

Third-order linear absorption by pairs of molecules

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A general theory is developed for third-order linear absorption of electromagnetic radiation propagating through a molecular gas. The process is obtained by pairs of molecules that are within a distance smaller than the wavelength. The resulting absorption coefficient is calculated using a statistical model. Numerical calculations of the third-order linear absorption of H₂O in the millimeter-wave region are made and the results are compared with the available empirical formula for the water-vapor continuum.

I. INTRODUCTION

This paper is a direct consequence of trying to answer the following questions.

(i) Is it possible for two molecules to absorb one photon whose frequency does not correspond to a transition of any one of them, but corresponds to a combined transition in which both undergo some electric dipole allowed transition?

(ii) How can such a process be described and the absorption rate calculated?

(iii) How does one calculate the effect of such a process on the absorption coefficient of molecular gases?

(iv) In what case, if any, can such an effect make an observable contribution to absorption by gases under normal conditions of pressure and temperature?

In the next three sections an attempt is made to give a detailed quantitative answer to these questions, while in this introduction the reason for our interest in the subject will be outlined. Consider a system consisting of a single molecule and an electromagnetic radiation field. The molecule can absorb a photon of energy $\hbar\omega_0$ (i.e., the system can make a transition from the initial state, where there are n photons in some radiation mode and the molecule is in a state $|i\rangle$, to a new state where the number of photons is $n-1$ and the molecule is in a state $|j\rangle$) only if such a transition is electric dipole (or some higher-order multipole) allowed and the energy is conserved, which means that $E_j - E_i \approx \hbar\omega_0$ (the almost equality sign is due to natural broadening). This absorption process will be called resonant absorption, and the frequencies at which it occurs will be called the spectral lines of the molecule.

The molecular gas, on the other hand, under high enough pressure can absorb any frequency, even those that are far away from any spectral line. The theory that explains this is called pressure broadening. Actually there are many, quite different, theories of pressure broadening with a common guiding principle, which will be described briefly below.

Interactions between molecules in a gas affect the energy levels of the individual molecules. As a consequence, instead of a constant energy difference ΔE_{ij} between levels i and j there is a certain probability $P_{ij}(\omega_0)$ to find this energy difference near any given energy $\hbar\omega_0$ (i.e., inside

some small interval $\Delta\omega$ centered at ω_0). The main goal of the pressure broadening theories is to calculate the probabilities $P_{ij}(\omega_0)$ from which the absorption coefficient at a given frequency ω_0 can be obtained.

Oversimplifying this idea we may say that, given all the probabilities and the number of photons in the incident radiation mode of frequency ω_0 , we can calculate an average number of molecules $N(\omega_0)$, out of the total number N_T in the gas sample, which will resonantly absorb one photon each per unit time interval.

In view of this very general and simplified analysis of existing pressure broadening theories, it seems natural to ask whether the remaining $N_T - N(\omega_0)$ (which is usually a number very close to N_T) molecules can still contribute, in some other way, to the absorption at a given frequency ω_0 .

Considering now a system of two molecules A and B and the radiation field, it is easy to see that there are additional possible resonant transitions. In principle, the system may now undergo a transition from a state with n photons in some mode and the molecules in the states $|i_A\rangle$ and $|i_B\rangle$, to a new state where there are $n-1$ photons and the molecules are in the states $|f_A\rangle$ and $|f_B\rangle$, providing of course that $E_{f_A} + E_{f_B} - E_{i_A} - E_{i_B} \approx \hbar\omega_0$. This leads naturally to the four questions introduced at the beginning.

It turns out that the simplest possible process that gives the desired effect consists of three interactions between the two molecules and the radiation field, only one of which is proportional to the incident radiation intensity of frequency ω_0 . We thus term it as third-order linear absorption by pairs of molecules.

In a search for the best way to describe the process, the approach of Craig and Thirunamachandran, given in Ref. 1, was chosen as the most suitable one. It should be mentioned that, especially in Sec. II, we rely heavily on similar calculations made there. In view of this it was decided to use similar notation as much as possible.

II. CALCULATION OF TRANSITION MATRIX ELEMENTS

In this section we calculate transition matrix elements for a third-order linear absorption process. The process

is obtained by a pair of molecules that are within a distance much smaller than the wavelength. The two molecules interact with a weak external monochromatic electromagnetic beam and with one another by dipole-dipole interaction. It is assumed that the frequency of the external beam is not resonant with the energy levels of the individual molecules, so that lower-order linear absorption processes are not possible.

For a pair of molecules interacting with the radiation field, the Hamiltonian is given by

$$H = H_{\text{mol}}(A) + H_{\text{mol}}(B) + H_{\text{rad}} + H_{\text{int}}. \quad (2.1)$$

$H_{\text{mol}}(A)$ and $H_{\text{mol}}(B)$ represent the Hamiltonians of the free molecules, H_{rad} is the Hamiltonian of the free radiation field, and H_{int} is the interaction term for the coupling of the pair of molecules with the radiation field.

In the electric dipole approximation the interaction Hamiltonian in the multipolar form (omitting self-interactions) is¹

$$H_{\text{int}} = -\epsilon_0^{-1} \boldsymbol{\mu}_A \cdot \mathbf{d}^\perp(\mathbf{R}_A) - \epsilon_0^{-1} \boldsymbol{\mu}_B \cdot \mathbf{d}^\perp(\mathbf{R}_B), \quad (2.2)$$

where $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}_B$ are the electric dipoles of the molecules A and B , respectively, and the radiation field $\mathbf{d}^\perp(\mathbf{r})$ is given by

$$\mathbf{d}^\perp(\mathbf{r}) = i \sum_{\mathbf{K}, \lambda} \left[\frac{\hbar c \mathbf{K} \epsilon_0}{2V} \right]^{1/2} \{ \hat{\mathbf{e}}^{(\lambda)}(\mathbf{K}) a^{(\lambda)}(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{r}} - \hat{\mathbf{e}}^{(\lambda)}(\mathbf{K}) a^{\dagger(\lambda)}(\mathbf{K}) e^{-i\mathbf{K} \cdot \mathbf{r}} \}, \quad (2.3)$$

where \mathbf{K} is the wave vector, $\lambda=1$ or 2 indicates the two polarizations of the radiation field, V is the quantization volume, and $\hat{\mathbf{e}}^{(\lambda)}(\mathbf{K})$, $a^{(\lambda)}(\mathbf{K})$, and $a^{\dagger(\lambda)}(\mathbf{K})$ are the unit vector in the direction of the field and the annihilation and creation operators of the mode (\mathbf{K}, λ) , respectively. The initial state of the system is given by

$$|0\rangle = |E_0(A), E_2(B), n(\mathbf{K}, \lambda)\rangle, \quad (2.4)$$

where the subscripts 0 and 2 correspond to the initial states of the molecules A and B , respectively, E_0 and E_2 are the corresponding energies, and there are n photons in the (\mathbf{K}, λ) mode of the radiation field.

