

The Cologne Database for Molecular Spectroscopy, CDMS: a useful tool for astronomers and spectroscopists

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Abstract

The general features of the internet browser-accessible Cologne Database for Molecular Spectroscopy (CDMS) and recent developments in the CDMS are described in the present article. The database consists of several parts; among them is a catalog of transition frequencies from the radio-frequency to the far-infrared region covering atomic and molecular species that (may) occur in the interstellar or circumstellar medium or in planetary atmospheres. As of December 2004, 280 species are present in this catalog. The transition frequencies were predicted from fits of experimental data to established Hamiltonian models. We present some examples to demonstrate how the combination of various input data or a compact representation of the Hamiltonian can be beneficial for the prediction of the line frequencies.

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1. Introduction

Spectral features in various frequency regions of the electromagnetic radiation are used to indicate the presence of atomic or molecular species in stellar or planetary atmospheres, including the Earth, or in the interstellar (ISM) or circumstellar medium (CSM). The availability of transition frequencies and intensities with appropriate accuracies is required to identify and quantify the abundance of a certain species unambiguously. Observations are currently performed routinely in the microwave and millimeter wave regions (8–300 GHz). However, in recent years the submillimeter region (300–1000 GHz) has become increasingly important for radio-astronomers, and not only satellite-based, but even ground-based observations in the terahertz region (~ 1 –10 THz), also known as the far-infrared region (~ 30 –300 cm^{-1}), have been performed, see e.g. Refs. [1,2]. The submillimeter and terahertz regions will become more important with the Atacama Pathfinder Experiment (APEX), which is about to start routine

observations, and future missions such as the Stratospheric Observatory For Infrared Astronomy (SOFIA), the HERSCHEL space observatory, and the Atacama Large Millimeter Array (ALMA).

More than 4 years ago, the internet browser-accessible Cologne Database for Molecular Spectroscopy (CDMS) has been created [3]. Its **Catalog** section contains mostly rotational transition frequencies, uncertainties, intensities, and a wealth of other information of atomic and molecular species that may occur in the ISM or CSM or in planetary atmospheres. An important incentive for the creation was that the relevant laboratory data on these molecules is scattered over many journals and very many issues, and the CDMS has the purpose to provide the relevant data to the astronomical community in a standardized way. Generally, emphasis has been put on creating new or updated entries taking into account particularly the submillimeter and terahertz regions. The basic features of this catalog have been described elsewhere [4]. Additional information, so far only provided in conference proceedings [5], will be included in the current article together with recent developments and suggestions for the near future. In Section 2, an update on the **Catalog** section of the CDMS is provided with the subsections *General*, *Entries*,

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and *Search*. Considerations for the choice of new entries will be described, and some suggestions for future laboratory work will be given. The new section **Molecules in space** will be presented briefly in Section 3, while Section 4 will give some information on the **Fitting spectra** section.

2. The Catalog

The **Catalog** section of the CDMS was formerly known as New line predictions section. The basic properties of the *Entries* and the *Search* subsections have been described previously [4]. Considerable background information is available on the internet [3] in the respective subsections and in the *General* subsection described below.

2.1. General

The *General* part provides information on the content and the format of the catalog, remarks on the partition function, and some equations useful for conversions. The catalog contains mostly rotational transition frequencies of atomic and molecular species of astronomical interest. Each entry refers to one atomic or molecular species. Particular emphasis has been put on providing separate entries for isotopomers or for excited vibrational states when appropriate. For diatomics, excited vibrational states are given generally in one entry together with the ground vibrational state. The main reason is that often several vibrational states were treated together in the spectral fits. In addition, vibrational designations are unambiguous for diatomic species. The entries are not restricted to species already observed in the ISM or CSM, but also include molecules that may be found there in the future. Therefore, the catalog can be, and has been used to identify new molecules in space. At present, the catalog covers mostly rotational transitions from the radio-frequency to the terahertz region and lower mid-infrared region, i.e. frequencies lower than ~ 18 THz or ~ 600 cm^{-1} , or wavelengths longer than ~ 16.5 μm . Even though ro-vibrational transitions were used frequently as input data to generate the entries, the ν_2 vibrational spectrum of C_3 is currently the only ro-vibrational entry featured in the CDMS catalog. Further such entries may be included in the near future.

The format of the entries has been described previously [4]. A color-coded version is available in the *General* part of the **Catalog** section. Moreover, the format of the catalog entries is identical to that in the JPL catalog [6]. It may be useful to emphasize the quantum number format in the present contribution because of the many requests concerning their meaning. Up to six quantum numbers are available each for the upper and for the lower state. Exactly two ascii characters are available for each quantum number. This affords a compact description of the quantum numbers. Therefore, half-integer quantum numbers are rounded up; these numbers may be necessary to describe splitting due to

