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ARTICLE TYPE

Is HO_3^- multiple-minimum and floppy? Covalent to van der Waals isomerization and bond rupture of a peculiar anion

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The singlet ground-state of the HO_3^- anion is studied with high level single- and multi-reference methods, and a scheme coined as Complete-Active-Space-Dynamical-Correlation which has been previously used to study the neutral HO_3 radical. It is found to have a planar *cis* isomeric structure with a long intermediate OO bond (≈ 1.75 Å) as it is now consensual in the literature. It has also a pyramidal-type branch-isomer, but its minimum lies ≈ 33 kcal mol^{-1} above the *cis* minimum. Interestingly, another isomer is here predicted with a planar geometry that can be even more stable than *cis*-HO_3^- at some levels of theory. It shows a hydrogen-bond (van der Waals) type structure, with an intermediate OO bond of ≈ 2.59 Å. All such minima lie on the lowest adiabatic potential energy surface, with the two lowest planar ones (*cis* and vdW) connected by a saddle point whose structure, also planar, is unveiled. All these lie on the first third of the optimum path for bond-rupture in $[HO - OO]^-$, which is predicted to yield ground state HO plus O_2^-, an asymptote lying 30 kcal mol^{-1} above the *cis*-HO_3^- minimum. Unprecedented in the literature of the key title anion, such features should bear strong implications on its preparation, spectroscopy, and role in chemistry.

1 Introduction

The neutral hydrogen trioxide radical (HO_3), its cation (HO_3^+), and its anion (HO_3^-) have all received substantial attention both experimentally[1–12] and theoretically,[2,5,6,8,9,11–41] with the former counting more than 100 ISI entries some even prior to experimental verification. Recent reviews on odd hydrogen[42] (species containg oxygen atoms but a single hydrogen atom) and hydrogen trioxide[43] (H_2O_3, of which the title anion is the conjugate base) are also available, where the reader may find further references through cross-referencing. The above interest may not be surprising since such species have been postulated to play important roles in air pollution and purification and treatment of water by ozone, in addition to other areas of environmental chemistry. They are also important in preparative organic chemistry, with trioxide anions such as HO_3^- or RO_3^- (R is an organic functional group) often invoked as key intermediates in mechanistic explanations of ozonation reactions.[44,45] Despite the fact that the neutral radical has been significantly studied, much less attention has been given to the HO_3^- anion.[5–7,14,21,29]

Regarding the title anion, most theoretical studies consider its ground singlet state,[5,14,21] although there has been a study[5] on its lowest triplet state. In fact, if HO_3^- is thought to be formed from a combination of $H(^2S)$ and O_3^- ($^2B_1$), both a singlet and a triplet state can result, with a similar reasoning applying if formed from $OH(^2\Pi)$ and O_2^- ($^2\Pi_g$). Note that the singlet and triplet states of HO_3^- are predicted to have rather different geometries and electronic structures: the former possesses a strong $O - OOH$ bond with some double bond char-

acter and a weakly covalent $OO - OH$ bond (which was considered at some stage[5] as the longest O-O bond ever found for a peroxide), while the triplet is predicted to have a weak stability of the van der Waals type.

The main difference between the singlet state of HO_3^- and the ground state of HO_3^+ (and even the ground state of the neutral radical) is the presence of a long O_bO_c bond[21] (1.883 Å or even[29] 1.713 Å) in $HO_aO_bO_c^-$ as compared to the same bond length in the cation[46] of 1.4 Å (or even to 1.650 Å in the neutral radical[37,39]). In the present work, we focus on the ground singlet state of HO_3^- whose signature has first been captured by Cacace and co-workers[1,7] using mass-spectroscopy. Thus, we extend previous work[35–37] on the neutral HO_3 radical to the title elusive anion.

2 Method

Geometries have first been optimized and frequencies calculated using the complete active space self-consistent field (CASSCF) method. Although all the electrons and orbitals were initially considered as active [*i.e.*, CASSCF(26, 16) or simply CAS(26, 16); the numbers specify the number of active electrons and orbitals], similar results were found to be obtained by considering the O 1s orbitals as closed. This is illustrated in Tables 1 and 2 where the properties of the *cis*-HO_3^- anion have been calculated with both approaches and Dunning's augmented correlated consistent triple-zeta basis set, aug-cc-pVXZ. Thus, a cheaper CASSCF(20,13) has been adopted except where explicitly indicated without sacrificing the accuracy. Basis sets of the cc-pVXZ and aug-cc-pVXZ Dunning's correlated consistent family, hereafter denoted for brevity as VXZ and AVXZ, were employed. Whenever vi-

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Table 1 Geometric and energetic properties of the HO_3^- anion at various levels of theory.[a]

Method/basis	E	ΔE[b]	$R_{O_bO_c}$	$R_{O_aO_b}$	$\angle O_aO_bO_c$	R_{O_aH}	$\angle O_bO_aH$
trans-HO_3^- (sp)							
CCSD(T)/AVTZ	−0.8397187	+3.3	1.3086	1.8615	111.75	0.9678	90.12
CCSD(T)/AVQZ[c]		+3.6	1.3014	1.8568	111.79	0.9650	90.17
CAS/VDZ	−0.0797649	+5.5	1.3380	1.8855	114.73	0.9797	84.32
CAS/AVTZ	−0.1715781	+4.4	1.3281	1.8519	113.00	0.9718	87.61
CAS/AVQZ	−0.1858551	+4.4	1.3240	1.8548	113.09	0.9702	87.48
MRCI/VDZ	−0.5014576	+8.0	1.3233	1.8910	114.89	0.9739	84.02
cis-HO_3^- (min)							
CCSD(T)/AVTZ	−0.8455274	0.0	1.3488	1.7241	106.95	0.9695	86.67
CCSD(T)/AVQZ[c]		0.0	1.3431	1.7125	106.89	0.9670	86.90
CAS/VDZ	−0.0894995	0.0	1.3666	1.8083	115.62	0.9794	81.11
CAS/VTZ	−0.1659818	0.0	1.3672	1.7495	106.05	0.9718	83.86
CAS(26,16)/AVTZ	−0.1794029	0.0	1.3758	1.7052	105.84	0.9730	86.10
CAS/AVTZ	−0.1792765	0.0	1.3756	1.7068	105.86	0.9730	86.05
CAS/AVQZ	−0.1934558	0.0	1.3655	1.7285	106.22	0.9711	85.58
MRCI/$6-311++G^{**}$[d]	−0.62795	0.0	1.341	1.761	108.8	0.958	88.5
MRCI/VDZ	−0.5151408	0.0	1.3466	1.8191	106.25	0.9735	80.43
MRCI/VTZ	−0.7279112	0.0	1.3482	1.7401	106.28	0.9652	83.56
MRCI/AVTZ[e]	−0.7588021	0.0	1.3481	1.7278	106.59	0.9672	85.58
CBS(T,Q)/CASDC[f]	−0.9137335	0.0		1.774			
CBS($Q,5$)/CASDC[f]	−0.9178568	0.0		1.753			
cis-vdW-HO_3^- (sp)							
CAS/VDZ	−0.0837772	+2.7	1.3720	2.3213	93.32	0.9824	49.54
CAS/VTZ	−0.1594146	+3.3	1.3612	2.3139	94.24	0.9742	49.96
CAS(26,16)/AVTZ	−0.1722225	+3.7	1.3577	2.3312	94.58	0.9746	50.12
CAS/AVTZ	−0.1721196	+3.7	1.3578	2.3310	94.59	0.9747	50.14
MRCI/VDZ	−0.5026930	+7.5	1.3596	2.3854	89.89	0.9825	42.15
MRCI/VTZ	−0.7180137	+5.7	1.3469	2.3883	90.10	0.9731	40.91
MRCI/AVTZ[c]	−0.7473642	+6.7	1.3440	2.4367	89.35	0.9748	39.09
CBS(T,Q)/CASDC[f]	−0.9008831	+7.5		2.451			
CBS($Q,5$)/CASDC[f]	−0.9044591	+7.9		2.461			
vdW-HO_3^- (min)							
CAS/VDZ	−0.0977018	−5.5	1.3720	2.6268	97.79	1.0078	1.50
CAS/VTZ	−0.1736456	−5.1	1.3666	2.6450	95.81	0.9949	1.99
CAS/AVTZ	−0.1857414	−4.3	1.3653	2.6635	96.87	0.9926	2.25
MRCI/VDZ	−0.5124046	+1.0	1.3598	2.5701	99.65	1.0351	0.92
MRCI/VTZ	−0.7265922	+0.1	1.3533	2.5698	96.80	1.0197	1.18
MRCI/AVTZ[e]	−0.7549444	+1.7	1.3526	2.5879	98.19	1.0170	1.51
CBS(T,Q)/CASDC[f]	−0.9077403	+3.0		2.601			
CBS($Q,5$)/CASDC[f]	−0.9109471	+3.6		2.583			
branch-HO_3^- (min)							
CCSD(T)/$6-311++G^{**}$[d]		+34	1.49	1.49	117.5	0.96	98.5
CCSD(T)/AVTZ[g]	−0.7927178	+33.1	1.4823	1.4823	116.66	0.9640	97.85
CAS/AVTZ[g]	−0.1327756	+29.2	1.4991	1.4991	115.89	0.9667	97.70

