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CaSDa24: Latest updates to the Dijon calculated spectroscopic databases

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ABSTRACT

We introduce CaSDa24, the latest iteration of our high-resolution molecular spectroscopy database cluster. Comprising ten independent databases, each dedicated to a specific molecule (CH₄, CH₃Cl, SF₆, C₂H₄, CF₄, GeH₄, RuO₄, SiF₄, UF₆, SiH₄), CaSDa24 integrates updated and new databases since our previous publication. These databases include detailed lists of calculated spectral lines, eigenvectors, energy levels, and additional relevant information derived from the latest experimental spectra analyses. This article provides an overview of the current state of molecular spectroscopy databases, explains the foundational principles of CaSDa24, and summarizes the significant updates and new data introduced.

1. Introduction

In this article, we present the latest version of our database cluster, which we have decided to call CaSDa24. This is a set of 10 high-resolution molecular spectroscopy databases, all built on the same general scheme, but each operating independently and dedicated to a single molecule. Several of them have been updated, and others have been added in regard to the last publication in Richard et al. [1]. These are databases containing not only lists of calculated lines, resulting from the latest line-by-line analyses of experimental spectra, but also eigenvectors, energy levels and lots of other relevant information. Calculations and modeling are carried out by the XTDS/SPVIEW tandem developed in the Dijon group. They use a tensorial model originally developed for spherical tops such as methane and now extended to different symmetries [2]. A state of the art is discussed in Section 2 to address the different databases used by the molecular spectroscopy community and to explain the origin of CaSDa. Section 3 describes the principle behind our databases and briefly recalls the mathematical formalism used in our group. Next, Sections 4 to 6 detail the new data introduced into the databases, molecule by molecule. Then, the Section 7 summarizes the elements of this important update, and we will discuss what has been done. Table 1 shows all the molecules present in CaSDa24 along with their status in this update, the name of the base, the corresponding HITRAN ID and the section of this article

where they are detailed. Finally, Section 8 will conclude and discuss the way forward, including the enhancements we plan to add.

2. Historical background

Molecular databases are an essential asset for the study of astrophysical environments, atmosphere of the Earth and the impact of industry on climate change. They provide valuable information that are used in radiative transfer calculations: characterizing molecules one by one is necessary for a global understanding of a more complex whole. There are several open-access databases, each specialized in a particular field. The most widely used are probably HITRAN [3] and GEISA [4]. The former, initially developed by the US Airforce, now contains data on 55 molecules whose study is dedicated to the atmospheres of the Earth and other planets. It was last updated in 2020 and should receive a new update soon. HITRAN mainly focuses on experimental data, but others may be present if no experimental data has been measured. Then, these line-by-line data are retrieved in a format that has since become a community standard and is described in Rothman et al. [5]. It is also possible to download absorption cross-section, collision induced absorption or high-temperature data for 13 molecules, with the subproject HITEMP. GEISA is the European equivalent of HITRAN.

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Table 1

Summary of molecules present in CaSDa24 with their status and the section in which a descriptive paragraph is devoted to them.

HITRAN ID	Molecule	Base name	Status	Section
6	CH ₄	MeCaSDa	Not Updated	4.1
24	CH ₃ Cl	ChMeCaSDa	New	6.2
30	SF ₆	SHeCaSDa	Updated	5.2
38	C ₂ H ₄	ECaSDa	Updated	5.1
42	CF ₄	TFMeCaSDa	Updated	5.3
52	GeH ₄	GeCaSDa	Updated	5.4
N/A	RuO ₄	RuCaSDa	Not Updated	4.2
N/A	SiF ₄	TFSiCaSDa	Updated	5.5
N/A	UF ₆	UHeCaSDa	New	6.1
N/A	SiH ₄	SiCaSDa	New	6.3

This database has a very similar purpose, and only the number and type of molecules that are included vary: the last updated version of 2020 contains line lists of 58 molecules. As both databases are mostly composed of experimental lines, they have the advantage of being very accurate, even if some (older) data may have origins that are difficult to trace. Their drawback is that they may be less complete than calculated databases in spectral regions where molecular absorption is very weak and/or complex, preventing detailed spectroscopic assignments.

There also exist similar experimental databases which are specialized into the microwave region for rotational spectra: the JPL [6] and the Cologne [7] databases.

After these four databases, there is ExoMol [8], another database of high temperature molecular line lists (96 molecules) whose primary purpose is the spectral characterization and simulation of the atmospheres of exoplanets, brown dwarfs and cold stars, or even sunspots. The ExoMol project has its own methodology based on *ab initio* calculations and therefore contains a large number of lines for certain molecules (there are over 50 billion lines for methane). Finally, TheoReTS [9], an acronym for *Theoretical Reims-Tomsk Spectral data*, is a specialized database devoted to making *ab initio* predictions of rotationally resolved spectra for specific, significant molecular entities. These data are derived from potential energy and dipole moment surfaces, which are computed through high-level electronic structure calculations employing variational techniques for energy levels and vibration-rotation transitions. The current version of TheoReTS contains line lists for 9 molecules (CH₄, PH₃, SF₆, C₂H₄, CF₄, GeH₄, SiH₄, CH₃F, NF₃) and 28 isotopologues. It also provides projected lists of spectral lines for high-temperature methane, reaching up to $T=2000$ K, a feature of considerable relevance for research related to hot Jupiter exoplanets. Both databases, ExoMol and TheoReTS, are very complete. However, as pure *ab initio* methods are used, they can suffer from a lack of accuracy in position in some complex polyads (although they can be refined using experimental data), but the accuracy of intensity predictions is excellent.

At the end of the 1960's, the Dijon group has developed theoretical tools that are a tremendous asset for analyzing and modeling molecules with high symmetry (see Section 3.1). It therefore seemed natural to make the results of these calculations available in a database. Nevertheless, during the creation of the CaSDa project (Calculated Spectroscopic Database), we realized that it was complicated to unify the notation of quantum numbers for all molecules. For example, they do not all have the same number of vibrational modes, which makes it very difficult to put them all in the same base. It was then decided to create a database for each molecule, which is ultimately easier to manage if we take into account the different symmetries and polyad schemes. A special case is that of CH₃D, which is the only isotopologue that we have studied so far to have a different symmetry compared to the main one (CH₄). It would have been incongruous to separate them. However, CH₃D is at present not well developed in MeCaSDa and thus we will not comment it any further in this paper. The CaSDa databases therefore contain spectroscopic lines resulting from fits of

line positions and/or intensities using experimental spectra, effective Hamiltonian and transition moments: calculations hence have experimental accuracy. In addition, the data are not extrapolated over a wide range of wavenumbers and rotational quantum numbers to prevent the polynomial model from diverging.

Finally, to bring as many databases as possible under a single standard, the Virtual Atomic and Molecular Data Centre (VAMDC) project has been set up to interconnect atomic and molecular databases, providing a single place¹ where users can access atomic and molecular data [10–13]. Spectroscopic data can be downloaded in a single format, the XML Schema for Atoms, Molecules and Solids (XSAMS) which has the huge advantage of bringing together all the major molecular spectroscopy databases, whether experimental or calculated, as we detail in Section 3.3.

3. Database generalities

Our databases are built on a relational model using SQL language. The simplified relational schema for each database is shown in Fig. 9 of our previous article [1]. They all have the same structure of 13 tables that are used to store calculated data. From transitions to symmetry names or vibrational levels, every molecular line is thus fully characterized.

Queries are made on a web page accessible at <https://vamdc.icb.cnrs.fr>. It is possible to select isotopologues and the desired wavenumber range, as well as the type of data (line-by-line or cross-sections). However, databases such as MeCaSDa for methane can take a long time to return results, due to the large size of the database. If one wish to download a wide range of data, we recommend splitting up the queries. Also, each query produces an interactive plot showing the data provided in the output file, as illustrated in Fig. 1. Again, if the query is too large, the interactive plot may be too heavy to load, and this is why, if more than 500,000 transitions are retrieved, a static image is displayed instead.

CaSDa24 mostly contains electric dipole transitions. Two databases also contain Raman lines (based on the electronic polarizability), but these only contain relative line intensities. These are MeCaSDa and SHeCaSDa, the bases of CH₄ and SF₆. They can be accessed via the web page by selecting “polarizability” in the “characterization” section. More information about the data output is given in Section 3.3.

3.1. Theoretical principles

The specificity of these databases is thus to contain only calculated line lists based on effective Hamiltonian and transition moment operators, whose parameters were fitted using assigned experimental spectra. The databases thus contain full descriptions of molecular eigenstates, including all necessary quantum numbers. This was detailed in the previous publication [1], but we feel it is necessary to briefly recall the theoretical part.

The general idea for all molecules is to consider polyads, *i.e.* groups of interacting vibrational levels. A polyad can either be a single vibrational level (for instance an isolated fundamental level) or a more complex set of interacting levels, like in the methane case [14]. Depending on the molecule and on the level of analysis that has been reached, different polyad schemes are used. Sometimes, several distinct polyad schemes can be used to deal with different spectral regions of the same molecule. Thus, in each database, one or several polyad schemes can be defined internally through a set of integers (i_1, i_2, \dots, i_N) , where N is the number of distinct normal modes of the considered species ($N = 4, 6$ or 12 for XY₄, XY₆ and X₂Y₄ molecules, respectively). Polyad number

¹ https://portal.vamdc.eu/vamdc_portal

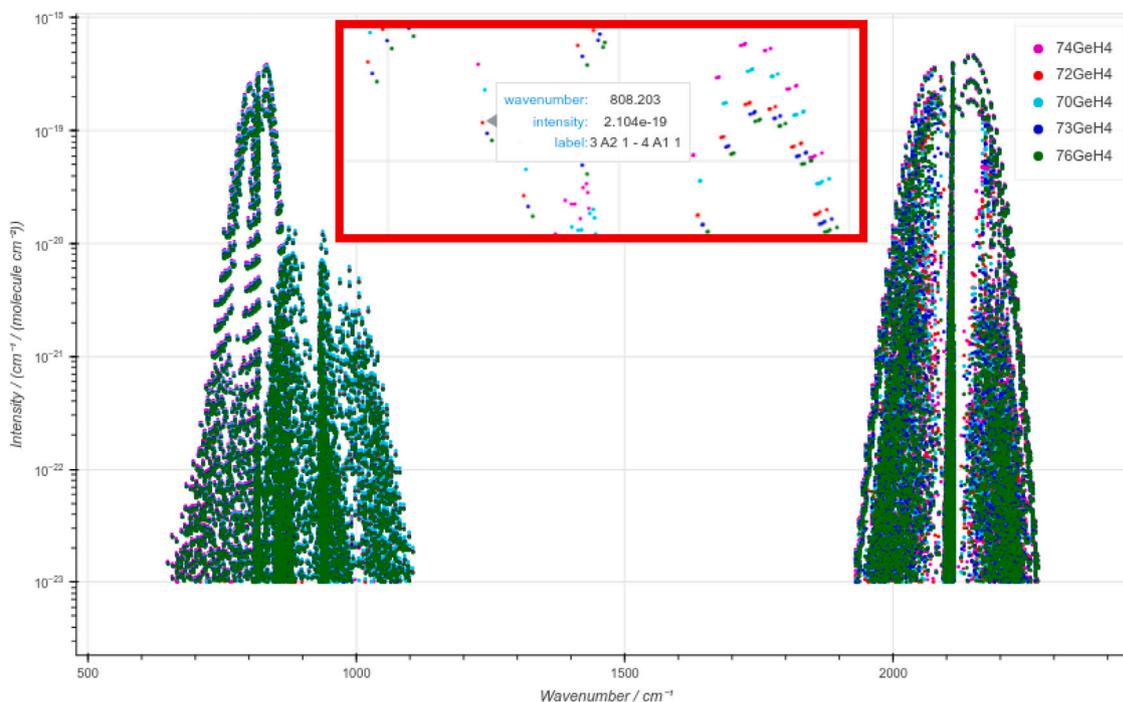


Fig. 1. Interactive graph preview for GeCaSDa. One can move around the plot and zoom in and out. Hovering the mouse over a point provides information on wavenumber, intensity and quantum numbers of the data. The inset shows the display produced by the feature.

