A discussion on molecular absorption noise in the terahertz band

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Abstract
This paper focuses on molecular absorption noise caused by molecular absorption in the higher frequency bands, such as THz band (0.1–10 THz). This transmission induced noise has been predicted to exist in the THz band, since the conservation of energy requires the conservation of the absorbed energy in the medium. There exist multiple models for the molecular absorption noise. Most of them focus only on the transformation of the absorbed energy directly into antenna temperature. This paper aims at giving additional perspectives to the molecular absorption noise. It is shown that the molecular absorption noise can be investigated with multiple different approaches, strongly affecting on the predicted strength and behavior of the noise. The full molecular absorption noise model is not given in this paper. Instead, we study the molecular absorption noise from different perspectives and give their derivations and the general ideas behind the noise modeling.

Keywords:
Einstein coefficients, molecular absorption, molecular absorption noise, radiative transfer, sky noise

1. Introduction

The higher frequency bands, such as millimeter-waves (30–300 GHz) and terahertz band (0.1–10 THz) have been seen as very promising platforms for...
many future wireless applications. The small cell deployment and nanocommun-

cations are among the considered applications for these extremely high

frequency bands [1, 2]. Since our main interest lies in the nanocommunica-
tions and the THz band, we use those as references. However, the theories
and discussion presented in this paper generally applies to all the absorbing
bands. The nanocommunications is a generic term for communication solu-
tions designed for the envisioned nanodevices. The nanodevices are expected
to be extremely small (a few cubic micrometers) biological or mechanical de-
vices capable of simple sensing and actuation tasks [2, 3]. Simple devices
can easily be integrated into almost any object, providing sensing and net-
working capabilities for the objects. Therefore, the nanodevices could be
harnessed to Internet-of-Things (IoT) applications. Other possible target
applications have been suggested, e.g., drug delivery and health monitoring
[2].

As it was mentioned above, our frequency band of interest is the THz
band. Along with very high free space path loss, molecular absorption be-
comes an issue. It causes loss to the signals, since the electromagnetic (EM)
energy is partially transformed into internal energy of the molecules. The
molecular absorption is a well known and investigated phenomenon (see,
e.g., [4, 5]), and is, therefore, not deeply covered in this paper. By the con-
servation of energy, it has been predicted that the molecular absorption of
the transmitted signals is an additional noise source in the THz band [4].
This is a very interesting idea, because it introduces a new type of a noise to
the communication systems, a *self-induced noise*, henceforth referred to as
a *molecular absorption noise*. It was first introduced in [4] and it has been
used in multiple papers, such as [6–10].

The existing molecular absorption noise models are based on so called *sky
noise* [11–16]. It is a simple model of the absorption energy transfer in the
atmosphere and it is present in all absorbing atmospheres, such as Earth’s
atmosphere. It is based on the Kirchhoff’s law of thermal radiation [17]. The
difference of the sky noise to the molecular absorption noise is that the sky
noise is caused by the radiation of the atmosphere due to the temperature
of the atmosphere, thus, ultimately by the sun. Molecular absorption noise,
on the other hand, is caused by the transmissions in the radio channel [4].
Since the sky noise is a foundation of the existing molecular absorption noise
models, we cover the sky noise in this paper along with the derivation and
an approximation for the THz band.

The existing research on the molecular absorption noise mostly focuses
on the frequency domain molecular absorption without considering its time
domain properties. In this paper, we present the different phenomena af-
fecting the molecular absorption noise. The main contribution is to present different perspectives how to model the molecular absorption noise. We will consider the following scenarios:

1. **A frequency domain model without time dependency.** The scenario assumes frequency dependent noise, directly linked to the absorption at THz band. This perspective represents most of the existing molecular absorption noise models [4, 6, 7, 9, 10].

2. **The additional propagation delay** compared to the line-of-sight (LoS) component due to the absorbed energy being re-emitted in a random direction, leading to an increased path length to a receiver. We assume zero emission delay (all the delay is due to the propagation delay), enabling modeling the multiple paths to the receiver with multiple scattering theory [18].

3. **The energy decay rate** of the molecules in the transmission medium assuming the energy remains in the absorption frequencies. For this, we utilize the Einstein coefficients [19] and the non-local thermodynamic equilibrium theories [20, 21]. Boronin et al. [9] considered the emission delay assuming a constant emission rate. We will derive a frequency dependent emission rate by utilizing the Einstein coefficients, which is a different approach to the problem.

4. **The energy** absorbed by the molecules (from the transmitted EM radiation) **transformed into heat.** In this approach, we calculate the temperature of the medium based on the heat induced by the absorbed energy density. This can be done by estimating the temperature with the heat capacity of the medium.

For all the above perspectives, we give the required background derivations and analysis. Our aim is not to introduce a closed form solution for the total molecular absorption noise, but to introduce the basic physical mechanisms behind the molecular absorption noise. There is no doubt about the existence of the molecular absorption noise. The question is, whether it is ever significant for the communication theoretic analysis (and if so, under what conditions)? Although we focus on the THz band, the theories are generally valid in all the absorbing bands.

The structure of this paper is as follows. Section 2 gives background knowledge on molecular absorption and the radiative transfer equation (RTE). In Section 3, the sky noise is reviewed and derived. Section 4 focuses on the frequency dependent molecular absorption noise and Section 5 focuses on the heat approximation. Finally, Section 6 concludes the paper. Fig. 1 clarifies the relationships of the phenomena considered.
2. Background

In this section, the core background on molecular absorption is given as it is the foundation of the molecular absorption noise and the sky noise as well. We often rely on the RTE. Therefore, the definition of the RTE is also given here. We utilize the RTE as it was defined by Chandrasekhar [22]. Also, the considered propagation environment is quickly went through in the end of this section.

