High Accuracy Resonator Spectroscopy of Atmospheric Gases at Millimetre and Submillimetre Waves

High Accuracy Resonator Spectroscopy of Atmospheric Gases at Millimetre and Submillimetre Waves

By

M. Yu. Tretyakov

Translated from Russian by Nadezhda Krivatkina
in close cooperation with the author

Proofreading by Eleanor Kate Brown

Cambridge
Scholars
Publishing

High Accuracy Resonator Spectroscopy of Atmospheric Gases at Millimetre and Submillimetre Waves

By M. Yu. Tretyakov

This book first published 2022

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN (10): 1-5275-7581-0
ISBN (13): 978-1-5275-7581-3

CONTENTS

Resonator spectrometer

Appendices

INTRODUCTION

Why atmosphere

Cognition of the surrounding world is closely connected with the evolution of civilisation and follows it step by step. At the initial stage, curiosity was the principal driving force, the pursuit of material goods frequently in the background. Later came the realisation that the familiar world is far from infinite, eternal and immutable. It is actually an infinitesimal, fragile framework capable of surviving under the conditions of unstable equilibrium for a brief moment of time at one of the interminable evolutionary stages of the Universe. The duration of this time flash may be cut short at any moment by various, negligible on the global scale, natural (meteor collision, volcanic eruption) or man-made (nuclear conflict, technological disaster) events. The established equilibrium will just break. The realisation of this fact gave a new impetus to learn more about the world so as to protect it. This requires understanding sources of danger, detecting, and preventing them well in advance, or at least forecasting a possible scenario of the upcoming event. At the state level, an understanding of the above implies rational environmental management as one of the priority areas in the development of science in all advanced countries worldwide. Therefore, the technologies of monitoring and forecasting the state of the atmosphere and hydrosphere are regarded to be the most important and even critical.

The atmosphere of the Earth is one of the key factors ensuring the existence of the familiar world. The Earth’s atmosphere is the source of oxygen and humidity that are indispensable for life, protects all living beings against hard cosmic radiation, and also works as a greenhouse film raising the average temperature of the Earth by more than 30°C. The atmosphere balances two basic mechanisms determining the average temperature of the Earth — heating by solar radiation, on the one hand, and energy loss due to self-radiation and the resulting cooling down, on the other hand. This process is called the *radiation balance* of the planet, which implies that the amount of the energy emitted into space must always be equal to that received from the Sun, thereby guaranteeing a stable climate on the planet. Thus, there exists a direct relationship between the climate and the factors influencing the radiation balance. The foremost of these are the solar radiation and the composition of the atmosphere. The oceans, the surface of the Earth, its vegetation, ice, and snow cover, as well as some other factors and processes of their interaction are also important, though to a lesser extent (fig. I.1).

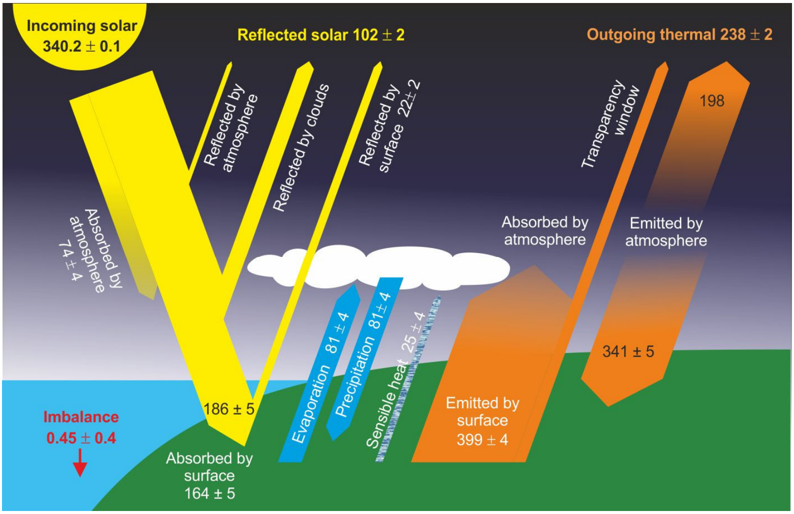

Fig. I.1. Approximate average annual radiation balance of the Earth [L'Ecuyer, 2015].

The author of the present work addresses different aspects of the atmosphere, with a focus on its major gas constituents and on the way, they absorb electromagnetic radiation and influence the radiation balance. Note that studying the problems of radiation propagation in the atmosphere is of great importance, and is closely connected with the development of systems for radio communication, radar and remote sensing, and weather forecasting.

To create a model of radiation propagation in the atmosphere one must know how the weak electromagnetic radiation of the wavelength range of interest interacts with the atmosphere, specifically, with its constituent gases. This interaction, or more precisely, the spectrum characterising the 'force' of radiation interaction with gas as a function of frequency, is the main subject of the study of molecular gas spectroscopy.

What is spectroscopy capable of?

Spectroscopy is a combination of theoretical and experimental methods that enable characterisation of the spectra of individual molecules and their ensembles, i.e., gases and their mixtures. These spectra possess the specific features of thermal motion of molecules and the effects of intermolecular interactions. Nitrogen and oxygen are the main constituents of the Earth's atmosphere, but it also contains molecules of all substances that can exist in the gas phase on our planet (fig. I.2). Despite the insignificant concentration, many of them take part in physical and chemical atmospheric processes and make a significant contribution to the global radiation balance.