Table 2

Molecules included in databases correlated with packages used for processing. Although not well developed, as explained above, CH₃D is reported for the record, sharing the same base with CH₄ but with a different symmetry.

C3vTDS	D2hTDS	HTDS	STDS
CH ₃ Cl	C ₂ H ₄	UF ₆ , SF ₆	CH ₄ , CF ₄
CH ₃ D			GeH ₄ , SiF ₄ RuO ₄ , SiH ₄

n , say P_n , is thus defined automatically by all the sets of vibrational quantum numbers $(\nu_1, \nu_2, \dots, \nu_N)$ that satisfy the relation:

$$n = \sum_{k=1}^{k=N} i_k \nu_k. \quad (1)$$

For instance, in the well-known case of the methane molecule (CH₄, MeCaSDa database), the approximate relation between its four normal mode frequencies, say $\nu_1 \simeq \nu_3 \simeq 2\nu_2 \simeq 2\nu_4$ leads to a single polyad scheme defined by $(i_1, i_2, i_3, i_4) = (2, 1, 2, 1)$ such that P_1 is the ν_2/ν_4 Dyad, P_2 is the $\nu_1/\nu_3/2\nu_2/2\nu_4/\nu_2 + \nu_4$ Pentad, etc [15].

The effective Hamiltonian operators are then decomposed into a series of contributions, one for each polyad, as:

$$\tilde{H} = \tilde{H}_{\{P_0\}} + \tilde{H}_{\{P_1\}} + \dots + \tilde{H}_{\{P_k\}} + \dots, \quad (2)$$

and the detailed writing of this operator, as well as that of the effective dipole moment (to calculate absorption line intensities) or effective polarizability (to calculate Raman scattering line intensities) has been described elsewhere, see for instance Refs. [2,16,17].

All calculations are performed in a symmetrized coupled rovibrational basis set:

$$\left| \Phi_{\sigma}^{\{s\}, C_v, J, n C_r, C} \right\rangle = \left| \Psi_r^{(J, n C_r)} \otimes \Psi_v^{\{s\}, C_v} \right\rangle_{\sigma}^{(C)}, \quad (3)$$

where all C symbols correspond to irreducible representations of the symmetry point group of the molecule and $\{s\}$ represents all other intermediate vibrational quantum numbers and symmetry symbols. The rotational part $\Psi_r^{(J, n C_r)}$ depends on the rotational quantum number J

and on a multiplicity index n that distinguishes levels within the same (J, C_r) block. The vibrational part $\Psi_v^{\{s\}, C_v}$ consists in the coupling of elementary wave functions for each normal mode number k in the general form for component σ_k :

$$\left| \Psi_{\nu_k \sigma_k}^{(l_k, n_k C_k)} \right\rangle = \left| \nu_k(l_k, n_k C_k, \sigma_k) \right\rangle, \quad (4)$$

where ν_k is the associated vibrational quantum number, l_k is the vibrational angular momentum quantum number ($l_k = 0$ for non-degenerate modes).

The eigenvectors of \tilde{H} are decomposed over the above-defined initial rovibrational basis set:

$$\left| \Psi_{\sigma}^{(J, C, \alpha)} \right\rangle = \sum_{\{s\}, C_r, C_v} C_{\{s\}, n C_r, C_v}^{\alpha} \left| \Phi_{\sigma}^{\{s\}, C_v, J, n C_r, C} \right\rangle. \quad (5)$$

Here, α numbers of eigenvectors within the same (J, C) block, in increasing eigenenergy order. Our databases contain this full decomposition through the full list of $C_{\{s\}, n C_r, C_v}^{\alpha}$ coefficients.

3.2. Software

Although this is not mandatory (but it is of course strongly adapted), the databases are built with a software suite developed in our Dijon group. These programs have already been presented in Wenger et al. [18] and consist of two main components:

- XTDS: a Java front-end to the different programs implementing the tensorial formalism developed in the Dijon group and described above. It allows the simulation and analysis of polyad systems for molecules of various symmetries (T_d and O_h spherical tops like CH₄ and SF₆, C_{2v} , C_{3v} , and C_{4v} quasi-spherical tops like SO₂F₂, CH₃D and SF₅Cl, D_{2h} molecules like C₂H₄).
- SPVIEW: a cross-platform Java application for the display and graphical assignment of high-resolution molecular spectra. Experimental and simulated spectra (XY ASCII or OPUS² formats) can

² Format developed by Bruker. It is a versatile and widely used closed file format in the field of spectroscopy and materials analysis.

Table 3

Comparison for the same line between the output produced by HITRAN (first line) and our database (second line) for the molecule CH₃Cl. We can clearly see that quantum numbers are assigned differently, and that the molecule is treated as a Group 3 molecule. The large intensity difference (third column) is due to the inclusion of the isotopic abundance in the HITRAN database.

241	662.530240	6.880E-24	...	V3	GROUND	62	2	0E	63	2	0E	334340	...
241	662.530500	1.031e-23	...	001000 1S+	000000 1S+	62	E	2	63	E	2	480000	...

Table 4

Rovibrational transitions of C₂H₄ in ECaSDa. Polyad schemes are described by (*i*₁; *i*₂; ...; *i*_N) multiplets as explained in Section 3.1.

Transitions	Number dipolar	Dipolar wavenumber cm ⁻¹	Dipolar intensity cm ⁻¹ / (molecule.cm ⁻²)
C ₂ H ₄ Scheme 1 (0,0,0,1,0,0,1,0,0,1,0,1) <i>P</i> ₁ - <i>P</i> ₀	54,755	620–1525	1×10 ⁻²⁷ –1×10 ⁻¹⁹
C ₂ H ₄ Scheme 2 (0,2,0,0,0,0,0,3,1,3,1) <i>P</i> ₃ - <i>P</i> ₀	41,642	2900–3300	1×10 ⁻²⁷ –1×10 ⁻²⁰
Total	96,397		

be loaded, displayed and manipulated, as well as stick spectra in various formats (including HITRAN). The software has been greatly improved since the version presented in the corresponding article, and is currently in version 2 natively available for GNU/Linux, MacOS and Microsoft Windows. A documentation is also available at <https://spview.rtfd.io>.

Both programs can be downloaded from the following address: <https://icb.u-bourgogne.fr/casda-soft> and although XTDS is cross-platform too, we strongly recommend using it under Linux or MacOS, due to the use of bash scripts. Table 2 illustrates the correspondence between molecules and packages used for analysis.

3.3. Database output format

Output files are available in two different formats: line lists are provided in the 160-character HITRAN2004 format [5], and cross-section data, that are computed by the binned sum of intensities, in a 2-column flat file. It is important to note, however, that unlike HITRAN, our databases do not include isotopic abundances.

Another detail worth highlighting here is the fact that the databases do not strictly adhere to the notation convention laid down in the article establishing the HITRAN2004 format, as far as quantum numbers and symmetry labels are concerned. Indeed, it should be remembered that the Dijon formalism was originally built for spherical rotors (Group 3 in Table 4 of the HITRAN article [5]), so we use the associated quantum numbers. Moreover, we have developed a similar formalism for some lower symmetry species, such as C_{3v} [19,20] and D_{2h} molecules [21]. Consequently, molecules such as ethene (C₂H₄), belonging to Group 1 of asymmetric rotors (described with *J*, *K*_a, *K*_c, *F* and *Sym*), or chloromethane (CH₃Cl) belonging to Group 4 (*J*, *K*, *l*, *C*, *Sym* and *F*) of symmetric rotors, have an output format corresponding to molecules in Group 3 (*J*, *C*, *α*, *F*). Table 3 shows an example of a CH₃Cl single line in the two different formats. Only the differing parts are shown. Our previous article presented the same table for the C₂H₄ molecule.

Our databases are compatible with the XSAMS (XML Schema for Atoms, Molecules, and Solids) format adopted as part of the European VAMDC project [10–13]. Because, despite being a standard, the XSAMS file format is still little used, if at all, in the molecular spectroscopy community, a tool is also available on the portal to convert an XSAMS file to the HITRAN format. However, not all our databases are yet accessible via the VAMDC portal³, especially the latest additions. In

fact, work is currently underway on the VAMDC servers to enable asynchronous queries. This update should resolve some of the problems associated with downloading large files through the portal.

4. Unchanged databases

Two databases have not been updated. Here we give a quick reminder of the molecules and their fields of application.

4.1. MeCaSDa, CH₄

Methane, under the isotopologue form of ¹²CH₄, is one of the most important and simplest organic compounds. It contributes from 4% to 9% to the greenhouse effect, with a relatively high lifetime of 8–10 years [22]. Methane is everywhere in the Solar System and plays an important role in the composition of the atmospheres of gas giants such as Jupiter [23] and Saturn [24], ice giants such as Uranus [25] and Neptune [26], as well as their main moons, notably Titan [27] and Triton [28], and the dwarf planet Pluto [29]. It is also one of the most important opacity sources in the atmospheres of exoplanets and brown dwarfs. For example, the very strong methane transition at 3 μm is the predominant feature in the spectrum of brown dwarfs at 1600 K, and remains discernible even at 1800 K.

No update has been performed on MeCaSDa in this release.

4.2. RuCaSDa, RuO₄

RuO₄, another tetrahedral molecule, has practical applications in various industrial sectors. The chemical toxicity of the compound and the radiological effects of its isotopologues ¹⁰³RuO₄ and ¹⁰⁶RuO₄ have led to renewed interest in studying its spectroscopic properties with a view to possible remote sensing in the atmosphere [30].

Ruthenium tetroxide database (RuCaSDa) has not been updated since Richard et al. [1].

