Far-IR Lasers: HCN, H O

Publication details
Wilhelm Prettl
Published online on: 24 Jun 2021

Accessed on: 28 Dec 2023

PLEASE SCROLL DOWN FOR DOCUMENT

Full terms and conditions of use: https://www.routledgehandbooks.com/legal-notices/terms

This Document PDF may be used for research, teaching and private study purposes. Any substantial or systematic reproductions, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The publisher shall not be liable for an loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.
30

Far-IR Lasers: HCN, H₂O

Wilhelm Prettl

CONTENTS

30.1 Introduction ........................................................................................................................................................................433
30.2 Laser Lines .............................................................................................................................................................................433
30.3 HCN Laser .............................................................................................................................................................................434
  30.3.1 Laser Mechanism ..................................................................................................................................................434
  30.3.2 Laser Fuels .............................................................................................................................................................435
  30.3.3 Wall Effects ...........................................................................................................................................................435
30.4 H₂O Laser ...........................................................................................................................................................................436
30.5 Resonator ............................................................................................................................................................................436
30.6 Glow Discharge and Additive Gases .................................................................................................................................437
30.7 Design and Operational Characteristics ............................................................................................................................437
30.8 Summary ............................................................................................................................................................................438
References ....................................................................................................................................................................................438
Further Reading ...........................................................................................................................................................................439

30.1 Introduction

This chapter deals with electric discharge pumped far-infrared lasers. The discovery of the H₂O and the HCN laser by Gebbie et al. [1–3] opened up a new age of spectroscopy in the far-infrared, a spectral range which had been notoriously hampered by the low power of thermal radiation sources. Many laboratories took up research on glow discharge excited molecular lasers, and suddenly a substantial number of fairly strong laser lines in the far-infrared were available. Many measurements of fundamental importance could be carried out in various fields. In particular, in solid-state physics, a new technique, magneto-spectroscopy, evolved which made use of fixed frequency laser lines, tuning the energy levels of the object of investigation by an external magnetic field. For instance, after its feasibility was first demonstrated [4], most effective masses and band parameters of semiconductors were determined by this method [5,6].

Besides HCN, H₂O and the isotopic derivatives DCN and D₂O, a number of other polyatomic molecules have been found to be suitable for laser action in an electric gas discharge. Among them are NH₃, OCS and SO₂. However, the lifetime of these molecules in a high voltage electric discharge is very short. Electrons with average kinetic energy in the range of ~10eV break chemical bonds and decompose molecules. Therefore, most polyatomic molecule lasers can only be operated in a pulsed mode with a duty cycle of the order of 1 cycle s⁻¹.

Among the many laser lines observed, there are a few strong laser lines in the cw mode lying in atmospheric windows. Today only these lines are of practical importance. These lines are currently used as an analytical tool in plasma diagnostics [7], to heat electrons in semiconductors [8] and in Stark spectroscopy on molecules [9]. Finally, it is interesting to note that one of the HCN laser lines belongs to about 100 cosmic laser transitions observed so far [10].

In this article, the basic physics, techniques and construction of HCN and H₂O lasers will be summarized.

30.2 Laser Lines

HCN and H₂O lasers may be electrically pumped in a longitudinal configuration of electrodes in the pulsed and cw mode of operation as well as transversely excited [11]. Laser action of HCN by HF pumping and for both lasers by flash lamp excitation has also been observed. However, today only longitudinally pumped cw lasers are in practical use.

Under longitudinal excitation, the gain bandwidth of both lasers is for practically all lines smaller than the frequency separation of the subsequent fundamental longitudinal modes or longitudinal and higher transverse modes. Hence, the output intensity as a function of the resonator length is modulated with sharp peaks at resonance between the molecular transition frequency and the resonances of the resonator. Therefore, a good estimate of the wavelength of an emission can easily be performed by monitoring the laser intensity as a function of the resonator length, a technique which has been termed resonator interferometry [12]. In many cases, more than one laser line or more than one mode can oscillate under the same operational conditions. Tuning the resonator length here is also a useful tool with which to obtain single-line and single-mode emission.
TABLE 30.1
Strong cw Laser Lines of the HCN and the H₂O Laser. The Highest Reported Power Is Given

