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On the $N_3O_2^-$ paradigm

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Dedicated to Lucjan Sobczyk on the occasion of his 80th birthday.

Abstract

A survey of the existing experimental and theoretical data on the trinitrogen dioxide anion $N_3O_2^-$ that manifests a controversy as to the number of isomers and their chemical structures is presented. To resolve the controversy, new computational studies are performed at the MP2/aug-cc-pVTZ computational level. Two hitherto unknown isomers are predicted, one with singlet and one with triplet spin multiplicity. The singlet isomer, structurally characterized as $N_2 \cdot [ONO]^-$, is the most stable among all known isomers and accounts for fragmentation patterns observed in the recent dissociative photodetachment experiments.

Keywords: $N_3O_2^-$; Theoretical calculations; Isomers; Electron detachment

1. Short introduction to the $N_3O_2^-$ paradigm

Writing on the special occasion is always a welcomed and pleasant work since it allows to explore some more unusual ideas, thoughts, and concepts that may not be fully appropriate for the standard mode of scientific paper. Some such speculative notions are perfectly suitable for the Festschrift publication and the authors do not necessarily need to worry of being carried away too far on their, if any, wings of imagination.

In the present work, we intend to take the full advantage of the aforementioned authors' freedom that any Festschrift kindly offers and address the topic that we have been thinking for quite some time on and off. We can only hope that Lucjan Sobczyk, whose 80th birthday this Festschrift is honorably dedicated to, will not be so displeased with our contribution. Bearing in mind this apology, we will now begin to expose our thoughts about the extremely simple, on one hand, and on the other, quite mysterious molecule that the trinitrogen dioxide anion $N_3O_2^-$ was and still is for those researchers who "touched" it at least once.

For the authors, the first impression was that this molecule is likely paradigmatic from its very beginning. The paradigm begins with the very name, "dinitrosoamide", which has sometimes been used in the literature (see Note 1 hereafter referred to as {1}). Let us now simply decompose its chemical formula in the most natural way, viz., in nitric oxide (NO) and nitrous oxide (N_2O), which are both well known as playing significant roles in the chemistry of the atmosphere, and the electron. Leaving the latter aside, we have the neutral trinitrogen dioxide molecule that is however thermodynamically unstable with respect to (w.r.t.) the dissociation limit composed of the former two by 1.17 eV [1]. The mysteries with $N_3O_2^-$ are pursued if we pose another simple question: where precisely is the excess electron located? Since the neutral parent is unstable w.r.t. the aforementioned asymptote, this question is quite meaningless unless the electron detachment fragmentation route accomodates the metastable (kinetically stable) state with a finite lifetime. It seems that this is not the case [2]. Thus, the stability of N_3 O_2^- is merely a matter of a

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three-body problem that is quite reluctantly separable in any two-body subproblems for the reason that both NO and N_2O are characterized by low electron affinities (EAs).

The nitric oxide anion NO^- has a triplet ground state like the isoelectronic oxygen molecule (see {2} and {3}). The experimental adiabatic electron affinity is $EA_a^{expt}(NO) = 0.026 \pm 0.005$ eV [3]. Actually, NO^- is classically unbound, and only the zero-point energy effects are responsible for its small and positive electron affinity [4] (see also {4}). The $EA_a(N_2O) \approx +0$ and arises according to the mechanism for the dissociative electron attachment process that involves the higher-energy cyclic isomer of N_2O and results in the cyclic anionic structure which is more stable than the bent-shaped isomer [8,9]. For this reason we may think that in some sense the $N_3O_2^-$ molecule crudely resembles a so called Efimov state [10]. Despite the low electron affinities of its constituent molecules, the trinitrogen dioxide anion was experimentally observed and it does therefore exist. With the present work we wish to contribute to an understanding of the immensely complicated picture of this anion that emerges from the experiments.

