

## Articles

# Density Functional Theory (DFT) studies on the ground state of $\text{NO}_3(^2A'_2)$ radical and the first triplet state of $\text{NO}_3^+$ cation

CAO, Xiao-Yan<sup>a</sup>(曹晓燕) HONG, Gong-Yi<sup>a</sup>(洪功义) WANG, Dian-Xun<sup>a,\*</sup>(王殿勋)LI, Le-Min<sup>b</sup>(黎乐民) XU, Guang-Xian<sup>b</sup>(徐光宪)<sup>a</sup>State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China<sup>b</sup>State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Density Functional Theory (DFT) studies on the ground states ( $^2A'_2$ ) of  $\text{NO}_3$  radical and on the ground state ( $^1A'_1$ ) and the first triplet state ( $^3E''$ ) of  $\text{NO}_3^+$  cation provide an unambiguous prediction about their geometrical structure: the ground states of both  $\text{NO}_3$  radical and  $\text{NO}_3^+$  cation have  $D_{3h}$  symmetry and the geometrical configuration of the first triplet state  $^3E''$  of  $\text{NO}_3^+$  cation has  $C_{2v}$  symmetry. It is shown that as far as the ionization energy calculations on  $\text{NO}_3$  radical are concerned, the results are only slightly different, no matter that gradient corrections of the exchange-correlation energy are included during self-consistent iterations or they are included as perturbations after the self-consistent iterations.

**Keywords**  $\text{NO}_3$ , symmetry, density functional theory

## Introduction

The determination of the ground electronic state and molecular structure of the nitrate radical ( $\text{NO}_3$ ) has been of great interests for both experimentalists and theorists.<sup>1-10</sup> A challenging question existing is to determine that the ground state of  $\text{NO}_3$  possesses  $D_{3h}$  or  $C_{2v}$  symmetry. It has been investigated by using various *ab initio* method, such as MPPT,<sup>4</sup> CASSCF theory,<sup>8,10</sup> Couple-Cluster method<sup>5a</sup> as well as MR-CI.<sup>4,9</sup> However, there are different answers to this question based on different levels of theory. For example, while MP2 and MP4 predict  $D_{3h}$  symmetry, MP3 favors  $C_{2v}$  symmetry.<sup>4</sup> The Couple-Cluster calculations both on Brueckner determi-

nants [ B-CC ] and quasi-restricted Hartree-Fock [ QRHF ] reference functions [ QRHF-CC ] predict a  $C_{2v}$  equilibrium geometry if triple excitations are not included, and predict an extremely flat potential surface which slightly favors the  $D_{3h}$  symmetry form of the molecule when an approximate treatment of the triple excitation effects is involved.<sup>5a</sup> While the CASSCF calculation at (17e/13MO) level with a DZ + P basis set prefers  $C_{2v}$  symmetry (with the total energy - 279.09660 au) rather than  $D_{3h}$  symmetry (with the total energy - 279.09434 au),<sup>8</sup> the more recent CASSCF calculation at (9e/13MO) level favors  $D_{3h}$  symmetry, using a concomitant basis set augmented by one d-polarization function for N and by two d-polarization functions for O atoms and using effective core potential to eliminate the K shell of all atoms.<sup>10</sup> In addition, Ref. 10 also reported the calculated energy of the ground state of  $\text{NO}_3^+$ . From the difference of the energies of  $\text{NO}_3$  and  $\text{NO}_3^+$  we can obtain the adiabatic ionization potential (IP): 10.60 eV which is much lower than the reported experimental value: 12.57 eV.<sup>10</sup> According to the variational principle, it thus can be derived that the error due to the incompleteness of the basis sets and of the configurations leads to an energy of the ground state of  $\text{NO}_3$ , at least higher for 1.97 eV in magnitude, than the exact one. On the other hand we obtained a value of 13.027 eV for the above-mentioned IP using density functional theory (DFT),<sup>11</sup> which is much closer to the experimental one.