2.1. Molecular absorption

The molecular absorption is caused by the transmitted EM wave is shifting the molecules in the medium to higher energy states. The energy, equivalent to the difference between the higher and the lower energy state of a molecule, determines the absorption energy that is drawn from the EM wave. This has a direct impact on the absorption frequency as the absorbed energy is $E = hf$, where $h$ is the Planck’s constant and $f$ is frequency [23, Chapter 17]. This process can be described stochastically by using the absorption coefficient $\kappa_a(f)$. This quantity describes the average effective area of the molecules per unit volume. The absorption coefficient depends on frequency and gives the THz band a very peculiar frequency selective spectral absorption profile. The amount of radiation that is capable of propagating through the absorbing medium is defined by transmittance, which is defined
by the Beer-Lambert’s law as [4, 5]

\[ \tau(r, f) = \frac{P_{Rx}(r, f)}{P_{Tx}(f)} = e^{-\kappa_a(f)r}, \]

(1)

where \( P_{Rx}(r, f) \) and \( P_{Tx}(f) \) are the received and the transmitted power, respectively, and \( r \) is the distance between the transmitter (Tx) and the receiver (Rx). The details on the calculation of the molecular absorption coefficient can be found, e.g., in [4] and [5]. Equation (1) is very well known and it is the foundation of the THz specific research, as well as it is a foundation of the derivation of the molecular absorption noise models presented in the following sections.

2.2. Radiative transfer equation

All the sky noise models, as well as the existing molecular absorption noise model are ultimately based on the RTE. Assuming a constant atmosphere, i.e., the absorption coefficient is constant in the path of radiation, the RTE can be presented as [22, Section 1.7]

\[ I(d, f) = I(0, f)e^{-\kappa_a(f)d} + \int_0^d B(T, f)\kappa_a(f)e^{-\kappa_a(f)s}ds, \]

(2)

where \( I(d, f) \) is the intensity of radiation at distance \( d \), \( I(0, f) \) is the intensity of the transmitted signal and \( B(T, f) \) is the source term, i.e., the Planck’s function

\[ B(T, f) = \frac{2h\pi f^3}{c^2} \left( e^{\frac{hf}{k_B T}} - 1 \right)^{-1}, \]

(3)

where \( c \) is the speed of light, \( k_B \) is the Boltzmann’s constant and \( T \) is the temperature. We have multiplied the above equation with \( \pi \) in order to transform the unit of the Planck’s function from \( \text{W/Hz/cm}^2/\text{sr} \) to \( \text{W/Hz/cm}^2 \) [24]. Then (3) corresponds to spectral excitance of the surface of the black body [24]. The first term on the right-hand side of (2) is the transmitted energy from the Tx and the second term is the radiative energy of the atmosphere. In the general case, it is described by the Planck’s law as the Planck’s law determines the radiation emitted by an object at temperature \( T \) (the black body radiation). The integral in the RTE describes the noise intensity at point \( d \) given the entire atmosphere contributes to the noise at point \( d \). That is, we sum the contribution of all the points \( s \) in the atmosphere. This is clear from the definition of RTE, as the term \( \exp(-\kappa_a(f)s) \) describes the transmittance at the surface of a sphere with radius \( s \).
2.3. Propagation environment

In all the following sections we consider the THz band (0.1–10 THz). A spherically symmetric free space environment is assumed in all the molecular absorption noise examples, i.e., the transmitter is at the center of a sphere and the receiver is at distance $r$ from the transmitter. We use the same parameters in all the examples, i.e., the distances and the atmospheric parameters. The distance between the transmitter and receiver is assumed to be $r = 10$ cm in all applicable cases. Other notations for the distances in this paper are $s$ for the infinitesimal distances and $d$ for the atmospheric thickness. Furthermore, the atmosphere itself is the only obstacle between the transmitter and the receiver. The atmosphere in all the examples is assumed to be homogenous at temperature $T = 300$ K, pressure $p = 101325$ Pa and 50% relative humidity. The transmit power spectral density is assumed to be $P_{Tx} = 2$ pW/Hz, leading to a transmit energy of 2 pJ per pulse. Similar values for the energy of a single pulse have been used in the previous works, such as 1 pJ per pulse in [25].

3. Sky Noise

The sky noise is caused by the temperature of the absorbing atmosphere, causing the atmosphere (or any medium) to be an effective black body radiator, or a gray body radiator in non-homogenously absorbing medium (in frequency domain). The sky noise is therefore known as a background noise and it is independent of the transmitted signals. There is a multitude of papers describing the sky noise, such as [11–16]. It is present, e.g., in satellite communications and it is commonly defined by the antenna temperature, i.e., an additional temperature accounting for the radiation from the absorbing atmosphere. The atmosphere is a dynamic medium, with roughly speaking decreasing temperature and pressure as a function of the elevation. Therefore, the total antenna temperature can be defined as an integral over the entire atmosphere [12, 14]

$$T_a(f) = \int_0^\infty T(s)\kappa_a(s, f)e^{-\gamma(s, f)}ds + T_\infty e^{-\gamma_\infty(f)}, \quad (4)$$

where $T_a(f)$ is the antenna temperature, or sky noise, $T(s)$ is the temperature of the atmosphere as a function of the distance $s$, $\kappa_a(s, f)$ is a distance dependent absorption coefficient, $\gamma(s, f) = \int_0^s \kappa_a(s', f)ds'$ is the optical depth of the medium [12, 14] and the term $T_\infty e^{-\gamma_\infty(f)}$ accounts for
the radiation coming outside the atmosphere. This last term is henceforth assumed to be small. In the general case, the absorption coefficient is a function of distance as in the above equation. This due to variable temperature and pressure in the atmosphere. If the distance is small, or the atmosphere is otherwise homogenous, \( \kappa_a(s, f) = \kappa_a(f) \). Assuming an isothermal atmosphere, (4) reduces to \([11, 13–16]\)

\[
T_a(d, f) = T_A(1 - e^{-\kappa_a(f)d})
\]

(5)

where \( T_A \) is the temperature of the atmosphere (or effective temperature of the atmosphere) and \( d \) is the thickness of the atmosphere. It can be seen that the antenna temperature is only present in the absorbing frequency bands. Therefore, it is not a problem, e.g., in the ultra high frequency (UHF, 0.3–3 GHz) band. However, the THz frequencies are highly absorbing and this additional noise source is present. It can also be seen in (5) that the antenna temperature is at maximum the atmospheric temperature \( T_A \). This is since the source of brightness temperature is the atmosphere at temperature \( T_A \), or an average temperature of the atmosphere as in [11].

