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Numerical simulations of nonequilibrium chemical reactions in a pulsating air bubble have been performed for various ultrasonic frequencies (20 kHz, 100 kHz, 300 kHz, and 1 MHz) and pressure amplitudes (up to 10 bars). The results of the numerical simulations have indicated that the main oxidant is OH radical inside a nearly vaporous or vaporous bubble which is defined as a bubble with higher molar fraction of water vapor than 0.5 at the end of the bubble collapse. Inside a gaseous bubble which is defined as a bubble with much lower vapor fraction than 0.5, the main oxidant is H2O2 when the bubble temperature at the end of the bubble collapse is in the range of 4000–6500 K and O atom when it is above 6500 K. From the interior of a gaseous bubble, an appreciable amount of OH radical also dissolves into the liquid. When the bubble temperature at the end of the bubble collapse is higher than 7000 K, oxidants are strongly consumed inside a bubble by oxidizing nitrogen and the main chemical products inside a bubble are HNO2, NO, and HNO3.© 2007 American Institute of Physics. [DOI: 10.1063/1.2790420]

I. INTRODUCTION

When a liquid is irradiated by a strong ultrasonic wave, many tiny gas bubbles appear, which is called acoustic cavitation. 1,2 The bubbles expand at the rarefaction phase of ultrasound and collapse at the compression phase. When the ambient bubble radius, which is defined as the bubble radius when ultrasound is absent, is in a certain range and the acoustic amplitude is above a threshold one, a bubble collapses very violently and the temperature inside a bubble increases dramatically due to the quasiadiabatic compression, where “quasi” means that appreciable thermal conduction takes place across the bubble surface. 3 At the final stage of the collapse, faint light is emitted from a bubble, which is called sonoluminescence. 4,5 In addition to the light emission, water vapor is dissociated inside the heated bubble in liquid water and chemical species such as OH radical and H atom are created inside the bubble. The oxidants such as OH radical and H2O2 have been detected experimentally in liquid water irradiated by ultrasound. 6,7 On the other hand, H atoms hardly penetrate into the liquid phase from the interior of a bubble. 8 Chemical reactions induced or accelerated by ultrasound are generally called sonochemical reactions. 9

Hart and Henglein 10 have suggested that oxygen atom may also be produced by ultrasound in liquid water in which oxygen is dissolved. Furthermore, the authors 11 have reported the results of numerical simulations of nonequilibrium chemical reactions inside a bubble under the condition of the experiment of single-bubble sonochemistry 12 and have suggested that an appreciable amount of oxygen atom could be produced by a bubble.

In the present study, numerical simulations of nonequilibrium chemical reactions inside an air bubble have been performed for various ultrasonic frequencies and pressure amplitudes in order to study the relationship between the bubble temperature and the main oxidant created inside a bubble.

II. MODEL

The present model has been fully described in Refs. 11 and 13–15 and has been validated for an isolated spherical bubble from the study of single-bubble sonochemistry. 11 An isolated bubble is defined as a bubble whose pulsation is described by the (modified) Rayleigh-Plesset equation neglecting the influence of neighboring bubbles or solid objects as in the case of the single-bubble sonoluminescence and sonochemistry.

The following is a brief description of the present model. The pressure and temperature inside a spherical bubble are assumed to be spatially uniform except at the thermal boundary layer near the bubble wall. The thickness of the thermal boundary layer is assumed as nλ where n=7 (Ref. 16) and λ is the mean free path of a gas molecule inside a bubble.

In the present model, the following effects are taken into account: nonequilibrium evaporation and condensation of water vapor at the bubble wall, nonequilibrium chemical reactions of gases and vapor inside a bubble, thermal conduction both inside and outside a bubble, diffusion of gases into or out of a bubble, and the liquid compressibility.