the presense of non-zero electronic or nuclear spins. Capital letters may be used to indicate numbers larger than 9, e.g. A0 and B1 stand for 100 and 111, respectively, while small letters signal numbers smaller than -9 , e.g. a stands for -10 . In the future, additional output options concerning the quantum numbers will be available. For linear or symmetric top molecules, symmetric rotor quantum numbers are commonly used in the following order: N , $\pm K$, ν , F_1, \dots, F_n , F ; unnecessary quantum numbers are generally omitted. N indicates the rotational angular momentum and K is its projection onto the symmetry axis; $N \equiv J$ for species without unpaired electrons; \pm signals the parity; K and the parity are sometimes combined to k ; ν is a state number, usually indicating different vibrational or electronic states; F_1, \dots, F_n are intermediate spin numbers, representing electronic or nuclear spins, and F is the total spin-angular momentum. Note that more than one state number ν may be needed to treat one degenerate vibrational or electronic state. For example, species 040504 is CH_3CCH , $\nu_{10}=1$. This state has been treated together with the ground vibrational state, among others. Thus, state numbers 1 and 2 together represent CH_3CCH , $\nu_{10}=1$. State number 2 is used for levels with $k>0$, whereas state number 1 indicates levels with $k \leq 0$. This information is gathered in the documentation file of the respective species. Redundant spin-numbers are often *not* omitted. Hence, for radicals such as NH_2 , H_2CN , PH_2 , etc. more than six quantum numbers would be needed to describe each level completely. In these cases, the intermediate spins F_1, \dots, F_n are replaced by an aggregate spin number n ; the coding of this aggregate spin number is given in separate files in each case for which links are available in the documentations. In the case of n equivalent nuclei, a symmetric coupling scheme may be employed; see Ref. [7] for cases with $n \geq 3$. For an asymmetric top molecule, the order of the quantum numbers is basically the same. However, the one field $\pm K$ is replaced by two, namely K_a and K_c , the projections of the rotational angular momentum onto the a and c axis, respectively.

The partition function Q is very important for deriving intensities of atomic or molecular lines. Some considerations are available in the *General* part of the CDMS catalog. Its values at selected temperatures are given in the respective documentation files for each entry. Quite recently, the decadic logarithms of these values have been gathered in a separate file for conversion purpose. Only the ground vibrational state has been considered in the calculation of Q for a certain species in many instances because no or very little information is available on low-lying excited vibrational states. If the partition function is calculated by summation over all states, as is generally the case in the CDMS, it is important to take into account states with sufficiently high quantum numbers. At elevated temperatures, which will be found in massive star-forming regions or in circumstellar shells, vibrational contributions to the partition function can be very substantial; see, e.g.

the discussion on HC₃N in the circumstellar shell CRL 618 in Ref. [8] for which a peak rotational temperature of ~520 K was inferred from the analyses of line shapes and intensities. However, it should be kept in mind that the rotational and the vibrational temperature are not necessarily the same. The vibrational energy and the degeneracy of the fundamental state are the most important informations to calculate or estimate vibrational contributions to the partition function. In contrast, changes in the rotational and centrifugal distortion constants of the excited vibrational state with respect to the ground state or effects of anharmonicity for multiply excited states usually cause minor modifications to the vibrational contributions of the partition functions. If these contributions are available in the CDMS for a certain species, this is indicated in the documentation. If the number of vibrational states to be considered is small, the individual contributions usually are given in the documentation, otherwise, a link to a separate file is provided instead.

Spin-statistical weight-ratios have been considered in the calculation of Q in general. However, common factors have been divided off frequently in order to keep Q and g_{up} small. Therefore, it is strongly advisable to look at Q/g_{up} rather than Q when data are compared from different databases. Non-trivial spin-statistical weight ratios are given explicitly in the documentation for a given species. Different ratios are the prime reason for Q values for different isotopomers to be quite dissimilar on occasion; other reasons may be the number of vibrational states considered in the calculation of Q .

In the very cold regions of the ISM it may be important to analyze *ortho* and *para* states separately—in particular for rather light species. The energy of the lowest rotational level is zero by definition, fine and hyperfine structure splitting has to be taken into account if applicable. Since fairly recently, the energy of the lowest level of a different spin-modification is given in the documentation throughout. Separate Q values for the different spin-modifications may be provided in the future.

The final aspects in the *General* part are some equations that may be useful for conversion purposes.

2.2. Entries, general information

The *Catalog Directory* lists all species available in the CDMS catalog. From the left to the right, it gives the six-digit tag, which is the identifying and sorting criterion, the name or formula of the species, the version number, the catalog file in HTML and ASCII format, the documentation for each species, and the date of creation of the current entry version. The catalog file is available separately with transition frequencies and uncertainties in units of cm⁻¹ for selected species. A pdf file containing the documentations will be available soon.

The first three digits of the six-digit tag represent the species' weight in atomic mass units, the fourth is the digit

'5' to avoid conflicts with the JPL catalog, which uses an equivalent scheme, and the last two digits are used for counting species with the same molecular weight.

The user of the catalog is strongly advised to read the documentation to the species of interest. It contains the tag, the name, and the chemical formula of the species and may indicate minor isotopomers or excited vibrational states. Furthermore, it lists the author and version of the entry, sources of the experimental data, special considerations for spin-statistics, fine and hyperfine structure, the partition function, etc. Rotational constants, dipole moment components, values of the partition function at selected temperatures, a comment on whether the species has been observed in the ISM or CSM along with additional information are also included.

The dipole moment components are very important for determining reliable line strengths or intensities. Therefore, we encourage laboratory spectroscopists to determine experimental values more often. Stark effect measurements are commonly employed to determine dipole components. Generally, one tries to resolve the individual Stark components as completely as possible. However, this method is often impracticable for transitions with high quantum numbers, at high frequencies, or for species with weak lines. Müller et al. [9] have described an alternative approach in which only small Stark shifts are measured quite accurately as long as (essentially) all Stark components are well within the absorption feature. Refs. [10,11] present further examples. This method may be less accurate than the more commonly known one, but the achievable accuracy of a few percent is definitely better than having no experimental value at all. Moreover, this accuracy should be sufficient in many instances. In cases with no experimentally determined dipole moment components available, *ab initio* values may be used instead. We encourage theoreticians to provide such data more often.

As of December, 2004, the catalog contains 280 species which are listed in Table 1 together with the tag. A comparison with Refs. [4,5] demonstrates that the catalog is growing rapidly: at the end of January 2001, there were 111 species in the catalog [4], this number has risen to 200 by the end of October 2003 [5]. All species that have been added or updated after January 2001 are indicated with an asterisk after the tag in Table 1.

