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Gaseous nitryl azide N_4O_2: A joint theoretical and experimental study

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Abstract

Gaseous nitryl azide N_4O_2 is generated by the heterogeneous reaction of gaseous $ClNO_2$ with freshly prepared AgN_3 at −50 °C. The geometric and electronic structure of the molecule in the gas phase has been characterized by *in situ* photoelectron spectroscopy (PES) and quantum chemical calculations. The experimental first vertical ionization energy of N_4O_2 is 11.39 eV, corresponding to the ionization of an electron on the highest occupied molecular orbital (HOMO) $\{4a''(\pi_{nb(N4-N5-N6)})\}^{-1}$. An apparent vibrational spacing of $1600 \pm 60\ \mathrm{cm}^{-1}$ (ν_{as}O1N2O3) on the second band at 12.52 eV ($\pi_{nb(O1-N2-O3)}$) further confirms the preference of energetically stable chain structure in the gas phase. To complement the experimental results, the potential-energy surface of this structurally novel transient molecule is discussed. Both calculations and spectroscopic results suggest that the molecule adopts a *trans*-planar chain structure, and a five-membered ring decomposition pathway is more favorable.

Keywords: Nitryl azide; HeI photoelectron spectroscopy (PES); Ionization energy; IRC

1. Introduction

Since the identification of N_2O, NO and NO_2 in the 18th century, many other oxides of nitrogen have also been known, such as N_2O_3, N_2O_5, NO_3 and several π^*–π^* bound binary complexes (N_2O_2, N_2O_4 $(N_2O)_2$ and $(N_2O)_3$) [1]. The research on them mainly focuses on structures and bonding, also their effects on the atmospheric environment (NO_x) through the combustion of fossil fuels [2], and their extensive applications as oxidizers in the rocket fuels [3]. Recently, large efforts have been made on understanding the structures and bonding properties of binary nitrogen oxides as well as isoelectronic high energetic homologues, such as N_4O [4], N_4O_2 [5], $O(N_3)_2$ [6], and ON–NCO, O_2N–NCO, N–NCO, ON–NC, O_2N–NC, etc. [7]. These novel nitrogen-containing compounds decompose at room temperature with large release of energy, which precludes the isolation of pure states under normal conditions, although there have been many theoretical discussions.

Similar to N_5^+ [8] and N_4O [4], nitryl azide N_4O_2 decomposes completely to two moles of thermodynamically stable N_2O with an energy release of 58.9 kcal mol^{-1} (MP2/6-31+G*) [5b]. The first attempt to prepare this novel compound was carried out by Doyle et al., they approached this unstable nitrogen oxide in CCl_4 solution through the “reaction between azide and nitronium ions (LiN_3 and NO_2BF_4)”, and pointed out that N_4O_2 is significantly more stable than nitrosyl azide (N_4O), which decomposes solely to nitrous oxide [5a]. Then Klapötke et al. achieved strong evidence for the formation of nitryl azide through the reaction of NO_2SbF_6 with NaN_3 in liquid CO_2 ($-55\ °C \leqslant T \leqslant -35\ °C$), and for the first time provided its experimental vibrational frequencies by means of low-temperature Raman spectroscopy [5b]. However, no further experimental properties for this intrinsically unstable molecule have been reported until now. As mentioned by Klapötke et al., N_4O_2 is highly unstable and reactive in the

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condensed phase at high temperature, so, similar to the preparation of ONNCO [7c] and $SO(N_3)_2$ [9a], we studied the gas–solid reaction of $ClNO_2$ with finely divided AgN_3 at different temperatures in vacuum (10^{-4} torr), the gaseous product was monitored in real time with *in situ* photoelectron spectroscopy (PES). Only decomposition product N_2O was observed above −30 °C, by lowering the temperature to −50 °C, the novel transient N_4O_2 was detected without decomposition. Its electronic structure was characterized for the first time by *in situ* photoelectron spectroscopy (PES), in combination with theoretical calculations. To elucidate the decomposition mechanism from the point of experimental results, the potential-energy surface was also discussed.

2. Experiment and quantum chemical calculations

Caution: Pure dried AgN_3 is extremely explosive, it should be handled only on a small scale with appropriate safety precautions (face shield, leather gloves, and protection clothing).