2. Experimental puzzles

What do the experiments tell us about the trinitrogen dioxide anion? $N_3O_2^-$ was first observed nearly forty years ago by Moruzzi and Dakin [11] who conjectured its appearance as the intermediate state in the reaction of NO^- with N_2O having the lifetime of 4×10^{-7} s. Four years later, Parkes [12] observed $N_3O_2^-$ as the product of the same reaction 'buffered' either by CO_2, or Ar, or another N_2O molecule:

$$NO^- + N_2O + M \rightarrow N_3O_2^- + M, M = CO_2, N_2O, Ar \quad (1)$$

The latter two reactions were further examined by Viggiano and co-workers [13] and Ferguson and co-workers [14]. Hayakawa et al. [15] studied the reaction (1) with $M = N_2O$

In the middle of the eighties, upon conducting the negative ion photoelectron (dissociative photodetachment) spectroscopy (DPS) experiments of N_2O^-, $(N_2O)_2^-$ and $N_3O_2^-$, Bowen and co-workers [16,17] (see also their recent work [18] and the review [19] by Chacko and Wenthold) concluded that the trinitrogen dioxide anion admits several isomeric forms. Before focusing on the latter issue that in fact, as we believe, leads to resolving the $N_3O_2^-$ paradigm, let us mention that the DPS can provide some insight into the structural and energetics motifs of a molecular anion and the dissociative states of the corresponding neutral species. The DPS is carried out by crossing a mass-selected beam of negative ions, which are somehow initially prepared, mainly in a mixture state, with a fixed-frequency photon beam and by analyzing the energy of the resultant photodetached electrons. Subtracting the center-of-mass electron kinetic energy of the revealed spectral feature from the photon energy yields the transition energy (or the bond dissociation energy ΔE) from the state of the negative ion to the energetically accessible state of the related neutral molecule. Two experimental regimes of the DPS are distinguished depending on whether a removal of the electron causes a substantial or small structural relaxation. In the former regime, the photodetached electron promotes the resultant neutral molecule to a strongly repulsive portion of the potential energy surface (PES) where it undergoes a direct fragmentation typically characterized by a large release of translational energy E_T and an unstructured photoelectron spectrum (PS). In the latter, the neutral molecule accesses a weakly repulsive portion of the PES that is accompanied by a small release of E_T and yields a structured PS.

The dynamics of $N_3O_2^-$ in the DPS experiments [16–18,20] has revealed both regimes, which straightforwardly implies the existence of at least two distinguishably different isomers: one being structurally similar to $NO^- \cdots N_2O$, since $EA(NO) > EA(N_2O)$ {5}, and another being significantly different. In these experiments, the PS of $N_3O_2^-$ was recorded at 514 nm (2.54 eV) [17], and at 532 nm (2.33 eV), 3.55 nm (3.49 eV) and 266 nm (4.66 eV) [20]. The PS at 514 and 532 nm are very similar and exhibit the general pattern of free NO^- [21] broadened due to the NO^- to NO vibrational transitions from $v'' = 0$ to $v' = 0$–6 (see Table 1 of Ref. [17]) and observed with an apparent photodetachment onset at the electron bond energy ΔE of ~0.24–0.25 eV w.r.t. to the dissociation asymptote $NO + N_2O + e^-$. Subtracting the center-of-mass kinetic energy of 2.282 eV that corresponds to the center of the peak of the transition $NO^-(X^3\Sigma^-, v'' = 0) \rightarrow NO(X^2\Pi, v' = 0)$ from the photon energy of 2.540 eV yields $EA(NO) = 0.037$ eV (corrected to 0.044 eV in Ref. [18] that nicely corroborates the MP2/aug-cc-pVTZ value of EA(NO) given in {3}). Accounting for the rotational and spin-orbit effects, we finally obtain the $EA_a(NO) = 0.024$–0.026 eV [17,18] that is close to the foregoing $EA_a^{expt}(NO)$. Therefore, such PS originate from NO^- which is insignificantly perturbed by N_2O, or in the other words, from a weakly bound ion-dipole cluster $NO^-(N_2O)$. This observation supports the original interpretation by Bowen and co-workers [17] that the excess charge of this cluster largely resides on the NO^- and $NO^-(N_2O)$ can be viewed as the almost intact $^3NO^-$ core ion solvated and presumably stabilized by N_2O due to purely electrostatic $^3NO^-$–N_2O interaction. The bond dissociation energy of this ion-dipole cluster is estimated equal to ~0.22 eV.

