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Ab initio study of spectroscopic constants and anharmonic force field of hypochlorous acid $HO^{35}Cl$

Junjie Liu[a,b], Meishan Wang[a*], Jing Li[a],
Meizhong Ma[a], Chuanlu Yang[a]

[a] *School of Physics and Photoelectrical Engineering, Ludong University, Yantai 264025, China*
[b] *Department of Physics, Binzhou Medical Ccollege, Yantai 264003, China*

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Abstract. The molecular geometries, spectroscopy constants, and anharmonic force field of hypochlorous acid have been calculated at B3PW91, MP2, CCSD(T) levels of theory employing three basis sets, 6-311g(3df,2p), 6-311g(3df,3pd) and cc-pVQZ, respectively. The equilibrium structures, rotational constants, anharmonicity constants, vibration-rotation interaction constants, quartic and sextic centrifugal distortion constants are compared with the available experimental data. Coriolis coupling constants are also calculated here. The partial spectroscopy constants show that the MP2 represent an improvement over the results obtained from B3PW91. The CCSD(T) method is also a good choice to study the anharmonic force field of this molecule.

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Key words: Anharmonic force field; spectroscopy constant; Ab initio study; hypochlorous acid.

1 Introduction

The molecules containing chlorine atoms are believed to act an important role in the atmosphere pollution and have attracted extensive attention. Hypochlorous acid (HOCl) which contains chlorine atom is considered to be a temporary reservoir for active chlorine and dissociates photochemically to produce chlorine atoms. Until now, it is believed to play a more important role in ozone depletion on polar stratospheric clouds [1, 2].

$$HOCl+hv \rightarrow HO+Cl$$
$$OH+O_3 \rightarrow HO_2+O_2$$
$$Cl+O_3 \rightarrow ClO+O_2$$
$$HO_2+ClO \rightarrow HOCl+O_2$$

*Corresponding author. *Email address:* mswang1971@163.com (M.-S. Wang)

In order to prevent the ozone hole from the further expansion, it is essential to get a better understanding of the properties of atmospheric molecule that participate in ozone depletion and of the chemical reactions themselves. Thus, a number of experimental and theoretical investigations have been undertaken in order to learn more about the properties of Hypochlorous acid (HOCl). As early as 1951, Hedberg and Badger [3] studied the initial infrared spectroscopy of HOCl and its isotopomer DOCl. Data of equilibrium rotational constants for HOCl and DOCl were determined from a lower resolution work by Deeley [4]. The near infrared high-resolution spectra [5] of the weak $3v_1+2v_2$ combination band of HOCl35(37) at 12600cm^{-1} were recorded in an ultrasensitive titanium: sapphire intracavity laser absorption spectrometer (ICLAS). The high resolution far-infrared spectrum [6] of HOCl were recorded between 20 and 360cm^{-1} by means of Fourier transform spectroscopy, which can observe the pure rotation lines involving rotational levels. Bellini *et al.* [7] reported the pure rotational spectrum of HOCl35(37) in the sub-millimeter wave region, from which one could obtain the rotational constants, quartic and sextic centrifugal distortion constants.

There have been a number of theoretical calculations on HOCl. Halonen and Ha [8] performed an *ab initio* calculation at MP3 level to determine the equilibrium structure and the anharmonic force field of this molecule. Escribano *et al.* [9] evaluated the geometrical parameters and determined the anharmonic force constants involving the equilibrium moments of inertia. From *ab initio* and scaled *ab initio* potential surfaces, Zhang and Ramachandran [10] reported the spectroscopic constants and anharmonic force fields for the HOCl and DOCl. From 1998 to 2000, Peterson *et al.* [11, 12-16] finished many theory computations about this molecule and its isotopomers on accurate *ab initio* potential energy surfaces.

The molecule is known to exhibit strong electron correlation effects, and it is therefore of interest to compare the quality of their B3PW91, MP2, and CCSD(T) anharmonic force fields. B3PW91 is the simplest correlated scheme but it has been rarely applied to this molecule. MP2 and CCSD(T) have all been applied and successfully in this area with very large basis sets.

In comparison to the present calculations, the former work has calculated the geometry, rotational constants, vibration-rotation constants, fourth centrifugal distortion constants, and quadratic, cubic, and quartic force constants in dimensionless normal coordinates, but they rarely calculated and discussed the quartic force constants and the sixth centrifugal distortion constants. In order to accurately calculate rotational spectra of molecules, it is necessary to take them into account. In the present case, we calculate the equilibrium geometry structure and the anharmonic force field by B3PW91, MP2, and CCSD(T) with 6-311g(3df,2p), 6-311g(3df,3pd) and cc-pVQZ basis sets.

2 Details of the calculations

All quantum-chemical calculations were carried out at B3PW91, MP2, and CCSD(T) levels using GAUSSIAN03 [17] and ACESII [18]. Three different basis sets were employed: