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Chunlei Guo, Subhash Chandra Singh

Chemical Lasers: COIL

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33 Chemical Lasers: COIL

B. D. Barmashenko and S. Rosenwaks

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33.1 Principle of Operation

The chemical oxygen iodine laser (COIL) [1] is the only known example of a high-power chemically driven electronic transition laser. Unlike other chemical lasers (e.g. HF (hydrogen fluoride) and DF (deuterium fluoride) lasers), which operate on rotational–vibrational transitions of molecules, the COIL operates on an atomic electronic transition. At present the COIL is the shortest wavelength chemical laser system [2,3]. Figure 33.1 shows the electronic states of the species participating in the pumping process of the COIL. The laser transition, at 1315 nm, takes place between the spin-orbit levels of the ground-state configuration of the iodine atom, I(5p52P3/2) → I(5p52P1/2). Basic chemical reactions taking place in the COIL are presented in Table 33.1 [4,5]. The iodine atoms are pumped by a near-resonant energy transfer from oxygen molecules in the excited singlet delta state, O2(a′ 1Δ) (reaction 1, Table 33.1). O2(1Δ) is a metastable molecule with a very long radiative lifetime (76 min) [6] and a pronounced stability against collisional deactivation processes in many environments. Hence, it can be used as the energy carrier for the COIL. Mixing of chemically produced O2(1Δ) with I2 molecules results in dissociation of molecular iodine to atomic iodine which is subsequently excited via reaction 1 (Table 33.1).

O2(1Δ) is produced in a chemical generator by the reaction of gaseous chlorine with basic hydrogen peroxide (BHP) solution. BHP is prepared by mixing an aqueous solution of HO2 with aqueous alkali metal hydroxide MOH (M≡Na or K). The mixing results in formation of HO2 ions in reaction 2 (Table 33.1). Due to the large value of the equilibrium constant of reaction 2 the BHP is composed of HO2, H2O2 and H2O with very little OH−. The BHP solutions used in the COIL are 6–8 molar in HO2, 1–3 molar in H2O2 and about 50% wt H2O [2,7]. Since reaction 2 is extremely exothermic (ΔH ≡ −50kJ mole−1), the BHP has to be cooled down during preparation and is kept at −10°C to −30°C. The chlorine molecules are transferred from the gas–liquid interface to the liquid and then enter the liquid. O2(1Δ) is then produced in the liquid (mainly in a layer that extends 100 nm from the interface) via reactions 3a–c (Table 33.1) with the overall reaction 3 between the chlorine and HO2 [8,9]. The O2(1Δ) product diffuses back to the interface and emerges from the liquid, some fraction of O2(1Δ) being quenched in the liquid by reaction 4. Key parameters of the O2(1Δ) chemical production are the O2(1Δ) yield Y and chlorine utilization U defined as

\[ Y = \frac{[O_2(1\Delta)]}{[O_2]_{\text{total}}} \]  \hspace{1cm} (33.1)

and

\[ U = \frac{[O_2]_{\text{final}}}{[Cl_2]} \]  \hspace{1cm} (33.2)

respectively, where \([O_2]_{\text{final}} = [O_2(1\Delta)] + [O_2(\Sigma)] + [O_2(\Sigma)]\) and \([Cl_2]\) is the chlorine density prior to its reaction with the BHP. Although the \(O_2(1\Delta)\) yield in reaction 3 is near one [8,10], the

FIGURE 33.1 Low-lying electronic states of O2, I2 and I. Energy gaps are given in cm−1.
TABLE 33.1
Basic Chemical Reactions in the COIL [4,5]. I* ≡ I(2P1/2), I ≡ I(2P3/2) I2 is the intermediate state of I2.

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>Rate Constant (cm³ s⁻¹) or Equilibrium Constant (Kₑ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Energy Transfer Pumping Reaction</strong></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>O₂(1∆) + I → O₂(Σ) + I*</td>
<td>k₁₁ = 7.8 × 10⁻¹¹, k₁₃ = k₁₁/Kₑ₁₁, Kₑ₁₁ = 0.75 exp (402/T)</td>
</tr>
<tr>
<td></td>
<td><strong>Liquid Phase O₂(1∆) Production</strong></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>O₂⁻ + H₂O₂ → HO₂⁻ + H₂O</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>HO₂⁻ + Cl₂ → HOOCl + Cl⁻</td>
<td>K₉₁ = 4 × 10⁴</td>
</tr>
<tr>
<td>3b</td>
<td>HO₂⁻ + HOOCI → ClO₂⁻ + H₂O₂</td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>ClO₂⁻ → Cl⁻ + O₂(1∆)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cl₂ + 2H₂O → O₂(1∆) + 2Cl⁻ + H₂O₂</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>O₂(1∆) → O₂(Σ)</td>
<td>k₄ = 5 × 10⁶ s⁻¹</td>
</tr>
<tr>
<td></td>
<td><strong>I₂ Dissociation by O₂ (IΣ)</strong></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>O₂(1∆) + O₂(IΣ) → O₂(Σ) + O₂(1∆)</td>
<td>k₅ = 2.7 × 10⁻¹³</td>
</tr>
<tr>
<td>6</td>
<td>O₂(IΣ) + I → O₂(Σ) + I</td>
<td>k₆ = 1.1 × 10⁻¹³</td>
</tr>
<tr>
<td>7</td>
<td>O₂(Σ) + H₂O → O₂(1∆) + H₂O</td>
<td>k₇ = 6.7 × 10⁻¹²</td>
</tr>
<tr>
<td>8</td>
<td>I₂(X) + O₂(Σ) → I + I + O₂(Σ)</td>
<td>k₈ = 4 × 10⁻¹²</td>
</tr>
<tr>
<td></td>
<td><strong>Hedin’s Auto Catalytic Mechanism of I₂ Dissociation</strong></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>O₂(1∆) + I → O₂(Σ) + I₂</td>
<td>k₉ = 7 × 10⁻¹⁵</td>
</tr>
<tr>
<td>10</td>
<td>I* + I → I + I*</td>
<td>k₁₀ = 3.8 × 10⁻¹¹</td>
</tr>
<tr>
<td>11</td>
<td>O₂(1∆) + I → O₂(Σ) + 2I</td>
<td>k₁₁ = 3 × 10⁻¹⁰</td>
</tr>
<tr>
<td>12</td>
<td>I* + H₂O → I + O₂(Σ)</td>
<td>k₁₂ = 2 × 10⁻¹²</td>
</tr>
<tr>
<td>13</td>
<td>I₂ + M → I₂ + M(M = H₂O₂O₂He)</td>
<td>k₁₃H₂O₂ = 2 × 10⁻¹², k₁₃O₂ = 5 × 10⁻¹⁵, k₁₃H₂ = 4 × 10⁻¹²</td>
</tr>
<tr>
<td></td>
<td><strong>HLAHP Mechanism of I₂ Dissociation</strong></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>O₂(1∆) + O₂(1∆) → O₂(Σ, v = 2) + O₂(1∆)</td>
<td>k₁₄ = 9.5 × 10⁻²⁸ T₀²⁺ exp(700/T₀)</td>
</tr>
<tr>
<td>15</td>
<td>O₂(1∆) + O₂(1∆) → 2O₂(Σ, v = 3)</td>
<td>k₁₅ = 1.7 × 10⁻¹⁷</td>
</tr>
<tr>
<td>16</td>
<td>O₂(Σ) + H₂O → O₂(1∆, v = 3) + H₂O</td>
<td>k₁₆ = 6.7 × 10⁻¹²</td>
</tr>
<tr>
<td>17</td>
<td>O₂(Σ, v = 1) + I → O₂(Σ) + I₂(A, A)</td>
<td>k₁₇(v = 2, v = 2, v = 3) = 3.0 × 10⁻¹¹, k₁₇(v = 2) = 1.0 × 10⁻¹¹</td>
</tr>
<tr>
<td>18</td>
<td>O₂(1∆) + I₂(A', A) → O₂(Σ) + 2I</td>
<td>k₁₈ = 3.0 × 10⁻¹⁰</td>
</tr>
<tr>
<td>19</td>
<td>I* + I → I + I*</td>
<td>k₁₉ = 3.8 × 10⁻¹¹ (1 - Γ), Γ = 0.25</td>
</tr>
<tr>
<td>20</td>
<td>O₂(1∆) + I → O₂(Σ) + I₂(A')</td>
<td>k₂₀ = 2 × 10⁻¹¹</td>
</tr>
</tbody>
</table>

yield obtained at the exit of the singlet oxygen generator (SOG) is usually smaller than unity, ranging from 0.5 to 0.7 [11,12] for the high-pressure SOGs used in the modern COIL devices (see Section 33.2). O₂(1∆) losses are due to both liquid-phase and gas-phase (reaction 5) quenching. For high pressures in the SOG, the liquid-phase losses are enhanced by HO₂ depletion near the gas–liquid interface, which results in the reaction zone shifting into the bulk of the liquid and an increase in the O₂(1∆) transport time to the interface. To estimate the values of Y and U, taking into account all the aforementioned processes, one can use simple analytical expressions [13–15]. Unlike Y, the utilization U is close to unity for almost all types of the SOG.

The mechanism by which O₂(1∆) dissociates I₂ is one of the most complex and least understood aspects of COIL chemistry. Since the loss of excited O₂(1∆) molecules in the iodine mixing–dissociation zone results in a decrease of laser power, this process is very important for the COIL operation. Three mechanisms have been suggested for iodine dissociation. The first [16] involves I₂ dissociation by energy transfer from O₂(1Σ) (reaction 8), which has sufficient energy to dissociate I₂ (see Figure 33.1). O₂(1Σ) is initially formed by the energy-pooling reaction 5 and then (once an appreciable amount of I₂ is formed) strongly supplemented by the pooling reaction 5, where I* (II(P₃/₂)) is formed by the pumping reaction 1. However, dissociation in COIL devices, where significant water concentrations severely reduce the steady-state density of O₂(1Σ) by the quenching reaction 7, is too fast to be attributed solely to this mechanism. Hence, reaction 8 is important only at the initiation stage of dissociation when a small fraction of I₂ is dissociated to atoms.
The second and most celebrated mechanism of iodine dissociation was suggested by Heidner et al. [4] (which for brevity will be referred to as Heidner's mechanism). They found that iodine dissociation is an autocatalytic chain reaction accelerated by $I^*$. A schematic representation of the dissociation mechanism is shown in Figure 33.2a. The dissociation is a two-step process. In the first step, $I_2$ is excited to an intermediate state $I_2^{(†)}$ by reaction 9 and the more rapid reaction 10. Then, excited $I_2^{(†)}$ molecules are dissociated by $O_2(1\Delta)$ in reaction 11. The dissociation rate is controlled by the rates of the excitation reactions 9 and 10. The slow reaction 9 initiates the process but after the buildup of $I$ atoms (excited to $I^*$ in reaction 1), the much faster reaction 10 dominates. Consequently, the rate of iodine dissociation is dependent on the number density of $I_2$ in the flow. Although the iodine intermediate $I_2^{(†)}$ was not observed directly, there is evidence that it is vibrationally excited $I_2(X, v \geq 25)$ and not one of the low-lying triplet $I_2$ electronic states shown in Figure 33.1 [4,17].

Subsequent kinetic studies have raised doubts concerning Heidner’s mechanism. As discussed in Refs. [18–20], the values of several reaction rate constants suggested in Heidner’s mechanism, and in particular the rate constant of reaction 9 which initiates the dissociation process, are substantially different from the directly measured values of these constants. To check the validity of Heidner’s mechanism, a three-dimensional (3D) computational fluid dynamics (CFD) modelling of a low-pressure supersonic COIL was carried out in Ref. [20]. Comparison between the calculated and experimental results (also obtained in Ref. [20]) showed that Heidner’s mechanism underestimates the dissociation rate of $I_2$ at the early initiation stage. As a result, the calculated small signal gain $g$, the temperature $T$ and the $I_2$ dissociation fraction $F$ were significantly different than those measured experimentally. As shown in Refs. [21,22], $g$, $F$, $T$ and the lasing power $P$ for different types of COIL can be predicted over the entire range of checked parameters using the Heidner–Lilenfeld–Azyazov–Heaven–Pichugin (HLAHP) mechanism [21,23], where pathways involving the excited species $I_2(A', A'')$ ($I_2(A'3\Pi_{u}, A'3\Pi_{u})$, $O_2(X^1\Sigma_{g}^+, v)$, $O_2(a^1\Delta, v)$, $O_2(b^1\Sigma_{g}^+, v)$ and $I(2P_{1/2})$ as intermediate reactants are included.

Table 33.1 lists the most important reactions considered in the modelling and their rate constants, the full list of reactions being presented in Refs. [21,22]. In the HLAHP mechanism, iodine dissociation involves at least three steps where $O_2(1\Delta, v = 1–3)$ by the sequence of $O_2(1\Delta)$ energy-pooling (reactions 14 and 15) and $O_2(1\Sigma)$ quenching by water (reaction 16), second in $I_2$ excitation to $I_2(A', A) (= I_2(A'3\Pi_{u}, A 3\Pi_{u}))$ by energy transfer from $O_2(1\Delta, v)$ via reaction 17 and third in
\(I_2(A', A)\) dissociation to I atoms via interaction with \(O_2(\Delta)\) (reaction 18); this is the initiation stage of \(I_2\) dissociation.

At the later stage of dissociation, when a substantial number of I atoms have been formed, an additional rapid three-step dissociation mechanism takes over, as shown in the schematics presented in Figure 33.1. In the first step of the rapid dissociation phase, \(P^*\) atoms (formed from \(I\) by reaction 1) excite \(I_2\) molecules to vibrational states via reaction 19 that splits to two channels: \((19')\) a small fraction \(\Gamma = 0.25\) of \(I_2\) molecules is excited to high vibrational levels \(I_2^*\) (\(\equiv I(X, 25 \leq v \leq 47)\)) which, in turn, dissociate via reaction 11; and \((19'')\) a larger fraction \(1 - \Gamma (\approx 0.75)\) of \(I_2\) is excited first to lower vibrational states, \(I_2^\prime (\equiv I(X, 10 \leq v \leq 25))\), then to \(I_2(A', A)\) by \(O_2(a)\) via reaction 5 which is the second step and finally \(I_2(A', A)\) is dissociated by another \(O_2(a)\) via reaction 18, just as in the above-mentioned initiation stage.

Zagidullin et al. revisited the values of some rate constants shown in Table 33.1 [24,25]. They claimed that according to their experimental observations, the rate constants of reactions 5 and 6, responsible for \(O_2(\Sigma)\) production, and reaction 18, responsible for \(I_2\) dissociation by \(O_2(\Sigma)\), are several times larger than the standard values presented in the table and concluded that the contribution of the \(I_2\) dissociation by \(O_2(\Sigma)\) is the same as that of Heidner’s mechanism. Note that neither of the revised \(I_2\) dissociation mechanism by \(O_2(\Sigma)\) [23,24] nor Heidner’s mechanism can explain the results of the measurements of the gain and iodine dissociation fraction in the supersonic COIL [20] since, as mentioned above, Heidner’s model and hence the mechanism of \(I_2\) dissociation by \(O_2(\Sigma)\) (which has a rate close to that predicted by Heidner’s model) strongly underestimate the iodine dissociation rate in typical supersonic COILs. At the same time, the supersonic COIL parameters predicted by the aforementioned HLAHP model are very close to the measured values.

The condition for the existence of population inversion between the levels involved in the \(I(2P_{1/2}) \rightarrow I(2P_{3/2})\) transition is

\[
\frac{[I(2P_{1/2})]}{[I(2P_{3/2})]} > 0.5. \tag{33.3}
\]

Taking into account that fast equilibrium between \(I^*\) and \(O_2(\Delta)\) is established in reaction 1, one can determine the yield \(Y_{th}\) necessary to achieve threshold population inversion in the \(O_2-I\) system:

\[
Y_{th} \equiv \frac{1}{2K_{e1} + 1} \tag{33.4}
\]

where \(K_{e1}\) is the equilibrium constant. At room temperature \((T = 300 \text{ K})\), \(Y_{th} = 0.15\).

To find the small signal gain, it is necessary to take into account that the upper laser level \(2P_{3/2}\) is split into two hyperfine sublevels with total angular moments of the I atom \(F = 2\) and 3 and the lower level \(2P_{3/2}\) consists of four hyperfine sublevels with \(F = 1\), 2, 3 and 4. Possible transitions between these sublevels and their wavelengths in vacuum are shown in Table 33.2. The largest value of the Einstein coefficient \(A = 5 \text{ s}^{-1}\) corresponds to the \(F = 3 \rightarrow F = 4\) which is the lasing transition. The gain coefficient for this transition is given by

\[
g = \frac{7}{12} \sigma_{34} \left[ \left( I(2P_{1/2}) \right) - 0.5 \left( I(2P_{3/2}) \right) \right] \tag{33.5}
\]

where \(\sigma_{34} = 1.29 \times 10^{-17}(300/T)^{1/2} \text{cm}^2\) is the stimulated emission cross section for Doppler broadening [27]. Taking into account the aforementioned assumption of the equilibrium between \(I^*\) and \(O_2(\Delta)\), the following equation for \(g\) is derived [27]:

\[
g = \frac{7}{12} \sigma_{34} \left( \frac{2K_{e1} + 1}{2} \right) \frac{Y - 1}{(K_{e1} - 1)Y + 1} \tag{33.6}
\]

where \([I]_{total} = [I(2P_{1/2})] + [I(2P_{3/2})]\). Hence, the gain increases with increasing iodine density and decreasing temperature and weakly depends on the yield \(Y\). At room temperatures and \(Y = 0.5-0.8\), \(g \text{ (cm}^{-1}) = (5-7) \times 10^{-16} [I]_{total}\), where \([I]_{total}\) is in \(\text{cm}^{-3}\). Hence, to get gain around \(10^{-3}-10^{-2} \text{cm}^{-1}\), the iodine densities in the COIL active medium should be around \(10^4-10^5 \text{cm}^{-3}\).

The lasing power \(P\) can be estimated with the aid of an energy book-keeping methodology such as the COIL heuristic equation [28]:

\[
P = 91 \left( \text{kJ mole}^{-1} \right) n\text{Cl}_2 U \left( Y_{\text{plan}} - Y_{\text{diss}} - Y_{\text{th}} \right) \eta_{\text{mix}} \eta_{\text{ext}} \tag{33.7}
\]

where \(91\text{kJ mole}^{-1}\) is the energy of \(I^*\), \(n\text{Cl}_2\) is the chlorine molar flow rate and \(Y_{\text{plan}}\) is the \(O_2(\Delta)\) yield just upstream of the iodine injection,

\[
Y_{\text{diss}} = NF \frac{nI}{n\text{Cl}_2 \eta_{\text{mix}}} \tag{33.8}
\]

is the \(O_2(\Delta)\) loss during iodine dissociation, \(\eta_{\text{mix}}\) is the mixing efficiency defined as the fraction of \(O_2(\Delta)\) mixed with iodine, \(\eta_{\text{ext}}\) is the optical extraction efficiency of the resonator, \(F\) is the iodine dissociation fraction and \(N\) is the number of \(O_2(\Delta)\) molecules lost in the region of iodine dissociation per \(I_2\) molecule. From energy considerations, \(N\) cannot be less than two. However, analytical and numerical computations [28,29] and experimental measurements [19,30] show that \(N\) can be appreciably larger, typically in

---

**TABLE 33.2**

Wavelengths of Transitions between the Hyperfine Sublevels of \(2P_{1/2}\) and \(2P_{3/2}\) States of I [26]

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavelength in Vacuum (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 → 4</td>
<td>1315.2463</td>
</tr>
<tr>
<td>3 → 3</td>
<td>1315.2220</td>
</tr>
<tr>
<td>3 → 2</td>
<td>1315.2106</td>
</tr>
<tr>
<td>2 → 3</td>
<td>1315.3360</td>
</tr>
<tr>
<td>2 → 2</td>
<td>1315.3246</td>
</tr>
<tr>
<td>2 → 1</td>
<td>1315.3204</td>
</tr>
</tbody>
</table>
the range 4–6. Exact value of $N$ was determined experimentally in [20,31] where direct measurements of the dissociation of I$_2$ molecules in the supersonic COIL were carried out: it is 4.5 ± 0.4 for typical conditions and I$_2$ densities applied for optimal operation of the COIL but increases at lower I$_2$ densities. The expressions for $\eta_{\text{ext}}$ for different types of optical resonators are presented later in Section 33.3. A very important parameter of the COIL is the chemical efficiency $\eta_{\text{chem}}$, defined as the number of emitted photons per number of chlorine molecules passed through the generator of O$_2$(1$^\Delta$) and, hence, given by

$$\eta_{\text{chem}} = \frac{P}{91(\text{kJ mole}^{-1}) \nu \text{Cl}_2} = U(Y_{\text{plen}} - Y_{\text{diss}} - Y_{\text{th}}) \eta_{\text{mix}} \eta_{\text{ext}}. \quad (33.9)$$

High values of the chemical efficiency can be achieved for efficient SOG with large values of $U$ and $Y_{\text{plen}}$, good mixing and optical extraction corresponding to large $\eta_{\text{mix}}$ and $\eta_{\text{ext}}$, small dissociation losses $Y_{\text{diss}}$ and low temperature in the resonator corresponding to small $Y_{\text{th}}$.