Conclusion 1. There exist at least two isomeric forms of $N_3O_2^-$. One of them is a weakly bound ion-dipole cluster $NO^-(N_2O)$ characterized by the bond dissociation energy of ~0.22 eV and its photodetachment fragmentation obeys the following reaction route

$$N_3O_2^- \rightarrow NO^- + N_2O \quad (2)$$

The structure of the other isomer cannot be deduced from this spectral feature.

Another PS of $N_3O_2^-$ recorded at 355 nm (3.49 eV) by Continetti and co-workers [20] is quite similar to that at 532 nm and corroborates the solvated NO^- interpretation given by Bowen and co-workers [17]. However, the 532-nm and 355-nm spectra reveal the high-E_T peaks, viz., at 0.7 and 0.9 eV, respectively, which are significantly different from each other. If at 532 nm the high-E_T channel is weak with negligible E_T probability distribution $P(E_T)$ at $E_T > 1.0$ eV that implies the existence of a minor isomer with the maximum bond dissociation energy of ca. 1.3 eV, at 355 nm the high-E_T limit moves to $E_T \approx 1.5$ eV. For a photon energy of 3.49 eV, the difference between these two values is ~2.0 eV.

In contrast to the former two, the third PS at 266 nm (4.66 eV) is markedly different and shows three key features indicated by A, B, and C in Fig. 2 of Ref. [20]. The feature A is characteristic to the isomer $NO^-(N_2O)$. The other two, viz., a large broad shoulder C at ~0.9 eV and a sharp peak and related shoulder (B) at 3.2 and 1.2 eV are novel. As concluded by Continetti and co-workers [20], the latter arises from the photodetachment of $O^- + \hbar\nu \rightarrow O(^3P)$, $O(^1D) + e^-$ that means that O^- is produced by photon absorption at 266 nm. Note that the channel with high photofragment translation energy release is not significant and its probability distribution extends beyond 2.0 eV. The peak B provides a clear evidence of the existence of the photodetachment channel that involves O^-.

Conclusion 2. An isomer of $N_3O_2^-$ exists that fragments via the following scenario

$$N_3O_2^- \rightarrow NO + N_2 + O^- \quad (3)$$

involving O^- as the product. It was postulated that the excess charge of this isomer is localized on the N_2O fragment [20]. Is this isomer precisely the second isomer suggested in Conclusion 1 or another one?

The feature C results in the observed maximum total E_T release of 2.7 eV. The difference between the photon energy of 4.66 eV and the latter value amounts to 2.0 ± 0.2 eV that was interpreted as the stability of $N_3O_2^-$ w.r.t. $NO + N_2O + e^-$ [20], and thus is the direct indication of the isomeric form of $N_3O_2^-$ different from the weakly bound ion-dipole cluster $NO^-(N_2O)$ (recall Conclusion 1). It was suggested that the feature C indicates the stability of the covalently bound isomer of $N_3O_2^-$ under the following assumptions [20]: (i) the $NO + N_2O$ products are formed without internal excitation; (ii) $N_3O_2^-$ is initially cold. Is the latter assumption a direct consequence of what the initially prepared state of the mass-selected beam of $N_3O_2^-$ is?

Conclusion 3. There exists a covalent isomer of $N_3O_2^-$ which is characterized by the bond dissociation energy of 2.0 ± 0.2 eV. Whether its photodetachment follows the following decomposition channel

$$N_3O_2^- \rightarrow NO + N_2O^- \quad (4)$$

that assumes the localization of the excess electron on the N_2O moiety is still an open question {6}. Another solid evidence of the existence of the $N_3O_2^-$ isomer distinct from $NO^-(N_2O)$ was demonstrated by Hayakawa et al. [15] for the reaction (1) in an $M = N_2O$ buffer at atmospheric pressure and temperature range from 300 to 500 K. At such conditions, the Gibbs free energy difference ΔG of the reaction (1) is always negative and the enthalpy of formation (or the bond enthalpy) indicates that this isomer is significantly stronger bonded as compared to $NO^-(N_2O)$. Hiraoka et al. [23] suggested that the bond dissociation energy of a covalently bound isomer amounts to at least 0.4 eV.

