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Journal of Quantitative Spectroscopy & Radiative Transfer ■ (■■■■) ■■■–■■■

Journal of
Quantitative
Spectroscopy &
Radiative
Transfer

www.elsevier.com/locate/jqsrt

Einstein *A*-coefficients and statistical weights for molecular absorption transitions in the *HITRAN* database

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Received 28 August 2004; received in revised form 22 July 2005; accepted 22 July 2005

Abstract

This paper describes the calculation of the statistical weights and the Einstein *A*-coefficients for the 39 molecules and their associated isotopologues/isotopomers currently present in the line-by-line portion of the *HITRAN* database. Calculation of the Einstein *A*-coefficients was carried out using the *HITRAN* line intensities and the necessary statistical weights. The Einstein *A*-coefficient and the statistical weights of the upper and lower levels of the transition were added in the new format of the line parameters for the most recent edition of the *HITRAN* database.

Keywords: Einstein *A*-coefficient; Statistical weight; Spectroscopic database; Atmospheric database; *HITRAN*

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0022-4073/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.jqsrt.2005.07.003

1. Introduction

The *HITRAN* molecular spectroscopic database [1] consists of several components essential for radiative transfer codes: high-resolution spectroscopic parameters of molecules in the gas phase, absorption cross-sections for molecules with very dense spectral features, aerosol refractive indices, ultraviolet line-by-line parameters and absorption cross-sections, and associated database management software. This compilation can be accessed at http://cfa-www.harvard.edu/HITRAN. The format of the line-by-line portion of the 2004 edition of *HITRAN* [1] has been expanded. The statistical weights and the Einstein *A*-coefficients have been added for the transitions of the thirty-nine molecules and their isotopologues/isotopomers[3] (currently 93, see Table 1 for the list). This paper discusses the motivation for adding these parameters and describes their calculation in order to provide users with a clearer understanding.

Section 2 describes the motivation that led to the replacement of the weighted square of the transition moment, $\Re$, that was present in the previous edition of *HITRAN* [2] by the Einstein *A*-coefficient. In order to understand how the Einstein *A*-coefficients are calculated from the line intensities given in *HITRAN*, the definition of the line intensity is presented in Section 3, and the definition of the Einstein *A*-coefficient follows in Section 4. Section 5 gives the relation between the line intensity and the Einstein *A*-coefficient. Section 6 clarifies the determination of the statistical weights that are necessary to calculate the Einstein *A*-coefficients from the line intensities. Furthermore, the determination of the so-called state-dependent nuclear spin statistical weights is explained for each isotopologue/isotopomer present in the *HITRAN* database. In Section 7, the relations between the Einstein *A*-coefficient, the oscillator strength, the line intensity and the weighted square of the transition moment are recalled. Section 8 discusses the non-additivity of the Einstein *A*-coefficients. Finally, Section 9 is devoted to inter-comparisons between the Einstein *A*-values in this work and the Cologne database for molecular spectroscopy [3].

2. Rationale for replacing the weighted square of the transition moment by the Einstein *A*-coefficient

The Einstein *A*-coefficient is desirable for applications in non-local thermodynamic equilibrium (non-LTE) problems of the atmosphere, astrophysics, and fundamental physics. Reasons for replacing the weighted square of the transition moment, $\Re$, by the Einstein *A*-coefficient in the *HITRAN* database are discussed below.

As has been mentioned by Goldman et al. [4], several inconsistencies can occur with the use of $\Re$. The first inconsistency is linked to the definition of the transition moment, which often differs from one author to another. Indeed, the definition sometimes includes the Hönl–London factors, sometimes not. For example, following Refs. [5–7], $\Re$ includes the Hönl–London factors, as in the definition for *HITRAN*. However in some studies [8,9], in order to reproduce the experimental *J*-

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[3] An isotopologue is a molecular variant that differs from the original molecule in the isotopic composition (number of isotopic substitutions) only; for example, $^{13}CH_4$ and $^{12}CH_3D$ are isotopologues of $^{12}CH_4$. An isotopomer (a contraction of ‘isotopic isomer’), on the other hand, has the same number of each of the isotopic atoms but differing in their orientation within the molecular structure (giving rise to different spectra), for example $^{16}O^{18}O^{16}O$ is an isotopomer of $^{16}O^{16}O^{18}O$ and so is $^{14}N^{15}NO$ of $^{15}N^{14}NO$.

dependence with the Herman Wallis factor, the Hönl–London factors were left out of $\mathfrak{R}$. This omission results in possible sources of error when data are incorporated into *HITRAN*.

Another inconsistency concerns the use of the statistical weights. In *HITRAN* [2], the parameter $\mathfrak{R}$ is the weighted square of the transition moment as defined in Refs. [5,6]. However, because this definition is sometimes overlooked, or because the terminology is not precise enough (see for example Table 6 of Ref. [10]), the unweighted square of the transition moment has occasionally been put into previous editions of *HITRAN*. The nuclear spin statistical weights can also be included or left out in the definition of $\mathfrak{R}$. In order to be consistent with the definition of $\mathfrak{R}$ with the Herman Wallis factor, these weights should not be included in the definition (see for example Jacquemart et al. [8]). Similarly, according to the convention adopted in Refs. [7,11], a supplemental weight equal to 2 can be introduced for the bands having l-type doubling. The fact that some authors neglect these supplemental weights, or use incorrect statistical weights (see for example Goldman et al. [4]), can lead to an erroneous value of $\mathfrak{R}$ in *HITRAN*.

Another difficulty is related to the set of units used for $\mathfrak{R}$ and to the expressions linking it to the *HITRAN* line intensity, which are different for electric-dipole, magnetic-dipole and electric-quadrupole transitions. The relation between the line intensity and $\mathfrak{R}$ in Refs. [5–7] is given only for electric-dipole transitions. This equation is not rationalized [12], that is to say, the unit coherence of the equation is not respected since the vacuum permitivity, ε_0, has been replaced by $1/4\pi$ in order to be in cgs electrostatic units. In *HITRAN*, the unit for $\mathfrak{R}$, which is valid for the electric-dipole transitions (the most prevalent cases in *HITRAN*), is Debye^2, but the standard unit is $\mathrm{C^2\,m^2}$. *HITRAN* also contains some magnetic-dipole transitions (O_2) and electric-quadrupole transitions (O_2 and N_2) for which the standard units are $\mathrm{A^2\,m^4}$ and $\mathrm{C^2\,m^4}$, respectively.

The choice of the Einstein A-coefficient is more standard and universal. There is only one definition and one unit for the Einstein A-coefficient ($\mathrm{s^{-1}}$). Moreover, the Einstein A-coefficient does not depend on the type of a transition (i.e. electric-dipole, magnetic-dipole, electric-quadrupole...). The Einstein A-coefficient is also preferred to the Einstein B-coefficients because for B there are at least four possible cases according to the meaning given to the amount of radiation used in its definition [12,13].

It is important to point out the existence of a wide variety of expressions for the different quantities related to the interactions between molecules and light [13]. The whole formalism for the Einstein coefficients and the intensity can be found in Refs. [13,14]. However, in order to have the same notations and the same equations as in previous *HITRAN* papers [2,5,6,15], we summarize the most important steps that are necessary to obtain a relation between the Einstein A-coefficient and the line intensity.

3. Definition of the line intensity

According to the Lambert–Beer law, the variation $\mathrm{d}I(\nu)$ of the intensity of a monochromatic radiance at wavenumber ν, going through a layer of a homogenous gas whose incremental depth is $\mathrm{d}l$, is proportional to the depth of this layer and to the intensity $I(\nu)$ of this radiance [14]

$$\mathrm{d}I(\nu) = -k(\nu)I(\nu)\,\mathrm{d}l, \tag{1}$$

where $k(\nu)$ (in $\mathrm{cm^{-1}}$) is the spectral absorption coefficient per unit length. Note, the variables and equations presented here adopt the notations used in *HITRAN* [2]; v is the wavenumber[4] and it is given in units of cm^{-1}. Care must be exercised when comparing the equations presented here with those found in other papers and texts where v can sometimes be the frequency in Hz.

The integrated absorption coefficient S (in cm^{-2}) of an isolated line centered at v_0 is defined as

$$S = \int_{-\infty}^{+\infty} k(v - v_0) d(v - v_0). \tag{2}$$

The spectral absorption coefficient can be expressed using S as a proportionality constant

$$k(v - v_0) = S\Phi(v - v_0), \tag{3}$$

since the integral of the normalized profile $\Phi(v - v_0)$ over the ~~all~~ spectral range is $\int_{-\infty}^{+\infty} \Phi(v - v_0) d(v - v_0) = 1$.

The absorption coefficient can be written as proportional either to the pressure P, or to the volumetric density ρ, or to the number N of absorbing molecules per unit volume

$$S = S_v^P P = S_v^\rho \rho = S_v^N N. \tag{4}$$

If P is in atm, ρ in $\mathrm{g\,cm^{-3}}$, and N in molecule cm^{-3}, the units of S_v^P, S_v^ρ, and S_v^N are cm^{-1} $(\mathrm{atm\,cm})^{-1}$, cm^{-1} $(\mathrm{g\,cm^{-2}})^{-1}$, and cm^{-1} $(\mathrm{molecule\,cm^{-2}})^{-1}$, respectively. Note that many other definitions and notations of the line intensity exist [16]. The notation of S_v^P, S_v^ρ and S_v^N is self-explanatory since the subscript v means that we use wavenumbers (cm^{-1}), and the superscripts P, ρ, N mean that the line intensity is defined for a unit pressure, for a unit volumetric density, and for one molecule per unit volume, respectively.

It is important to note that in *HITRAN*, the given line intensity is S_v^N ($T = 296\,\mathrm{K}$). Moreover, because S_v^P and S_v^N are the most common quantities used, it is useful to recall the relations between these two quantities

$$S_v^N(T) = \frac{P}{N} S_v^P(T). \tag{5}$$

For an ideal gas, we have

$$\frac{N}{P} = \frac{1}{k_\mathrm{B} T} = \frac{1}{k_\mathrm{B} T_\mathrm{S}} \frac{T_\mathrm{S}}{T}, \tag{6}$$

where $k_\mathrm{B} = 1.38065 \times 10^{-16}\,\mathrm{erg\,K^{-1}}$ is the Boltzmann constant ($1\,\mathrm{erg} = 10^{-7}\,\mathrm{J}$), T is the temperature of the gas, T_S is the standard temperature ($T_\mathrm{S} = 273.15\,\mathrm{K}$) and

$$\frac{1}{k_\mathrm{B} T_\mathrm{S}} = \frac{L(T_\mathrm{S})}{P_0}, \tag{7}$$

where $L(T_\mathrm{S})$ is the Loschmidt number ($L(T_\mathrm{S}) = 2.68676 \times 10^{19}\,\mathrm{molecule\,cm^{-3}}$), and P_0 the pressure unit (equal to 1 atm). Finally, we obtain

$$S_v^N(T) = \frac{P_0}{L(T_\mathrm{S})} \frac{T}{T_\mathrm{S}} S_v^P(T). \tag{8}$$

Eq. (8) provides the conversion between the two most common definitions of the line intensity.