PES was recorded on a double-chamber UPS-II machine [9] which was built specifically to detect transient species at a resolution of about 30 meV indicated by the standard $Ar^+(^2P_{2/3})$ photoelectron band. Experimental vertical ionization energies (IP in eV) are calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample.

Recently, many azide-containing compounds have been successfully prepared and characterized, and found that AgN_3 is an ideal precursor for *in situ* preparation of highly explosive azides, through heterogeneous reactions with reactive halogen-containing molecules [9]. The freshly prepared AgN_3 (0.5 g) [10] should be dried in vacuum (10^{-4} torr) prior to the PES experiment, and the silver salt was supported on glass wool and loosely packed into a 5 cm inlet column. By lowering the temperature of the reaction tube to −50 °C, the reaction went smoothly by passing $ClNO_2$ vapor over the solid AgN_3 (Eq. (1)), new spectrum was obtained in comparison to the known PE spectrum of N_2O [11]. While, when the temperature was slowly increased to −30 °C, spectrum of pure decomposition product N_2O appeared. Attempts have been made to isolate pure nitryl azide by condensing $ClNO_2$ on the surface of AgN_3 at −195.8 °C (liquid nitrogen), but failed in fierce explosion when the temperature was increased to −55 °C. $ClNO_2$ was synthesized according to the literature [12].

$$ClNO_2(g) + AgN_3(s) \underset{10^{-4}\text{torr}}{\overset{-50°C}{\rightarrow}} N_4O_2(g) + AgCl(s) \qquad (1)$$

To assign the PE spectrum of nitryl azide, Outer valence Green's function (OVGF) [13] calculations with 6-311+G(d) basis sets based on the B3LYP [14] optimized geometry were performed for isomers of N_4O_2. The vertical ionization energies (Ev) were calculated at the *ab initio* level according to Cederbaum's OVGF method, including the effect of electron correlation and reorganization beyond the Hartree-Fock approximation. The self-energy part was expanded up to third-order, and contributions of higher-orders were estimated by means of a renormalization procedure. On discussing the N_4O_2 potential-energy surface, all the geometric structures and the harmonic vibrational frequencies of two isomers of N_4O_2, three transition states during the decomposition process were calculated at B3LYP/6-311+G(d) level, the single point of energy for all species were calculated with CCSD(T)/6-311+G(d) [15] and MP2/6-311+G(3df) [16] levels of theory; the minimum-energy pathways for decomposition of the N_4O_2 were confirmed using the intrinsic reaction coordinate (IRC) method [17]. All above calculations were performed using Gaussian 98 Program [18].

3. Results and discussions

3.1. Calculated structure

There have been many theoretical investigations on the cyclic and chain isomers of N_4O_2 [19]. All the results predicted the trans bent structure (chain isomer in Fig. 1) to be the most stable, the preference for this trans planar molecule can be rationalized by a higher degree of π delocalization in comparison to the cyclic isomer (Fig. 1) as explained by Klapötke et al., according to the experimental vibrational frequencies (Raman) and theoretical predictions (RHF/6-31+G*). They concluded that the cyclic isomer does not represent a local minimum at correlated level (RMP2/6-31+G*) [5b].

The geometrical features for two planar isomers are summarized in Fig. 1 and Table 1, respectively, and corresponding energies are listed in Table 2. As for the optimized stable chain and cyclic isomers, the latter shows 11.5 kcal mol^{-1} less stable at B3LYP/6-311+G(d) level, including ZPE corrections, and the other two levels of theory (CCSD(T) and MP2) predict similar relative energies (Table 2). However, previous detailed theoretical calculations on nitrosyl azide N_4O predicted that the cyclic isomer (O–NONNN) is more stable than the open chain trans isomer by 11.3 kcal mol^{-1} (including ZPE), the reverse in stability between two isomers can be ascribed to the different degree of π delocalization in N_4O and N_4O_2 [5b,20]. The N2–N4 bond length in the chain isomer is calculated to be 1.491 Å, which is very close to that of calculated *trans*-ONN_3 (1.501 Å) [20], O_2NNCO (1.451 Å) [7a], and *trans*-NNCO (1.498 Å) [7d], this rather long bond (typical values: N–N single bond, 1.447 Å in N_2H_4, N=N double bond, 1.252 Å in N_2H_2) indicates a significant donor-acceptor interaction (hyperconjugation) [7a,20], of the lone-pairs on both oxygen atoms with the unoccupied, antibonding σ^* orbitals of the N–N bond (LP(O) → σ^* (N–N)). The O–N bond length in this weakly bound molecule is predicted to be 1.212 and 1.199 Å for O1–N2 and N2–O3, respectively, a little longer than the undisturbed NO_2 (1.197 Å) [21].