[a] Energies in hartree (added 225 E_h), distances in angstrom, angles in degrees. Except for the *trans* entry where the torsion angle is 180 deg, in all others it is 0 deg. Most numbers should be realistic up to the quoted figures. [b] Exothermicity corrected for the ZPE effect (in kcal mol^{-1}) with reference to *cis*-HO_3^-. [c] From Ref. [21] with geometry optimized assuming a planar *cis* structure; see paper for other estimates. [d] From Ref. [29] See paper for other estimates. [e] Converged down to MOLPRO's threshold value; vibrational frequencies to obtain ΔE considered at MRCI/VTZ level. [f] From MRCI/VXZ raw energies, including the Davidson correction. ΔE from vibrational frequencies at MRCI/VTZ level. [g] $O_aO_bO_c$ define the three oxygen atoms, with H attached to O_b. The dihedral angle is $\angle HO_bO_cO_a = 102.48$ deg.

able, optimizations have also been carried out using the single-reference coupled cluster method with single and double electron excitations plus perturbative triples, CCSD(T), mostly with the AVTZ basis. Optimizations have additionally been carried out with the multireference configuration interaction singles and doubles (MRCI) method. In all the expensive multireference calculations, core electrons were kept frozen in treating the electron correlation. All employed the internally contracted MRCI[47,48] method as implemented in the MOL-PRO suite of electronic structure programs,[49] with MOLDEN and locally written codes used to process graphically the calculated data.

The following are diatom+diatom dissociation processes that are allowed by the spin-spatial Wigner-Witmer correlation rules for the title anion:

$$HO_3^- \, (^1A') \rightarrow OH^- \, (X\,^1\Sigma^+) + O_2 \, (a\,^1\Delta_g) \qquad (1)$$

$$\rightarrow OH(X\,^2\Pi) + O_2^- \, (X\,^2\Pi_g) \qquad (2)$$
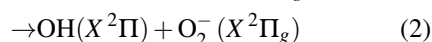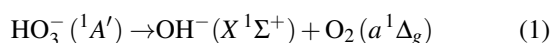
with OH$^-$ carrying the excess charge in channel (1), and O$_2^-$ in channel (2). Dissociation processes involving other types of fragmentation are possible, but knowledge from the neutral HO$_3$ radical suggests the above to lie lowest in energy. The energy for the asymptote in Eq. (2) has been estimated at the CCSD(T)//6-311++G-(2df,2pd)+ZPE level of theory[21] to lie approximately $+25\,kcal\,mol^{-1}$ above the energy of equilibrium HO$_3^-$. Because the $a\,^1\Delta_g$ state lies $22.64\,kcal\,mol^{-1}$ above the ground $^3\Sigma_g^-$ state[50,51] of O$_2$, the two channels may compete, despite the fact that channel (2) should be preferred since it correlates with both fragments in the ground electronic state. In fact, even though against common sense to some extent, the negative charge from the HO$_3^-$ breakdown will be shown to be carried out by the O$_2^-$ anion. Parenthetically, Miller[52] has attempted to produce the *cis*-HO$_3^-$ anion (see later) via reaction (1), hoping to elucidate the much debated dissociation energy of the neutral.[10,32,37] Unfortunately, despite the attempts[52] made to produce the *cis*-HO$_3^-$ anion using a variety of mixtures and combinations of precursor gases where the gas pulse is ionized by a beam of electrons and/or a pulsed electrical discharge or even improvements and modifications made to the anion source, the expected photoelectron spectrum could not match observation. As Miller states:[52] "The current photoelectron spectrum is presented, which is most likely not from *cis*-HO$_3^-$ but from another isomer". Can the present work help in offering a clue?

The first step in characterizing the title anion consisted of examining the known estimates available in the literature for the location of its minimum geometry. Exploratory calculations mostly at the CASSCF level of theory were then pursued using the VDZ basis set of Dunning's correlation consistent family,[53] and subsequently followed for quantitative accuracy with larger basis sets of the same type but augmented

with diffuse functions.[54] Thus, we treat the problem with basis sets similar to the largest used in previous work.[29] To explore regions away from equilibrium where bonds are broken or formed, the use of a multireference electronic structure approach reveals itself to be of crucial importance. Most calculations employed the MRCI method as noted above. Because these calculations are highy expensive, they will employ mostly the smaller VXZ basis, but the calculated raw energies energies are extrapolated to the complete-basis-set (CBS) limit[55,56] (and references therein). Previous work on the neutral has shown this to be a quite reliable methodology, and hence is here too adopted.[35–37] The results predict a *cis*-HO$_3^-$ minimum very much in agreement with previous work. In fact, a similar search for the *trans* attribute has shown it to be a saddle point, since it has a negative curvature for the motion that leaves planarity, thence in agreement with earlier work.[21] Thus, unlike the work by Mazziotti[29] (this is restricted to in-plane motion of the atoms) may eventually suggest, *trans*-HO$_3^-$ is not a stable species but a saddle-point structure that $3\,kcal\,mol^{-1}$ or so above *cis*-HO$_3^-$. Besides confirming such features, novel attributes have been found, as it will be described in the following.

The accurate prediction of a bond-breaking/bond-forming reaction course is not trivial. For this, we have recently suggested a cost-effective scheme comprising the following four-point premise:[36,37]

1. Bond-breaking/bond-forming reactions are best treated at MRCI level of theory, preferably when the Davidson correction (MRCI + Q) is added.

2. A convenient reference for MRCI is the full-valence-complete-active-space[57–59] (FVCAS) wave function, warranting a correct dissociation.

3. Such processes can be described by a single reactive coordinate (*e.g.*, O$_a$O$_b$ in HO$_3^-$).

4. Single-point MRCI + Q calculations of the optimized FV-CAS path should differ little from expensive directly optimized MRCI + Q ones.

where $+Q$ implies to have added the Davidson correction for quadruple excitations. The above scheme, referred to as CASDC[60] (the sum of the optimized CASSCF energy, CAS for brevity, plus the dynamical correlation calculated pointwise) can therefore be viewed as a generalization of the popular Hartree-Fock plus dispersion model for closed-shell interactions.[61–63] Thus, it is based on the largely untested idea of performing single point calculations with a high-level method at stationary points (or optimized paths) determined at a lower level of theory. To our knowledge, this will be first test of the CASDC model chemistry for any anion which, despite having

Table 2 Harmonic frequencies$^{a)}$ of the HO$_3^-$ anion at various levels of theory.$^{b)}$