5. Spectroscopic data updates

5.1. ECaSDa, C₂H₄

Ethylene (or ethene) is a natural gas compound present in our atmosphere but also in the atmospheres of outer Solar System planets and moons such as Jupiter [31], Saturn [32], Titan [33] and Neptune [34]. However, a better knowledge of spectroscopic parameters is needed

³ https://portal.vamdc.org/vamdc_portal

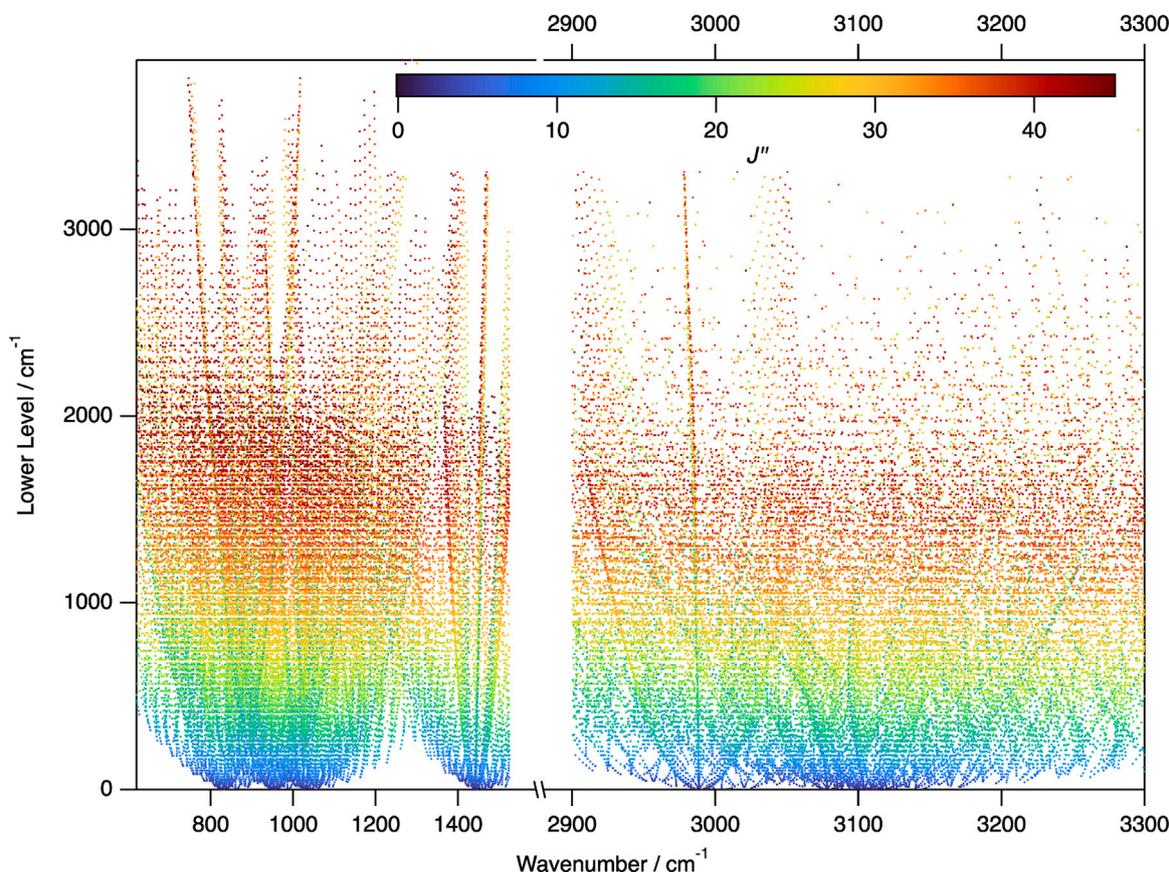


Fig. 2. Representation of the lower level wavenumber for all transitions present in the ECaSDa database. Colors are used to display the lower state rotational quantum number value, J'' .

for this molecule in order to detect its presence and/or to derive its accurate concentration in these atmospheres.

Two polyad schemes were considered, which are specified in Table 4. The first one was used for the $\nu_4/\nu_7/\nu_{10}/\nu_{12}$ tetrad in Ref. [35] which is not updated in this release.

We have recently performed a detailed analysis and modeling of the strongly absorbing ν_9 and ν_{11} fundamental bands in the 3000 cm^{-1} ($3.3\ \mu\text{m}$) region. Due to the complexity of the observed spectra, we have built a second polyad scheme taking into account some fundamental bands previously analyzed thanks to the tensorial formalism developed in Dijon for asymmetric-top molecules [36]. A four polyad system has been settled and the last P_3 polyad contains four rovibrational bands: ν_9 , ν_{11} , $\nu_2 + \nu_{12}$ and $2\nu_{10} + \nu_{12}$. A first line position analysis has been performed, leading to 3328 assignments with a root mean square deviation of $5.927 \times 10^{-3}\text{ cm}^{-1}$ and a standard deviation of 1.965 using 88 adjusted parameters. Line intensities have also been fitted with a relative root mean square deviation of 3.77% [37]. A new list of lines calculated in the $2900\text{--}3300\text{ cm}^{-1}$ region has been added to the database, bringing 41,642 new transitions, and is summarized in Table 4. It is also important to note that an intensity threshold of $10^{-27}\text{ cm}^{-1}/(\text{molecule cm}^{-2})$ has been added to the old data, which are integrated into scheme 1, reducing their number from 96,756 [1] to 54,755. This choice of cutoff seemed judicious in retrospect, and allows us to eliminate weak transitions that seemed unreliable. Fig. 2 displays the distribution of the lower states of all ECaSDa transitions.

5.2. SHeCaSDa, SF₆

SF₆ is a strong greenhouse gas whose origin is purely anthropogenic, see for instance papers [38], [39] and references therein. Since many years, our group, in collaboration with various experimentalists, has

undertaken a systematic study of the many fundamental, overtone and combination bands of this molecule in the far and near infrared ranges [40]. This is important to be able to calculate hot bands in the strongly absorbing ν_3 region around 940 cm^{-1} ($10.6\ \mu\text{m}$) since such hot bands involve vibrational levels that can be studied separately thanks to combination and overtone bands [41]. The main difficulty with such a heavy species is that it is almost impossible to measure intensities of individual lines; SF₆ lines form clusters of many transitions, even at high-resolution. Thus, it is necessary to use calculated estimates of the dipole moment derivatives [42].

We have recently reinvestigated the $\nu_3 + \nu_5$ combination band around 1450 cm^{-1} ($6.9\ \mu\text{m}$). This one presents a very unusual asymmetric intensity profile, as it was shown for the first time at high-resolution in Ref. [43]. Thanks to a new perturbative calculation to be detailed in a forthcoming paper [44], we could provide better estimates of the effective dipole moment parameters for this band. We have used these values to include it in the SHeCaSDa database. Table 5 shows this addition with the 31,553 new transitions added in $P_3 - P_0$ of scheme 3.

Fig. 3 displays the distribution of the lower states of all SHeCaSDa transitions.

5.3. TFCaSDa, CF₄

Tetrafluoromethane CF₄ is another greenhouse gas whose contribution is far from negligible, even if its abundance is far behind that of CO₂ with an atmospheric concentration almost five million times weaker. The molecule has a warming power 6500 times greater and a lifetime 200 times longer (50,000 years) in the atmosphere [45]. It is therefore crucial to study this perfluorocarbon (PFC) molecule, as its concentration must be monitored and reduced, as stipulated by the Kyoto Protocol [46], in order to limit emissions of this powerful

Table 5Rovibrational transitions of SF₆ in SHeCaSDa. Polyad schemes are described by (i₁; i₂; ...; i_N) multiplets as explained in Section 3.1.

Transitions	Number dipolar	Nb. Raman	Dipolar wavenumber cm ⁻¹	Dipolar intensity cm ⁻¹ / (molecule.cm ⁻²)	Raman wavenumber cm ⁻¹	Raman intensity arbitrary unit
³² SF ₆						
Scheme 1 (2,1,3,0,0,0)						
P ₁ - P ₀		42,983			600-687	2×10 ¹⁸ -6×10 ²⁰
P ₂ - P ₀		7,861			773-775	2×10 ¹⁷ -3×10 ²¹
P ₄ - P ₂		11,797			770-773	2×10 ¹⁷ -2×10 ²⁰
P ₃ - P ₀	53,996		935-957	1×10 ⁻²³ -2×10 ⁻²⁰		
P ₄ - P ₁	32,371		932-959	1×10 ⁻²³ -8×10 ⁻²²		
P ₅ - P ₂	11,473		937-949	1×10 ⁻²³ -4×10 ⁻²²		
Scheme 2 (0,0,0,2,0,1)						
P ₂ - P ₀	14,941		593-637	1×10 ⁻²³ -1×10 ⁻²¹		
P ₃ - P ₁	34,575		593-637	1×10 ⁻²³ -2×10 ⁻²²		
P ₁ - P ₀	62,895		320-374	1×10 ⁻²⁸ -6×10 ⁻²⁶		
Scheme 3 (0,0,2,0,1,0)						
P ₁ - P ₀		59,842			475-562	2×10 ¹⁸ -4×10 ⁻²⁰
P ₃ - P ₀	31,553		1425-1496	8×10 ⁻²⁷ -4×10 ⁻²⁵		
P ₃ - P ₁	121,841		932-964	1×10 ⁻²³ -1×10 ⁻²¹		
Scheme 4 (0,4,0,2,1,0)						
P ₁ - P ₀		17,987			772-773	3×10 ¹⁷ -2×10 ²⁰
P ₃ - P ₁	3,935		599-630	1×10 ⁻²³ -3×10 ⁻²³		
³³ SF ₆						
Scheme 5 (0,0,1,0,0,0)						
P ₁ - P ₀	1,620		937-941	2×10 ⁻²² -2×10 ⁻²⁰		
³⁴ SF ₆						
Scheme 5 (0,0,1,0,0,0)						
P ₁ - P ₀	1,620		928-933	2×10 ⁻²² -2×10 ⁻²⁰		
Scheme 6 (0,0,0,1,0,0)						
P ₁ - P ₀	3,920		600-624	1×10 ⁻²³ -1×10 ⁻²¹		
³⁶ SF ₆						
Scheme 5 (0,0,1,0,0,0)						
P ₁ - P ₀	7,843		908-920	1×10 ⁻²¹ -2×10 ⁻²⁰		
Total	382,583	140,470				

Table 6Rovibrational transitions of CF₄ in TFMeCaSDa. Polyad schemes are described by (i₁; i₂; ...; i_N) multiplets as explained in Section 3.1.

Transitions	Number dipolar	Dipolar wavenumber cm ⁻¹	Dipolar intensity cm ⁻¹ / (molecule.cm ⁻²)
¹² CF ₄			
Scheme 1 (0,2,6,3)			
P ₆ - P ₀	39,086	1230-1305	8×10 ⁻²³ -8×10 ⁻²⁰
P ₃ - P ₀	15,149	583-682	1×10 ⁻²⁴ -8×10 ⁻²²
P ₈ - P ₂	33,430	1231-1330	8×10 ⁻²⁵ -1×10 ⁻²⁰
P ₆ - P ₆	284,350	1-114	1×10 ⁻³⁰ -8×10 ⁻²⁷
Scheme 2 (3,0,4,2)			
P ₆ - P ₀	3408	1270-1283	8×10 ⁻²⁵ -1×10 ⁻²¹
Total	375,423		

greenhouse gas which, once emitted, remains in the atmosphere for a long time on a human scale and contributes to radiative forcing [47].

The molecule is a spherical top with no permanent dipole moment. As a consequence, rotational lines, forbidden in first approximation, are very faint, and recording them is always a technical challenge for such a molecule. Lately, Simon et al. [48] reported a new contribution in the ν₃ - ν₃ pure rotation band thanks to a Cavity Ring-Down Spectroscopy (CRDS) experiment. More than 50 lines were measured with great precision in terms of position and intensity, and added to the database. In order to achieve that, the latter had to be restructured and the third polyad scheme, initially used to describe these pure rotational lines of ν₃ = 1, and based on earlier work by Boudon et al. [49], has been removed. Instead, we defined the transition P₆ - P₆ in the scheme 1, adding 284,350 new transitions in the range 1 to 114 cm⁻¹, for a total of 375,423 lines. Table 6 illustrates the update.

Table 7Rovibrational transitions of GeH₄ in GeCaSDa. Polyad schemes are described by (i₁; i₂; ...; i_N) multiplets as explained in Section 3.1.