There are two types of COILs: subsonic and supersonic. The first COIL [1] used subsonic flow of the reagents in the resonator. Due to small flow velocities, low densities of iodine are needed to provide for the total dissociation of I$_2$ and to extract energy O$_2$(1$^\Delta$) while maintaining a reasonable laser mode volume [32]. Small values of the iodine density and, hence, of the small signal gain forces the laser beam region to become unbearably long. For example, the first 100–500 W class subsonic devices [33,34] had a gain length of 0.5 to 2 m, and an output power of 4.6 kW was eventually obtained from a 4 m gain-length device [2]. In the supersonic COILs, the flow is brought to supersonic velocity via expansion in a converging–diverging nozzle. The supersonic COILs, which have been intensively studied during the last decade, have several advantages over the subsonic devices. Most importantly, the low temperature achieved by supersonic expansion (predicted to be 150 K for typical devices) displaces the equilibrium of reaction 1 (Table 33.1) in favour of I$^\nu$ production. The equilibrium constant increases from $K_{I^\nu} = 2.88$ at room temperature to 10.9 at 150 K. Using Equation (33.4), one obtains that the threshold yield $Y_{\text{th}}$ falls to 0.044; hence, both the gain and power, given by Equations (33.6) and (33.7), respectively, rise. Also, supersonic flow stretches the gain region, which facilitates power extraction from the optical cavity. In addition, the low temperature reduces the Doppler linewidth of the lasing transition, thereby increasing the gain at the line-centre. These advantages were demonstrated in a supersonic COIL with a 25 cm length nozzle, which yielded powers comparable to the 4 m subsonic device mentioned earlier [2].

### 33.2 Construction and Components

A block diagram of a typical COIL is shown in Figure 33.3. The major components of the COIL are the SOG, water vapour trap (WVT) for H$_2$O removal (in most modern COILs, this trap is not used), iodine supply system, iodine–oxygen mixing system, optical resonator and reactant exhaust system.

Figure 33.4 shows four main types of SOGs: bubbler (or sparger), wetted wall with rotating discs, jet and aerosol generators. In a bubbler or sparger generator (Figure 33.4a), O$_2$(1$^\Delta$) is produced by bubbling (sparging) of the Cl$_2$ gas through a batch of pre-cooled BHP. Cl$_2$ is injected into the BHP through small orifices in a plate located in the lower part of the generator. Chlorine bubbles formed in this way float up and react with the BHP. The chlorine is absorbed by the solution and reacts in the liquid phase generating O$_2$(1$^\Delta$), which in its turn is transferred from the liquid to the interior of the bubble. This generator has a very simple configuration and a very high specific surface area for the gas–liquid interface, $S$ (the area per active unit volume in the generator), which can reach 300 cm$^{-1}$ and ensures high utilization of chlorine (close to 100%). However, the yield is sufficiently high (above ~0.3) only when the partial pressure of oxygen in the generator is relatively low ~1–2 torr.

In a wetted wall SOG, the gaseous Cl$_2$ reacts with a thin film of the BHP solution on the surface of packing placed inside the SOG. This generator evolved from falling film generators [35] to the current rotating-disc generator, as shown in Figure 33.4b [36]. In this generator, closely spaced discs rotate through a pool of BHP producing a set of parallel-plate surfaces coated with a

![FIGURE 33.3 Block diagram of a typical COIL.](image-url)
thin BHP film. The Cl₂ gas is forced through the discs, producing O₂(1∆). This generator operates better at higher pressures, the chlorine utilization and O₂(1∆) yield being about 0.9 and 0.5–0.55 [12], respectively, at a partial oxygen pressure of 11.5 torr. The specific surface S for disc generators reaches 10 cm⁻¹.

The third type of the SOG shown in Figure 33.4c is a jet generator [37]. The BHP is pushed through holes of 0.6–0.8 mm diameter in a perforated plate into the generator, producing jets at a velocity of 6 m s⁻¹ in the reaction zone. Cl₂ is delivered into the reaction zone at the lower part of the generator and flows at a velocity of 10 m s⁻¹ between the BHP jets, against their flow direction, to the generator exit. Most of the Cl₂ (80%–90%) reacts with the BHP to produce singlet oxygen at a yield of 0.6–0.7 [11] and a partial oxygen pressure of 20–30 torr. An increase in the velocity of the jets to 20 m s⁻¹ and of the chlorine to 30 m s⁻¹ enables the oxygen pressure to be increased to 100 torr, and the yield is then about 0.6 [38].

In aerosol SOGs, the gaseous Cl₂ reacts with the BHP delivered in the form of droplets. The best design is the uniform droplets SOG [39], as shown in Figure 33.4d. Just as in the jet SOG, BHP is sprayed through a large number of holes in an injector plate located at the top of the generator. The plate is vibrated by a piezoelectric actuator at a frequency of 4 kHz to generate a field of uniformly sized 0.5 mm diameter droplets at a velocity 12 m s⁻¹. Mutual orientation of the chlorine and droplet flows of 90°, as suggested and analysed by Barmashenko et al. [13], is employed in this generator. Application of a uniform droplet field and 90° orientation in this SOG enables the separation of the droplets from the gas flow to be precluded.

FIGURE 33.4 Different types of singlet oxygen generators. (a) Bubble. (Reprinted with permission of SPIE from Ref. [5]). (b) Wetted wall with rotating discs. (Reprinted with permission of SPIE from Ref. [5]).

(Continued)
At the nominal conditions of 10 torr partial oxygen pressure, the chlorine utilization and \( \text{O}_2(1\Delta) \) yield are 0.8 and 0.7, respectively. The uniform droplet SOG is used in the multi-megawatt COIL for the US Air Force Airborne Laser [40].