We look for the transition amplitude from this initial state to a final state:

$$|F\rangle = |E_1(A), E_3(B), (n-1)(\mathbf{K}, \lambda)\rangle. \quad (2.5)$$

In this process one photon with energy $\hbar c K$ is absorbed, exciting the molecules to their final states with energies $E_1(A)$ and $E_3(B)$. Conservation of energy requires

$$E_1(A) + E_3(B) - E_0(A) - E_2(B) = E_{10} + E_{32} = \hbar c K. \quad (2.6)$$

The transition amplitude follows from perturbation theory and is given by

$$M = M_0 + M_1 + M_2 + M_3 + \dots = \langle F|0\rangle + \langle F|H_{\text{int}}|0\rangle + \sum_{\text{I}} \langle F|H_{\text{int}}|\text{I}\rangle \langle \text{I}|H_{\text{int}}|0\rangle + \sum_{\text{II}} \sum_{\text{I}} \frac{\langle F|H_{\text{int}}|\text{II}\rangle \langle \text{II}|H_{\text{int}}|\text{I}\rangle \langle \text{I}|H_{\text{int}}|0\rangle}{(E_{\text{II}} - E_0)(E_{\text{I}} - E_0)} + \dots. \quad (2.7)$$

In the present process the lowest-order contribution to M is the third order, defined above as M_3 . There are six possibilities for the process that may be described by time-ordered graphs enabling the perturbation matrix elements to be listed and calculated. We give here a list of intermediate states I and II, which are denoted here as (a), (b), (c), (d), (e), and (f), and are described graphically in Fig. 1:

$$\begin{aligned} \text{(a)} \quad |\text{I}\rangle &= |E_0(A), E_r(B), (n-1)(\mathbf{K}, \lambda)\rangle, \\ |\text{II}\rangle &= |E_0(A), E_3(B), (n-1)(\mathbf{K}, \lambda), 1(\mathbf{P}, \lambda')\rangle, \end{aligned}$$

where r denotes all the one molecule states that are connected with the states E_2 and E_3 by electric dipole matrix elements and $1(\mathbf{P}, \lambda')$ denotes the photon, with wave vector \mathbf{P} and polarization λ' , exchanged between the two molecules:

$$\begin{aligned} \text{(b)} \quad |\text{I}\rangle &= |E_0(A), E_r(B), 1(\mathbf{P}, \lambda'), n(\mathbf{K}, \lambda)\rangle, \\ |\text{II}\rangle &= |E_0(A), E_3(B), 1(\mathbf{P}, \lambda'), (n-1)(\mathbf{K}, \lambda)\rangle, \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad |\text{I}\rangle &= |E_0(A), E_r(B), 1(\mathbf{P}, \lambda'), n(\mathbf{K}, \lambda)\rangle, \\ |\text{II}\rangle &= |E_1(A), E_r(B), n(\mathbf{K}, \lambda)\rangle, \\ \text{(d)} \quad |\text{I}\rangle &= |E_0(A), E_r(B), (n-1)(\mathbf{K}, \lambda)\rangle, \\ |\text{II}\rangle &= |E_1(A), E_r(B), (n-1)(\mathbf{K}, \lambda), 1(\mathbf{P}, \lambda')\rangle, \\ \text{(e)} \quad |\text{I}\rangle &= |E_1(A), E_2(B), n(\mathbf{K}, \lambda), 1(\mathbf{P}, \lambda')\rangle, \\ |\text{II}\rangle &= |E_1(A), E_r(B), (n-1)(\mathbf{K}, \lambda), 1(\mathbf{P}, \lambda')\rangle, \\ \text{(f)} \quad |\text{I}\rangle &= |E_1(A), E_2(B), n(\mathbf{K}, \lambda), 1(\mathbf{P}, \lambda')\rangle, \\ |\text{II}\rangle &= |E_1(A), E_r(B), n(\mathbf{K}, \lambda)\rangle. \end{aligned}$$

In interpreting the graphs of Fig. 1 time flows upwards. The vertical lines represent the changes taking place in the two molecules. The wavy lines represent photons in (\mathbf{K}, λ) or (\mathbf{P}, λ') modes. The initial and the final states are shown by the horizontal lines $|0\rangle$ and $|F\rangle$, respectively, and the intermediate states are shown by the horizontal lines $|\text{I}\rangle$ and $|\text{II}\rangle$. The intersection of a wavy

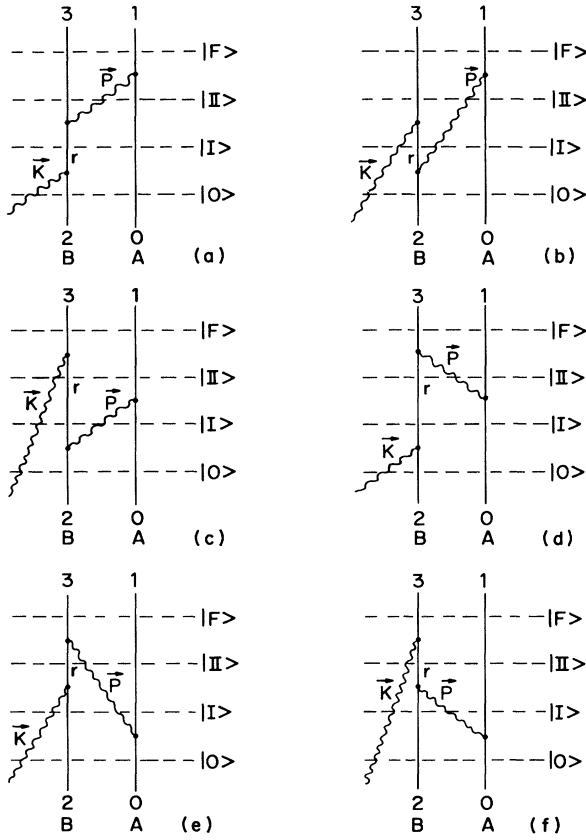


FIG. 1. Six diagrams showing the processes contributing to the third-order linear absorption by pairs of molecules.

line with the solid vertical line represents changes in the states that take place via the interaction term (2.2). The energies of the various states represented by the dashed horizontal lines are easily read from the graphs.