Transitions	Number dipolar	Dipolar wavenumber cm ⁻¹	Dipolar intensity cm ⁻¹ / (molecule.cm ⁻²)
⁷⁰ GeH ₄			
Scheme 1 (1,0,1,0)			
P ₁ - P ₀	6426	1930-2266	1×10 ⁻²³ -4×10 ⁻¹⁹
Scheme 2 (0,1,0,1)			
P ₁ - P ₀	5666	650-1106	1×10 ⁻²³ -4×10 ⁻¹⁹
⁷² GeH ₄			
Scheme 1 (1,0,1,0)			
P ₁ - P ₀	6462	1930-2265	1×10 ⁻²³ -4×10 ⁻¹⁹
Scheme 2 (0,1,0,1)			
P ₁ - P ₀	5679	649-1106	1×10 ⁻²³ -4×10 ⁻¹⁹
⁷³ GeH ₄			
Scheme 1 (1,0,1,0)			
P ₁ - P ₀	6470	1930-2265	1×10 ⁻²³ -4×10 ⁻¹⁹
Scheme 2 (0,1,0,1)			
P ₁ - P ₀	5700	649-1105	1×10 ⁻²³ -4×10 ⁻¹⁹
⁷⁴ GeH ₄			
Scheme 1 (1,0,1,0)			
P ₁ - P ₀	6509	1929-2265	1×10 ⁻²³ -4×10 ⁻¹⁹
Scheme 2 (0,1,0,1)			
P ₁ - P ₀	5700	649-1105	1×10 ⁻²³ -4×10 ⁻¹⁹
⁷⁶ GeH ₄			
Scheme 1 (1,0,1,0)			
P ₁ - P ₀	6525	1929-2265	1×10 ⁻²³ -4×10 ⁻¹⁹
Scheme 2 (0,1,0,1)			
P ₁ - P ₀	5741	648-1105	1×10 ⁻²³ -4×10 ⁻¹⁹
Total	60,878		

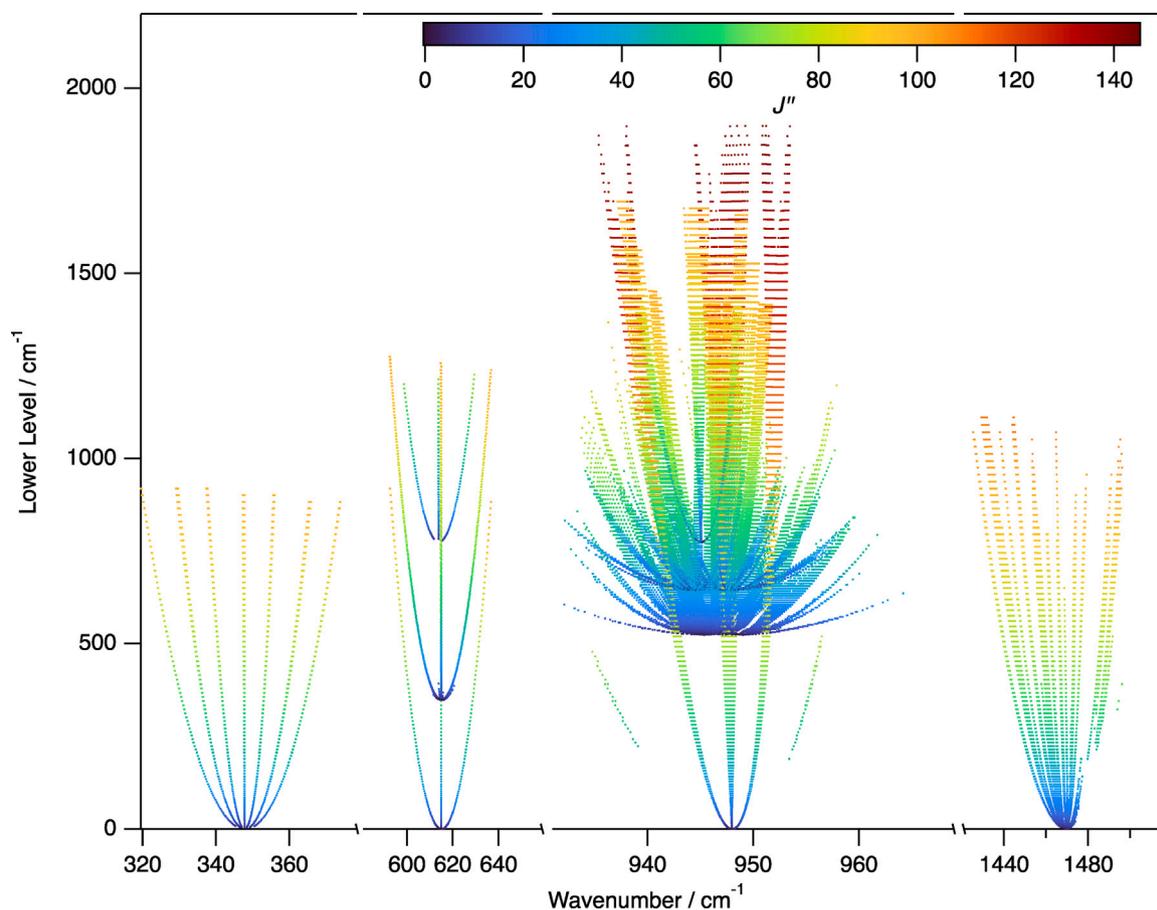


Fig. 3. Representation of the lower level wavenumber for all transitions present in the SHeCaSDa database. Colors are used to display the lower state rotational quantum number value, J'' .

Fig. 4 displays the distribution of the lower states of all TFMCaSDa transitions; this illustrates the recent addition of hot band lines in this base.

5.4. GeCaSDa, GeH_4

Germane (GeH_4) is a tetrahedral molecule present in small amount in the atmospheres of the giant planets Jupiter [50] and Saturn [51]. The ongoing NASA mission Juno has renewed interest in the spectroscopy of Jupiter, since its accurate modeling is essential for the retrieval of other tropospheric species [52].

Because the region is of high interest for planetology, the database was first built with the strongly absorbing ν_1/ν_3 stretching dyad region near 2100 cm^{-1} ($4.8\ \mu\text{m}$), for all five germane isotopologues in natural abundance [53]. Since then, GeCaSDa has been updated with the ν_2/ν_4 bending dyad centered around 900 cm^{-1} ($11.1\ \mu\text{m}$) [54] and 28,486 new transitions have been included in the database, bringing the total number of lines to 60,878 (see Table 7). Fig. 5 displays the distribution of the lower states of all GeCaSDa transitions for the main isotopologue: $^{74}\text{GeH}_4$.

5.5. TFSiCaSDa, SiF_4

Silicon tetrafluoride (SiF_4) is considered a major byproduct of phosphorus fertilizer production and certain ore enrichment processes [55]. It finds application in the electronics and semiconductor industry, as well as in the purification and etching of silicon. This molecule also forms during volcanic activity [56,57]. The presence of SiF_4 in volcanic plumes may serve as an indicator of the deep-seated magma source in certain volcanoes [58,59] and is thus adapted to remote IR

spectroscopy using its strong absorption band ν_3 at 1032 cm^{-1} ($9.7\ \mu\text{m}$). Moreover, it has been suggested that SiF_4 may be present in the volcanic emissions of Jupiter's moon Io [60].

The silicon tetrafluoride is also a tetrahedral spherical top molecule with T_d symmetry. As shown in Ref. Merkulova et al. [61], its infrared spectrum presents a series of regularly spaced rovibrational polyads (see for instance Figure 2 of this reference). However, when studying only the lowest vibrational levels, the contribution of interactions between different modes is remarkably small. Therefore, it is possible to analyze the rovibrational band implying these levels with satisfactory accuracy using an isolated band model. Consequently, at present, we did not use the full polyad scheme for this molecule, but only simple reduced schemes adapted to the bands under consideration.

The present update of the TFSiCaSDa database of calculated SiF_4 lines is based on the recent analyses of combination bands $\nu_1 + \nu_3$, $\nu_2 + \nu_3$ [61] and $\nu_3 + \nu_4$ [62]. We did not model the line intensities of these combination bands themselves, so they are not included in the database. Their rovibrational levels which were determined through these two analyses, however, are also the upper levels of important hot bands. Combined with those of the fundamental bands [63], they can therefore be used to deduce the (hot) difference bands in question: $\nu_3 + \nu_1 - \nu_1$, $\nu_3 + \nu_2 - \nu_2$ and $\nu_3 + \nu_4 - \nu_4$ which lie in the strongly absorbing ν_3 region. In order to calculate line intensities, we used the ν_3 effective dipole moment parameters [63] for all these (cold and hot) ν_3 -based bands. Calculations were performed for the $^{28}\text{SiF}_4$, $^{29}\text{SiF}_4$ and $^{30}\text{SiF}_4$ isotopologues.

A total of 677,519 lines are now available in TFSiCaSDa as part of this major update. Table 8 illustrates the content of the 5 polyad schemes used, as well as the ranges in wavenumber and intensity. Finally, Fig. 6 displays the distribution of the lower states of all transitions for the main isotopologue: $^{28}\text{SiF}_4$.

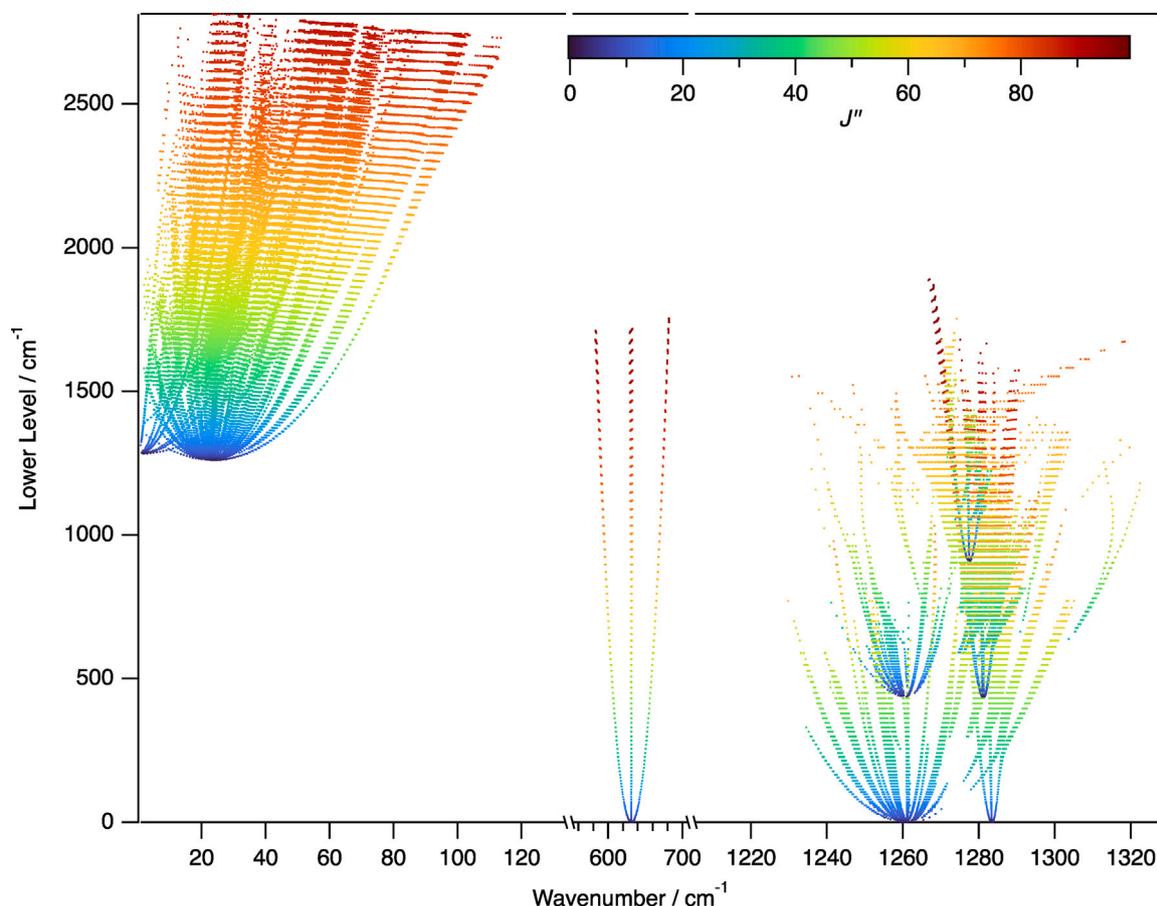


Fig. 4. Representation of the lower level wavenumber for all transitions present in the TFM_eCaSDa database. Colors are used to display the lower state rotational quantum number value, J'' .