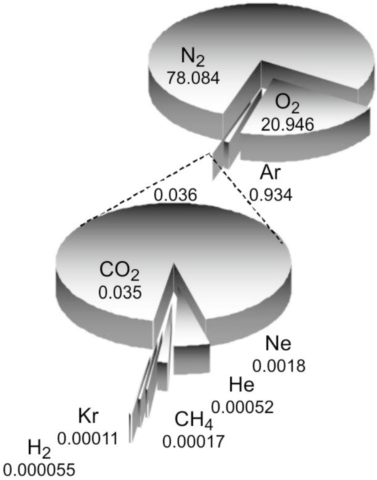

Fig. I.2. Approximate composition of dry atmospheric air with percentage indicated for each.

The most typical example is a molecule of water H_2O. Water vapour constitutes less than 1 % of the mass of the atmosphere but it is the main absorber of radiation. CO_2, O_3, CH_4, N_2O, and many other gases also have a strong immediate impact on the radiation balance (fig. I.3), although the fraction of even the most common of these molecules in the atmosphere is merely a few hundredths of a percent.

To control this atmospheric diversity and properly take into consideration the absorption of the radiation propagating in the atmosphere, spectroscopic databases, which contain detailed information needed for modelling molecular spectra, are created. The most known ones are the open access international databases HITRAN (HIgh-resolution TRANsmission molecular absorption database) [Gordon, 2021] and GEISA (Gestion et Etude des Informations Spectroscopiques Atmosphériques = Management and Study of Atmospheric Spectroscopic Information) [Jacquinet–Husson, 2016].

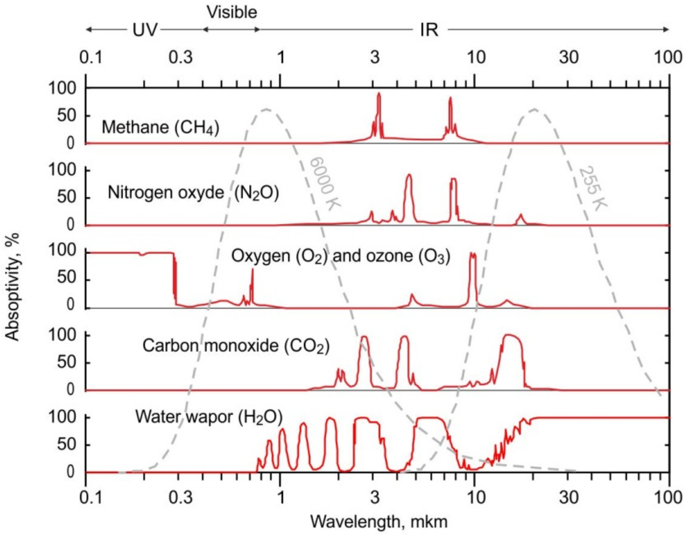

Fig. I.3. The contribution of major greenhouse gases to the absorption of the radiation that has passed through the atmosphere to the surface of the Earth [Peixoto, 1992]. The dashed curves show spectral density of the radiation power of the Sun (6000 K) and the Earth (255 K). The arrows on top indicate approximate borders of ultraviolet (UV), visible, and infrared (IR) ranges.

A huge amount of spectroscopic information, which is constantly updated and supplemented, has been accumulated by now. For instance, the HITRAN-2008 database [Rothman, 2009] contained a little more than 1 million spectral lines of atmospheric gases, whereas its current version HITRAN-2021 [Gordon, 2021] contains over 11 million lines belonging to 55 different molecules in 146 various isotopic combinations, and the ExoMol database [Tennyson, 2016] comprises billions of lines for NH_3, SO_2, H_2CO, CH_4, and other molecules. As a result, many projects on global monitoring of the atmosphere and the underlying surface of the planet that seemed fantastic not long ago can now be implemented from space satellites. As new achievements are made and new technically advanced equipment is developed, mankind poses even more ambitious tasks, the solution of which demands new and more accurate spectroscopic data.

Despite the recent breakthrough in the field of direct numerical computations of molecular spectra on supercomputers, high accuracy experimental research of the radiation absorption by atmospheric gases and their mixtures in well controlled laboratory conditions is still of primary significance. The experiment is required not only for assessing the quality of the known or new calculated data but also for gaining an insight into the physical mechanisms affecting the magnitude of absorption that underlie the propagation models.

What is high accuracy needed for?

High accuracy is critically important for both the models and the underlying spectroscopic data used for calculating the radiation balance and the solution of remote sensing problems, as they are aimed at determining integrated absorption over very long paths with greatly differing conditions of radiation propagation. The calculations should take into account a large range of factors affecting the amount of absorption. With increasing distance from the surface, all major parameters — temperature, pressure, gas concentration — change, even without allowance for turbulent motions of the air (fig. I.4). Hence, the smallest error in the spectroscopic parameters or the inaccuracy of the propagation model may result in significant uncertainties in the interpretation of the computation results.

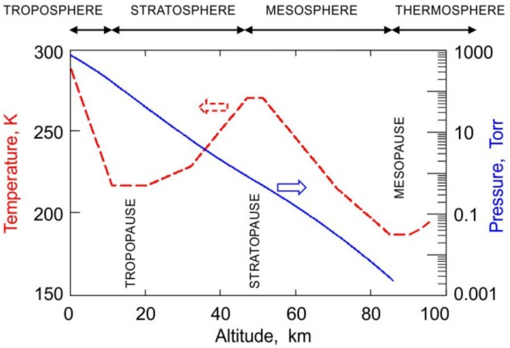

Fig. I.4. Approximate profiles of pressure (solid line, right scale) and temperature (dashed curve, left scale) of the Earth's atmosphere in the mid-latitudes (according to the data of the 'Standard Atmosphere calculator and table generator'). The division of the atmosphere into constituent layers is shown on top.