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[4] Throughout this paper we use the symbol v for wavenumber (in units of cm^{-1}), rather than $\tilde{v}$ since there will be no confusion with frequency (units of s^{-1}).

The formula allowing the temperature conversion of the line intensity can be obtained by performing the ratio of the expressions of S_ν^N (see Eq. (19) below and notations in Section 5) at two different temperatures, T and T'

$$S_\nu^N(T) = S_\nu^N(T') \frac{Q'_{\text{tot}}(T')}{Q_{\text{tot}}(T)} e^{-c_2 E_1((1/T)-(1/T'))} \left[\frac{1 - e^{-c_2\nu/T}}{1 - e^{-c_2\nu/T'}}\right], \tag{9}$$

where $Q_{\text{tot}}(T)$ is the total internal partition sum of the absorbing gas at the temperature T and E_1 is the energy of the lower state (cm^{-1}). c_2 is the second radiation constant, hc/k_{B}, where c is the speed of light and h is the Planck constant.

4. Definition of the Einstein coefficients

The Einstein A-coefficient for spontaneous emission is a first-order decay constant in units of s^{-1} [14]. If we consider that the number of atoms in the initial upper level m at time zero is $N_m(0)$, then, in the absence of an external radiation field, the number remaining after time t is

$$N_m(t) = N_m(0) e^{-\sum_n A_{mn} t}, \tag{10}$$

where the summation is performed over all the lower energy levels n.

Several definitions of the Einstein B-coefficients for induced absorption and emission exist, according to the meaning given to the amount of radiation of an external radiation field. In this work, the "amount of radiation", u_ω, is taken as the energy density per unit frequency interval at the frequency of the line, ω, and it is expressed in $\text{J}\,\text{cm}^{-3}\,\text{Hz}^{-1}$. Hence, the unit for B-coefficients is $\text{s}^{-1}/(\text{J}\,\text{cm}^{-3}\,\text{Hz}^{-1})$, which is also written as $\text{cm}^3(\text{J}\,\text{s}^2)^{-1}$. If we consider that the number of atoms in the initial level m is N_m, then the number of induced downward transitions to the lower level n per unit time is given by $N_m B_{mn} u_{\omega_{mn}}$. Similarly, the number of induced upward transitions to the upper level n' per unit time is $N_m B'_{mn} u_{\omega'_{mn}}$.

The rate at which N_m decreases with time as a result of these three radiative processes is described as

$$-\frac{\mathrm{d}N_m}{\mathrm{d}t} = N_m \sum_n A_{mn} + N_m \sum_n B_{mn} u_{\omega_{mn}} + N_m \sum_{n'} B_{mn'} u_{\omega_{mn'}} \tag{11}$$

(the replenishment of level m by transitions from other levels or its depletion or replenishment by collisional processes can be involved in further considerations).

In an approximation of a two level system (upper m and lower n levels are denoted as 2 and 1, respectively), we have the well-known equations linking the Einstein A- and B-coefficients

$$g_1 B_{12} = g_2 B_{21}, \tag{12}$$

$$A_{21} = 8\pi h \nu^3 B_{21}, \tag{13}$$

where A_{21} is in s^{-1}, and B_{12} and B_{21} are in $\text{cm}^3\ (\text{J}\,\text{s}^2)^{-1}$, and g_1 and g_2 are the statistical weights of the levels 1 and 2, respectively. It is important to stress that Eq. (13) can be different if the units of the Einstein B-coefficients are different.

5. Relation between the line intensity and the Einstein *A*-coefficient

In order to obtain a relation between the line intensity and the Einstein *A*-coefficient, the first step is to express the variation of the intensity $\mathrm{d}I(\nu-\nu_0)$ (see Eq. (1)) using the Einstein *B*-coefficients [14]

$$\mathrm{d}I(\nu-\nu_0) = -(N_1B_{12}-N_2B_{21})\frac{h\nu_0}{c}\,I(\nu-\nu_0)\Phi(\nu-\nu_0)\,\mathrm{d}l, \tag{14}$$

where N_2 and N_1 are the numbers of molecules per unit volume in the energy levels E_2 and E_1 (expressed in cm^{-1}), respectively, such that $E_2-E_1=\nu_0$ is the wavenumber of the line.

The spectral absorption coefficient can be deduced from Eqs. (1) and (14):

$$k(\nu-\nu_0) = (N_1B_{12}-N_2B_{21})\,\frac{h\nu_0}{c}\,\Phi(\nu-\nu_0) \tag{15}$$

and the relation linking the line intensity to the Einstein *B*-coefficients is obtained from Eqs. (2)–(4), (15)

$$S_\nu^N(T) = \frac{1}{N}\int_{-\infty}^{+\infty} k(\nu-\nu_0)d(\nu-\nu_0) = \frac{1}{N}\,(N_1B_{12}-N_2B_{21})\,\frac{h\nu_0}{c}. \tag{16}$$

If *N* is the total number of molecules per unit volume at the temperature *T*, the population N_1 of the energy level E_1 is equal to

$$N_1 = \frac{g_1N}{Q_{\mathrm{tot}}(T)}e^{-c_2E_1/T} \tag{17}$$

with a similar expression for N_2. Combining Eqs. (16) and (17), we obtain

$$S_\nu^N(T) = \frac{1}{Q_{\mathrm{tot}}(T)}(e^{-c_2E_1/T}g_1B_{12}-e^{-c_2E_2/T}g_2B_{21})\frac{h\nu_0}{c}. \tag{18}$$

Then using Eqs. (12) and (13), we have a relation between the line intensity and the Einstein *A*-coefficient

$$S_\nu^N(T) = \frac{g_2}{Q_{\mathrm{tot}}(T)}\,\frac{A_{21}}{8\pi c\nu_0^2}\,e^{-c_2E_1/T}(1-e^{-c_2\nu_0/T}). \tag{19}$$

It is important to note that the line intensity given in these equations is defined for a pure gas. The line intensity in *HITRAN* is defined at the reference temperature $T_0 = 296\,\mathrm{K}$ for an isotopic abundance, I_a. Calling this line intensity S_{HIT}, the conversion of the Einstein A_{21} coefficients from the line intensities S_{HIT} is performed according to

$$A_{21} = \frac{8\pi c\nu_0^2Q_{\mathrm{tot}}(T_0)S_{\mathrm{HIT}}}{e^{-c_2E_1/T_0}(1-e^{-c_2\nu_0/T_0})I_\mathrm{a}g_2}. \tag{20}$$

Eq. (20) is valid for the electric-dipole, magnetic-dipole, and electric-quadrupole transitions that exist in *HITRAN*. It is equivalent to substituting Eq. (A~~-~~5) into Eq. (A~~-~~9) in Appendix A of Ref. [5]. However there is an error when similarly substituting Eq. (39) into Eq. (42) of Ref. [6] because the factor *c* had been omitted in Eq. (39). It is important to note that whereas the line intensities are additive, the Einstein *A*-coefficients are not (see Section 8).

In *HITRAN*, the conversion of the Einstein A_{21} coefficients from the line intensities S_{HIT} was performed using Eq. (20) with the recommended values of the physical constants c, h, and k_{B} (taken from Table XXIV of Mohr and Taylor [17]). All the other quantities, i.e. the lower state energy E_1, the wavenumber of the transition ν_0, the total internal partition function $Q_{\mathrm{tot}}(T_0 = 296)$, the isotopic abundance I_{a}, the line intensity S_{HIT}, and the degeneracy factor g_2 of the upper level required in Eq. (20) are in the *HITRAN* database [1] either in the line-by-line portion (ν_0, S_{HIT}, E_1, and g_2), or in separate small files attached to the compilation ($Q_{\mathrm{tot}}(T_0)$ and I_{a}). Table 1 summarizes the quantities $Q_{\mathrm{tot}}(T_0)$ and I_{a} for each isotopologue present in *HITRAN*.

6. Calculation of the statistical weights

This section is devoted to the determination of the statistical weights that are required in the calculations of the Einstein A-coefficients from the line intensities (see Eq. (20)) and of the total internal partition functions of the molecules. In the *HITRAN* database, the partition functions come from the work of Refs. [4,18–20], and the statistical weights used in these studies agree with the definitions in Refs. [12,21–24]. The statistical weight g (also called the degeneracy factor) must be determined based on the quantum structure of the level:

$$g = g_{\varepsilon} g_{\mathrm{rot}}. \tag{21}$$

The factor g_{ε} represents the total degeneracy due to all non-rotational factors, i.e. the product of the electronic statistical weight g_{e} and the vibrational statistical weight g_{v}, and the g_{rot} factor includes all the degeneracy factors related to the rotational state.

The statistical weight g of the level (g_2 of the upper level in Eq. (20)) is equal to g_{rot} for the transitions in *HITRAN*, which have the complete electronic, vibrational and rotational assignments (hyperfine assignments not considered, see Tables 3 and 4 of Ref. [1]). When the quantum numbers are not available in *HITRAN* (unassigned lines), zero values have been assigned for the statistical weights and likewise for the Einstein A-coefficients.

We will now consider several cases that appear in *HITRAN* requiring different formulae for the calculation of the statistical weights g_{rot}. In order to simplify the notations, the indices 1 and 2 for the lower and upper levels, respectively, are not reported in Eqs. (21)–(30).

6.1. Case where the hyperfine structure is not listed in HITRAN

For the transitions in *HITRAN* for which there is no F quantum number in the rotational field of the transition (see notations of local quanta identification in Ref. [1]), either because there is no hyperfine structure for the line or because it is not listed for the line, the statistical weight g_{rot} is equal to

$$g_{\mathrm{rot}} = g_J = (2J + 1) g_{\mathrm{s}} g_{\mathrm{i}}, \tag{22}$$

where each state labeled by J has a $(2J + 1)$ degeneracy in the absence of an external electromagnetic field and g_{s} and g_{i} are the state-dependent and state-independent nuclear spin statistical weights, respectively.

