

H₂O₂+Ng Excited Electronic State Description

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Keywords: Excited Electronic States, Potential Energy Curve, H₂O₂-Ng systems, Time-Dependent Density Functional Theory.

INTRODUCTION

Hydrogen peroxide (H₂O₂) plays an important role in several chemical and physical processes, evidenced in astronomy, medicine, and chemical reactions. Due its importance and diversity of applications, this molecule has been subject of several studies^{1,2}. Recently, our research group has developed an analytical interpretation of noble-gases influence on hydrogen peroxide by means of a potential energy surface that involves angular and radial coordinates of noble gases. The Improved Lennard Jones (ILJ) analytical form², widely applied in this kind of systems, was used in order to represent the Van der Waals interaction of noble gas and O-H bond. In this work, we present the H₂O₂-Ng (with Ng=He,Ne, Ar, and Kr) potential energy curves (PEC) in the excited electronic states. Furthermore, these new PEC are exploited to describe the dynamical properties (ro-vibrational energies and spectroscopic constants) of the H₂O₂-Ng systems.

METHODS AND DISCUSSION

It is large known that the study of excited states is not an easy task. It request a long computational simulation time and depending on electrons quantity it may be not viable. Considering this facts, it becomes crucial cost-benefits considerations. By these assumptions, we considered H₂O₂ + He, H₂O₂ + Ne, H₂O₂ + Ar, H₂O₂ + Kr on equilibrium geometries given by Table below (geometrical definition are shown in Figure 1).

Ng	$\alpha = \alpha_{eq}$	θ_1	θ_2
He	0°	30°	217°
Ne	0°	32°	215°
Ar	0°	38°	209°
Kr	0°	47°	200°

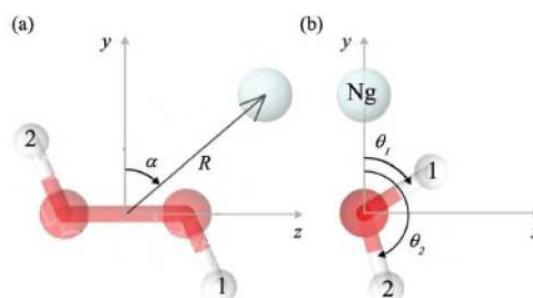


Figure 1: H₂O₂-Ng geometrical representation. (a) R is the distance from noble-gas and center of O-O bond. (b) θ_1 and θ_2 are the angles between O-H bond and y axis.

For all complexes, we calculated the electronic energies as a function of R (from 3Å to 10Å, with 0,2Å of step) considering 15 excited states. All these calculations were performed using the TDDFT method (implemented in the NWCHEM code³), with the cam-qtz-00 functional and the aug-cc-pVTZ basis set. These excited electronic energies were adjusted by generalized rydberg functions, as shown in Figure 2. Then, these analytical PEC were used to determine the ro-vibrational energies and spectroscopic constants. for all studied systems. These properties were calculated by two different methods: Solving the nuclear Schrodinger's equation (by Discrete Variable Representation⁴) and Dunham⁵ method. The results obtained through Dunham and DVR methodologies are in an excellent agreement. This fact demonstrates the reliability of our study.

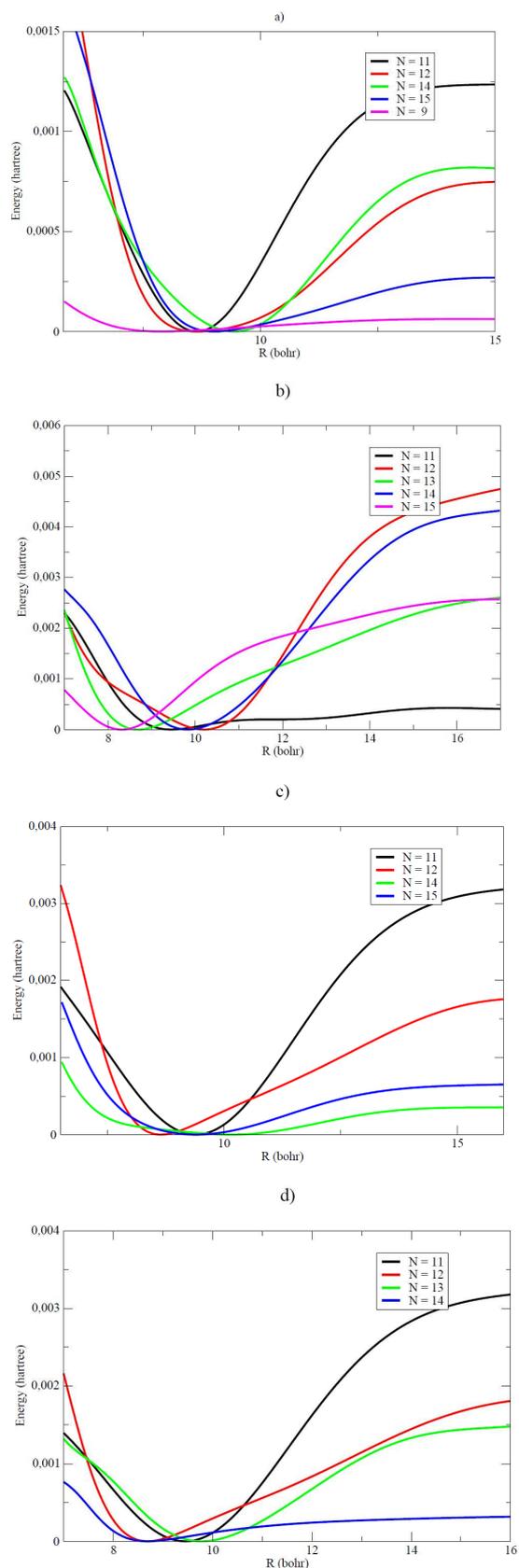


Figure 2: Potential Energy Curves of (a) $\text{H}_2\text{O}_2 + \text{Ne}$, (b) $\text{H}_2\text{O}_2 + \text{Kr}$, (c) $\text{H}_2\text{O}_2 + \text{He}$, (d) $\text{H}_2\text{O}_2 + \text{Ar}$ systems for different excited states ($n = 9, 15$).

CONCLUSIONS

In this work, we have presented a study of the interaction among the H_2O_2 molecule with noble-gases (He, Ne, Ar, and Kr) on the excited electronic states. Analytical PEC, ro-vibrational energies and spectroscopic constants were determined considering fifteen electronic states for each system. These kind of results represent the main novelty of this work, since they are presented for first time in the literature.

ACKNOWLEDGMENTS

The authors are grateful for the support given by the CNPq, and SEE-DF.

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