<table>
<thead>
<tr>
<th>Wavelength Approximate (µm)</th>
<th>Wavelength High Resolution (µm)</th>
<th>Frequency (GHz)</th>
<th>Power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN 337</td>
<td>336.5578</td>
<td>890.7607</td>
<td>250</td>
</tr>
<tr>
<td>H₂O 28</td>
<td>27.971</td>
<td>10.718.073</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>3821.755</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>119</td>
<td>2527.9528</td>
<td>52</td>
</tr>
</tbody>
</table>

Ref. [17].
Ref. [18].
Ref. [19].
Ref. [20].
Ref. [21].

The laser wavelengths were determined with high accuracy by long path-difference Michelson interferometry [13]. Very high precision measurements of laser line frequencies were carried out by heterodyning the laser emission with the high harmonics of coherent microwave sources like the klystron [14].

The gain in energy per pulse due to transverse excitation is not much larger than that at longitudinal excitation; however, discharge instabilities occurring at high longitudinal currents are avoided. In addition, transverse excitation increases the gain bandwidth, which makes tuning and stabilization of the resonator length unnecessary.

With HCN as a laser medium essentially two groups, each of four or five laser lines, may be obtained. One group is around the strongest HCN laser line at \( \lambda = 337 \) µm (see Table 30.1) and the other is in the range of 130 µm. With DCN, a similar set of lines may be obtained around 190 µm. The longest wavelengths with an electric discharge pumped molecular laser were observed by Steffen et al. with ICN at 538 µm [15] and at 774 µm [16]. These lines had not been assigned until then.

The 337 µm line of HCN is the strongest far-infrared laser emission of an electrically pumped molecular laser. It may yield cw power around 250 mW [18].

With the water vapour laser in the pulsed mode more than 100 laser lines and over a dozen lines in the cw mode have been found in the wavelength range 7–220 µm. In addition to these lines attributed to the isotopic species H\(_2\)\(^{18}\)O, a comparable number of laser lines have been obtained with H\(_2\)\(^{16}\)O and D\(_2\)\(^{16}\)O. The molecular transitions of most but not all of these lines have been identified. A list of the wavelengths is given in [22,23].

The wavelengths of the strong lines in the cw mode of the H₂O laser are 28, 78 and 119 µm, as summarized in Table 30.1. Only these lines are of practical importance. An exhaustive list of experimentally observed lines of glow discharge pumped far-infrared lasers is given in [24].

30.3 HCN Laser

30.3.1 Laser Mechanism

The history of the identification of the energy levels involved in the far-infrared transitions of the HCN and the H₂O laser and even the recognition of the laser active molecules illustrates the complexity of molecular spectra and molecular kinetics. The striking feature of these triatomic molecular lasers is that there is no regularity in the emission-line spectra as in the case of the CO\(_2\) or CO laser. It took three years of controversial discussions in the literature until Lide and Maki [25] succeeded in assigning the strong 337 µm line and the neighbouring line at 311 µm of the HCN laser correctly.

The essential physical background of laser transitions comprises the resonance perturbations in the vibrational–rotational system due to the Coriolis force acting in the frame of the rotating molecule and anharmonic resonances like the Fermi resonance [26]. The electric discharge creates a population inversion between low-lying predominantly stretching modes and bending modes. Laser action occurs by rotational–vibrational inter-mode transitions. In the harmonic approximation, inter-mode transitions are forbidden; therefore, anharmonicity of the molecular vibrations is important for laser action.¹ The transition probabilities between different vibrational modes are usually too small to give sufficient gain for laser oscillation. However, if two molecular states belonging to the same symmetry species come accidentally close in energy, their wavefunctions may mix. The mixing of vibrational states of identical symmetry occurs due to anharmonicity. A coupling of vibrational states of differing symmetry may be accomplished by the Coriolis interaction of nearly degenerate rotational–vibrational states if the overall symmetry species are the same. In particular, the angular momentum quantum number \( J \) and the parity of the interacting rotational states must be identical. In some sense, the inter-mode vibrational transition borrows oscillator strength from rotational transitions. If laser oscillation occurs between two different modes, rotational states in the individual modes are populated and depopulated. Hence, laser action may also occur by cascades of purely rotational transitions. Therefore, HCN as well as H₂O lasers have a tendency towards simultaneous multi-line emission.

