Gas-Phase Experiments Aimed at Probing the Existence of the Elusive Water Oxide Molecule**

Detlef Schröder,* Christoph A. Schalley, Norman Goldberg, Jan Hrůšák, and Helmut Schwarz

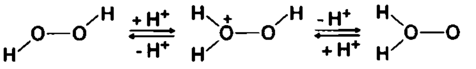
Dedicated to Professor Gerhard Ertl on the occasion of his 60th birthday

Abstract: Collisional activation, charge reversal, and six different neutralization – reionization mass spectrometric experiments with $[H_2,O_2]^{\cdot+}$ radical cations and $[H_2,O_2]^{\cdot-}$ radical anions were performed in order to probe the predicted existence of neutral water oxide, H_2OO, the long sought after tautomer of hydrogen peroxide, HOOH. The experiments together with ab initio calculations indicate that H_2OO is a local minimum on the $[H_2,O_2]$ potential-energy surface, and the elusive molecule seems to be formed as a transient upon neutralization of the corresponding radical cation $H_2OO^{\cdot+}$ in the gas phase.

Keywords
computer chemistry · electron transfer · hydrogen peroxide · mass spectrometry · water oxide

Introduction

Despite the enormous progress in the development of spectrometric methods, there remain a few elusive, long sought after species in chemistry. One of these molecules is water oxide, H_2OO, the tautomer of hydrogen peroxide, HOOH. Although several high-level theoretical studies[1, 2] have amply demonstrated that water oxide represents a local minimum on the $[H_2,O_2]$ potential-energy surface and most recently even led to the statement that "oxywater awaits synthesis",[3] no experimental evidence for the existence of H_2OO has been reported so far. Besides the fundamental interest in probing elusive molecules, the search for water oxide is motivated by the fact that H_2OO has been postulated to play a key role in several chemical and biochemical oxidation processes involving peroxides.[1, 4] While H_2OO is conceptually accessible from hydrogen peroxide by a simple protonation/deprotonation sequence (Scheme 1), this is not a viable experimental approach, because the equilibrium is shifted way over to the left.



Scheme 1.

Some of the problems associated with the generation of water oxide become obvious on inspecting the calculated potential-energy surface of neutral $[H_2,O_2]$ (Fig. 1); note that throughout this article superscripts serve as a simplified notation for spin multiplicities. As shown in previous calculations,[1–3] the global minimum corresponds to singlet ^1HOOH; ^1H_2OO is 47 kcal mol^{-1} less stable. We will use this result in the discussion below. Further, we have examined possible triplet states of these two tautomers—^3HOOH and ^3H_2OO—which turn out to be hardly stable towards dissociation into two $^2OH^{\cdot}$ radicals and $^1H_2O + {}^3O$, respectively.[5–8] The barrier to 1,2-hydrogen migration associated with the transition structure ^1TS amounts to only a few kcal mol^{-1} with respect to ^1H_2OO and is further

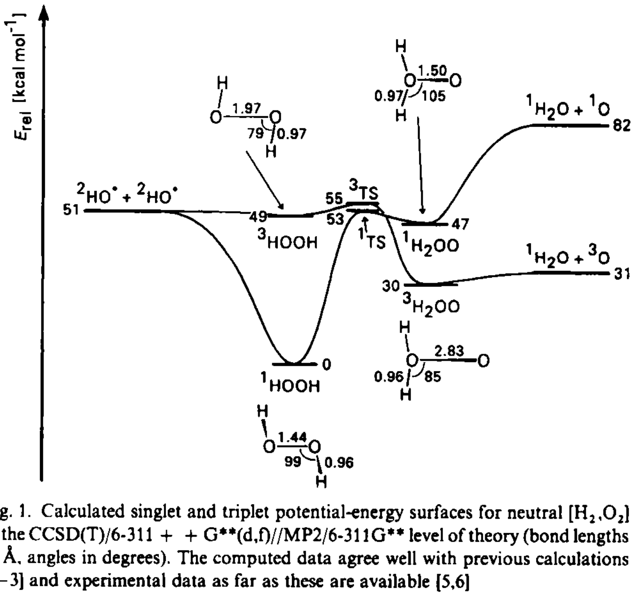


Fig. 1. Calculated singlet and triplet potential-energy surfaces for neutral $[H_2,O_2]$ at the CCSD(T)/6-311 + + G**(d,f)//MP2/6-311G** level of theory (bond lengths in Å, angles in degrees). The computed data agree well with previous calculations [1–3] and experimental data as far as these are available [5,6]

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reduced upon inclusion of zero-point energy.[2,3] From a practical point of view, such a small activation barrier together with the huge exothermicity of the isomerization $^1H_2OO \rightarrow {}^1H_2O_2$ will not allow "pure" water oxide to be generated in bulk at room temperature. In addition, deprotonation of protonated hydrogen peroxide according to Scheme 1, will largely, if not exclusively, result in the formation of ^{1}HOOH. Further, dissociative hydrogen atom abstractions [Eq. (1)] will be exo-

$$^1H_2OO + {}^1R{-}H \longrightarrow {}^1H_2O + {}^2HO^{\bullet} + {}^2R^{\bullet} \qquad (1)$$

thermic[6] for all molecules with R–H bond energies of less than 115 kcal mol^{-1}. Consequently, any attempt to probe the existence of water oxide at a molecular level requires a less traditional approach as well as sensitive, highly selective detection techniques.

Neutralization–reionization (NR) mass spectrometry in its many variants is well suited for this particular purpose,[9,10] as it takes advantage of the powerful repertoire of state-of-the-art mass-spectrometric techniques. In NR experiments, mass-selected ions having several keV kinetic energy are subjected to a double-collision event: in a first collision some of the ions are neutralized and then the remaining ions are deflected away from the beam by a kV potential. Subsequently, the fast neutrals are reionized in a second collision, and the ionic species formed are analyzed and detected by mass-spectrometric means. In order to probe the potential-energy surface of $[H_2,O_2]$, six different variants of the NR method have been used here, which are denoted according to the charges of the projectiles and product ions:[11] 1) neutralization of cations and subsequent reionization to cations ($^+NR^+$); 2) collisional activation (CA) of mass-selected $[H_2,O_2]^{\bullet+}$ ions stemming from reionized neutrals of a $^+NR^+$ experiment ($^+NR^+$/CA); 3) neutralization of cations and reionization to anions ($^+NR^-$); 4) neutralization of anions and reionization to cations ($^-NR^+$); 5) neutralization of anions and reionization to anions ($^-NR^-$); and 6) neutralization of cations, followed first by collision-induced dissociation of the neutrals and then reionization to cations ($^+NCR^+$).[12]

Experimental Details

The experiments were performed with a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors) [13]. Briefly, $[H_2,O_2]^{\bullet+}$ were generated by electron ionization (EI, 70 eV) of concentrated hydrogen peroxide (90%), and $[H_2,O_2]^{\bullet-}$ were obtained by chemical ionization (CI) of water with dinitrogen oxide as reagent gas. In order to avoid decomposition of hydrogen peroxide and achieve maximum intensities of $[H_2,O_2]^{\bullet+}$, the use of a metal-free Teflon/glass inlet system is essential [14]. For the variation of the energy of the ionizing electrons (E_e), the repeller was grounded to the ion source in order to avoid unintentional electron acceleration by the potentials inside of the ion source. Note that the ionizing electrons are not energy-selected and certainly have a broad distribution of kinetic energies, so that the dependencies observed (see below) should only be regarded in a qualitative sense. Owing to decreasing ion intensities, NR experiments were no longer possible at nominal electron energies lower than 20 eV; similarly, self-CI of H_2O_2 to achieve collisional cooling of the ions [15] was not practicable, because the $[H_2,O_2]^{\bullet+}$ disappears when the ion source pressure increases.

