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MeCaSDa and ECaSDa: Methane and Ethene Calculated Spectroscopic Databases for the Virtual Atomic and Molecular Data Centre

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Abstract

Two spectroscopic relational databases, denoted MeCaSDa and ECaSDa, have been implemented for methane and ethene, and included in VAMDC (Virtual Atomic and Molecular Data Centre, http://portal.vamdc.eu/vamdc_portal/home.seam). These databases collect calculated spectroscopic data from the accurate analyses previously performed for the electronic ground state of methane, ethene, and some of their isotopologues: $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, and $^{12}\text{C}_2\text{H}_4$. Both infrared absorption and Raman scattering lines are included. The polyad structures are reported and the transitions are precisely described by their energy, their intensity and the full description of the lower and upper states involved in the transitions. The relational schemas of ECaSDa and MeCaSDa databases are equivalent and optimized to enable the better compromise between data retrieval and compatibility with the XSAMS (XML Schema for Atoms, Molecules, and Solids) format adopted within the VAMDC European project.

1. Introduction

Methane (CH_4) and ethene (or ethylene, C_2H_4) have been thoroughly studied by both experimental and theoretical spectroscopic techniques during the past decades.

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As a matter of fact, these two molecules are of great interest for various applications, among which atmospheric sciences and planetology are the most important. CH_4 is one of the most important greenhouse gases in the Earth’s atmosphere and it is present in significant quantities in the atmosphere of the Solar System’s giant planets, on Titan, but also on brown-dwarfs and some exoplanets. C_2H_4 is a pollutant produced by biomass fires and is also present on some astronomical objects like Jupiter, Saturn, Neptune, Titan and maybe some exoplanets. It is thus important, in order to perform remote concentration measurements or to run radiative transfer codes to model such atmospheres, to have extensive and accurate line lists for these molecules. A close collaboration between the ICB group in Dijon and the GSMA groups in Reims has allowed to perform extensive high resolution spectroscopic studies on these two species and develop specific formalisms and models helpful for fitting experimental data and producing synthetic line lists [1, 2].

Initiated mid-2009, the Virtual Atomic and Molecular Data Centre (VAMDC) European FP7 project aims to build an interoperable e-infrastructure for relating atomic and molecular databases and make them easily accessible by the scientific community [3]. The databases involved in this project cover a wide range of systems from atoms with databases such as the Vienna Atomic Line Database (VALD) [4] or the CHIANTI database [5], to molecules of interest in astrochemistry and atmospheric physics with databases such as the High-resolution TRANsmission molecular absorption database (HITRAN) [6, 7], the Spectroscopic and Molecular Properties of Ozone database (S&MPO) [8] or the MeCaSDa (Methane Calculated Spectroscopic Database) and ECaSDa (Ethene Calculated Spectroscopic Database) databases described in the present paper, and also solids with the Grenoble astrophysics and planetology Solid Spectroscopy and Thermodynamics database (GhoSST) [9] or the Laboratorio di Astrofisica Sperimentale (LASp) database [10, 11]. The MeCaSDa and ECaSDa databases only collect theoretical data although the spectroscopic data included in other VAMDC databases come from both experimental studies such as Fourier transform infrared spectroscopy or Cavity ring-down spectroscopy and semi-empirical lines resulting from analyses.

In this paper, we first describe in Section 2 the data included in the MeCaSDa and ECaSDa databases and briefly recall the theoretical techniques used to derive them. The relational schema of the databases is then detailed in Section 3 and Section 4 explains how to query the databases through the VAMDC portal. Section 5 gathers concluding remarks on the interest of these databases, especially within the scope of the VAMDC European project.

2. Data included in MeCaSDa and ECaSDa

2.1. Generalities

All the line lists included in MeCaSDa and ECaSDa have been assigned using the SPVIEW software and molecular effective parameters (Hamiltonians and dipole moments) have been fitted using the XTDS software [12]. Then, XTDS was also used to generate the calculated lists (line positions and intensities).