Method/basis	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ZPE
trans-HO$_3^-$ (sp)							
CCSD(T)/AVTZ	228.4i	262.5	456.0	803.3	1133.8	3753.6	3204.7
CAS/VDZ	215.4i	260.5	494.6	843.5	1072.4	3575.3	3123.2
CAS/AVTZ	218.6i	261.6	483.9	862.6	1066.2	3643.0	3158.7
CAS/AVQZ	217.2i	263.3	485.5	861.4	1072.8	3655.9	3169.5
MRCI/VDZ	219.9i	262.0	498.2	810.2	1132.2	3692.0	3197.4
cis-HO$_3^-$ (min)							
CCSD(T)/AVTZ	151.8	173.8	465.0	952.8	1157.9	3717.9	3309.6
CAS/VDZ	244.8	336.8	455.4	900.8	1181.1	3582.2	3350.6
CAS/VTZ	211.3	293.7	443.9	923.0	1164.5	3641.4	3338.9
CAS(26,16)/AVTZ	156.1	272.0	458.9	894.7	1187.2	3632.6	3300.8
CAS/AVTZ	157.4	270.7	458.2	895.3	1185.8	3632.4	3299.9
CAS/AVQZ	179.4	258.3	450.7	910.3	1169.4	3651.0	3309.6
MRCI/VDZ	278.4	282.8	425.5	973.6	1128.2	3703.0	3395.8
MRCI/VTZ	220.2	287.0	456.9	977.6	1178.7	3745.5	3432.9
MRCI/AVTZ	189.0	238.9	457.4	960.0	1166.6	3729.6	3370.5
cis-vdW-HO$_3^-$ (sp)							
CAS/VDZ	259.5i	239.9	373.7	850.9	1043.2	3583.4	3045.5
CAS/VTZ	267.6i	228.8	368.2	823.7	1069.8	3624.1	3057.3
CAS(26,16)/AVTZ	262.2i	219.0	343.3	793.0	1066.6	3625.6	3023.7
CAS/AVTZ	262.1i	219.0	342.2	793.2	1066.5	3625.3	3023.1
MRCI/VDZ	251.5i	244.5	797.9	884.8	1080.0	3588.2	3297.7
MRCI/VTZ	256.9i	238.3	738.6	778.0	1111.1	3632.0	3249.0
vdW-HO$_3^-$ (min)							
CAS/VDZ	117.7	328.1	971.6	981.8	1090.6	2984.5	3237.1
CAS/VTZ	113.7	300.8	900.6	944.7	112.2	3113.8	3242.9
CAS/AVTZ	107.8	279.7	862.9	904.2	1101.6	3149.8	3203.0
MRCI/VDZ	119.2	370.3	1015.8	1037.8	1119.0	2650.2	3156.2
MRCI/VTZ	120.6	350.1	980.5	985.8	1145.2	2771.5	3176.8
MRCI/AVTZ$^{c)}$	116.3	326.5	930.8	942.1	1128.8	2811.2	3127.9
branch-HO$_3^-$ (min)							
CCSD(T)/AVTZ	399.4	637.9	756.5	980.8	1147.1	3789.1	3855.5
CAS/AVTZ	396.9	733.6	750.0	989.5	1183.8	3731.8	3892.8

$^{a)}$ For simplicity, all real frequencies (in cm^{-1}) are ordered by magnitude. See also text. $^{b)}$ Acronyms as in Table 1. $^{c)}$ Shows two small negative imaginary frequencies of 27 and 20 cm^{-1}, which upon eye-analysis of the vibrational modes are likely to be low vibrations.

only four atoms in the present case, is known to pose enormous problems to accurate electronic structure calculations. Conversely to other model chemistries,[64,65] the appealing attribute of CASDC is that both steps utilize a multireference wavefunction and fully complement each other. Of course, one could think of going a step ahead and base the optimization on a MRCI calculation with a smaller basis.[42] Although bound to success if a large enough basis set were used, such an approach would be extremely more expensive than CASDC, and hence it is not pursued.

To construct the CASDC optimized reaction path (ORP) for rupture/formation of the O_aO_b bond in $[HO_aO_bO_c]^-$, a grid of 40 distinct points between 1.1 and 1000 Å has been calculated and all other degrees of freedom (DOF) fully optimized at the CAS(26,19)/VDZ level of theory. A convergence of typically $10^{-6}\,E_h\,Å^{-1}$ in the gradient has been warranted. Exploratory calculations with the AVTZ basis have also been done to assess the potential energy surface at a higher level of theory. The optimum geometrical parameters so obtained are shown in Figure 2 as a function of the inactive bond distance. As it is shown, the calculated VDZ and AVTZ curves reveal consistency in shape, with minor differences occurring only near 2.3 Å where a saddle point arises connecting the minimum of the cis-HO_3^- anion and the one of a new isomer here predicted with $R_{O_aO_b} = 2.63$ Å. Because the latter is located at a distance where electrostatic and induction (plus dispersion) forces are expected to play a significant role, it will be denoted as vdW-HO_3^-, although such a bonding format is commonly known as hydrogen-bonding. The parallelity of the two curves also suggests that MRCI/AVXZ//CASSCF/VDZ or even MRCI/VXZ//CASSCF/VDZ calculations should provide reliable reaction attributes (vs actually optimized MRCI ones with AVXZ or VXZ basis). It turns out that the optimization of all 5 DOF is easy to perform only up to $R_{O_aO_b} = 3$ Å, since after this distance the dominant contributions to the energy arise mainly from variations in R_1 and R_3. These are the results actually displayed in Figure 2, with the CASSCF having no closed orbitals. After 3 Å, the optimization gets unstable and difficult to converge. To overcome this, only two DOF (R_1 and R_3) were optimized beyond $R_{O_aO_b} = 3$ Å, keeping the angles fixed at the values of the last fully optimized point.

For enhanced accuracy, the ORP should be extrapolated to the complete basis set (CBS) limit. Due to their distinct nature, both components of the energy (the CASSCF and correlation terms) are extrapolated separately. Because the procedure is described in the literature[56,66,67] (and references therein), it is here only briefly addressed. The protocol of Karton and Martin suggested[68] to extrapolate the Hartree-Fock energy is here utilized for the akin CASSCF energy as postulated and tested elsewhere.[56] For the pair (T, Q), it is an empirical two-point extrapolation of the form $A + BX^{-5.34}$ which is believed[68] to yield AVXZ converged energies with a root mean
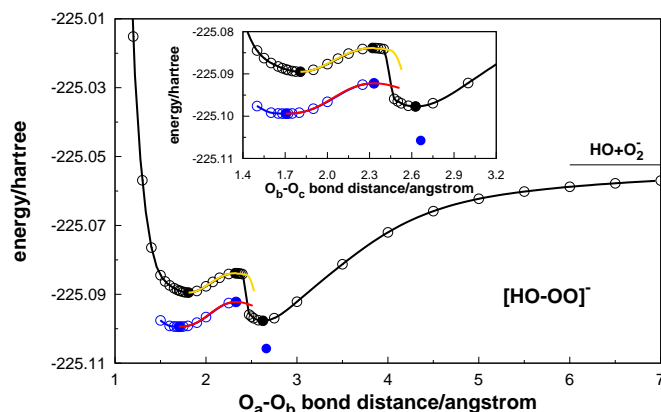

Fig. 1 (color online) Calculated ORP for dissociation of the HO_3^- anion. The open circles indicate the ORP grid at CAS(26,19)/VDZ level of theory. Also shown is a portion of the corresponding CAS(26,19)/AVTZ path. Only the CAS/VDZ curve is in proper scale, with the AVTZ one shifted for clarity. The solid dots indicate optimized VDZ (in black) and AVTZ (blue) stationary points, with portions of the IRC curves shown in gold (VDZ) and red (AVTZ).

square error of $\sim 0.12\,kcal\,mol^{-1}$. For the $(Q, 5)$ pair, the form $E^{CAS} = E_\infty^{CAS} + A(X+1)\exp(-9X)$ is found to perform better with HF/AVXZ energies,[68] and hence is here too adopted. Regarding the dynamical correlation, the CBS extrapolation schemes find a basis on studies of its dependence on the partial wave quantum number for two-electron atomic systems and second-order pair energies in many-electron atoms,[69,70] with $E_X^{cor} = E_\infty^{cor} + A_3/(X+\alpha)^3$ being a popular one[56,71,72]; E_X^{cor} is the correlation energy obtained with cardinal number X, E_∞^{cor} and A_3 parameters determined from calculations for the two highest affordable values of X, and α is an offset parameter fixed from an auxiliary condition.[56] The asymptotic nature of the above rule makes it reliable only when based on values of X typically larger than Q. To overcome this difficulty, we suggested the following uniform singlet-pair and triplet-pair extrapolation (USTE) scheme[56] (see also elsewhere[73]):

$$E_X^{cor} = E_\infty^{cor} + A_3 Y^{-3} + A_5 Y^{-5} \qquad (3)$$

where $Y = X + \alpha$, and A_5 is related to A_3 via the auxiliary relation $A_5 = A_5^\circ + cA_3^m$; A_5°, c, and m are 'universal' parameters for a chosen level of theory. For MRCI energies and $\alpha = -3/8$: $A_5^\circ = 0.0037685459$, $c = -1.17847713\,E_h^{-m}$, and $m = 1.25$. The above two-parameter (E_∞^{cor}, A_3) scheme has been shown[74] to yield accurate results for a variety of systems and theoretical approaches.[56,74–76] Note that the method has no parameters alien to the theory for which they have been defined, with the coefficients showing no visible difference for methods and basis sets that belong to related families.
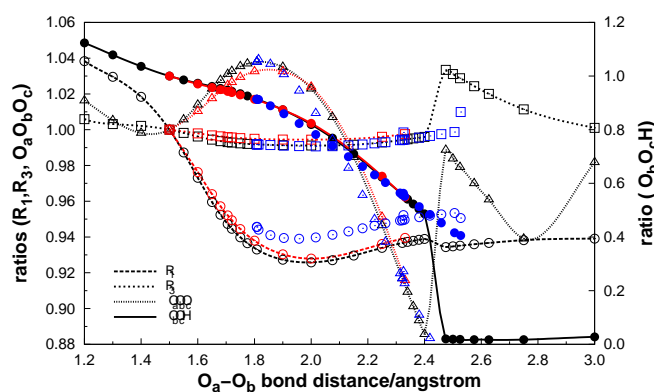
Fig. 2 (color online) Dependence of geometrical parameters in $R_{O_aO_b}$ as shown by the ratios relative to a reference value taken as $R_{O_aO_b} = 1.5$ Å. The online version shows the results obtained at the CAS/VDZ level of theory in black, while the AVTZ ones are in red. Shown in blue are IRC calculations at CAS/VDZ level, starting at the isomerization saddle point. For visibility, these do not include guiding line.