¹ In fact, all electric discharge pumped molecular infrared gas lasers are based on inter-mode transitions made possible by anharmonicity.
optical inter-mode transitions. In the electric discharge of a HCN laser, the molecule is formed with a high amplitude for the stretching mode \((\nu_1, \nu_2, \nu_3) = (100)\) which is mostly made up of CN vibrations. This is due to the fact that the (100) state is practically metastable [27]. Vibrational transitions from (100) to the (000) ground state are almost three orders of magnitude slower than the (010)–(000) and (001)–(000) transitions [28]. In the gas discharge of HCN laser, molecules are distributed over all vibrational states which are quickly depopulated by spontaneous emission cascading down the vibrational levels to the ground state. The metastable (100) state and all combinations based on it become overpopulated compared to other vibrational modes. Such combinations are obtained by adding one or two quanta of the bending mode \(\nu_3\) yielding a combination of the vibrational states (100) and (120) which are very close in energy to the pure bending modes (040) and (050), respectively. The bending and stretching combination states give the upper laser levels whereas the purely bending states represent the lower laser levels. This is due to faster relaxation of the bending modes compared to stretching–bending equilibria [29].

The pumping mechanism is not very effective as the majority of the molecules relax back to the ground state without passing through the laser transitions. This correlates to the low small-signal gain of the order of 0.1 dB m\(^{-1}\) and the corresponding moderate output power of the order of magnitude of 10–100 mW.

In the case of HCN transitions around the strong 337 \(\mu\)m line, two rotational levels of the combined stretching and bending mode (11\(^0\)) and the bending mode (04\(^0\)0) having the same rotational quantum number and parity, \(J(10)\), lie sufficiently close together that the Coriolis interaction relaxes the selection rule of forbidden inter-mode transitions. In addition, the inter-vibrational transitions pump purely rotational transition cascades at 284, 310, 335 and 373 \(\mu\)m. High-precision measurements of the frequencies of these laser lines support this level assignment. The sum of the frequencies of the 311 and 335 \(\mu\)m lines differ by less than one part in 10\(^6\) from the sum of the frequencies of the 310 and 337 \(\mu\)m lines [17]. A schematic energy-level diagram and the corresponding laser transitions are displayed in Figure 30.1.

The same mechanism can be assumed for other groups of laser lines. In the HCN laser, the coupling of \(J=26\) rotational states of the 12\(^0\)0 and the 05\(^0\)0 vibration ladders leads to an emission of laser lines in the region of ~130 \(\mu\)m and in the DCN laser, a similar perturbation occurs between \(J=21\) states of the (22\(^0\)) and (09\(^0\)) vibrations generating laser emission in the vicinity of 190 \(\mu\)m.

### 30.3.2 Laser Fuels

HCN molecules are not stable in the glow discharge. They are decomposed by the impact of high-energy electrons and form again in excited vibrational–rotational states. Thus, the HCN laser is a chemical laser. In fact, it is not necessary to use poisonous HCN as a laser medium but almost any compound or mixture of molecules containing C, N and H, with a sufficient excess of H, may produce HCN in the gas discharge and generate laser action. Several chemical reactions have been discussed, making population inversion conceivable [30].

Gas mixtures are selected from the point of view of high output power and small polymer deposition on the resonator wall (see later). A standard fuel is the gas mixture N\(_2\)+CH\(_4\) in volume ratios ranging from 1:1 to 1:3. Other laser media are CH\(_3\)N, C\(_2\)H\(_5\)CN and CH\(_4\)+NH\(_3\). Remarkably, C\(_2\)H\(_2\)+N\(_2\) is laser inactive but may be activated by adding H\(_2\) [31].