The flow emerging from the SOG contains water vapour that strongly quenches both \( I^* \) and \( I_2 \) by reactions 13 and 14 (Table 33.1) and, hence, decreases laser power. To minimize this effect, two approaches have been used: (1) WVT to freeze the water downstream of the SOG; and (2) lower BHP temperature to minimize water vapour formation [41]. The first approach works well for the bubble SOG used in subsonic COILs, where pressure is low and losses of \( \text{O}_2(1\Delta) \) due to the pooling reaction 5 (Table 33.1) are small. Different types of WVTs are used: cold-finger-style WVTs [5], finned WVT [5]...

and rotational/scraping finned cold traps [42] to remove the ice forming on the trap walls. The WVT temperature is usually about 200 K. For the disc, jet and aerosol SOGs used mainly in supersonic COILs, the pressure is significantly higher and, therefore, the WVT cannot be used due to large O$_2$(1Δ) losses. In this case, the second approach is employed and the BHP is kept at $-15^\circ$C to $30^\circ$C. It is worth noting that the harmful effect of the water on the COIL operation is determined by the ratio [H$_2$O]/[O$_2$(1Δ)] rather than by the absolute H$_2$O vapour density [9]. In the case of high O$_2$(1Δ) partial pressure, this ratio just after the generator is not larger than that after the WVT in the case of low O$_2$(1Δ) pressure. That means that COILs using high-pressure SOG can work without WVT.

The I$_2$ supply system uses the following two methods of iodine vapour production: (i) sublimation of solid I$_2$ into a carrier gas (Ar, He or N$_2$) by heat lamps or circulating oil heater [5,43,44] and (ii) iodine boilers where I$_2$ is swept out of molten iodine by heated carrier gas [45,46]. The tubes delivering the iodine vapours to the iodine–oxygen mixing system are heated to avoid I$_2$ condensation.

Subsonic and supersonic COILs use different kinds of iodine–oxygen mixing systems. For subsonic COILs, the primary stream emerging from the WVT, and typically carrying the oxygen and a diluent (buffer) gas, flows in a rectangular duct with constant cross section. The secondary stream carrying the iodine and additional diluent is injected into the primary stream through either small (~0.5 mm diameter) holes, uniformly distributed across the primary flow (with a distance of several millimetres between adjacent holes), or a narrow slit in metal (brass or stainless steel) tubes. Due to low pressure and flow velocity, almost total mixing is achieved several centimetres downstream of the injection location.

In supersonic COILs, as previously mentioned (Section 33.1), the primary stream is expanded in a supersonic nozzle with ~2:1 area ratio and ~10:1 pressure ratio [2]. Both slit mono-nozzles [46] (see Figure 33.5) and grid nozzles, i.e. arrays of several supersonic nozzles [2,45] (see Figure 33.6), are used. The secondary flow is injected into the primary flow at some location in the nozzle, i.e. in the subsonic, transonic or supersonic part of the flow (see Figure 33.5). Usually one or two rows of small injection holes, uniformly distributed across the flow, are drilled in each side of the nozzle wall. Most of the supersonic COILs operating with He primary diluent use a subsonic mixing scheme [2,46]. In subsonic mixing, He is preferred due to the high velocity of flows diluted with He. For conditions where a nitrogen buffer gas or no primary buffer gas is used, this scheme is not optimal and transonic [44] or quasi-transonic (with injection holes located several millimetres upstream of the critical cross section [47,48]) mixing schemes are employed. A supersonic mixing scheme uses either iodine injection in the diverging section of a slit nozzle [7,49], or supersonic mixing of parallel jets of O$_2$ and of I$_2$/N$_2$ with Mach number Ma $\approx$ 1.5 [50] created by a two-dimensional conical nozzle array, referred to as a Cassady grid nozzle [51].

Another concept of ejector COIL also uses supersonic mixing [52,53]. In order to achieve good pressure recovery and effective exhaust of the laser gas into the atmosphere, it is necessary to increase the stagnation pressure at the supersonic section of the flow, which usually is less than 100 torr. To this end special grid nozzles were designed where a transonic (Ma = 1) oxygen flow is mixed with hypersonic (Ma = 4–5) I$_2$/N$_2$ flow, the N$_2$ flow rate being five to ten times larger than that of the oxygen. If the total momentum of the N$_2$ stream is much larger than the momentum of oxygen stream, the latter is pulled into the laser cavity by the nitrogen flow and the stagnation pressure of completely mixed stream is determined mainly by the N$_2$ + I$_2$ flow. Figure 33.7 shows one such mixing nozzle with separate supplies of N$_2$ and I$_2$ [52]. The ejector COIL operates at stagnation pressure in the cavity of 200 torr and a Mach number of about 3 and, hence, is able to ensure a good pressure recovery using small pumping rates.
The optical resonator where the energy of $O_2(^1\Delta)$ is converted into the laser radiation is located several centimetres downstream of the iodine injectors. The optical axis of the resonator is usually transverse to the flow direction. The design and extraction efficiency of the resonators are discussed later in Section 33.3. The laser effluent is then exhausted into a diffuser-pumping system where the pressure is recovered to the atmospheric pressure [54]. The pumping system usually consists of one or two Roots stages on the vacuum side followed by a rotary pump [45]. Sometimes a cryogenic trap is installed upstream of the pumps to remove iodine and residual chlorine from the exhaust gas in order to prevent corrosion in the pumps. For high stagnation pressures in supersonic COILs, ejectors can be used for pressure recovery [54].

Considerable heat release downstream of the supersonic nozzle (and thus in the optical cavity) driven by the water deactivation of the excited iodine atoms (reaction 13, Table 33.1) has a direct impact on the hardware design of the supersonic part of the flow channel and on the performance of the gas recovery system. To preclude a temperature rise in the gas the floor and the ceiling of the supersonic flow duct usually diverge at an angle of $4^\circ–8^\circ$ [28,55]. Calculations of the shape of the flow duct for the supersonic diffuser should also take into account the aforementioned heat release [56].

33.3 Cavity Design and Extraction Efficiency

The measured values of the small signal gain are typically smaller than 1–1.5 and 0.15 m$^{-1}$ in supersonic [7,46,57] and subsonic [58,59] COILs, respectively. Hence, stable resonators have been commonly used in these lasers. The mirror separation depends on the gain length $L$ of the COIL and is usually in the range of 0.5–3 m, the mirror radius of curvature being 2–10 m. The outcoupling mirror transmissions for supersonic COILs with large gain length are about 10%–20%, whereas for subsonic COILs a typical transmission coefficient does not exceed 5%. The mirrors are isolated from the gas flow by ducts purged with He or N$_2$ to protect the mirror coatings from BHP contamination as well as to prevent iodine from entering the ducts. To extract most of the energy stored by $O_2(^1\Delta)$, the aperture of the mirrors in the flow direction should be 3–10 cm, hence, 5 or 10 cm diameter mirrors are typically used in COILs. Since each iodine atom is repumped and cycled many times throughout the flow field during the lasing process, the saturation characteristics of the COIL are different than in other lasers. To find the extraction efficiency $\eta_{\text{ext}}$ appearing in Equation (33.7) for the laser power, simple models for gain saturation and power extraction in the COIL should be used [29,60,61]. In particular, if the mirror’s aperture is much larger than the $O_2(^1\Delta)$ energy extraction distance along the flow, the efficiency $\eta_{\text{ext}}$ for Fabry–Pérot resonator is given by

$$\eta_{\text{ext}} = \frac{t}{t + a} \left( 1 - \frac{g_n}{g} \right) \left[ 1 - \frac{Y - 1/(2K_d + 1)}{Y + 1/(K_d + 1)} \right]$$

where $t$ and $a$ are the transmission and loss of the mirrors, respectively, and $g_n \equiv (t + a)/2L$ is the threshold gain of the resonator. The values of $\eta_{\text{ext}}$ of stable and unstable resonators are shown to be higher than those of a Fabry–Pérot resonator [29,61].