The antenna orientation has an impact on the received sky noise \([11, 12, 15, 16]\). This due to the thickness of the atmosphere changes with the elevation angle. The effect of the elevation angle has been estimated to be \([12]\)

\[
T_a(d, f, \Theta) = T_A(1 - e^{-\kappa_a(f)\text{csc}(\Theta)})
\]

(6)

where \( \text{csc}(\Theta) \) is a cosecant of the elevation angle \( \Theta \) with 90 degree angle at the zenith. This has been estimated to be rather accurate down to elevation angles from 10 to 15 degrees \([12]\). We can see that the antenna temperature is at highest when antenna is pointed in horizontal direction and lowest when pointed at the zenith \([11, 12]\). This is due to the fact that the length of atmosphere is shortest in the zenith direction. However, it can also be calculated that the antenna temperature in the THz band is approximately constant \( T_A \) regardless of the antenna orientation due to very high absorption.

Given the antenna temperature, assuming no other losses, the sky noise can be approximated as \([13]\)

\[
N_{sn}(T_A, d, f) = k_B T_A W F(1 - e^{-\kappa_a(f)d}).
\]

(7)

where \( W \) is the bandwidth of the system and \( F \) is a sky noise acceptance factor of the receiver (an aperture term for the noise). In the general case, the term \( k_B T \) should be replaced with the Planck’s law (3). However, there
is a difference in the unit of these two terms. The unit of $k_B T$ is J or W/Hz. Integrating it over the bandwidth of the system yields W. The Planck’s law (3) has a unit of W/Hz/cm$^2$. Integrating (3) over the bandwidth yields W/cm$^2$. This is since the Planck’s law is a general radiative function of the surface of the black body. Thus, the antenna aperture term is required if one wants to describe it as power.

We are mostly interested in the general behavior of the noise in the absorbing medium. Therefore, we will describe the sky noise with the Planck’s law (3) and the RTE (2). Assuming highly absorbing medium, such as the THz band, the sky noise reduces to the Planck’s function

$$N_{sn}(T_A, d, f) = \int_0^d B(T_A, f)\kappa_a(f)e^{-\kappa_a(f)s}ds$$

assuming large $d$ (the whole atmosphere contributes to the sky noise). This is a good approximation, since as it was stated, it can be shown that the antenna temperature is approximately constant in the THz band (by utilizing large $d$). As a consequence, in this approximation, the atmosphere radiates according to the Planck’s law. We use the Planck’s function as a background radiation and the molecular absorption noise is an additional noise source, caused by the transmission. As stated above, the sky noise is not caused by the transmissions, but by the atmosphere. Since we approximate the sky noise with the Planck’s function, the unit of the sky noise is W/Hz/cm$^2$. The sky noise can be further approximated by taking into account the (ideal) antenna aperture term $c^2/(4\pi f^2)$:

$$N_p(T_A, f) = \frac{c^2}{4\pi f^2}B(T_A, f),$$

where $N_p(T_A, f)$ is the sky noise power spectral density (PSD) due to the Planck’s function. The unit of this sky noise is therefore W/Hz. The sky noise without the antenna aperture is plotted in Fig. 2. The antenna aperture was discarded in this figure since the most of the molecular absorption noise figures are given in W/Hz/cm$^2$ due to interest in the pure radiative behavior of the molecular absorption noise.

4. Frequency Dependent Molecular Noise

The next two sections consider the molecular absorption noise. The difference to the sky noise is that the molecular absorption noise is induced
by the transmissions of the users sharing the medium. We will go through
the frequency dependent molecular absorption noise models in this section.
First, the existing molecular absorption noise model is derived. Then we
take a look at the propagation delay of the molecular absorption noise as-
suming instantaneous emission of the absorbed energy in a random direc-
tion. Finally, we consider the emission delay due to the spontaneous and
the stimulated emissions.

4.1. General frequency dependent molecular noise

While the sky noise is caused by the atmosphere, the transmission in-
duced molecular absorption noise requires a different approach. In the case
of sky noise, we integrated the RTE over all distances in order to achieve
the contribution of the entire atmosphere. Since we now consider a point
source, a transmitter, the integral in the right-hand term in (2) vanishes and
the source term (the Planck’s function) must be replaced by an appropriate
transmit energy function. Furthermore, we notice that

$$\kappa_a(f) e^{-\kappa_a(f)r} = \frac{d}{dr} \left( 1 - e^{-\kappa_a(f)r} \right).$$

(10)

This derivative is the molecular absorption noise density of a point source
with unit transmit power at distance $r$. This is very easy to verify by
calculating the derivative. On the other hand, we can also verify this by
looking at the purpose of the derivative in the above equation. The difference
of the absorbed energy between two points, infinitesimally close to each
other, tells the energy that was absorbed between these points. There is also
another way to think about the correctness of this approach: the fraction
$$(1 - \exp(-\kappa_a(f)r))$$
gives a cumulative fraction of the energy absorbed. This
is clear when we take the distance to the limit: all the energy is absorbed
and \( \lim_{r \to \infty} (1 - \exp(-\kappa_a(f)r)) = 1 \), unless the absorption coefficient is zero.
The derivative of a cumulative distribution is a probability density function.
Then the above equation is an exponential random variable with a mean
given by an inverse of the absorption coefficient. This is what we seek: an
energy density function of the absorbed energy, i.e., the spatial distribution
of the absorbed energy. Thus, the molecular absorption noise energy at
point $r$ depends on the derivative of the complement of the transmittance.