3   Results and discussion

The striking observation from Figure 1 is the double minimum nature of the ground state adiabatic potential energy surface of the HO_3^- anion, with both minima connected by a saddle point for isomerization. All such stationary points have been accurately determined, and their geometries and harmonic vibrational frequencies gathered in Tables 1 and 2. In turn, Figure 1 illustrates their location while the corresponding structures are shown as stick-and-ball drawings in Figure 3. Interestingly, they fit well into the CASDC ORP, which shows as expected[60] a sudden change in energy in the region between the saddle point and the vdW-HO_3^- minimum. Such a topography is fully unexpected from the literature on the title anion. This is not to say that other structures were not predicted. For example, a kind of pyramidal- or branch-structure [structure (2) in[21] Figure 1] in which the H atom is attached to the central oxygen atom was predicted at the CCSD(T)/6-311++G** level of theory but 34 kcal mol^{-1} less stable than cis-HO_3^-. We have confirmed such a prediction both at the single- and multireference levels of theory, with the stick-and-ball plot corresponding to the optimized CASSCF/AVTZ structure shown in Figure 4. Of course, there is another isomer which corresponds to the image of Figure 4 on the plane defined by the three oxygen atoms. The message to emphasize at this point is perhaps that it lies close or even above the $HO + O_2^-$ dissociation channel, thence contrasting with vdW-HO_3^- that can be even the most stable form at some levels of theory.
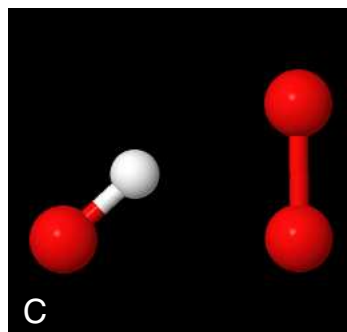
Also shown for comparison in Figures 1 and 2 are the intrinsic-reaction coordinate (IRC) paths[77–79] (see elsewhere[60] for further references) connecting the covalent and
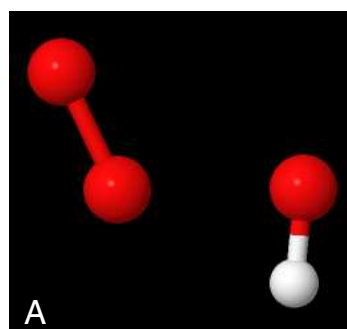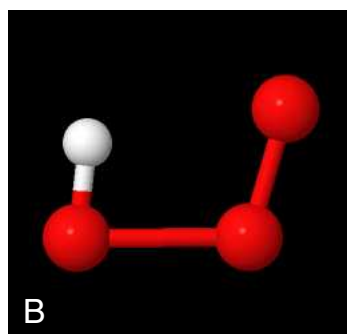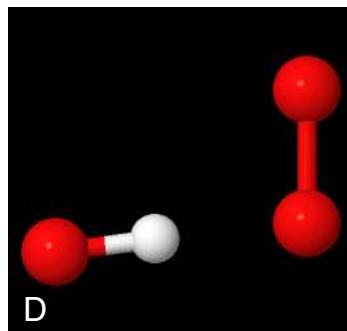

| Basis	ΔE_{ZPE}^{MRCI}
VDZ	8.0
VDZ	0.0
VTZ	0.0
CBS	0.0
VDZ	7.5
VTZ	5.7
CBS	7.7 ± 0.2
VDZ	1.0
VTZ	0.1
CBS	3.3 ± 0.3

Fig. 3 (color online) Co-planar stationary structures of the HO_3^- anion at MRCI and CBS(Q,5)/CASDC levels of theory: B and D represent minima of the cis and vdW isomers, while A and C are the $trans$ and cis to vdW saddle points. Shown in the right-hand-side are the ZPE-corrected stabilities (in kcal mol^{-1} relative to the cis structure) here predicted with the MRCI/VXZ and CBS/CASDC methods. Error bars in the latter are determined such as to encompass both (T,Q) and (Q,5) estimates; see also Table 1 for the branch-HO_3^- isomer, and the text.
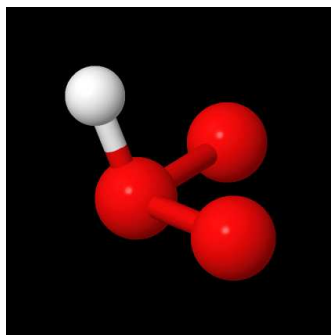
Fig. 4 (color online) The branch-isomer of the HO_3^- anion. For the geometrical and energetic properties, see Table 1.

vdW minima which have been calculated by finding the minimum energy path away (both in the backwards and forward directions) of the saddle point. Note that the IRC is prematurely interrupted before the vdW-HO_3^- minimum. This is due to the presence of a conical intersection as discussed later. In fact, there is close agreement between the ORP and IRC except in the region that mediates the saddle point and the vdW-HO_3^- minimum where such a sudden change occurs. This implies the opening of a more favorable path, as discussed elsewhere[60] for the HO_2 radical. In fact, such quick changes are mostly the result of mapping the intricate topography of a multi-dimensional potential energy surface into a curve.

Because a saddle point can be the result of an avoided crossing between two states of the same spin-spatial symmetry, we have performed 2- and 4-state CASSCF/VDZ calculations along the ORP determined above. The former are shown in Figure 5. Apparently, a crossing occurs at $R_{O_aO_b} \sim 2.425\,\text{Å}$,
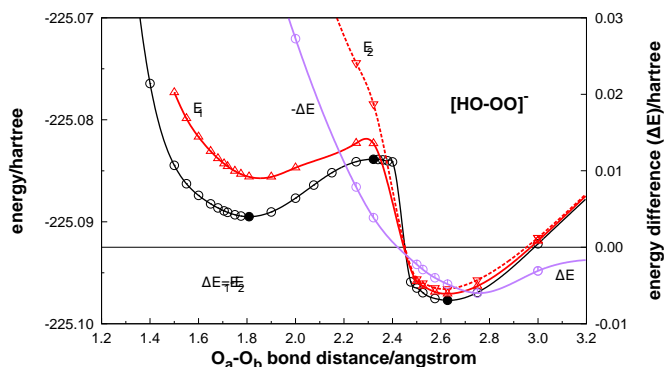
Fig. 5 (color online) Calculated two-state CASSCF/VDZ energies for OO bond-rupture in the HO_3^- anion. Also shown for comparison is the single-state ORP at the CASSCF/VDZ level of theory, and the energy difference ΔE between the two states, sign-changed at the crossing point. Cubic splines are employed to connect the calculated points, which may explain some wiggly behavior.