Why millimetres and submillimetres

Despite the fact that the millimetre and submillimetre waves, even if taken together, constitute only a minor part of the range of electromagnetic radiation interacting with the atmosphere, this monograph is dedicated to this wave range for several reasons.

The atmosphere in the millimetre and submillimetre ranges is more transparent for radiation than in the ultraviolet and visible ranges, especially in the conditions of fog, smoke, dust, and other factors of this sort. This occurs partly because of a much longer radiation wavelength compared to the characteristic size of volatile particles, which makes radiation scattering negligibly small.

The lines of the rotational spectra of all light molecules possessing a magnetic or an electric dipole moment and a small number of atoms fall within this range. This universality makes it extremely attractive for a quantitative molecular analysis, which is the basis of remote sensing of the atmosphere of the Earth and other planets. That is why the number of ground-based, airborne, and satellite-based instruments using the millimetre and submillimetre ranges for monitoring is growing every year.

The considered range is interesting and actively mastered by traditional radar and radiometry methods. The higher the operating frequency of the radiometer (the shorter its wavelength), the higher its spatial resolution and the smaller the size and weight of the instrument. Not a single large satellite mission on remote sensing of the Earth works without devices operating in the millimetre and submillimetre wavelength ranges.

Also worthy of note is the recent actively developing ‘teravision’ — visualisation using terahertz waves. These are the submillimetre waves that must pass through the atmosphere to illuminate or transilluminate the object. Finally, still another reason for choosing the considered range is the fact that the majority of physical mechanisms determining the characteristic features of the spectra of gases and gas mixtures are common for all spectral ranges. The microwave methods of research, that gave birth to high and superhigh resolution molecular spectroscopy and laid the bases for high accuracy millimetre and submillimetre spectroscopy, ensure higher quality data at a lower cost than the studies in other regions of electromagnetic radiation.

Why resonator

The longer the distance passed by the radiation interacting with matter, the weaker the interaction registered by the spectrometer. Therefore, the interaction *path length* and the related sensitivity to radiation absorption are the two principal parameters characterising the instrument. The advantage of a resonator over a conventional gas cell is the possibility of achieving a very long path length. The radiation bouncing between the reflecting mirrors passes the distance between them many times. In a well-made desktop resonator, the radiation can pass several hundred metres. Such a path length in conventional gas cells is possible theoretically, but it is unfeasible in the millimetre and submillimetre ranges primarily because it is impossible to form a narrow non-divergent beam.

A rather long interaction path length may be attained in an open atmosphere in field conditions, but continuously varying, uncontrolled parameters of the object under study, that are quite natural for these conditions, create insurmountable difficulties for accurate measurements.

Still another merit of the *resonator spectrometer* (also referred to as the *cavity spectrometer*) is that for measuring the magnitude of absorption there is no need to know the path length as, in resonance conditions, an integer number of radiation half-waves fit in between the resonator mirrors. Consequently, the radiation-gas interaction path length may be expressed in units of the frequency at which the measurements are performed. In all other spectrometer types, the path length is a multiplier of the measured absorption. The geometrical length of a cell can be measured accurately, but the path length may differ significantly (always being longer) from the geometrical length because of unknown spatial radiation diagram and the presence of inevitable parasitic reflections, due to which part of the radiated power returns to the cell and interacts with the gas. The uncertainty of the length leads to ambiguity of the measured absorption.

Finally, the main advantage of the resonator spectrometer is the practicability of studying broad molecular lines (for example, pressure-broadened lines of atmospheric gases under ambient conditions) and non-resonant absorption slowly varying with frequency. This feature is also connected with a more regular field pattern inside the resonator compared to gas cells of other types. It is especially pronounced in traditional microwave video spectrometers, in which the radiation is transmitted through the studied gas and arrives at the radiation power receiver. The molecular lines in this case are observed as dips in the power *versus* frequency curve. The output power is frequency dependent in all real radiation sources. This dependence is aggravated by the interference of the source radiation with inevitable parasitic reflections from the receiver, gas cell windows, and other spectrometer elements. It is not a simple task to distinguish a broad molecular line from interference dips of comparable width. The frequency period of the amplitude-frequency dependence of the radiation power in the spectrometer is the shorter the longer the gas cell length. There arises a contradiction: a large path length is demanded for a high spectrometer sensitivity, whereas for studying broad lines, the length must be small. As priority is always given to sensitivity, traditional spectrometers of the millimetre and submillimetre ranges are restricted to studying narrow lines corresponding to the uppermost atmospheric layers at extremely low pressures. Therefore, many physical mechanisms affecting the shape of gas spectra remain outside the performed research. One such mechanism is the collisional coupling of molecular lines (also referred to as spectral exchange, line interference, or line mixing). Some spectra consisting of closely spaced molecular lines cannot be represented as a sum of individual components. This effect occurs only at high pressures when the line contours overlap strongly. Another example is molecular spectra arising due to the collisions of molecules with each other. Collisional interaction leads to transient polarisation of molecules. So, even non-polar molecules of noble gases may form short-lived pair states and start to absorb radiation. The corresponding spectral manifestations of such processes are very broad because of a short time scale of collisions. In the millimetre and submillimetre ranges, they may be investigated only by means of resonator spectrometers.