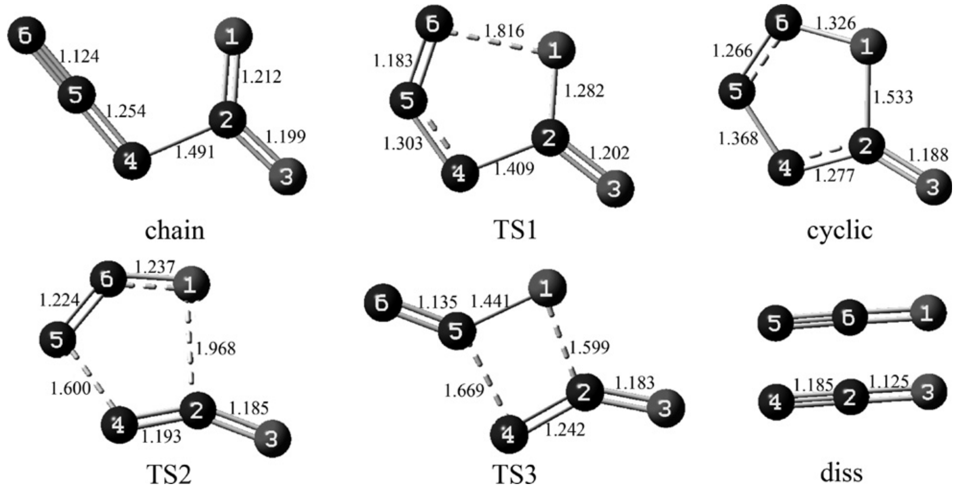

Fig. 1. Optimized geometries (B3LYP/6-311+G(d)) of the isomers and transition structures on the potential-energy surfaces of the decomposition of N_4O_2. Bond distances in Å.

Table 1
Distances and angles for N_4O_2 isomers calculated at B3LYP/6-311+G(d) level (refer to Fig. 1)

Molecule	Distances (Å)						
	O1–N2	N2–O3	N2–N4	N4–N5	N5–N6	N5–O1	N6–O1
Chain	1.212	1.199	1.491	1.254	1.124		
TS1	1.282	1.202	1.409	1.303	1.183		1.861
Cyclic	1.533	1.188	1.277	1.368	1.266		1.326
TS2	1.968	1.185	1.193	1.600	1.224		1.237
TS3	1.599	1.183	1.242	1.669	1.135	1.441	
Diss		1.125	1.185				

Molecule	Angles (deg)				
	O1–N2–O3	O1–N2–N4	N2–N4–N5	N4–N5–N6	N5–N6–O1
Chain	129.4	118.2	109.5	173.8	43.5
TS1	124.4	115.7	103.5	126.3	96.2
Cyclic	119.4	105.8	108.6	111.6	111.1
TS2	113.3	99.2	113.1	106.9	125.3
TS3	120.9	99.5	87.6	137.8	26.2
Diss					180.0

Table 2
Energies (hartrees), ZPE corrections (kcal mol^{-1}) and energies relative to the chain isomer (kcal mol^{-1}) for N_4O_2 isomers, transition states, and decomposition product, $2N_2O$

Molecule	E(B3LYP)[a]	ZPE[a]	E(CCSD(T))[a,c]	E(MP2)[b,c]	ΔE[d]
Chain	−369.363518	15.1	0.0	0.0	0.0
TS1	−369.327663	14.6	21.7	29.6	21.2
Cyclic	−369.340584	15.2	11.4	10.3	11.5
TS2	−369.334312	14.2	18.2	12.5	17.3
TS3	−369.267241	13.8	59.3	59.7	58.0
Diss	−369.434036	13.8	−48.7	−54.9	−50.0

[a] At 6-311+G* basis set.