thus in the region where a sudden change in geometry occurs;

see Figure 2. To rationalize the results, we have plotted the energy difference $\Delta E = E_1 - E_2$ and its symmetrical along the ORP. A smooth transition between $-\Delta E$ and ΔE is observed at the crossing point, which may support its occurrence. However, an apparently vanishing ΔE cannot warrant per se a conical intersection, with a demonstration requiring topological arguments.[80–83] Suffice to recall that, for a N-atom system, the conical intersection involves a $3N - 8$ dimensional subset of the $3N - 6$ dimensional configuration space.[84] In fact, the degeneracy at a conical intersection is lifted in only two directions: one, is the direction of the gradient of the difference of the expectation values,

$$\mathbf{g}_1 = \frac{\partial \left(H_{AA} - H_{BB}\right)}{\partial \mathbf{R}}\Big|_{\mathbf{R}_c}\,, \tag{4}$$

the other is the gradient of the nonadiabatic matrix element,

$$\mathbf{g}_2 = \langle \psi_A | \frac{\partial H}{\partial \mathbf{R}} | \psi_B \rangle |_{\mathbf{R}_c} = \frac{\partial H_{AB}}{\partial \mathbf{R}}\Big|_{\mathbf{R}_c}\,, \tag{5}$$

where $H_{ij} = \langle \psi_i | H | \psi_j \rangle$, ψ_i the wave function of state $i = A, B$, and $\mathbf{R}_c$ is the crossing geometry. Bearpark *et al.*[85] used the above arguments to devise an algorithm to locate conical intersections in quantum chemical calculations. We have also utilized their procedure but with other basis sets (*e.g.*, STO-3G) since MOLPRO only supports segmented basis. Although gradients down to $< 10^{-3}\,\text{E}_h\,\text{Å}^{-1}$ were obtained, the search failed to indicate a crossing within the specified (default) tolerance. Despite this, the two states are seen to approach rather close to each other, which may explain both the appearance of the $cis-$vdW saddle point and the premature termination of the IRCs in Figure 1. A word of caution to emphasize that the above 2-state CASSCF calculations have been carried out along the ORP, and hence the curves shown may not correspond to optimized paths.

The calculated CASDC energies are shown in Figure 6. Note that the role of excitations beyond singles and doubles in the MRCI expansion is far from negligible. Also significant for the low-rank basis is likely to be the basis set superposition error[86] (BSSE). This should though be largely absent[66,87] at the CBS level, with the extrapolated energies being obtained with the dual-level USTE protocol.[56] They are shown in Figure 6 for CBS$(Q,5)$/MRCI/VXZ, both with the $+Q$ correction and without considering it. Full optimizations of the HO_3^- anionic structures at the MRCI/VXZ level of theory here done for the first time with $X = D, T$ are also shown. Parenthetically, a saddle point is predicted at all levels of theory here considered for *trans*-HO_3^-. This should be emphasized since it could be understood to be a stable isomer from Mazziotti's[29] work. However, as stated in his paper,[29] the calculated harmonic frequencies are only for planar internal motion, thus leaving aside the frequency for torsion, which turns out to be imaginary at the *trans*-HO_3^- geometry. We should add that
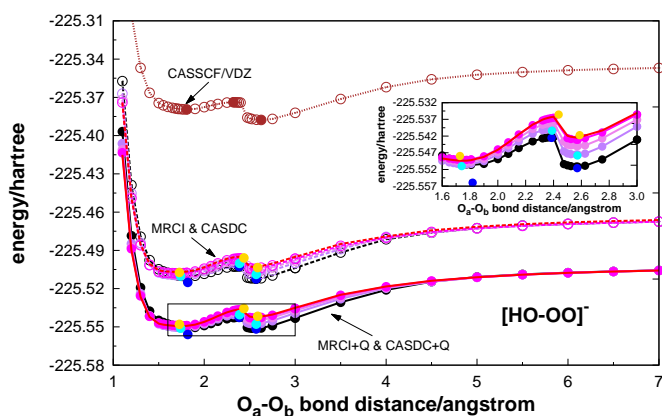
Fig. 6 (color online) Calculated CASSCF/VDZ ORP and stationary points (shifted down by $-0.29\,E_h$; top line, dotted, and solid points in brown), along with MRCI/VXZ and MRCI+Q/VXZ energies (middle and bottom curves, respectively) for OO bond-rupture in the HO$_3^-$ anion. Also shown are CASDC/VXZ ($X = D, T, Q, 5$) and CBS$(Q,5)$ ORPs, the former with the actual calculated points (open if without Davidson's correction, solid otherwise), the others drawn such as to share the same asymptote at 10^3 Å. Indicated are also the *cis*-HO$_3^-$ minimum, *cis*-vdW saddle point, and vdW-HO$_3^-$ minimum at the MRCI/VDZ (solid dots, in blue), MRCI/VTZ (in cyan), and MRCI/AVTZ (in gold) levels of theory.

the agreement with the best available data[29] for the *cis*-HO$_3^-$ isomer is fair, although the diversity of reported attributes is huge[21] as opposed to the focused values here reported.

Being the MRCI approach quite expensive, one may ask whether the popular single-reference CCSD(T) method could be sufficient for accurate values. The answer is positive, if the analysis is restricted to the equilibrium region of both *cis* and *trans* structures. At the *cis*-HO$_3^-$ equilibrium geometry, only 6 reference coefficients exceed 0.05, with the largest being 0.89, thence far larger than all others together. In fact, even at the *trans*-HO$_3^-$ saddle point the single-particle diagnostics[88–90] assume values of $T_1 = 0.033$ and $D_1 = 0.124$, thence $T_1/D_1 = 0.269$. Thus, one expects the CCSD(T) method to perform well[90] in the vicinity of the above stationary points. An additional item for positive judgment refers to the largest T_1 and T_2 amplitudes: the print threshold value of 0.05 is only sporadically attained even at the *trans* saddle point. However, the situation worsens when at the saddle point for *cis*-vdW isomerization, and from there onwards toward dissociation where two open-shell species are formed. In fact, besides unreasonable T_1 and D_1 diagnostics, many singles and doubles amplitudes exceed the recommended threshold at the vdW-HO$_3^-$ minimum. This may explain the lack of convergence in trial attempts, and hence it has not been pursued. Both methods must then be used to obtain a global coverage of the potential energy surface. Because it would be computationally heavy and parallelity is to a large extent ex-

pected, no attempt has been made to get the full ORP at MRCI/AVXZ//CASSCF/AVTZ level. Stating differently, previous work on the neutral HO$_3$ radical may support the idea that the cost-effective CBS/MRCI+Q/VXZ//CASSCF/VDZ model chemistry here utilized should mimic the results of higher-ranked versions without sacrificing the accuracy. It goes without saying that calculations to test the role of additional diffuse functions should still be valuable.

As already noted, the double-minimum nature of the title anion is, to our knowledge, unprecedented. Striking is also the strong binding energy of the vdW-HO$_3^-$ anion which, at some levels of *ab initio* theory, can be even slightly more stable than the covalent *cis*-HO$_3^-$ isomer. Furthermore, despite the diversity of geometries, all them fit into a planar bond breaking/bond-forming mechanism. Note that previous work has only shown the *cis*-isomer, either at a high level of accuracy but restricted to 5 dimensions[29] or at a fair accuracy[21] and hence inconclusive. In contrast with this, our extrapolated energies for the ORP, including the *cis* and vdW-HO$_3^-$ isomers, should be reliable within a fraction of a kcal mol^{-1}, although the model chemistry itself may suffer from a somewhat larger uncertainty.

Regarding charge evolution upon rupture of the intermediate OO bond, Elliot *et al.*[21] remarked that the reaction of Eq. (2) would be endothermic if dissociating to OH($X\,^2\Pi$) + O$_2^-$($X\,^2\Pi_g$) or exothermic if the channel OH$^-$($X\,^1\Sigma^+$) + O$_2$($X\,^3\Sigma_g^-$) were considered. Because a nonadiabatic transition from the singlet into a triplet potential energy surface should have a low probability [this does not imply that intersystem crossings cannot have a significant role, as shown recently[91] for the electronic quenching of N(^2D) by N$_2$], they concluded that it would enhance the lifetime of HO$_3^-$, thence corroborating experimental observation.[1] Our results not only support that HO$_3^-$ is a stable anion but anticipate a complicated spectroscopy due to the existence of two isomers and a low isomerization barrier (high floppiness).