An entry is created by fitting (essentially) all available rotational data to established Hamiltonian models. Rovibrational or rovibronic transitions may be considered in the fit also. The resulting spectroscopic parameters with their uncertainties together with the variance-covariance matrix is used to generate predictions of the rotational spectrum. For this purpose, it is of utmost importance to have reasonable uncertainties assigned to the experimental transition frequencies. Unfortunately, rather frequently no uncertainties are given at all, or the stated uncertainties appear to be too optimistic or too pessimistic. In other cases, which may be viewed as almost satisfactory, uncertainties

Table 1
Species in the CDMS catalog as of December 2004

Tag ^a	Name ^b	Tag ^a	Name ^b
005501* ⁺	HD ₂ ⁺	051503 ⁺	HC ₃ N, (0002)
012501 ⁺	C-atom	051504 ⁺	HC ₃ N, (0010)
013501 ⁺	¹³ C-atom	051505 ⁺	HC ₃ N, (0011)
013502 ⁺	CH	051506 ⁺	HC ₃ N, (1000)
015501* ⁺	NH	051507 ⁺	HC ₃ N, (1001)
016501* ⁺	NH ₂	051508 ⁺	HC ₃ N, (0100)/ (0003)
016502*	ND	051509	HC ₃ N, (1002)/ (0200) ^{oc}
016503*	CH ₂ D ⁺	051510	KC
017501*	OH ⁺	051511* ⁺	¹³ CCCN
018501* ⁺	NH ₂ D	051512* ⁺	C ¹³ CCN
019501* ⁺	NHD ₂	051513* ⁺	CC ¹³ CN
020501* ⁺	ND ₃	051514*	C ₃ ¹⁵ N
024501	NaH	052501	C ₃ O
025501 ⁺	CCH, $\nu=0$	052502	³⁶ SO
025502*	MgH	052503 ⁺	HC ₃ NH ⁺
025503*	CCH, $\nu_2=1$	052504	KCH
026501 ⁺	CCD	052505*	CaC
026502 ⁺	¹³ CCH	052506*	H ₂ CCHCCH (C ₄ H ₄)
026503 ⁺	C ¹³ CH	052507*	(<i>c</i> -C ₃ H ₂)CH ₂ (C ₄ H ₄)
027501* ⁺	HCN, $\nu=0$	052508* ⁺	DC ₃ N, $\nu=0$
027502 ⁺	HNC, $\nu_2=0, 1$	052509* ⁺	H ¹³ CCCN, $\nu=0$
027503* ⁺	HCN, $\nu_2=1$	052510* ⁺	HC ¹³ CCN, $\nu=0$
028501 ⁺	H ¹³ CN	052511* ⁺	HCC ¹³ CN, $\nu=0$
028502 ⁺	H ₂ CN	052512* ⁺	HCCC ¹⁵ N, $\nu=0$
028503 ⁺	CO, $\nu=0$	053501* ⁺	AiNC
028504* ⁺	HCNH ⁺	053502*	SiCCH
029501 ⁺	¹³ CO	053503*	HC ¹³ C ¹³ CN
029502*	HCND ⁺	053504*	H ¹³ CC ¹³ CN
029503* ⁺	C ¹⁷ O	053505*	AiNC
029504* ⁺	HOC ⁺ , $\nu_2=0$	053506*	HCC ¹³ C ¹⁵ N
029505*	HOC ⁺ , $\nu_2=1$	053507*	<i>a</i> -HC ₃ O
030501* ⁺	H ₂ CO	053508*	H ¹³ C ¹³ CCN
030502* ⁺	C ¹⁸ O	054501* ⁺	SiCN
030503* ⁺	¹³ C ¹⁷ O	054502* ⁺	SiNC
030504* ⁺	H ¹³ CO ⁺	054503*	<i>l</i> -H ₂ C ₃ O
030505* ⁺	HC ¹⁷ O ⁺	054504*	<i>c</i> -H ₂ C ₃ O
030506*	DOC ⁺	056501	HCCP
031501 ⁺	HD ₂ CO	056502* ⁺	CCS
031502 ⁺	¹³ C ¹⁸ O	056503*	ONCN
031503 ⁺	H ₂ ³ CO	058501*	H ₂ C ₂ S
031504 ⁺	H ₂ COH ⁺	058502* ⁺	NaCl, $\nu=0, 1$
031505	CF	058503*	KF, $\nu=0, 1$
031506* ⁺	HC ¹⁸ O ⁺	058504*	NCS
032501*	PH	059501	MgCl
032502 ⁺	D ₂ CO	059502*	CaF
032503 ⁺	H ₂ C ¹⁸ O	060501* ⁺	CH ₂ (OH)CHO
032504** ⁺	CH ₃ OH, $\nu_i=0, 1$	060502* ⁺	Na ³⁷ Cl, $\nu=0, 1$
033501*	PH ₂	061501*	PNO
033502** ⁺	¹³ CH ₃ OH, $\nu_i=0, 1$	062501* ⁺	<i>l</i> -C ₅ H ₂
033503*	NH ₂ OH	062502*	TiN
035501*	NaC	062503*	<i>aGg'</i> -(CH ₂ OH) ₂
036501	NaCH	062504*	<i>Gg'</i> -(CH ₂ OH) ₂
036502* ⁺	C ₃ , ν_2 band	063501* ⁺	<i>l</i> -HC ₄ N
037501* ⁺	C ₃ H, $\nu=0, \nu_4=1, \mu^2\Sigma$	064501 ⁺	<i>l</i> -SiC ₃
038501* ⁺	<i>l</i> -C ₃ H ₂	064502 ⁺	SO ₂ , $\nu=0$