There is an additional proof of the molecular absorption noise being
proportional to (10), which gives the fraction of the energy absorbed at the
surface of a sphere with radius $r$. This is very easy to verify by stating that
the total energy $E(f)$ at frequency $f$ is either transmitted a distance $r$ or is
absorbed along the path from zero to \( r \). This corresponds to a transmittance at distance \( r \) plus integral over the path of propagation:

\[
E(f)e^{-\kappa_a(f)r} + \int_0^r E(f) \frac{d}{ds} \left( 1 - e^{-\kappa_a(f)s} \right) ds
\]

\[
= E(f)e^{-\kappa_a(f)r} + E(f) \left( 1 - e^{-\kappa_a(f)r} \right) = E(f).
\]

As it can be seen, this is valid for all \( r \). This verifies the absorbed energy density at point \( r \) to be

\[
E_p(r, f) = P_{Tx}(f) \frac{d}{dr} \left( 1 - e^{-\kappa_a(f)r} \right) = P_{Tx}(f) \frac{\kappa_a(f)e^{-\kappa_a(f)r}}{4\pi r^2},
\]

where \( P_{Tx}(f) \) is a transmit signal PSD, \( 1/(4\pi r^2) \) accounts for the spreading loss.

From the above expression for the energy density, we can easily derive the existing molecular absorption noise models [4, 6]. Without time dependency, the energy flux through the surface of a sphere with radius \( r \) is obtained with

\[
\int_0^r P_{Tx}(f) \frac{d}{ds} \left( 1 - e^{-\kappa_a(f)s} \right) ds = P_{Tx}(f) \left( 1 - e^{-\kappa_a(f)r} \right).
\]

By dividing by the area of the sphere, we get the existing molecular absorption noise models for the receiver at distance \( r \) from the transmitter

\[
N_m(r, f) = \frac{P_{Tx}(f)}{4\pi r^2} \left( 1 - e^{-\kappa_a(f)r} \right).
\]

There are some variations in the existing models [4, 6–10] how to take into account the spreading loss and the antenna aperture, but this is the core model. For instance, taking into account the antenna aperture term in (14) leads to the molecular absorption noise models presented in [6, Eq. (16)], [7, Eq. (8)], and [8, Eq. (12)].

An example of this kind of a noise is given in Fig. 2. The molecular absorption noise is given for the transmit power \( P_{Tx} = 2 \) pW/Hz and the distance \( r = 10 \) cm. For reference purposes, the Planck’s function according to (3) at temperature \( T = 300 \) K is also shown and it corresponds to the sky noise (without the antenna aperture term). It can be seen that with the above assumptions on the noise, the molecular absorption noise is a potential source of interference in the THz band.
4.2. Propagation delay for the molecular absorption noise

The above approach did not take into account that the absorbed energy has a propagation delay dependent on the absorption properties of the atmosphere. We get the spatial energy density from (12) assuming spherically symmetric space. We notice that the representation of the noise density is the same as the average path length in the multiple scattering models [18, 26]. Therefore, we propose utilization of the multiple scattering channel models for the molecular absorption noise under the assumption of no emission delay. Because of the zero delay assumption, the whole propagation process is similar to the scattering of energy. The difference is that the scatterers are not particles but molecules, which do not scatter at THz frequencies. The reason is too long wavelength compared to the size of the molecules. Instead, the “scattering” here refers to the release of the absorbed energy without any time delay.

We used the multiple scattering models [18, 26] in [27] to derive a wide-band multiple scattering channel model. However, this time we will stay with the three-dimensional model given by Paasschens in [18] due to the interest on emissions on individual frequencies. The multiple scattering theory comprises the LoS and the non-LoS (NLoS) parts of the radiation. The NLoS is the interesting part of the theory for the molecular absorption noise, because it gives the delayed tail response, or the molecular absorption noise in our case. The LoS component is always the desired signal component. The multiple scattering model for the transient response per unit power is
given by [18]

$$I(r, t, f) = \sum_{N_c=1}^{\infty} \kappa_a(f)^3 e^{-\kappa_a(f)ct} \frac{\Gamma(\frac{3}{4}N_c + \frac{3}{2})}{\pi \sqrt{\pi} N_c! \Gamma(\frac{3}{4}N_c)} \times \left( ct\kappa_a(f) \right)^{N_c-3} \left( 1 - \frac{r^2}{c^2t^2} \right)^{\frac{3}{4}N_c-1} \Theta(r - ct),$$

(15)

where $I(r, t, f)$ is the energy flux per hertz in unit W/Hz/cm$^2$ (J/s/Hz/cm$^2$) at the receiver at the distance $r$ from the isotropic transmitter, $N_c$ is the number of collisions, i.e., the absorptions before a photon reaches the receiver, $\Gamma(\cdot)$ is the gamma function and $\Theta(x)$ is a step function, which one for $x > 0$ and zero elsewhere. The transmit power spectral density is required, since the theory in [18] is for unit transmit power.

Figure 3 shows the behavior of the intensity according to (15). An impulse-like signal in time domain with power spectral density $P_{Tx}(f) = 2$ pW/Hz is assumed. The distance between Tx and Rx is assumed to be $r = 10$ cm. We can see that the transient caused by the continuous absorption-emission process is strongly frequency dependent and locally rather long. This is due to differences in the absorption properties from frequency to frequency. This causes variations in the effective path length before the next absorption occurs, which is given by an inverse of the absorption coefficient. We can also see that the noise level is quite small compared to the one in Fig. 2. The main reason is because the noise energy is distributed over time on the contrary to the case in Fig. 2. Also, the LoS path was excluded since the LoS energy was considered to be the desired signal energy. For
these reasons, the contribution of the molecular absorption noise is small compared with the sky noise.