Regarding bond-rupture, Figure 7 suggests the formation of OH($X\,^2\Pi$) + O$_2^-$($X\,^2\Pi_g$). Indeed, on evolving from the *cis*- to vdW-HO$_3^-$ forms, thence toward the products, the negative charge is seen to be larger in O$_2$: it changes from $-0.71\,e$ to $-0.84\,e$. Figure 1 corroborates such a prediction by showing that the CASSCF/VDZ dissociation asymptote lies 19.98 kcal mol^{-1} above the *cis*-HO$_3^-$ (28.66 kcal mol^{-1} over vdW-HO$_3^-$) anion. This mimics within 0.2 kcal mol^{-1} the sum of energies of the fragments (thus ignoring any BSSE,[86] and any further optimization of the O$_a$O$_b$O$_c$ angle). It should be noted though that our best result for the reaction exothermicity to form the *cis*-HO$_3^-$ anion at 0 K (thus, ignoring the ZPE correction) is 30.10 kcal mol^{-1} from CBS$(Q,5)$/MRCI+Q. Such a result may be compared with the corresponding MRCI/AVTZ (MRCI+Q/AVTZ) value of 32.55 kcal mol^{-1} (31.36 kcal mol^{-1}) also from the present
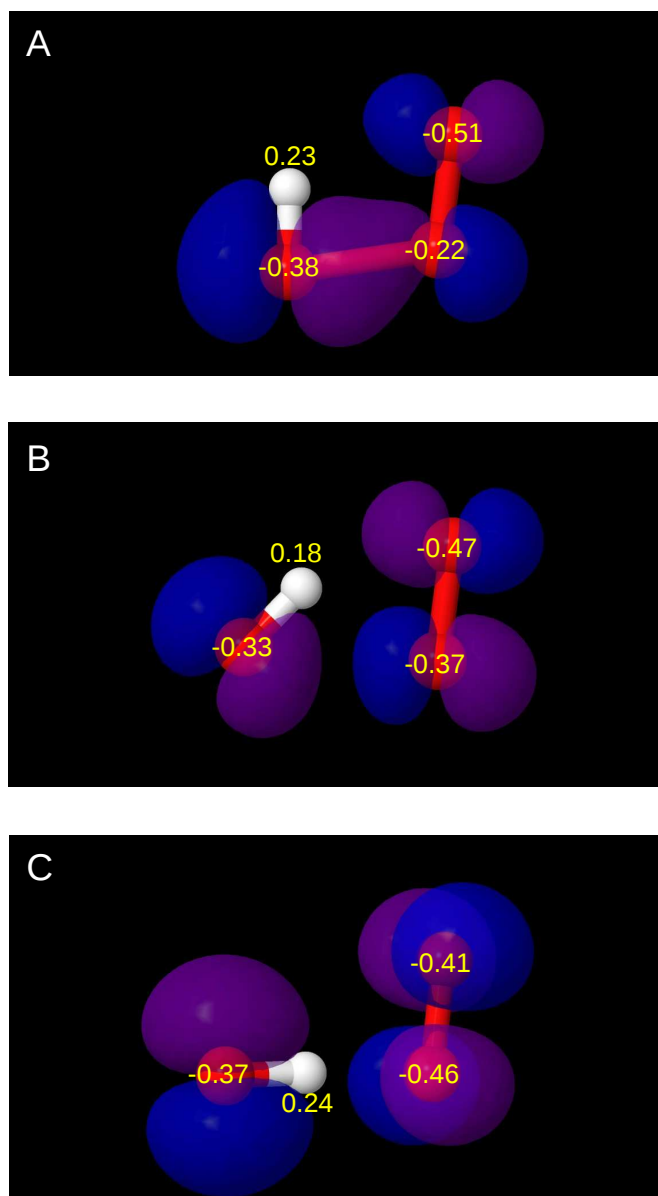
Fig. 7 (color online) HOMO of HO_3^- at various critical points along the *cis* dissociation path. At the vdW minimum, the two single-electron occupied orbitals are shown, one localized in HO, the other in O_2. Also indicated are the Mulliken populations.

work, and ignoring in this case too the BSSE.

On examining the *cis*-HO_3^- structure, Elliot *et al.*[21] concluded that the title anion should be chemically bound rather than a vdW complex between HO^- and O_2. Their argument follows from a natural bond-order analysis[92] and calculated effective atomic charges. From the left- to right-hand-side atoms in $HO_aO_bO_c$, they have obtained: $+0.38e$, $-0.79e$, $-0.14e$, and $-0.45e$. Although their atomic charges for HO differ somewhat from ours, this may partly reflect the dependence of the population analysis on the basis sets.[64,93,94] Because their net charges in HO and O_2 are $-0.41e$ and $-0.69e$, a substantial charge transfer has taken place from HO^- to O_2, which may support chemical bonding between the two. However, despite some further charge transfer to O_2, covalent bonding cannot exist in vdW-HO_3^- although this is nearly as stable as (or even slightly more than) the covalent isomer.

To determine the stability of the title anion, one requires the ZPE correction. This can be calculated very precisely for a diatomic molecule from the known spectroscopic constants, but its determination for a polyatomic requires the knowledge of the harmonic vibrational frequencies, anharmonicities and a constant term which is often not considered but can be sizable (say $100\,cm^{-1}$ for molecular species with large rotational constants).[95–97] Since an accurate anharmonic frequency analysis is unaffordable for the title floppy anion, we use the harmonic frequencies here reported. The ZPE-corrected stabilities so obtained are given in Table 2 and Figure 3. Because harmonic frequencies are unavailable at CBS/CASDC level, they have been approximated by MRCI/VTZ ones that are frequently accepted as highly reliable. Other simplifications require a justifying word. First, a computational one: we refrained for affordability to the cheapest among the family of correlation consistent basis. Second, core correlation effects, relativistic and spin-orbit corrections for the neutral radical have been found[33] to play a minor role, which supports their neglect also for the anion. Conversely, the effect of extra diffuse basis functions is hard to anticipate, and should be examined in future work. Regarding electronic excitations beyond those in MRCI+Q: coping with them requires the exact solution of the electronic Schrödinger equation, a task not foreseeable at present for the title anion.

Table 1 and Figure 6 show that an enhancement of the basis set tends to stabilize more the *cis*-HO_3^- anion than the vdW isomer. This may be attributed to the fact that the CASSCF energy accounts for the dominant long-range interaction involving the permanent electrostatic moments of HO and O_2^- but lacks the dynamical correlation that should be of primary importance at long range distances. In fact, an increase of the basis flexibility should affect primarily the *cis* structure due which entails a situation of covalent bonding. One may then raise the question of how should the true relative positioning look like. One could be led prima facie to think

that the vdW minimum tends to evolve to its typical weak well-depth format as in the HO_3 radical. In an attempt to answer this question, we have carried out MRCI optimizations of the above two minima with the AVTZ basis. The results are found to support the double-minimum nature of the HO_3^- anion, with ball-and-stick structures similar to the ones in panels B and D of Figure 3. Indeed, the MRCI/AVTZ results corroborate the slightly smaller stability of the vdW-HO_3^- anion relative to the *cis* isomer. Furthermore, Figure 6 shows that the CBS/CASDC results are in striking agreement with the fully optimized MRCI/AVTZ values. Yet, a remark is due on the CASDC scheme. Despite the error made by approximating the ZPE correction with the MRCI/VTZ values, the CASDC results must reflect a slight imbalance inherent to the underlying model chemistry. This should not be surprising, since it must at least embed the error due to the lack of parallelity between the CASSCF/VDZ ORP and the higher-ranked CASSCF paths used in the CASDC scheme. Such an error could possibly be mitigated by adopting an ORP at CASSCF/AVTZ level or even at an affordable level of MRCI theory, an issue not attempted here. Finally, we should note that the dynamical correlation has a significant impact on the potential energy surface. For example, the harmonic frequency for torsion of the *cis*-vdW saddle point is $885\,cm^{-1}$ at the MRCI/VTZ level, while the CAS/VTZ value is $368\,cm^{-1}$ ($343\,cm^{-1}$ for CAS/AVTZ). In a smaller scale, an enhancement of the correlation description by augmenting the basis set tends to decrease the intermediate OO distance of the *cis*-HO_3^- isomer, while increasing it in vdW-HO_3^- and the isomerization saddle point. This trend is perhaps best visible from the location of the MRCI/VDZ, MRCI/VTZ, and MRCI/AVTZ stationary points in Figure 6. In fact, our best equilibrium $R_{O_aO_b}$ CASDC values are $(1.75 \pm 0.01)\,\text{Å}$ and $(2.59 \pm 0.01)\,\text{Å}$, with the former only slightly different from the most recent single-reference CCSD(T)/AVQZ estimate[29] of $1.713\,\text{Å}$ or the present directly optimized MRCI/AVTZ value of $1.728\,\text{Å}$. This is particularly close to the value of $1.723\,\text{Å}$ that is obtained by numerically interpolating the three or four calculated points that encompass and lie closest to the CASDC/AVTZ minimum ($1.766\,\text{Å}$ at the CASDC+Q/AVTZ level), thus via exploratory MRCI/AVTZ//CASSCF/VDZ and MRCI+Q/AVTZ//CASSCF/VDZ calculations. If the CASDC approach is pushed further by utilizing the AVQZ basis, the corresponding results are $1.717\,\text{Å}$ and $1.758\,\text{Å}$. The above results also underscore the importance of the $+Q$ correction in obtaining a slightly longer equilibrium geometry for the *cis*-HO_3^- anion. In summary, we emphasize the remarkable agreement between the highly computationally expensive directly optimized MRCI/AVTZ attributes and the CBS/MRCI+Q/VXZ//CASSCF/VDZ ones (see the insert of Figure 6), even when the most cost-effective CASDC approach has been considered.