The vibrational structure of a molecule is considered as a series of polyads which are groups of interacting vibrational levels. The theoretical model implemented in XTDS [12] is based on the tensorial formalism developed in the ICB group [13, 14, 15] in line with earlier implementations for the databases of tetrahedral molecules [16]. This model allows the construction of effective Hamiltonian and transition moment (dipole moment or polarizability) operators adapted to a given polyad scheme. We define a polyad scheme as follows. Let n be the polyad number. A vibrational level with quantum numbers (v_1, v_2, \dots, v_N) of a molecule with N normal modes of vibration belongs to polyad P_n if:

$$n = \sum_{j=1}^{j=N} i_j v_j, \quad (1)$$

where the $\{i_j\}$ is a set of integers. For example, in the case of CH_4 , since the stretching modes (ν_1, ν_3) have close harmonic wavenumbers which are approximately twice those of the bending modes (ν_2, ν_4) , we choose $(i_1, i_2, i_3, i_4) = (2, 1, 2, 1)$ and the polyad number is:

$$n(\text{CH}_4) = 2v_1 + v_2 + 2v_3 + v_4, \quad (2)$$

leading to the well-known sequence of polyads: Ground State (one level), Dyad (two levels), Pentad (five levels), Octad (eight levels), *etc* [17].

2.2. Spectroscopic data

All the calculated line lists included in the MeCaSDa and ECaSDa databases result from the most recent line by line analyses of high resolution infrared and Raman experimental spectra.

For $^{12}\text{CH}_4$, the line list mostly results from the global analysis of the first four polyads (Ground State, Dyad, Pentad and Octad) performed by Albert *et al.* [17] and recently updated by Daumont *et al.* [1]. Ground State (*i.e.* pure rotational lines) intensities have been recently revised by Boudon *et al.* [18]. Preliminary results of an ongoing analysis of the Tetradecead region are also included. Note that an accurate WKMC (Wang, Kassi, Mondelain, Campargue) experimental methane line list above 5850 cm^{-1} has been recently measured in Grenoble [19] by means of laser cavity-ring-down spectroscopy technique. However, only a small fraction of this list (945 lines in the $5\nu_4/\nu_2 + 4\nu_4$ region and 164 lines in the $\nu_2 + 2\nu_3$ region), namely lines at the beginning of the icosad range, has been theoretically assigned up to now [20]. The MeCaSDa database does not yet include these data as our approach requires a full theoretical description of the included polyad.

For $^{13}\text{CH}_4$, a global analysis of the infrared spectrum in the spectral range $0 - 3200 \text{ cm}^{-1}$ has been recently performed by Niederer *et al.* [21] and will be completed by additional results [22].

In the case of ethene, global analyses are less advanced than for methane, but are in progress. Contrary to methane, this molecule has no clear and unique polyad scheme. We thus use different polyad schemes (*i.e.* different $(i_1, i_2, \dots, i_{12})$ sets of integers for this species with 12 normal modes) for each spectral region under consideration. These polyad schemes are chosen to get a proper grouping of the vibrational levels that are considered together. Moreover, line intensities are still under investigation. At present,

only the ν_{12} band intensities have been analyzed [2]. Line positions in the 3000 and 6000 cm^{-1} C–H stretching regions have been fitted [23], but the intensity analysis is in progress. This is also the case for the $\nu_{10}/\nu_7/\nu_4/\nu_{12}$ bending tetrad.

We wish to emphasize that the present databases contain calculated lines (positions and intensities). It is thus “complete” for a given set of transitions between two polyads (up to a given rotational quantum number), but not necessarily highly accurate in all regions, depending on the quality of the fit of experimental data that led to this list. No intensity cutoff is applied. On the other hand, our lists are also combined with experimental line positions and intensities to give semi-empirical line lists that are used to update the HITRAN [6, 7] and GEISA 2009 [24] databases as described for instance by Brown et al. [25, 26]. These lists are less “complete” (in the sense defined above *i.e.* they may contain less lines in some regions) but composed of more accurate lines. In this respect, MeCaSDa and ECaSDa do not directly compete with other experimental or semi-empirical databases but bring added value to the community of spectroscopists. As a first example, Figure 1 shows a comparison between the lines included in HITRAN 2008 [6] (or GEISA 2009 [24]) and in MeCaSDa.

