Efficient electrochemical splitting of H₂O to O₂ and H₂ fuels has become an important goal in the quest for a renewable source of energy.[1] A major source of the inefficiency of this process is the significant overpotential associated with the anodic oxygen evolution reaction (OER). Understanding the mechanism of the OER could help in identifying the elementary processes contributing to OER overpotential and their relationship to the anode composition and morphology. While the OER has been investigated both experimentally and theoretically for over 50 years, its mechanism and the identity of the chemical intermediates involved remain uncertain.[2–7] Two principal pathways have been postulated for the OER on metal surfaces, such as gold (Au). The first involves a direct recombination of oxygen atoms to give O₂, as shown in Equations (1)–(4):

\[
\begin{align*}
M + H_2O &\rightarrow M-OH + H^+ + e^- \quad \text{(in acids)} \\
M-OH &\rightarrow M-O + H^+ + e^- \quad \text{(M = metal site, e = electron)} \\
M-OH + M-OH &\rightarrow M-O + H_2O + M \\
M-O + M-O &\rightarrow O_2 + 2M 
\end{align*}
\]

(1)–(4)

The second mechanism consists of a sequence of four consecutive one-electron oxidations, the first two of which are identical to those of the first mechanism, and the next two are as shown in Equations (5) and (6):

\[
\begin{align*}
M-O + H_2O &\rightarrow M-OOH + H^+ + e^- \quad \text{(in acids)} \\
M-OOH &\rightarrow M+O_2 + H^+ + e^- 
\end{align*}
\]

(5)–(6)

In this case, the oxygen coupling step produces a hydroperoxy species (M–OOH), which then dissociates to produce O₂. Recent theoretical studies indicate that the second mechanism for oxygen coupling should be favored because it has a lower activation barrier.[4,5] Hydroperoxy species have also been suggested as key intermediates in the electrochemical reduction of O₂ (ORR), and initial experimental evidence for their presence has been presented.[6,7] It is notable nonetheless, that while OOH species have been envisioned to be critical for OER, the species have not been observed under electrochemical conditions.

Herein we report the first spectroscopic identification of surface-bound OOH as intermediates of oxygen evolution reaction occurring on the surface of a gold catalyst. The presence of OOH species was observed by in situ electrochemical surface-enhanced Raman spectroscopy (SERS) in both acidic and basic electrolytes. Roughened gold, rather than a more active catalyst such as platinum, was chosen for investigation because it is an excellent SERS substrate.[10] It was also anticipated that the decomposition of hydroperoxy species on Au might be slower than on more active metals, which would result in a higher accumulation of OOH species and facilitate their spectroscopic detection. A confocal Raman microscope coupled with a high numerical aperture water-immersion objective and 633 nm excitation was used to record these spectra. Real-time SER spectra of a Au electrode in 1 M HClO₄ during a linear voltammetry sweep from 1.0 to 1.65 V are shown in Figure 1. At 1.0 V, the Au surface is reduced, as can be seen from its relatively featureless SER spectrum. The peak at 934 cm⁻¹ is assigned to the symmetric stretching mode of ClO₄⁻.[11] The elevated spectral background is associated with high SERS activity exhibited by a metal surface, and has been previously assigned to photons emitted during the annihilation of inelastically scattered localized surface plasmons.[12] At 1.1 V, a feature appears at 568 cm⁻¹ that can be attributed to Au–O stretching [ν(Au-O)] vibrations of Au oxide. As the potential increases, the position of this band blue shifts to 598 cm⁻¹. Assignment of this band to a ν(Au–O) vibration as opposed to a ν(Au–OH) vibration is supported by the following observations: 1) A recent theoretical and high-resolution electron energy loss spectroscopy study has affirmed that the Au–O band lies at 580 cm⁻¹.[13] 2) Vibrational studies of gaseous Au(OH)₂ and bulk Au(OH)₃ have shown that the ν(Au–OH) vibration is observed at 677 and 635 cm⁻¹ respectively.[14,15] 3) Au has been shown to have a greater propensity to form metal oxides compared to metal hydroxides, especially in an acidic environment.[16]

At 1.4 V and above where O₂ gas evolution occurs, a feature was observed reproducibly at ~820 cm⁻¹ (Figures 1a,b and
Additional information about this band was also obtained from SER spectra recorded from a Au surface held at 1.4 V, and then reduced to 1.2 V. The spectra are presented in Figure 2 a. It can be seen that the peak at 822 cm\(^{-1}\) is only visible at 1.4 V. This band reappears if the potential is again increased from 1.2 to 1.4 V, whereas the rest of the spectrum remains unchanged. These observations demonstrate that the generation and stability of the band at \(\approx 820\) cm\(^{-1}\) is dependent on the applied potential.

Repeating the same experiments with 0.1 m KOH yields the same signal at 827 cm\(^{-1}\), albeit with weaker intensity (Figure 2 b) possibly due to more extensive deprotonation of Au–OOH in the basic solution. Galvanostatic/SERS measurements were also performed on the Au electrode and the same results were obtained (Section S3 in the Supporting Information).