Table 8

Rovibrational transitions of SiF₄ in TFSiCaSDa. Polyad schemes are described by $(i_1; i_2; \dots; i_N)$ multiplets as explained in Section 3.1.

Transitions	Number dipolar	Dipolar wavenumber cm ⁻¹	Dipolar intensity cm ⁻¹ / (molecule.cm ⁻²)
Scheme 1 (0, 0, 1, 0)			
²⁸ SiF ₄			
$P_1 - P_0$	17,139	1010–1049	1×10^{-23} – 2×10^{-20}
²⁹ SiF ₄			
$P_1 - P_0$	23,660	1000–1041	1×10^{-23} – 2×10^{-20}
³⁰ SiF ₄			
$P_1 - P_0$	22,269	993–1032	1×10^{-23} – 2×10^{-20}
Scheme 2 (0, 0, 0, 1)			
²⁸ SiF ₄			
$P_1 - P_0$	44,564	356–426	1×10^{-24} – 3×10^{-21}
²⁹ SiF ₄			
$P_1 - P_0$	45,113	354–424	1×10^{-24} – 3×10^{-21}
³⁰ SiF ₄			
$P_1 - P_0$	57,656	353–421	1×10^{-24} – 3×10^{-21}
Scheme 3 (1, 0, 2, 0)			
²⁸ SiF ₄			
$P_3 - P_1$	8201	1014–1037	1×10^{-23} – 3×10^{-22}
²⁹ SiF ₄			
$P_3 - P_1$	7949	1005–1029	1×10^{-23} – 3×10^{-22}
³⁰ SiF ₄			
$P_3 - P_1$	7931	996–1020	1×10^{-23} – 3×10^{-22}
Scheme 4 (0, 1, 2, 0)			
²⁸ SiF ₄			
$P_3 - P_1$	42,822	1012–1050	1×10^{-23} – 4×10^{-21}

(continued on next page)

Table 8 (continued).

Transitions	Number dipolar	Dipolar wavenumber cm ⁻¹	Dipolar intensity cm ⁻¹ / (molecule.cm ⁻²)
²⁹ SiF ₄			
$P_3 - P_1$	45,682	1003–1041	1×10^{-23} – 4×10^{-21}
³⁰ SiF ₄			
$P_3 - P_1$	45,318	994–1032	1×10^{-23} – 4×10^{-21}
Scheme 5 (0, 0, 2, 1)			
²⁸ SiF ₄			
$P_3 - P_1$	100,998	991–1061	1×10^{-23} – 2×10^{-21}
²⁹ SiF ₄			
$P_3 - P_1$	102,150	981–1051	1×10^{-23} – 2×10^{-21}
³⁰ SiF ₄			
$P_3 - P_1$	106,067	975–1042	1×10^{-23} – 2×10^{-21}
Total	677,519		

6. New molecules

New molecules have also been added to CaSDa24 and are discussed in the present section.

6.1. UHeCaSDa, UF₆

UF₆ has always been a molecule of interest to the nuclear industry for isotope separation. It stands as the sole uranium-containing compound exhibiting noteworthy volatility, boasting well-established industrial production and handling procedures. Additionally, only minimal photolysis energy is needed to induce its dissociation or reaction.

Unable to obtain experimental spectra of UF₆ due to the potentially hazardous nature of uranium, coupled with data disclosure restrictions

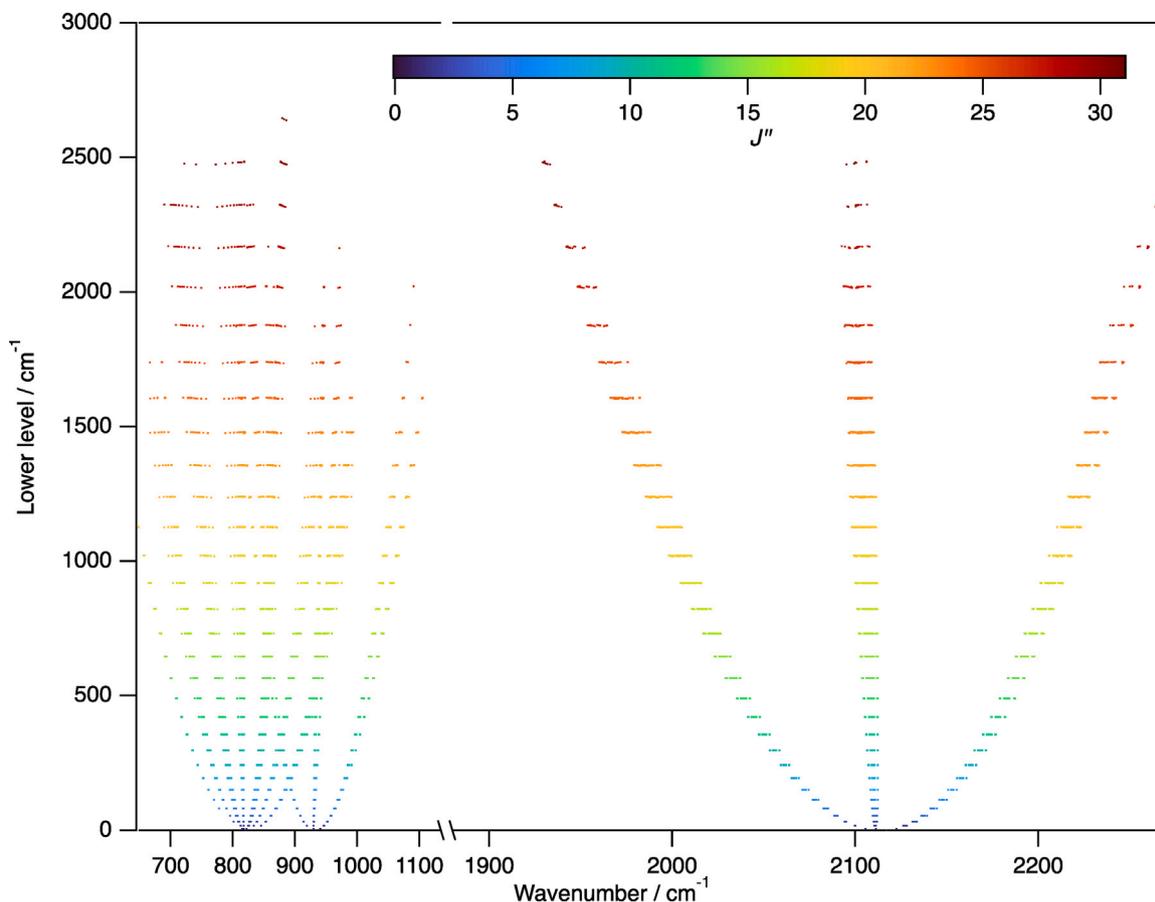


Fig. 5. Representation of the lower level wavenumber for all transitions present in the GeCaSDa database, for the main isotopologue: $^{74}\text{GeH}_4$. Colors are used to display the lower state rotational quantum number value, J'' .

stemming from security and confidentiality concerns, we turned to computer modeling using Hamiltonian parameters for the ν_3 fundamental band near 627 cm^{-1} ($15.9\text{ }\mu\text{m}$) found in Ref. [64] and dipole moment value taken in Ref. [65]. As the recovered data were only available for the two main isotopologues ($^{235}\text{UF}_6$ and $^{238}\text{UF}_6$), and based on the conclusions of the paper of Loète et al. [66] for RuO_4 and SF_6 , which shows a linear dependence of band centers between isotopologues, we extrapolated the experimental data for the other six isotopologues, as illustrated in Fig. 7. More precisely, we took effective Hamiltonian parameters from Aldridge et al. [64], using those for $^{238}\text{UF}_6$ for all isotopologues, except for the band center that was shifted using the $^{235}\text{UF}_6$ - $^{238}\text{UF}_6$ separation from this reference to calculate the isotopic shift per atomic mass unit. For such heavy molecules, other effective parameters, including that of the dipole moment, usually show negligible variations with isotopic substitution of the central atom. We thus obtained parameter files that were used to calculate the database, and Table 9 summarizes the addition of these 110,041 transitions. Except for $^{238}\text{UF}_6$, for which the existing data are accurate, the data of this database may not be as accurate as for the other CaSDa databases described in the present paper, but this is the best that can be done at present. There also exist other effective Hamiltonian parameters for this molecule, for instance for the $3\nu_3$ overtone [67] or the $\nu_1 + \nu_3$ combination band [68], but with no dipole moment value, so we do not include this here, as it is not possible to provide absolute intensity values. Fig. 8 displays the distribution of the lower states of all UHeCaSDa transitions for the main isotopologue: $^{138}\text{UF}_6$.

6.2. ChMeCaSDa, CH_3Cl

Chloromethane (CH_3Cl) is a symmetric-top molecule belonging to the C_{3v} symmetry group. It has six vibrational modes: three parallel

Table 9

Rovibrational transitions of UF_6 in UHeCaSDa. Polyad schemes are described by $(i_1; i_2; \dots; i_N)$ multiplets as explained in Section 3.1.