The state-independent weight g_{i} is caused by the spins of the nuclei that are not interchanged in symmetry operations of a point group of a molecule [24]. It is given by the product over n nuclei of

Table 1
Molecular entities in HITRAN with general quantities required to calculate the Einstein *A*-coefficient from the line intensity

Molecule number	Isotopologue	State-independent weight, g_i	State-dependent weight, g_s	Total internal partition sum $Q_{tot}(T = 296\,K)$	Fractional abundance I_a
1	$H_2{}^{16}O$	1	1:3	1.7464E + 02	0.997317
	$H_2{}^{18}O$	1	1:3	1.7511E + 02	1.99983E − 03
	$H_2{}^{17}O$	6	1:3	1.0479E + 03	3.71884E − 04
	$HD^{16}O$	6	1	8.5901E + 02	3.10693E − 04
	$HD^{18}O$	6	1	8.7519E + 02	6.23003E − 07
	$HD^{17}O$	36	1	5.2204E + 03	1.15853E − 07
2	${}^{12}C^{16}O_2$	1	1:0	2.8694E + 02	0.984204
	${}^{13}C^{16}O_2$	2	1:0	5.7841E + 02	1.10574E − 02
	${}^{16}O^{12}C^{18}O$	1	1	6.0948E + 02	3.94707E − 03
	${}^{16}O^{12}C^{17}O$	6	1	3.5527E + 03	7.33989E − 04
	${}^{16}O^{13}C^{18}O$	2	1	1.2291E + 03	4.43446E − 05
	${}^{16}O^{13}C^{17}O$	12	1	7.1629E + 03	8.24623E − 06
	${}^{18}O^{12}C^{18}O$	1	1:0	3.2421E + 02	3.95734E − 06
	${}^{17}O^{12}C^{18}O$	6	1	3.7764E + 03	1.47180E − 06
3	${}^{16}O_3$	1	1:0	3.4838E + 03	0.992901
	${}^{16}O^{16}O^{18}O$	1	1	7.4657E + 03	3.98194E − 03
	${}^{16}O^{18}O^{16}O$	1	1:0	3.6471E + 03	1.99097E − 03
	${}^{16}O^{16}O^{17}O$	6	1	4.3331E + 04	7.40475E − 04
	${}^{16}O^{17}O^{16}O$	6	1:0	2.1405E + 04	3.70237E − 04
4	${}^{14}N_2{}^{16}O$	9	1	5.0018E + 03	0.990333
	${}^{14}N^{15}N^{16}O$	6	1	3.3619E + 03	3.64093E − 03
	${}^{15}N^{14}N^{16}O$	6	1	3.4586E + 03	3.64093E − 03
	${}^{14}N_2{}^{18}O$	9	1	5.3147E + 03	1.98582E − 03
	${}^{14}N_2{}^{17}O$	54	1	3.0971E + 04	3.69280E − 04
5	${}^{12}C^{16}O$	1	1	1.0712E + 02	0.986544
	${}^{13}C^{16}O$	2	1	2.2408E + 02	1.10836E − 02
	${}^{12}C^{18}O$	1	1	1.1247E + 02	1.97822E − 03
	${}^{12}C^{17}O$	6	1	6.5934E + 02	3.67867E − 04
	${}^{13}C^{18}O$	2	1	2.3582E + 02	2.22250E − 05
	${}^{13}C^{17}O$	12	1	1.3809E + 03	4.13292E − 06
6	${}^{12}CH_4$	1	5:2:3	5.9045E + 02	0.988274
	${}^{13}CH_4$	2	5:2:3	1.1808E + 03	1.11031E − 02
	${}^{12}CH_3D$	3	8:4	4.7750E + 03	6.15751E − 04
7	${}^{16}O^{16}O$	1	1:0	2.1577E + 02	0.995262
	${}^{16}O^{18}O$	1	1	4.5230E + 02	3.99141E − 03
	${}^{16}O^{17}O$	6	1	2.6406E + 03	7.42235E − 04
8	${}^{14}N^{16}O$	3	1	1.1421E + 03	0.993974
	${}^{15}N^{16}O$	2	1	7.8926E + 02	3.65431E − 03
	${}^{14}N^{18}O$	3	1	1.2045E + 03	1.99312E − 03
9	${}^{32}S^{16}O_2$	1	1:0	6.3403E + 03	0.945678
	${}^{34}S^{16}O_2$	1	1:0	6.3689E + 03	4.19503E − 02

Table 1 (*continued*)

Molecule number	Isotopologue	State-independent weight, g_i	State-dependent weight, g_s	Total internal partition sum $Q_{tot}(T = 296\,K)$	Fractional abundance I_a
10	$^{14}N^{16}O_2$	3	1:0	1.3578E + 04	0.991616
11	$^{14}NH_3$	3	4:2	1.7252E + 03	0.995872
	$^{15}NH_3$	2	4:2	1.1527E + 03	3.66129E − 03
12	$H^{14}N^{16}O_3$	6	1	2.1412E + 05	0.989110
13	^{16}OH	2	1	8.0362E + 01	0.997473
	^{18}OH	2	1	8.0882E + 01	2.00014E − 03
	^{16}OD	3	1	2.0931E + 02	1.55371E − 04
14	$H^{19}F$	4	1	4.1466E + 01	0.999844
15	$H^{35}Cl$	8	1	1.6066E + 02	0.757587
	$H^{37}Cl$	8	1	1.6089E + 02	0.242257
16	$H^{79}Br$	8	1	2.0018E + 02	0.506781
	$H^{81}Br$	8	1	2.0024E + 02	0.493063
17	$H^{127}I$	12	1	3.8900E + 02	0.999844
18	$^{35}Cl^{16}O$	4	1	3.2746E + 03	0.755908
	$^{37}Cl^{16}O$	4	1	3.3323E + 03	0.241720
19	$^{16}O^{12}C^{32}S$	1	1	1.2210E + 03	0.937395
	$^{16}O^{12}C^{34}S$	1	1	1.2535E + 03	4.15828E − 02
	$^{16}O^{13}C^{32}S$	2	1	2.4842E + 03	1.05315E − 02
	$^{16}O^{12}C^{33}S$	4	1	4.9501E + 03	7.39908E − 03
	$^{18}O^{12}C^{32}S$	1	1	1.3137E + 03	1.87967E − 03
20	$H_2{}^{12}C^{16}O$	1	1:3	2.8467E + 03	0.986237
	$H_2{}^{13}C^{16}O$	2	1:3	5.8376E + 03	1.10802E − 02
	$H_2{}^{12}C^{18}O$	1	1:3	2.9864E + 03	1.97761E − 03
21	$H^{16}O^{35}Cl$	8	1	1.9274E + 04	0.755790
	$H^{16}O^{37}Cl$	8	1	1.9616E + 04	0.241683
22	N_2	1	6:3	4.6598E + 02	0.992687
23	$H^{12}C^{14}N$	6	1	8.9529E + 02	0.985114
	$H^{13}C^{14}N$	12	1	1.8403E + 03	1.10676E − 02
	$H^{12}C^{15}N$	4	1	6.2141E + 02	3.62174E − 03
24	$^{12}CH_3{}^{35}Cl$	4	8:4	1.1583E + 05	0.748937
	$^{12}CH_3{}^{37}Cl$	4	8:4	1.1767E + 05	0.239491
25	$H_2{}^{16}O_2$	1	1:3	9.8198E + 03	0.994952
26	$^{12}C_2H_2$	1	1:3	4.1403E + 02	0.977599
	$^{12}C^{13}CH_2$	8	1	1.6562E + 03	2.19663E − 02
27	$^{12}C_2H_6$	1	24:20:16:8	7.0881E + 04	0.976990
28	PH_3	2	8:4	3.2486E + 03	0.999533
29	COF_2	1	1:3	7.0044E + 04	0.986544
30	SF_6	1	2:10:8:6	1.6233E + 06	0.950180
31	$H_2{}^{32}S$	1	1:3	5.0307E + 02	0.949884
	$H_2{}^{34}S$	1	1:3	5.0435E + 02	4.21369E − 02
	$H_2{}^{33}S$	4	1:3	2.0149E + 03	7.49766E − 03
32	HCOOH	4	1	3.9133E + 04	0.983898
33	HO_2	2	1	4.3004E + 03	0.995107

Table 1 (*continued*)

Molecule number	Isotopologue	State-independent weight, g_i	State-dependent weight, g_s	Total internal partition sum $Q_{tot}(T = 296\,K)$	Fractional abundance I_a
34	O	1	See text	6.7212E + 00	0.997628
35	$^{35}Cl^{16}O^{14}N^{16}O_2$	12	1	4.7884E + 06	0.749570
	$^{37}Cl^{16}O^{14}N^{16}O_2$	12	1	4.9102E + 06	0.239694
36	NO^+	3	1	3.1168E + 02	0.993974
37	$H^{16}O^{79}Br$	8	1	2.8339E + 04	0.505579
	$H^{16}O^{81}Br$	8	1	2.8238E + 04	0.491894
38	$^{12}C_2H_4$	1	7:3	1.1041E + 04	0.977294
	$^{12}C^{13}CH_4$	2	10:6	4.5197E + 04	2.19595E − 02
39	CH_3OH	2	8:4	3.5314E + 04	0.985930

Note: All the values of the partition functions come from [18], except for the oxygen atom (see Section 6.3.34) and for CH_3OH [39].

2 times the nuclear spin I_n plus 1:

$$g_i = \prod_n (2I_n + 1). \tag{23}$$

The state-dependent weights g_s depend on the values of the total spin of the identical nuclei, which are interchanged in symmetry operations. Since, in this case, not all the nuclear spin states are always allowed to be associated with a specific rotational level, these weights vary from one transition to another and lead to the intensity alternation in the spectrum.

For example, the weights g_s of linear symmetrical molecules (point group $\boldsymbol{D}_{\infty h}$) are different for the symmetric *s* (species Σ_g^+ and Σ_u^-) and antisymmetric *a* (species Σ_u^+ and Σ_g^-) rotational levels (see Fig. 99b of Ref. [24]). The following relation holds for those molecules with one pair of identical nuclei of spin I_x (see Eqs. (I.8) and (I.9) of Ref. [24, p. 17] for an arbitrary number of pairs of identical nuclei)

$$\begin{array}{l}\text{Fermi system — } s \text{ levels}\\ \text{Bose system — } a \text{ levels}\end{array} \quad g_s = \tfrac{1}{2}[(2I_x + 1)^2 - (2I_x + 1)], \tag{24a}$$

$$\begin{array}{l}\text{Fermi system — } a \text{ levels}\\ \text{Bose system — } s \text{ levels}\end{array} \quad g_s = \tfrac{1}{2}[(2I_x + 1)^2 + (2I_x + 1)]. \tag{24b}$$

This is the case of a molecule such as $^{12}C^{16}O_2$, which has two identical oxygen nuclei with spin zero. Substituting this value into the above equations yields a one-fold degeneracy for the even rotational *J* levels (symmetric *s*) and a zero-fold degeneracy for the odd rotational *J* levels (antisymmetric *a*) in the vibrationless electronic ground state (a totally symmetric state Σ_g^+).