[Insert Figure 1 here.]

As a second example of available spectral lines in these databases Figure 2 shows the Raman scattering lines of $^{12}\text{CH}_4$ included in MeCaSDa. It is noteworthy that MeCaSDa and ECaSDa are probably the only databases featuring Raman scattering rotation-vibration lines, which constitutes one of their specificities.

[Insert Figure 2 here.]

At present, the databases do not contain line broadening coefficients, but such data will be included in the near future, based on theoretical calculations developed by the ICB group [27, 28]. As described hereafter, the database structure has been conceived in order to allow the inclusion of pressure broadening data for various collisional partners. Tables 1 and 2 display the number of levels and transitions, respectively, for both databases at the time of the redaction of the present paper. Table 2 also show the wavenumber and intensity ranges for all transitions included in the databases.

[Insert Table 1 here.]

[Insert Table 2 here.]

3. Structure of the databases

The MeCaSDa and ECaSDa databases share the same structure since they contain the same types of data. They are compatible with the XSAMS (XML Schema for Atoms, Molecules, and Solids) [29] format adopted within the VAMDC European project [3]. Their structure is based on a set of fourteen database tables (hereafter called DB tables), as shown in Figure 3 (more detailed relational schemas for the MeCaSDa

and ECaSDa databases are supplied as Supplementary Material), that are related together through external key indices chosen to optimize both the size and query execution time of the database. Table 3 details the physical quantities (with units), main quantum numbers and chemical names used in the three main DB tables.

[Insert Figure 3 here.]

[Insert Table 3 here.]

The specificity of each database is determined by the energy level labeling which differs for methane and ethene due to the multiple choices of polyad schemes in the case of ethene. The quantum numbers and the isotopologues also differ for these molecules.

The main DB table of these databases is called “transitions”. This DB table precisely documents transitions between rovibrational states by indicating their computed wavenumber, intensity, pressure-induced line broadenings, and pressure-induced line shifts as illustrated in Figure 4. The accuracy and least-squares fit residuals of all the previous quantities and the Einstein coefficient are also provided. The remaining fields correspond to indices that refer to some other DB tables, namely “sources”, “characterisation”, “transition_types”, “molecules_isotopes”, and “molecular_states”, that enable a full description of the transition. DB table “sources” collects the references of all the publications on spectroscopic analyses (see Section 2) of methane or ethene. DB table “characterisation” specifies the physical origin of the transition (*i.e.*, electric dipole or polarizability). DB table “transition_types” indicates the spectroscopic technique corresponding to the data under consideration, such as microwave absorption, infrared absorption, or stimulated Raman spectroscopy. Each isotopologue of methane or ethene present in the MeCaSDa and ECaSDa databases are defined in DB table “molecules_isotopes” by its chemical formula in text and \TeX formats, its international chemical identifier (InChI) and corresponding InChiKey [30], and its chemical abstract service registry number. This DB table also contains an identifier for the state taken as energy reference and an identifier that refers to the molecular type (DB table “molecule_types”). For instance, the methane isotopologues currently included in MeCaSDa are of XY_4 molecular type. In ECaSDa, the ethene isotopologues have molecular type X_2Y_4 .

[Insert Figure 4 here.]

The lower and upper states involved in the transitions are described in DB table “molecular_states” by means of their term value, polyad index, total angular momentum J , irreducible symmetry group representation C of the rovibrational wavefunction, multiplicity index α , and nuclear spin statistical weight g (as mentioned above, a detailed correspondence between physical quantities and DB table labels is given in Table 3). For each wavefunction, we only provide the squared coefficients and sublevels corresponding to its decomposition on the initial normal mode basis set. Supplying both coefficients and their signs instead of squared coefficients would be feasible but requires bigger storage capacity and this would also be impractical for most users that do not need such information. In other words, we provide the most useful data on all the

Hamiltonian eigenvectors that can be used in various applications such as line-mixing calculations. The squared coefficients of the decomposition are sorted in decreasing order. The vibrational sublevels indices refer to DB table “vibrational_sublevels” that contains vibrational quantum numbers of the initial normal mode states as described in Ref. [15] for CH₄ and in Ref. [31] for C₂H₄.