The modified Keller equation (the modified Rayleigh-Plesset equation) of the bubble radius R is numerically integrated with time by Euler’s method.
The rate of each chemical reaction is calculated using the modified Arrhenius equation. For example, the rate of the reaction \( \text{H}_2\text{O} + M \rightarrow \text{H} + \text{OH} + M \) is

\[
r_f = A_f T^{b_f} \exp(-C_f / T)[\text{H}_2\text{O}][M],
\]

where the rate constants \( A_f, b_f, \) and \( C_f \) are given in Table I of Ref. 11. \( T \) is the temperature, \( [\text{H}_2\text{O}] \) is the concentration of water vapor molecules, and \( [M] \) is the concentration of particles (the third body). \( T^{b_f} \) means \( T \) to the \( b_f \). The subscript \( f \) denotes the forward reaction. The error bars of the reaction rates calculated by the chemical kinetics model used in the present numerical simulations are less than one order of magnitude. Details of the error bars have also been described in Refs. 15–20.

The rate of the backward reaction is calculated in a similar manner.

\[
r_b = A_b T^{b_b} \exp(-C_b / T)[\text{H}[\text{OH}][M],
\]

where the rate constants \( A_b, b_b, \) and \( C_b \) are given in Table I of Ref. 11, and \( [\text{H}] \) and \( [\text{OH}] \) are the concentration of hydrogen atom and that of \( \text{OH} \) radical, respectively. The subscript \( b \) denotes the backward reaction.

In the present model, the temperature inside a bubble (\( T \)) is calculated as follows:

\[
T = \frac{(E + a n_i^2 / V)}{C_V n_i},
\]

where \( E \) is the thermal energy of the bubble, \( a \) is the van der Waals constant, \( n_i \) is the total number of molecules inside the bubble in mol, \( V \) is the bubble volume, and \( C_V \) is the molar heat of the gases and vapor inside the bubble.

The change of the thermal energy of a bubble (\( \Delta E \)) in time \( \Delta t \) is expressed by

\[
\Delta E(t) = -p(t)\Delta V(t) + 4\pi R^2 \frac{N_A e_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} m \Delta t + 4\pi R^2 \Delta t - \frac{2}{3} M \Delta t^2,
\]

where \( p \) is the pressure inside a bubble which is calculated using van der Waals equation of state, \( \Delta V \) is the change in the bubble volume, \( R \) is the bubble radius, \( N_A \) is the Avogadro constant, \( M_{\text{H}_2\text{O}} \) is the molecular weight of water, \( m \) is the rate of evaporation of water at the bubble wall, \( e_{\text{H}_2\text{O}} \) is the energy carried by an evaporating or condensing vapor molecule, \( k \) is the thermal conductivity of the gas, \( \partial T / \partial r |_{r=R} \) is the temperature gradient at the bubble wall, \( r_{sf} (r_{sh}) \) is the forward (backward) reaction rate per unit volume and unit time, \( \Delta H_{sf} \) is the enthalpy change in the forward reaction (when \( \Delta H_{sf} < 0 \), the reaction is exothermic), \( M \) is the total mass of the gases and vapor inside the bubble, and the dot denotes the time derivative (\( d/dt \)). The first term in the right-hand side of Eq. (6) is the work by pressure (\( pV \) work). The second term is the energy carried by evaporating or condensing vapor molecules. The third term is the energy change due to thermal conduction. The fourth term is the heat of chemical reactions and their backward reactions are taken into account involving \( \text{N}_2, \text{O}_2, \text{H}_2\text{O}, \text{OH, H, O, HO}_2, \text{H}_2\text{O}_2, \text{O}_3, \text{N, HNO}_2, \text{HNO}, \text{HNO}_3, \text{NO, NO}_2, \) and \( \text{N}_2\text{O} \). Detailed information of the chemical kinetic model used in the present study is described in Refs. 11, 13, and 18–20.
cal reactions inside the bubble. The last term is the change in macroscopic kinetic energy of the gas inside a bubble that is transferred to heat. The brackets in Eq. (6) mean that this term is excluded when both the bubble wall velocity and the acceleration are negative \((R<0, \dot{R}<0)\). It is because in this case the increase in the macroscopic kinetic energy of the gas does not decrease the thermal energy of the bubble as it is a result of the work by the surrounding liquid that is not taken into account in the first term of Eq. (6).