For collisional activation (CA), the ions were selected by means of B(1)/E(1), collided with helium (80% transmission, T) in the field-free region preceding B(2), and the products were subsequently monitored by scanning this sector. $^+NR^+$/CA experiments [16,17] were performed by selecting the recovery ions of an NR experiment by means of B(2), colliding them with helium (80% T), and monitoring the ionic products with E(2). For a direct comparison with the $^+NR^+$/CA spectrum of $[H_2,O_2]^{\bullet+}$, the CA spectrum of source-generated ions was also recorded by mass-selection with B(1)/E(1)/B(2), collision with helium (80% T) in the field-free region preceding E(2), and monitoring the products by scanning this sector. For $^+NR^+$ and $^-NR^+$ experiments, the ions were mass-selected by means of B(1)/E(1), neutralized by collisions with xenon and oxygen (80% T), respectively, reionized by collision with oxygen (80% T), and the resulting mass spectra subsequently recorded by scanning B(2). In the $^+NR^+$ experiments two different lifetimes of the neutrals were sampled by variation of the length of the flight path from 10 to 80 cm [17]; this gives minimum lifetimes of ca. 0.5 and 4 µs, respectively, for 8 keV ions with a mass of 34 amu. Owing to their lower intensities, $^+NR^-$ (xenon, 80% T; benzene, 70% T) and $^+CR^-$ mass spectra (benzene, 70% T) were obtained by mass-selection with B(1) and scanning E(1) [18]. Because mass-selection with a magnet alone does not guarantee sufficient separation of the ions of interest [19], the E(1) spectra were carefully checked for interferences, which were, however, not observed. The experimental setup allowed us not only to perform $^+NR^+$ mass spectra as described above, but also to collisionally activate the neutral beam to give $^+NCR^+$ mass spectra [17]. To this end, ions were neutralized (Xe, 80% T) and remaining ions were deflected away; the neutrals collided with helium at various transmittances and were reionized (O_2, 70% T), and the cations formed were monitored by scanning B(2). In certain favorable cases, the $^+NCR^+$ technique allows for the investigation of unimolecular and collision-induced dissociations of neutrals, although fragmentations of the corresponding cations may complicate the mass spectra and their interpretation [12]. Spectra were accumulated and processed on-line with the AMD-Intectra data system; 5 to 30 scans were averaged to improve the signal-to-noise ratio. HOOD and D_2O_2 were simply prepared by mixing H_2O_2 (90%) with the same amount of D_2O in the reservoir of the Teflon/glass inlet system.

The calculations were performed with standard routines of the GAUSSIAN 94 suite of programs [20], and will, therefore, not be described in detail. In general, zero-point vibrational energies (ZPVEs) were neglected, because of the limitations of the computational approaches used. For discussions of the importance of ZPVE effects for the potential-energy surface of $^1[H_2,O_2]$, see refs. [1–3].

Results

Before describing the results of the mass-spectrometric experiments aimed at probing neutral $[H_2,O_2]$, we will present some experimental and theoretical results concerning the potential-energy surfaces of ionic species $^2[H_2,O_2]^{\bullet+}$ and $^2[H_2,O_2]^{\bullet-}$. As for the potential-energy surface of the neutral species $^1[H_2,O_2]$ and $^3[H_2,O_2]$ described above (Fig. 1), these results were in part taken from previous computational studies, and only values relevant to the present context were calculated independently.

The radical cation $[H_2,O_2]^{\bullet+}$ is easily available by ionization of hydrogen peroxide, which has an ionization energy (IE) of 10.5 eV.[6] The global minimum of the $[H_2,O_2]^{\bullet+}$ system corresponds to ionized hydrogen peroxide in its doublet ground state (i.e., $^2HOOH^{\bullet+}$). However, the radical cation of water oxide, $^2H_2OO^{\bullet+}$, resides in a significantly deeper well than the corresponding neutral species (Fig. 2). The stability difference between the two $[H_2,O_2]^{\bullet+}$ tautomers is 24 kcal mol^{-1};[21] for the neutral counterparts this difference has been calculated to be 47 kcal mol^{-1} (Fig. 1).[1,2] Moreover, the calculated barrier associated with the 1,2-hydrogen migration from $^2H_2OO^{\bullet+}$ is

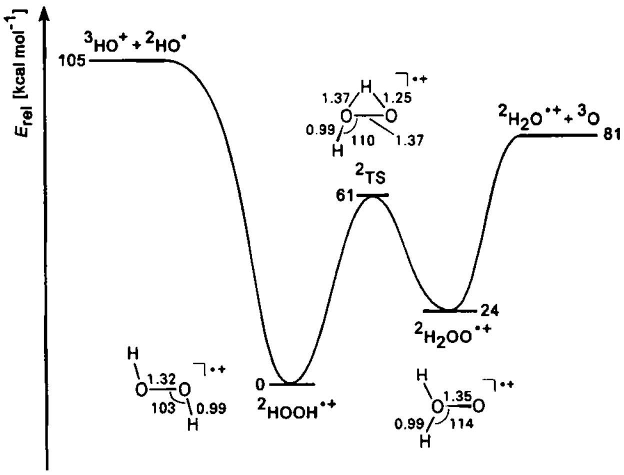

Fig. 2. Calculated doublet potential-energy surface for the radical cation $^2[H_2,O_2]^{\bullet+}$ at the CCSD(T)/6-311++G**(d,f)//MP2/6-311G** level of theory (bond lengths in Å, angles in degrees). The computed data agree well with previous calculations [21] and experimental data [6].

37 kcal mol^{-1}, compared to a barrier of only a few kcal mol^{-1} in the neutral case. Further, dissociation into $^2H_2O^{\cdot+} + {}^3O$ is a high-energy process (81 kcal mol^{-1}), although it requires 24 kcal mol^{-1} less energy than the dissociation to $^3OH^+ + {}^2OH^{\cdot}$. Thus, in the ionization with 70 eV electrons, the tautomer $^2H_2OO^{\cdot+}$ is expected to form to some extent. In fact, EI does not only lead to the formation of ground-state ions, but also of rovibrationally and/or electronically excited ions, owing to the large excess energy imparted in the course of electron bombardment. As a consequence, other "hot" isomers, for example, $^2H_2OO^{\cdot+}$, may also be formed by EI with energetic electrons (see below).