The process is described by three matrix elements corresponding to the molecular transitions:

$$A: 0 \rightarrow 1, \quad (2.8)$$

$$B: 2 \rightarrow r \rightarrow 3.$$

It is assumed that there is no one molecule excited state in the energy neighborhood of the one-photon process. The transitions $A: 0 \rightarrow 1$ and either $B: 2 \rightarrow r$ or $B: r \rightarrow 3$ are produced by the interactions with the vacuum or with one-photon fields so that the total process is linear in the intensity of the external field. We introduce the following definitions:

$$\begin{aligned} \mu_i^{mn}(A) &= \langle E_m(A) | \mu_i | E_n(A) \rangle, \\ \mu_i^{mn}(B) &= \langle E_m(B) | \mu_i | E_n(B) \rangle, \end{aligned} \quad (2.9)$$

$$E_{mn} = E_m - E_n,$$

and the summation notation for repeating indices:

$$a_i b_i = \sum_{i=1}^3 a_i b_i. \quad (2.10)$$

To simplify calculations we assume $\mathbf{R}_A = \mathbf{0}$, $\mathbf{R}_B = \mathbf{R}$. By adding the contributions of processes described by the six diagrams of Fig. 1 and after some simple algebra we get the total transition amplitude:

$$\begin{aligned} M = -i \left[\frac{nc\hbar K}{2\epsilon_0 V} \right]^{1/2} \sum_{\mathbf{P}, \lambda', r} \left[\frac{\hbar c P}{2\epsilon_0 V} \right] \hat{e}_i^{\lambda'}(\mathbf{P}) \hat{e}_j^{\lambda'}(\mathbf{P}) \hat{e}_k(\mathbf{K}) \mu_i^{10}(A) \left[\frac{e^{i(\mathbf{K}-\mathbf{P})\cdot\mathbf{R}}}{(E_3 - \hbar c K + \hbar c P)} \left[\frac{\mu_j^{3r} \mu_k^{r2}}{E_{r2} - \hbar c K} + \frac{\mu_i^{3r} \mu_k^{r2}}{E_{r2} + E_{10}} \right] \right. \\ \left. + \frac{e^{i(\mathbf{K}+\mathbf{P})\cdot\mathbf{R}}}{E_{10} + \hbar c P} \left[\frac{\mu_k^{2r} \mu_j^{r2}}{E_{r2} + E_{10}} + \frac{\mu_k^{3r} \mu_j^{r2}}{E_{r2} - \hbar c K} \right] \right]. \end{aligned} \quad (2.11)$$

By using the equality

$$E_{r2} + E_{10} = E_{r2} - E_{32} + \hbar c K = \hbar c K - E_{3r} \quad (2.12)$$

we introduce the symbol $\alpha_{jk}^{32}(B)$, defined by

$$\alpha_{jk}^{32}(B) = \sum_r \left[\frac{\mu_j^{3r} \mu_k^{r2}}{E_{r2} - \hbar c K} + \frac{\mu_k^{3r} \mu_j^{r2}}{\hbar c K - E_{3r}} \right] \quad (2.13)$$

and then we obtain

$$M = -i \left[\frac{n\hbar c K}{2\epsilon_0 V} \right]^{1/2} \sum_{\mathbf{P}, \lambda'} \left[\frac{\hbar c P}{2\epsilon_0 V} \right] \hat{e}_i^{\lambda'}(\mathbf{P}) \hat{e}_j^{\lambda'}(\mathbf{P}) \hat{e}_k(\mathbf{K}) \mu_i^{10}(A) \alpha_{jk}^{32}(B) \left[\frac{e^{i(\mathbf{K}-\mathbf{P})\cdot\mathbf{R}}}{\hbar c P - E_{10}} + \frac{e^{i(\mathbf{K}+\mathbf{P})\cdot\mathbf{R}}}{E_{10} + \hbar c P} \right]. \quad (2.14)$$

The sum over the polarization is performed as usual by writing

$$\sum_{\lambda'} \hat{e}_i^{\lambda'}(\mathbf{P}) \hat{e}_j^{\lambda'}(\mathbf{P}) = \delta_{ij} - \hat{P}_i \hat{P}_j \quad (2.15)$$

and the sum over \mathbf{P} is converted to an integral by using the relation

$$\frac{1}{V} \sum_{\mathbf{P}} \Rightarrow \frac{1}{(2\pi)^3} \int d^3\mathbf{P}. \quad (2.16)$$

From (2.16) we obtain the transition amplitude as

$$M = -i \left[\frac{n\hbar c K}{2\epsilon_0 V} \right]^{1/2} \hat{e}_k(\mathbf{K}) \mu_i^{10}(A) \alpha_{jk}^{32}(B) e^{i\mathbf{K}\cdot\mathbf{R}} \frac{1}{2\epsilon_0} \int \frac{d^3\mathbf{P}}{(2\pi)^3} P \frac{(\delta_{ij} - \hat{P}_i \hat{P}_j)}{P^2 - K_{10}^2} [P(e^{i\mathbf{P}\cdot\mathbf{R}} + e^{-i\mathbf{P}\cdot\mathbf{R}}) - K_{10}(e^{i\mathbf{P}\cdot\mathbf{R}} - e^{-i\mathbf{P}\cdot\mathbf{R}})] , \quad (2.17)$$

where $K_{10} = E_{10}/\hbar c$. Integrals identical to this have been calculated in Ref. 1 and using their results we get

$$M = -i \left[\frac{n\hbar c K}{2\epsilon_0 V} \right]^{1/2} \hat{e}_k(\mathbf{K}) \mu_i^{10}(A) \alpha_{jk}^{32}(B) V_{ij}(K_{10}, \mathbf{R}) e^{i\mathbf{K}\cdot\mathbf{R}} ,$$

$$V_{ij}(K_{10}, \mathbf{R}) = \frac{1}{4\pi\epsilon_0 R^3} \{ (\delta_{ij} - 3\hat{R}_i \hat{R}_j) [\cos(K_{10}R) + K_{10}R \sin(K_{10}R)] - (\delta_{ij} - \hat{R}_i \hat{R}_j) K_{10}^2 R^2 \cos(K_{10}R) \} . \quad (2.18)$$

Equation (2.18) describes the transition amplitude for the absorption of a photon (\mathbf{K}, λ) by a pair of molecules undergoing the transitions: $A(0 \rightarrow 1)B(2 \rightarrow r \rightarrow 3)$.