In their collision-induced dissociation experiments, Torchia et al. [22] estimated the bond energy of $N_3O_2^-$ as equal to 0.76 ± 0.10 eV and observed the three reaction routes (2)–(4). However, they found a certain disagreement with the DPS experiments by Continetti and co-workers [20] and concluded that there are two main reasons of such disagreement: (i) their covalently bound isomer of $N_3O_2^-$ differs from the strongly bound one observed in Ref. [20] and even "may not be apparent in the present experimental data, since it may have a small cross section for the dissociation without electron photodetachment"; (ii) "essentially none of the dissociative photodetachment products are formed vibrationally cold". Summarizing, we arrive at

Conclusion 4. There exist at least four isomeric forms of $N_3O_2^-$: a weakly bound ion-dipole cluster $NO^-(N_2O)$, two covalently bound isomers, and one isomer that produces O^-.

In other words: $N_3O_2^-$ is a pretty bizarre molecule with a plethora of isomers!

3. Experiment–theory controversy

The rather vague and perplexing picture which has emerged from the experiments and which we have to admit as the truth, that such a simple molecule as $N_3O_2^-$ might possess so many isomeric forms, has generated a long-standing controversy between experiment and theory. Paradoxically, the theoretical studies which were mostly conducted by Hiraoka et al. [23] in 1994 and Torchia et al. [22] in 1999, only partially concurred with the experimental Conclusions 1–4 on the existence of a weakly bound ion–dipole cluster $NO^-(N_2O)$ and a single covalently bound $N_3O_2^-$ isomer, and did not predict its other isomeric forms. The summary of these studies are presented in Fig. 1 and Table 1.

The agreement between the theoretical bond energy $\Delta E^{theor}(^3NO^-(N_2O))$ calculated at the MP2/6-31+G(d)//R(O)HF/6-31+G [23] and the DPS experimental one obtained from the PS of $N_3O_2^-$ recorded at 514 nm (2.54 eV) [17] and at 532 nm (2.33 eV) [20] is seeming because the mentioned computational level poorly

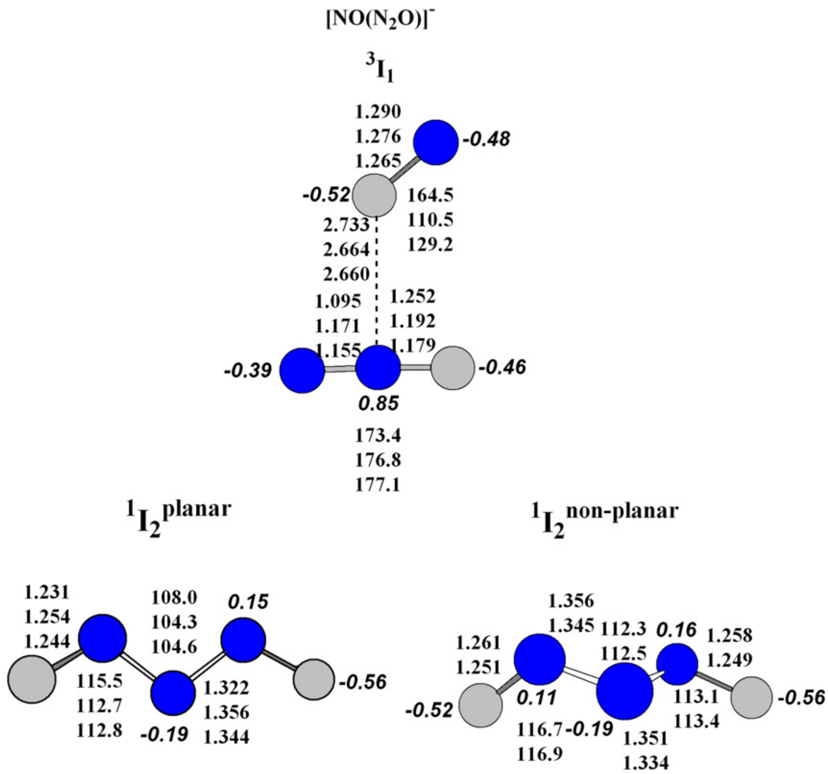

Fig. 1. The MP2/aug-cc-pVTZ T structures of the $N_3O_2^-$: $^3I_1$, $^1I_2^{planar}$, and $^1I_2^{non\text{-}planar}$. Bond lengths are given in Å and bond angles in °: the upper entry corresponds to the MP2/6-31+G(d)//R(O)HF/6-31+G [23], the middle to the MP2/aug-cc-pVDZ [22], and the lower to the MP2/aug-cc-pVTZ computational level invoked in the present work. The last two levels are only applied to $^1I_2^{non\text{-}planar}$. The nitrogen and oxygen atoms are represented by dark and light circles, respectively. The corresponding Mulliken charges are indicated in italics.