The radical anion $[H_2,O_2]^{\cdot-}$ has also been studied repeatedly, and we adopt the results of previous experimental and theoretical studies.[5, 22–24] First, it should be pointed out that hydrogen peroxide itself has a negative, vertical electron affinity (EA$_v$) of ca. −58 kcal mol^{-1}, and electron attachment to ground-state ^{1}HOOH thus cannot occur without substantial structural rearrangement.[23] However, two stable isomers of the radical anion are known, and these are best described as the electrostatic complexes $^1HO^- \cdot {}^2HO^{\cdot}$ and $^2O^{\cdot-} \cdot {}^1HOH$.[24] According to the ab initio computations,[22, 23] these two species are separated by an extremely small barrier (Fig. 3), so that they are, in practice, indistinguishable at room temperature.

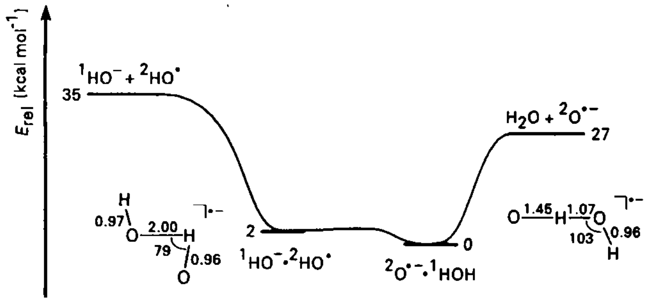

Fig. 3. Calculated doublet potential-energy surface for the radical anion $^2[H_2,O_2]^{\cdot-}$ taken from ref. [23] (bond lengths in Å, angles in degrees).

Collisional activation of $[H_2,O_2]^{\cdot+}$: Due to reasons which will become clear below, we would like to begin with discussing the collision-induced fragmentation of $[H_2,O_2]^{\cdot+}$. The properties of the $^2[H_2,O_2]^{\cdot+}$ potential-energy surface are reflected in the CA mass spectrum of the ion (Fig. 4a): $H_2O^{\cdot+}$ formed by loss of an oxygen atom is much more abundant than the OH^+ ion simply because the corresponding exit channel is lower in energy. In addition, the loss of one and two hydrogen atoms (or molecular H_2) is observed, which leads to the formation of HO_2^+ and $O_2^{\cdot+}$, respectively. However, the loss of hydrogen atoms is not instructive with respect to connectivity, and thus we restrict the following discussion to the $H_2O^{\cdot+}$ and HO^+ fragments.

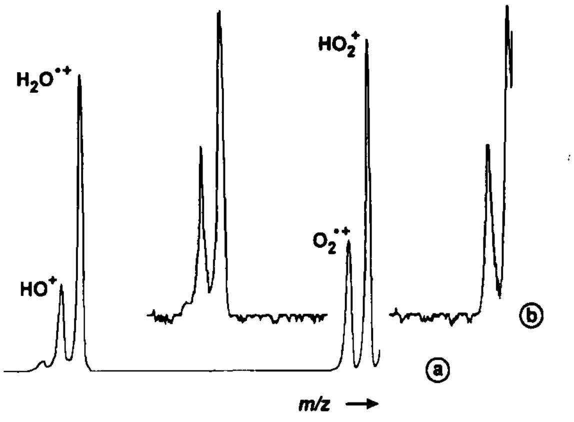

Fig. 4. a) CA mass spectrum (He, 80% T) of B(1)/E(1)/B(2) mass-selected $[H_2,O_2]^{\cdot+}$. b) $^+NR^+$/CA mass spectrum (Xe, 80% T; O_2, 80% T; He, 80% T) of $[H_2,O_2]^{\cdot+}$. These ions were generated by neutralization–reionization of B(1)/E(1) mass-selected $[H_2,O_2]^{\cdot+}$, followed by mass-selection of the recovery ions with B(2); the spectrum was then recorded by scanning E(2).

In order to examine the proposal made above, namely, that EI of hydrogen peroxide may result in the formation of a mixture of $^2HOOH^{\cdot+}$ and $^2H_2OO^{\cdot+}$, CA mass spectra were recorded at different kinetic energies of the ionizing electrons in the ion source. Regarding the potential-energy surface of $^2[H_2,O_2]^{\cdot+}$ (Fig. 2), we considered the dependence of the $H_2O^{\cdot+}/OH^+$ ratio on the electron energy (E_e) as an indicator for the presence of a mixture of two different isomers formed upon EI. An electron energy of ca. 12.5 eV serves as a suitable reference point, because at this energy the $^2HOOH^{\cdot+} \rightarrow {}^2H_2OO^{\cdot+}$ rearrangement is largely suppressed;[25] of course, isomerization following collisional activation can still take place. In the experiment (Table 1), the ratio $H_2O^{\cdot+}/OH^+$ remains constant (ca. 4.3) upon lowering E_e from 100 eV down to ca. 20–25 eV; however, below 20 eV the $H_2O^{\cdot+}/OH^+$ ratio depends on the electron energy with an increasing probability for formation of OH^+ relative to $H_2O^{\cdot+}$ upon decreasing E_e. This observation suggests that a mixture of two $^2[H_2,O_2]^{\cdot+}$ isomers is formed with energetic electrons, because otherwise a constant ratio $H_2O^{\cdot+}/OH^+$ would be expected over the whole energy range. One might argue, that the changing ratio of $H_2O^{\cdot+}$ and OH^+ signals is due to different internal energies of the ions at different electron energies. However, with respect to the $^2[H_2,O_2]^{+\cdot}$ potential-energy surface presented in Figure 2, one would expect the ratio to change in favor of $H_2O^{\cdot+}$ on lowering the internal energy with E_e. In contrast, at lower E_e values the OH^+ signal increases relative to $H_2O^{\cdot+}$. As some other experimental findings support the generation of both tautomers of $^2[H_2,O_2]^{\cdot+}$ as well, we will return to this topic further below.

Table 1. $H_2O^{\cdot+}/OH^+$ ratio observed in the collisional activation (CA) mass spectra of $[H_2,O_2]^{\cdot+}$ at different kinetic energies (E_e) of the ionizing electrons.

E_e [eV] [a]	12.5	14	15	17.5	20	25	50	70	100
$H_2O^{\cdot+}/OH^+$ [b]	3.03	3.28	3.45	4.17	4.22	4.35	4.34	4.33	4.36

[a] The electron energies are rough estimates and are given as the potential of the filament relative to the source block; no energy selection of the electrons is performed; see Experimental Section. [b] The experimental uncertainty in $H_2O^{\cdot+}/OH^+$ is ±0.05 for $E_e > 20$ eV and increases to ±0.2 at $E_e = 12.5$ eV.