It should be mentioned that in the general case there could be additional contributions to the above result.

(i) First of all, to give the total transition amplitude for the absorption of a photon (\mathbf{K}, λ) , Eq. (2.18) should be summed over all possible pairs of final states of molecules A and B that satisfy the resonance condition (2.6) and are allowed by appropriate selection rules for one- and two-photon absorption processes, respectively.

(ii) If molecules A and B are identical and if their initial states are the same ($\langle 0| \equiv \langle 2|$), then there is an additional set of six diagrams contributing to the transition amplitude. This set is obtained by interchanging the place of molecules A and B in Fig. 1.

(iii) If the molecules are not identical or if they are identical but their initial states are different, there is still a possibility of a contribution from the interchanged set of diagrams (i.e., third-order absorptions in which A undergoes two interactions and B undergoes one interaction). In this case, however, just interchanging the molecules A and B in Fig. 1 is not enough. An allowed dipole transition between an initial and a final state of a molecule obeys either the one- or the two-photon selection rules. In view of this one should also provide a new pair of final states for molecules A and B ($\langle 1'|$ and $\langle 3'|$), which do obey the appropriate selection rules and, at the same time, obey the resonance condition:

$$E_{1'0} + E_{3'2} = \hbar c K .$$

Whether one or more of those additional contributions do actually exist depends on the specific application. In our treatment of water-vapor absorption (Sec. IV), we have found that the contributions from cases 2 and 3 could be practically ignored. In principle, the inclusion of the contributions of cases 2 and 3 can be done in a straightforward way by following the same steps used in the derivation of Eq. (2.18).

In view of this, and in order to simplify the following calculations, which will be applied later to water vapor, we will assume that Eq. (2.18) represents practically the only third-order linear absorption process that contributes to the absorption of a photon (\mathbf{K}, λ) by a pair of

molecules A and B . Assuming for simplicity that \hat{e}_K and μ_i are real, we get

$$|M|^2 = \left[\frac{n\hbar c K}{2\epsilon_0 V} \right]^2 \hat{e}_k^\lambda(\mathbf{K}) \hat{e}_n^\lambda(\mathbf{K}) V_{ij} V_{lm} \mu_i^{10}(A) \times \mu_l^{10}(A) \alpha_{jk}^{32}(B) \alpha_{mn}^{32}(B) . \quad (2.19)$$

The above result gives the absorption probability for a specific orientation of molecule A , molecule B , vector \mathbf{K} , and vector \mathbf{R} relative to each other. In a gas these orientations are usually randomly distributed, therefore a rotational averaging of (2.19) must be performed.

By associating the vector \mathbf{R} with some frame fixed in space, it is easy to see that the expressions (2.19) should be averaged over all possible orientations of vector \mathbf{K} , molecule A , and molecule B relative to such a frame. This may be written as

$$\langle |M|^2 \rangle = \left[\frac{n\hbar c K}{2\epsilon_0 V} \right]^2 \langle \hat{e}_k \hat{e}_n \rangle_{\mathbf{K}} V_{ij} V_{lm} \times \langle \mu_i^{10} \mu_l^{10} \rangle_A \langle \alpha_{ik}^{32} \alpha_{mn}^{32} \rangle_B . \quad (2.20)$$

The averaging is performed using the general technique described in Ref. 2. The averaging over molecule A gives

$$\langle \mu_i^{10} \mu_l^{10} \rangle_A = \frac{1}{3} \delta_{il} |\boldsymbol{\mu}^{10}|^2 . \quad (2.21)$$

The averaging over molecule B gives

$$\langle \alpha_{jk}^{32} \alpha_{mn}^{32} \rangle_B = \frac{1}{30} (\delta_{ik} \delta_{mn} U + \delta_{jm} \delta_{kn} V + \delta_{jn} \delta_{km} W) , \quad (2.22)$$

where

$$U = 4\alpha_{\lambda\lambda}\alpha_{\nu\nu} - \alpha_{\lambda\mu}\alpha_{\lambda\mu} - \alpha_{\lambda\mu}\alpha_{\mu\lambda} ,$$

$$V = -\alpha_{\lambda\lambda}\alpha_{\nu\nu} + 4\alpha_{\lambda\mu}\alpha_{\lambda\mu} - \alpha_{\lambda\mu}\alpha_{\mu\lambda} ,$$

$$W = -\alpha_{\lambda\lambda}\alpha_{\nu\nu} - \alpha_{\lambda\mu}\alpha_{\lambda\mu} + 4\alpha_{\lambda\mu}\alpha_{\mu\lambda} .$$

The averaging over \mathbf{K} gives

$$\langle \hat{e}_k \hat{e}_n \rangle_{\mathbf{K}} = \frac{1}{3} \delta_{kn} |\hat{e}|^2 = \frac{1}{3} \delta_{kn} . \quad (2.23)$$

Substituting Eqs. (2.21) and (2.23) into Eq. (2.20) we get

$$\begin{aligned} \langle |M|^2 \rangle &= \left[\frac{n \hbar c K}{2 \epsilon_0 V} \right] \frac{1}{270} |\boldsymbol{\mu}^{10}|^2 \delta_{kn} (V_{lk} V_{ln} U + V_{lm} V_{lm} \delta_{kn} V + V_{ln} V_{lk} W) \\ &= \left[\frac{n \hbar c K}{2 \epsilon_0 V} \right] \frac{1}{27} |\boldsymbol{\mu}^{10}|^2 V_{lm} V_{lm} \alpha_{\lambda\mu} \alpha_{\lambda\mu}. \end{aligned} \quad (2.24)$$