The COIL using stable resonator with mirror aperture of several centimetres has a large Fresnel number and, hence, oscillates on high-order transverse modes. Therefore, it has a large mode volume and is well suited for the extraction of high power. However, this advantage is associated with a large beam divergence and, thus, with a beam quality that is far from what is required for the general applications of such a laser. This problem can be solved by using an unstable resonator which, on the one hand, has a large mode volume and, on the other hand, is capable of discriminating the high-order transverse modes [62]. A conventional confocal unstable resonator consists of either concave and convex (positive branch) or two concave (negative branch) spherical mirrors. The most important parameter of this kind of resonator is the magnification $M$, which is equal to the ratio between the mirror apertures. $M$ describes the outcoupled fraction of the mode volume by simple geometry, being also a measure of the amount of power (intensity) that can be concentrated in the central peak of the far-field mode pattern. In addition to the central peak, this pattern has also side diffraction maxima. Low power in the side maxima is obtained only for large $M$. However, for small- and medium-sized COILs, only a small fraction of the intracavity power can be coupled out without a serious loss in the total lasing power. For small values of $M$ (close to unity), the radiation field forms a narrow ring with only a small fraction of power in the central peak and the beam divergence is large. This means that a conventional unstable resonator is unable to provide for high lasing power and good quality of the laser beam. In experiments carried out in China [63], an output power of 7.1 kW was achieved at a chlorine flow rate of 450 mmole s$^{-1}$ for a 1 m gain-length COIL a using confocal, conventional unstable resonator with $M = 1.39$. However, the experimental beam divergence angle was almost six times larger than the beam diffraction angle, defined as the divergence of a filled-in beam with uniform amplitude and phase; and the aforementioned ring intensity profile pattern was
observed in the near field. One way for improving this situation was suggested by Anan’ev et al. [64] and investigated for the COIL by Latham et al. [65]. Their resonator utilizes an oblique roof-top reflector to turn the phase by 90° with each path (Figure 33.8). This resonator (named UR-90) was used to obtain a uniform intensity profile pattern in the near field. The same output power as for a conventional unstable resonator was obtained with a beam divergence angle only twice the beam diffraction angle. Another unstable double-pass resonator of the hybrid, confocal type was designed for outcoupling the radiation of a 10 kW class COIL with a gain length of 20 cm developed at the Deutsche Zentrum fur Luft und Raumfahrt (DLR) in Germany [62]. This positive branch unstable resonator uses two cylindrical mirrors with $M = 1.17$. While being unstable in the flow direction, it is of the common Fabry– Pérot type in the other direction. Predicted mode field distribution shows excellent beam quality in the far field with over 95% of the outcoupled power in the central peak with $0.3 \times 0.5$ mrad divergence. Further experimental studies of DLR 10 kW class COIL operation with hybrid resonator and other kinds of unstable resonators were reported in [66–68].

### 33.4 Operating Characteristics, Performance and Modes of Lasing

Operating characteristics and performance of different cw COIL devices are shown in Table 33.3. The first lasers, starting with the 4 mW COIL (No 1, Table 33.3) demonstrated in 1977 [1], used subsonic velocity gas in the laser cavity. After an initial scaling from the milliwatt level to 100 W by Benard et al. [33], the subsonic COIL was further scaled to 4.6 kW (No 2, Table 33.3 [5]). The chemical efficiencies of these COILs were smaller than 10%. Much higher values of the efficiencies were achieved at the end of the 1980s in Japan. In particular, a COIL with extremely high efficiency of 42% (No 3, Table 33.3), was demonstrated by Yoshida et al. [69]. The highest reported chemical efficiency of both subsonic and supersonic COILs is 42%. The same authors developed the first subsonic industrial COIL (No 4, Table 33.3) with a power of 1 kW and a highest efficiency of 23% at the same power level. Long-term stable operation was demonstrated with the output power kept within 3% at 1 kW for over 1 h [70,71].

As has already been mentioned in Section 33.1, most subsonic devices have a very large gain length and, therefore, are inconvenient for operation and upscaling. The first compact, 10 cm gain length subsonic COIL [72] was developed in Israel (No 5, Table 33.3). In spite of relatively high efficiency, low (~0.5 torr) pressure in the cavity resulted in a very small output power. Later 5–7.5 cm gain-length compact supersonic COILs with an output power of several hundred watts (No 6, Table 33.3) have been developed in Russia and Japan [73,74]. Unlike the first COIL devices, these COILs are energized by jet SOGs and have chemical efficiencies larger than 20%. To increase the efficiency of these compact COILs, pre-cooling of the primary buffer gas, previously demonstrated by Blayvas et al. [75] for supersonic COIL, was employed.

From the end of the 1980s, the emphasis of COIL research switched to the supersonic devices first demonstrated in 1982 in the Phillips Laboratory in Albuquerque, NM [2]. For the VertiCOIL (shown in Figure 33.9), RADICL and RotoCOIL devices (Nos 7–10, respectively, Table 33.3) power larger than 1, 10 and 30 kW, respectively, were achieved. Both VertiCOIL and RADICL used slit supersonic nozzles, whereas a grid nozzle array was employed in the 54-cm gain-length RotoCOIL. Very high chemical efficiency of 29.6%, was obtained for the RADICL device energized by the jet SOG, (No 9, Table 33.3). These COILs served as the prototypes for the multi-megawatt supersonic COIL (No 11, Table 33.3) employed in the US Air Force Airborne Laser [40,78]. The multi-megawatt COIL used the aforementioned uniform droplet SOG (shown in Figure 33.4d) and supersonic injection of the $I_2/He$ mixture into the helium-singlet delta oxygen mixture. Then, the oxygen / helium / Iodine mixture accelerates through a supersonic nozzle and enters the laser cavity [78].