[b] At 6-311+G(3df) basis set.

[c] Based on the B3LYP/6-311+G(d) optimized structure.

[d] Including ZPE corrections.

3.2. Potential-energy surface

To explore both isomerization and decomposition mechanism, an exhaustive theoretical study was performed for stable isomers, transition states (TS) and decomposition products $2N_2O$. Structures were fully optimized and confirmed to be local minima or transition states on the potential-energy surface. IRC studies were carried out at the B3LYP/6-311+G(d) level of theory to connect minima with the corresponding TS.

The first decomposition pathway for nitryl azide is: chain $O_2N–N_3 \rightarrow TS1 \rightarrow$ cyclic ONONNN $\rightarrow TS2 \rightarrow 2N_2O$. Similar to the decomposition of N_4O [20], a five-membered cyclic isomer C_s–ONONNN forms properly in this process. Based on IRC analysis, the cyclic isomer formed via a transition state TS1, this can be mechanistically thought to be driven by a nucleophilic attack of O1 of the nitryl group on the N6 of the azido moiety, and similar transition states have been discussed during the decomposition of ON–NCO, O_2N–NCO etc. [7a]. The transition state TS1 is basically a distorted O1–N2–N4–N5–N6 ring, with rather long O–N bond distance of 1.816 Å, this distance resembles more the cyclic isomer O–N, 1.326 Å,

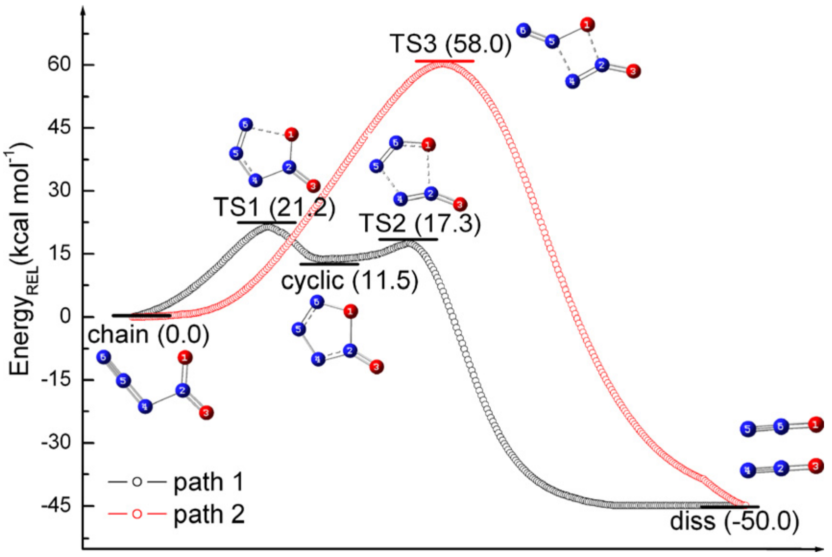

Fig. 2. Qualitative description of the N_4O_2 potential-energy surface.

this is in agreement with Hammond's postulates that the TS lies more towards the higher energy side [22]. Meanwhile, by vibrational analysis, an imaginary vibration occurs for TS1 at $-386.6\ cm^{-1}$, it embodies the concerted in-plane stretching vibration of bonds O1–N6 and N2–N4, the vibration shortens the distances between the nitryl group and the azido moiety, which makes the cyclization possible. Energetically, to form the cyclic isomer, a barrier of 21.2 kcal mol^{-1} needs to be surmounted, indicating that the chain isomer should be intrinsically more stable. The decomposition of cyclic isomer to experimentally observed $2N_2O$ experiences a transition state TS2 as well, during this process, the bonds of O1–N2 and N4–N5 become longer to 1.968 and 1.600 Å, respectively, an imaginary vibrational frequency at $-472.1\ cm^{-1}$ of TS2 helps it further decompose to two moles of thermally stable N_2O, with an energy release of 67.3 kcal mol^{-1}. The dissociation barrier for the cyclic isomer C_s–ONONNN is computed to be only 5.8 kcal mol^{-1} (including ZPE) at B3LYP/6-311+G(d) level, similar to the low decomposition barrier of ring isomer of N_4O [20], a barrier of this size lies much lower than its ZPE (15.2 kcal mol^{-1}), throwing doubt on the existence of the cyclic isomer of N_4O_2.