The evolution of resonator spectroscopy

The history of the resonator spectroscopy started almost simultaneously with the high-resolution microwave spectroscopy. In the early spectrometers, the resonator was a box (sometimes the size of a room) with polished copper walls, in which the problem of a huge number of spatial modes excited in such a cavity was solved by means of a fan ‘mixing’ the radiation inside the box and a large number of thermocouples measuring the temperature of the gas heated by the radiation (see, for instance, Becker [1946]). Charles Townes and Arthur Schawlow, the authors of the classical book ‘Microwave Spectroscopy’ [Townes, 1955] widely known in the spectroscopic community, stated that the use of a resonator allows measuring absorption in broad lines and obtaining long path lengths in a gas cell of small size. A few years later, in a paper on the theory of the cavity spectrometer [Beers, 1959] it was shown that, other conditions being equal, its limiting sensitivity may be up to 300 times higher than that of the video spectrometer with a conventional 3-metere cell. Beer’s paper was published at a time when the culture of work with open resonators with two reflecting surfaces (Fabry-Perot resonators) had been formed. In the 1960s it gave an impetus to creating resonator spectrometers, considered at that time as an alternative to video spectrometers that would provide a better sensitivity retaining the high resolution inherent to the microwave spectroscopy. A typical example is a resonator spectrometer created by E. Valkenburg, and V. Derr [Valkenburg, 1966] that was used to investigate the high-resolution spectra of D_2O molecules [Benedict, 1970] and N_2O molecules [Pearson, 1970] in the 70—310 GHz range. The real sensitivity of the resonator spectrometers, on account of their technical features, proved not to be higher than that of conventional video spectrometers. The main reason for this was complexity of employing modulation methods, which was mentioned by Beers but was undervalued by other researchers.

The resonator spectrometers did not reach a record sensitivity in investigations of high-resolution spectra, but they demonstrated their advantages both in accurate measurements of the magnitude of absorption coefficient [Gilbert, 1970] and in studies of broad atmospheric lines [Frenkel, 1966-1] and even of non-resonant absorption [Frenkel, 1966-2].

The next impetus for the development of the resonator spectroscopy was offered by systems of remote sensing and radars that demanded accurate models of millimetre and submillimetre wave radiation propagation in the atmosphere, whereas the high-resolution molecular spectroscopy could not provide sufficient information. Typical examples of the instruments capable of solving these tasks are the spectrometers developed by Hans Liebe [Liebe, 1975, 1984, 1992] and at the University of Lille (France) [Bauer, 1986].

The progress in the modern resonator spectroscopy was stimulated by the increasing requirements for accuracy in the radiation propagation models, as well as by the desire to find a modulation method efficient for the resonator spectrometer and to realise its potential advantage in sensitivity. A possible approach to the solution of this problem is fast, repeated recording of the resonant response in the frequency domain over a maximum short time stipulated by the resonator time constant. A special high-accuracy frequency modulation of the exciting radiation is used for recording, this approach is used in the spectrometer created at the Institute of Applied Physics in Nizhny Novgorod [Krupnov, 2000; Tretyakov, 2009; Koshelev, 2018-1].

Another approach with analogous underlying physics is pulse excitation of a resonator and recording of its response in the time domain over the same minimal time. The attempt to implement this approach was made at the Ohio State University (USA) [Meshkov, 2005]. This approach was, for the time being, fully realised and demonstrated record sensitivity to radiation absorption in molecular lines ($5 \cdot 10^{-13}$ cm^{-1}) only in the resonator spectrometer of the IR wavelength range [Burkart, 2014], in which the reflection coefficient of the mirrors can be an order of magnitude higher than in the millimetre and submillimetre ranges.

The structure of the book

The first chapter of the book is a brief introduction to the molecular gas spectroscopy, in which the basic definitions, terminology, and concepts needed for modelling atmospheric absorption in the millimetre and submillimetre wavelength ranges are introduced. Special attention is given to resonant molecular lines and non-resonant absorption. The physical mechanisms determining line shape and leading to non-resonant absorption are also addressed. The second chapter is dedicated to the resonator spectroscopy technique. The principles of the operation of the resonator spectrometer and of all systems needed for its functioning are considered in detail. The absorption measurement methods are surveyed. The resonator spectrometer developed at the Institute of Applied Physics of the Russian Academy of Sciences (IAP RAS) is considered as a practical example. Its basic parameters are compared with analogous parameters of the other best-known instruments of such class. Chapter 3 is primarily a retrospective overview of the studies of the specific features of atmospheric absorption in the millimetre and submillimetre wavelength ranges. Particular attention is paid to the information regarding the spectra of atmospheric gases obtained using the resonator spectroscopy. The results of analogous investigations employing other methods are presented for comparison. The theoretical fundamentals on the oxygen and water vapour spectra are provided at the beginning of the corresponding sections. A significant part of Chapter 3 is devoted to the investigation of non-resonant absorption and experimental analysis of its causes. The contribution of the resonator spectrometry to the research concerned with the absorption of the millimetre and submillimetre waves by the Earth's atmosphere is summarized in the Conclusion. The materials presented in the Appendices may be helpful to the readers interested in practical details. They may also be useful for a deeper understanding of the processes and phenomena considered in the book.

CHAPTER 1

THE BASICS OF ATMOSPHERIC ABSORPTION MODELLING

1.1. Absorption coefficient

The absorption of sunlight by the atmospheric air has been attracting the attention of researchers for about three centuries. Back in the 1720s, the French physicist Pierre Bouguér assessed the transparency of the atmosphere by measuring changes of the solar light at different heights. In 1729, he published the 'Essay on the Gradation of Light' ('Essai d'Optique, sur la gradation de la lumiere') [Bouguér, 1729], in which he proposed methods for measuring attenuation of the light propagating through the atmosphere and was the first to formulate the basic law of spectroscopy known as the Bouguér law (also referred to as the Beer–Lambert–Bouguér law).