Using the approximation $K_{10}R \ll 1$ in Eq. (2.18) we can write

$$V_{lm} \simeq \frac{\delta_{lm} - 3\hat{R}_l \hat{R}_m}{4\pi\epsilon_0 K R^3}, \quad (2.25)$$

$$V_{lm} V_{lm} \simeq \frac{6}{(4\pi\epsilon_0)^2 R^6}. \quad (2.26)$$

By substituting Eq. (2.26) into Eq. (2.24) we get our final result for the averaged square of the absolute value of the matrix element of the third-order linear absorption:

$$\langle |M|^2 \rangle = \left[\frac{n \hbar c K}{2 \epsilon_0 V} \right] \frac{1}{(4\pi\epsilon_0)^2 R^6} \frac{2}{9} |\boldsymbol{\mu}^{10}|^2 \alpha_{\lambda\mu}^2 \alpha_{\lambda\mu}^2. \quad (2.27)$$

III. STATISTICAL MODEL OF THIRD-ORDER LINEAR ABSORPTION

We analyze here a statistical model for third-order linear absorption of electromagnetic radiation propagating through a molecular gas. Statistical models that take into account binary interactions of atoms have been described previously for broadening of spectral atomic lines in the visible or ultraviolet regime.^{3,4} In these models the broadening has been related to the difference between the interaction potential between the two atoms in their initial and final states, i.e., before and after the absorption process. By these statistical models the profiles of the spectral lines, including the appearance of satellite bands, in the atomic spectra have been successfully analyzed.

The statistical model discussed here is different and appears to be more appropriate for analyzing absorption effects in the infrared, millimeter, and microwave regions. For such absorption transitions, with relatively low frequencies, the change in the interaction potential between the two molecules, before and after the transition, is significant. Therefore we develop here a different statistical model which incorporates the effect described in the preceding section.

First the integrated absorption resulting from a third-order linear transition of molecular pairs from an initial state $|E_0(A), E_2(B)\rangle$ to a final state $|E_1(A), E_3(B)\rangle$ will be calculated.

According to the Fermi golden rule, the energy absorbed by a gas sample of small length ΔZ containing $N_i(R)dR$ pairs in the initial state and $N_f(T)dR$ in the final state is given by

$$\hbar\omega_0 [N_i(R) - N_f(R)] dR \frac{2\pi}{\hbar} \rho \langle |M|^2 \rangle \frac{\Delta Z}{c}, \quad (3.1)$$

where the distance between the molecules in the pairs is assumed to lie in the interval R to $R + dR$, ω_0 is the frequency of transition and M is the transition matrix element for a given R calculated in Sec. II.

The number of levels per unit energy, ρ , is related to the incident radiation energy flux per unit area per unit frequency interval $I_0(\omega)$. Assuming a broadband slowly varying $I_0(\omega)$ centered around the transition frequency ω_0 , the relation is given by

$$\rho = \frac{I_0(\omega_0)V}{2\pi n \hbar^2 \omega_0 c}. \quad (3.2)$$

The total energy absorbed by the sample due to a certain third-order linear transition is calculated by integrating (3.1) over all possible values of R between R_{\min} and R_{\max} .

The need to limit the minimum possible value of the intermolecular distance arises from the use of the interaction term (2.2) in calculating the matrix elements. This term is valid only for the range of intermolecular separations outside the molecular overlap region. Obviously, the use of the results of the preceding section should be limited to intermolecular distances greater than some appropriate R_{\min} .

For $R > R_{\min}$ (neglecting the interaction energy) and using the binary approximation, the number of pairs with intermolecular distance between R and $R + dR$ is given by

$$N(R)dR = N^2 4\pi R^2 dR. \quad (3.3)$$

This formula has been used by all statistical theories and gives good results provided R is much smaller than the average distance between molecules.

The number of pairs in which one of the molecules is in state E_0 and the other in E_2 is given by

$$\begin{aligned} Gg_0g_2 N(R)dR \frac{\exp[-(E_0 + E_2)/k_B T]}{Q^2} \\ = N(R)dR \frac{g'_i \exp(-E_i/k_B T)}{Q^2}, \end{aligned} \quad (3.4)$$

where g_0, g_2 are the statistical weights of the states E_0 and E_2 ; Q is the appropriate partition function of the gas molecule; $G=1$ if the two states E_0 and E_2 are equal and $G=2$ if they are different; $g'_i = Gg_0g_2$ is the overall statistical weight of the pair state.

Finally, the total energy absorbed by the sample due to some specific third-order linear transition by molecular pairs is given by

$$I_0(\omega_0) \frac{V}{n\hbar^2 c} \frac{\Delta Z}{c} 4\pi \frac{N^2}{Q^2} [g'_i \exp(-E_i/k_B T) - g'_f \exp(-E_f/k_B T)] \int_{R_{\min}}^{R_{\max}} \langle |M|^2 \rangle R^2 dR . \quad (3.5)$$

Inserting (2.26) for $\langle |M|^2 \rangle$ and performing the integration up to $R_{\max} = \infty$ we get

$$\frac{1}{27} I_0(\omega_0) \frac{4\pi\omega_0}{\hbar c \epsilon_0} \frac{\Delta Z}{c} \frac{1}{R_{\min}^3} \frac{|\mu^{10}|^2}{(4\pi\epsilon_0)^2} \alpha_{\lambda\mu}^{32} \alpha_{\lambda\mu}^{32} \frac{N^2}{Q^2} [g'_i \exp(-E_i/k_B T) - g'_f \exp(-E_f/k_B T)] . \quad (3.6)$$

On the other hand, assuming validity of the Beer-Lambert law, the connection between the incident $I_0(\omega)$ and the transmitted irradiance per unit frequency interval is given by

$$I(\omega) = I_0(\omega) e^{-\alpha(\omega)\Delta Z} , \quad (3.7)$$

where $\alpha(\omega)$ is the absorption coefficient. For ΔZ sufficiently small we can write

$$I(\omega) - I_0(\omega) \simeq I_0(\omega) \alpha \Delta Z \quad (3.8)$$

and the total energy absorbed by the sample, for a broadband slowly varying $I_0(\omega)$, is

$$\frac{I_0(\omega_0)}{c} \Delta Z \int \alpha(\omega) d\omega = I_0(\omega_0) \frac{\Delta Z}{c} \gamma_{\text{int}} , \quad (3.9)$$

where γ_{int} is the integrated absorption coefficient. Equating (3.6) and (3.9) we get finally

$$\gamma_{\text{int}} = \frac{\omega_0}{27\hbar c} \frac{|\mu^{10}|^2 \alpha_{\lambda\mu}^{32} \alpha_{\lambda\mu}^{32}}{4\pi\epsilon_0^3 R_{\min}^3} \frac{N^2}{Q^2} \{ g'_i \exp[-E_i/(k_B T)] - g'_f \exp[-E_f/(k_B T)] \} . \quad (3.10)$$

An average absorption coefficient in a certain frequency interval, due to third-order linear absorption by pairs, can be calculated by summing the integrated absorption of all pair absorption lines falling in the interval and dividing by the interval length. If the number of pair absorption lines in the interval is large enough this will lead us to a very good approximation of the actual absorption coefficient.