Neutralization–Reionization Experiments: Two salient features of NR experiments should be pointed out at the outset. First, the velocity of keV ions is so large (about 10^5 m s^{-1}) that collisions with molecular targets usually produce only vertical transitions, that is, geometry changes are negligible.[26–28] Second, the detection of a reionized parent ion ("recovery signal") proves that the corresponding neutral has a lifetime τ equal to (or more likely exceeding) the time interval between the two collision events. In the present experiments the time interval is of the order of µs, which defines a lower boundary of τ for the neutral formed in the electron-transfer process.

Irrespective of the flight time of the neutral species, the recovery signals of the reionized neutral constitute the base peaks in the $^+NR^+$ mass spectra of $[H_2,O_2]^{\cdot+}$ (Fig. 5). In fact, the geometries of $^2HOOH^{\cdot+}$ and $^2H_2OO^{\cdot+}$ resemble closely those of the corresponding neutral species (see above); this favors the

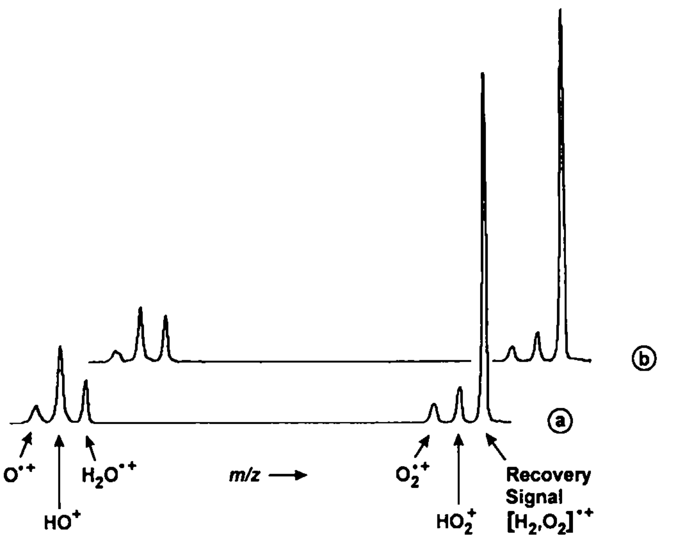

Fig. 5. a) $^+NR^+$ mass spectrum (Xe, 80% T; O_2, 80% T) of B(1)/E(1) mass-selected $[H_2,O_2]^{\cdot+}$ with a neutral flight path of ca. 10 cm. b) $^+NR^+$ mass spectrum (Xe, 80% T; O_2, 80% T) of B(1)/E(1) mass-selected $[H_2,O_2]^{\cdot+}$ with a neutral flight-path of ca. 80 cm [17].

vertical electron-transfer processes during the NR procedure. As far as the fragments are concerned, the relative intensities of the $H_2O^{\cdot+}$ and OH^+ signals differ from those observed in the CA mass spectra (see above) in that OH^+ is much more prominent in the $^+NR^+$ mass spectra. This change is completely in line with the relative energies of the corresponding exit channels for the cationic and neutral species: at the neutral stage homolytic cleavage of hydrogen peroxide into two hydroxyl radicals prevails; these are then reionized, while formation of water is suppressed. Overall, the NR spectra obtained with two different flight paths are quite similar. A minor change occurs in the $H_2O^{\cdot+}/OH^+$ ratio: the amount of reionized water is larger in Figure 5b. This suggests that unimolecular decay of the neutral proceeds by dehydration according to Equation (2). However,

$$^1HOOH \longrightarrow {}^1H_2OO \longrightarrow {}^1H_2O + {}^1O \qquad (2)$$

with respect to the neutral species, the $^+NR^+$ mass spectra alone cannot be regarded as evidence for the formation of water oxide, because the slight differences can also be explained without involving the presence of water oxide.

The intensity of the $^+NR^+$ recovery signal is sufficient to allow a $^+NR^+$/CA experiment with reionized $[H_2,O_2]^{\cdot+}$ ions to be performed, in order to characterize their connectivity (Fig. 4b). It has been demonstrated earlier that, owing to the vertical nature[26–28] of the electron-transfer processes in a NR experiment, the efficiencies for neutralization and reionization may differ substantially for isomeric ions.[29, 30] Consequently, if mixtures of $^2HOOH^{\cdot+}$ and $^2H_2OO^{\cdot+}$ were formed in the ion source, the ratio of these ions may differ from those extracted directly from the source. This is indeed indicated by the comparison of the $^+NR^+$/CA with the CA spectrum of ions generated in the source: the ratio $H_2O^{\cdot+}/HO^+$ decreases from ca. 4:1 in Figure 4a to ca. 2:1 in Figure 4b. With regard to the potential-energy surface of the neutral (Fig. 1), this change can be traced back to the fact that, upon neutralization of $^2H_2OO^{\cdot+}$, the more energetic product ^1H_2OO 1) is less likely to be reionized intact than ^1HOOH because its dissociation is facile and 2) will rearrange to some extent to the more stable hydrogen peroxide. According to this line of reasoning, the recovery ions contain more $^2HOOH^{\cdot+}$ than those generated in the ion source, so that HO^+ gains in intensity relative to $H_2O^{\cdot+}$, which is precisely what is observed in the experiment. Further, the difference between the CA and the $^+NR^+$/CA spectra lends further support to the suggestion that a mixture of $^2HOOH^{\cdot+}$ and $^2H_2OO^{\cdot+}$ is formed by EI of hydrogen peroxide. Thus, the question arises, whether water oxide is indeed formed as a transient neutral in the $^+NR^+$ experiments.

Another, less frequently used variant of the NR methods involves reionization of neutrals to anions.[11, 12] Without going into details, one important feature of this method should, however, be pointed out: in $^+NR^-$ and $^-NR^-$ experiments only neutrals with positive electron affinities (EAs) give rise to recovery signals.[11, 31] In view of the huge negative EA of hydrogen peroxide, the presence of a signal for $[H_2,O_2]^{\cdot-}$ in the $^+NR^-$ spectrum of $[H_2,O_2]^{\cdot+}$ (Fig. 6a) is therefore of prime impor-