The second dissociation channel is: chain O_2N–$N_3 \rightarrow$ TS3 $\rightarrow 2N_2O$. The barrier for the formation of this four-membered ring transition state TS3 is calculated to be 58.0 kcal mol^{-1} at the B3LYP/6-311+G(d) level of theory. According to the previously NBO analysis [5b], the negative oxygen atom O1 of nitryl group can also take nucleophilic attack on the positive nitrogen atom N5 of the azido moiety to form this four-membered ring TS3, similar four-membered transition states have also been proposed during the decomposition of ON–NCN [23], and N_4 [24], this assumption is confirmed by IRC analysis (Fig. 2). However in contrast to the five-membered ring transition state TS1, the latter pathway is considered more favorable due to lower decomposition barrier.

3.3. Photoelectron spectrum

The PE spectra of the gaseous product obtained by the reaction (1) at different temperatures are given in Fig. 3. It can be clearly seen that there are three clear peaks at 12.89, 16.38, and 18.20 eV, respectively, as depicted in Fig. 3b, which corresponds to the characteristic HeI photoelectron

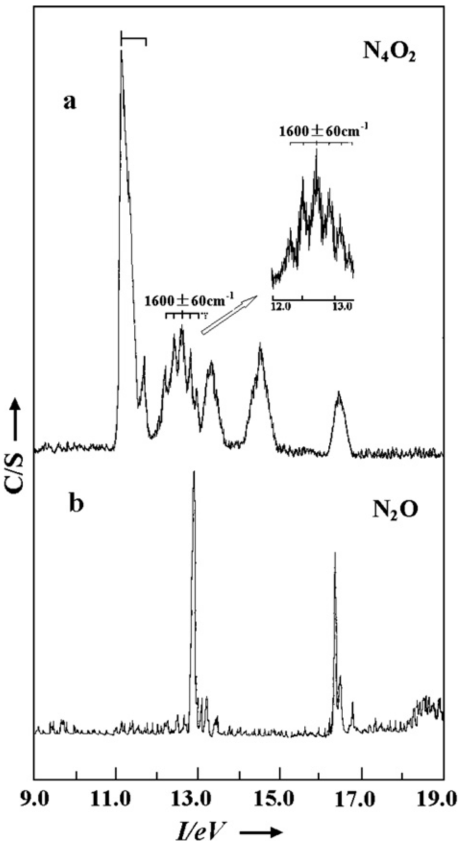

Fig. 3. HeI photoelectron spectrum of the gaseous products of the reaction (1) at different temperatures (a, −50 °C; b, −30 °C).

Table 3
Experimental (IP in eV) and calculated (Ev in eV) vertical ionization energies, and molecular orbital characters for the chain isomer of N_4O_2

IP (eV)	Ev (eV)[a]		MO	Character
	Chain[b]	Cyclic		
11.39	11.19 (0.90)	11.36 (0.90)	4a″ (22)	$\pi_{nb(N4–N5–N6)}$
12.52	12.12 (0.91)	12.29 (0.90)	3a″ (21)	$\pi_{nb(O1–N2–O3)}$
13.32	12.37 (0.88)	13.53 (0.89)	18a′ (20)	n_{O1}, n_{N4}
	12.49 (0.89)	13.64 (0.89)	17a′ (19)	$\pi'_{nb(O1–N2–O3)}$
14.52	14.80 (0.89)	14.05 (0.89)	16a′ (18)	$\pi_{b(O1–N2–O3)}$, $\pi_{b(N4–N5–N6)}$
16.65	17.66 (0.87)	15.60 (0.85)	15a′ (17)	$\sigma_{(O1–N2–O3)}$, $\pi_{(N4–N5–N6)}$

[a] OVGF calculations with 6-311+G(d) basis set.
[b] Polestrength in parentheses.