Table 1
The bond dissociation energies ΔE (in eV) of the $N_3O_2^-$ isomers

Isomer	MP2/6-31+G(d)//R(O)HF/6-31+G [23]	MP2/aug-cc-pVDZ [22]	B3LYP/6-311+G(d) [2]	Experiment
$^3NO^-(N_2O)$				0.22 [17], 0.21 ± 0.04 [15]
Planar	0.21	0.139		
Non-planar		0.143		
$^1N_3O_2^-$				2.0 ± 0.2 [20], 0.76 ± 0.10 [22]
Planar	1.25	0.876	1.5[a], 1.45[b]	
Non-planar		0.497		

Among them are considered the weakly bound ion-dipole triplet-state cluster $^3NO^-(N_2O)$ and w-shaped singlet-state cluster $^1N_3O_2^-$. Both admit the planar and non-planar forms. The planar isomer of the former one is denoted hereafter as the isomers $^3I_1$, and the isomers of the latter by $^1I_2^{planar}$, and $^1I_2^{non\text{-}planar}$, respectively. Their structures are displayed in Fig. 1. The superscripts [a] and [b] indicate the ZPE-uncorrected and ZPE-corrected bond dissociation energies, respectively.

describes the structure of the weakly bound isomer $^3NO^-(N_2O)$ (cf. its geometry with the MP2/aug-cc-pVDZ one in Fig. 1). On the other hand, the MP2/aug-cc-pVDZ underestimates $\Delta E^{expt}(^3NO^-(N_2O))$ by ca. 37%. A more substantial underestimation (∼56%) is obtained, at this computational level, for the planar w-shaped covalently bound isomer $^1N_3O_2^-$ [22]. We are impressed by the much better agreement that B3LYP/6-311+G(d) offers [2] and wonder why it largely diverges from the former.

Theoretical impasse? Not actually, though after the works [23,22], what else can we tell the readers from a theoretical point of view? In our naïve endeavor of putting "all ends together" towards a better agreement between experiment and theory, we have performed a rather exhaustive search of the PES of $N_3O_2^-$, and the results of this search and our way of thinking developed in the present work to explain the experiments are presented in the next Section for the readers' consideration.

4. Toward resolving the $N_3O_2^-$ paradigm: some clues

As promised in the Introduction, we now engage in some speculations regarding the existence of additional isomers of $N_3O_2^-$ which are postulated experimentally in Conclusions 2–4:

Speculation 1. Consider the weakly bound isomer $^3I_1$ $NO^-(N_2O)$. It is largely stabilized by pure electrostatic interaction of the polarized NO^- ion with the N_2O molecule where the ion is directed through the oxygen atom to the latter unit. Since in isolated NO^- the negative charge is nearly equally (~45% vs. ~55%) distributed over the N and O atoms, respectively, let us suggest another isomer, precisely the rotamer of $^3I_1$, where NO^- is directed towards N_2O via the nitrogen.

Speculation 2. As noticed in the introduction, the mechanism for the dissociative electron attachment process that determines $EA_a(N_2O) \approx +0$ involves the higher-energy cyclic isomer of N_2O and leads to the cyclic anionic structure which is more stable than the obsolete bent-shaped isomer [8]. Interacting with NO, this cyclic anion N_2O^- may form a molecular anion with a quite specific structure.