4.3. Emission rate in THz band

In this section, we consider purely radiative properties of the radiative decay of the energy through the spontaneous and the stimulated emissions. The absorbed energy is assumed to remain at the absorption frequencies and the emissions are only caused by the radiative effects.

The problem of the absorbed and thereafter re-emitted energy requires non-local thermal equilibrium (non-LTE) assumption due to the LTE condition is broken by the absorbed energy from the transmission. This phenomenon is purely related to the molecular absorption noise, theoretically locally disturbing the thermal equilibrium. There are two good books explaining the non-LTE phenomena [20, 21] with a similar approach to the problem. We cannot entirely abandon the LTE, as the full non-LTE problems may be very demanding.

The two-level absorption/emission model can be used to describe energy transitions in the absorption process, which can be explained through the Einstein coefficients. The idea behind the two-level model is that each energy transition is seen as an energy transition between lower and upper energy states. There are in total of \(N\) molecules per unit volume of the medium. As a consequence, there are \(N\) possible energy transitions in the unit volume per frequency. These \(N\) energy transitions populate either the upper or the lower energy state of each molecule at frequency \(f\). Knowing the Einstein coefficients, the time dependent energy state populations can be derived as we did in Appendix A:

\[
n_2(t, f) = \pi_2(f) + (n_2(0, f) - \pi_2(f))e^{-R_{21}(f)t}, \quad (16)
\]

\[
n_1(t, f) = \pi_1(f) - (n_2(0, f) - \pi_2(f))e^{-R_{21}(f)t}, \quad (17)
\]

where \(n_1(t, f)\) and \(n_2(t, f)\) are the time dependent population of the lower and higher energy states, respectively, \(\pi_1(f)\) and \(\pi_2(f)\) are the equivalent for the LTE situation, \(R_{21}(f) = B_{21}(f)B(T, f) + A_{21}(f)\) is the rate of decay of population in \(n_2(t, f)\), where \(A_{21}(f)\) is the Einstein coefficient for the spontaneous emission and \(B_{21}(f)\) is the Einstein coefficient for the stimulated emission. The detailed derivation of the time dependent populations, as well as the related issues, with discussion on the assumptions is given in Appendix A. Knowing the time dependent populations \(n_1(t, f)\) and \(n_2(t, f)\), we can estimate the additional energy density at point \(r\) due to absorption.
Figure 4: Energy decay according to the non-LTE theories.

as was shown in Appendix A:

\[ J_n(T, r, t, f) = B(T, f) \left( \frac{n_2(t, f)}{n_1(t, f)} \pi_1(f) \frac{1 - \exp \left( -\frac{hf}{k_B T} \right)}{1 - \frac{n_1(f)n_2(t, f)}{g_2(f)n_1(t, f)}} - B(T, f) \right) \]  

where \( g_1(f) \) and \( g_2(f) \) are the degeneracies of states 1 and 2 respectively. The dependence of \( J_n(T, r, t, f) \) on \( r \) comes through \( n_1(t, f) \) and \( n_2(t, f) \) as shown in Appendix A. It should be noticed that the Planck’s function in this equation is the energy density as in Eq. (A.3) in Appendix A instead of energy flux as in Eq. (3). The subtraction with the Planck’s law is due to we are only interested in the excess energy in the system, i.e., the molecular absorption noise. This energy approximation is true for the energy decay in a single point \( r \) in the space. The validity of this model is discussed in Appendix A and it can be shown that the model is valid at the boundaries \((t = 0 \text{ and } t = \infty)\). At \( t = 0 \), with simple manipulations, it can be shown that (A.23) is equivalent to the absorbed energy density at the distance \( r \). On the other hand, (A.23) is zero at \( t = \infty \). Therefore, the model is correct at the boundaries. However, the validity of the decay rate is not easy to show in the absence of measurement data. Also, the Authors are unaware of any additional and independent method to validate the rate. Thus, it is not possible to fully validate this model.

Figure 4 shows the decay of the energy density according to the above non-LTE theories assuming a transmit power \( P_{Tx} = 2 \text{ pW/Hz} \). We can see that the energy decay is rather slow, causing large temporal distribution of the energy. Therefore, the energy of the noise is quite low. Furthermore, the energy decay rate varies with the frequency. This is a direct consequence of
the frequency selective absorption as it is (indirectly) shown in Appendix A.

5. Heat Approximation

If we assume all the energy in the absorption is transformed into heat, we get one more approach to the molecular absorption noise. In this case, we must look into the heat capacity of the medium. The heat capacity in general terms is the amount of energy to be transferred to a substance in order to change its temperature by one degree [28]. It is usually given as specific heat capacity, or specific heat, which tells the heat capacity per unit mass of the substance. We know the energy density of the absorbed energy (Eq. (12)). If we assume all this energy is transformed into heat, we can calculate the temperature increase of the medium due to the absorbed energy. Assuming constant pressure, we can use tabled values (e.g., [29]) for the heat capacity, i.e., the isobaric mass heat capacity. Since we know the energy density of the absorbed energy, we need the isobaric volumetric heat capacity \( C_{P,V} \) in order to calculate the temperature increase due to the absorbed energy density. We get it from the density of the air. Then, \( C_{P,V} = \rho C_{P,m} \text{ J/cm}^3/\text{K} \), where \( \rho \) is the density of the air, which can be obtained from the tabled values, e.g., [30]. The temperature increase due to the absorption is given by [28, Chapter 17.5]

\[
\Delta T = \frac{Q(r)}{C_{P,V}}, \tag{19}
\]

where

\[
Q(r) = \int_{W} P_{Tx}(f) \frac{d}{dr} \left( 1 - e^{-\kappa_{x}(f)r} \right) T_{p} df \tag{20}
\]