### 30.3.3 Wall Effects

Physical and chemical processes at the inner walls of the discharge tube are of central importance for the operation of an HCN laser. A characteristic feature of the HCN laser is the deposit of a polymer layer on the discharge tube and on the mirrors of the resonator. The deposited film, coloured between yellow and dark brown, causes a substantial reduction in output power and, if the layer gets too thick, laser emission ceases. The deposit can be removed by running the discharge with H\(_2\)O for several hours. Adding oxygen speeds up the process of converting the deposit into gaseous products.

Chemical analysis and infrared spectroscopy showed that the main constituent of the electric discharge polymerized material is (CN)\(_2\) [32]. Laser emission of the 337 \(\mu\)m HCN line may be obtained in a discharge tube with the polymer deposit running the discharge with pure H\(_2\)O, H\(_2\) or NH\(_3\). Laser action occurs because HCN molecules are formed in sufficient concentration by the discharge from the wall deposit.

The generation of laser active molecules at the walls leads to a surprising dependence of the gain on the laser tube as a function of the distance from the tube axis. In typical low-pressure gas lasers, the gain drops rapidly as it approaches the discharge tube walls. Atoms or molecules excited in the volume diffuse to the wall and lose their energy there. In contrast, the gain in the HCN laser is almost constant over the whole cross section of the discharge tube [33].
behaviour was explained by taking the volume and wall processes in the plasma into account simultaneously [32].

### 30.4 H₂O Laser

The physical mechanisms and operating conditions of the water vapour laser are very similar to those of the HCN laser. Both Coriolis and Fermi resonances yield the transition probability between different vibrational modes. The coupling occurs between rotational levels of the (100) and (001) vibrational states of the ν₁ and ν₃ modes, respectively, and the first overtone (020) of the symmetric bending mode of frequency ν₂. The strong interaction is caused by large anharmonicity and the fact that the frequencies of the symmetric (ν₁) and antisymmetric (ν₃) OH stretching modes are almost exactly twice the frequency of the bending fundamental vibration (ν₂).

Symmetry analysis [27] shows that Fermi resonances cause perturbations of rotational levels in (100) and (020), whereas the Coriolis force is responsible for the interaction between (020) and (001).

As an asymmetric top molecule, the rotational energy-level structure of H₂O is considerably more complex than that of the linear molecule HCN. A very detailed discussion of the water vapour laser and an assignment of a large number of observed laser lines is given in [22]. In Figure 30.2, part of the energy-level scheme of H₂O is shown which accounts, among other lines, for the stronger laser lines given in Table 30.1. A concise discussion of the inversion mechanism is given in [34].

The H₂O laser is very convenient to operate as there are no problems of wall depositions in the laser tube and the lifetime of the molecule is quite long. In contrast to the HCN laser, H₂O is directly excited in the glow discharge without being dissociated. This was concluded from the observation that, in the pulsed mode of operation, H₂O lases during the exciting current pulse and decays rapidly when the excitation terminates. HCN and other molecular species lase with characteristic temporal delay in the afterglow of the current pulse [35].

### 30.5 Resonator

The glow discharge and the resonator mirrors of electrically pumped far-infrared lasers are usually confined in glass or Pyrex tubes. Typical dimensions of laser resonators are several centimetres in radius a and a few metres in length b. These units result in Fresnel numbers \( N = a^2 / 2b = 1 \) where \( \lambda \) is the laser wavelength. This is in contrast to lasers in the visible or near-infrared which have Fresnel numbers much larger than one. Thus, taking into account the low gain, diffraction losses cannot limit the laser threshold. This fact was first recognized by Schwaller et al. [36] who pointed out the discrepancy between diffraction-selected resonator modes and actually observed modes. Steffen and Kneubühl [12] showed that, in fact, the resonator works like an oversized leaky waveguide. Instead of diffraction, the losses are due to reflection at the dielectric resonator walls. The attenuation in a low-index leaky guide decreases with increasing radius like \( \alpha \sim \lambda a \) [37]. The loss of fundamental longitudinal modes is vanishingly small in oversized resonators due to the almost grazing incidence of radiation on the wall. The curvature of the mirrors is still important as it affects the mode volume [38].