For quantitative measurements of light attenuation or radiation absorption by a medium, it is convenient to use a characteristic that is related only to the medium and depends neither on the radiation properties nor on the interaction volume. The radiation receiver response is usually proportional to the power W of the radiation absorbed by the medium on the path having length Δl. Therefore, the amount of radiation absorption by gas may be characterised by a relative change of the radiation power normalised to the interaction path length:

$$\frac{1}{\Delta l}\frac{\Delta W}{W}\,.$$

Assuming the radiation wavefront to be plane, in the limit as the path length approaches zero, this quantity is called the *absorption coefficient*:

$$\alpha = \lim_{\Delta l \to 0}\left(\frac{1}{\Delta l}\frac{\Delta W}{W}\right) = \frac{1}{W}\frac{dW}{dl}\,. \tag{1.1}$$

Most generally, the absorption coefficient is defined as the relative change in the radiation energy per unit volume of the medium per unit time. By solving this differential equation, taking into consideration that it is more convenient to regard α to be positive, we obtain the formula for the radiation power variation during propagation in the medium known as the Beer–Lambert–Bouguér law:

$$W(l) = W_0 \cdot \exp(-\alpha \cdot l), \tag{1.2}$$

where W_0 is the initial power, and l is the distance passed by the radiation.

In classical electrodynamics, the propagation of electromagnetic waves is described by Maxwell's equations, from which it follows that, in a nonconducting medium having dielectric constant ε and magnetic permeability μ, any Cartesian component of electromagnetic field, E and B, must meet the wave equation

$$\nabla^2 u - \frac{1}{\upsilon^2}\frac{\partial^2 u}{\partial t^2} = 0, \tag{1.3}$$

where the constant $\upsilon = \frac{c}{\sqrt{\mu\varepsilon}}$ characterises the wave propagation velocity in the medium (c is the speed of light in vacuum). The quantity $n = \sqrt{\mu\varepsilon}$ is called the index of refraction or *refractive index* of the medium and is a complex value:

$$n = n_1 + in_2. \tag{1.4}$$

The wave equation has a solution in the form of a plane wave

$$u = \exp(i\mathbf{k} \cdot \mathbf{r} - i\omega t), \tag{1.5}$$

where the circular frequency ω and the absolute value of the wave vector $\mathbf{k}$ are related by

$$k = \frac{\omega}{\upsilon} = \frac{\omega}{c} n. \tag{1.6}$$

If the wave is propagating only in the x direction, the fundamental solution will be written as

$$u(x,t) = A\exp(ikx - i\omega t) + B\exp(-ikx - i\omega t). \tag{1.7}$$

From the relations (1.4) and (1.6) we obtain

$$u(x,t)=\left[A\exp\left(-\frac{\omega}{c}n_2x\right)\exp\left(i\frac{\omega}{c}n_1x\right)\right.$$
$$\left.+B\exp\left(\frac{\omega}{c}n_2x\right)\exp\left(-i\frac{\omega}{c}n_1x\right)\right]e^{-i\omega t}, \tag{1.8}$$

from which it is clear that during the wave propagation in conventional dielectrics ($n_2 > 0$), the wave amplitude decreases exponentially as

$$u(x,t)=A\exp\left(-\frac{\omega}{c}n_2x\right)\exp\left(-i\omega\left(t+\frac{n_1}{c}x\right)\right). \tag{1.9}$$

Considering that the wave power is proportional to its amplitude squared and comparing the form of the solution (1.9) with the expression (1.2), we obtain the following formula for the absorption coefficient of the medium:

$$\alpha=\frac{2\omega}{c}n_2\,. \tag{1.10}$$

For strict compliance with the Beer–Lambert–Bouguér law, the following conditions shall be met:

1) The absorbing medium shall be homogeneous throughout the interaction volume.
2) The medium shall not be turbid, i.e., it must not scatter radiation.
3) The radiation shall propagate through the medium with all its beams being of equal length of the interaction with the absorbing medium.
4) The radiation intensity shall be sufficiently small so as not to disturb the thermodynamic balance of the medium (in particular, the energy distribution of the gas molecules shall be Boltzmann distribution).
5) The radiation shall be monochromatic or at least have a spectral width narrower than the characteristic scale of the dependence of the absorption coefficient of the medium on radiation frequency.

Let us consider how radiation interacts with gases and why the result of the interaction depends on radiation frequency.

The origin of this interaction is the same as the interaction of the electric field with spaced apart unlike charges (electric dipole) or the magnetic field with a current loop (magnetic dipole). In either case, additional energy of the object, arising as a result of the object’s dipole moment interaction with the field, is equal to the scalar product of the dipole moment and the field intensity.

The electric dipole arises in molecules because different atoms attract electrons of the neighbouring atoms in a different way (electronegativity of atoms), leading to a nonuniform distribution of positive and negative charges in the molecule, and to the appearance of the electric dipole moment. The presence of spin in the nuclei and electrons in the molecules or the orbital motion of unpaired electrons is equivalent to the magnetic dipole (fig. 1.1).

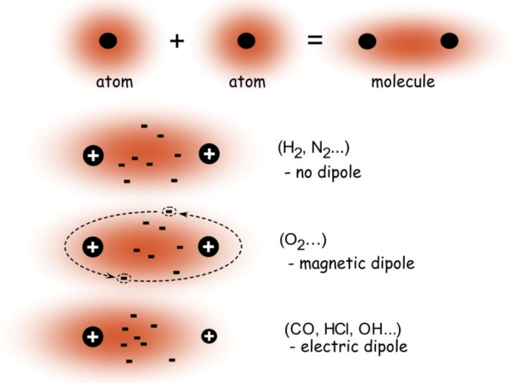

Fig. 1.1. Dipole moment in a diatomic molecule.