Transitions	Number dipolar	Dipolar wavenumber cm^{-1}	Dipolar intensity $\text{cm}^{-1} / (\text{molecule}\cdot\text{cm}^{-2})$
$^{232}\text{UF}_6$			
Scheme 1 (0,0,1,0,0,0)			
$P_1 - P_0$	13,761	618–639	1×10^{-23} – 9×10^{-23}
$^{233}\text{UF}_6$			
Scheme 1 (0,0,1,0,0,0)			
$P_1 - P_0$	13,759	618–639	1×10^{-23} – 9×10^{-23}
$^{234}\text{UF}_6$			
Scheme 1 (0,0,1,0,0,0)			
$P_1 - P_0$	13,756	617–639	1×10^{-23} – 9×10^{-23}
$^{235}\text{UF}_6$			
Scheme 1 (0,0,1,0,0,0)			
$P_1 - P_0$	13,754	617–638	1×10^{-23} – 9×10^{-23}
$^{236}\text{UF}_6$			
Scheme 1 (0,0,1,0,0,0)			
$P_1 - P_0$	13,753	617–638	1×10^{-23} – 9×10^{-23}
$^{237}\text{UF}_6$			
Scheme 1 (0,0,1,0,0,0)			
$P_1 - P_0$	13,751	617–638	1×10^{-23} – 9×10^{-23}
$^{238}\text{UF}_6$			
Scheme 1 (0,0,1,0,0,0)			
$P_1 - P_0$	13,748	617–638	1×10^{-23} – 9×10^{-23}
$^{239}\text{UF}_6$			
Scheme 1 (0,0,1,0,0,0)			
$P_1 - P_0$	13,748	616–638	1×10^{-23} – 9×10^{-23}
Total	110,041		

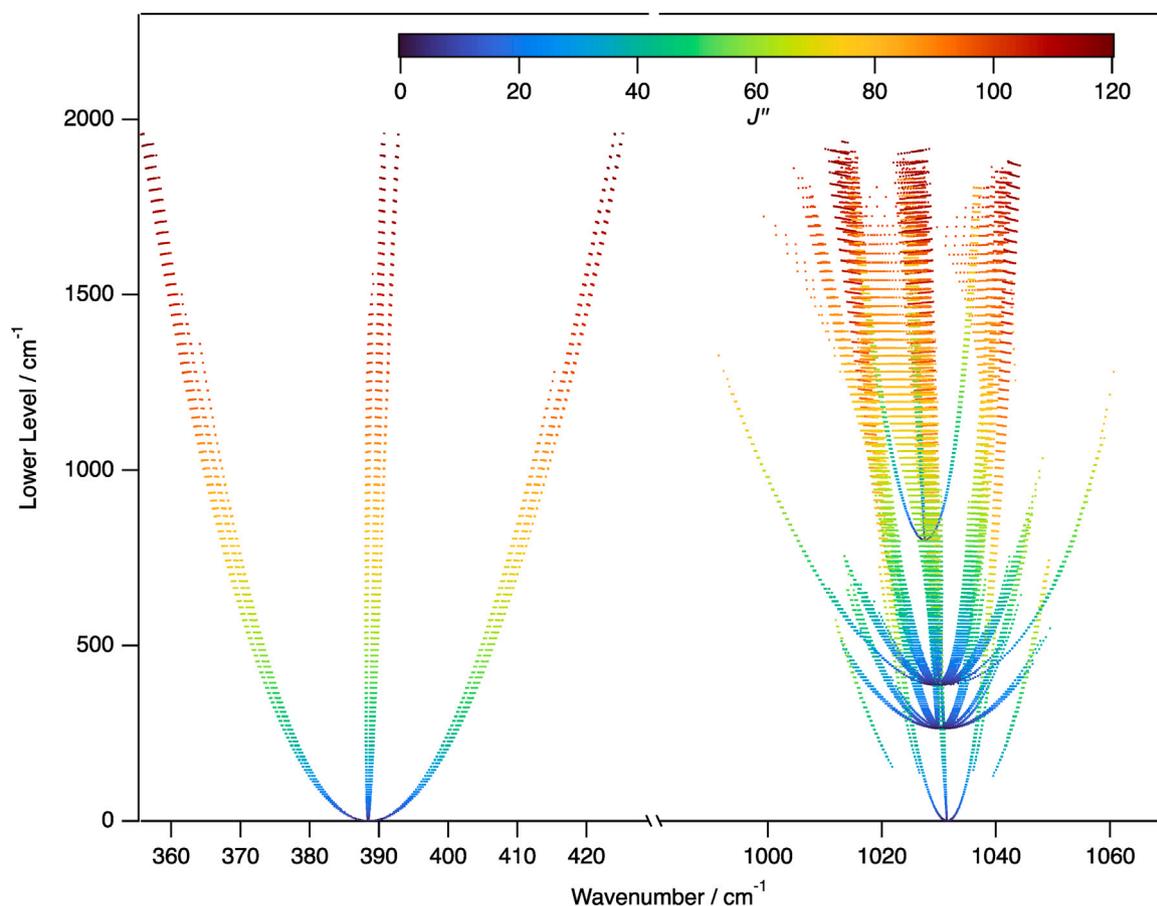


Fig. 6. Representation of the lower level wavenumber for all transitions present in the TFSiCaSDa database, for the main isotopologue: $^{28}\text{SiF}_4$. Colors are used to display the lower state rotational quantum number value, J'' .

Table 10

Rovibrational transitions of CH_3Cl in ChMeCaSDa. Polyad schemes are described by $(i_1; i_2; \dots; i_N)$ multiplets as explained in Section 3.1.

Transitions	Number dipolar	Dipolar wavenumber cm^{-1}	Dipolar intensity $\text{cm}^{-1} / (\text{molecule}\cdot\text{cm}^{-2})$
$\text{CH}_3^{35}\text{Cl}$			
Scheme 1 (0,0,1,0,0,1)			
$P_1 - P_0$	2601	663–773	$1 \times 10^{-23} - 1 \times 10^{-20}$
$P_2 - P_0$	3460	915–1146	$1 \times 10^{-23} - 2 \times 10^{-21}$
$\text{CH}_3^{37}\text{Cl}$			
Scheme 1 (0,0,1,0,0,1)			
$P_1 - P_0$	2593	658–767	$1 \times 10^{-23} - 1 \times 10^{-20}$
$P_2 - P_0$	3498	913–1145	$1 \times 10^{-23} - 2 \times 10^{-21}$
Total	12,152		

vibrations of type A_1 , and three degenerate pairs of perpendicular vibrations of type E .

This molecule is one of the simplest haloalkanes, belonging to the more general family of organohalogens which are abundant in the Earth's atmosphere, due to biological and industrial processes [69]. Through catalytic processes, they lead to the destruction of atmospheric ozone [70].

While CH_3Cl was detected for the first time in 1975 by Lovelock [71], its detection beyond the Earth's atmosphere is much more recent. Indeed, CH_3Cl was only detected in the surrounding of a protostar through submillimeter-wave spectroscopy in 2017, and in the coma of comet 67P/Churyumov-Gerasimenko through *in situ* mass spectrometry [72] the same year. The ν_3 and ν_6 bands respectively located at $650\text{--}800\text{ cm}^{-1}$ ($12.5\text{--}15.4\ \mu\text{m}$) and $920\text{--}1150\text{ cm}^{-1}$ ($8.7\text{--}10.9\ \mu\text{m}$) were

recently analyzed for the two most abundant isotopologues ($\text{CH}_3^{35}\text{Cl}$ and $\text{CH}_3^{37}\text{Cl}$) by Hardy et al. [73]. An accurate model of the positions and intensities of 12,152 lines was produced and was included in the new ChMeCaSDa database. They are summarized in Table 10.

Fig. 9 displays the distribution of the lower states of all ChMeCaSDa transitions for the main isotopologue: $\text{CH}_3^{35}\text{Cl}$.

The ν_1 and ν_4 bands ($2900\text{--}3200\text{ cm}^{-1}$) were recently observed at high-resolution at the LISA facility. Both bands will be added to the database by adapting the polyad scheme lately used for ν_3 and ν_6 and described in Section 6.2. In the future polyad scheme, P_0 , P_1 , P_2 , P_3 and P_4 will respectively be associated to the ground state, ν_3 , ν_6 , ν_5 , and $\nu_1/\nu_4/2\nu_5/3\nu_6$ band.

6.3. SiCaSDa, SiH_4

Silane (SiH_4) shares similarities with methane (CH_4) as a typical spherical-top molecule but exhibits greater reactivity, being pyrophoric. Despite its simplicity as the most basic stable silicon compound, silane possesses a complex rovibrational spectrum [74–76]. It serves as a crucial precursor for chemical vapor deposition of silicon. Moreover, it has also been detected in circumstellar envelopes, such as around IRC +10216 [77–79] and recent laboratory research has investigated the chemistry of silicon and silane in such environments [80].

As a tetrahedral spherical top molecule with T_d symmetry, silane is not currently covered by line-by-line spectroscopic databases. However, the Pacific Northwest National Laboratory (PNNL) spectral library [81] covers the range from 600 to 6500 cm^{-1} (0.15 to $1.67\ \mu\text{m}$) with a resolution of around 0.06 cm^{-1} for temperatures of 5 , 25 and $50\text{ }^\circ\text{C}$ with cross-section data.

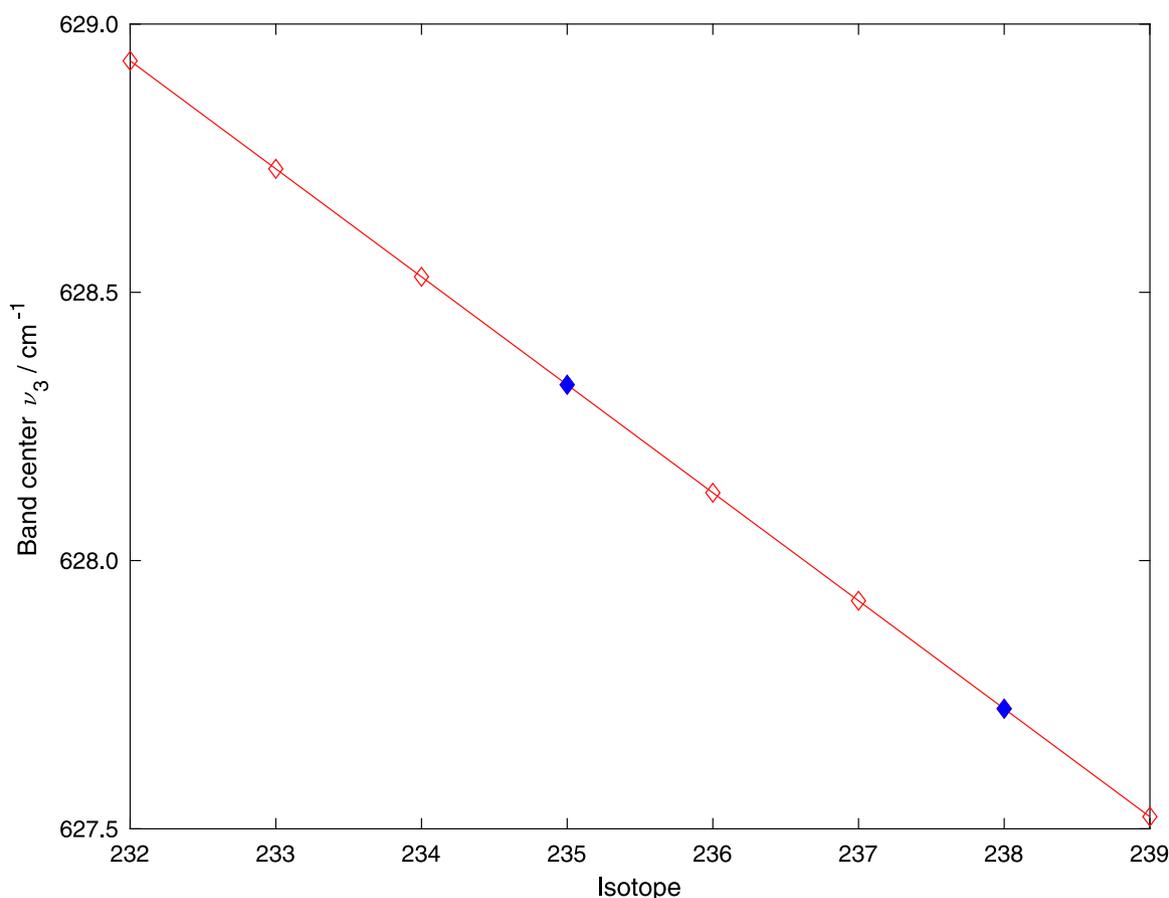


Fig. 7. Band center for the different isotopologues of UF_6 . In blue, the two experimental values from Ref. [64] used to linearly extrapolate the others.

It was then decided to create a new database based on new, modern spectra, in order to improve molecular parameters and thus obtain better modeling with our software packages.