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In the previous paper,<sup>11</sup> we reported a complete HeI photoelectron spectrum (PES) of NO<sub>3</sub> radical which is produced *in situ* by the pyrolysis of pure gas phase N<sub>2</sub>O<sub>5</sub> at 280°C (±0.5°C) in a double-heater inlet system on a double-chamber UPS Machine-II built specifically to detect transient species. In the present paper, we focus the attention on the study of the geometry of neutral ground and two ionic states of the NO<sub>3</sub> radical by using DFT method, especially on the geometry of the first triplet state of the NO<sub>3</sub><sup>+</sup> cation which was suggested to deserve further discussion.<sup>10</sup> In addition, the vertical ionization energies of HOMO, SHOMO and the adiabatic ionization energy of the SHOMO have been studied by using several gradient correction schemes to the exchange-correlation energy.

## Calculations

All the calculations were carried out with the Amsterdam Density Functional (ADF) program package,<sup>12-14</sup> in which a density fitting procedure<sup>12</sup> was used to obtain the Coulomb potential, and an elaborate 3D numerical integration technique<sup>13,14</sup> was employed to calculate the Hamiltonian matrix elements. The geometry optimization was performed using local spin density functional theory<sup>15</sup> which acquired great success in the prediction of molecular structure.<sup>16</sup> High numerical integration accuracy and extended basis sets (triple  $\zeta$  + double P) as well as analytical first order derivative were adopted in practical computation.

## Results and discussion

In the geometry optimization of the ground states of both NO<sub>3</sub> and NO<sub>3</sub><sup>+</sup>, the input initial data are in the C<sub>2v</sub> symmetry with one longer bond and two shorter bonds, or with one shorter bond and two longer bonds. The geometries of both NO<sub>3</sub> and NO<sub>3</sub><sup>+</sup> in ground states are always converged to the one with D<sub>3h</sub> symmetry. Table 1 gives the results of the optimized geometry for both NO<sub>3</sub> and NO<sub>3</sub><sup>+</sup>.

Thus in the photoionization process from the ground state of NO<sub>3</sub> neutral radical to the ground state of NO<sub>3</sub><sup>+</sup> cation, corresponding to the NO<sub>3</sub><sup>+</sup>(<sup>1</sup>A'<sub>1</sub>) ← NO<sub>3</sub>(<sup>2</sup>A'<sub>2</sub>) ionization, there is no significant distortion of the configuration of the species. This result is consistent with a

very sharp peak with the lowest ionization potential (12.55 ± 0.01 eV) in the HeI photoelectron spectrum (PES) of the NO<sub>3</sub> radical.<sup>11</sup>

**Table 1** Optimized geometry<sup>a</sup> for NO<sub>3</sub> and NO<sub>3</sub><sup>+</sup>

	NO <sub>3</sub> ( <sup>2</sup> A' <sub>2</sub> )	NO <sub>3</sub> <sup>+</sup> ( <sup>1</sup> A' <sub>1</sub> )	NO <sub>3</sub> <sup>+</sup> ( <sup>3</sup> E'')
N—O(1)	1.230	1.220	1.315
N—O(2)	1.230	1.220	1.315
N—O(3)	1.230	1.220	1.152
O(1)—N—O(2)	120.0	120.0	97.30
O(1)—N—O(3)	120.0	120.0	131.80

<sup>a</sup> Bond lengths are in angstrom and bond angles are in degree. The threshold for the convergence is taken as 0.005 angstrom for bond length and 0.1 degree for bond angle.

From the shape of the second band of the PE spectrum of NO<sub>3</sub> radical, it can be inferred that the second band should come from electron ionization of a strong bonding orbital in the molecule. Associating with the photoionization process of the electron on the strong orbital, the molecular geometry should change considerably.