Thus, the electric and magnetic components of radiation may interact with the molecules, triggering changes in spin orientation, rotation of a molecule as a whole, vibration of atoms, electron transitions to higher orbitals, and so on. In all cases, the interaction results in the conversion of the radiation energy to one or another form of a molecule's internal energy.

The dependence of the interaction on the radiation frequency originates from the quantum nature of light. A molecule can absorb only one radiation quantum (photon) at each moment of time, this results in an abrupt change in its state, for example, it starts to rotate or to vibrate[1]. As the energy of a quantum is directly proportional to the radiation frequency, and the energy needed to excite motions of different types in a molecule may differ strongly, the result of the radiation–molecules interaction strongly depends on the radiation frequency.

Moreover, in each spectral region corresponding to some type of motion, the radiation may interact with molecules in a resonant or non-resonant manner. Resonant interaction and absorption are typical for

---

[1] Strictly speaking, two or more photons may be absorbed by a molecule simultaneously (see, for example, Bonch-Bruevich [1965] and references therein). However, this probability is many orders of magnitude smaller than a one-photon transition and may be disregarded in the majority of cases.

individual molecules. They occur only at definite frequencies, for instance, the ones related to changes in the angular velocity (frequency of rotation) of a molecule or to changes in the vibrational frequency of atoms. Non-resonant absorption is caused by the inelastic (non-instantaneous, leading to changes in internal energy) interaction of molecules with each other. Even at the instant of collision, that may be regarded to be almost elastic from the classical point of view, the field of one molecule induces charge redistribution in another one, resulting in a transient induced dipole moment. Inelastic collision may cause short-term ‘adhesion’ of molecules and formation of a new object absorbing radiation. In either case a new additional absorption mechanism comes into play that acts for a very short time and, hence, its manifestation in the frequency domain is very smooth compared to the resonant lines. Such smooth broadband spectral features are responsible for non-resonant absorption.

The general dependence of absorption coefficient on frequency is called the *spectrum of gas*. Different types of motion in a molecule correspond to different regions of the spectrum: the spectrum of nuclear magnetic and electron spin (paramagnetic) resonance, rotational spectrum, vibrational spectrum, electron spectrum, and others. The region of frequencies where the resonant interaction occurs is called *the spectral line of gas*.

In section 1.2 we will show where particular frequencies of spectral lines come from, specifically, when a molecule rotating as a whole changes its angular speed. Different aspects of non-resonant absorption will be addressed in section 1.3.

1.2. Resonant lines

In this section we will consider how molecules absorb radiation and what happens in this case. Assume that a hypothetical gas consists of identical molecules that do not possess translational motion and do not interact with each other but are in thermodynamic equilibrium. The spectrum of such a gas depends on the properties of the individual molecules and is actually a stick diagram, in which the lines are delta functions at certain frequencies multiplied by the corresponding amplitudes. We will also address different aspects of resonant line shapes and, in particular, the way molecular motion and almost elastic collisions affect the spectrum of individual molecules.

1.2.1. Spectrum stick diagram

A detailed analysis of the classical [Townes, 1955; Gordy, 1984; Herzberg, 1949-1, -2] and more recent [Jensen, 2000; Banker, 2004] *ab initio* methods of calculating spectra of different molecules based on numerical solution of the Schrödinger equation is not directly related to this book. Here, we intend to demonstrate why, how, and what should be taken into consideration in modelling the spectra of atmospheric absorption in the millimetre and submillimetre wavelength ranges that are the domains of the rotational molecular spectra.

Molecular rotation

In classical physics, the rotations of macroscopic objects are described by angular momentum (the rotational equivalent of linear momentum) and rotational kinetic energy, the essential parameters of the objects being the values of the principal moments of inertia with respect to three mutually perpendicular axes of rotation. This allows the rotation to be considered as a combination of the components along these axes. The rotational spectra of molecules are calculated analogously. This approach is physically correct when the displacement of the atoms in a molecule, from the equilibrium positions, are small compared to the distance between the atoms (bond length). The principal moments of inertia are generally designated in ascending order by I_A, I_B and I_C. According to the values of the moments of inertia, all molecules are divided into groups which are unambiguously related to the geometrical structure of the molecules.

1. *Linear molecules are the molecules in which all atoms are arranged along one line.* Typical atmospheric representatives are the molecules of carbon dioxide (CO_2), nitrous oxide (N_2O), and carbonyl sulphide (OCS). Diatomic molecules such as carbon oxide (CO), molecular oxygen (O_2) or nitrogen (N_2) are the simplest cases of linear molecules. The moment of inertia with respect to the axis of a linear molecule I_A is infinitesimal, as it is determined by the size of the atoms that are negligibly small compared to the bond length and by the electron mass, which is much less than the mass of the atoms. It can be asserted that, under normal conditions, linear molecules do not rotate about their axis, as the energy of such rotation greatly exceeds the average thermal energy of the molecules. The moments of inertia, I_B and I_C, corresponding to the rotation in two mutually perpendicular planes passing through the axis of the molecule are identical. Therefore, it can be assumed that in linear molecules $I_B = I_C$, $I_A = 0$.

2. *Symmetric tops are the molecules with two identical moments of inertia and one moment of inertia different from them and from zero.* Typical representatives are, for example, molecules of ammonia (NH_3) and methyl fluoride (CH_3F). These molecules have a symmetry axis at the rotation about which they resemble tops; that's where the name of the group comes from. Obviously, in this case too, the moments of inertia corresponding to the rotation of mutually perpendicular planes passing through the axis of the molecule are identical. If these moments of inertia are greater than the moment of inertia with respect to the symmetry axis ($I_B = I_C > I_A$), the top is called oblate, and if they are smaller ($I_A = I_B < I_C$), the top is called prolate. Accordingly, the molecule of ammonia is an oblate top, and the molecule of methyl fluoride is a prolate top.