The MP2/aug-cc-pVTZ computational proof of the above speculations is provided in Table 2 and Fig. 2. Altogether, we now have five isomers of $N_3O_2^-$, two triplets and three singlets, which are likely pretty good candidates for explaining the experiments surveyed in Section 2. The key properties of all those isomers which can be used for their experimental "fingerprinting" are collected in Table 2. It is anticipated that the two triplet-state isomers $^3I_1$ and $^3I_3$, both mapping the weakly bound cluster $NO^-(N_2O)$, are nearly isoenergetic – precisely, the latter is slightly more stable by 0.012 eV, and exhibit very similar properties (vide Table 2). As pointed out in Figs. 1 and 2, the excess charge of these two isomers is fully localized on the NO^- unit that remains largely preserved upon interacting with N_2O: cf. the data in {2} with the R(N–O) = 1.265 and 1.262 Å, and ν(N–O) = 1431 cm^{-1} (116 km mol^{-1}) and 1445 cm^{-1} (106 km mol^{-1}) of Table 2. We suggest that these two isomers both contribute to the subtle patterns of the PS which are experimentally recorded at 514 nm (2.54 eV) [17] and at 532 nm (2.33 eV) [20], and fragment according to Eq. (2).

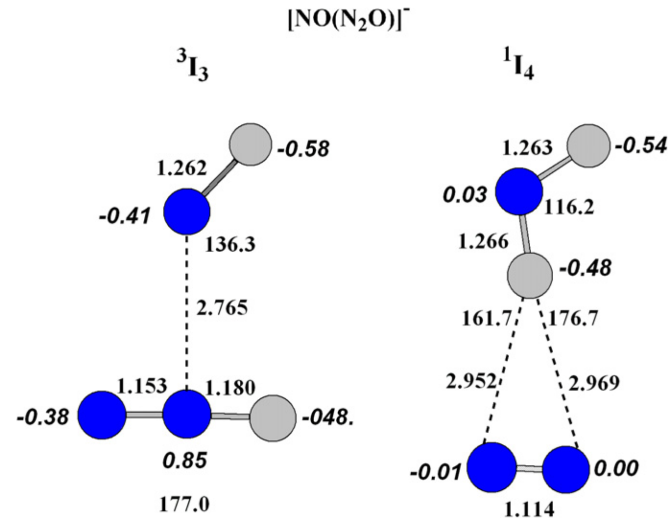

Fig. 2. The novel MP2/aug-cc-pVTZ structures of $N_3O_2^-$: $^3I_3$ and $^1I_4$. For the notation, we refer to the legend of Fig. 1.

The isomers $^1I_2^{planar}$ and $^1I_2^{non\text{-}planar}$ mapping the covalently bound structure $[ONNNO]^-$ of $N_3O_2^-$ are stabilized by charge delocalization via the bond formation. The excess charge is located on the two terminal oxygen atoms. The planar isomer is essentially stronger bound than the non-planar.

The last isomer $^1I_4$ is quite specific in all meanings. It is formed between the most stable cyclic anion N_2O^- [8] and NO through the strong $O^{-\delta}$–NO bond that can be interpreted as the NO_2^- unit and characterized by the large bond

Table 2
Key features of the isomeric forms of $N_3O_2^-$ studied in the present work at the MP2/aug-cc-pVTZ computational level: rotational constants (in GHz), vibrational frequencies (in cm^{-1}), IR intensities (in km mol^{-1}, in parentheses), the enthalpy of formation, ΔH_f, the ZPE-corrected bond dissociation energy, ΔE, (both in eV), and the entropy difference, ΔS (in cal mol^{-1} T^{-1})

Features	$^3I_1$	$^1I_2^{planar}$	$^1I_2^{non\text{-}planar}$	$^3I_3$	$^1I_4$
Rotational constants	11.4091	60.2297	22.9632	11.5173	30.3580
	2.7967	2.8205	3.6124	2.4923	1.6367
	2.2461	2.6943	3.1742	2.0489	1.5529
Frequencies	47 (~1)	199 (~1)	196 (8)	37 (~1)	14 (~0)
	51 (8)	332 (~1)	320 (5)	68 (6)	37 (~1)
	131 (16)	347 (0)	359 (64)	128 (24)	38 (~2)
	146 (5)	609 (~0)	605 (2)	173 (7)	86 (11)
	544 (16)	761 (137)	853 (~1)	534 (19)	95 (~0)
	587 (2)	1146 (838)	1105 (242)	587 (2)	797 (~2)
	1331 (23)	1259 (4)	1140 (744)	1293 (13)	305 (11)
	1431 (116)	1431 (725)	1384 (252)	1445 (106)	1363 (738)
	2298 (323)	1502 (3)	1444 (224)	2238 (332)	2182 (~1)
ΔH_f	0.252	1.046	0.673	0.259	3.755
ΔE	0.292	0.887	0.515	0.304	3.656
ΔS	−18.2	−33.3	−32.8	−18.4	−11.2