In the present study, a bubble is assumed to disintegrate into daughter bubbles when the amplitude of the nonspherical component of the bubble shape exceeds the mean bubble radius. A small distortion of the spherical surface is described by \(R(t)+a_n(t)Y_n\), where \(R(t)\) is the mean radius of a bubble at time \(t\), \(Y_n\) is a spherical harmonic of degree \(n\), and \(a_n(t)\) is the amplitude of the nonspherical component. The dynamics for the amplitude of nonspherical component \(a_n(t)\) is given by

\[
\ddot{a}_n + B_n(t)a_n - A_n(t)a_n = 0, \tag{7}
\]

where the overdot denotes the time derivative \((d/dt)\),

\[
A_n(t) = \left( n - 1 \right) \frac{\dot{R}}{R} - \frac{\beta_n \sigma}{\rho t R^3} - \left[ (n-1)(n+2) + 2n(n+2)(n-1) \frac{\delta}{R} \right] \frac{2\mu \dot{R}}{R^3}, \tag{8}
\]

and

\[
B_n(t) = \frac{3\dot{R}}{R} + \left[ (n+2)(n+1) - 2n(n+2)^2 \frac{\delta}{R} \right] \frac{2\mu \ddot{R}}{R^3}, \tag{9}
\]

where \(\beta_n = (n-1)(n+1)(n+2)\), \(\sigma\) is the surface tension, \(\rho t\) is the liquid density, \(\mu\) is the liquid viscosity, and \(\delta\) is the thickness of the thin layer where fluid flows

\[
\delta = \min \left( \sqrt{\frac{\mu}{\omega \rho}} \frac{R}{2n} \right),
\]

where \(\omega\) is the angular frequency of ultrasound.

It should be noted here that there are other theoretical models for chemical reactions inside an isolated spherical bubble reported by other groups.\(^{22-30}\)

### III. RESULTS AND DISCUSSIONS

Numerical simulations of chemical reactions have been performed for various ultrasonic frequencies (20 kHz, 100 kHz, 300 kHz, and 1 MHz) and various acoustic amplitudes (up to 10 bars) inside an isolated spherical air bubble. According to the experimental data reported in Refs. 31 and 32, the ambient radius of a typical active bubble, which is defined as the bubble radius when ultrasound is absent, is nearly independent of ultrasonic frequency in the range of \(20-500\) kHz. Above about 500 kHz, however, it decreases considerably as ultrasonic frequency increases. The range of ambient bubble radius for a typical active bubble is rather narrow according to the experimental observations; from 3 to 6 \(\mu\)m at 27 kHz for shock-wave emitting bubbles\(^{31}\) and from 2.8 to 3.7 \(\mu\)m at 515 kHz for sonoluminescing bubbles.\(^{35}\) In the present numerical simulations, the ambient radii of a typical bubble active for sonochemical reactions have been assumed as 5 \(\mu\)m for 20 kHz, 3.5 \(\mu\)m for 100 and 300 kHz, and 1 \(\mu\)m for 1 MHz according to the experimental data for active bubbles.\(^{31,32}\) The initial bubble radius in the present numerical simulations has been assumed as the ambient bubble radius.

In Fig. 1, the calculated bubble radius has been shown as a function of time for one acoustic cycle (3.3 \(\mu\)s) when the frequency and pressure amplitude of an ultrasonic wave are 300 kHz and 3 bars, respectively. The ambient radius of an isolated spherical air bubble is 3.5 \(\mu\)m. The dotted line is the acoustic pressure (plus the ambient pressure) as a function of time.
the pressure inside a bubble, the bubble collapse stops suddenly when the density inside the bubble (650 kg/m³) becomes nearly that of the condensed phase.