For each isotopologue/isotopomer of each molecule in *HITRAN*, the values of g_i and g_s are summarized in Table 1. The description of the g_s calculation is also developed in Section 6.3.

6.2. Case where the hyperfine structure is listed in HITRAN

Hyperfine structure results from the intramolecular electromagnetic interactions of the nuclei with non-zero spins. For most of the transitions in *HITRAN*, the hyperfine structure is not resolved, that is to say, the hyperfine lines are not listed as separate transitions in the database. In these cases we have applied Eq. (22) to calculate the statistical weights g_{rot}. However, when the hyperfine structure is resolved (or partially resolved), Eq. (22) is no longer applicable.

Three cases altogether occur in *HITRAN* requiring different formulae for the calculation of the statistical weights g_{rot}, when the hyperfine structure is resolved. The first case, most common here, involves molecules such as $^{16}O^{12}C^{17}O$, $^{16}O^{17}O^{16}O$,$^{16}O^{16}O^{17}O$, $^{16}O^{17}O$, $^{14}N^{16}O$, $^{14}N^{16}O_2$, ^{16}OH, $^{35}Cl^{16}O$, $^{37}Cl^{16}O$, $^{12}CH_3{}^{35}Cl$, $^{12}CH_3{}^{37}Cl$, where there is only one nucleus that has non-zero spin (identical nuclei interchangeable in symmetry operations are not considered here). In the vector model, the $\mathbf{I}_1$ nuclear spin and $\mathbf{J}$ molecular angular momenta are coupled together to form $\mathbf{F}_1$, the total angular momentum of the molecule, which gives the splitting of each rotational J level into the hyperfine levels $F_1 = |J - I_1|, |J - I_1 + 1|, \ldots, J + I_1$, each of them having $(2F_1 + 1)$ degeneracy in the absence of an external electromagnetic field. The statistical weight g_{rot} of the hyperfine level $F_1 (F_1 \equiv F)$ is equal to

$$g_{\mathrm{rot}} = g_{F_1} = (2F_1 + 1)g_{\mathrm{s}} \tag{25}$$

and the total number of Zeeman states is equal to the sum of the degeneracies of the hyperfine components

$$g_J = \sum_{F_1=|J-I_1|}^{J+I_1} g_{F_1} = g_{\mathrm{s}} \sum_{F_1=|J-I_1|}^{J+I_1} (2F_1 + 1) = g_{\mathrm{s}}(2J + 1)(2I_1 + 1) = (2J + 1)g_{\mathrm{i}}g_{\mathrm{s}}. \tag{26}$$

In this equation, the product in Eq. (23) reduces to $(2I_1 + 1)$.

The case where two nuclear spins are coupled together and to $\mathbf{J}$ appears for a few molecules in *HITRAN* (some authors call this situation *hyperhyperfine* structure [21]). Examples in *HITRAN* include $H^{79}Br$, $H^{81}Br$, $H^{35}Cl$, $H^{37}Cl$, $H^{127}I$, and $H^{12}C^{14}N$. In the pure-rotation region, the hyperfine assignments for these molecules come from the JPL catalog [25]. The nuclear spin of Br, Cl, I, N,... (denoted $\mathbf{I}_1$) is strongly coupled to $\mathbf{J}$ to form $\mathbf{F}_1$, and the spin of hydrogen (denoted $\mathbf{I}_2$) is weakly coupled to $\mathbf{F}_1$ to form $\mathbf{F}$. As a consequence, each J level is split into the levels $F_1 = |J - I_1|, |J - I_1 + 1|, \ldots, J + I_1$, and further each F_1 level is split into the levels $F = |F_1 - I_2|, |F_1 - I_2 + 1|, \ldots, F_1 + I_2$. In the JPL catalog (as in *HITRAN*), the quantum number associated with the hyperfine structure is just F_1, not F (the hyperfine structure due to the hydrogen nucleus is not resolved at all). Note that there are no lines in the *HITRAN* database assigned with more than F_1 quantum number (we set $F_1 \equiv F$ for such cases).

The statistical weight g_{rot} of the hyperfine level F_1 in this case is equal to

$$g_{\mathrm{rot}} = g_{F_1} = (2F_1 + 1)(2I_2 + 1)g_{\mathrm{s}} \tag{27}$$

and the total number of Zeeman states is equal to the sum of the degeneracies over the states F_1

$$g_J = \sum_{F_1=|J-I_1|}^{J+I_1} g_{F_1} = g_\mathrm{s} \sum_{F_1=|J-I_1|}^{J+I_1} (2F_1+1)(2I_2+1) = g_\mathrm{s}(2J+1)(2I_1+1)(2I_2+1) = (2J+1)g_\mathrm{i}g_\mathrm{s}, \tag{28}$$

or to the sum of the degeneracies over the states F_1, F:

$$g_J = \sum_{F_1=|J-I_1|}^{J+I_1} \sum_{F=|F_1-I_2|}^{F_1+I_2} g_F = g_\mathrm{s} \sum_{F_1=|J-I_1|}^{J+I_1} \sum_{F=|F_1-I_2|}^{F_1+I_2} (2F+1) = g_\mathrm{s} \sum_{F_1=|J-I_1|}^{J+I_1} (2F_1+1)(2I_2+1). \tag{29}$$

Fig. 1 represents a schematic example of the multiplets of HBr levels resulting from the coupling between **J** and the nuclear spins $\mathbf{I}_1$ and $\mathbf{I}_2$. In this figure, the statistical weights g_J, g_{F_1}, and g_F are indicated, allowing us to verify Eqs. (27)–(29).

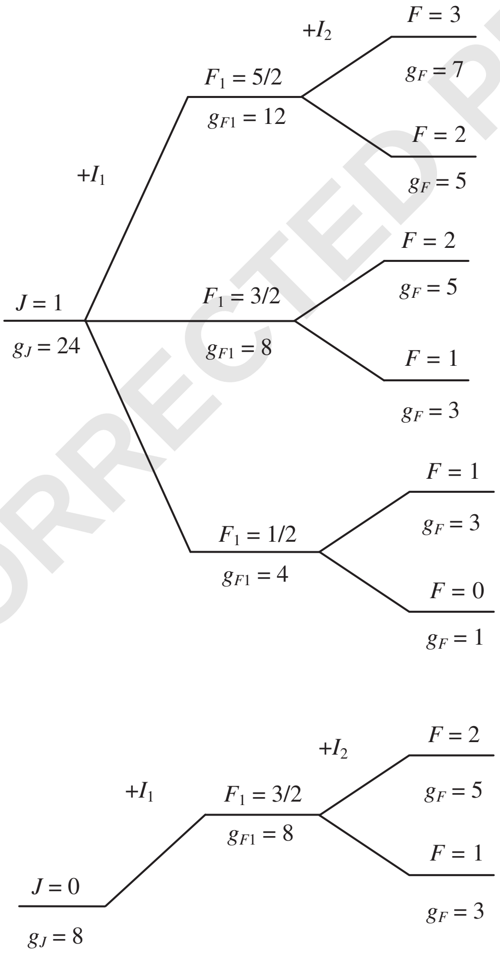

Fig. 1. Schematic example of the multiplets of HBr levels.

The case of $H^{13}C^{14}N$ is a little more complicated, since we have three nuclear spins different from zero: $I(\mathrm{H}) = I(^{13}\mathrm{C}) = 1/2$, and $I(^{14}\mathrm{N}) = 1$. In the *HITRAN* database (as in the JPL catalog), the F quantum number is in fact F_1 ($\mathbf{F}_1$ is the result of the coupling of $\mathbf{J}$ and $\mathbf{I}(^{14}\mathrm{N})$). In this case, the statistical weight of the level F_1 is equal to

$$g_{\mathrm{rot}} = g_{F_1} = (2F_1 + 1)(2I_2 + 1)(2I_3 + 1)g_{\mathrm{s}}, \tag{30}$$

where I_2 is the nuclear spin of H, and I_3 of ^{13}C.

6.3. Determination of the statistical weights for each isotopologue/isotopomer

The statistical weights have been calculated for the upper and lower levels of each transition present in the *HITRAN* database [1]. The statistical weight, g, has been expressed as the product of g_ε and g_{rot} (see Eq. (21)). For the calculation of g_{rot} we need to know the nuclear spin statistical weights g_{i} and g_{s} together with the quantum number J, where no hyperfine structure is resolved (Eq. (22)). Where the hyperfine structure due to the nucleus with the spin I_1 is resolved, the quantum number F_1 and the nuclear spin statistical weights $g_{\mathrm{i}}/(2I_1 + 1)$ and g_{s} are needed (Eqs. (25), (27), (30)). The quantum numbers J and F_1 (denoted F in Table 4 of Ref. [1]) are given in the *HITRAN* line-by-line file of each molecule. The weights g_{s} and g_{i} are given in Table 1 for all the isotopologues present in *HITRAN*.

It follows from the selection rules that the nuclear spin statistical weights are the same for both the lower and upper levels of a transition. The state-dependent weights g_{s} are determined from the symmetries of the rotational levels (the electronic–vibration–rotation states) as described in the following subsections. In this text, the symmetries are the species of the point group of a molecule or the species of its rotational subgroup. In each subsection, we also indicate when hyperfine structure appears for an isotopologue, in order to determine which equation ((25), (27), (30)) has been used to calculate the statistical weights g_{rot}.

6.3.1. H_2O (molecule 1)

For the $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$ isotopologues ($\boldsymbol{C}_{2\mathrm{v}}$), the statistical weights g_{s} of the A and B rotational levels are 1 and 3, respectively. The symmetry of the rotational level is A if $K_a + K_c + v_3$ is even and B if $K_a + K_c + v_3$ is odd in the ground electronic state (the symmetry of the vibrational state is A if v_3 is even and B if v_3 is odd, see Figs. 17 and 144 of Ref. [24]). For the $HD^{16}O$, $HD^{18}O$, $HD^{17}O$ isotopologues, the statistical weights g_{s} of all the rotational levels are 1.

No hyperfine structure is reported in the H_2O line list of the *HITRAN* database [1]. Consequently, Eq. (22) has been used to calculate the statistical weights g_{rot} for all the levels.