The latter three are taken w.r.t. to the dissociation asymptote $NO + N_2O + e^-$.

dissociation energy of ca. 3.7 eV. The excess charge of this isomer fully resides on the NO_2^-. By all features, this isomer $N_2 \cdot [ONO]^-$ contributes to the PS recorded at 266 nm (4.66 eV) [20] and fragments via Eq. (3).

5. Résumé

First of all, we think that the problem posed in this work to resolve the paradoxical situation with the trinitrogen dioxide anion $N_3O_2^-$ that has emerged from the experimental and early theoretical studies is rather a worth scientific problem than a "gardening" on its intricate PES. In particular, we have explored a quite rich physics that lies behind the mechanism of the dissociative electron attachment to the N_2O molecule and demonstrated that it is indeed the most stable cyclic anion N_2O^- that, while interacting with NO, yields the most stable isomer $N_2 \cdot [ONO]^-$ of $N_3O_2^-$.

Actually, the present work is aimed to study the monosolvation of NO^- "dissolved" into the nitrous oxide solvent which has been of the longstanding interest as itself. What we have shown is the striking existence of the additional "restructive–destructive" solvation scenarios that lead to the covalently bound cluster $[ONNNO]^-$ and to a novel cluster $N_2 \cdot [ONO]^-$, how these clusters accomodate the excess negative charge and how they can be experimentally identified.

Another important observation for us is that the weakly bound isomer $NO^-(N_2O)$ admits two rotamers, one where the oxygen atom as the more favorable site for nesting the excess charge of NO interacts with N_2O and the other, new rotamer with a flipped NO unit w.r.t. N_2O. We will leave aside (actually, that is a quite big "aside") the question of how all these isomers $^3I_1$, $^3I_3$, and $^1I_4$ are formed in a mixture state of a mass-selected beam of negative ions initially prepared in the discussed experiments {7} and hope to return to it in the forthcoming work.

6. Notes

1. In the literature, $N_3O_2^-$ is sometimes referred to as "dinitrosoamide anion" which is however quite misleading. A dinitrosoamide would have the structure R–$N(NO)_2$ where R might be hydrogen or some organic rest. The complexes like $N_2O \cdot NO^-$ or $N_2 \cdot NO_2^-$ that will be addressed in the present work are certainly not amides. A more appropriate designation would be "trinitrogen dioxide anion".
2. All computations, framing the present work, were performed within the second-order Møller-Plesset perturbation method (MP2) [5] with a frozen-core approximation using the GAUSSIAN 03 package of programs [6]. The Dunning's correlation consistent polarized valence basis set of triple-zeta quality cc-pVTZ [7] was employed. The analytical harmonic vibrational frequencies were calculated in order to distinguish whether the stationary structures belong to the energy minima or to saddle points and kept unscaled together with the corresponding zero-point energies (ZPE). Thermodynamic quantities, enthalpies and entropies, were evaluated from the partition functions at the temperature of 298.15 K and the pressure of 1 atm, using Boltzmann thermostatistics and the rigid-rotor-harmonic-oscillator approximation.
3. At the MP2/aug-cc-pVTZ computational level, the triplet ground state $^3NO^-(X^3\Sigma^-)$, characterized by the bond length R(N–O) = 1.265 Å (R^{expt}(N–O) = 1.258 Å [21], 1.267 Å [24]) and the stretching vibrational frequency ν(N–O) = 1423 cm^{-1} (123 km mol^{-1}), differs from the lowest singlet-state $^1NO^-$, with R(N–O) = 1.254 Å and the stretching vibrational frequency ν(N–O) = 1394 cm^{-1} (143 km mol^{-1}), by 1.18 eV.
4. The MP2/aug-cc-pVTZ difference in energy between the ground state of $NO(^2\Pi)$ and $^3NO^-$ amounts to −0.0707 eV without the ZPE correction and 0.048 eV with the ZPE correction. The latter value is the MP2/aug-cc-pVTZ estimate of EA_a(NO).
5. All the ambiguities with the EA(N_2O) have recently been resolved in Ref. [8].
6. Note that there is not any direct evidence that this isomer of $N_3O_2^-$ should be referred to as a covalently bound. What is known from the DPS experiments is that there exists a regime where the photodetached electron causes a significant structural relaxation.
7. The conditions of the DPS experiments were discussed by Hiraoka et al. [23] in Concluding Remarks with relation to the existence of the $[ONNNO]^-$ isomer. It is also worth mentioning the large entropy effect for the reported isomers of $N_3O_2^-$ (see Table 2) that was already pointed out for $^3I_1$ in Ref. [23].