3. *Spherical tops are the molecules with three identical moments of inertia* ($I_A = I_B = I_C$). An example is a tetrahedron-shaped molecule of methane (CH_4).

4. *Asymmetric tops are the molecules that have three different moments of inertia* ($I_A \neq I_B \neq I_C$). The majority of molecules are asymmetric tops. Typical atmospheric representatives are molecules of water (H_2O), nitrogen dioxide (NO_2), ozone (O_3), sulphur dioxide (SO_2), and hydrogen sulphide (H_2S).

We will consider the rotational spectrum in the simplest case of a diatomic molecule, since much of this consideration can be generalised to more complex molecules.

To begin with, we will assume that the atoms are rigidly bonded with each other (fig. 1.2), i.e., we will use *the rigid top approximation*.

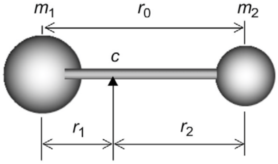

Fig. 1.2. Rigid diatomic molecule. m_1, m_2 and r_1, r_2 are, respectively, atomic masses and distances from the position of the centre of mass (c), and r_0 is bond length.

The principal axis of rotation of such a molecule is normal to its axis and passes through the centre of mass, the position of which is found from the equilibrium condition (the equality of rotational momenta):

$$m_1 r_1 = m_2 r_2 . \qquad (1.11)$$

The moment of inertia with respect to this axis is defined by

$$I_C = m_1 r_1^2 + m_2 r_2^2 = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu \cdot r_0^2 , \qquad (1.12)$$

where μ is the reduced atomic mass. A classical angular momentum **J** of such a system rotating with angular velocity ω_r is

$$\mathbf{J} = I_C \boldsymbol{\omega}_r . \qquad (1.13)$$

The kinetic energy of rotation of such a system is

$$E = \frac{I_C \omega_r^2}{2} = \frac{\mathbf{J}^2}{2 I_C} . \qquad (1.14)$$

Quantum mechanics postulates that the square of the angular momentum is quantised, i.e., it can take on only discrete values proportional to the square of Planck’s constant $\hbar$:

$$\mathbf{J}^2 = \hbar^2 J(J+1), J = 0, 1, 2... \qquad (1.15)$$

The number J is called a *rotational quantum number*. The absolute value of the vector of angular momentum at large values of J is an integer number of Planck’s constants:

$$|\mathbf{J}| \approx J\hbar.$$

Therefore, the angular momentum is frequently represented as a vector having length $J\hbar$.

The dependence of the kinetic energy on the rotational quantum number is found by the substitution of (1.15) into (1.14):

$$E = hBJ\left(J+1\right), \qquad (1.16)$$

where $h = 2\pi \cdot \hbar$, and $B = \frac{h}{8\pi^2 I_c}$ is the *rotational constant* of the molecule.

Exactly the same expression may be rigorously derived for the energy of rotation of a diatomic molecule from the solution of the Schrödinger equation (see, for example, Townes [1955]), from which follows quantisation of rotational energy. Values of the energy determine the position of rotational *energy levels* (stationary molecular states) usually depicted as a diagram (fig. 1.3).

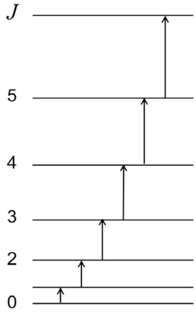

Fig. 1.3. Diagram of rotational energy levels of a diatomic molecule. The arrows show allowed transitions with photon absorption.

A molecule can interact with radiation, absorb a photon, and make a transition from one rotational level to another, only if it has a permanent electric or magnetic moment. Undoubtedly, the necessary condition for absorption to occur is to meet the law of conservation of energy, i.e., the change in the molecule energy must be equal to the energy of the absorbed photon:

$$\Delta E = h\nu\,. \qquad (1.17)$$

Moreover, since the rotational state of the molecule changes as a result of the interaction with the field, i.e., its angular momentum changes, according to the laws of conservation the angular momentum of the field shall change as well. However, a plane electromagnetic wave has no definite angular momentum. To solve this problem, the field is expanded into *multipole waves* (see, for example, Rose [1955] or Berestetskii [1982]). The individual terms of this expansion correspond to the photons having various values of angular momentum, which may be absorbed by molecules. The main term of this expansion is dipole waves. All the other terms of the expansion in molecular spectroscopy may be neglected in most cases (*dipole approximation*). Photons in this case may be in two states corresponding to the projections of their spin (angular momentum) onto the propagation direction equal to $+\hbar$ and $-\hbar$ (in classical electrodynamics this corresponds to the right and left circular polarisations of the electromagnetic wave). Consequently, the molecule that has absorbed a photon can change its total angular momentum only by $\hbar$. This means that, at each act of the interaction of the molecule-dipole with radiation, the rotational quantum number can change only by unity:

$$\Delta J = \pm 1\,. \qquad (1.18)$$

This relation is referred to as the *selection rule* for dipole transitions. The selection rule also follows from the solution of the Schrödinger equation. It determines the molecular energy levels between which transitions are allowed when the molecule interacts with the field. All other transitions are *forbidden*. For the rotational spectrum of a polar diatomic molecule, only the transitions to the neighbouring levels are *allowed*. The plus sign corresponds to the absorption of a photon by a molecule, and the minus sign to photon emission. The transitions with photon absorption are shown by arrows in fig. 1.3.