A polyad (DB table “polyads”) is defined by a polyad number and a polyad scheme (DB table “polyad_schemes”). As presented in Section 2 several polyad schemes can be used to describe the vibrational energy levels of a given molecule. Each polyad scheme is a set of polyads (DB table “polyad_descriptions”) composed of a limited number of vibrational levels described in DB table “vibrational_levels”.

4. Querying MeCaSDa and ECaSDa through the VAMDC portal

The MeCaSDa and ECaSDa databases can be queried from the online VAMDC portal (<http://portal.vamdc.eu/vamdc.portal/home.seam>). Through this interface, it is possible to retrieve lines within a given wavenumber and/or intensity range. Examples are given in Figures 5 and 6. The VAMDC portal also searches entries for methane and ethene in other databases such as HITRAN.

[Insert Figure 5 here.]

[Insert Figure 6 here.]

5. Conclusion

The approach adopted in the MeCaSDa and ECaSDa relational databases relies on good quality extrapolation properties of the underlying spectroscopic models, particularly for high J values and hot band intensities based on accurate fits of experimental data obtained for smaller sets of quantum numbers values. This approach could help interpret future observations, in particular for atmospheric and planetary applications. MeCaSDa and ECaSDa do not compete with other public databases containing either experimental or semi-empirical transitions. This is a complementary approach, giving complete line lists, but with a lower accuracy for some regions, depending on the status of line-by-line analyses of experimental spectra (see Section 2.2). These two databases will be regularly updated in the future, as soon as some new analyses are performed, leading to improved spectroscopic models. We also intend to include soon some other molecules that are studied in our groups, like CF₄ [32] or SF₆.

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TABLE 1: Number of vibrational levels and sublevels, maximum J value (rotational quantum number) and rovibrational states included in the databases..

TABLE 2: Rovibrational transitions included in the databases (see Table 1 for polyad definitions).

TABLE 3: Correspondence between physical quantities and labels in the DB tables “transitions”, “molecule_isotopes”, and “molecular_states”. In DB table “transitions” the index i stands for the collision partner responsible for line broadenings or line shifts (ie, self, N₂, O₂, air, H₂O, CO₂, H₂, He, Ar).

Table 1: Number of vibrational levels and sublevels, maximum J value (rotational quantum number) and rovibrational states included in the databases.

MeCaSDa	$^{12}\text{CH}_4 / ^{13}\text{CH}_4$	Vib. levels	Vib. sublevels	Max. J	Rovib. states
	P_0 GS	1	1	25 / 25	282 / 282
	P_1 Dyad	2	2	25 / 25	1408 / 1408
	P_2 Pentad	5	9	25 / 25	5352 / 5352
	P_3 Octad	8	24	22 / 12	12142 / 3874
	P_4 Tetradecad	14	60	17 / 0	18900 / 0
ECaSDa	$^{12}\text{C}_2\text{H}_4$	Vib. levels	Vib. sublevels	Max. J	Rovib. states
Scheme 1	P_0 GS	1	1	45	2116
	P_1 $\nu_4/\nu_7/\nu_{10}/\nu_{12}$	4	4	45	8464
Scheme 2	P_0 GS	1	1	36	1369
	P_1 ν_5	1	1	35	1296
	P_2 ν_9/ν_{11}	2	2	35	2592
	P_3 $\nu_5 + \nu_9/\nu_5 + \nu_{11}$	2	2	35	2592

Table 2: Rovibrational transitions included in the databases (see Table 1 for polyad definitions).