The first calculated line list included in the present work contains the ν_2/ν_4 dyad, located in the $820\text{--}1150\text{ cm}^{-1}$ ($0.87\text{--}12.2\text{ }\mu\text{m}$) range. We also added the pure rotational transitions which have been recently recorded at the SOLEIL Synchrotron facility, allowing to extract line intensities using the method described in Ref. [82] and to fit the centrifugal-distortion-induced dipole moment parameters for the first time. This work will be described in a forthcoming paper [83].

For the ν_2/ν_4 Dyad, the three isotopologues $^{28}\text{SiH}_4$, $^{29}\text{SiH}_4$ and $^{30}\text{SiH}_4$ were analyzed. For the pure rotational transitions, the $^{29}\text{SiH}_4$ and $^{30}\text{SiH}_4$ minor isotopologues were extrapolated by using their own effective Hamiltonian parameters, but calculating intensities using the same effective dipole moment parameters as for $^{28}\text{SiH}_4$ (since this operator does not strongly depend on the isotope of the central atom for such molecules). All this results in a new database called SiCaSDa with a total of 33,910 lines as shown in Table 11. Fig. 10 displays the distribution of the lower states of all transitions for the main isotopologue: $^{28}\text{SiH}_4$.

7. Discussion

CaSDa24 represents a major release of our databases, updating five of them and introducing three new ones. However, the structure remains identical and is detailed in Refs. [1,84]. The names of the bases

Table 11

Rovibrational transitions of SiH_4 in SiCaSDa. Polyad schemes are described by $(i_1; i_2; \dots; i_N)$ multiplets as explained in Section 3.1.

Transitions	Number dipolar	Dipolar wavenumber cm^{-1}	Dipolar intensity $\text{cm}^{-1} / (\text{molecule}\cdot\text{cm}^{-2})$
$^{28}\text{SiH}_4$			
Scheme 1 (2,1,2,1)			
$P_0 - P_0$	4606	0–276	1×10^{-30} – 2×10^{-23}
$P_1 - P_0$	6649	714–1154	1×10^{-23} – 6×10^{-19}
$^{29}\text{SiH}_4$			
Scheme 1 (2,1,2,1)			
$P_0 - P_0$	4607	0–274	1×10^{-30} – 2×10^{-23}
$P_1 - P_0$	6920	732–1180	1×10^{-23} – 6×10^{-19}
$^{30}\text{SiH}_4$			
Scheme 1 (2,1,2,1)			
$P_0 - P_0$	4607	0–274	1×10^{-30} – 2×10^{-23}
$P_1 - P_0$	6521	711–1154	1×10^{-23} – 6×10^{-19}
Total	33,910		

may seem surprising and complicated to pronounce, but they follow the following logic. Each base name ends with the suffix CaSDa (case-sensitive) which stands for Calculated Spectroscopic Database, then the prefix is determined by the literal name of the molecule. For CH_4 , the name is Methane, so MeCaSDa. For SF_6 , which is Sulfur Hexafluoride, a compound name in which each part is used, the name becomes SHeCaSDa, and so on.

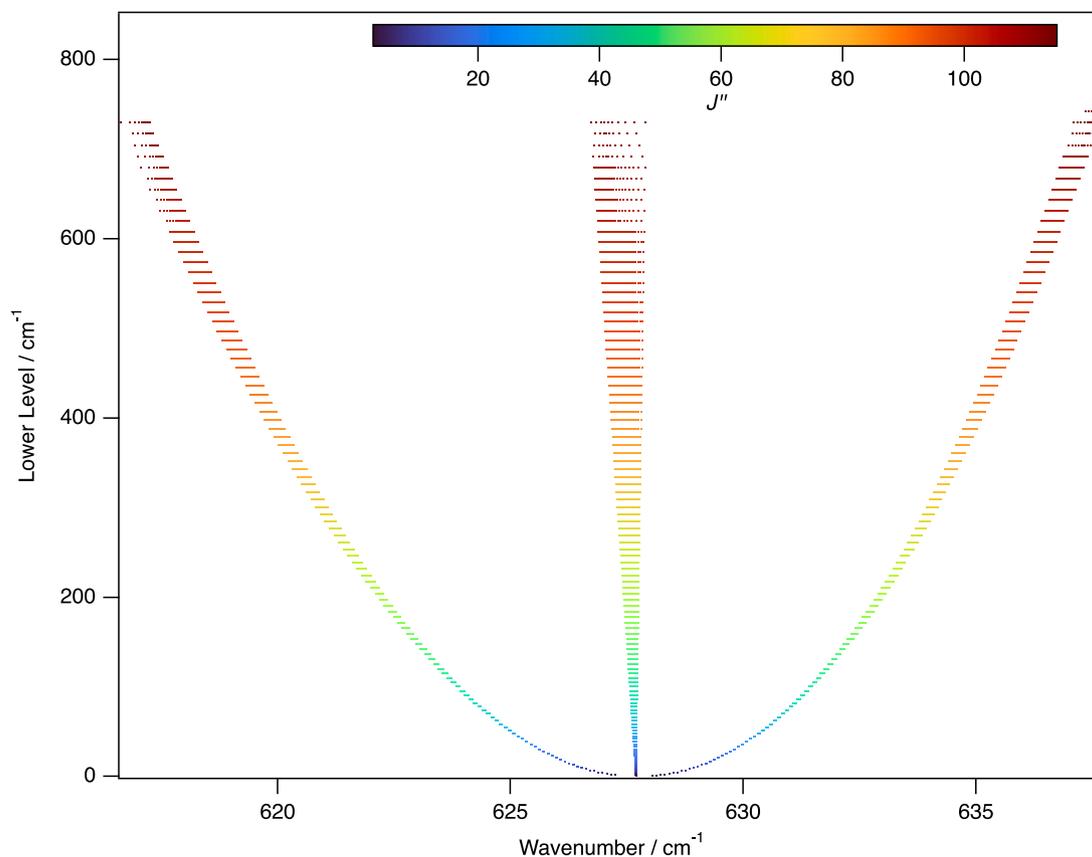


Fig. 8. Representation of the lower level wavenumber for all transitions present in the UHeCaSDa database, for the main isotopologue: $^{138}\text{UF}_6$. Colors are used to display the lower state rotational quantum number value, J'' .

All our databases are calculated from high-resolution experimental spectra, for which we have applied position fits to determine the Hamiltonian parameters, and intensity fits to derive the dipole moment values. One exception is the UHeCaSDa database (UF_6), for which we were unable to obtain experimental data for the reasons explained in Section 6.1 and had to make do with the few published parameters for only two isotopologues. As a result, this database is certainly the least accurate of all, and its results should be used with caution.

With the availability of multiple high-resolution spectroscopic databases, it is valuable to compare their data when the same molecules and vibrational bands are present. As an example, a comparison between the HITRAN database and one of the CaSDa24 databases (ChMeCaSDa) is presented below.

In the current version of HITRAN, theoretical line intensities in the 640–2600 cm^{-1} region were rescaled to fit experimental data [85]. Conversely, in the ChMeCaSDa database, the intensities of ν_3 and ν_6 bands were calculated using dipole moment parameters fitted from experimental lines intensities. To calculate ChMeCaSDa, we used 827 line intensities coming from Ref. [86] for the ν_3 band of $\text{CH}_3^{35}\text{Cl}$, and 1777 line intensities coming from Ref. [87] for the ν_6 band of $\text{CH}_3^{35}\text{Cl}$. The natural abundances of CH_3Cl (0.7577 for $\text{CH}_3^{35}\text{Cl}$, 0.24423 for $\text{CH}_3^{37}\text{Cl}$) were taken into account to compare both databases.

In Fig. 11, we represent the relative difference between experimental intensities and both databases, for the ν_3 band of $\text{CH}_3^{35}\text{Cl}$.

Due to a different intensity cutoff, HITRAN2020 contains more lines (4127) for this band and this isotopologue than ChMeCaSDa (2601). However, we observe better agreement with experimental data in our database. The root mean square deviation (d_{RMS}) of the relative differences is 17.04% for HITRAN and 15.83% for ChMeCaSDa.

The same comparison was performed for the ν_6 band of $\text{CH}_3^{35}\text{Cl}$, and is represented in Fig. 12. Again, HITRAN2020 contains more lines (5064) for this band and this isotopologue than ChMeCaSDa (3460), but the root mean square deviation (d_{RMS}) of the relative differences is 14.94% for HITRAN and 12.77% for ChMeCaSDa. Moreover, the slope in HITRAN2020 residuals does not appear in the ChMeCaSDa residuals.

As far as the databases for other molecules are concerned, some of them in HITRAN2020 come directly from the corresponding CaSDa24 databases; these are GeH_4 , C_2H_4 and SF_6 . A comparison between these databases and HITRAN is therefore not necessary in these cases.



Access to our databases is free and requires no registration on the website. Simply scan the QR Code or follow the URL <https://vamdc.icb.cnrs.fr> to access the database web page and select the molecule you are interested in. These are sorted following their HITRAN molecular species identification (ID) number, with molecules not present in HITRAN at the end of the table, returning a fixed-value 99 field. As already explained, it is important to note that unlike HITRAN, our databases do not contain isotopic abundances, and corrective factors should be applied in the case of atmospheric calculations, for instance.

The establishment of standards for the characterization of molecular data is imperative for their effective use in research into terrestrial and extraterrestrial atmospheres. The adoption of a standardized framework encompassing species description, quantum states and spectroscopic processes thus promotes compatibility between simulation codes and enables transparent and facilitated data exchange between researchers. Combined with free availability, this guarantees

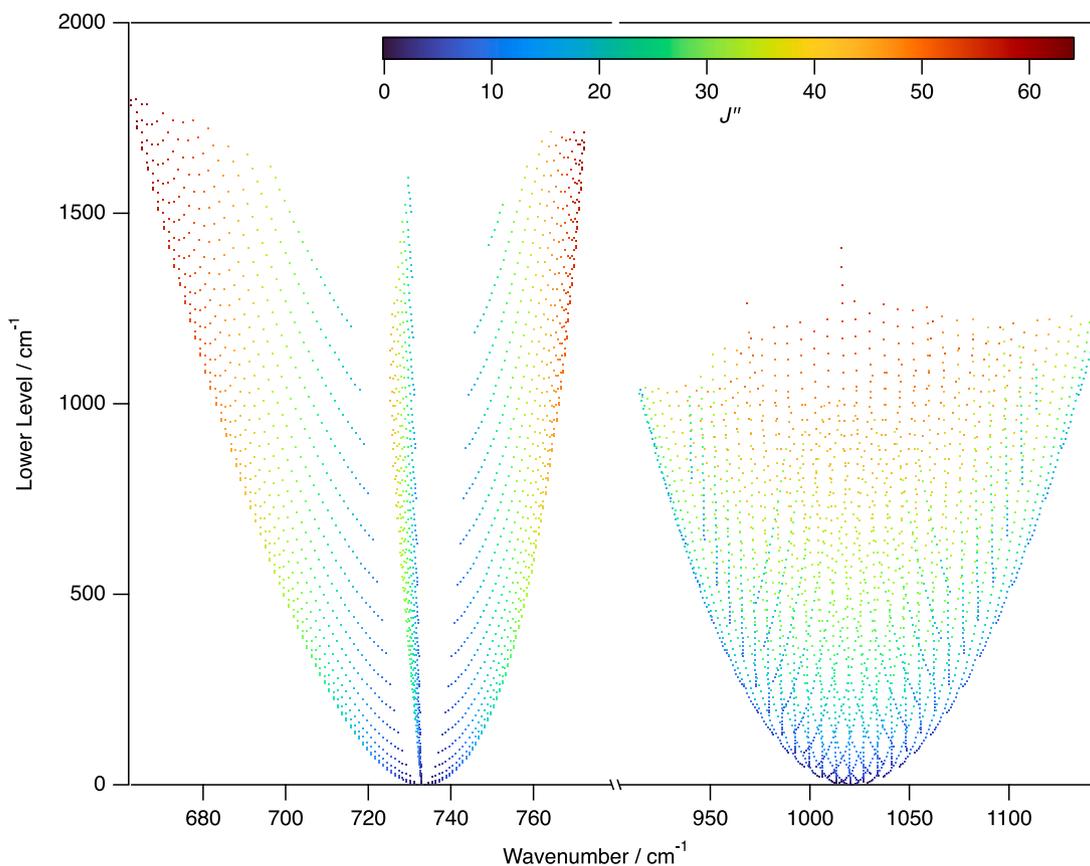


Fig. 9. Representation of the lower level wavenumber for all transitions present in the ChMeCaSDa database, for the main isotopologue: $\text{CH}_3^{35}\text{Cl}$. Colors are used to display the lower state rotational quantum number value, J'' .

the long-term preservation of data, which is key to the success of any database.