4 Concluding remarks

The HO_3^- anion has been studied with an accurate multi-reference scheme previously utilized for the neutral. Single-reference coupled-cluster calculations have also been done. Two stable isomers are predicted, and their harmonic vibrational frequencies calculated. One has a structure reminiscent of the neutral *cis*-HO_3 radical. However, unlike the latter where *trans*-HO_3 is the most stable isomer, in the anion the *trans* form is a saddle point lying at least $3\,kcal\,mol^{-1}$ above the *cis* minimum. As in the neutral, the intermediate OO bond of the *cis*-HO_3^- anion is found unusually long, even longer than in the neutral. Yet, the *cis*-HO_3^- anion is a chemically bound species rather than a van der Waals complex resulting from the interaction of HO^- and O_2 (note that the negative charge in O_a exceeds that of O_b; Figure 7). In fact, the long OO bond in *cis*-HO_3^- may be attributed to a bond-order smaller than unit.[21] Remarkably, another almost equally stable isomer of the title anion is also predicted. In this, the HO moiety is allowed to flip and turn its H side to the O_2 part where the charge starts to pile up. In view of its geometrical arrangement and importance of van der Waals forces, it has been denoted as vdW-HO_3^-. The above minima are connected by a saddle point in the ground adiabatic potential energy surface of HO_3^-, which has been here too characterized. Moreover, the dissociative asymptote of the title anion has been shown to be $HO(X\,^2\Pi) + O_2^-(X\,^2\Pi_g)$, and to lie about $30\,kcal\,mol^{-1}$ above the minimum of the *cis*-HO_3^- anion. Notably, $\lesssim 8\,kcal\,mol^{-1}$ are needed for the molecule to visit both isomeric forms and the *trans* saddle point: they all lie in the first third of the HO_3^- well. Such a high floppiness may be explained by the small O_aO_b bond-order, with HO_a performing a full rotation along the IRC at the CASSCF/AVTZ level without altering $\angle O_aO_bO_c$ by more than ≈ 5 deg and $\angle HO_aO_b$ by ≈ 3 deg, all in a smooth, nearly monotonic, way while the remaining bond distances are affected only to a minor extent. In answering the title question, we then conclude that the two minima here discussed should dominate the landscape of the ground-state potential energy surface of HO_3^-, but the existence of shallower ones (less stable isomers) cannot be ruled out prior to further work, an issue outside the scope of the present work.

Because the hydroxyl radical is abundant in the atmosphere and O_2^- anions can also be produced by lightning or by solar radiation from molecular oxygen, the HO_3^- anion should easily be formed via a highly exothermic process. Indeed, no barrier has been predicted along the ORP here calculated, which suggests a fast rate constant for HO_3^- formation via a reaction dominated by strong long-range forces. Thus, the title anion is expected to exist as an isolated species with a long lifetime, as it has been first shown by Cacace *et al.*[1] who predicted a lifetime $> 0.8\,\mu s$. How much will be the structure and energetics of the HO_3^- anion influenced by water or other

solvents is an interesting issue that may not be answered at the present level of accuracy. However, our recent approach to the neutral radical may suggest itself as a viable route [42,65] (and references therein) of study. It is therefore hoped that the present work may stimulate further experimental and theoretical studies of the HO_3^- anion, thence helping the latter to find the right place in environmental and atmospheric chemistry. In particular, the two lowest isomeric structures (planar) and floppiness here revealed for the title anion may help experimentalists to unravel its formation, spectroscopy, and role in chemistry. Specifically, can the data here reported help on rationalizing the photoelectron spectrum[52] of the HO_3^- anion? Suffice it here to be a little speculative. Indeed, if the two isomers are taken together for the analysis, which may be a fair assumption given the low isomerization barrier, the electron binding energy (taken as an average of the individual values) turns out to be $1.47\,eV$, a result in striking coincidence with one of the observed (and, to our knowledge, unexplained) peaks by Miller[52] at $1.46\,eV$. As for the CASDC method, its use on searching for other possible isomers could be illuminating. Finally, despite preliminary results suggesting that the addition of diffuse functions onto the basis may not have a drastic effect on the results, further calculations toward higher accuracy would per se be valuable.

5 Acknowledgement

References

1 F. Cacace, G. de Petris, F. Pepi and A. Troiani, *Science*, 1999, **285**, 81.

2 M. Speranza, *Inorg. Chem.*, 1996, **35**, 6140–6151.

3 A. Engdahl and B. Nelander, *Science*, 2002, **295**, 482–483.

4 J. Cerkovnik and B. Plesničar, *J. Am. Chem. Soc.*, 1993, **115**, 12169–12170.

5 J. Koller and B. Plesničar, *J. Am. Chem. Soc.*, 1996, **118**, 2470–2472.

6 E. Kraka, D. Cremer, J. Koller and B. Plesnicarar, *J. Am. Chem. Soc.*, 2002, **124**, 8462–8470.

7 F. Cacace, R. Cipollini, G. de Petris and A. Troiani, *Int J Mass Spectrom*, 2003, **228**, 717–722.

8 E. L. Derro, T. D. Sechler, C. Murray and M. I. Lester, *J. Phys. Chem. A*, 2008, **112**, 9269–9276.

9 E. L. Derro, T. D. Sechler, C. Murray and M. I. Lester, *J. Chem. Phys.*, 2008, **128**, 244313.

10 S. D. Le Picard, M. Tizniti, A. Canosa, I. R. Sims and I. W. M. Smith, *Science*, 2010, **328**, 1258–1262.

11 E. P. Hoy, C. A. Schwerdtfeger and D. A. Mazziotti, *J. Phys. Chem. A*, 2013, **117**, 1817–1825.

12 T. Liang, D. B. Magers, P. L. Raston, W. D. Allen and G. E. Douberly, *J. Phys. Chem. Lett.*, 2013, **4**, 3584–3589.

13 R. J. Blint and M. D. Newton, *J. Chem. Phys.*, 1973, **59**, 6220–6228.

14 K. B. Mathisen, O. Gropen, P. N. Skancke and U. Wahlgren, *Acta Chem. Scand. A*, 1983, **37**, 817–822.

15 M. Dupuis, G. Fitzgerald, B. Hammond, W. A. Lester Jr. and H. F. Schaefer III, *J. Chem. Phys.*, 1986, **85**, 2691–2697.

16 T. H. Lay and J. W. Bozzelli, *J. Phys. Chem. A*, 1997, **101**, 9505–9510.

17 H. G. Yu and A. J. C. Varandas, *J. Chem. Soc. Faraday Trans.*, 1997, **93**, 2651–2656.

18 M. Speranza, *J. Phys. Chem.*, 1998, **102**, 7535.

19 H. G. Yu and A. J. C. Varandas, *Chem. Phys. Lett.*, 2001, **334**, 173–178.

20 P. A. Denis, M. Kieninger, O. N. Ventura, R. E. Cachau and G. H. F. Diercksen, *Chem. Phys. Lett.*, 2002, **365**, 440–449.

21 B. Elliott, A. N. Alexandrova and A. I. Boldyrev, *J. Phys. Chem. A*, 2003, **107**, 1203–1206.

22 K. Suma, Y. Sumiyoshi and Y. Endo, *Science*, 2005, **308**, 1885–1886.

23 W. M. F. Fabian, J. Kalcher and R. Janoschek, *Theor. Chem. Acc.*, 2005, **114**, 182–188.

24 A. Mansergas and J. M. Anglada, *Comp. Phys. Comm.*, 2006, **7**, 1488–1493.

25 C. Murray, E. L. Derro, T. D. Sechler and M. I. Lester, *J. Phys. Chem. A*, 2007, **111**, 4727.

26 E. L. Derro, C. Murray, T. D. Sechler and M. I. Lester, *J. Phys. Chem. A*, 2007, **111**, 11592–11601.

27 A. Mansergas and J. M. Anglada, *Phys. Chem. Chem. Phys.*, 2007, **9**, 5865–5873.

28 A. Mansergas, J. M. Anglada, S. Olivella, M. F. Ruiz-López and M. Martins-Costa, *Comp. Phys. Comm.*, 2007, **8**, 1534–1539.