Table 1 (continued)

Tag ^a	Name ^b	Tag ^a	Name ^b
038502*	C ₂ N	064503 ⁺	SO ₂ , $\nu_2=1$
038503*	C ₃ D, $\nu=0, \nu_4=1, \mu^2\Sigma$	064504*	TiO
038504*	¹³ CCCH, $\nu=0, \nu_4=1, \mu^2\Sigma$	064505	<i>l</i> -SiC ₃
038505*	C ¹³ CCH, $\nu=0, \nu_4=1, \mu^2\Sigma$	064506*	CuH
038506*	CC ¹³ CH, $\nu=0, \nu_4=1, \mu^2\Sigma$	064507* ⁺	CH ₃ C ₄ H
039501 ⁺	HCCN	064508*	ScF
039502*	<i>l</i> - ¹³ CCCH ₂	065501 ⁺	³³ SO ₂
039503*	<i>l</i> -C ¹³ CCH ₂	065502	SO ¹⁷ O
039504*	<i>l</i> -CC ¹³ CH ₂	065503* ⁺	CH ₃ C ₃ N
039505*	H ₂ C ₃ H	065504*	ZnH
040501 ⁺	SiC, $\nu=0$	066501 ⁺	³⁴ SO ₂
040502* ⁺	CH ₃ CCH, $\nu=0$	066502 ⁺	SO ¹⁸ O
040503	KH	066503	CaNC
040504*	CH ₃ CCH, $\nu_{10}=1$	066504*	⁶⁵ CuH
040505* ⁺	H ₂ CCN	067501*	⁶⁶ ZnH
040506*	<i>c</i> -C ₃ H ₄	068501	FeC
041501*	CH ₃ CCD	068502	HC ₃ P
041502* ⁺	CH ₂ DCCH	068503* ⁺	C ₃ S
042501* ⁺	H ₂ CCO	069501	NC ₂ P
042502*	NaF, $\nu=0, 1$	069502*	C ¹³ CCS
042503*	NCO	069503*	¹³ CCCS
043501	CP	069504*	⁶⁸ ZnH
043502	<i>c</i> -C ₂ H ₄ NH	070501*	NiC
043503	MgF	070502* ⁺	C ₃ ³⁴ S
043504	C ₂ H ₃ NH ₂	070503*	H ₂ C ₃ S
043505*	H ₂ C ¹³ CO	071501*	CoC
043506*	H ¹³ CCO	074501 ⁺	C ₅ N
043507*	HDCCO	074502* ⁺	<i>l</i> -C ₆ H ₂
044501*	CS, $\nu=0-2$	074503*	<i>aa</i> -(C ₂ H ₅) ₂ O
044502	HCP, $\nu=0$	074504*	NiO
044503	HCP, $\nu_2=1$	074505* ⁺	KCl, $\nu=0, 1$
044504	<i>c</i> -C ₂ H ₄ O	075501*	HC ₄ NC
044505	SiO, $\nu=0-6$	075502*	CaCl
044506* ⁺	<i>s</i> -H ₂ C=CHOH	075503* ⁺	HC ₅ N, $\nu=0$
044507* ⁺	<i>a</i> -H ₂ C=CHOH	075504* ⁺	HC ₅ N, $\nu_{11}=1$
044508*	H ₂ CC ¹⁸ O	075505*	HC ₅ N, $\nu_{11}=2$
044509*	D ₂ CCO	075506* ⁺	HC ₅ N, $\nu_{10}=1$
045501* ⁺	¹³ CS, $\nu=0, 1$	075507*	HC ₅ N, $\nu_{11}=3$
045502* ⁺	C ³³ S, $\nu=0, 1$	075508*	HC ₅ N, $\nu_{11}=4$
045503	DCP	075509*	HC ₅ N, $\nu_9=1$
045504 ⁺	²⁹ SiO, $\nu=0-3$	076501	NC ₃ NC
045505*	H ₂ CP	076502 ⁺	SiC ₄
045506* ⁺	HCS ⁺	076503*	<i>c</i> -C ₆ H ₄
045507*	HCS	076504*	K ³⁷ Cl, $\nu=0, 1$
045508*	HSC	076505*	⁴¹ KCl, $\nu=0, 1$
046501* ⁺	C ³⁴ S, $\nu=0, 1$	076506* ⁺	DC ₅ N
046502 ⁺	³⁰ SiO, $\nu=0-3$	076507* ⁺	H ¹³ CC ₄ N
046503	Si ¹⁸ O, $\nu=0-3$	076508* ⁺	HC ¹³ CC ₃ N
046504*	H ¹³ CS ⁺	076509* ⁺	HC ₂ ¹³ CC ₂ N
046505*	DCS ⁺	076510* ⁺	HC ₃ ¹³ CCN
046506* ⁺	<i>a</i> -HCOOH	076511* ⁺	HC ₄ ¹³ CN
046507*	<i>s</i> -HCOOH	076512*	HC ₅ ¹³ N
046508*	¹³ C ³³ S	080501*	C ₄ S
047501* ⁺	¹³ C ³⁴ S	080502*	ScCl
047502*	HC ³⁴ S ⁺	082501*	Sc ³⁷ Cl
047503*	<i>a</i> -H ¹³ COOH	084501*	FeCO
047504* ⁺	HD ₂ CS	085501* ⁺	C ₇ H
048501 ⁺	SO, $\nu=0$	086501*	<i>l</i> -C ₇ H ₂

(continued on next page)

Table 1 (continued)

