



Theoretical double-core-hole spectroscopy of cytosine tautomers

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ABSTRACT

Double-core-hole potentials of cytosine tautomers were calculated within the framework of the density functional theory. The differences between the relaxation energies of these tautomers were visualized using a Wagner plot. Relationship of molecular structure with relaxation energies among tautomers was discussed.

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1. Introduction

X-ray photoelectron spectroscopy using a single core hole (SCH) is widely used in the chemical analysis of molecules [1,2]. In the mid-1980s, Cederbaum et al. presented a theoretical proposal for double core hole (DCH) spectroscopy at the K-shell [3–6]. Their pioneering work revealed that DCH spectroscopy was more sensitive than SCH spectroscopy. It should be noted that there are two DCH states, one in which the DCH state is at a single site (ssDCH) and the other in which there are DCH states at two sites (tsDCH). To analyze the double ionization energy of the tsDCH states, it is necessary to extract chemical information related to hole–hole distance, relaxation energy, and their relation to charge transfer. A detailed history and an account of recent progress in DCH spectroscopy have already been described in the literature [7,8]. Notably, it is now possible to detect DCH states experimentally owing to recent progress in synchrotron radiation instrumentation and the emergence of intense free electron lasers. In the early stages of development, DCH state measurements were limited to small molecules such as NH_3 , CH_4 [9], N_2 [10], CO [11], H_2O [12], NO , N_2O [13], and a series of hydrocarbons [14–17]. Recently, the measurement of larger molecules such as uracil [18], aminophenol [19], and C_{60} [20] was also made possible. Several groups of theoretical researchers became interested in understanding and developing models for this system. Tashiro et al. [21,22] enriched the description of DCH spectroscopy using modern theoretical procedures at the complete active space self-consistent field (CASSCF) level. Kryzhevoi et al. [23,24] studied

DCH states of aminophenol isomers by means of Green's function or propagator methods within algebraic diagrammatic construction (ADC) schemes, and their studies prompted several experimental [19] and theoretical works [25]. These discoveries were followed by the work of Takahashi et al. [8,26–29], who demonstrated that density functional theory (DFT) can describe the SCH and DCH states of formamide at a comparable level with that of the CASSCF theory [27]. The merit of DFT lies in its simplicity, which translates into the ability to apply to relatively large molecules. Thomas [30] proposed the use of Wagner plots to describe differences in relaxation energy graphically. More recently, Hua et al. [25,31] calculated the DCH states of aminophenol using the state-averaged restricted-active space SCF (SA-RASSCF) theory.

Tautomers are readily interconvertible isomers that differ only in the position of protons and electrons. A typical example of tautomerism is that between keto and enol forms. For general carbonyl compounds, the keto form is most stable; however, there are some exceptions in which the enol form is more stable. The ratio of tautomeric forms is often controlled by the pH in solution, and can be measured using spectroscopic techniques such as IR, UV–vis, and NMR [32,33]. Many theoretical studies of tautomerism have been performed for keto–enols [34] and nucleic acids [35]. Different from the above conventional spectroscopies, core-level electron spectroscopies such as SCH spectroscopies [36,37] are performed under vacuum conditions, and it is performed on environments to examine properties in molecule without interaction with any solvents. Furthermore through SCH and DCH spectroscopies, correlation of molecular structure with relaxation energy can be examined. To examine the fundamental molecular properties in molecule in the gas phase has a great significance.

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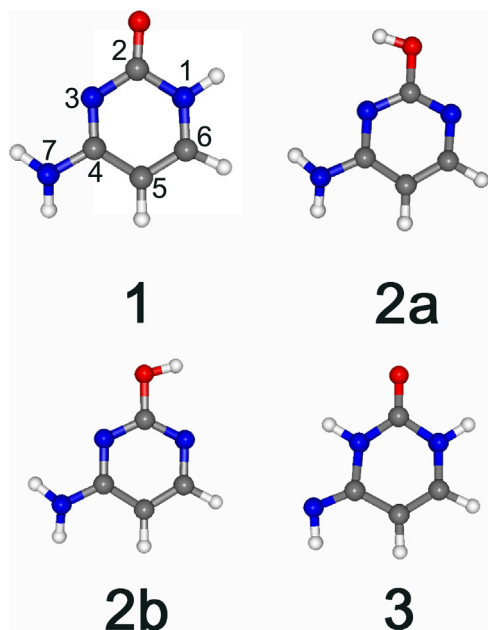


Fig. 1. Low energy tautomers of cytosine. **2a** and **2b** are rotamers. The numbering of atoms is defined for **1** only.