MeCaSDa $^{12}\text{CH}_4 / ^{13}\text{CH}_4$	Transitions	Nb. dipolar	Nb. Raman	Dipolar wavenumber range / cm^{-1}	Dipolar intensity range / $\text{cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$	Raman wavenumber range / cm^{-1}	Raman intensity range / arbitrary unit
$^{12}\text{CH}_4$	$P_0 - P_0$	1222	0	0-253	$8 \times 10^{-49} - 8 \times 10^{-25}$		
	$P_1 - P_0$	13025	19207	911-1868	$1 \times 10^{-39} - 2 \times 10^{-19}$	671-2076	$4 \times 10^{-1} - 4 \times 10^{18}$
	$P_1 - P_1$	31510	0	0-688	$3 \times 10^{-61} - 8 \times 10^{-25}$		
	$P_2 - P_0$	49475	72954	2075-3483	$2 \times 10^{-41} - 4 \times 10^{-20}$	1842-3685	$6 \times 10^{-3} - 2 \times 10^{20}$
	$P_2 - P_1$	247325	0	456-2303	$8 \times 10^{-49} - 4 \times 10^{-22}$		
	$P_2 - P_2$	459276	0	0-1132	$4 \times 10^{-61} - 2 \times 10^{-27}$		
	$P_3 - P_0$	97581	141446	3322-5011	$3 \times 10^{-37} - 8 \times 10^{-21}$	3123-5179	$2 \times 10^{-2} - 2 \times 10^{17}$
	$P_3 - P_1$	267105	375012	1854-3685	$1 \times 10^{-39} - 2 \times 10^{-22}$	1696-3804	$3 \times 10^{-1} - 2 \times 10^{17}$
	$P_3 - P_2$	1015053	0	274-2473	$8 \times 10^{-45} - 1 \times 10^{-24}$		
	$P_4 - P_0$	114580	0	4670-6446	$2 \times 10^{-36} - 2 \times 10^{-21}$		
	$P_4 - P_1$	572747	0	3095-5223	$8 \times 10^{-46} - 2 \times 10^{-23}$		
	$P_4 - P_2$	2176493	3024031	1520-4005	$1 \times 10^{-45} - 8 \times 10^{-25}$	1378-4097	$6 \times 10^{-7} - 9 \times 10^{14}$
ECaSDa $^{12}\text{C}_2\text{H}_4$	Transitions	Nb. dipolar	Nb. Raman				
Scheme 1	$P_1 - P_0$	123205	0	500-1750	$3 \times 10^{-45} - 8 \times 10^{-18}$		
Scheme 2	$P_1 - P_0$	0	6791			3000-3150	$2 \times 10^{-6} - 2 \times 10^{20}$
	$P_2 - P_0$	68549	0	1500-5500	$3 \times 10^{-38} - 8 \times 10^{-18}$		
	$P_3 - P_0$	59440	0	5000-7499	$4 \times 10^{-39} - 4 \times 10^{-17}$		

Table 3: Correspondence between physical quantities and labels in the DB tables “transitions”, “molecule_isotopes”, and “molecular_states”. In DB table “transitions” the index i stands for the collision partner responsible for line broadenings or line shifts (ie, self, N₂, O₂, air, H₂O, CO₂, H₂, He, Ar).

DB Table name	Physical quantity	Label in the databases	Unit (if relevant)
transitions	Wavenumber, $\tilde{\nu}$	wavenumber	cm ⁻¹
	Wavenumber accuracy, $\delta\tilde{\nu}$	wavenumber_prec	cm ⁻¹
	Wavenumber residual, $\Delta\tilde{\nu}$	wavenumber_residual	cm ⁻¹
	Intensity, I	intensity	cm ⁻² .atm ⁻¹ at 296 K
	HITRAN intensity (see for instance Ref. [7])	intHITRAN	cm ⁻¹ /(molecule.cm ⁻²)
	Intensity accuracy, δI	intensity_prec	%
	Intensity residual, ΔI	intensity_residual	%
	Einstein coefficient, A	einstein	s ⁻¹
	Pressure-induced line broadening, γ_i	gamma	cm ⁻¹ .atm ⁻¹
	Pressure-induced line broadening accuracy, $\delta\gamma_i$	gamma_prec	cm ⁻¹ .atm ⁻¹
	Pressure-induced line shift, δ_i	deltai	cm ⁻¹ .atm ⁻¹
	Pressure-induced line shift accuracy, $\delta\delta_i$	deltai_prec	cm ⁻¹ .atm ⁻¹
	Coefficients for temperature dependence of γ_i , n_i	nexpi	unitless
	Accuracy on coefficients for temperature dependence of γ_i , δn_i	nexpi_prec	unitless
molecule_isotopes	Isotope name	isotope_name	
	InChi number	inchi	
	InChi key	inchikey	
	Chemical formula in TeX format	formtex	
	Chemical abstract service registry number	casregnum	
	Energy reference	eostateid	
molecular_states	Term value, F	position	cm ⁻¹
	Total angular momentum, J	j	
	Irreducible representation, C	symname	
	Multiplicity index, α	alpha	
	Nuclear spin statistical weight, g	weight	