Tag ^a	Name ^b	Tag ^a	Name ^b
048502	SO, $\nu=1$	086502*	NiCO
058503* ⁺	C ³⁶ S	087501*	<i>I</i> -HC ₆ N
048504	SO, a ¹ Δ , $\nu=0, 1$	088501	SiC ₅
048505	NaCCH	088502*	CH ₃ C ₆ H
048506*	HPO	089501*	CH ₃ C ₅ N
049501 ⁺	³³ SO	097501 ⁺	C ₈ H
049502 ⁺	S ¹⁷ O	099501* ⁺	HC ₇ N, $\nu=0$
049503 ⁺	C ₄ H, $\nu=0$	099502*	HC ₇ N, $\nu_{15}=1$
049504 ⁺	C ₄ H, $\nu_7=1$	099503*	HC ₇ N, $\nu_{15}=2$
049505 ⁺	C ₄ H, $\nu_7=2^0$	100501	SiC ₆
049506 ⁺	C ₄ H, $\nu_7=2^2$	100502*	DC ₇ N
049507	MgCCH	100503*	H ¹³ CC ₆ N
049508*	¹³ C ³⁶ S	100504*	HC ¹³ CC ₅ N
050501 ⁺	³⁴ SO	100505*	HC ₂ ¹³ CC ₄ N
050502 ⁺	S ¹⁸ O	100506*	HC ₃ ¹³ CC ₃ N
050503* ⁺	<i>I</i> -C ₄ H ₂	100507*	HC ₄ ¹⁴ CC ₂ N
050504 ⁺	MgNC, $\nu=0$	100508*	HC ₅ ¹³ CCN
050505	MgNC, $\nu_2=1$	100509*	HC ₆ ¹³ CN
050506 ⁺	C ₄ D	100510*	HC ₇ ¹⁵ N
050507* ⁺	¹³ CCCCH	109501	C ₉ H
050508* ⁺	C ¹³ CCCH	112501*	CH ₃ C ₈ H
050509* ⁺	CC ¹³ CCH	113501*	CH ₃ C ₇ N
050510* ⁺	CCC ¹³ CH	121501	C ₁₀ H
050511* ⁺	C ₃ N, $\nu=0$	123501* ⁺	HC ₉ N
050512*	C ₃ N, $\nu_5=1$	137501*	CH ₃ C ₉ N
051501 ⁺	HC ₃ N, (0000)	147501* ⁺	HC ₁₁ N
051502 ⁺	HC ₃ N, (0001)	171501*	HC ₁₃ N

^a The six-digit tag consists of the molecular weight in atomic mass units for the first three digits, of a 5, and of two counting numbers to distinguish between entries with the same molecular weight. An asterisk after the tag indicates a new or an updated version with respect to Table 1 in Ref. [4] (January 2001). The second asterisk for two CH₃OH isotopomers signals that $S\mu^2$ is given instead of the intensity *I*. A plus after the tag signals that the species has been detected in the ISM or CSM, uncertain or tentative detections have been omitted; if one entry contains several vibrational states or bands the documentation for the entry will contain information on which of these have been detected.

^b The *I* indicates a linear molecule or a molecule that contains a linear backbone; the *c* indicates a cyclic molecule or a molecule with a cyclic subunit; *s*, *g*, and *a* signal syn, gauche, and anti conformers, respectively. Numbers in parentheses after HC₃N designate the quanta of the lowest four vibrational states ($\nu_4\nu_5\nu_6\nu_7$).

are stated that are reasonable on average, but seem to be both too optimistic and too pessimistic for certain subsets of the data. As a consequence, rather often experimental uncertainties have to be guessed or have to be adjusted—at least in part. Therefore, careful selection and evaluation of the input data are important preconditions for obtaining reliable transition frequencies. Lastly, transitions, which deviate from the calculated ones by several times their uncertainties will be omitted from the final fit in general. There are two important reasons for this procedure. First, wherever available, calculated transition frequencies and uncertainties usually will be overwritten by experimental ones in each entry, see below. Second, even a small number of data with comparatively large residuals may bias spectroscopic parameters, in particular those of highest

order, which generally are determined least significantly. Obviously, this will have an effect on the quality of the predictions.

Each atomic or molecular species, actually, each isotopomer or each vibrational state are given in separate entries—even if several isotopomers or vibrational states have been treated together in a common fit. However, for diatomic species, excited vibrational states will be given together with the ground vibrational state as long as these excited states may be of relevance for astronomical observations. When fine or hyperfine splitting is of relevance for astronomical observations only for part of the transitions, most commonly the general entry will not include this splitting; instead, separate files will contain this information for a selected quantum number or frequency range. Still existing inconsistencies in the catalog are intended to be resolved in the near future.

Each transition is given in exactly one line that contains the transition frequency, its uncertainty, intensity, the degree of freedom in the rotational partition function, the lower state energy, the upper state degeneracy, a flag that indicates whether the line frequency and uncertainty refer to experimental or calculated values, the tag, a code for the format of the quantum numbers, and finally the upper and lower state quantum numbers. Special considerations as well as details on the format and the units are given in the *General* part of the CDMS web page, in the preceding chapter of this article, and in Ref. [4].

In each entry, calculated transition frequencies and uncertainties are overwritten by the experimental values wherever they are available and as long as the experimental uncertainties are deemed to be accurate enough with respect to the other experimental data. The documentation provides information on this matter. Generally, the experimental uncertainties provide a more conservative measure on the accuracy of the predicted transition frequencies. While statistics often may provide calculated line positions that are more accurate than the experimentally determined ones, this cannot be guaranteed *in general*. Moreover, while interpolations may be reliable quite frequently, extrapolations should always be viewed with some caution—even if extrapolations are reasonable to a considerable extent in some instances. Extrapolations should be viewed with particular caution if the input data set is small, if the Hamiltonian converges slowly, e.g. for light hydride species such as H₂O, NH₂, and even more pronounced, CH₂, or for species with large amplitude motions or with vibration–rotation interactions.