The band observed at 815–830 cm\(^{-1}\) in Figures 1, 2 is characteristic of the \(\nu(O–O)\) vibration in both peroxo (M–OO) and hydroperoxy (M–OOH) species. For example, the \(\nu(O–O)\) band lies between 817 and 824 cm\(^{-1}\) for Fe–OO complexes, whereas the \(\nu(O–O)\) band lies between 796–810 cm\(^{-1}\) for Fe–OOH complexes and between 824 and 830 cm\(^{-1}\) for Co–OOH complexes.\(^{18–20}\) The assignment of the band at 815–830 cm\(^{-1}\) to the \(\nu(O–O)\) vibration of Au–OOH was corroborated by performing OER/SERS with deuterated electrolytes. The position of the band shifted from 818 to 821 cm\(^{-1}\) in 1 m DCIO\(_4/D_2O\), and from 826 to 830 cm\(^{-1}\) in 0.1 m KOD/D\(_2O\) (Figure S8 in the Supporting Information). These reproducible shifts are consistent with predictions for a hydroperoxy complex: similar observations have been made for the \(\nu(O–O)\) vibration of OOH (810 cm\(^{-1}\)) and OOD (814 cm\(^{-1}\)) ligands in Fe complexes, as well as for H\(_2O_2\) (876 cm\(^{-1}\)) and D\(_2O_2\) (878 cm\(^{-1}\)).\(^{18,20,21}\) The small increase in the \(\nu(O–O)\) frequency for the deuterated hydroperoxy has been attributed to coupling between the O–O stretching and O–D bending modes.\(^{22}\)

The possibility that the 815–830 cm\(^{-1}\) band is due to Au–peroxy species can be excluded for two reasons. First, the energy shift of this band by \(\pm 3–4\) cm\(^{-1}\) upon substitution of H\(_2O\) for D\(_2O\) cannot be attributed to differences in hydrogen bonding between light and heavy water with Au–OO. This conclusion is supported by previous studies of metal-peroxy complexes. The \(\nu(O–O)\) frequencies of these species were not affected by the medium (H\(_2O\) or D\(_2O\)) in which they were dissolved.\(^{18,20,21}\) Second, at the high anodic potentials where the band at 815–830 cm\(^{-1}\) is observed, O\(_2^2–\) would be readily oxidized to O\(_2^2+\).\(^{23}\)

The assignment of the band at 815–830 cm\(^{-1}\) to other forms of oxygen associated with Au (e.g. superoxo, oxo, and hydroxy) can also be excluded. The \(\nu(O–O)\) vibration for superoxo spe-
cies (O\textsubscript{2}−) occurs in the range of 1000–1200 cm\textsuperscript{-1}, as previously shown for Pt electrodes (1005–1016 cm\textsuperscript{-1}) and for pure or mixed cerium oxides (1126 cm\textsuperscript{-1}).\textsuperscript{[24, 25]} We have also considered the possibility that ν(Au−O) vibrations of the Au−oxo moieties are responsible for the 815−830 cm\textsuperscript{-1} band. This species, however, is intrinsically unstable and has never been generated on gold surfaces.\textsuperscript{[13]} Furthermore, Au−oxo species with an intermediate Au−O bond strength [ν(Au−O) expected at 700 cm\textsuperscript{-1}] were not observed during the voltammetry sweep (Figure 1a).\textsuperscript{[26]} The presence of Au−O can also be ruled out based on XPS studies of electrochemically oxidized Au surfaces. Only O\textsubscript{1}s photoelectrons with a binding energy of 530 eV (Au oxide) were recorded for Au surfaces held at OER potentials.\textsuperscript{[27, 28]} O\textsubscript{1}s photoelectrons expected for Au−O at 531.5 eV [O\textsubscript{2}− (532 eV), O\textsubscript{2}− (535 eV)] were not detected. The small H/D isotopic shift of the 815−830 cm\textsuperscript{-1} band also excludes the likelihood that the signal originates from Au−O−H bending [δ(Au−O−H)] vibrations, since this vibration will decrease by 150−250 cm\textsuperscript{-1} for the deuterated isotope. For example, δ(Ag−O−H) and δ(Ag−O−D) bands occur at ~800 and ~550 cm\textsuperscript{-1} respectively.\textsuperscript{[29]}

