” representation of the surface based on DFT calculations [35], and as it has been generated with a completely different procedure, one expects several differences with respect to the analytical ones. For this reason we choose this latter PES in the present study, while for comparison with the present results the earlier analytical PES by Xie et al. [33] has been used. This surface has been employed, up to date, in the majority of the dynamics studies, as it is computationally the most efficient one.

The work presented here expands our previous efforts to evaluate the PESs of such cations obtained from first principles computations, by direct comparison with the experiment. In this way we can study the role of the uncertainties in the PES on the spectroscopic properties. This involves to carry out quantum dynamics simulations, and here we take advantage of the availability of performing them within the MCTDH framework [36–38].

The plan of the article is as follows: In the next section we discuss on the aspects of the potential energy surfaces, we describe the computational details of the time-independent and time-dependent MCTDH calculations, together with the results obtained from the spectral simulations. Their comparison with previous theoretical studies and the experimental data available is also provided. A summary and some conclusions are given in the closing section.

Computational details and results

Potential energy surfaces

In Fig. 1 we show the internal coordinates employed to describe the H_5^+/D_5^+ cluster. the R and z coordinates are the distance between the centers of mass of the H_2 units, and the distance of the proton (see atom label 5) from the origin of the body-fixed (BF) XYZ-system, respectively, while R_1 and R_2 are the bondlengths of the two H_2 monomers (see atom labels 1, 2 and 3, 4), with the torsional angle between the two H_2 units being 90°.

As we mentioned above, we employed here an “on the fly” DFT surface [35]. This PES is generated by carrying out DFT electronic structure calculations at each point of the whole grid, using the B3(H) hybrid functional, which has been designed for

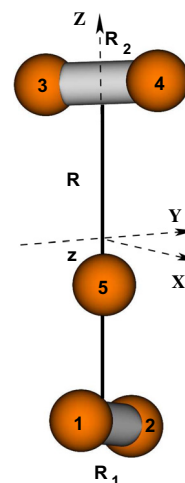


Fig. 1. The R , z , R_1 , and R_2 coordinates used in this study for the H_5^+ and D_5^+ .

Download English Version:

<https://daneshyari.com/en/article/1233082>

Download Persian Version:

<https://daneshyari.com/article/1233082>

[Daneshyari.com](https://daneshyari.com)