IV. THIRD-ORDER LINEAR ABSORPTION BY WATER VAPOR IN THE MILLIMETER-WAVE REGION

Although there is no doubt that the general process described in detail above exists, it is obviously a very weak (compared to ordinary first order) absorption process. Therefore the question arises whether it can have any observable effect on the absorption of electromagnetic radiation by gases.

It is quite clear that one should look for such effects in those parts of a gas spectrum where the ordinary absorption is weak, i.e., in the windows between spectral lines.

Under normal conditions the absorption by gases is determined by pressure broadening of the first-order linear absorption lines. This is an extremely well-studied subject, theoretically and experimentally. So the chances are that if the third-order linear absorption by pairs of

molecules can make an observable effect, and if, as far as we know, it has never been taken into account, there should be a reported discrepancy between theoretically calculated and measured absorption.

At least one such discrepancy has been known for a long period of time. It is a well-established fact that the measured absorption in the atmospheric "windows" is greater (sometimes much greater) than calculated, using known pressure broadening theories. The discrepancy is strongly correlated with the amount of water vapor in the air and is known as the water-vapor continuum or EWA (excess water absorption).⁵⁻⁷ The phenomenon exists over a large part of the spectrum spreading from microwaves to the near infrared. Although many attempts have been made to give a theoretical explanation for EWA, none of them, until now, can give quantitatively solid results. Over the years several empirical formulas describing the discrepancy in different spectral regions have emerged.⁶ In the millimeter-wave region one of the most widely used and accepted is the Liebe continuum formula:⁷

$$\alpha = f^2 [2.548 \times 10^{-8} p e \Theta^{2.5} + 9.846 \times 10^{-6} e^2 \Theta^{5.5}] , \quad (4.1)$$

where α is the absorption coefficient in dB/km, f is the frequency in GHz, e is the partial pressure of water vapor in kPa, p is the partial pressure of all other gases in the atmosphere in kPa, and $\Theta = 300/T$, where T is the temperature in K.

Figure 2 shows the atmospheric attenuation in the

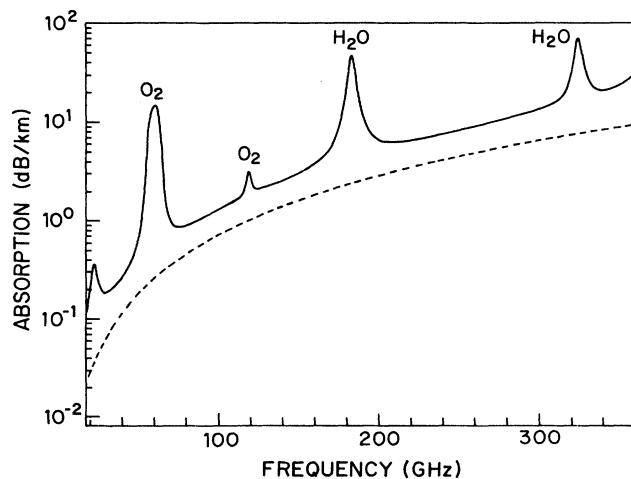


FIG. 2. The sea-level atmospheric absorption (solid line) and the Liebe continuum (dashed line) in the 20–360-GHz region for $T=293$ K, the absolute humidity is 12 g/m^3 .

20–350-GHz region (solid line) and the value of the Liebe continuum (dashed line) at typical sea-level atmospheric conditions. The solid line is obtained by adding, to the theoretical value of the attenuation, the empirical continuum based on experimental results.

It will be shown later in this section that in this region third-order linear absorption by pairs of water molecules makes a significant contribution to the observed discrepancy between the theoretical and measured absorption described empirically by the above formula.

The general process of calculating the absorption by pairs of given molecules is simple. First one writes down all the electric dipole allowed transitions and the corresponding frequencies ω_{10} . Then one lists all possible “Raman type” transitions $2 \rightarrow r \rightarrow 3$ and the corresponding frequencies ω_{32} (each transition contributes two terms—one for absorption, $\omega_{ij} > 0$, and one for emission, $\omega_{ij} < 0$). Then one finds all third-order linear transitions that con-

tribute to absorption in the region of interest ($\omega_{\min} < \omega < \omega_{\max}$) by looking for all combinations that give

$$\omega_{\min} < \omega_{32} + \omega_{10} < \omega_{\max} . \quad (4.2)$$

The integrated absorption of each line is then calculated using (3.10) and spectroscopic data of the molecule (energy levels, transition strength, and statistical weights).

This procedure was applied to calculate the absorption by pairs of H_2O molecules in the millimeter wave region. Since the absorption of H_2O in this region is determined by a pure rotational spectrum, we include only rotational transitions in our calculation. H_2O is an asymmetric top molecule with a permanent dipole moment coinciding with the intermediate axis of rotation. Therefore, using the standard $J_{K-1}K_1$ notation, the rotational transition rules for a one-photon process (ω_{10}) are^{8,9}