6.3.2. CO_2 (molecule 2)

For the $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{18}O_2$ isotopologues ($\boldsymbol{D}_{\infty\mathrm{h}}$), the statistical weights g_{s} of the symmetric s and antisymmetric a rotational levels are 1 and 0, respectively (see Fig. 99 of Ref. [24], Fig. 17-6 of Ref. [26]). For the $^{16}O^{12}C^{18}O$, $^{16}O^{12}C^{17}O$, $^{16}O^{13}C^{18}O$, $^{16}O^{13}C^{17}O$, $^{17}O^{12}C^{18}O$ isotopologues, the statistical weights g_{s} of all the rotational levels are 1.

The statistical weights g_{rot} have been calculated using Eq. (25) for around 300 transitions of the $^{16}O^{12}C^{17}O$ isotopologue in the pure-rotation region, where the hyperfine structure is reported, and using Eq. (22) for all the other CO_2 lines in the *HITRAN* database.

6.3.3. O_3 (molecule 3)

For the $^{16}O^{16}O^{16}O$, $^{16}O^{17}O^{16}O$, $^{16}O^{18}O^{16}O$ isotopologues ($\boldsymbol{C}_{2v}$), the statistical weights g_s of the A and B rotational levels are 1 and 0, respectively. The symmetry of the rotational level is A if $K_a + K_c + v_3$ is even and B if $K_a + K_c + v_3$ is odd in the ground electronic state (the symmetry of the vibrational state is A if v_3 is even and B if v_3 is odd, see Figs. 17 and 144 of Ref. [24]). For the $^{16}O^{16}O$ ^{18}O, $^{16}O^{16}O^{17}O$ isotopologues, the statistical weights g_s of all the rotational levels are 1.

In the current *HITRAN* edition [1], the hyperfine structure is reported for 78705 pure-rotational transitions of the $^{16}O^{17}O^{16}O$ and $^{16}O^{16}O^{17}O$ isotopomers in the spectral region between 0 and 156 cm^{-1}. The statistical weights g_{rot} have been calculated using Eq. (25) for the hyperfine lines and Eq. (22) for all the other ozone lines in the *HITRAN* database.

6.3.4. N_2O (molecule 4)

The statistical weights g_s of all the rotational levels are 1 for the nitrous oxide molecule.

No hyperfine structure is reported in the N_2O line list of the *HITRAN* database. Consequently, Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.5. CO (molecule 5)

The statistical weights g_s of all the rotational levels are 1 for the carbon monoxide molecule.

No hyperfine structure is reported in the CO line list of the *HITRAN* database. Consequently, Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.6. CH_4 (molecule 6)

For the $^{12}CH_4$ and $^{13}CH_4$ isotopologues ($\boldsymbol{T}_d$), the statistical weights g_s of the A, E and F rotational levels are 5, 2 and 3, respectively [24,26]. The symmetry of the rotational level can be determined from the local quanta identification in *HITRAN*.

The symmetries of the rotational levels (and the statistical weights g_s) in the non-degenerate A and degenerate E vibrational states of the $^{12}CH_3D$ isotopologue ($\boldsymbol{C}_{3v}$) in the electronic ground state are given in the Section 6.3.24. The $^{12}CH_3D$ isotopologue has three non-degenerate, $v_1(A_1), v_2(A_1), v_3(A_1)$, and three degenerate, $v_4(E), v_5(E), v_6(E)$, normal modes of vibration. The vibrational state has the A_1 symmetry if an arbitrary number of quanta of A_1 vibrations are excited ($\ell = 0$) and the E symmetry if one quantum of an E vibration is excited ($\ell = \pm 1$). If two quanta of an E vibration are excited the vibrational state split into the substates with the A_1 symmetry ($\ell = 0$) and the E symmetry ($\ell = \pm 2$). Similarly if one quantum of each of two different E vibrations are excited the vibrational state split into the substates with the $A_1 + A_2$ symmetry ($\ell = 0$) and the E symmetry ($\ell = \pm 2$). If $\ell = \pm 2$, each $K = |k| > 0$ rotational level is split into the so-called $+\ell$ and $-\ell$ levels (if these levels are assigned as $+\ell(k\ell < 0)$ and $-\ell(k\ell > 0)$, they have the same symmetries as if $\ell = \pm 1$, see Section 6.3.24).

No hyperfine structure is reported in the methane line list of the *HITRAN* database. Consequently, Eq. (22) has been used to calculate the statistical weights g_{rot} for all the methane lines.

6.3.7. O_2 (molecule 7)

For the $^{16}O^{16}O$ isotopologue ($\boldsymbol{D}_{\infty h}$), the statistical weights g_s of the symmetric s and antisymmetric a rotational levels are 1 and 0, respectively (see Figs. 114b, 115b of Ref. [27]). For the $^{16}O^{18}O$ and $^{16}O^{17}O$ isotopologues, the statistical weights g_s of all the rotational levels are 1.

In the current *HITRAN* edition [1], the hyperfine structure is reported for the pure-rotational transitions of the $^{16}O^{17}O$ isotopologue in the spectral region between 0 and 251 cm^{-1}. The statistical weights g_{rot} have been calculated using Eq. (25) for the hyperfine lines and Eq. (22) for all the other oxygen lines in the *HITRAN* database.

6.3.8. NO (molecule 8)

The statistical weights g_s of all the rotational levels are 1 for the nitric oxide molecule. Hyperfine structure is reported in *HITRAN* for the transitions of the following bands of $^{14}N^{16}O$: $^2\Pi_{1/2}(v=1)–^2\Pi_{1/2}(v=0)$, $^2\Pi_{3/2}(v=1)–^2\Pi_{1/2}(v=0)$, $^2\Pi_{1/2}(v=1)–^2\Pi_{3/2}(v=0)$, $^2\Pi_{3/2}(v=1)–^2\Pi_{3/2}(v=0)$, $^2\Pi_{1/2}(v=2)–^2\Pi_{1/2}(v=0)$, $^2\Pi_{3/2}(v=2)–^2\Pi_{3/2}(v=0)$, $^2\Pi_{1/2}(v=2)–^2\Pi_{1/2}(v=1)$, and $^2\Pi_{3/2}(v=2)–^2\Pi_{3/2}(v=1)$. The statistical weights g_{rot} have been calculated using Eq. (25) for the hyperfine lines and Eq. (22) for all the other NO lines in the *HITRAN* database.

6.3.9. SO_2 (molecule 9)

For the $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ isotopologues ($\boldsymbol{C}_{2v}$), the same rule holds as for the $^{16}O^{16}O^{16}O$ isotopologue (see Section 6.3.3).

No hyperfine structure is reported in the SO_2 line list of the *HITRAN* database. Consequently, Eq. (22) has been used to calculate the statistical weights g_{rot} for all the levels.

6.3.10. NO_2 (molecule 10)

For the $^{14}N^{16}O_2$ isotopologue ($\boldsymbol{C}_{2v}$), the same rule holds as for the $^{16}O^{16}O^{16}O$ isotopologue (see Section 6.3.3).

Hyperfine structure is reported for all the NO_2 lines in *HITRAN* and the statistical weights g_{rot} have been calculated using Eq. (25).

6.3.11. NH_3 (molecule 11)

The ammonia molecule was for a long time classified among the pyramidal molecules ($\boldsymbol{C}_{3v}$) with the normal modes of vibration, $v_1(A_1), v_2(A_1), v_3(E), v_4(E)$, where the doublet levels are labeled s and a (symmetric and antisymmetric with respect to molecular inversion, respectively). In the ($\boldsymbol{D}_{3h}$) labeling system, the normal modes of vibration are $v_1(A_1'), v_2(A_2''), v_3(E'), v_4(E')$, where the strongly anharmonic bending mode v_2 is defined as the inversion and the quantum number v_{inv} is introduced. There is the following correspondence between both the labeling systems: the $v_{inv} = 0$ (A_1') corresponds to $v_2 = 0$ (s) ground state; $v_{inv} = 1$ (A_2'') corresponds to $v_2 = 0$ (a); $v_{inv} = 2$ (A_1') corresponds to $v_2 = 1$ (s); $v_{inv} = 3$ (A_2'') corresponds to $v_2 = 1$ (a); etc. This means that the symmetry of the inversion state v_2 is A_1' if v_{inv} is even (s state) and A_2'' if v_{inv} is odd (a state) where $v_{inv} = 0, 1$ if $v_2 = 0$; $v_{inv} = 2, 3$ if $v_2 = 1$, etc. [26].

If only non-degenerate vibrations are excited ($\ell = 0$), the symmetry of the vibrational state is A_1' (s state) or A_2'' (a state). If one quantum of an E' vibration is excited ($\ell = \pm 1$) the symmetry of the vibrational state is E' (s state) or E'' (a state). If two quanta of an E' vibration are excited the vibrational substates are *s* with the symmetries A_1' ($\ell = 0$) and E' ($\ell = \pm 2$) or *a* with the symmetries A_2'' ($\ell = 0$) and E'' ($\ell = \pm 2$). Similarly if one quantum of each of two different E' vibrations are excited, the vibrational substates are *s* with the symmetries $A_1' + A_2'$ ($\ell = 0$) and E' ($\ell = \pm 2$) or *a* with the symmetries $A_2'' + A_1''$ ($\ell = 0$) and E'' ($\ell = \pm 2$), see Sections 6.3.6 and 6.3.24.

The rotational structures of the non-degenerate *A* and degenerate *E* vibrational states of the electronic ground state can be deduced from parts (a) and (b), respectively, of Fig. 118 of Ref. [24]. The prime and double prime should be added over the symmetries of the rotational levels with the even and odd *K*, respectively, in the *s* states, and with the odd and even *K*, respectively, in the *a* states. Note that the A_1 and A_2 symmetries of the rotational levels in the A_2 vibrational states are interchanged (see also Table 15-1 and Fig. 15-5 of Ref. [26]).

The statistical weights g_s of the A_2', A_2'' and E', E'' rotational levels are 4 and 2, respectively, while the A_1', A_1'' rotational levels are entirely missing [26,28].

No hyperfine structure is reported in the NH_3 line list of *HITRAN* and the statistical weights g_{rot} have been calculated using Eq. (22).

6.3.12. HNO_3 (molecule 12)

The statistical weights g_s of all the rotational levels are 1 for the nitric acid molecule.

No hyperfine structure is reported in the HNO_3 line list of *HITRAN* and the statistical weights g_{rot} have been calculated using Eq. (22).

6.3.13. OH (molecule 13)

The statistical weights g_s of all the rotational levels are 1 for the hydroxyl radical, OH.