Two 10 kW class supersonic COIL devices operating with a grid nozzle array were developed at the DLR in Germany and in China (Dalian) (Nos 12 and 13, respectively, Table 33.3). The aforementioned supersonic COILs used He as the diluent gas and, hence, a subsonic mixing scheme (see Section 33.2). In order to obtain high gas velocity and a low partial stagnation pressure for $O_2(C\Delta)$, the He molar flow rates were three to five times higher than that of the chlorine.
For industrial applications, the use of large amounts of He is expensive. Therefore, supersonic COILs with a nitrogen diluent (which is more readily available and cheaper than He) or without a primary buffer gas were developed at the end of the 1990s. A supersonic COIL with N₂ buffer gas using subsonic mixing scheme was first demonstrated by Blayvas et al. [75], the chemical efficiency being only about 13%. Much higher chemical efficiencies (over 20%) were achieved by moving the mixing location downstream to the nozzle throat, i.e. by using quasi-transonic mixing scheme [47,48]. Twenty-three percent chemical efficiency with a room-temperature nitrogen diluent was obtained by Carroll et al. [47] using a VertiCOIL with modified iodine injector blocks (No 14, Table 33.3). A higher efficiency, with room-temperature N₂, 24.6%, was obtained by Endo et al. [81]; however, in these experiments a much larger gain length, 22.5 cm, was employed. The highest power, with room-temperature nitrogen, 1.4 kW, was achieved by Zagidullin et al. [82] using a 5-cm gain-length supersonic COIL (No 15, Table 33.3). A highly efficient ejector COIL (No 16, Table 33.3) has been demonstrated by Nikolaev et al. [52]. Efficient supersonic COILs without any primary diluent applying either transonic or supersonic mixing schemes have been demonstrated in Ben-Gurion University, Israel [44,49,55]. The maximum chemical efficiencies were 18% and 21% for transonic [55] and supersonic [49] mixing schemes, respectively. Later even higher values of the efficiencies were achieved at this laboratory [83,84]. By carefully studying and optimizing the operation of the chemical generator, 0.73 yield of singlet oxygen was obtained for conditions corresponding to the highest efficiency. As a result, 30% efficiency was exceeded for the first time and ~33% efficiency was achieved [83] (No 17, Table 33.3). Then, further optimization of the supersonic nozzle and iodine temperature made it possible to achieve ~40% efficiency (No 18, Table 33.3) [84], the highest reported value of any supersonic COIL, and the closest to the theoretical limit. Also, ~33% efficiency was obtained using a COIL with a supersonic mixing scheme where the primary buffer gas was pre-cooled by liquid nitrogen (No 19, Table 33.3) [85] (pre-cooling leads to ~20% power increase [75]).

### TABLE 33.3

<table>
<thead>
<tr>
<th>No</th>
<th>Name of the COIL and Comment</th>
<th>Type of the SOG</th>
<th>Gain Length (cm)</th>
<th>Cl₂ Flow Rate (mmole s⁻¹)</th>
<th>Power, (W)</th>
<th>Chemical Efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The first COIL</td>
<td>Bubble</td>
<td>70</td>
<td>4</td>
<td>0.004</td>
<td>10⁻⁴</td>
<td>[1]</td>
</tr>
<tr>
<td>2</td>
<td>COIL-IV</td>
<td>Bubble</td>
<td>400</td>
<td>600</td>
<td>4600</td>
<td>8.4</td>
<td>[5]</td>
</tr>
<tr>
<td>3</td>
<td>Extremely efficient COIL</td>
<td>Bubble</td>
<td>35</td>
<td>5</td>
<td>192</td>
<td>42</td>
<td>[69]</td>
</tr>
<tr>
<td>4</td>
<td>Industrial COIL</td>
<td>Bubble</td>
<td>100</td>
<td>69</td>
<td>1015</td>
<td>16</td>
<td>[70,71]</td>
</tr>
<tr>
<td>5</td>
<td>Compact subsonic COIL</td>
<td>Bubble</td>
<td>10</td>
<td>0.4</td>
<td>5</td>
<td>13.7</td>
<td>[72]</td>
</tr>
<tr>
<td>6</td>
<td>High pressure subsonic COIL</td>
<td>Jet</td>
<td>7.5</td>
<td>19.7</td>
<td>448</td>
<td>25</td>
<td>[73]</td>
</tr>
<tr>
<td>7</td>
<td>VertiCOIL with primary He</td>
<td>Disc</td>
<td>5</td>
<td>70.8</td>
<td>1730</td>
<td>27</td>
<td>[46]</td>
</tr>
<tr>
<td>8</td>
<td>RADICL</td>
<td>Disc</td>
<td>25</td>
<td>500</td>
<td>12790</td>
<td>28.1</td>
<td>[76,77]</td>
</tr>
<tr>
<td>9</td>
<td>RADICL</td>
<td>Jet</td>
<td>25</td>
<td>509</td>
<td>13690</td>
<td>29.6</td>
<td>[77]</td>
</tr>
<tr>
<td>10</td>
<td>RotoCOIL</td>
<td>Disc</td>
<td>54.1</td>
<td>1800</td>
<td>39000</td>
<td>24</td>
<td>[2]</td>
</tr>
<tr>
<td>11</td>
<td>COIL for Airborne Laser</td>
<td>Uniform droplet</td>
<td>-</td>
<td>-</td>
<td>&gt; 10⁶</td>
<td>-</td>
<td>[78]</td>
</tr>
<tr>
<td>12</td>
<td>DLR (Germany) 10kW class</td>
<td>Disc</td>
<td>20</td>
<td>500</td>
<td>9700</td>
<td>21.3</td>
<td>[79]</td>
</tr>
<tr>
<td>13</td>
<td>Dalian (China) 10kW class COIL</td>
<td>Jet</td>
<td>100</td>
<td>450</td>
<td>8800</td>
<td>21.4</td>
<td>[80]</td>
</tr>
<tr>
<td>14</td>
<td>VertiCOIL with primary N₂</td>
<td>Disc</td>
<td>5</td>
<td>23.8</td>
<td>490.6</td>
<td>23</td>
<td>[47]</td>
</tr>
<tr>
<td>15</td>
<td>Compact COIL with primary N₂</td>
<td>Jet</td>
<td>5</td>
<td>75</td>
<td>1408</td>
<td>20.7</td>
<td>[82]</td>
</tr>
<tr>
<td>16</td>
<td>Ejector COIL</td>
<td>Jet</td>
<td>5</td>
<td>39.2</td>
<td>700</td>
<td>19.7</td>
<td>[52]</td>
</tr>
<tr>
<td>17</td>
<td>COIL without primary buffer gas</td>
<td>Jet</td>
<td>5</td>
<td>17.4</td>
<td>517</td>
<td>32.7</td>
<td>[83]</td>
</tr>
<tr>
<td>18</td>
<td>COIL with efficiency approaching the theoretical limit</td>
<td>Jet</td>
<td>5</td>
<td>17.4</td>
<td>627</td>
<td>39.6</td>
<td>[84]</td>
</tr>
<tr>
<td>19</td>
<td>COIL with precooling of primary N₂</td>
<td>Jet</td>
<td>7.5</td>
<td>20</td>
<td>599</td>
<td>32.9</td>
<td>[85]</td>
</tr>
</tbody>
</table>

**FIGURE 33.9** Three-dimensional view of VertiCOIL generator, duct and cavity hardware. (Reprinted with permission from Ref. [39]. Copyright © 1999 IEEE.)
The range of applications of the COIL can be extended considerably by pulsed or pulse-periodic operation. A cw COIL can be transformed into a pulse-periodic laser by using either gain-switching (which is similar to Q-switching) or mode-locking methods.