spectrum of N_2O [11]. That is, the gaseous product of the reaction at −30 °C leads completely to N_2O, derived from the dissociation of N_4O_2 (Eq. (1)). This is in agreement with the previous report by Klapötke et al. that N_4O_2 decomposes to yield N_2O at room temperature [5b]. By lowering the temperature to −50 °C, five different bands occur in the region of 10.0–17.0 eV, which are considered to be the PE spectrum of another sole gaseous product of the reaction (1), N_4O_2. To make assignment of the observed PE bands to nitryl azide N_4O_2, OVGF calculations in combination with molecular orbital analysis based on the optimized stable chain and cyclic isomers at the 6-311+G(d) basis set were performed. Table 3 presents experimental (IP in eV) and calculated (Ev in eV) vertical ionization energies, and corresponding ionized molecular orbital characters. It can be seen clearly that the experimental results match well with the ionization potentials calculated for both the chain and the cyclic isomers, we could not exclude the existence of the latter simply from the ionization energies. However, an apparent vibrational spacing of $1600 \pm 60\ \mathrm{cm^{-1}}$ is observed on the band centered at 12.52 eV (Fig. 3), it is assigned to the typical asymmetric stretching (ν_{as}O1N2O3) of the nitro group (Table 4), which confirms the dominant existence of energetically favorable chain isomer in the gas phase, as reported by previous theoretical predictions [5].

Since it is a planar open-chain molecule, $O_2N–N_3$ can be described quite adequately as a loosely bound combination of a reorganized O_2N and a N_3 radical. More specifically, the molecular orbitals (MOs) of $O_2N–NNN$ can be treated as MOs localized on either the O_2N or the N_3 fragment of the neutral molecule. So, in comparison to the known PE spectra of HN_3 [25], $SO(N_3)_2$ [9a], CH_3NO_2 [11], the assignments of the PE bands in Fig. 3 will be relatively straightforward.

The first band at 11.39 eV (Fig. 3) exhibits a narrow Frank-Condon profile in agreement with its assignment as a non-bonding orbital high symmetry molecule, and the ionization potential is higher than those of HN_3 (10.72 eV) [25] and $SO(N_3)_2$ (10.18 eV) [9a]. As we know, the first ionization energies of HN_3 (10.72 eV) [25] and CH_3NO_2 (11.29 eV) [11] are assigned to the non-bonding orbitals with $\pi_{nb(N–N–N)}$ and $\pi_{nb(O–N–O)}$ characters, respectively. Since the bonding orbitals (π_b) in both moieties are delocalized all over the three atoms, whereas the non-bonding orbitals (π_{nb}) have a nodal plane at the central atom, perpendicular to the frame of the moiety. Then, the π_{nb} orbital is primarily localized on the two outer atoms, which for ONO is the two more electronegative oxygen atoms leading to a higher ionization potential in comparison to the orbital embodying $\pi_{nb(N–N–N)}$ character. So, this band with high intensity can be easily assigned to the ionization of the HOMO (4a″) electron on the azido group with primary $\pi_{nb(N4–N5–N6)}$ character, as is shown in Fig. 4.

The second broad band at 12.52 eV with apparent vibration spacing of $1600 \pm 60\ \mathrm{cm^{-1}}$ (Fig. 3a) is designated to the result of ionizing an electron on the second HOMO (SHMO) 3a″(21) of the N_4O_2 molecule, not only owing to the fact that its value is close to computed value of

Table 4
Computed vibrational frequencies ($\mathrm{cm^{-1}}$) of the chain and cyclic isomers of N_4O_2, respectively

Mode	Chain			Cyclic	
	Calcd.[a,b]	Exptl[c]	Assignment	Calcd.[a]	Assignment
ν_1	2237 (320)	2107 (8)	ν_{as}N4N5N6	1738 (512)	νO3N2
ν_2	1689 (428)	1556 (2)	ν_{as}O1N2O3	1378 (6)	ν_sN5N6
ν_3	1320 (211)	1151 (3)	ν_sO1N2O3	1194 (60)	δN_4O_2
ν_4	1173 (313)	1060 (10)	ν_sN4N5N6	1054 (16)	δ_sO1N6N5
ν_5	837 (238)	758 (8)	δN_4O_2	1033 (40)	ν_sN4N5
ν_6	773 (0.8)		δN_4O_2	980 (10)	δN_4O_2
ν_7	736 (11)	605 (3)	γN_4O_2	809 (24)	δN_4O_2
ν_8	530 (6)	485 (7)	δN_4O_2	687 (0.8)	γN_4O_2
ν_9	512 (16)		δN_4O_2	646 (2)	γN_4O_2
ν_{10}	440 (49)	398 (2)	γN_4O_2	543 (7)	δN_4O_2
ν_{11}	189 (0.9)			308 (2)	
ν_{12}	100 (0.01)			270 (25)	

[a] Calculated at B3LYP/6-311+G(d) level.
[b] Intensities in parentheses.
[c] Raman data taken from Ref. [5b].