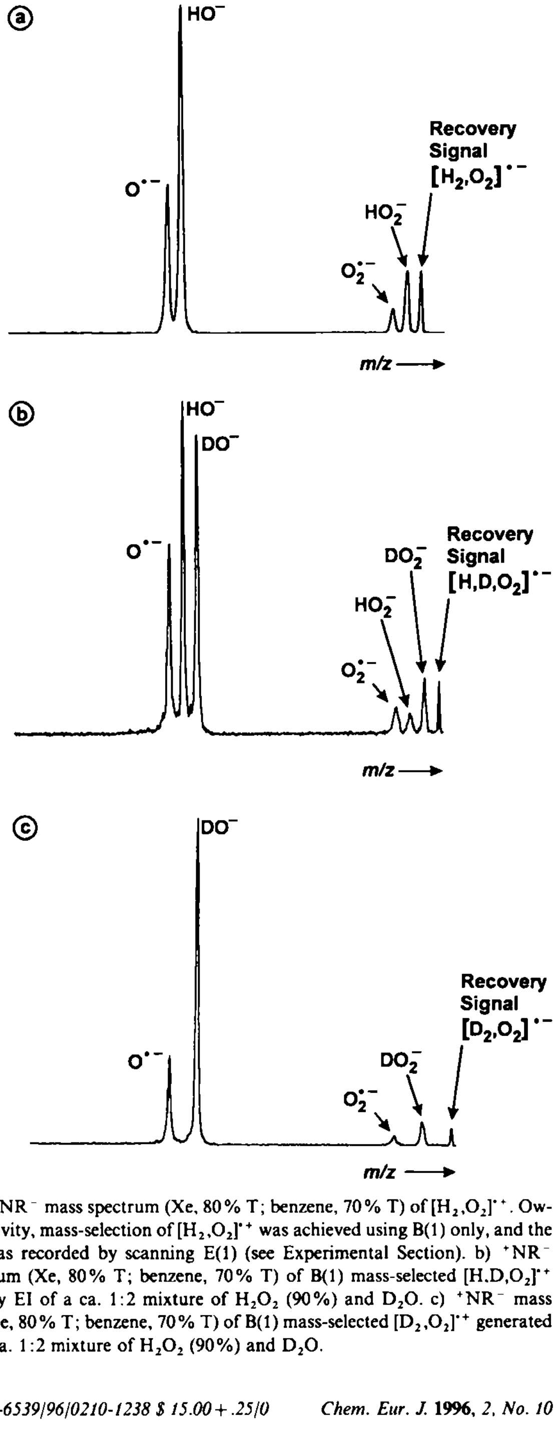

Fig. 6. a) $^+NR^-$ mass spectrum (Xe, 80% T; benzene, 70% T) of $[H_2,O_2]^{\cdot+}$. Owing to sensitivity, mass-selection of $[H_2,O_2]^{\cdot+}$ was achieved using B(1) only, and the spectrum was recorded by scanning E(1) (see Experimental Section). b) $^+NR^-$ mass spectrum (Xe, 80% T; benzene, 70% T) of B(1) mass-selected $[H,D,O_2]^{\cdot+}$ generated by EI of a ca. 1:2 mixture of H_2O_2 (90%) and D_2O. c) $^+NR^-$ mass spectrum (Xe, 80% T; benzene, 70% T) of B(1) mass-selected $[D_2,O_2]^{\cdot+}$ generated by EI of a ca. 1:2 mixture of H_2O_2 (90%) and D_2O.

tance, because it cannot be explained in terms of ground-state ^{1}HOOH. Regarding the identity of the recovery signals, the spectra of the isotopologues (Fig. 6a–c) confirm that neither ^{17}O- nor ^{18}O-containing isobaric species can account for these signals. Rather, the recovery signals must constitute genuine $[H_2,O_2]^{\cdot-}$, $[H,D,O_2]^{\cdot-}$, and $[D_2,O_2]^{\cdot-}$ radical anions, respectively. Also of interest is the apparent slight decrease of the recovery ion intensities upon deuterium incorporation, which indicates the operation of a kinetic isotope effect disfavoring the $^+NR^-$ process.

In order to gain insight into the energetics of the $^+NR^-$ process leading to the formation of $[H_2,O_2]^{\cdot-}$, we have performed the $^+NR^-$ experiment at higher energy resolutions. In this way, the energy offset between the high-energy tails of the precursor ion $[H_2,O_2]^{\cdot+}$ and the recovery signal $[H_2,O_2]^{\cdot-}$ can be determined.[32] To a first approximation, the energy difference (ΔE) for stepwise electron attachments to a cation A^+ in the sequence 1) $A^+ + T \rightarrow A + T^+$ and 2) $A + T \rightarrow A^- + T^+$ to yield the corresponding anion A^- is given by Equation (3), where T stands for the target gas and EA_v for vertical electron

$$\Delta E = IE(T) - EA_v(A^+) + IE(T) - EA_v(A) \qquad (3)$$

affinities.[33] For a calibration of the energy scale in this kind of experiment, we used the process given in Equation (4). When

$$O_2^{\cdot+} \longrightarrow O_2 \longrightarrow O_2^{\cdot-} \qquad (4)$$

xenon is used in both collisions, we obtain ΔE(Xe/Xe) $= 13.6 \pm 0.6$ eV for the formation of $[H_2,O_2]^{\cdot-}$ from the radical cation. When xenon is used for neutralization and benzene for reionization to the anion, we measure $\Delta E(Xe/C_6H_6) = 10.0 \pm 0.6$ eV. Taking $IE(Xe) = 12.1$ eV and $IE(C_6H_6) = 9.3$ eV,[6] we arrive at an average of $EA_v(H_2,O_2^{\cdot+}) + EA_v(H_2,O_2) = 11 \pm 1$ eV.

Remarkably, the charge-reversal signal and also the signals for HO_2^- and $O_2^{\cdot-}$ are much more intense in the $^+CR^-$ spectrum of $[H_2,O_2]^{\cdot+}$ than in the $^+NR^-$ spectrum (Fig. 7). This finding suggests that most of the neutrals formed by electron transfer from the target to the radical cations undergo dissociation, most likely upon reionization, while in the direct charge-reversal process short lifetimes are sampled, and double electron transfer without involving an intermediate also becomes feasible. Again, this finding is in line with the presence of $^2H_2OO^{\cdot+}$ in the beam of cations mass-selected from the ion source and the formation of water oxide as a transient, while for $^2HOOH^{\cdot+}$ the formation of a radical anion in a two-electron transfer is even less likely than in a stepwise sequence (see below).

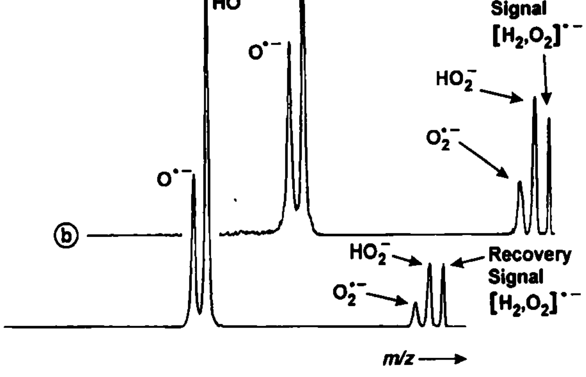

Fig. 7. a) $^+NR^-$ mass spectrum (Xe, 80% T; benzene, 70% T) of B(1) mass-selected $[H_2,O_2]^{\cdot+}$. b) $^+CR^-$ mass spectrum (benzene, 70% T) of B(1) mass-selected $[H_2,O_2]^{\cdot+}$.