The vertical ionization potential corresponding to the NO<sub>3</sub><sup>+</sup>(<sup>3</sup>E''<sub>1</sub>) ← NO<sub>3</sub>(<sup>2</sup>A'<sub>2</sub>) ionization has been given in the previous paper.<sup>11</sup> In order to obtain the adiabatic ionization potential corresponding to the NO<sub>3</sub><sup>+</sup>(<sup>3</sup>E''<sub>1</sub>) ← NO<sub>3</sub>(<sup>2</sup>A'<sub>2</sub>) ionization, the geometry of the first triplet state of the NO<sub>3</sub><sup>+</sup> cation has been optimized. The converged geometry has C<sub>2v</sub> symmetry. The result is also presented in Table 1. This result shows that in the photoionization process corresponding to the NO<sub>3</sub><sup>+</sup>(<sup>3</sup>E''<sub>1</sub>) ← NO<sub>3</sub>(<sup>2</sup>A'<sub>2</sub>) ionization, the geometry of the species is changed from D<sub>3h</sub> to C<sub>2v</sub> symmetry. The adiabatic ionization potential for the ionization NO<sub>3</sub><sup>+</sup>(<sup>3</sup>E''<sub>1</sub>) ← NO<sub>3</sub>(<sup>2</sup>A'<sub>2</sub>) is calculated from the difference of the total energy of the NO<sub>3</sub><sup>+</sup> cation at its optimized geometry and that of NO<sub>3</sub> radical in the ground state. Of course, the different zero-point vibrational energies in different electronic states should be considered, but they are very small and may be neglected. The calculations are performed with using both LSDA and non-local gradient corrections to the LSDA exchange-correlation energy. The results are presented in Table 2, in which Bx, P86x, PW91x, P86c, PW91c denote the gradient correction to the correlation energy due to Becke<sup>17</sup> and Perdew<sup>18,19</sup>, respectively. The vertical ionization potentials for the ioniza-

tions  $\text{NO}_3^+ (^1A'_1) \leftarrow \text{NO}_3 (^2A'_2)$  and the ionization  $\text{NO}_3^+ (^3E''_2) \leftarrow \text{NO}_3 (^2A'_2)$  have also been calculated. The results are presented in Table 2 too. It can be seen from Table 2 that the results derived from several non-local density functional schemes are very close and agree rather well with the PES experiment. This fact supports,

in turn, the above-mentioned prediction of a  $C_{2v}$  symmetry for the first state of the  $\text{NO}_3^+$  cation. Furthermore, it gives also a strong evidence in favor of the ground state of  $\text{NO}_3$  radical having  $D_{3h}$  symmetry, taking into account the vibrational structure of the second PES band, which corresponds to the geometry with  $D_{3h}$  symmetry.

**Table 2** Calculated vertical ionization potentials ( $I_v$  in eV) for HOMO and SHOMO and adiabatic ionization potentials ( $I_a$ ) for SHOMO (in eV)

Orbital	BxP86c <sup>a</sup>	P86xPW91c <sup>a</sup>	PW91xPW91c <sup>a</sup>	LSDA	BxP86c <sup>b</sup>	EXP.
SHOMO ( $I_a$ )	13.375	13.350	13.371	13.629		13.05
SHOMO ( $I_v$ )	13.560	13.535	13.551	13.747	13.507	13.18
HOMO ( $I_v$ )	13.075	13.094	13.053	13.124	13.027	12.55

<sup>a</sup> The gradient corrections are added self-consistently. <sup>b</sup> The gradient correction are added as a perturbation after LDA SCF calculation has been finished.

Table 2 also shows that the adopted three kinds of gradient correction schemes yield very similar results, and give better results than those from the local spin density approximation. The calculated vertical ionization energies for HOMO and SHOMO presented in this paper are a little larger, about 0.05 eV in magnitude, than those in the previous paper,<sup>11</sup> with the same gradient correction schemes, due to the inclusion of the gradient corrections into the LSDA exchange-correlation potential in the self-consistent iterations in the present studies, while in the previous paper, the gradient corrections to the exchange-correlation energy were included after the LSDA self-consistent calculations. It thus can be concluded that inclusion or not inclusion of the gradient corrections into the exchange-correlation potential in the self-consistent iterations only results in a negligible difference as far as the ionization energy is concerned. But inclusion of gradient corrections in the SCF calculations results in much large computation expenses.

In a word, the present DFT study shows that (1) the geometries of  $\text{NO}_3$  and  $\text{NO}_3^+$  in ground state both possess  $D_{3h}$  symmetry; (2) the geometry of  $\text{NO}_3^+$  in the first triplet state  $^3E''$  possesses  $C_{2v}$  symmetry; (3) whether or not including the gradient corrections into the exchange-correlation potential in the self-consistent iterations only results in a negligible difference in the ionization energy calculations on  $\text{NO}_3$  radical.

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(E9909134 JIANG, X.H.; DONG, L.J.)