The design of a pulsed COIL is practically identical to that of a cw laser. This means that all the characteristic features of the operation of a COIL associated with dissociation of molecular iodine and relaxation are still retained. The advantage of this method is that there is no need to alter the laser design in going from pulsed to cw operation, i.e. both may be achieved in the same device. The principle of gain switching, first suggested by Schmiedberger et al. [86], is based on magnetic suppression or modulation of the gain by means of applying strong (hundreds of Gauss) magnetic field directly to the COIL cavity. Increasing the magnetic field in the range 1–500 G causes splitting of the hyperfine levels of the I atom due to the Zeeman effect and a significant monotonic decrease in the gain coefficient on the strongest \( F = 3 \rightarrow F = 4 \) transition. Modulation of the gain of a kilowatt-class COIL was demonstrated in the Phillips Laboratory in Albuquerque, NM [87]. Initially, a static magnetic field of 400 G was applied to the cavity of a supersonic COIL, with an output power of 3 kW. An alternating magnetic field, directed opposite to the static field, compensated the latter at certain moments and the lasing pulse appeared at these moments. The peak power in the pulse, 39 kW, was about 13 times larger than the average power corresponding to cw operation, the pulse duration and repetition rate being of 10–20 \( \mu \) s and 500 Hz, respectively.

The mode-locking experiments were carried out at the Phillips Laboratory using the RADICL device [88]. To achieve mode locking, an acousto-optic modulator was inserted into the resonator and lasing was demonstrated on the TEM\(_{00}\) mode with a small intracavity aperture. A dc magnetic field was used to increase the number of axial modes. The field broadened the gain by weakly splitting the Zeeman components of the I(\( F = 4 \)\) \( \rightarrow \) I(\( F = 3 \)) hyperfine transition. A peak power of 2.5 kW was reached with a pulse width of 2.1 ns at a repetition rate of 43.68 MHz.

Pulsed operation in COILs can also be obtained in a flowing gas mixture containing \( O_2(\Delta) \) and an iodide (CH\(_3\)I, CF\(_3\)I or C\(_2\)F\(_2\)I) exposed to a pulse (e.g. a light flash) which generates iodine atoms throughout the whole volume [3]. Optimization of the laser performance made it possible to generate 4.4 J pulses of 15 \( \mu \) s duration, which corresponds to a pulse power of 300 kW [3]. This is the highest value reported so far. These results were obtained at a chlorine flow rate of 17 mmole s\(^{-1}\), when under the best circumstances the cw output power could be 680 W (assuming that the laser chemical efficiency is 40%). Thus, the power of a pulsed COIL (with flash formation of iodine) was over 400 times higher than the cw power. Different methods of the pulsed operation of the COIL have been comprehensively analysed by Yurychev [3].

The high power of both the cw and pulsed COIL devices makes it possible to generate second harmonics in these devices. The frequency doubling of 1315 nm radiation is very important since chemical lasers in the visible wavelength region have not yet been constructed. Different research groups have carried out both intra- and extra-cavity frequency-doubling experiments. The maximum second-harmonic power was obtained in a series of extracavity frequency-doubling tests performed using the output from a RotoCOIL at the Phillips Laboratory [89]. The diffraction-limited radiation of 6.8 kW power was focused into an LiIO\(_3\) crystal. Conversion efficiencies of 8% were achieved resulting in visible (657 nm) cw outputs of nearly 700 W. It was found that the optical strength of the non-linear crystals was insufficient: it fractured after 1 s exposure to a focused beam. Intracavity frequency-doubling experiments was carried out using both LiIO\(_3\) [90] and LBO crystals [91], the maximum conversion efficiency being about 8% [90].

An interesting alternative to the COIL is the electrically driven oxygen-iodine laser (ElectricOIL), which was first demonstrated by Carroll et al. [92]. This laser operates on the same electronic transition of the iodine atom at 1315 nm as does COIL. The lasing state \( ^1 \)I\(_2\) in the ElectricOIL is also produced by near-resonant energy transfer from the singlet oxygen metastable \( O_2(\Delta)\); however in this case the \( O_2(\Delta) \) is generated by an “electric” discharge rather than via a “chemical” reaction (as is the case of the COIL). The highest reported output power of ElectricOIL was 481 W [93].

### 33.5 Conclusions

Since the invention of the COIL in 1977, this laser has made impressive progress and is now one of the most powerful and efficient lasers. It can operate at multi-megawatt power levels with 30% chemical efficiency at a wavelength of 1315 nm, favourable for fibre and atmospheric transmission. Employment of unstable resonators offers excellent beam quality. Development of COILs with a small consumption of a nitrogen diluent makes their operation inexpensive. These characteristics make COIL an ideal laser for both military and industrial applications, in particular for laser cutting, decommissioning of nuclear power facilities and the removal of space debris [19]. COIL technology culminated with the Advanced Tactical Laser demonstrating penetration of the hood of a moving truck [94], and the Airborne Laser successfully shooting down a ballistic missile in the boost phase [94]. However, despite the successful demonstration, the range for shooting down the missiles was too short and to reach the program goals, the onboard COIL had to be by an order of magnitude more powerful which made the program too expensive and impractical; as a result it was eventually discontinued [95].

COILs have higher investment and operation costs than the classical \( CO_2 \) and Nd:YAG lasers if they are compared on the basis of equal power [96]. However, the advantages of the COIL, which has a much better beam quality than the Nd:YAG laser and a much shorter wavelength and, hence, a much higher material processing speed than the \( CO_2 \) laser, may more than compensate for these higher costs.

In spite of the progress in laser technology, some fundamental processes in the COIL active medium are not still properly understood. In particular, one of the more critical issues, the kinetics of iodine dissociation, is still obscure. Other important issues are understanding the hydrodynamics in the supersonic COIL and finding new mixing schemes resulting in minimal losses of singlet oxygen and ensuring a good mixing efficiency.
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FURTHER READING


Basic principles of the COIL operation are presented; the main equations for the gain and power are derived.

Basov N G 1990 Chemical Lasers 1st edn (Berlin: Springer).

Main principles of the chemical lasers operation are described, theoretical description of different processes in the COIL is given.


Overview of photolytic iodine lasers, COILs, COIL diagnostics, singlet oxygen yield, the all gas-phase iodine laser and electric oxygen-iodine laser.

Kodymova J 2007 Overview on the chemical oxygen-iodine laser technology SPIE 6346 634609.

The overall COIL technology is considered as a sequence of coexistent technologies of main laser components with a mutual impact: a technology of the singlet oxygen generator, gasdynamic mixing and expansion nozzle, energy extraction and optical resonator and the exhaust and pressure recovery systems.