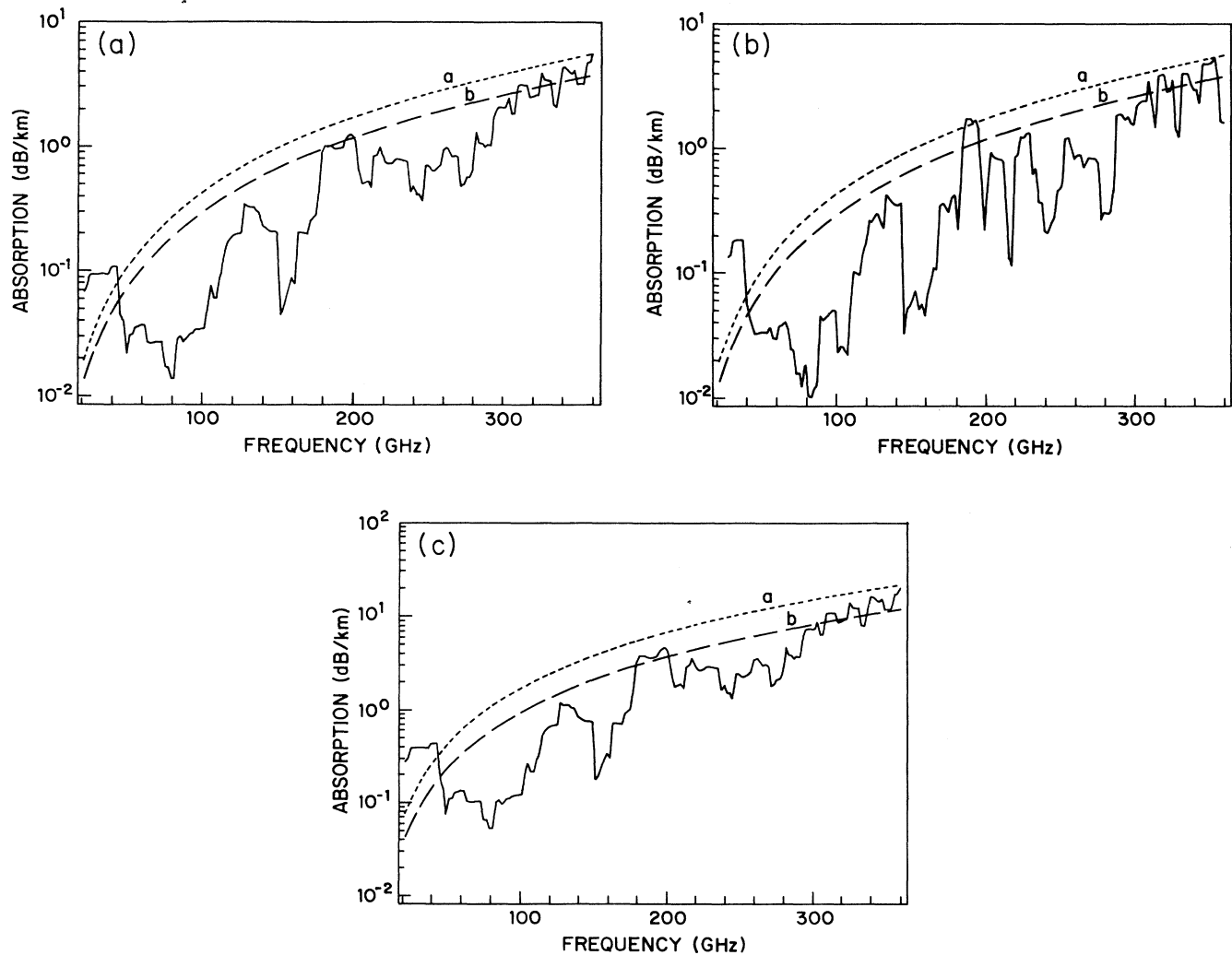


FIG. 3. Comparison of the third-order linear absorption of H_2O molecules (solid line) and the Liebe continuum (labeled *a*) in the 20–360-GHz region. Also shown is the part of the Liebe continuum that depends on the square of the water concentration (labeled *b*). (a) $T=293$ K, the absolute humidity is 12 g/m^3 , with an averaging interval of $\Delta f=24$ GHz. (b) $T=293$ K, 12 g/m^3 , and $\Delta f=12$ GHz. (c) $T=313$ K, 25 g/m^3 , and $\Delta f=24$ GHz.

$$\begin{aligned} \Delta J &= 0, \pm 1, \\ ee &\leftrightarrow oo, \quad eo \leftrightarrow oe. \end{aligned} \quad (4.3)$$

(Rotational levels are specified by evenness or oddness of $K_{-1}K_1$) and for a two-photon process (ω_{32})

$$\begin{aligned} \Delta J &= 0, \pm 1, \pm 2 \\ ee &\leftrightarrow ee, \quad oo \leftrightarrow oo, \quad eo \leftrightarrow eo, \quad oe \leftrightarrow oe. \end{aligned} \quad (4.4)$$

In the summation over the virtual states r we have included all possible intermediate rotational states allowed by one-photon selection rule. In this way we guarantee that the two-photon selection rules are obeyed completely. However, we have neglected the much weaker contributions from intermediate excited r states, which are vibrationally excited. A detailed numerical example of the calculations made for the integrated absorption of one of the third-order absorption lines is given in the Appendix. Use was made of energy-level data from Ref. 10 and transition-strength data from Refs. 11 and 12 and the calculation was limited to transitions up to $J=9$. This produced 449 transitions of type ω_{10} and 4008 Raman-type transitions ω_{32} .

It was found that there are 3168 third-order linear absorption lines in the 20–360-GHz region. Weak transitions of type $R_{3\bar{3}}$, $P_{3\bar{3}}$, $Q_{3\bar{3}}$ and higher were excluded. Lines with either $2 \rightarrow r$ or $r \rightarrow 3$ transitions near resonance with the incident radiation frequency were excluded also. The integrated absorption of these lines was subsequently calculated according to (3.10), assuming $R_{\min} = 10 \text{ \AA}$. This choice of R_{\min} was used to ensure the validity of the interaction term (2.2). The actual intermolecular separation of two H_2O molecules at which overlapping effects become appreciable is estimated at $5\text{--}7 \text{ \AA}$.⁵

No adjustable parameters, other than R_{\min} , were used in this calculation. Figures 3(a)–3(c) show the attenuation in dB/km caused by third-order linear absorption of water vapor (solid line) obtained by averaging the integrating absorptions over frequency intervals of 24 GHz. The figures also show the Liebe continuum formula (labeled a) and that part of the formula which depends on e^2 (labeled b). Since the present results are also a function of e^2 , it is more appropriate to compare them with that part only.

V. CONCLUSIONS

It is not the purpose of the present paper to go into more detailed analysis of the effect of third-order linear absorption on the problem of the water-vapor continuum. The only conclusions we would like to obtain from these preliminary results are the following.

(i) In view of the results described in Figs. 3(a)–3(c) it seems that in analyzing the absorption by water vapor in the millimeter wave windows regions, one should take into account the significant contribution of the third-order linear absorption.

(ii) In view of (i), it is reasonable to expect that third-order linear absorption can also have an observable effect

on attenuation in spectral “windows” in other regions and by other gases.