The statistical weights g_{rot} of the hyperfine lines in the pure-rotation region have been calculated using Eq. (25); otherwise Eq. (22) has been used where no hyperfine structure is reported.

6.3.14. HF (molecule 14)

The statistical weights g_s of all the rotational levels are 1 for the hydrogen fluoride molecule.

Hyperfine structure is not reported in the HF line list of *HITRAN*. Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.15. HCl (molecule 15)

The statistical weights g_s of all the rotational levels are 1 for the hydrogen chloride molecule.

For the hyperfine lines of $H^{35}Cl$ and $H^{37}Cl$ in the pure-rotation region, Eq. (27) has been used to calculate the statistical weights g_{rot}. Let us recall that for these levels, the hyperfine quantum number *F* given in *HITRAN* is F_1 (the nuclear spin of Cl (denoted $\mathbf{I}_1$) is strongly coupled to $\mathbf{J}$ to form $\mathbf{F}_1$, see Section 6.2). For all the other lines, where no hyperfine structure is reported, Eq. (22) has been used.

6.3.16. HBr (molecule 16)

The statistical weights g_s of all the rotational levels are 1 for the hydrogen bromide molecule.

For the hyperfine lines of $H^{79}Br$ and $H^{81}Br$ of the (0–0) and (1–0) bands, Eq. (27) has been used to calculate the statistical weights g_{rot}. For these levels, the hyperfine quantum number *F* given in

HITRAN is F_1 (the nuclear spin of Br (denoted $\mathbf{I}_1$) is strongly coupled to $\mathbf{J}$ to form $\mathbf{F}_1$, see Section 6.2). For all the other lines, where no hyperfine structure is reported, Eq. (22) has been used.

6.3.17. HI (molecule 17)

The statistical weights g_s of all the rotational levels are 1 for the hydrogen iodide molecule.

For the hyperfine lines of $H^{127}I$ of the (0–0) and (1–0) bands, Eq. (27) has been used to calculate the statistical weights g_{rot}. For these levels, the hyperfine quantum number F given in *HITRAN* is F_1 (the nuclear spin of I (denoted $\mathbf{I}_1$) is strongly coupled to $\mathbf{J}$ to form $\mathbf{F}_1$, see Section 6.2). For all the other lines, where no hyperfine structure is reported, Eq. (22) has been used.

6.3.18. ClO (molecule 18)

The statistical weights g_s of all the rotational levels are 1 for the chlorine monoxide molecule.

Hyperfine structure is reported in *HITRAN* for the transitions of the $^2\Pi_{1/2}(v=0)-{}^2\Pi_{1/2}(v=0)$, $^2\Pi_{3/2}(v=0)-{}^2\Pi_{3/2}(v=0)$ bands of $^{35}Cl^{16}O$ and $^{37}Cl^{16}O$. The statistical weights g_{rot} of the hyperfine levels have been calculated from Eq. (25), otherwise Eq. (22) has been used where no hyperfine structure is reported.

6.3.19. OCS (molecule 19)

The statistical weights g_s of all the rotational levels are 1 for the carbonyl sulfide molecule.

Hyperfine structure is not reported in the OCS line list of *HITRAN*. Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.20. H_2CO (molecule 20)

For the H_2CO molecule ($\boldsymbol{C}_{2v}$), the statistical weights g_s of the A and B rotational levels are 1 and 3, respectively. The symmetry of the rotational level is A if $K_a+v_3+v_4+v_5$ is even and B if $K_a+v_3+v_4+v_5$ is odd in the ground electronic state (the symmetry of the vibrational state is A if $v_3+v_4+v_5$ is even and B if $v_3+v_4+v_5$ is odd, see Figs. 17 and 143 of Ref. [24]).

Hyperfine structure is not reported in the H_2CO line list of *HITRAN*; thus Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.21. HOCl (molecule 21)

The statistical weights g_s of all the rotational levels are 1 for the hypochlorous acid molecule. No hyperfine structure is reported in the HOCl line list of the *HITRAN* database. Consequently, Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.22. N_2 (molecule 22)

For the nitrogen molecule ($\boldsymbol{D}_{\infty h}$) in the ground electronic state, the statistical weights g_s of the symmetric s (even J) and antisymmetric a (odd J) rotational levels are 6 and 3, respectively (see Figs. 64b, 114b of Ref. [27]).

No hyperfine structure is reported in the N_2 line list of the *HITRAN* database. Consequently, Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.23. HCN (molecule 23)

The statistical weights g_s of all the rotational levels are 1 for the hydrogen cyanide molecule.

The statistical weights g_{rot} of the hyperfine components of the $R(0)$ lines in the pure-rotational bands (000–000) of $H^{12}C^{14}N$ and $H^{13}C^{14}N$ were calculated from Eqs. (27) and (30), respectively. Let us recall that for these levels, the hyperfine quantum number F given in *HITRAN* is F_1 (the nuclear spin of ^{14}N (denoted $\mathbf{I}_1$) is strongly coupled to $\mathbf{J}$ to form $\mathbf{F}_1$, see Section 6.2). For all the other lines, where no hyperfine structure is reported, Eq. (22) has been used.

6.3.24. CH_3Cl (molecule 24)

The symmetries A and E of the rotational levels of a $\boldsymbol{C}_{3\mathrm{v}}$ molecule in a totally symmetric electronic state are determinable from the values of the quantum number $G = \ell - k$ introduced by Hougen [29] ($\ell = \sum_i \ell_i$ runs over all degenerate normal modes, where $\ell_i = v_i, v_i - 2, \ldots, -v_i$ is the vibrational angular momentum quantum number associated with the ith mode, and $k = 0, \pm 1, \pm 2, \ldots, \pm J$). The rotational level has the $A_1 + A_2$ symmetry if $G = 0, \pm 3, \pm 6, \pm 9, \ldots$ (an exception occurs if $k = 0$ and $\ell = 0$ see below) and the E symmetry if $G = \pm 1, \pm 2, \pm 4, \pm 5, \ldots$. The statistical weights g_{s} of the A_1, A_2 and E rotational levels are 4 (the weight is 8 for the $A_1 + A_2$ level) [26,28]. The symmetry of the rotational level has been added in the local quanta field of the current *HITRAN* edition, but only for the recent work between 6 and 8 μm [30].

The CH_3Cl molecule has three non-degenerate, $v_1(A_1), v_2(A_1), v_3(A_1)$, and three degenerate, $v_4(E), v_5(E), v_6(E)$, normal modes of vibration. If an arbitrary number of quanta of A_1 vibrations are excited ($\ell = 0$) the symmetry of the vibrational state is A_1 and the symmetries of the rotational levels are $A_1 + A_2$ if $K = 3, 6, 9, \ldots$ and E if $K = 1, 2, 4, 5, \ldots$; the $K = 0$ level has the symmetry A_1 if J is even and A_2 if J is odd (see Figs. 118a of Ref. [24], 9.1A of Ref. [28]).

If one quantum of an E vibration is excited ($\ell = \pm 1$) the symmetry of the vibrational state is E and each $K = |k| > 0$ rotational level is split into the so-called $+\ell$ level ($k\ell > 0$ and $G = \pm(|\ell| - |k|)$) and $-\ell$ level ($k\ell < 0$ and $G = \pm(|\ell| + |k|)$). The $+\ell$ and $-\ell$ levels have the symmetries $A_1 + A_2$ and E, respectively, if $K = 1, 4, \ldots$; E and $A_1 + A_2$, respectively, if $K = 2, 5, \ldots$; E and E, respectively, if $K = 3, 6, \ldots$; and the symmetry is E if $K = 0$ (see Figs. 118b of Ref. [24], 9.1B of Ref. [28]).

If three quanta of an E vibration are excited, the vibrational state splits into the substates with the $A_1 + A_2$ symmetry ($\ell = \pm 3$) and the E symmetry ($\ell = \pm 1$). The symmetries of the rotational levels in the A_1 and E vibrational states are given above. (The rotational structure of the A_2 vibrational state is similar to that of the A_1 vibrational state except that the A_1 and A_2 symmetries of the rotational levels are interchanged.)

Hyperfine structure is reported in *HITRAN* for the transitions of the pure-rotational bands of $^{12}CH_3{}^{35}Cl$ and $^{12}CH_3{}^{37}Cl$. The statistical weights g_{rot} have been calculated using Eq. (25) for the hyperfine lines and Eq. (22) for all the other lines.

6.3.25. H_2O_2 (molecule 25)

For the hydrogen peroxide molecule ($\boldsymbol{C}_2$), the statistical weights g_{s} of the A and B rotational levels are 1 and 3, respectively. The symmetry of the rotational level is A if K_c is even and B if K_c is odd in the ground and $v_3 = 1$ vibrational states (A symmetry), while the reverse is true for the $v_6 = 1$ vibrational state (B symmetry) of the electronic ground state. These rules hold independently of the values of the torsional quantum numbers n and τ (see note of Table 3 of Ref. [1]).

No hyperfine structure is reported in the H_2O_2 line list of the *HITRAN* database. Consequently, Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.26. C_2H_2 (molecule 26)

For the $^{12}C_2H_2$ isotopologue ($\boldsymbol{D}_{\infty\mathrm{h}}$), the statistical weights g_{s} of the symmetric s and antisymmetric a rotational levels are 1 and 3, respectively. The symmetries s/a of the rotational levels of a given vibrational state ($\Sigma^{+}_{g(u)}, \Sigma^{-}_{g(u)}, \Pi_{g(u)}, \Delta_{g(u)}$) of the electronic ground state can be deduced from Fig. 99 of Ref. [24] (Fig. 17-6 of Ref. [26]).

The rotational levels in *HITRAN* are assigned as *e* and *f*, respectively: the *e* levels are those with the parity $+(-1)^J$ and the *f* levels are those with the parity $-(-1)^J$ [26,31]. The symmetry of the vibrational state can be determined from the local quanta identification in *HITRAN* (note that the characters *u* (ungerade) and *g* (gerade) have been added in the new vibrational format, see Table 3 of Ref. [1]).

For the $^{12}C^{13}CH_2$ isotopologue, the statistical weights g_{s} of all the rotational levels are 1.

No hyperfine structure is reported in the C_2H_2 line list of the *HITRAN* database and Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.27. C_2H_6 (molecule 27)

The symmetries of the rotational levels of the ethane molecule (staggered model, $\boldsymbol{D}_{3\mathrm{d}}$ point group) in the ground electronic state can be deduced from Fig. 118a of Ref. [24] for the A_1 and A_2 vibrational states (note that the A_1 and A_2 symmetries of the rotational levels in the A_2 vibrational states are interchanged) and from Fig. 118b of Ref. [24] for the E vibrational states. All the rotational levels are g and u levels in the g and u vibrational states, respectively. The statistical weights g_{s} of the A_1, A_2 and E rotational levels are 8, 16 and 20, respectively [26,32].