In Fig. 2(c), the calculated number of molecules inside a bubble has been shown as a function of time with the logarithmic vertical axis. As the calculations were performed for an air bubble, the main bubble contents are nitrogen molecule, oxygen molecule, and water vapor. At the final stage of the bubble collapse, most of water vapor and some of nitrogen and oxygen molecules are dissociated and many chemical products are created such as H₂O₂, HO₂, O, O₃, HNO₂, HNO₃, H₂, and OH radical. It is seen from the figure that not only OH radical but also an appreciable amount of H₂O₂ and O atom are created inside a bubble. It is also seen that the amount of each chemical species becomes nearly constant after about τ=0.05 μs which is 0.05 μs after the end of the bubble collapse as the temperature and density inside the bubble decrease suddenly. Thus, in the present study, the amount of each chemical species created inside a bubble is defined as that after it becomes nearly constant (about 0.05–0.1 μs after the end of the bubble collapse).

In Fig. 3, the calculated result for the whole lifetime of an isolated air bubble has been shown under the condition of Figs. 1 and 2 (300 kHz, 3 bars, R₀=3.5 μm). According to the numerical simulation, a bubble disintegrates into daughter bubbles at the end of the fourth collapse (τ~13.4 μs). In Fig. 3(a), the bubble radius has been shown as a function of time. It is seen that the maximum bubble radius at each acoustic cycle increases as the number of the acoustic cycle increases. As a result, the temperature inside a bubble at the end of the bubble collapse increases from 5100 K at the first collapse to 6000 K at the fourth collapse. It should be noted, however, that near the end of the fourth collapse the deviation from the spherical shape may not be neglected and that the actual bubble temperature at the end of the fourth collapse may be lower than that calculated by the present model (6000 K).

In Fig. 3(c), the number of molecules of each chemical species has been shown with the logarithmic vertical axis. It is seen that the main chemical species inside a bubble are nitrogen, oxygen, and water vapor for the whole lifetime. The amount of water vapor increases significantly during the bubble expansion due to the evaporation of water vapor at the bubble wall and decreases during the bubble collapse due to the condensation at the bubble wall. As seen in Fig. 3(c), argon is also present inside a bubble as air contains about 1% of argon in molar fraction. The amount of each oxidant (H₂O₂, O, O₃, and OH) inside a bubble varies only a few tens of percent from acoustic cycle to cycle. Thus, in the following, the main oxidant has been studied only at the first bubble collapse. On the other hand, the amount of HNO₃ and HNO₂ increases more than an order of magnitude in the whole lifetime, as seen in Fig. 3(c).

In Fig. 4, the calculated results for the first collapse of an isolated spherical air bubble have been shown as a function of acoustic amplitude for various ultrasonic frequencies. In Fig. 4(a), the temperature inside a bubble at the final stage of the bubble collapse has been shown. It is seen that for 20 kHz there is a sharp peak of the bubble temperature.
at relatively low acoustic amplitude (1.5 bars) and that the bubble temperature is nearly constant (6300 K) at higher acoustic amplitude than 3 bars, which has been reported previously. The reason for the sharp peak at relatively low acoustic amplitude is as follows. Initially, the bubble temperature increases as acoustic amplitude increases due to the increase in the maximum bubble radius resulting in more violent bubble collapse. On the other hand, the molar fraction of water vapor inside a bubble at the end of the bubble collapse increases as the acoustic amplitude increases, as shown in Fig. 4. Too much vapor fraction decreases the bubble temperature because water vapor has a larger molar heat than that of air and the endothermic dissociation of water vapor cools the bubble considerably. This is the reason for the peak in the bubble temperature at relatively low acoustic amplitude both for the cases of 20 and 100 kHz.

The reason for the increase in molar fraction of water vapor at the end of the bubble collapse as acoustic amplitude increases is as follows. As the acoustic amplitude increases, a bubble expands more resulting in more evaporation of water vapor at the bubble wall. As the bubble collapse is so fast, condensation of water vapor at the bubble wall is in nonequilibrium during the bubble collapse. It means that more amount of water vapor is trapped inside a bubble at the end of the bubble collapse when more amount of water vapor

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**FIG. 3.** The calculated results under the condition of Figs. 1 and 2 as a function of time for the whole lifetime of an isolated air bubble. A bubble disintegrates into daughter bubbles just at the end of the fourth collapse (t~13.4 μs). (a) The bubble radius. (b) The temperature inside a bubble. (c) Number of molecules of each chemical species inside a bubble with the logarithmic vertical axis.