Partially reflecting loss-free solid-state mirrors, such as those used as output reflectors in optical lasers, do not exist in the far-infrared due to phonon absorption at room temperature. Therefore, there is no standard scheme to couple radiation from the resonator. Several coupling systems have been developed and applied. The most used among them include hole coupling, coupling with a thin dielectric film, coupling with a Michelson interferometer and coupling by a metallic mesh.

Coupling through a hole in the centre of one of the resonator mirrors is technically simple and thus mostly applied. The disadvantage is the diffraction widening of the beam and the need for an individual hole diameter for each laser line in order to optimize output. The latter requirement is in fact nowadays no real restriction as most discharge-pumped lasers are used with one line only.

Coupling is performed by mounting a thin (5–20 μm) Mylar or polyethylene film with a tilt angle of 45° to the resonator axis. Absorption losses in the thin films can be ignored. The reflection coefficient is independent of the wavelength in a...
Wide wavelength range, but it is polarization dependent. Thus, the output beam is polarized. Two output ports may be used yielding two low-divergence beams of the same cross section as the resonator.

A Michelson interferometer with a dielectric film, usually Mylar, as beamsplitter is very reliable making the operation of a laser on different lines easier. By varying the length of one interferometer arm, the output can be tuned and optimized for different laser lines.

Thin metallic meshes represent low-loss partial reflectors in the far-infrared [39] and have been frequently used [40,41]. The advantage is that they retain the laser beam and the linear structure of the resonator. The pitch has to be adapted to the particular laser line. Using two parallel metallic meshes with adjustable spacing gives the arrangement of a Fabry–Pérot interferometer. As an output coupler, it allows the reflectivity and selection of single laser lines to be tuned [12].

Films of Mylar or polyethylene as well as sheets of TPX or crystalline quartz are used as window materials.

### 30.6 Glow Discharge and Additive Gases

The optimum radiation power of a longitudinally pumped cw laser is obtained with a pressure in the range of 0.2–0.8 mbar. The output power of the laser increases with rising current until it assumes a maximum and drops on further increase in current. The optimum current is in the range 1–3 A, yielding a voltage drop of about 2–4 kV. The peak output is found with a wall temperature between 100°C and 150°C. The wall temperature has been controlled by thermostatically temperature-stabilized oil flowing in a jacket around the laser tube. In the case of the HCN laser, a higher temperature is advantageous even if the power is not optimal because it reduces the wall deposit rate. The glow discharge of a cw laser is in the diffusion-dominated regime where the positive column fills almost the whole plasma tube. In the positive column, striations are formed which become unstable at higher current densities, shifting the current of maximum output power to higher values or, in turn, lowering the required discharge voltage for a given current. H2 and H2O have a similar effect on the discharge. In addition, H2 may compensate for a shortage of hydrogen in the laser fuel and helps to relax the energy of the lower laser level bending mode by hydrogen bonding effects.

### 30.7 Design and Operational Characteristics

In Figure 30.3, a standard design of a cw HCN laser is shown. The characteristic data are given in Table 30.2.

The laser oscillates on the 337 µm line only. The gain of the laser is too small to obtain other HCN lines. The length of the laser tube is made of glass (Schott Duran 50) and is thermally stabilized by four invar rods. Sufficient thermal stability is achieved after running the laser for about 1 h. The temperature at the wall of the tube is then 150°C. The stability of the laser also depends critically on the electrode configuration. As an anode, a stainless steel ring 7 cm wide attached concentrically onto the inner wall of the discharge tube and as a cathode, a hollow copper cylinder in a side arm of the tube have proved to provide a stable discharge. The cathode is cooled by water flow. Another important parameter with respect to stability is the gas pressure. The discharge runs smoothly below about 0.6 mbar forming stable mushroom-like striations. Above this pressure, the striations start irregular motions and mixing until any regular pattern in the discharge disappears. In this state, the output power strongly fluctuates; however, the average power is two to three times higher than in the smoothly running mode. Adding small amounts of water vapour to the discharge increases stability, adding He does not have much effect.