The rotational levels of the vibrational ground state ($A_{1\mathrm{g}}$ symmetry) have the symmetries $A_{1\mathrm{g}} + A_{2\mathrm{g}}$ if $K = 3, 6, 9, \ldots$ (the weight factor is 24); E_{g} if $K = 1, 2, 4, 5, \ldots$ (the weight factor is 20); $A_{1\mathrm{g}}$ if $K = 0$ and J is even (the weight factor is 8); $A_{2\mathrm{g}}$ if $K = 0$ and J is odd (the weight factor is 16). All these levels change from g to u if an odd number of torsional quanta is excited ($v_4 = 1$ vibrational state, $A_{1\mathrm{u}}$ symmetry).

In the $v_7 = 1$ vibrational state (E_{u} symmetry), the so-called $+\ell$ and $-\ell$ levels ($\ell = \pm 1$, see Section 6.3.24) have the symmetries $A_{1\mathrm{u}} + A_{2\mathrm{u}}$ and E_{u}, respectively, if $K = 1, 4, \ldots$; E_{u} and $A_{1\mathrm{u}} + A_{2\mathrm{u}}$, respectively, if $K = 2, 5, \ldots$; E_{u} and E_{u}, respectively, if $K = 3, 6, \ldots$; and the symmetry is E_{u} if $K = 0$ (the weight factor is 24 for $A_{1\mathrm{u}} + A_{2\mathrm{u}}$ and 20 for E_{u} levels). All these levels change from u to g if an odd number of torsional quanta is excited ($v_7 = 1,\ v_4 = 1$ vibrational state, E_{g} symmetry).

If the internal rotation tunneling leads to observable splitting in the spectrum, the rotational levels (electronic–vibration–rotation–torsion states) have the symmetry species s of the $\boldsymbol{G}^{+}_{36}$ permutation-inversion group: $A_{1\mathrm{g}}(8) \rightarrow A_{1\mathrm{s}}(6) + E_{3\mathrm{s}}(2)$, $A_{2\mathrm{g}}(16) \rightarrow A_{2\mathrm{s}}(10) + E_{4\mathrm{s}}(6)$, $E_{\mathrm{g}}(20) = E_{1\mathrm{s}}(4) + G_{\mathrm{s}}(16)$ and $A_{1\mathrm{u}}(8) \rightarrow A_{3\mathrm{s}}(6) + E_{3\mathrm{s}}(2)$, $A_{2\mathrm{u}}(16) \rightarrow A_{4\mathrm{s}}(10) + E_{4\mathrm{s}}(6)$, $E_{\mathrm{u}}(20) = E_{2\mathrm{s}}(4) + G_{\mathrm{s}}(16)$, the statistical weights g_{s} are given in parentheses [33] ($A_{1\mathrm{g}} + A_{2\mathrm{g}} \rightarrow A_{\mathrm{s}}(16) + E_{\mathrm{s}}(8)$ in the *HITRAN* file where the splitting is only partially resolvable).

No hyperfine structure is reported in the C_2H_6 line list of the *HITRAN* database and Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.28. PH_3 (molecule 28)

The symmetries of the vibrational states of the phosphine molecule, which has four normal modes of vibration, $v_1(A_1), v_2(A_1), v_3(E), v_4(E)$, and the symmetries of the rotational levels (and the statistical weights g_s) in the non-degenerate A and degenerate E vibrational states of the electronic ground state are determinable under the rules given for $\boldsymbol{C}_{3v}$ molecules in the Sections 6.3.6 and 6.3.24.

No hyperfine structure is reported in the PH_3 line list of the *HITRAN* database. Consequently, Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.29. COF_2 (molecule 29)

For the carbonyl fluoride molecule ($\boldsymbol{C}_{2v}$), the same rule holds as for the formaldehyde molecule (see Section 6.3.20).

No hyperfine structure is reported in the COF_2 line list of the *HITRAN* database. Consequently, Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.30. SF_6 (molecule 30)

The statistical weights g_s of the A_1, A_2, E, F_1 and F_2 rotational levels of the sulfur hexafluoride molecule ($\boldsymbol{O}_h$) are 2, 10, 8, 6 and 6, respectively [26,32,34]. This symmetry appears in the rotational assignment of *HITRAN* (designated by assignment C in *HITRAN*, see Table 4 of Ref. [1]).

No hyperfine structure is reported in the SF_6 line list of the *HITRAN* database and Eq. (22) has been used to calculate the statistical weights g_{rot} for all the levels.

6.3.31. H_2S (molecule 31)

For the $H_2{}^{32}S$, $H_2{}^{33}S$ and $H_2{}^{34}S$ isotopologues ($\boldsymbol{C}_{2v}$), the same rule holds as for the $H_2{}^{16}O$ isotopologue (see Section 6.3.1).

No hyperfine structure is reported in the H_2S line list of the *HITRAN* database. Consequently, Eq. (22) has been used for all the levels to calculate the statistical weights g_{rot}.

6.3.32. HCOOH (molecule 32)

The statistical weights g_s of all the rotational levels are 1 for the formic acid molecule.

No hyperfine structure is reported in the HCOOH line list of the *HITRAN* database and Eq. (22) has been used to calculate the statistical weights g_{rot}.

6.3.33. HO_2 (molecule 33)

The statistical weights g_s of all the rotational levels are 1 for the hydroperoxy radical, HO_2.

Hyperfine structure is reported in *HITRAN* for the transitions of the (000–000) band of HO_2. The statistical weights g_{rot} have been calculated using Eq. (25) for the hyperfine lines and Eq. (22) for all the other lines.

6.3.34. O (molecule 34)

The oxygen atom is unique in the database, having no vibration-rotation states. Only two electronic transitions are present in *HITRAN*: the first one is at 68.716 cm^{-1} between the upper level $2s^22p^4\ {}^3P_0$ and the lower level $2s^22p^4\ {}^3P_1$, the second is at 158.303 cm^{-1} between the upper level $2s^22p^4\ {}^3P_1$ and the lower level $2s^22p^4\ {}^3P_2$. The statistical weight, which appears in Eq. (20), is equal to 5 for the level $2s^22p^4\ ^3P_2$, 3 for the level $2s^22p^4\ ^3P_1$, and 1 for the level $2s^22p^4\ ^3P_0$. The electronic partition sum used to obtain the Einstein *A*-coefficients from the *HITRAN* line intensities is equal to 6.72123. It has been calculated as usual

$$Q = \sum_i g_i e^{-c_2 E_i/T}, \tag{31}$$

where g_i and E_i are the statistical weight and the energy of the level *i*, respectively. The summation is performed over all the possible states *i*. In our case, the summation has been performed over the three *P* states.

No hyperfine structure is reported in the oxygen-atom line list of the *HITRAN* database. Consequently, Eq. (22) has been used for all the levels to calculate the statistical weights g_{rot}.

The calculated values of the Einstein *A*-coefficients in this work have been compared with the values in the literature. For the 68.716 cm^{-1} transition, we obtain $1.74 \times 10^{-5}\,\mathrm{s}^{-1}$, as compared to $1.78 \times 10^{-5}\,\mathrm{s}^{-1}$ from Galavís et al. [35]; for the 158.303 cm^{-1} transition, we obtain $8.80 \times 10^{-5}\,\mathrm{s}^{-1}$, as compared to $8.86 \times 10^{-5}\,\mathrm{s}^{-1}$ from Ref. [35] and to $8.46 \times 10^{-5}\,\mathrm{s}^{-1}$ from Vastel et al. [36].

6.3.35. $ClONO_2$ (molecule 35)

The statistical weights g_s of all the rotational levels are 1 for the chlorine nitrate molecule.

No hyperfine structure is reported in the $ClONO_2$ line list of the *HITRAN* database and Eq. (22) has been used for all the levels to calculate the statistical weights g_{rot}.

6.3.36. NO^+ (molecule 36)

The statistical weights g_s of all the rotational levels are 1 for the NO^+ cation.

No hyperfine structure is reported in the NO^+ line list of the *HITRAN* database. Consequently, Eq. (22) has been used for all the levels to calculate the statistical weights g_{rot}.

6.3.37. HOBr (molecule 37)

The statistical weights g_s of all the rotational levels are 1 for the hypobromous acid molecule.

No hyperfine structure is reported in the HOBr line list of the *HITRAN* database and Eq. (22) has been used for all the levels to calculate the statistical weights g_{rot}.

6.3.38. C_2H_4 (molecule 38)

For the $^{12}C_2H_4$ isotopologue ($\boldsymbol{D}_{2h}$), the statistical weights g_s of the A, B_1, B_2 and B_3 rotational levels are 7, 3, 3, and 3, respectively. The symmetries of the rotational levels in the A, B_1, B_2 and B_3 vibrational states of the electronic ground state can be deduced from Figs. 145a–d of Ref. [24], respectively. (Note, that Herzberg's convention of the symmetry labeling of the normal modes of vibration is adopted here, see Fig. 44 of Ref. [24] and Table 6 of Ref. [37]).

In the ground vibrational state (*A* symmetry), the symmetry of the rotational level is *A* if both K_a and K_c are even, and *B* if K_a or K_c is odd (see Figs. 17 and 145a of Ref. [24]); in the $v_{10} = 1$ vibrational state (B_2 symmetry), the symmetry of the rotational level is *A* if both K_a and K_c are odd and *B* if K_a or K_c is even (see Figs. 17 and 145c of Ref. [24]) [38].

For the $H_2{}^{12}C^{13}CH_2$ isotopologue ($\boldsymbol{C}_{2v}$), the statistical weights g_s of the *A* and *B* rotational levels are 10 and 6, respectively. In the ground vibrational state (*A* symmetry), the symmetry of the rotational level is *A* if K_a is even and *B* if K_a is odd (see Figs. 17 and 143a of Ref. [24]).

No hyperfine structure is reported in the C_2H_4 line list of the *HITRAN* database. Consequently, Eq. (22) has been used for all the levels to calculate the statistical weights g_{rot}.

6.3.39. CH_3OH (molecule 39)

The statistical weights g_{s} are 8 for the A rotational levels if the splitting is not observable (4 for each member of a resolvable $A\pm$ doublet) and 4 for the E rotational levels [39].

No hyperfine structure is reported in the CH_3OH line list of the *HITRAN* database, and Eq. (22) has been used for all the levels to calculate the statistical weights g_{rot}.