Next, we examined the radical anion, that is, the mixture of $^1HO^- \cdot {}^2HO^{\cdot}$ and $^2O^{\cdot-} \cdot {}^1H_2O$ formed upon CI of water with N_2O.[23, 24] In the corresponding $^-NR^+$ and $^-NR^-$ spectra of $[H_2,O_2]^{\cdot-}$, recovery signals for $[H_2,O_2]^{\cdot+}$ and $[H_2,O_2]^{\cdot-}$, respectively, are hardly observed (Fig. 8). In fact, the intensities of these signals are so low that within the experimental accuracy these may be completely due to interferences with isobaric $^{16}O^{18}O^{\cdot-}$, which is co-generated in the ion source under the CI conditions applied. Thus, vertical electron detachment from either $^1HO^- \cdot {}^2HO^{\cdot}$ or $^2O^{\cdot-} \cdot {}^1H_2O$ has a low or even negligible probability of leading to the global minimum ^{1}HOOH or to ^1H_2OO, which are expected to be reionized in the $^-NR^+$ experiment. Rather, upon neutralization, the neutral hydrogen-bonded complexes,[5, 6] $^2HO^{\cdot} \cdot {}^2HO^{\cdot}$ (either singlet or triplet coupled) and $^3O \cdot {}^1H_2O$, fall apart into their components, which give rise to $H_2O^{\cdot+}$, HO^+, and $O^{\cdot+}$ upon reionization in the $^-NR^+$ experiment (Fig. 8a) or HO^- and $O^{\cdot-}$ in the $^-NR^-$ experiment (Fig. 8b), respectively.

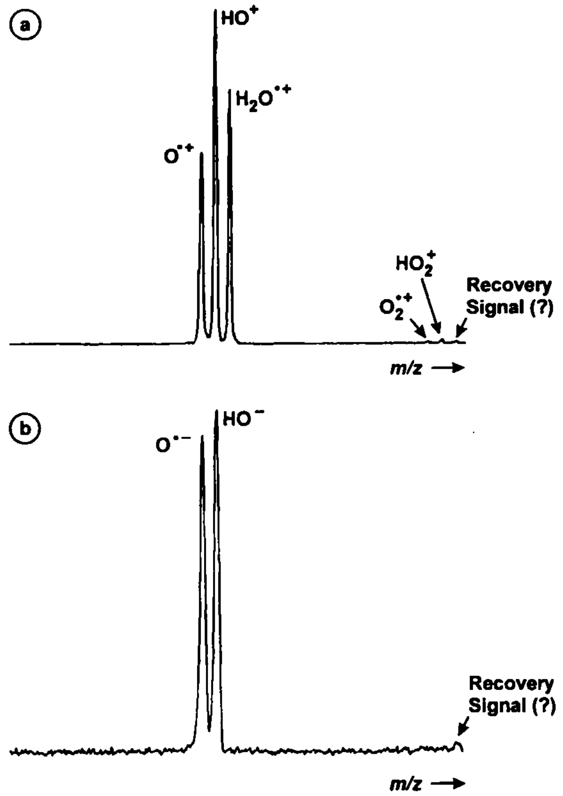

Fig. 8. a) $^-NR^+$ mass spectrum (O_2, 80% T; O_2, 80% T) of B(1)/E(1) mass-selected $[H_2,O_2]^{\cdot-}$. Within experimental error it cannot be assessed whether part of the recovery signal stems from $[H_2,O_2]^{\cdot+}$ or whether it is completely due to isobaric $^{16}O^{18}O^{\cdot+}$ and $H^{16}O^{17}O^+$. b) $^-NR^-$ mass spectrum (O_2, 80% T; benzene, 70% T) of $[H_2,O_2]^{\cdot-}$. Due to sensitivity, mass-selection of $[H_2,O_2]^{\cdot-}$ was achieved using B(1) only, and the spectrum was recorded by scanning E(1); again, within experimental error the recovery signal may be completely due to isobaric $^{16}O^{18}O^{\cdot-}$.

Figure 9 shows the $^+NCR^+$ spectra of $[H_2,O_2]^{\cdot+}$ in which the recovery signals represent the base peaks and fragment ions increase from Figure 9a to e. For a qualitative analysis of the fragmentation patterns in terms of structural implications, we

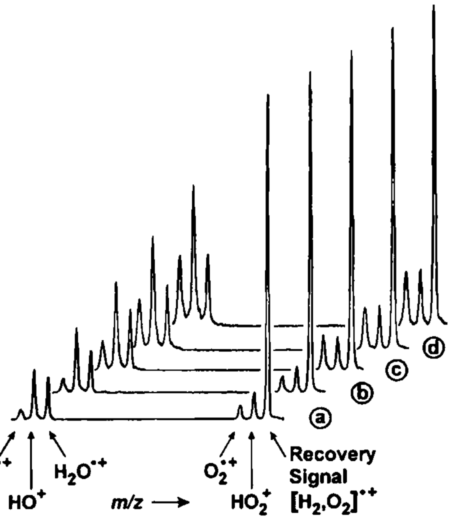

Fig. 9. $^+NCR^+$ mass spectra (Xe, 80% T; O_2, 80% T) of B(1)/E(1) mass-selected $[H_2,O_2]^{\cdot+}$, in which the neutrals were collided with helium at various transmissions: a) no helium, 100% T; b) He, 80% T; c) He, 65% T; d) He, 50% T; and e) He, 35% T.

again consider the HO^+ signal as being characteristic for an O–O bond cleavage in hydrogen peroxide, while $H_2O^{\cdot+}$ points to the presence of a water oxide structure. Upon increasing the helium pressure for collisional activation of the neutrals in the $^+NCR^+$ experiments, the signal for $H_2O^{\cdot+}$ gains in intensity (Fig. 9). Because the conditions of neutralization and reionization are kept constant in these experiments, the increased formation of $H_2O^{\cdot+}$ must be due to unimolecular or collision-induced loss of atomic oxygen from neutral $[H_2,O_2]$. With regard to the potential-energy surface of the neutral (Fig. 1), loss of an oxygen atom may occur directly from neutral ^1H_2OO or, after curve crossing,[34] from ^3H_2OO. According to thermochemistry,[6] dissociation of neutral ^1HOOH into two $^2HO^{\cdot}$ radicals, which are subsequently reionized, should always greatly exceed formation of H_2O and atomic oxygen. Thus, with the collision gas pressure in the $^+NCR^+$ experiments, the HO^+ signal should gain much more in intensity than $H_2O^{\cdot+}$, if ^1HOOH were the only species present in the ion beam. The experimentally observed increase of HO^+ *and* $H_2O^{\cdot+}$ in the series of $^+NCR^+$ mass spectra suggests that in the neutralization of $[H_2,O_2]^{\cdot+}$ the elusive water oxide ^1H_2OO may indeed be formed, at least to some extent.

Discussion

In this section we would like to address two questions in more detail: 1) Is any $^2H_2OO^{\cdot+}$ formed upon EI of hydrogen peroxide? 2) Which species of the potential-energy surfaces can account for the observation of the recovery signal in the $^+NR^-$ experiment?