FIG. 1: $^{12}\text{CH}_4$ lines included in MeCaSDa (red points) and corresponding lines included in HITRAN 2008 [6] and GEISA 2009 [24] (blue points) at $T = 296$ K. Polyad names are indicated.

FIG. 2: $^{12}\text{CH}_4$ Raman lines included in MeCaSDa at $T = 296$ K. Polyad names are indicated.

FIG. 3: Simplified relational schema of the MeCaSDa and ECaSDa databases. A complete relational schema of the MeCaSDa and ECaSDa databases is provided in Figs 1 and 2 of supplementary materials.

FIG. 4: Definition of line parameters: intensity I , wavenumber $\tilde{\nu}$, pressure-induced line broadening γ_i , and pressure-induced line shift δ_i where i represents the collision partner (ie, self, N_2 , O_2 , air, H_2O , CO_2 , H_2 , He, Ar). The exponent $^\circ$ is added on top of some symbols to remind that they are obtained for standard pressure conditions.

FIG. 5: Simple example of methane lines query through the VAMDC portal.

FIG. 6: VAMDC portal response to the query shown on Figure 5. Methane lines can be retrieved from either the HITRAN database (experimental and semi-empirical lines) or from the MeCaSDa database (calculated lines).

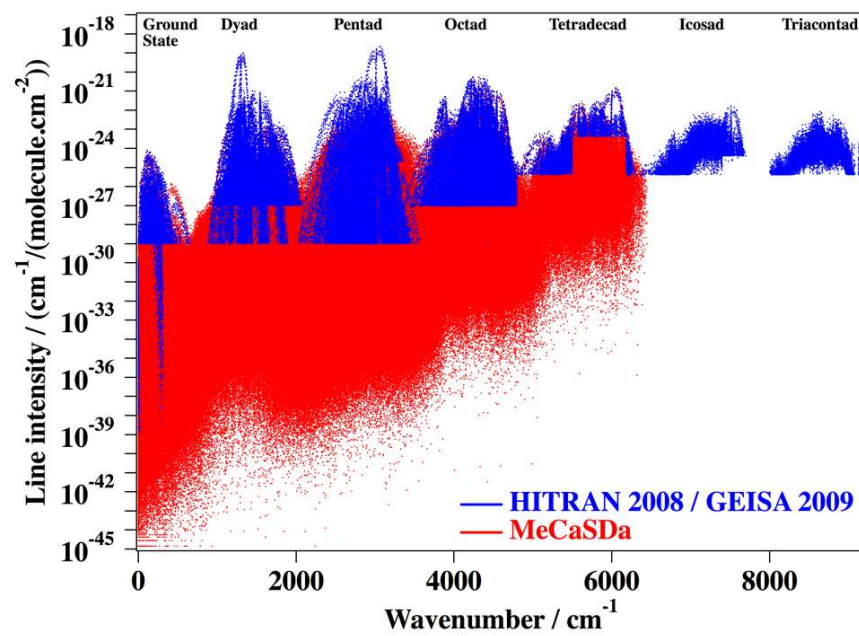


Figure 1: $^{12}\text{CH}_4$ lines included in MeCaSDa (red points) and corresponding lines included in HITRAN 2008 [6] and GEISA 2009 [24] (blue points) at $T = 296$ K. Polyad names are indicated.