The VAMDC project, whose standard XSAMS format is described in Section 3.3, is a consortium that also promotes open data and standards through its portal to the most important molecular and atomic spectroscopic databases.

DataUBFC⁴ (formerly Dat@OSU) is a platform that fits in perfectly with this approach, and aims to provide a description of digital datasets from scientific research in the form of standardized metadata records. DataUBFC is harvested by national and international research catalog or data infrastructures (datacite, <https://recherche.data.gouv.fr>, ...). Our databases can be accessed at the following URL: <https://search-data.ubfc.fr/icb/coll/4>, where each molecule is referenced in a data sheet that provides a description of the calculated data.

8. Conclusion

In this paper, we present a major update of our databases called CaSDa24. To date, 10 molecules have been included, which contains valuable information on molecular spectroscopy data that are useful in many fields of application.

In a future update, we intend to add the possibility to download, from the website, the full decomposition of molecular eigenstates on the initial basis, that is the complete description of eigenvectors. This information, which is contained in the CaSDa databases (but not yet directly accessible), is of great interest for some calculations such as line-mixing effects for instance.

Finally, we are currently working on the analysis of several SiH_4 bands and should be updating SiCaSDa in a near future. We are also

developing a software version that would be able to give K values for symmetrical tops such as CH_3Cl .

CRediT authorship contribution statement

C. Richard: Supervision, Software, Investigation, Data curation.
O. Ben Fathallah: Investigation. **P. Hardy:** Investigation. **R. Kamel:** Investigation. **M. Merkulova:** Investigation. **M. Rotger:** Investigation. **O.N. Ulenikov:** Investigation. **V. Boudon:** Validation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data can be accessed via databases.

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⁴ <https://search-data.ubfc.fr/>

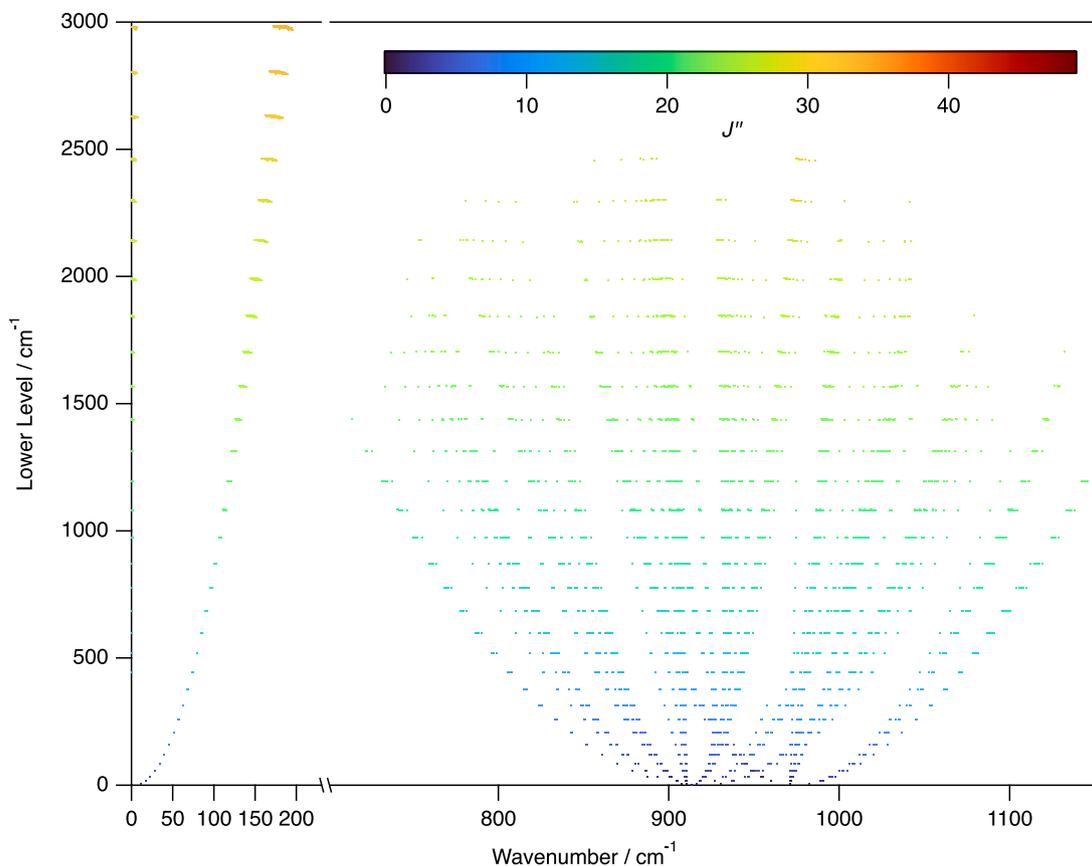


Fig. 10. Representation of the lower level wavenumber for all transitions present in the SiCaSDa database, for the main isotopologue: ²⁸SiH₄. Colors are used to display the lower state rotational quantum number value, J'' .

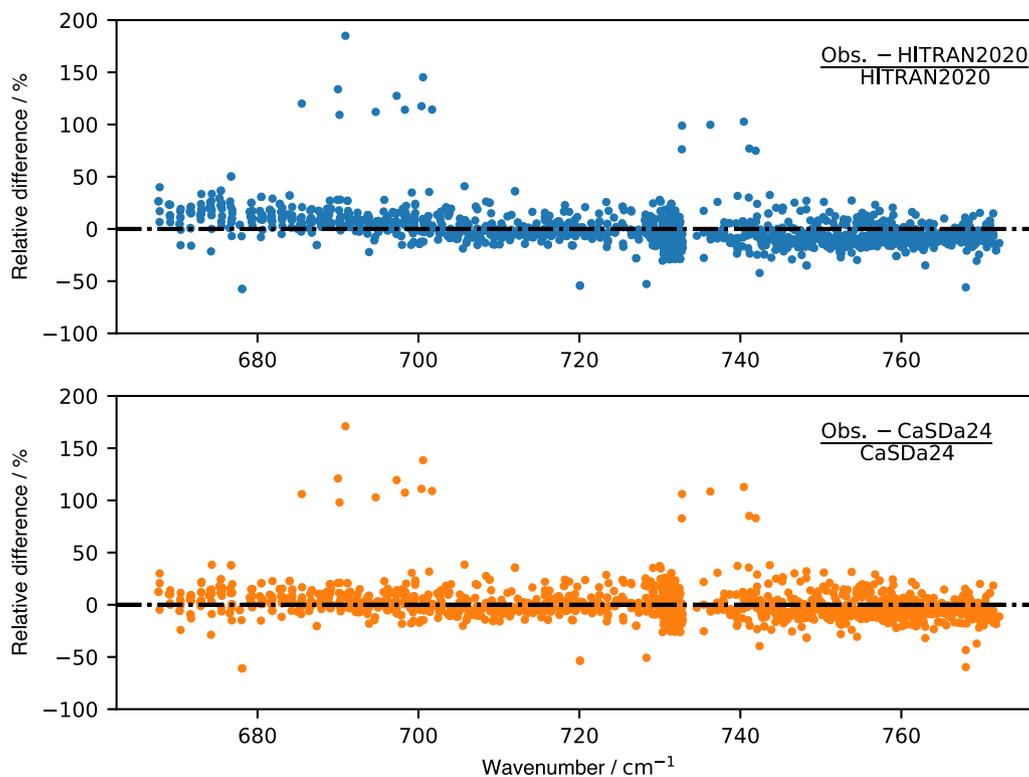


Fig. 11. Comparison between experimental line intensities from [86] and HITRAN2020 (blue) or CaSDa24 (orange) of the ν_3 band of CH₃³⁵Cl.

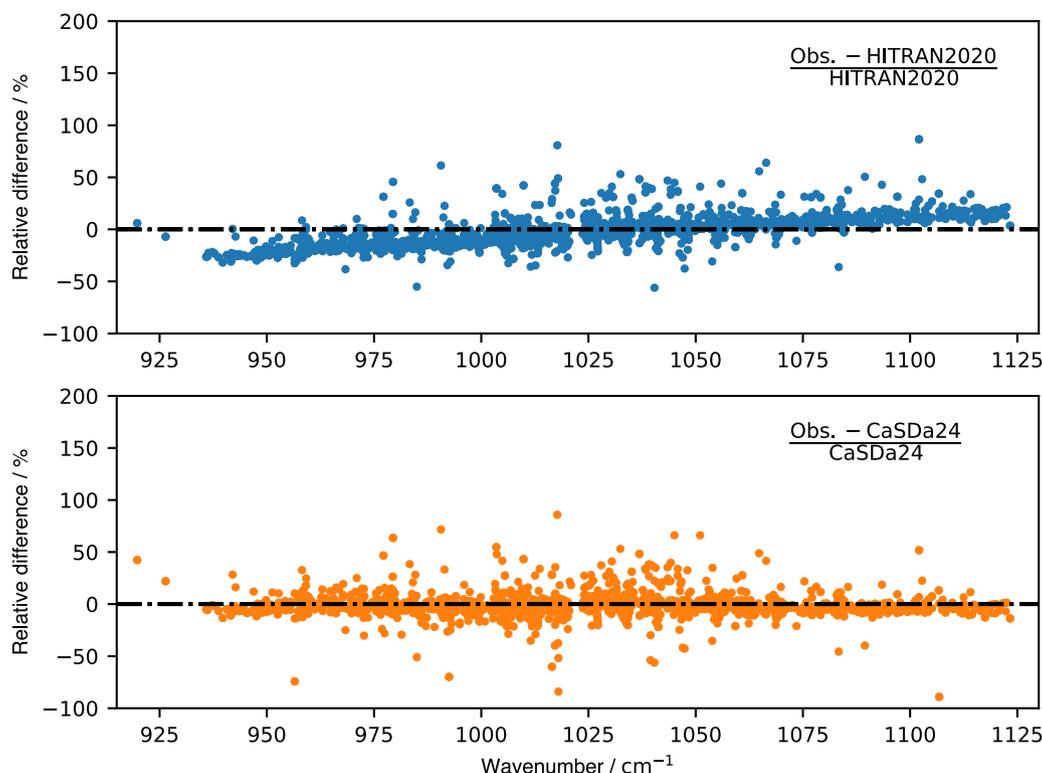


Fig. 12. Comparison between experimental line intensities from [87] and HITRAN2020 (blue) or CaSDa24 (orange) of the ν_6 band of $\text{CH}_3^{35}\text{Cl}$.

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