7. Relation between the Einstein A-coefficient, the weighted square of the transition moment, the line intensity and the oscillator strength

The relation between the Einstein A-coefficient and the unweighted square of the transition moment depends on the type of a transition [12,21]

$$\text{For an electric-dipole transition} \quad g_2A_{21} = \frac{16\pi^3}{3h\varepsilon_0}\, v^3|R_{12}|^2. \tag{32}$$

$$\text{For a magnetic-dipole transition} \quad g_2A_{21} = \frac{16\pi^3\mu_0}{3h}\, v^3|R_{12}|^2. \tag{33}$$

$$\text{For an electric-quadrupole transition} \quad g_2A_{21} = \frac{8\pi^5}{5h\varepsilon_0}\, v^5|R_{12}|^2. \tag{34}$$

The factors ε_0 and μ_0 are the fundamental physical constants, the permitivity and the permeability of vacuum, respectively. The transition moment squared has the units $\mathrm{C}^2\,\mathrm{m}^2$, $\mathrm{A}^2\,\mathrm{m}^4$ and $\mathrm{C}^2\,\mathrm{m}^4$ in Eqs. (32), (33) and (34), respectively. Eq. (32) can be found in Refs. [6,13].

From Eqs. (20) and (32) in cgs units (for conversion to cgs electrostatic units, ε_0 should be replaced by $1/4\pi$ [12]), we obtain the relation linking the line intensity S_{HIT} (in cm^{-1} (molecule $\mathrm{cm}^{-2})^{-1}$) to the weighted square of the transition moment $\Re_{12} \equiv 1/g_1|R_{12}|^2$ (in Debye^2, $1\,\mathrm{Debye} = 10^{-18}\,\mathrm{cgs\,esu}$), which has been used for the previous *HITRAN* compilations [2,5,6,10,15] (the majority of the transitions in *HITRAN* are electric-dipole)

$$S_{\mathrm{HIT}} = I_{\mathrm{a}}\,\frac{v_0}{Q_{\mathrm{tot}}(T_0)}\,\frac{8\pi^3}{3hc}\,e^{-c_2E''/T_0}(1-e^{-c_2v_0/T_0})g_1\Re_{12}\times 10^{-36}. \tag{35}$$

In many studies, especially in astrophysics, we find the dimensionless oscillator strength, also called the *f*-value, instead of the Einstein A-coefficient, the transition moment or the line intensity. It is thus useful to recall the relation between the oscillator strength and the Einstein A-coefficient [6,13,14]

$$f_{12} = \frac{g_2}{g_1}\,\frac{\varepsilon_0 mc}{2\pi e^2v_0^2}\,A_{21}, \tag{36}$$

where e and m are the charge and the mass of the electron, respectively. One can note that g_1f_{12} is also called the weighted oscillator strength. The relation between the oscillator strength and the line intensity or the transition moment squared can easily be obtained by combining Eq. (36) with Eq. (20) or Eqs. (32)–(34), respectively, depending on the type of the transition.

8. Non-additivity of the Einstein *A*-coefficients

Contrary to the line intensities, the Einstein *A*-coefficients and the oscillator strengths are not additive. If we consider the upper state noted η' and the lower state noted η'' with the degeneracies $d_{\eta'}$ and $d_{\eta''}$, respectively, the Einstein *A*-coefficient $A_{\eta'\to\eta''}$ for spontaneous emission from the state η' to η'' can be expressed from the Einstein *A*-coefficients $A_{\eta'\xi'\to\eta''\xi''}$ for spontaneous emissions from the substates $\eta'\xi'$ to $\eta''\xi''$ using the following equation [6]

$$A_{\eta'\to\eta''} = \frac{1}{d_{\eta'}} \sum_{\xi',\xi''} A_{\eta'\xi'\to\eta''\xi''}. \tag{37}$$

For the lines with the hyperfine structure listed in *HITRAN*, we can express the Einstein *A*-coefficient of the transition from the Einstein *A*-coefficients of its hyperfine components

$$A_{\mathrm{e'v'}J'\to \mathrm{e''v''}J''} = \frac{1}{d_{J'}} \sum_{F'_1,F''_1} A_{\mathrm{e'v'}J'F'_1\to \mathrm{e''v''}J''F''_1}, \tag{38}$$

where the indices $\mathrm{e}, \mathrm{v}, J$, and F_1 (denoted F in *HITRAN*, see Section 6.2) correspond to the electronic, vibrational, rotational, and hyperfine levels, respectively. In this case, $d_{J'}$ represents the hyperfine multiplicity of the level J', that is, the number of its hyperfine sublevels F'_1.

9. Comparisons between the Einstein *A*-values from this work and submillimeter catalogs

It is informative to make comparisons of the values calculated here with similar quantities used in archival databases. Verdes et al. [40] made extensive comparisons for the partition sum data between *HITRAN* and the JPL submillimeter catalog [25]. The JPL catalog is limited to lines below 300 cm^{-1}, and is focused on constituents in the interstellar medium. Verdes et al. [40] concluded that the agreement between the *HITRAN* and *JPL* values was generally quite good, provided that one took into account that the JPL catalog did not contain the vibrational partition sum. Some differences that did exist, for example for nitric oxide, have since been corrected in the HITRAN calculation.

We made a comparison of Einstein *A*-coefficients between *HITRAN* [1] and *CDMS* [3]. Similar to the JPL catalog, *CDMS* is limited to the submillimeter region, and isotopologues in common between *HITRAN* and *CDMS* are not numerous. However, the *CDMS* web-site allows users to have both the intensities and Einstein *A*-coefficients, as does the new format of *HITRAN* [1]. For example, Fig. 2 represents the ratio of the Einstein *A*-coefficients from Refs. [3,1] for the (0–0) bands of $^{12}C^{16}O$ and $^{12}C^{18}O$ isotopologues. These plots show systematic discrepancies of about 1–3% increasing with the wavenumber. The two databases also give very similar results for the (01^10–01^10) band of $H^{12}C^{14}$ (the differences are less than 1%, see Fig. 3). Comparisons are also possible for the pure-rotational bands of H_2CO, and SO_2. The difference between *HITRAN* and *CDMS* values does not exceed 2% for $H_2{}^{13}C^{16}O$ and $H_2{}^{12}C^{18}O$; however the discrepancies reach

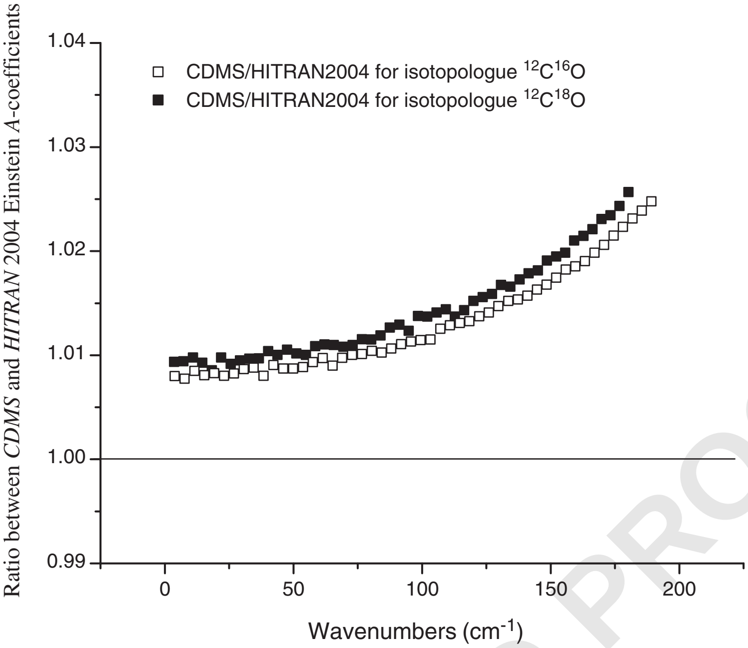

Fig. 2. Comparisons of the Einstein *A*-coefficients for the (0–0) bands of the $^{12}C^{16}O$ and $^{12}C^{18}O$ isotopologues.

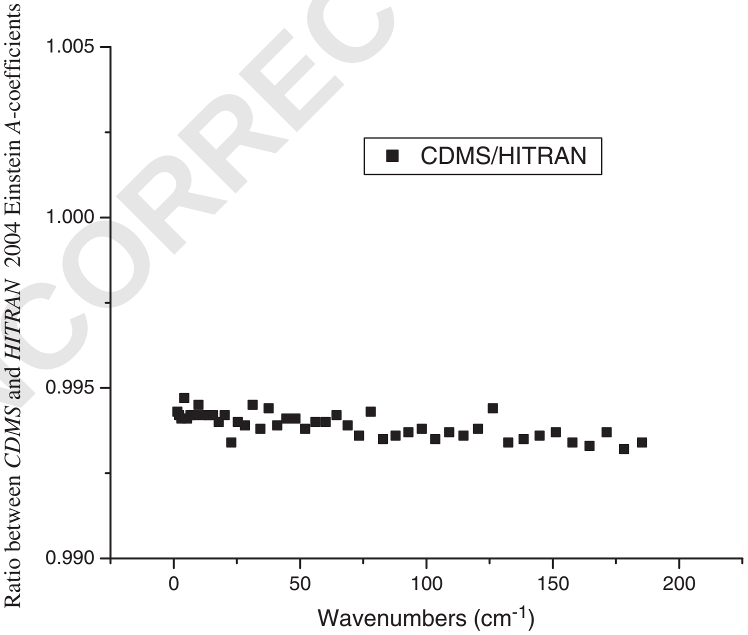

Fig. 3. Comparison of the Einstein *A*-coefficients for the (01^10–01^10) band of the $H^{12}C^{14}N$ isotopologue.

almost 25% for $H_2{}^{12}C^{16}O$ and $^{32}S^{16}O_2$. In these cases the ratio~~n~~s of the Einstein *A*-coefficients are almost (±5%) identical with the ratios of the line intensities. The discrepancies are probably attributable to the different values of the dipole-moment expansion used in the two databases.

Acknowledgements

The authors thank V. Boudon, I. Kleiner, A. Perrin, and J.B. Tatum for useful discussions and comments concerning the calculation of statistical weights. We also wish to acknowledge P. Bernath and J.-Y. Mandin for helpful comments regarding the manuscript.

The current effort has been supported by the NASA Earth Observing System (EOS), Grant NAG5-13534, and funding from the Office of the Secretary of Defense (OSD) High Energy Laser Joint Technology Office. One of the authors (RRG) is pleased to acknowledge support of this research by the National Science Foundation (NSF) through Grant No. ATM-0242537.

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