**FIG. 4.** The calculated result as a function of acoustic amplitude for various ultrasonic frequencies (20 kHz, 100 kHz, 300 kHz, and 1 MHz) for the first collapse of an isolated spherical air bubble. The ambient bubble radii are 5 μm for 20 kHz, 3.5 μm for 100 and 300 kHz, and 1 μm for 1 MHz. (a) The temperature inside a bubble at the final stage of the bubble collapse. (b) The molar fraction of water vapor inside a bubble at the end of the bubble collapse.
evaporates into the bubble during the bubble expansion. Thus, the vapor fraction inside a bubble at the end of the bubble collapse increases as the acoustic amplitude increases. Due to the similar mechanism, the vapor fraction at the end of the bubble collapse increases as ultrasonic frequency decreases, as seen in Fig. 4.

In Fig. 4, it is seen that for ultrasonic frequencies of 300 kHz and 1 MHz the bubble temperature continuously increases as the acoustic amplitude increases in contrast to the cases of 20 and 100 kHz. It is due to the much lower molar fraction of water vapor at the end of the bubble collapse for the cases of 300 kHz and 1 MHz, as seen in Fig. 4.

In Fig. 5, the rate of production of each oxidant inside an isolated spherical air bubble per second calculated by the first bubble collapse has been shown with the temperature inside a bubble at the end of the bubble collapse as a function of acoustic amplitude for various ultrasonic frequencies. In Fig. 5, the rate of production of each oxidant inside an isolated spherical air bubble per second calculated by the first bubble collapse as a function of acoustic amplitude with the temperature inside a bubble at the end of the bubble collapse (the thick line): (a) 20 kHz and \( R_0 = 5 \mu m \), (b) 100 kHz and \( R_0 = 3.5 \mu m \), (c) 300 kHz and \( R_0 = 3.5 \mu m \), (d) 1 MHz and \( R_0 = 1 \mu m \).

At acoustic amplitudes above 2 bars at 20 kHz and above 5 bars at 100 kHz, the molar fractions of water vapor at the end of the bubble collapse are larger than 0.4 and 0.3, respectively, and the main oxidant created inside a bubble is OH radical. In other words, inside a nearly vaporous or vaporous bubble which is defined as a bubble with higher molar fraction of vapor than 0.5 at the end of the bubble collapse, the main oxidant created is OH radical. At 20 kHz, the molar fraction of \( \text{H}_2\text{O}_2 \) inside a bubble is much smaller than that at 100 kHz because the duration of high temperature is much longer than that at 100 kHz and most of \( \text{H}_2\text{O}_2 \) is dissociated inside a bubble by the reaction \( \text{H}_2\text{O}_2 + M \rightarrow 2\text{OH} + M \).

When the molar fraction of water vapor inside a bubble at the end of the collapse is much less than 0.5 (we may call such a bubble a gaseous bubble) and the temperature inside a bubble at the end of the bubble collapse is in the range of 4000–6500 K, the main oxidant created inside a bubble is \( \text{H}_2\text{O}_2 \). When it is above about 6500 K, the main oxidant is

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**Fig. 5.** The rate of production of each oxidant inside an isolated spherical air bubble per second calculated by the first bubble collapse as a function of acoustic amplitude with the temperature inside a bubble at the end of the bubble collapse (the thick line): (a) 20 kHz and \( R_0 = 5 \mu m \), (b) 100 kHz and \( R_0 = 3.5 \mu m \), (c) 300 kHz and \( R_0 = 3.5 \mu m \), (d) 1 MHz and \( R_0 = 1 \mu m \).
oxygen atom in a gaseous bubble. It should be noted that an appreciable amount of OH radical also dissolves into the liquid from a gaseous bubble because the amount of OH radical inside a bubble as a function of time peaks at the end of the bubble collapse and decreases sharply with time, as seen in Fig. 2. The rate of OH radical production inside a bubble shown in Fig. 5 could be underestimated.