After starting the paper with four questions and, as we hope, giving them the right answers, it seems appropriate to end it by discussing some of the most interesting subjects for future research.

First of all, the investigation of third-order linear absorption by water vapor should be extended to the infrared (i.e., to the vibrational transitions of H_2O). Although the two molecules in the pairs were referred to as being of the same type, it is not a necessary condition. In addition to this, magnetic dipole or higher-order multipole interactions can be included in the theory. In view of the last two points, it would be interesting to study the contribution of oxygen-water pair absorption to the EWA in the millimeter-wave region.

Finally, it should be mentioned that there are reports of discrepancies between calculated and measured continuum absorption by other gases. For example, NH_3 absorption in the $1900\text{--}2100\text{-cm}^{-1}$ region exhibits such a discrepancy. Not accidentally, the reason for the NH_3 investigation arises from the interest in the “windows” of the Jovian atmosphere.¹³

APPENDIX

One of the third-order linear absorption lines of water vapor in the 20–350-GHz region is obtained when one of the molecules in a pair undergoes a transition $A(4_{22} \rightarrow 4_{13})$ with $f_{10} = -1208 \text{ GHz}$ and the other $B(2_{11} \rightarrow r \rightarrow 3_{13})$ with $f_{32} = 1413 \text{ GHz}$. The usual $J_{K_{-1}K_1}$ notation for an asymmetric rotor is used to designate various rotational energy levels of an H_2O molecule.⁹ The frequency of the radiation absorbed in the above process is

$$f_0 = f_{32} + f_{10} = 205 \text{ GHz}. \quad (A1)$$

The integrated absorption of this line will be calculated now using spectroscopic data about H_2O from the following.^{10–12}

1. Calculation of $|\mu^{10}|^2$ and $\alpha_{\lambda\mu}^{32}\alpha_{\lambda\mu}^{32}$

The dipole moment of H_2O coincides with the intermediate axis of rotation b (i.e., only $\mu_b^{ij} \neq 0$). In view of this we can write

$$|\mu^{10}|^2 = (\mu_b^{10})^2 = \mu_{\text{H}_2\text{O}}^2 S_{10}^b, \quad (A2)$$

where S_{10}^b is a tabulated quantity for a given asymmetric rotor and $\mu_{\text{H}_2\text{O}}$ is the dipole moment of H_2O ,

$$\mu_{\text{H}_2\text{O}} \simeq 6.14 \text{ C m}. \quad (A3)$$

For the $A(4_{22} \rightarrow 4_{13})$ transition we get¹¹

$$|\mu^{10}|^2 \simeq 8.2 \times 10^{-59} \text{ C}^2 \text{ m}^2. \quad (A4)$$

In the same way $\alpha_{\lambda\mu}^{32}\alpha_{\lambda\mu}^{32}$ for H_2O is given by

$$\alpha_{\lambda\mu}^{32}\alpha_{\lambda\mu}^{32} = \left[\sum_r \left[\frac{\mu_b^{3r}\mu_b^{r2}}{E_{r2} - \hbar cK} + \frac{\mu_b^{3r}\mu_b^{r2}}{\hbar cK - E_{3r}} \right] \right]^2. \quad (\text{A5})$$

There are two possible Raman-type transitions from 2_{11} to 3_{13} :

$$(a) \quad 2_{11} \rightarrow 2_{20} \rightarrow 3_{13},$$

$$(b) \quad 2_{11} \rightarrow 2_{02} \rightarrow 3_{13}.$$

From Ref. 10 the corresponding energy differences are

$$(a) \quad \frac{1}{h}E_{r2} = 1230 \text{ GHz}; \quad \frac{1}{h}E_{3r} = 183 \text{ GHz}, \quad (\text{A6})$$

$$(b) \quad \frac{1}{h}E_{r2} = -753 \text{ GHz}; \quad \frac{1}{h}E_{3r} = 2166 \text{ GHz}.$$

In view of the fact that $f_0 = 205 \text{ GHz}$ it is clear that we can approximate

$$\alpha_{\lambda\mu}^{32}\alpha_{\lambda\mu}^{32} \equiv \left[\frac{\mu_b^{3t}\mu_b^{t2}}{h(205 - 183) \times 10^9} \right]^2, \quad (\text{A7})$$

where t now stands for 2_{20} .

From Ref. 11 we get

$$(\mu_b^{3t})^2 = 3.8 \times 10^{-60} \text{ C}^2 \text{ m}^2, \quad (\text{A8})$$

$$(\mu_b^{t2})^2 = 4.7 \times 10^{-59} \text{ C}^2 \text{ m}^2,$$

and finally

$$\alpha_{\lambda\mu}^{32}\alpha_{\lambda\mu}^{32} \approx 8.4 \times 10^{-73} \text{ C}^4 \text{ m}^4 \text{ J}^{-2}. \quad (\text{A9})$$

2. Calculation of Q

For $T > 100 \text{ K}$ a good approximation for the rotational partition function of an asymmetric rigid rotor is given by⁸

$$Q \equiv 2 \left[\frac{\pi}{ABC} \left(\frac{k_B T}{h} \right)^3 \right]^{1/2}, \quad (\text{A10})$$

where A , B , and C are the rotational constants of the molecule. Inserting the data for H_2O (Ref. 8) into (A10) we obtain

$$Q \approx 3.2 \times 10^{-2} T^{3/2}. \quad (\text{A11})$$

3. Calculation of the statistical factor

For the above specified initial and final levels of A and B molecules, we get from Ref. 8

$$g'_i = g'_f = 2 \quad (\text{A12})$$

and using the fact that $hf_0 \ll k_B T$ we obtained

$$\begin{aligned} & g'_i \exp(E_i/k_B T) - g'_f \exp(E_f/k_B T) \\ &= 2 \frac{hf_0}{k_B T} \exp(-E_i/k_B T) \\ &\approx 6.5 \times 10^{-2}. \end{aligned} \quad (\text{A13})$$

Inserting all that into (3.10) and assuming $T = 300 \text{ K}$ and $N = 2.5 \times 10^{23} \text{ m}^{-3}$ (i.e., water-vapor density of 7.5 g/m^3), we obtained the integrated absorption of the line,

$$\gamma_{\text{int}} \approx 1.7 \times 10^6 \text{ m}^{-1} \text{ Hz}. \quad (\text{A14})$$

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