At the anodic potentials applied during SERS, the main reactions are those for oxygen evolution; neither oxygen reduction nor irreversible gold oxide desorption (Figure S2, Supporting Information) occur at these potentials. There is the possibility, though, for anodic oxidation of H\textsubscript{2}O to H\textsubscript{2}O\textsubscript{2} (in acid) or OOH\textsuperscript{−} (in base) at the highest potentials used herein.\textsuperscript{[30]} Therefore, control experiments were performed to exclude the effects of these reactions on our observations. We set the potential of the Au electrode in 1 M HClO\textsubscript{4} at 1.45 V, at which the maximum equilibrium concentration of H\textsubscript{2}O\textsubscript{2} is 2.6 × 10\textsuperscript{−4} M. 1 × 10\textsuperscript{−3} M of H\textsubscript{2}O\textsubscript{2} was then added to the electrolyte. The SER spectra collected before and after adding H\textsubscript{2}O\textsubscript{2} exhibited the same spectral features. Identical findings were obtained for experiments performed in 0.1 M KOH + H\textsubscript{2}O.\textsuperscript{[31]} These experiments demonstrate unambiguously that any H\textsubscript{2}O\textsubscript{2} or OOH\textsuperscript{−} generated from the oxidation of H\textsubscript{2}O do not contribute to the 815−830 cm\textsuperscript{-1} band. Both H\textsubscript{2}O\textsubscript{2} and OOH\textsuperscript{−} are expected to be unstable compared to surface-bound OOH, and should dissociate spontaneously to O\textsubscript{2} gas at the Au electrode (Section S4 in the Supporting Information).

A mechanism for the electrochemical evolution of O\textsubscript{2} on Au can now be proposed on the basis of our observations. At 1.0 V, the surface is devoid of observable adspecies, with the exception of ClO\textsubscript{4}− anions present near the anode surface. As the potential increases, Au oxide is formed in agreement with both the work of Desilvestro and Weaver, and with the four one-electron transfer mechanism.\textsuperscript{[14, 15]} Above 1.4 V, oxygen coupling occurs to produce surface-bound OOH. The appearance of the 815−830 cm\textsuperscript{-1} band only after Au oxide has formed indicates that Au−OOH is not an intermediate in Au oxide formation (Figure 1a). This conclusion is also supported by the theoretical calculations of Rossmeisl et al., which shows that OOH species are formed on Au only at potentials above which a surface oxide layer has been formed.\textsuperscript{[32]} On the other hand, the observation of OOH species in both the acidic and basic systems is consistent with the work of Rossmeisl et al., in which OOH was postulated to be the intermediate from which O\textsubscript{2} is formed.\textsuperscript{[33]}

Thus, it is not surprising that OOH species are observed before the visible commencement of O\textsubscript{2} gas evolution at 1.6 V because the elementary steps of the OER process occur sequentially over a range of potentials starting from 1.1 V (Figure 1).\textsuperscript{[31]} The shifts in frequencies of the ν(O−O) and ν(Au−O) bands with potentials can be attributed to an electrochemical vibrational Stark effect.

While OOH has been implicated as an intermediate during the OER on various transition metal electrodes, this species has hitherto never been identified spectroscopically.\textsuperscript{[2, 4, 6, 7]} The elementary reaction that forms Au−OOH cannot be deduced directly from the present study. Recent theoretical work by Fang and Liu on oxygen coupling on Pt(111) and stepped Pt(211) surfaces indicates that this process is likely to occur via the reaction O−O−OH−OOH only on an oxygen-covered Pt(211) surface, since the activation barrier for this process on the Pt(111) surface is in excess of 1 eV.\textsuperscript{[21]} These authors also show that oxygen coupling via the reactions O−O−O\textsubscript{2} or OH−OH−HO\textsubscript{2} on either surface should not occur because the activation barriers are prohibitively high. Oxygen coupling via O−O−O\textsubscript{2} on both clean and oxidized Au surfaces has also been excluded by Rossmeisl et al.\textsuperscript{[34]} Thus, it is reasonable to infer that oxygen coupling on Au occurs only on the stepped oxidized surfaces via the reaction O−OH−OOH. However, other pathways to OOH are also possible, such as O−H\textsubscript{2}O−O−OOH + H\textsuperscript{+} + e.\textsuperscript{[18]}

In summary, surface-bound OOH was observed on a Au anode at potentials where O\textsubscript{2} is released from the electrode surface, leading us to conclude that Au−OOH species are the precursors to O\textsubscript{2}, as has been suggested by theoretical studies of OER on Au and Pt.\textsuperscript{[4, 5]} The identification of this species is a result of the judicious choice of OER potentials, isotope labeling experiments and the high detection sensitivity afforded by the Raman microscope system (with a water immersion objective) used. We believe that the findings of this study will contribute significantly to the understanding of the elementary processes involved in the electrochemical oxidation of water.

**Experimental Section**

Details of the experiments are described in Section S1 of the Supporting Information. In brief, SERS experiments were performed with an epi-illumination confocal Raman microscope, using a 633 nm HeNe laser as the excitation source. A high numerical aperture (N.A. 1.23) water immersion objective was used to collect the Raman signals. The electrochemical cell was based on a round teflon dish. The counter and reference electrodes were respectively a Pt wire, and a Ag/AgCl (in acids) or Hg/HgO (in bases). The Au disc electrode was roughened electrochemically for enhanced SERS activity. The cell potential was controlled by a galvanostat/potentiostat and referenced to the Ag/AgCl.

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