The quality of the entry depends quite obviously on the amount and the accuracy of the experimental data. Since reliable information on the accuracy of this data is not always available, the quality of the entry depends also on the critical evaluation of the experimental data. Finally, choosing an adequate Hamiltonian model is a decisive issue, in particular for extensive data sets and for species with a complex spectrum. As a rule of thumb, higher order

spectroscopic parameters not determined significantly are retained in the fit only if their values appear to be of the right order of magnitude. This results in mostly larger predicted uncertainties compared to a fit without these parameters.

2.3. Entries, recent developments and future needs

A review article on methanol maser and dark cloud transitions [12] has emphasized the need for accurate laboratory data in particular in the microwave and lower millimeter wave regions up to about 120 GHz or even somewhat higher. The line widths in these astronomical sources may be around 10^{-6} . Therefore, corresponding laboratory rest frequencies should be known to about 10^{-7} or better. Ref. [12] summarized those CH_3OH transition frequencies previously published or measured newly that are or may be observable in dark clouds or are known to be masing in certain sources. Other examples on recent accurate laboratory measurements are those on CS in the microwave [13] and millimeter wave regions [14]. Further examples are available, e.g. in the recent documentations on HCN, H_2CO , CH_3CCH , or various isotopomers of HC_5N or are intended to be made available in the near future in new or updated documentations for H_2O , HCN, CO, SiS, including many of their isotopic species, or for CH_2 .

On occasion, astronomical observations are used to determine rest frequencies. As an example, the recently published deep line survey of TMC-1 [15] should be mentioned with data on C_3H —among many other species. Of course, the question of the precision and the accuracy of the data is an important issue. The partial resolution of hyperfine structure in astronomical observations of H^{13}CO^+ may serve as an example that even for cationic species transitions of minor isotopic species are observable with very good signal-to-noise [16]. Since this transition is frequently used in studies of molecular clouds associated with the formation of low-mass stars, this observation demonstrates that not only accurate line positions, but also the knowledge of possible hyperfine splitting is important for the analyses of the dynamics in the molecular clouds.

Species for which more or more accurate data are needed include the minor isotopomers of CH, HCO^+ , and N_2H^+ as well as CH^+ and H_2CS and their minor isotopic species—with the possible exception of HDCS.

Even though on average deuterium is about four to five orders of magnitude less abundant in the ISM than hydrogen, it may be significantly enhanced in molecular species occurring in very cold sources or sources that had been very cold until fairly recently because of the much lower zero point vibrational energy of deuterated isotopomers compared to their fully hydrogenated counterparts. Recently, D_2S [17], HD_2^+ [18], D_2CS [19], ND_3 [20,21], and CD_3OH [22], have been detected. As can be seen in Table 1, several deuterated species have been included in the CDMS catalog in the past 3 years.

CH_2D^+ , CHD_2^+ , H_2DO^+ , HD_2O^+ , HDC_3 , and HDC_4 are some of the deuterium-containing species for which more or more accurate data are needed; the isomers with linear carbon backbones are meant in case of the latter two molecules. Also worthwhile mentioning are the asymmetrically deuterated isotopomers of CH_3OH . Because of their rather complex spectra, considerably more data are needed even though several studies have been published. Unfortunately, some of them provide no or only very sparse experimental transition frequencies and reliable uncertainties.

Several of the more complex molecules have been included in the CDMS catalog recently. Ethylene glycol [23] is an example for which the entry led to the detection in the comet Hale-Bopp [24]. There are certainly several alcohols, aldehydes, ethers, esters, amides, cyanides, etc. with two to four carbon atoms for which more or more accurate data are needed.

As a final aspect, several species with rotational transitions within excited vibrational states have been included in the CDMS catalog lately. The recent detections of direct-*l*-type transitions of HCN, $\nu_2=1$ [25], vibrationally excited HNC [26] or $\text{C}_2\text{H}_5\text{CN}$ [27] indicate that in the area of excited vibrational states a lot of new detections can be expected. This will be of importance for APEX, HERSCHEL, and SOFIA, but even more so for telescope arrays such as the Submillimeter Array (SMA) and ALMA which will provide very high spatial resolution. In this context it is worthwhile mentioning that many line surveys, in particular those toward hot-core sources, revealed several unidentified lines (U-lines). An apparent record was set recently with a survey in selected 3 mm windows towards Sagittarius B2 North-Large Molecule Heimat (Sgr B2(N-LMH)) in which more than half of the lines or about 6 per 100 MHz were unidentified [28]. Even though some of these lines may be due to new species or may turn out to be unusual and weak velocity components of known species, it is quite likely that several of these are caused by minor isotopomers or by vibrationally excited states of already identified molecules. It is very useful for the unambiguous identification of new species in the ISM or CSM to reduce the number of unidentified lines.

Rotational spectra within low-lying excited vibrational states of organic molecules with one to four carbon atoms as well as their corresponding ro-vibrational bands need particular attention. The detection of a structured band contour near 174 cm^{-1} in several sources in spectra obtained with the ISO satellite by Cernicharo et al., that has been tentatively assigned to C_4 or C_4H [29], is a particular good example for the need of ro-vibrational spectra in the submillimeter and terahertz regions because existing laboratory data do not permit an unambiguous assignment of this feature. Moreover, with increased sensitivity and resolution available with future missions such as HERSCHEL or SOFIA, many more such features are likely to be revealed.

It is worthwhile mentioning that some of the proposed laboratory work is under way currently but has not yet been submitted for publication.