Making full use of the waveguide effect of rather thin discharge tubes, similar but more compact cw laser designs have been reported by Belland and Veron [38], Véron et al. [43] and Bruneau et al. [44]. In these devices, the temperature of the tube wall could be actively controlled by the flow of oil in an outer jacket around the tube. This gives another parameter at hand to optimize laser operation.
30.8 Summary

Glow discharge lasers were coherent sources of substantial intensity which bridged the gap between the microwave range and near-infrared. The revolution in the field of coherent far-infrared sources was concluded by the discovery of the CO₂ laser pumped molecular laser by Chang and Bridges [45] and approached maturity with the advent of the free-electron laser [46]. Optically pumped molecular lasers deliver thousands of laser lines in the far-infrared, they may be operated as cw or pulsed, they produce short pulses or extremely high intensities when transversely excited atmospheric pressure (TEA)-CO₂ lasers are applied as the pump source. To all these the free-electron laser adds tunability in a wide wavelength range. Thus, these laser concepts superseded the electrically pumped far-infrared laser in most cases. However, there are still areas of research where it is reasonable to apply H₂O and HCN lasers. Both lasers are low cost, reliable and of simple construction. In the cw mode, they are easy to handle due to direct electrical excitation and deliver on a few lines with a rather high power.

REFERENCES


### TABLE 30.2

The characteristic data of HCN laser.

<table>
<thead>
<tr>
<th>Resonator</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>2.4 m</td>
</tr>
<tr>
<td>Curvature of movable mirror</td>
<td>4 m</td>
</tr>
<tr>
<td>Curvature of coupling mirror</td>
<td>∞</td>
</tr>
<tr>
<td>Hole coupling, bore</td>
<td>15 mm</td>
</tr>
<tr>
<td>Output window</td>
<td>TPX sheet, 3 mm thick</td>
</tr>
<tr>
<td>Thermal stabilization</td>
<td>4 invar rods, 25 mm diameter</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Discharge</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser gas</td>
<td>CH₂ and N₂, 1:1</td>
</tr>
<tr>
<td>Optical additive gases</td>
<td>H₂O, He</td>
</tr>
<tr>
<td>Pressure</td>
<td>0.4...0.6 mbar</td>
</tr>
<tr>
<td>Flow rate</td>
<td>500 cm³/min⁻¹</td>
</tr>
<tr>
<td>Anode</td>
<td>Stainless steel ring, 70 mm wide</td>
</tr>
<tr>
<td>Cathode</td>
<td>Hollow copper structure</td>
</tr>
<tr>
<td>Voltage</td>
<td>1.0...2.5 kV</td>
</tr>
<tr>
<td>Current</td>
<td>0.5...1.5 A</td>
</tr>
<tr>
<td>Load resistor</td>
<td>600 Ω</td>
</tr>
<tr>
<td>Power</td>
<td></td>
</tr>
<tr>
<td>Gain</td>
<td>0.5 dB m⁻¹</td>
</tr>
<tr>
<td>Output power</td>
<td>5 mW</td>
</tr>
</tbody>
</table>
Far-IR Lasers: HCN, H2O


FURTHER READING

Chantry G W 1984 Long-Wave Optics (London: Academic)

A concise textbook presentation of the inversion mechanism and energy-level scheme of the HCN and H2O laser (Vol 1: Basics, pp 150–3) and technical performance (Vol 2: Applications, pp 570–3) in the context of other infrared lasers.


Kneubühl pioneered submillimetre glow discharge lasers. This review was written after understanding of the physics background was settled and after the technology had approached a certain technological maturity. Coverage of all excitation mechanisms (cw, pulsed longitudinal, transversely excited).


A review with emphasis on the kinetic and transport processes in the laser plasma. A very thorough discussion of chemical processes, excitation and relaxation in the plasma and rate equation models.