29 D. A. Mazziotti, *J. Phys. Chem. A*, 2007, **111**, 12635–12640.

30 B. J. Braams and H. Yu, *Phys. Chem. Chem. Phys.*, 2008, **10**, 3150–3155.

31 M. E. Varner, M. E. Harding, J. Gauss and J. F. Stanton, *Chem. Phys.*, 2008, **346**, 53–55.

32 C. Murray, E. L. Derro, T. D. Sechler and M. I. Lester, *Acc. Chem. Res.*, 2009, **212**, 419–427.

33 M. E. Varner, M. E. Harding, J. Vázquez, J. Gauss and J. F. Stanton, *J. Phys. Chem. A*, 2009, **113**, 11238–11241.

34 P. A. Denis and F. R. Ornellas, *J. Phys. Chem. A*, 2009, **113**, 499–506.

35 A. J. C. Varandas, *Phys. Chem. Chem. Phys.*, 2011, **13**, 9796–9811.

36 A. J. C. Varandas, *Phys. Chem. Chem. Phys.*, 2011, **13**, 15619–15623.

37 A. J. C. Varandas, *J. Chem. Theory Comput.*, 2012, **8**, 428–441.

38 P. L. Raston, T. Liang and G. E. Douberly, *J. Chem. Phys.*, 2012, **137**, 184302.

39 M. C. McCarthy, V. Lattanzi, D. Kokkin, J. Oscar Martinez and J. F. Stanton, *J. Chem. Phys.*, 2012, **136**, 034303.

40 K. Suma, Y. Sumiyoshi and Y. Endo, *J. Chem. Phys.*, 2013, **139**, 094301.

41 Y. Zhou, H. Hu, L. Li, H. Hou and B. Wang, *Computational and Theoretical Chemistry*, 2013, **1026**, 24–30.

42 A. J. C. Varandas, *Int. J. Quantum Chem.*, 2013, **000**, 000.

43 J. Cerkovnik and B. Plesnicar, *Chem. Rev.*, 2013, **113**, 7930–7951.

44 P. S. Bailey, *Ozonation in Organic Chemistry*, Academic Press: New York, 1982.

45 S. S. Razumovskii and G. E. Zaikov, *Studies in Organic Chemistry, Vol. 15*, Elsevier: New York, 1984.

46 C. Meredith, G. E. Quelch and H. F. Schaefer III, *J. Am. Chem. Soc.*, 1991, **113**, 1186–1193.

47 P. J. Knowles and H. J. Werner, *Chem. Phys. Lett.*, 1988, **145**, 514–522.

48 H. J. Werner and P. J. Knowles, *J. Chem. Phys.*, 1988, **89**, 5803.

49 H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, A. Mitrushenkov, G. Rauhut, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dob-

byn, F. Eckert, E. Goll, C. Hampel, G. Hetzer, T. Hrenar, G. Knizia, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang and A. Wolf, *MOLPRO, version 2010.1, a package of* ab initio *programs*, see http://www.molpro.net.

50 G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, (2nd edition)*, Van Nostrand, New York, 1950.

51 P. H. Krupenie, *J. Phys. Chem. Ref. Data*, 1972, **1**, 423.

52 E. M. Miller, *PhD thesis*, University of Colorado, 2012.

53 T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007–1023.

54 D. Woon and T. Dunning Jr., *J. Chem. Phys.*, 1993, **98**, 1358.

55 F. Jensen, *Theor. Chem. Acc.*, 2005, **113**, 267–273.

56 A. J. C. Varandas, *J. Chem. Phys.*, 2007, **126**, 244105.

57 B. O. Roos, *Adv. Chem. Phys.*, 1987, **69**, 399–445.

58 K. Ruedenberg, M. W. Schmidt, M. M. Gilbert and S. Elbert, *Chem. Phys.*, 1982, **71**, 41–49.

59 K. Ruedenberg and K. R. Sundberg, *Quantum Science*, Plenum, New York, 1975, p. 505.

60 A. J. C. Varandas, *J. Phys. Chem. A*, 2013, **117**, 7393–7407.

61 J. Hepburn, G. Scoles and R. Penco, *Chem. Phys. Lett.*, 1975, **36**, 451–456.

62 J. N. Murrell and A. J. C. Varandas, *Mol. Phys.*, 1975, **30**, 223–236.

63 R. Podeszwa, K. Pernal, K. Patkowski and K. Szalewicz, *J. Phys. Chem. Lett.*, 2010, **1**, 550–555.

64 F. Jensen, *Introduction to Computational Chemistry*, Wiley, Chichester, 2nd edn, 2006.

65 L. P. Viegas and A. J. C. Varandas, *J. Comp. Chem.*, 2014, **35**, 507–517.

66 A. J. C. Varandas, *J. Phys. Chem. A*, 2010, **114**, 8505–8516.

67 A. J. C. Varandas, *Int. J. Quantum Chem.*, 2010, **111**, 416–429.

68 A. Karton and J. M. L. Martin, *Theor. Chem. Acc.*, 2006, **115**, 330–333.

69 C. Schwartz, *Phys. Rev.*, 1962, **126**, 1015.

70 W. Kutzelnigg and J. D. Morgan III, *J. Chem. Phys.*, 1992, **96**, 4484–4508.

71 T. Helgaker, W. Klopper, H. Koch and J. Noga, *J. Chem. Phys.*, 1997, **106**, 9639–9646.

72 A. J. C. Varandas, *J. Phys. Chem. A*, 2008, **112**, 1841–1850.

73 A. J. C. Varandas, *J. Chem. Phys.*, 2000, **113**, 8880–8887.

74 A. J. C. Varandas, *Physica Scripta; Comm. At. Opt. Mol. Phys.*, 2007, **76**, C28–C35.

75 A. J. C. Varandas, *Chem. Phys. Lett.*, 2007, **443**, 398–407.

76 A. J. C. Varandas, *J. Chem. Phys.*, 2007, **127**, 114316.

77 K. Fukui, *J. Phys. Chem.*, 1970, **74**, 4161–4163.

78 J. W. McIver and A. Komornicki, *J. Am. Chem. Soc.*, 1972, **94**, 2625–2633.

79 S. Maeda and K. Morokuma, *J. Chem. Theory Comput.*, 2011, **7**, 2335–2345.

80 H. C. Longuet-Higgins, *Proc. R. Soc. Ser. A*, 1975, **344**, 147.

81 A. J. C. Varandas, J. Tennyson and J. N. Murrell, *Chem. Phys. Lett.*, 1979, **61**, 431.

82 D. R. Yarkony, *Rev. Mod. Phys.*, 1996, **68**, 985.

83 A. J. C. Varandas, *Chem. Phys. Lett.*, 2010, **487**, 139–146.

84 E. Teller, *J. Phys. Chem.*, 1937, **41**, 109.

85 M. J. Bearpark, M. A. Robb and H. B. Schlegel, *Chem Phys Lett*, 1994, **223**, 269–274.

86 F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553–566.

87 A. J. C. Varandas, *Theor Chem Acc*, 2008, **119**, 511–521.

88 T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem.*, 1989, **S23**, 199–207.

89 M. L. Leininger, I. M. B. Nielsen, T. D. Crawford and C. L. Janssen, *Chem. Phys. Lett.*, 2000, **328**, 431.

90 T. J. Lee, *Chem. Phys. Lett.*, 2003, **372**, 362–367.

91 B. R. L. Galvão, A. J. C. Varandas, J. P. Braga and J. C. Belchior, *J. Phys. Chem. Lett.*, 2013, **4**, 2292–2297.

92 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.

93 J. F. Harrison, *J Phys Chem A*, 2006, **110**, 10848–10857.

94 A. J. C. Varandas, *Comp. Theor. Chem.*, 2014, **1036**, 61–71.

95 I. M. Mills, Theoretical Chemistry *(Specialist Periodical Report, The Chemical Society, London, 1974), Vol. 1, p.110*.

96 D. G. Truhlar, *J. Comput. Chem.*, 1991, **12**, 266–270.

97 M. S. Schuurman, S. R. Muir, W. D. Allen and H. F. Schaefer III, *J. Chem. Phys.*, 2004, **120**, 11586.