The analysis of tautomers using DCH spectroscopy presents another interesting application of this spectroscopic method. Here, cytosine was selected as the target molecule because it is a nucleobase, and therefore, one of the most important molecules for conserving genetic information. Recently, Feyer et al. studied tautomerism in cytosine and uracil experimentally and theoretically [36], and later, Plekan et al. studied it in guanine [37]. Feyer et al. detected three types of tautomers, illustrated in Fig. 1, one of which had a rotamer based on the rotation of the OH bond. In a previous study, [27] we used DCH spectroscopy to study nucleobases; however, a detailed investigation of their tautomerism was not conducted. In addition to providing an insight into this area, the present study can reveal information about the effect of intense X-ray exposure on cytosine.

2. Computational methods

Vertical SCH and DCH ionizations were considered in the present work, and the molecular geometries of the target molecules were calculated by geometry optimization at the MP2/cc-pVTZ level of theory using the Gaussian09 suite of programs [38]. Rotamers and tautomers of cytosine are illustrated in Fig. 1, where they are identified by their atom numbering. The optimized structures of the target molecules are given by their Cartesian coordinates in the Supplementary material.

DFT calculations of the SCH and DCH states were performed by the Δ Kohn-Sham (Δ KS) method, [39] i.e., allowing full relaxation of the core-hole states to compute the relaxed ionization potentials (IPs) and double IPs (DIPs). The basis set dependence of the DFT calculations was examined for the *K*-shell DCH states with the IGLO-III [40] and cc-pCVTZ basis sets. The gradient-corrected exchange (PD86) [41] and correlation functional (PD91) [42] described by Perdew and Wang were used for the correlation-exchange functional in the DFT calculations. The Generalized Gradient Approximation (GGA) exchange and correlation functional prepared by Perdew, Burke, and Ernzerhof [43] were also used. For example, the functional combination “PD86-PD91” implies the use of PD86 as the exchange functional and PD91 as the correlation

Table 1

SCH IPs (in eV) for cytosine as calculated with the DFT/IGLO-III method and the PD86-PD91 functional.

Core holes	Calculations		Experiment
	This work	Feyer ^(a)	Feyer ^(a)
Tautomer 1			
C2	293.7	294.10	293.9
C4	293.1	293.14	293.2
C5	290.7	290.61	290.6
C6	292.4	292.39	292.4
N1	406.5	406.09	406.1
N3	404.2	404.04	404.5
N7	406.1	405.95	406.1
O	536.5	536.22	536.5
Tautomer 3			
C2	294.7	295.24	295.1
C4	293.0	293.18	293.2
C5	290.9	290.78	290.6
C6	292.4	292.46	292.4
N1	406.9	406.49	406.1
N3	406.5	406.14	406.1
N7	403.9	404.10	404.5
O	537.4	537.23	537.3
Rotamer 2a			
C2	293.6	293.76	293.9
C4	292.9	293.08	293.2
C5	290.4	290.46	290.6
C6	291.6	291.56	291.7
N1	406.2	404.49	404.5
N3	404.4	404.95	404.5
N7	404.8	406.10	406.1
O	539.5	539.46	539.4
Rotamer 2b			
C2	293.6	293.75	293.9
C4	292.9	293.03	293.2
C5	290.4	290.47	290.6
C6	291.6	291.62	291.7
N1	406.1	404.58	404.5
N3	404.5	404.77	404.5
N7	404.6	405.97	406.1
O	539.5	539.43	539.4

(a) Reference [36].

functional, respectively. All DFT calculations were performed using the STOBE-DEMON program [44].

3. Quick review of DCH spectroscopy

Following Refs. [21] and [27], the SCH IP is given by:

$$IP = -\varepsilon_a - RC(a^{-1}), \quad (1)$$

where ε_a is the Hartree-Fock energy of the orbital a (a is a $1s$ core orbital) and $RC(a^{-1})$ is the generalized relaxation energy, which includes orbital relaxation and electron correlation. In the case of the *K*-shell IPs, the effect of orbital relaxation is much larger than that of electron correlations. Analogously, the DIP of a state with two core vacancies $a^{-1}b^{-1}$ is given by:

$$DIP = -\varepsilon_a - \varepsilon_b - RC(a^{-1}b^{-1}) + RE(a^{-1}b^{-1}), \quad (2)$$

where $RC(a^{-1}b^{-1})$ is the generalized relaxation energy of the DCH state and $RE(a^{-1}b^{-1})$ is the repulsion-exchange energy of the two core holes. The DCH generalized relaxation energy can be decomposed into three terms:

$$RC(a^{-1}b^{-1}) = RC(a^{-1}) + RC(b^{-1}) + ERC(a^{-1}b^{-1}), \quad (3)$$

where $ERC(a^{-1}b^{-1})$ is the generalized excess relaxation energy, representing a non-additive contribution to the DCH relaxation energy.

In the case where two core holes are created on the same atomic site, $ERC(a^{-2})$ measures the local properties of a core ionized atom. When two core holes are created on different atomic sites,

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