2.4. Search

A search and conversion form is available to search in the catalog for transition frequencies of selected or all species in a specific frequency region. As the catalog contains a rather large number of transition frequencies already, it is strongly recommended to scan in small frequency windows. Recently, an option has been implemented to search for selected groups of species, e.g. all those that have been detected in the ISM or CSM, or for silicon-containing compounds. It is possible to extend these options to lists of species related to certain selected sources, e.g. Sgr B2(N), the carbon star IRC + 10216, or the proto-planetary nebula CRL 618. Because of extensive work needed to implement this feature we welcome support of radio-astronomers in this field, e.g. by supplying lists of species found in their favorite sources, preferably with some literature references.

Several output options are available in the search and conversion routine. These include graphical output as well as output in text form with several sorting options; an example of a graphical output has been presented previously [4]. By default, the intensity of a transition at 300 K is provided, several other, lower temperatures can be selected. In addition, the Einstein *A*-value can be requested. Several additional output and conversion options are intended to be implemented in the near future. Moreover, resources different from the CDMS catalog, e.g. the JPL catalog [6], may be included in the search and conversion routine at some point.

3. Molecules in space

A new section in the CDMS lists the approximately 120–130 molecules that have been detected in the ISM or CSM, in part with some background information on their detection. Species detected in stellar or planetary atmospheres, comets, or interstellar ices only are not (yet) included. Table 2 presents the status as of December 2004. The exact number depends very much on whether some doubtful or uncertain detections are included. An interesting example is the recent report on the detection of the aldehydes with three carbon atoms, propynal, propenal, and propanal toward Sgr B2(N) [30]. While propynal was detected in the ISM much earlier, and while several lines were observed for propanal, only two lines were detected for propenal. Therefore, the detection of propenal should be viewed with some caution. However, since propanal is suggested to be formed on grain surfaces from propynal by addition of H₂ twice via propenal, the presence of the latter species in the ISM appears to be very plausible.

Rotational diagrams are quite commonly used to establish the presence of a certain species in the ISM and to derive its abundance and excitation temperature. Very recently, Fuchs et al. attempted to detect C₂N toward IRC + 10216 [31]. When they used their putative lines to derive a rotational diagram, they obtained an abundance, excitation temperature, and uncertainties for both that seemed plausible. However, when they synthesized a spectrum from their rotational diagram they should have seen lines in certain frequency regions where there were none. Therefore, C₂N remains to be identified in the ISM or CSM. Moreover, this work has shown that rotational diagrams should be viewed with some caution. More recently, Snyder et al. used similar arguments to cast serious doubt on the reported detection of the amino acid glycine [32].

4. Fitting spectra

4.1. General considerations

Almost all of the fitting and prediction of the spectral features present in the CDMS catalog has been done with Pickett's SPFIT/SPCAT program suite [33]. It is a rather general program written to fit and predict spectra of asymmetric top molecules involving spin- and rotation-vibration interaction. Symmetric top or linear molecules are treated as special cases. Up to 9 spins with $g_1 > 1$ and more than 100 states (e. g. vibrational) can be considered simultaneously. However, because of the very general character and the many options available, its use may be non-trivial for the unexperienced user. Therefore, the **Fitting spectra** section has been an integral part of the CDMS from the start. As a service for the spectroscopic community, it contains various examples on how the programs may be used to solve specific problems; several of these examples include detailed documentations or will so in the near future.

Simple examples include CO, CO⁺ (²Σ), HNC, FeCO (³Σ), C₆ (³Σ), TiO (³Δ) as diatomic or linear molecules, CH₃CCH (propyne) as a symmetric top, and protonated formaldehyde and DS₂ as asymmetric tops; some of these do not have any unpaired electron while others have. Several examples demonstrate the use of ro-vibrational and rotational data simultaneously in a straightforward manner. If the spectroscopic parameters are defined in units of megahertz, the transition frequencies can be both in megahertz and in reciprocal centimeters. Examples with vibration-rotation interaction are CH₃CCH, HD₂⁺, *aGg'* ethylene glycol, and C₃H; the latter is documented in detail on the web and is discussed also below. The *aGg'* ethylene glycol conformer is also one of the examples that involve large amplitude tunneling between two equivalent positions. An example how Dunham type fits may be performed even in the presence of extensive hyperfine splitting is shown by means of the IF molecule. In this and similar cases

Table 2
Molecules^a detected in the interstellar or circumstellar medium

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	> 12 atoms
H ₂	C ₃ *	<i>c</i> -C ₃ H	C ₅ *	C ₅ H	C ₆ H	CH ₃ C ₃ N	CH ₃ C ₄ H	CH ₃ C ₅ N (?)	HC ₉ N	C ₆ H ₆ * (?)	HC ₁₁ N
AlF	C ₂ H	<i>l</i> -C ₃ H	C ₄ H	<i>l</i> -H ₂ C ₄	CH ₂ CHCN	HCOOCH ₃	CH ₃ CH ₂ CN	(CH ₃) ₂ CO			
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄ *	CH ₃ C ₂ H	CH ₃ COOH	(CH ₃) ₂ O	(CH ₂ OH) ₂ (?)			
C ₂ **	C ₂ S	C ₃ O	<i>l</i> -C ₃ H ₂	CH ₃ CN	HC ₅ N	C ₇ H	CH ₃ CH ₂ OH	H ₂ NCH ₂ COOH, Glycine?			
CH	CH ₂	C ₃ S	<i>c</i> -C ₃ H ₂	CH ₃ NC	CH ₃ CHO	H ₂ C ₆	HC ₇ N	CH ₃ CH ₂ CHO			
CH ⁺	HCN	C ₂ H ₂ *	CH ₂ CN	CH ₃ OH	CH ₃ NH ₂	CH ₂ OHCHO	C ₈ H				
CN	HCO	NH ₃	CH ₄ *	CH ₃ SH	<i>c</i> -C ₂ H ₄ O	<i>l</i> -HC ₆ H* (?)					
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	H ₂ CCHOH	CH ₂ CHCHO (?)					
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO							
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO							
SiC	H ₂ O	HNCS	H ₂ CNH	C ₃ N							
HCl	HOCO ⁺	HOCO ⁺	H ₂ C ₂ O	<i>l</i> -HC ₄ H* (?)							
KCl	HNC	H ₂ CO	H ₂ NCN	<i>l</i> -HC ₄ N							
NH	HNO	H ₂ CN	HNC ₃								
NO	MgCN	H ₂ CS	SiH ₄ *								
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺								
NaCl	N ₂ H ⁺	<i>c</i> -SiC ₃									
OH	N ₂ O	CH ₃ *									
PN	NaCN										
SO	OCS										
SO ⁺	SO ₂										
SiN	<i>c</i> -SiC ₂										
SiO	CO ₂ *										
SiS	NH ₂										
CS	H ₃ ⁺ *										
HF	H ₂ D ⁺ , HD ₂ ⁺										
SH*	SiCN										
HD	AlNC										
FeO?	SiNC										
O ₂ ?											