is the absorbed energy density integrated over the bandwidth \( W \) of the system. The pulse length \( T_{p} \) is required in order to describe the energy over the bandwidth \( W \), i.e., the heat which warms the system. We have shown the temperature increase according to (19) in Fig. 5 for one pulse. The parameters for this figure were as follows: the atmospheric density is \( \rho = 1.191 \times 10^{-6} \text{ kg/cm}^3 \) at 294 K and 101.3 kPa [30] and the specific heat is \( C_{P,m} = 1.011.7 \text{ J/kg/K} \) at 293 K, 101.325 kPa and the relative humidity of 50% [29]. Furthermore, transmit power is ranging from \( P_{Tx}(f) = 10^{-12} \text{ W/Hz} \) to \( P_{Tx}(f) = 10^{-9} \text{ W/Hz} \), the bandwidth is \( W = 9.87 \text{ THz} \) and the pulse length is \( T_{p} = 100 \text{ fs} \). This gives a pulse energy \( E_{p} = P_{Tx}W T_{p} = 0.987 \text{ pJ} \). We can see that the temperature increase due to one pulse is modest. Even with a billion pulses per second, the temperature increase
would be small. This is even when assuming a stationary environment, i.e.,
the temperature is not allowed to disperse, e.g., due to the Brownian motion.
However, the above model is only for one point in space. What is subject
to the future research is to study the contribution of the entire space to
the receiver. That is, to investigate the aggregate radiative noise due to
all points in space. Each point experiences a temperature increase due to
transmitted power and each point in space radiates according to the Planck’s
function. Then it is possible to model the entire space. This requires further
investigation and is therefore subject to the future work. However, it is
possible that the noise contribution with the heat approximation will remain
very small due to the modest effect of the small temperature increase to the
Planck’s function. Especially, since the THz band is not at the peak of
the Planck’s function even at temperatures around 300 K. Therefore, larger
effect of the temperature increase is caused to frequencies above 10 THz.
This is easy test and see with the Planck’s function 3.

Figure 5: Temperature increase due to absorption as a function of distance with several
transmit powers.

6. Discussion and the Future Work

Several different approaches for the molecular absorption noise modeling
were given. However, the true nature of the molecular absorption noise re-
 mains unrevealed. We focused on the different physical phenomena behind
the absorption and emission. The true molecular absorption noise contribu-
tion is a combination of the phenomena presented in Sections 4.1– 5. One
important task for future work is to unify the models. That is, to con-
sider the molecular noise at the receiver due to one or more different noise
induction mechanisms.
The nano-scale device-to-device communications in the THz band is expected to utilize extremely wide bandwidths. Therefore, it is important to consider the temporal properties of the noise. They determine the amount of energy received in the detection window of the receiver. The delayed noise response may lead to inter-symbol interference. This may be a problem for low transmit power devices operating in extremely dense nanonetworks. Although the distances in the nanonetworks are potentially very low, decreasing the instantaneous noise contribution, all the energy will be consumed by the medium. As a consequence, the delayed noise response is important to study. Especially in the case of dense networks, potentially aggregating the noise level in the entire network.

Based on the provided analysis, the truth behind the molecular absorption noise is very complex. We can assume that the molecular absorption noise is a combination of several phenomena. However, several open questions remain to be investigated:

- What are the proportions of the above phenomena to each other? This ultimately determines the intensity of the molecular absorption noise at the receiver. This also determines the frequency domain correlation of these phenomena. For instance, some theories assume the absorbed energy remains at the absorption frequencies (Sections 4.1–4.3), while the thermal assumptions distribute the energy across the spectrum according to the Planck's law. The truth most likely lies between these two assumptions.

- The full analysis on the temporal properties of the absorption. We gave some temporal properties, but only from narrow point of view, e.g., an analysis on a single point of space. This research question determines the time delay properties of the molecular absorption, thus, the intensity of the molecular absorption noise as a function of time. This is, of course, also dependent on the channel sharing of the close-by nanodevices and the symbol separation, i.e., a certain kind of an inter-symbol molecular absorption noise interference.

- Are there any other phenomena that influences the molecular absorption noise? The real atmosphere is very complex medium which cannot be easily modeled with just a few assumptions. For instance, we did no take into account, nor studied the possible existence of the Stokes shift in the THz band causing the re-emission of energy to occur on the lower frequency than the absorption [31, Section 1.3].
• The full spatiotemporal molecular absorption noise model should comprise all the possible phenomena, i.e., the delay, frequency dependent absorption, heat approximation, dynamics of the medium, etc. that can have effect on the radiative noise energy at the receiver.

The full molecular absorption noise model is hard to derive. Still, all the required phenomena for the noise modeling are well known, but most likely never combined due to the unique demands of the communication engineering specific problems.

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Appendix A. Derivation of the Emission Rate

The famous Einstein coefficients and their relationships are [19]

\[ A_{21} = \frac{8\pi hf^3}{c^3}B_{21}, \quad (A.1) \]

\[ g_1B_{12} = g_2B_{21}, \quad (A.2) \]

where \( A_{21} \) is the Einstein coefficient for spontaneous emission, \( B_{21} \) is the Einstein coefficient for stimulated emission, \( B_{12} \) is the Einstein coefficient for absorption and constants \( g_1 \) and \( g_2 \) are statistical weights (degeneracies) of the states 1 and 2, respectively. These coefficients correspond to the two-level approximation of the system and can be obtained from the HITRAN catalogue [32], except for the \( B \) coefficients, but which depend directly on the \( A \) coefficient and the degeneracies of the states as shown above. The unit of the Einstein \( A \)-coefficient is 1/s, i.e., the decay as a function of time, or the probability that the upper state will decay to the lower state. Thus, the inverse of Einstein \( A \)-coefficient is telling the lifetime of the state. The unit of the Einstein \( B \)-coefficients is \( s^{-1}/(J \ cm^{-3} \ Hz^{-1}) \). As a consequence, the \( B \)-coefficients must be multiplied with energy density per unit frequency interval at frequency of the line, or in J cm\(^{-3}\)Hz\(^{-1}\).
The energy density at frequency $f$ in LTE can be obtained from the Planck's law [20, Chapter 3.6]