For the ultrasonic frequency of 1 MHz, the main oxidants are H₂O₂ and oxygen atom at almost any acoustic amplitude because even at higher bubble temperature than 7000 K there is not enough time for H₂O₂ to be dissociated due to the short duration of the high temperature for \( R_0 = 1 \mu m \).

It should be noted that the results in Figs. 5 and 6 have been derived for the first collapse of a bubble. Thus, the above discussions are valid at least for bubbles of relatively short lifetime such as those at relatively high acoustic amplitude and high ultrasonic frequency. The composition of the bubble contents may be changed dramatically during the lifetime of a bubble by the accumulation of the chemical products inside a bubble and should be studied in future in more details.

As has been suggested by Hart and Henglein and the authors, oxygen atom may also dissolve into the liquid from the interior of a bubble. In order to confirm the hypothesis, experimental detection of oxygen atom in liquid irradiated by ultrasound is required. The methods to detect oxygen atom in liquid have been reported in the literatures. For example, a nonvolatile solute having a branched carbon chain such as \( \text{CH}_3\text{CH}_2\text{COO}^- \) can be used to detect oxygen atoms in liquid: \( \text{CH}_3\text{CH}_2\text{COO}^- + \text{O} \rightarrow (\text{CH}_3)_2\text{C(OH)CH}_2\text{COO}^- \), where \( \text{O}(3P) \) is an oxygen atom in its triplet ground state. It should be noted that only nonvolatile solute can be used to detect oxygen atoms in liquid phase because volatile solutes enter bubbles and may react with oxygen atoms in the gas phase inside bubbles. Another method is to use a nonvolatile solute of high molecular weight having a carbon double bond such as

![FIG. 6. The rate of production of other main chemical species inside an isolated spherical air bubble per second calculated by the first bubble collapse as a function of acoustic amplitude (a) 20 kHz and \( R_0 = 5 \mu m \). (b) 100 kHz and \( R_0 = 3.5 \mu m \). (c) 300 kHz and \( R_0 = 3.5 \mu m \). (d) 1 MHz and \( R_0 = 1 \mu m \).](image-url)
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C₆H₄(CH=CH₂)SO₃ which reacts with an oxygen atom to form an epoxide: C₆H₄(CH=CH₂)SO₃+O(3P) → C₆H₄(COCH₂)SO₃.

The production of oxygen atoms inside a bubble is mainly by the following reactions: O₂+→O+OH, O₂+M→O+O+M, OH+M→O+H+M, and H+OH→O+H₂. With regard to the chemical reactions at the bubble interface or in the liquid phase outside a bubble, it is required to model them and numerically simulate them in future.

In Fig. 6, the rate of production of other main chemical species inside an isolated spherical air bubble per second calculated by the first collapse has been shown as a function of acoustic amplitude for various ultrasonic frequencies [(a) 20 kHz, (b) 100 kHz, (c) 300 kHz, and (d) 1 MHz]. For all the frequencies, when the bubble temperature at the bubble collapse is higher than about 7000 K, the main chemical products are HNO₂, NO, and HNO₃ because oxidants react with nitrogen inside a bubble and produce them at such a high temperature.

The dissociation of N₂ is mainly by N₂+→NO+N. The creation of HNO₂ is mainly by OH+NO+M→HNO₂+M. The creation of HNO₃ is mainly by OH+NO₂+M→HNO₃+M. The formation of NO₂ is mainly by OH+HNO₂→NO₂+H₂O. The following reactions are also important inside a bubble: NO₂+H→NO+OH and HNO₂+H→H⁺NO₂.