To answer the first question, it is necessary to recall the essential aspects of the doublet potential-energy hypersurface of the radical cation (Fig. 2). Both isomers of $^2[H_2,O_2]^{\cdot+}$ are trapped in relatively deep wells with respect to the thermochemical thresholds[6] of the possible homolytic bond cleavages ($^2H_2OO^{\cdot+} \rightarrow {}^2H_2O^{\cdot+} + {}^3O$, 81 kcal mol^{-1}; $^2HOOH^{\cdot+} \rightarrow {}^3HO^+ + {}^2HO^{\cdot}$, 105 kcal mol^{-1}; $^2[H_2,O_2]^{\cdot+} \rightarrow HO_2^+ + {}^2H^{\cdot}$, 106 kcal mol^{-1}) as well as with respect to dehydrogenation to yield $^2O_2^+ + {}^1H_2$, which has a barrier in excess of the thermochemical threshold of 69 kcal mol^{-1}. Thus, ionization with energetic electrons may lead to formation of radical cations with significant internal energies. There can therefore be no principle argument against formation of $^2H_2OO^{\cdot+}$ by rearrangement of $^2HOOH^{\cdot+}$ via ^2TS (61 kcal mol^{-1}). The experimental findings provide two pieces of evidence in favor of the concomitant formation of $^2H_2OO^{\cdot+}$ upon electron ionization of hydrogen peroxide: 1) The dependence of the CA spectra of $^2[H_2,O_2]^{\cdot+}$ on the energy of the ionizing electrons (Table 1) is exactly in line with the formation of $^2H_2OO^{\cdot+}$: the $H_2O^{\cdot+}$ fragment, assumed to be characteristic for water oxide, increases with increasing electron energy and reaches a plateau at $E_e > 20$ eV. 2) The difference between the CA and the $^+NR^+$/CA spectra (Fig. 4) indicates a change in the composition of the reionized beam and an enrichment of $^2HOOH^{\cdot+}$; this also suggests that water oxide radical cations were formed to some extent in the ionization event. Further, the deuterium isotope effects on the recovery ion intensities in the $^+NR^-$ spectra are in line with a decreasing fraction of water oxide radical cation in the beam upon increasing deuteration, because the rearrangement $^2HOOH^{\cdot+} \rightarrow {}^2H_2OO^{\cdot+}$ is hindered. Finally, simply the formation of $^2H_2O^{\cdot+}$ upon collisional activation of $^2[H_2,O_2]^{\cdot+}$ is indicative for the presence of $^2H_2OO^{\cdot+}$, because an intact water molecule can only be formed by fragmentation of water oxide. Thus, for the following, we assume that $^2H_2OO^{\cdot+}$ is indeed co-generated upon EI of hydrogen peroxide, although, strictly speaking, we have no *direct* evidence for its formation.

Of the various NRMS studies presented here, the recovery signal in the $^+NR^-$ spectrum of $^2[H_2,O_2]^{\cdot+}$ is the most telling with respect to the formation of water oxide, because it certainly cannot be explained by invoking only the presence of hydrogen peroxide. This conclusion follows directly from the fact that it is established beyond any reasonable doubt that the singlet ground state of hydrogen peroxide exhibits a large, negative EA_v (ca. -58 kcal mol^{-1}).[23]

Let us now consider in more detail the various possible neutrals that may be formed upon neutralization of the radical cation and their reionization to anions [Eq. (5)]. Here, reac-

$$^2HOOH^{\cdot+} \longrightarrow {}^1HOOH \qquad (5a)$$

$$^2HOOH^{\cdot+} \longrightarrow {}^3HOOH \qquad (5b)$$

$$^2H_2OO^{\cdot+} \longrightarrow {}^1H_2OO \qquad (5c)$$

$$^2H_2OO^{\cdot+} \longrightarrow {}^3H_2OO \qquad (5d)$$

$$^2HOOH^{\cdot+} \longrightarrow {}^1HOOH^{*} \qquad (5e)$$

tion (5e) denotes the formation of vibrationally excited hydrogen peroxide; this possibility was not considered for the other species, because both triplet states will immediately dissociate upon significant excitation, while singlet water oxide will immediately rearrange to ^1HOOH.

The crucial question with respect to the $^+NR^-$ experiment is which of the reactions (5) leads to a species with a positive vertical electron affinity (EA_v), so that reionization to an anion can occur. Certainly, reaction (5a) can be excluded, because even though hydrogen peroxide is a stable neutral, its $EA_v(^1HOOH)$ is very negative (see above). Reactions (5b) and (5d) lead to the respective triplet species. In their ground-states ^3HOOH and ^3H_2OO may well have positive electron affinities,[22] because they contain long O–O bonds and can thus be regarded as loose complexes of fragments (e.g., $^2HO^{\cdot}$ and ^3O), which have significant EAs (1.8 and 1.5 eV, respectively).[6] However, when these triplets are formed upon vertical neutralization of the corresponding cations [Eq. (5 b) and (5 d)], owing to large geometry differences, the Franck-Condon factors will be very unfavorable and lead to a significant energy deposition in the triplets. The weak binding forces in the triplet species will then lead to their dissociation within a few vibrational periods (i.e., a ps lifetime), rather than generating neutrals with μs lifetimes, which are sampled in the $^+NR^-$ experiment.

Following these arguments, the only ground-state species that can give rise to the $[H_2,O_2]^{\cdot -}$ signal is ^1H_2OO, because water oxide in its singlet state resides in a potential well and may exhibit a positive electron affinity. In order to assess the magnitude of the latter, we calculated $EA_v(^1H_2OO)$, which turned out to be slightly negative ($-7\,kcal\,mol^{-1}$) at the CCSD(T)/6-311 + + G**//MP2/6-311G** level of theory.[35] Thus, for water oxide no recovery signal is expected. However, a fraction of these neutrals is certainly rovibrationally excited and may explore geometries with a positive EA_v. Basically, a positive EA_v requires elongation of the O–O distance (r_{O-O}) in order to reduce electron repulsion in the corresponding radical anion. In order to test this hypothesis, we examined EA_v of ^1H_2OO as a function of r_{O-O} (Fig. 10). In fact, the energy demand for stretching the O–O bond in ^1H_2OO from $r_{O-O} \approx 1.5$ Å to $r_{O-O} \approx 1.9$ Å is relatively small even in the vicinity of the barrier for rearrangement to ^1HOOH. On the other hand, in the same range of O–O distances $EA_v(^1H_2OO)$ increases significantly and even becomes positive at $r_{O-O} > 1.75$ Å.

Although the basis set used in these computations (6-311 + + G**) is by no means complete, implying that $EA_v(^1H_2OO)$ may even be larger,[36] these results can be combined to a consistent scenario for the formation of the recovery signal in the $^+NR^-$ experiment: vertical neutralization of slightly excited $^2H_2OO^{\cdot +}$ leads to ^1H_2OO [Eq. (5 c)] with a small amount of excess internal energy such that rearrangement to the much more stable ^1HOOH is slow or even prevented; thus, singlet water oxide may well survive within the μs timeframe.[3] However, even a small amount of excitation energy in the neutral may suffice to allow ^1H_2OO to adopt geometries with larger r_{O-O} and positive electron affinities. Hence, though with low efficiency, reionization to the radical anion becomes feasible. Further, this scenario does not conflict with the energy demand of the $^+NR^-$ process ($IE_v + EA_v = 11 \pm 1$ eV, see above) in that neutralization occurs close to the ground-state geometry of the cation ($IE_v \approx 9.5$ eV). Neutral water oxide survives for several thousands of vibrational periods within the potential well. Finally, those vibrationally excited species with $r_{O-O} > 1.75$ Å ($EA_v > 0$ eV) can pick up an electron in the reionization event to yield $H_2OO^{\cdot -}$; probably, the latter anion only serves as a transient species en route to $^1HO^- \cdot {}^2HO^{\cdot}$ and/or $^2O^{\cdot -} \cdot {}^1H_2O$.