$$B_f = \frac{A_{21}}{B_{21}} \left( \frac{\bar{n}_1 g_2}{\bar{n}_2 g_1} - 1 \right)^{-1} = \frac{8\pi hf^3}{c^3} \left( \exp \left( \frac{hf}{k_B T} \right) - 1 \right)^{-1}, \quad (A.3)$$

where $\bar{n}_1$ and $\bar{n}_2$ are populations of the upper and lower energy levels under LTE condition, respectively. It should be noticed that $B_f$, $\bar{n}_1$, $\bar{n}_2$, $g_1$, $g_2$, $A_{21}$ and $B_{21}$ are all functions of frequency. Furthermore, this Planck’s law is different to (3) as it gave the energy flux and the above Planck’s law is for energy density, which is obtained by relations [20, Chapter 3.6]

$$\frac{A_{21}}{B_{21}} = \frac{8\pi hf^3}{c^3} \quad (A.4)$$

and

$$\frac{\bar{n}_1}{\bar{n}_2} = \frac{g_1}{g_2} \exp \left( \frac{hf}{k_B T} \right). \quad (A.5)$$

We denote the populations in the non-LTE with $n_1$ and $n_2$, which should not be confused with the LTE populations ($\bar{n}_1$ and $\bar{n}_2$). Under the LTE assumption, a detailed balance between the decay rates is required [20, Chapter 3.6]

$$\bar{n}_1 B_{12} B_f = \bar{n}_2 A_{21} + \bar{n}_2 B_{21} B_f, \quad (A.6)$$

The population of states can be obtained as [19]

$$\bar{n}_1 = \frac{g_1 N}{Q_{tot}(T)} \exp \left( -\frac{hc E_1}{k_B T} \right), \quad (A.7)$$

$$\bar{n}_2 = \frac{g_2 N}{Q_{tot}(T)} \exp \left( -\frac{hc E_2}{k_B T} \right), \quad (A.8)$$

where $N$ is the total number of molecules ($N = p N_A/(RT)$, where $p$ is pressure, $N_A$ is Avogadro’s number and $R$ is gas constant) and $Q_{tot}(T) = \Sigma q g_q \exp(-hc E_q/(k_B T))$ is the total partition function, where $g_q$ is the degeneracy of state $q$ ($\{1, 2\}$) and $E_q$ is the corresponding energy of the state (given by the HITRAN in units 1/cm, thus the $c$ as a multiplier). These parameters are unique for each molecule and the absorption line of the molecule. It is easy to show that $N(f) = \Sigma f n_{1,f} + \Sigma f n_{2,f}$. Therefore, (A.7) and (A.8) hold.
The full detailed balance can be given as [20, Chapter 3.6]

\[ n_1 B_{12} B_f - n_2 A_{21} - n_2 B_{21} B_f + n_1 C_{12} - n_2 C_{21} = 0, \quad (A.10) \]

where \( C_{12} \) and \( C_{21} \) are the collision rates of the states 1 and 2 respectively.

The collisional effects cancel in the LTE (as do the radiative effects). In the further calculations, we assume the environment to be in the LTE, while the transmission breaks the LTE locally, i.e., we neglect the collisional effects and focus on the radiative transfer of energy. Furthermore, the absorbed power is assumed to be small enough to prevent the local warming of the environment. This assumption is directly related to the collisional effects being assumed to remain in the LTE. This is also shown to be rather good approximation based on our calculations on the temperature increase due to the absorbed energy density in Section 5.

We begin the calculation of the molecular absorption noise from the rate between the populations in the non-LTE. It can be derived from the non-LTE Planck’s function [20, Chapter 8.2.1]

\[ J_f = B_f \frac{n_2 \bar{k}_f}{n_2 k_f}, \quad (A.11) \]

where \( \bar{k}_f \) is absorption coefficient in the LTE and \( k_f \) is absorption coefficient in the non-LTE. Ratio of the non-LTE and LTE absorption coefficients is defined as

\[ \frac{k_f}{\bar{k}_f} = \frac{n_1}{n_1} \frac{1 - \frac{g_1 n_2}{g_2 n_1}}{1 - \exp\left(-\frac{h_f}{k_B T}\right)}. \quad (A.12) \]

From these two equations we can derive the population ratios in the non-LTE at point \( r \) at the zeroth time instant with respect to the re-emission of the energy as

\[ \frac{n_1(t = 0)}{n_2(t = 0)} \equiv C(r) = \frac{g_1}{g_2} + \frac{B_f}{J(r) n_2} - \frac{B_f}{J(r) n_2} \frac{n_1}{n_2} \exp\left(-\frac{h_f}{k_B T}\right), \quad (A.13) \]

where \( C(r) \) is the ratio between \( n_1(t) \) and \( n_2(t) \). \( J(r) \) is now the total energy in the system. In the non-LTE, the populations can be solved, given the total energy density \( J(r) \) is known and the collision rates are known. Regarding the collision rates, we rely on the assumptions given above. The total energy density at distance \( r \) is estimated by a summation of the Planck’s law and the absorbed energy at point \( r \) as in (12)

\[ J(r) = B_f + P_{Tx} \frac{\kappa_a e^{-\kappa_a r}}{4 \pi r^2}. \quad (A.14) \]
It can be seen that if \( \kappa_a = 0 \), \( J(r) = B_f \). Then (A.11) reduces to the Planck’s function in the LTE. From (A.13) we can solve \( n_1(0) \) and \( n_2(0) \) from the relationships: \( n_1(0)/n_2(0) = C(r) \), \( n_1(0) = N X \), and \( n_2(0) = N - n_1(0) \), where \( X \) is an arbitrary constant for which \( n_1(0) = NX \), where \( N \) is the total number of molecules. This yields \( n_1(0) = NC(r)/(C(r) + 1) \) and \( n_2(0) = N/(C(r) + 1) \). By knowing the initial populations and the LTE values for them (Eqs. (A.7) and (A.8)), we can derive the populations of the upper and lower states.