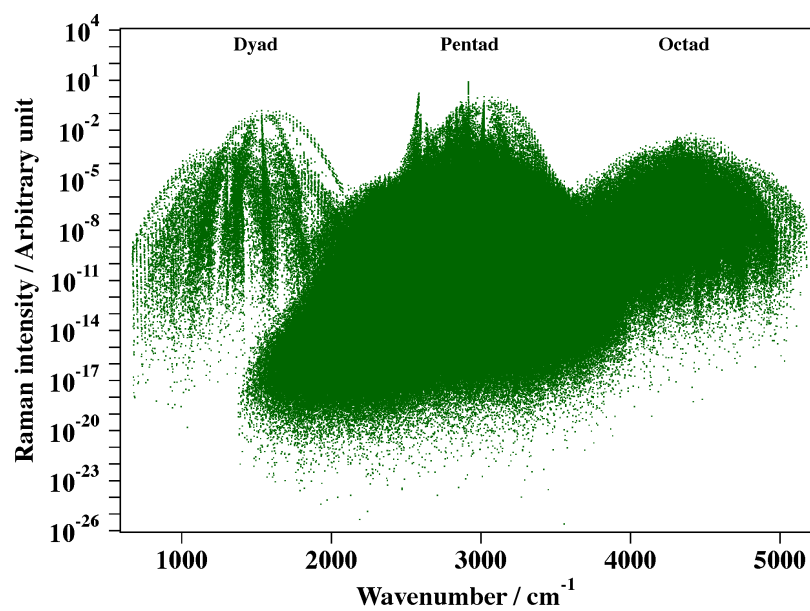


Figure 2: $^{12}\text{CH}_4$ Raman lines included in MeCaSDa at $T = 296$ K. Polyad names are indicated.

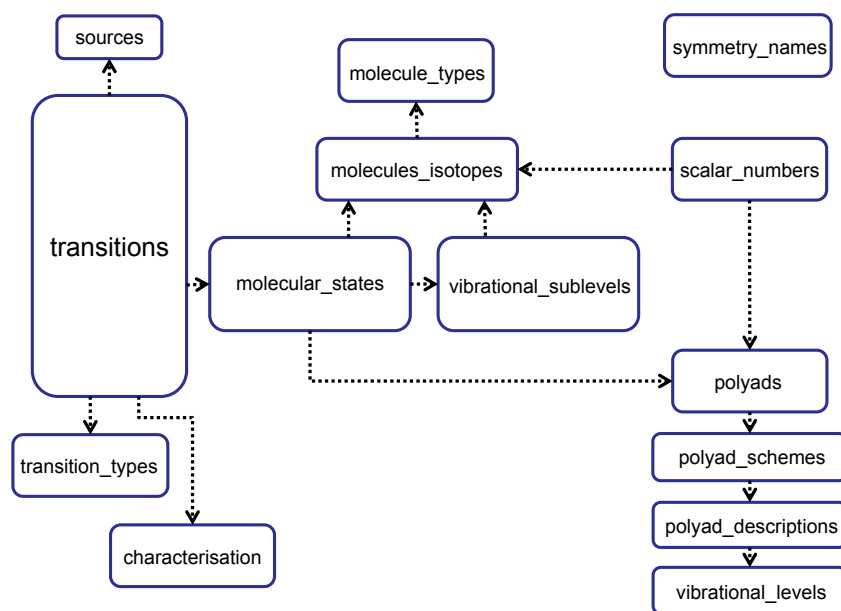


Figure 3: Simplified relational schema of the MeCaSDa and ECaSDa databases. A complete relational schema of the MeCaSDa and ECaSDa databases is provided in Figures 1 and 2 of supplementary materials.