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References

[1] I. Pápai, A. Stirling, Chem. Phys. Lett. 253 (1996) 196.
[2] A. Snis, I. Panas, Chem. Phys. Lett. 305 (1999) 285.
[3] M.J. Travers, D.C. Cowles, G.B. Ellison, Chem. Phys. Lett. 164 (1989) 449.
[4] M.C. McCarthy, J.W.R. Allington, K.S. Griffith, Chem. Phys. Lett. 289 (1998) 156.
[5] C. Møller, M.S. Plesset, Phys. Rev. 46 (1934) 618.
[6] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa,

M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision A.1, Gaussian Inc., Pittsburgh, PA, 2003.

[7] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. 96 (1992) 6796.

[8] E.S. Kryachko, C. Vinckier, M.T. Nguyen, J. Chem. Phys. 114 (2001) 7911.

[9] O. Tishchenko, E.S. Kryachko, M.T. Nguyen, in: E.J. Brändas, E.S. Kryachko (Eds.), Fundamental World of Quantum Chemistry: A Tribute Volume to the Memory of Per-Olov Löwdin, vol. 2, Kluwer, Dordrecht, 2003, pp. 393–423.

[10] V. Efimov, Phys. Lett. 33 B (1970) 563.

[11] J.L. Moruzzi, J.T. Dakin, J. Chem. Phys. 49 (1968) 5000.

[12] D.A. Parkes, J. Chem. Soc. Faraday Trans. I 68 (1972) 2103–2121.

[13] A.A. Viggiano, R.A. Morris, J.F. Paulson, J. Phys. Chem. 94 (1990) 3286.

[14] R. Marx, G. Mauclaire, F.C. Fehsenfeld, D.B. Dunkin, E.E. Ferguson, J. Chem. Phys. 58 (1973) 3267.

[15] S. Hayakawa, A. Matsumoto, M. Yoshioka, S. Matsuoka, T. Sugiura, Mass Spectrosc. (Tokyo) 34 (1986) 147.

[16] J.V. Coe, J.T. Snodgrass, C.B. Friedhoff, K.M. McHugh, K.H. Bowen, Chem. Phys. Lett. 124 (1986) 274.

[17] J.V. Coe, J.T. Snodgrass, C.B. Friedhoff, K.M. McHugh, K.H. Bowen, J. Chem. Phys. 87 (1987) 4302.

[18] J.H. Hendricks, H.L. de Clercq, C.B. Freidhoff, S.T. Arnold, J.G. Eaton, C. Fancher, S.A. Lyapustina, J.T. Snodgrass, K.H. Bowen, J. Chem. Phys. 116 (2002) 7926.

[19] S.A. Chacko, P.G. Wenthold, Mass Spectrom. Rev. 25 (2006) 112.

[20] M. Sowa Resat, V. Zengin, M.C. Garner, R.E. Continetti, J. Phys. Chem. A 102 (1998) 1719.

[21] M.W. Siegel, R.J. Celotta, J.L. Hall, J. Levine, R.A. Bennett, Phys. Rev. A 6 (1972) 607.

[22] J.W. Torchia, K.O. Sullivan, L.S. Sunderlin, J. Phys. Chem. A 103 (1999) 11109.

[23] K. Hiraoka, S. Fujimaki, A. Kazuo, S. Yamabe, J. Phys. Chem. 98 (1994) 8295.

[24] D. Teillet-Billy, F. Fiquet-Fayard, J. Phys. B 10 (1977) L111.