Our derivation of the time dependent populations begins with assumption that the upward and downward rates are equal in LTE. Furthermore, we assume that in non-LTE, the upper state population has increased due to absorption and the population rate change is

\[
\frac{d n_2}{d t} = -(n_2(t) - \bar{n}_2) R_{21},
\]  

(A.15)

where \( n_2(t) - \bar{n}_2 \) describes the deviation of the upper state population from the LTE value and \( R_{21} \) is the rate at which the overloaded upper state decays towards the LTE value. The lower state is assumed to have small effect on the upper state since it is underpopulated compared to the LTE. The minus sign is due to the derivative is negative as a consequence of decaying upper population. In LTE, \( d n_2/dt = 0 \). The above equation meets this demand as in LTE \( n_2(t) = \bar{n}_2 \) and due to \( d n_2/dt = 0 \).

We can derive the time domain population of the upper state by rearranging (A.15) and multiplying with \( \exp(R_{21}t) \):

\[
\frac{d n_2}{d t} e^{R_{21}t} + n_2(t) R_{21} e^{R_{21}t} = \bar{n}_2 R_{21} e^{R_{21}t}.
\]  

(A.16)

The term \( d n_2/dt \exp(R_{21}t) + n_2(t) R_{21} \exp(R_{21}t) = d/dt(n_2(t) \exp(R_{21}t)) \) by partial derivative rule. Integrating both sides

\[
\int \frac{d}{d t}(n_2(t)e^{R_{21}t})dt = \int \bar{n}_2 R_{21} e^{R_{21}t} dt
\]  

(A.17)

yields

\[
n_2(t)e^{R_{21}t} = \bar{n}_2 e^{R_{21}t} + D,
\]  

(A.18)

where \( D \) is integration constant. From the initial value for \( n_2(t = 0) \), we get \( D = n_2(0) - \bar{n}_2 \). Thus,

\[
n_2(t) = \bar{n}_2 + (n_2(0) - \bar{n}_2)e^{-R_{21}t}.
\]  

(A.19)
We can check the correctness of this equation by inspecting the value of $n_2(t)$ at the boundaries. At $t = 0$, (A.19) gives $n_2 (0)$ and at $t = \infty$, (A.19) gives $\bar{n}_2$ as it could be expected as the overloaded upper state should decay towards the LTE value after some time from the excitation event. Knowing the $n_2(t)$, we can write $n_1 (t) = N - n_2(t)$. The number of possible transitions remains at constant value $N = \bar{n}_1 + \bar{n}_2 \equiv n_1(t) + n_2(t)$. Therefore, we can write the lower state population as

$$n_1(t) = \bar{n}_1 - (n_2(0) - \bar{n}_2) e^{-R_{21} t}.$$  

(A.20)

It should be noticed that this derivation is an approximation of the reality. We do not take into account the fact, that even in the LTE, there are upward and downward fluxes of energy due to the Einstein coefficients. However, we assume that the LTE, the fluxes cancel each other. Furthermore, we assume that in the non-LTE, the upward flux is negligible as is the downward flux of the LTE value. As a consequence, we assume that only the overloaded part of the population decays and the equations above holds. The full non-LTE problem is not easy to solve. This can be seen by starting from the full problem:

$$\frac{dn_2}{dt} = n_1(t) R_{12} - n_2(t) R_{21},$$

(A.21)

where $R_{12} = B_{12} B_f$, $n_1(t) R_{12}$ is a source term for $n_2(t)$ and $n_2(t) R_{21}$ is a sink term. Similarly, for $n_1(t)$, we can write

$$\frac{dn_1}{dt} = n_2(t) R_{21} - n_1(t) R_{12}.$$  

(A.22)

With similar approach we did above, it is easy to derive the populations. However, assuming constant rates $R_{12}$ and $R_{12}$, the end result does not hold. The full non-LTE problem would therefore require time dependent rates. That will increase the complexity of the calculations significantly. Therefore, we will stay with the approximation for the populations given above.

With the known time dependent populations $n_1(t)$ and $n_2(t)$, we can estimate the additional energy density at point $r$ due to absorption by subtracting from (A.11) the LTE energy density, i.e.,

$$J_n(T, r, t, f) = B_f \frac{n_2(t)}{n_1(t)} \frac{\bar{n}_1}{\bar{n}_2} \frac{1 - \exp \left( - \frac{hf}{k_B T} \right)}{1 - \frac{g_1 n_2(t)}{g_2 n_1(t)}} - B_f.$$  

(A.23)
The validity of this excess energy can be shown at the boundaries. When
time approaches infinity, it is easy to see that (A.23) is zero by looking at
(A.19) and (A.20). When, on the other hand, time is zero, we can show
that the energy in the system is the same as the absorbed energy at point
$r$. This can straightforwardly be shown by calculating the equality

\[ B_f \frac{n_2}{n_1} \frac{1}{\pi_2} \frac{1 - \exp \left( -\frac{h_f}{k_B T} \right)}{1 - \frac{g_1 n_2}{g_2 n_1}} - B_f = \frac{4}{\pi r^2} \frac{1 - e^{-\kappa(r)} r}{4 \pi r^2}. \]

This is easy to confirm by simple manipulations and with the relations given
by (A.13) and (A.14). This proves that the approach is correct at the bound-
aries. However, this is only a partial validation. The energy decay is hard
to validate, mainly because of the absence of the measurement data on the
noise.

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