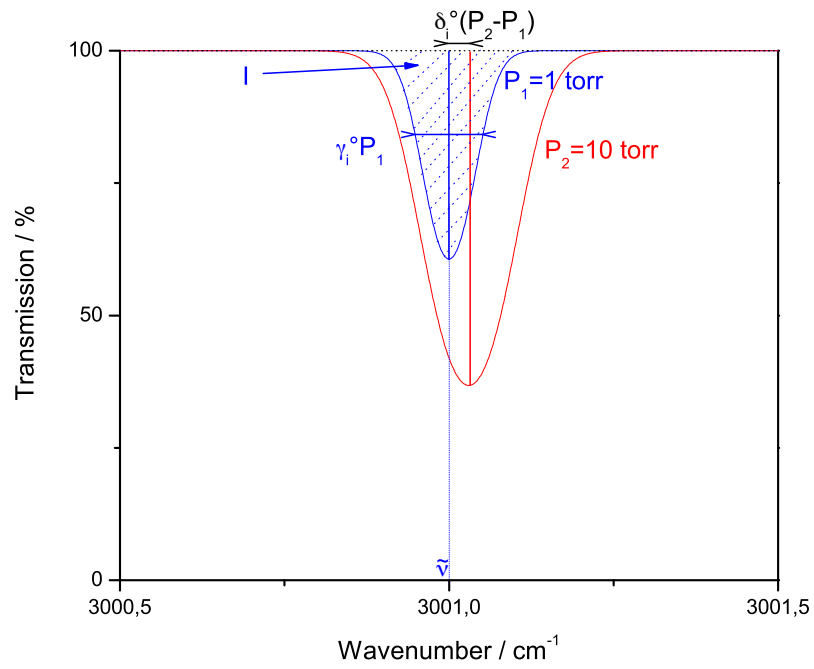


Figure 4: Definition of line parameters: intensity I , wavenumber $\tilde{\nu}$, pressure-induced line broadening γ_i , and pressure-induced line shift δ_i where i represents the collision partner (ie, self, N_2 , O_2 , air, H_2O , CO_2 , H_2 , He, Ar). The exponent $^\circ$ is added on top of some symbols to remind that they are given for standard pressure conditions.

Molecules

Clear Remove

Chemical name

Methane

Stoichiometric formula

CH4

Structural formula

Spin isomer

Standard InChIKey

VNWKOKETHGBQD-UHFFFAOYSA-N,
VNWKOKETHGBQD-OUBTZVSYSA-N

Select All None

Search by stoichiometric formula if no isotopologue is selected.

Isotopologue

☒ Methane ¹²CH₄
☒ Methane ¹³CH₄
☐ Methane ¹²CH₃D
☐ Methane ¹³CH₃D

Radiative

Clear Remove

Wavenumber

1300 to 1400

cm-1

Equivalent Wavelength

Wavelength from to 76923.07692307692A

Upper state energy

to

1/cm

Equivalent to

1/cm

Lower state energy

to

1/cm

Equivalent to

1/cm

Probability, A

to

1/s

Find data

Save query

Legend

available, can answer

available, don't support query

unsupported keyword

Theoretical spectral database of polycyclic aromatic hydrocarbons

Chianti

Cologne Database for Molecular Spectroscopy: VAMDC-TAP service

GSMA Reims S&MPO

ECaSDa - Ethene Calculated Spectroscopic Database

GhoSST

Lund laboratory spectroscopy database

Stark-b

HITRAN-UCL resource

VALD sub-set in Moscow (obs)

Cologne Database for Molecular Spectroscopy: VAMDC-TAP service

MeCaSDa - Methane Calculated Spectroscopic Database

VALD (atoms)

Carbon Dioxide Spectroscopic Databank (VAMDC-TAP)

VAMDC species-DB

OACT - LASP Database

TOPbase : VAMDC-TAP interface

DESIRE database (Moscow mirror)

BASECOL: VAMDC-TAP interface

TIPbase : VAMDC-TAP interface

Carbon Dioxide Spectroscopic Databank 296K (VAMDC-TAP)

SpEctroScopy of Atoms and Molecules

Carbon Dioxide Spectroscopic Databank 1000K (VAMDC-TAP)

Spectr-W3

Water internet Accessible Distributed Information System

KIDA: VAMDC-TAP interface

Figure 5: Simple example of methane lines query through the VAMDC portal.