HNO₂ is a weak acid as HNO₂⇌H⁺+NO₂⁻, where pKₐ=3.3. 47 When pH<3.3, most of HNO₂ are in their neutral state in an aqueous solution and may work as an oxidant or a reductant. As an oxidant, HNO₂ may oxidize O₂ as follows: 2HNO₂+2H⁺+2O₂→I₂+2NO₂+2H₂O. It means that when pH<3.3 the KI dosimetry may quantify not only the oxidants such as OH radical, H₂O₂, O atom, and O₃ but also HNO₂. As a reductant, HNO₂ consumes the oxidants, for example, HNO₂+H₂O→HNO₃+H₂O. When pH>3.3, on the other hand, most of HNO₂ are in their ionic state (NO₂⁻) and the oxidizing or reducing power is weaker than that in their neutral state (HNO₂). 47 It suggests that HNO₂ may play an important role in some sonochemical reactions especially when pH<3.3. 48–51

As seen in Fig. 6(a), an appreciable amount of hydrogen molecule is created inside a bubble when the acoustic amplitude is higher than about 3 bars at 20 kHz. It is created mainly by H+OH→H₂+O. Hydrogen molecules might also play some role in some sonochemical reactions.

Although Henglein ⁸ argued that H atoms which are formed inside a bubble by the dissociation of water molecules hardly penetrate into the liquid phase due to the recombination of H atoms in the gas phase or at the edge of the interface (H+→H₂), the result of the present numerical simulation has indicated that the mechanism for the consumption of H atoms inside a bubble is not the recombination of H atoms but the following reactions: H₂+O→O +OH, H+O₂+M→HO₂+M, H+OH→H₂+O, H+HNO₂→H₂+NO₂, and H+NO₂→NO+OH. The main mechanism of H₂ formation is not the recombination of H atoms but the following reactions; H+OH→H₂, and H+HNO₂→H₂+NO₂. It should be noted that Henglein ⁸ has pointed that the reaction H₂+→HO₂ is important.

The results of the present numerical simulations have suggested that an appreciable amount of HO₂ could dissolve into the liquid from the interior of a bubble for all the ultrasonic frequencies. Kondo et al. ⁵² have detected HO₂ experimentally when argon-saturated aqueous solution is irradiated by 50 kHz ultrasonic wave. It means that an appreciable amount of superoxide radicals (O₂⁻) could be formed in liquid water due to the following reaction: HO₂⇌H⁺+O₂⁻, where pKₐ(HO₂)=4.7.

It should be noted that all the calculated results in the present paper are for an isolated spherical bubble. In order to understand the multibubble system completely, the other categories of bubbles should be studied further including isolated nonspherical bubbles, spherical, and nonspherical ones pulsating under a strong influence of neighboring bubbles. ³³⁻³⁴,³⁵ For example, nonspherical bubble collapse may result in droplet injection into the bubble and may affect the amount of vapor and the temperature inside the bubble.³³,³⁴ Thus, for nonspherical bubble collapse, the amount of chemical products may differ from that for spherical bubble collapse. It is also required to study the spatial distribution of acoustic amplitude and that of the number density of bubbles for each category of bubbles.⁵⁴⁻⁵⁷

IV. CONCLUSION

Numerical simulations of chemical reactions in an isolated spherical air bubble have been performed for various ultrasonic frequencies (20 kHz, 100 kHz, 300 kHz, and 1 MHz) and acoustic amplitudes (up to 10 bars). The numerical simulations have revealed that in a nearly vaporous or vaporous bubble OH radical is the main oxidant created inside a bubble. On the other hand, in a gaseous bubble, it is H₂O₂ when the bubble temperature is in the range of 4000–6500 K, and O atom when it is above about 6500 K. An appreciable amount of OH radical also dissolves into the liquid from the interior of a gaseous bubble. When the bubble temperature at the bubble collapse is higher than about 7000 K, the oxidants are strongly consumed inside a bubble by oxidizing nitrogen and the main chemical products are HNO₂, NO, and HNO₃.

4 F. R. Young, Sonoluminescence (CRC, Boca Raton, FL, 2005).