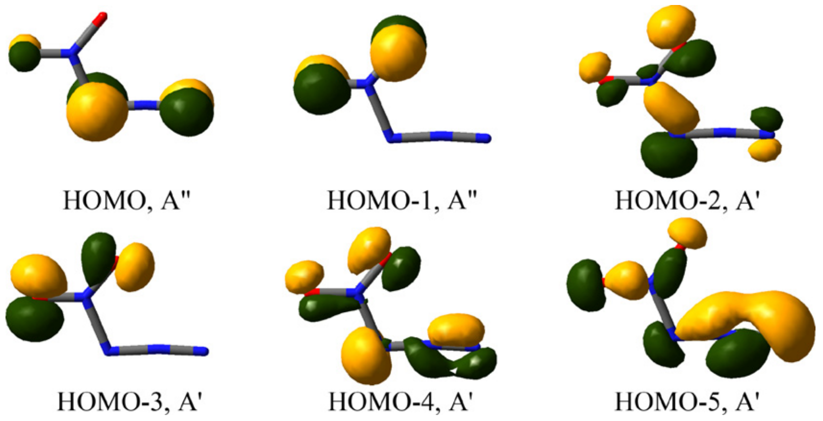

Fig. 4. Selected molecular orbitals of N_4O_2.

12.12 eV, but also the vibration spacing $1600 \pm 60\ cm^{-1}$ on this band is in well agreement with the calculated asymmetric stretching (ν_{as}O1N2O3) vibrational frequency $1689\ cm^{-1}$ (B3LYP/6-311+G(d)) of nitro group, this value is very close to the experimentally determined $1556\ cm^{-1}$ (Raman), reported by Klapötke et al. [5b]. With the aid of molecular orbital analysis (Fig. 4), this band is the ionization result of a π non-bonding electron mainly localized on the NO_2 group, similar to the first ionization process of CH_3NO_2 (11.29 eV) [11].

The third band, ranging from 12.90 to 13.70 eV can be tentatively assigned to the ionization of electrons of both 18a′ and 17a′ orbitals according to the OVGF calculations and molecular orbital analysis (Fig. 4); the remaining bands at 14.52 and 16.65 eV should be the results of ionization of electrons of deeper orbitals in N_4O_2, which could hardly be accurately assigned.

4. Conclusion

In summary, novel unstable compound N_4O_2 has been prepared by heterogeneous reaction of $ClNO_2$ with AgN_3 at −50 °C at low pressure (10^{-4} torr). The geometric and electronic structure has been characterized by *in situ* photoelectron spectroscopy (PES) and quantum chemical calculations. It is a planar chain molecule with C_s symmetry in the gas phase, the first vertical ionization energy is experimentally determined to be 11.39 eV, in well agreement with the OVGF calculated 11.19 eV, corresponding to the ionization of the electron on the highest occupied molecular orbital (HOMO) 4a″, with dominant character of $\pi_{nb(N4–N5–N6)}$ on the N_3 moiety. A apparent vibrational spacing of $1600 \pm 60\ cm^{-1}$ (ν_{as}O1N2O3) on the second band at 12.52 eV ($\pi_{nb(O1–N2–O3)}$) further confirms the preference of chain structure. At −30 °C this novel oxide of nitrogen decomposes completely into N_2O. By potential-energy surface analysis, the cyclic isomer C_s–ONONNN is less stable than the experimentally observed C_s-nitryl azide: $O_2N–N_3$, the former is just $5.8\ kcal\ mol^{-1}$ lower in energy than the transition state leading to decomposition products $2N_2O$, which precludes the attempt to isolate the cyclic isomer. Meanwhile, a five-membered ring decomposition pathway is more favorable, and it is accompanied by an energy release of $50.0\ kcal\ mol^{-1}$.

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