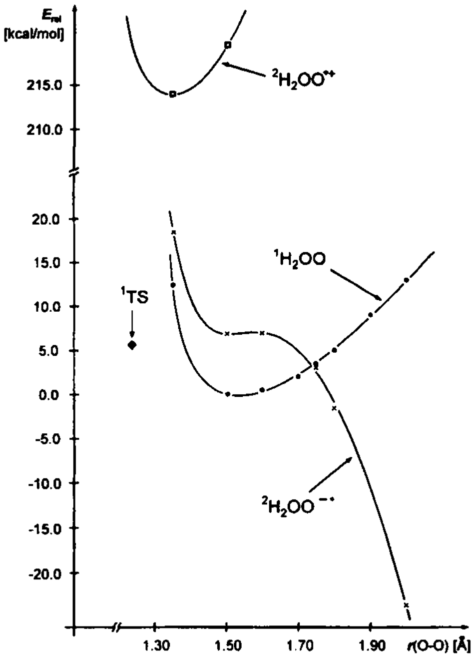

Fig. 10. Projection of the potential-energy surfaces of $^2H_2OO^{\cdot +}$ (□), ^1H_2OO (●), and $^2H_2OO^{\cdot -}$ (×) on the O–O coordinate determined by single-point energy calculations (CCSD(T)/6-311G**//MP2/6-311 + + G**) [35,36]. Here, the O–O distances were kept frozen, while all other parameters of the neutral species were fully optimized, and these geometries were used to calculate the energetics for the vertical transitions to the corresponding cationic and anionic species. The relative energy of ^1TS to yield hydrogen peroxide at this level of theory is displayed (◆), though it cannot be regarded as a part of this projection of the potential-energy surface.

In this context, we would like to refer to a possible pitfall of the NRMS technique: it has repeatedly been argued that the NR technique suffers from the fact that the state(s) in which the neutrals are generated are ill defined. For example, in the case of $^+NR^+$ and $^-NR^+$ experiments, the neutral may be formed in a highly excited Rydberg state,[37] which then gives rise to a recovery signal. In fact, invoking these highly excited states is a good option in $^+NR^+$ and $^-NR^+$ experiments, because detachment of the loosely bound electron in a Rydberg state is facile, and the reionization step is thus relatively efficient. However, the opposite applies for $^+NR^-$ and $^-NR^-$ experiments, because electron attachment to a Rydberg state is expected to be difficult and will lead either to a collapse into the ground state (which exhibits no EA_v for ^1HOOH) or to a double Rydberg anion. According to the arguments put forward by Simons and Gutowski[38] the formation of a double Rydberg molecular anion of hydrogen peroxide in the $^+NR^-$ experiment is also unlikely, because Rydberg states of neutral HOOH are likely to dissociate.[39] Moreover, formation of highly excited Rydberg states can be excluded on energetic grounds, as this would be associated with much larger energy differences ΔE than obtained experimentally (see above), because the excitation energy to a Rydberg state must be taken from the kinetic energy of the projectile.

Hence, apart from water oxide, there are two other options that remain to be considered as possible sources of the recovery signal in the $^+NR^-$ spectrum of $[H_2,O_2]^{\cdot +}$:

1) Despite the large negative EA_v of ^1HOOH, the neutral may attach an electron to form a very loosely bound Rydberg state of the anion, which is better described in terms of a complex of the type $[^1HOOH \cdot e^-]$. The energy required to detach an electron from such an anion will be rather small, and it will hardly survive an NR experiment; however, we cannot rigorously exclude this possibility, because it does not conflict with the measured energy demand of the $^+NR^-$ process.

2) Reaction (5 e) may lead to a vibrationally highly excited neutral ^1HOOH in which the O–O bond length is stretched to such an extent that the corresponding neutral may exhibit a positive EA_v.[22] However, this conjecture can certainly not be evaluated in terms of the static pictures of the potential-energy surfaces applied here.

These two options are far beyond the scope of the present study. Nevertheless, the transient formation of neutral water oxide in terms of the scenario depicted in Figure 10 not only accounts for the $^+NR^-$ spectrum, but also for the other experiments, namely, the isotope effect on the $^+NR^-$ efficiencies, the increase of the recovery signal in the $^+CR^-$ experiment, the practical absence of survivor signals in the $^+CR^-$ and $^+NR^-$ spectra, and the trend of the ratio $H_2O^{\cdot +}/HO^+$ upon $^+NCR^+$ (see above). Thus, the present experiments provide a credible, though not ultimate experimental proof for the existence of neutral water oxide.[3]

Conclusion

Six different types of NR experiments together with detailed theoretical considerations provide strong support for the formation of singlet water oxide as a transient upon neutralization of $[H_2,O_2]^{\cdot+}$ (i.e., upon electron ionization hydrogen peroxide is thought to rearrange to $^2H_2OO^{\cdot+}$). The recovery signal in the $^+NR^-$ spectrum of $[H_2,O_2]^{\cdot+}$ can be explained consistently by postulating ^1H_2OO as intermediate. In a strict sense, these experiments provide only an indirect proof for the existence of water oxide, and other states may play a role (e.g., neutrals of quartet species $^4HOOH^{\cdot+}$ arising from high-spin coupling of $^3HO^+$ and $^2HO^{\cdot}$, or excited singlet states of water oxide). For an ultimate assignment of the recovery signal in the $^+NR^-$ experiment, sophisticated theoretical treatments including excited states and reaction dynamics are required. With regard to the potential-energy surface of neutral $[H_2,O_2]$, it remains questionable whether a *direct* experimental detection of water oxide will ever be possible, not to mention its bulk production.

The combination of experimental and theoretical methods demonstrates that 1) the shallow minimum of water oxide may be accessible by one-electron reduction of the radical cation, and 2) within its potential well, water oxide can adopt geometries which can exist in the cationic, neutral, and anionic state. Thus, these findings show once more that vertical electron transfer can be used to generate elusive neutral species which are difficult to obtain otherwise.[9, 10, 12]

Finally, the present results suggest that water oxide is a viable molecule in the gas phase and that it may play a role as an intermediate in oxidation reactions involving hydrogen peroxide.[1, 4] In fact, in the condensed phase, the vacant site of the oxo atom in ^1H_2OO can interact by quite a variety of possible mechanisms, which could help to stabilize the water oxide molecule and facilitate O atom transfer from peroxides to other substrates. Consequently, hydrogen peroxide activation may have to be reexamined to take into account, not only classical homo- or heterolytic mechanisms, but also pathways involving water oxide.[40, 41, 42]

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