The substitution of the values of the energy levels from (1.16) into (1.17) applying the selection rule (1.18) yields an expression for the frequencies at which the molecule can absorb radiation:

$$\nu = 2B\left(J+1\right). \tag{1.19}$$

They are the frequencies of the rotational spectrum lines at which the resonant interaction of radiation with a rigid diatomic molecule occurs. From the expression (1.19), it follows that the lines of this spectrum are spaced apart by the same distance equal to $2B$. Such a spectrum is called *equidistant.*

In real conditions, atoms in a molecule are not rigorously bonded; the distance between them during the rotation of the molecule will increase due to centrifugal forces stretching the molecule: the higher the rotation speed (or the value of J), the greater the stretching. If the stretching is small, we can speak of an elastic deformation of the molecule. Then, according to classical physics, an increase in the moment of inertia I_C and the related decrease of the rotational constant B must be proportional to the square of angular velocity or the square of angular momentum (1.14), i.e., in conformity with (1.15), the rotational constant at the state J may be written as

$$B_J = B - DJ(J+1), \tag{1.20}$$

where D is the linear centrifugal stretching constant.

The substitution of this expression into (1.16) yields the energies of the levels

$$E = hBJ\left(J+1\right) - hDJ^2\left(J+1\right)^2. \tag{1.21}$$

The frequencies of rotational lines of a nonrigid molecule obtained by analogy with the derivation of (1.19) are

$$\nu = 2B\left(J+1\right) - 4D\left(J+1\right)^3. \tag{1.22}$$

For the majority of molecules, the constant D is very small, not more than $10^{-4}B$. Therefore, the rotational spectrum of diatomic molecules is almost equidistant, but its lines are gradually approaching each other with increasing J.

A still more exact expression for line frequencies may be obtained by taking into consideration nonlinearity of the centrifugal stretching or, which is the same, anharmonicity of the molecule's field of force. This is done by means of still another small molecular constant H, the magnitude of which depends on the geometry of the molecule (see, for instance, Gordy [1984]). For the energy of the levels, we obtain

$$E = hBJ\left(J+1\right) - hDJ^2\left(J+1\right)^2 + hHJ^3\left(J+1\right)^3, \qquad (1.23)$$

and for the frequencies

$$\nu = 2B\left(J+1\right) - 4D\left(J+1\right)^3 + H\left(J+1\right)^3\left[\left(J+2\right)^3 - J^3\right]. \quad (1.24)$$

The expression (1.23) is actually a power series expansion of energy in terms of $J(J+1)$, which may be expanded, if necessary, to any number of terms. It should be kept in mind that all the other terms of this series do not have such a clear physical meaning as the initial ones. Values of molecular constants are determined by the best possible fit with the experimentally measured line frequencies. For example, the frequencies of the rotational spectrum lines of a molecule of carbon monoxide CO reproducing all currently known accurate measurements may be calculated by three constants: B =57.635968019(28) GHz, D = 0.18350489(16) MHz, and H = 0.17168(10) Hz [Winnewisser, 1997]. The uncertainties of the values of constants related to a measurement error are indicated in parentheses in units of the last significant digit. This notation of a parameter uncertainty will be used throughout this book.

Let us now consider what the amplitude of the spectral lines depends on, i.e., what determines the value of the gas absorption coefficient at the resonance frequency. The radiation power absorbed by the gas is equal to the energy of the absorbed quanta per unit time, which is equal to the number of quanta absorbed per unit time multiplied by the energy of one quantum (we assume for definiteness that there occurs a rotational transition from level a to level b):

$$\Delta E = N_q \cdot h\nu_{ab}. \qquad (1.25)$$

The number of the absorbed quanta is equal to the number of molecules able to absorb a quantum, multiplied by the probability of absorption:

$$N_q = N_{ab} p_{ab}. \tag{1.26}$$

If the medium is in thermodynamic equilibrium with the field, then the number of molecules at the level *a* (energy level *population*) is defined by the Boltzmann distribution

$$N_a = N \exp\left(-\frac{E_a}{kT}\right), \tag{1.27}$$

where N is the total number of molecules, E_a is the energy of the low level, k is the Boltzmann constant, and T is the temperature of gas.

It should be taken into consideration that, in the resonant field, the molecules of the lower-level *a* will absorb photons and jump to the upper-level *b*, and the molecules of the level *b* will, at the same time, emit photons indistinguishable from the photons of the field and will drop to level *a*. We will show below that both processes are equiprobable for the millimetre and submillimetre wavelength ranges. This means that the resulting decrease of the number of field photons, which from the point of view of an external observer corresponds to the number of molecules able to absorb a photon and characterises the radiation power absorbed by the gas, will be proportional to the difference of the populations of levels *a* and *b*:

$$N_a - N_b = N_a\left(1 - \exp\left(-\frac{E_b - E_a}{kT}\right)\right) = N_a\left(1 - \exp\left(-\frac{h\nu_{ab}}{kT}\right)\right). \tag{1.28}$$

It should be taken into account that molecules in different states may have equal energies. Such states are called *degenerate.* The number of the states having the same energy is referred to as the degree of degeneracy. Such states include, in particular, rotational states of molecules with different projections of the total angular momentum in the absence of a permanent external field. In conformity with the quantisation rules, the projection of the total angular momentum of such a system may have values equal to the integer number of Planck's constants:

$$\mathrm{J}_z = m\hbar\,,\ m = 0, \pm1, \pm2\ldots\,. \tag{1.29}$$

Consequently, in a molecule with the angular momentum characterised by the rotational quantum number J, m may take on values from $-J$ to $+J$,