^a All species were detected by radio-astronomy except molecules marked with one or two asterisks which were detected by means of their ro-vibrational or rovibronic spectrum. Entries with a question mark are tentative or questionable detections—some are presented as detections in the literature. Entries with a question mark in parentheses are likely detections viewed as tentative ones because of the small number of (unambiguous) lines—some are presented as detections in the literature. In some instances detections are viewed as secure in spite of a small number of lines; available documentations give further details. The *l* indicates a linear molecule or a molecule that contains a linear backbone; the *c* indicates a cyclic molecule or a molecule with a cyclic sub-unit.

the spectroscopic parameters for various vibrational states (and isotopomers) are locked together according to certain ratios. Similarly, five KCl isotopomers were fit simultaneously to determine isotope-invariant parameters plus Born-Oppenheimer breakdown terms. OH⁺, BrF, and CS are additional examples that are described briefly below. The effects of off-diagonal quadrupole coupling were demonstrated in detail for SOCl₂. In addition, the options of coupling two spin-angular momenta to the rotational angular momentum parallel ($\mathbf{I}_1 + \mathbf{I}_2 = \mathbf{I}$, $\mathbf{J} + \mathbf{I} = \mathbf{F}$) or sequentially ($\mathbf{J} + \mathbf{I}_1 = \mathbf{F}_1$, $\mathbf{F}_1 + \mathbf{I}_2 = \mathbf{F}$) are discussed. While the sequential coupling scheme may be employed always, only two arbitrary spins or up to six equivalent spins may be coupled in parallel [7]. Finally, FCIO₃ is one of several examples to demonstrate how several (here: three) states may be defined to fit various degrees of hyperfine splitting for transitions within the ground vibrational state. Many other examples are available on the web on these and other aspects.

Among the many interesting features available in the SPFIT/SPCAT program suite, it should be mentioned that overlapping lines are treated as (intensity-) weighted averages, provided the overlapping lines appear immediately one after the other in the line list. Alternative formulations of the Hamiltonian, so-called Euler series, are available for spectra where the conventional Watson-type Hamiltonian converges very slowly or even diverges. Currently, work is under way in Cologne on isotopomers of H₂O, on NH₂, and on CH₂, and some of the results will be added to this section.

4.2. Selected examples

4.2.1. Oxoniumylidene, OH⁺

Even though the SPFIT/SPCAT program suite is a rather general one, the input transition frequencies are limited to field free data. Frequencies determined in the presence of an electric or magnetic field cannot be used. As a result, data obtained by laser-magnetic resonance (LMR) for some short-lived radicals cannot be used properly in the fitting procedure. Nevertheless, in many cases sufficient field-free data is available to permit the prediction of the rotational spectrum with reasonable accuracy as will be demonstrated for the ³Σ⁻ radical OH⁺. The *N*=1–0 hyperfine components of the ground vibrational state were recorded near 1 THz by Bekooy et al. with an accuracy of about 1 MHz [34]. The *N*=13–12 transition [35] and the ro-vibrational spectrum up to *v*=5–4 [36] were recorded in the laboratory of Oka. For the high *N* transition, an uncertainty of 0.003 cm⁻¹ was stated [35]; the same uncertainty was used for all ro-vibrational transitions except for the *v*=5–4 for which 0.010 cm⁻¹ was used because of the small signal-to-noise ratio and the large residuals. Transitions with residuals exceeding three times the ascribed uncertainty by a considerable amount were omitted from the final fit.

The ro-vibrational part of the energy levels was represented by:

$$E(v, J) = \sum_{ij} Y_{ij} (v + 1/2)^i J^j (J + 1)^j \quad (1)$$

were the *Y_{ij}* are the customary Dunham parameters. This representation of the data is fairly compact and can be implemented in a fit straightforwardly. The rotational and vibrational dependences of the fine structure spin–spin and spin–rotation coupling parameters λ and γ, respectively, were expressed accordingly. Hyperfine splitting was resolved for the 1–0 ground vibrational transition only, therefore, no rotational or vibrational correction terms could be determined for the scalar and tensorial electron spin–nuclear spin coupling parameters *b_F* and *c*, respectively. The resulting spectroscopic parameters are gathered in Table 3; some were not or just barely determined significantly. Since their magnitudes appeared to be reasonable they were retained in the fit in order to obtain more conservative uncertainties for the predicted transition frequencies. The present parameters compare very favorably with those in Refs. [34,36]. However, the combination of rather accurate data [34] with a very extensive data set [36] yields greatly improved values for *Y₀₁*, *Y₀₂*, and the corresponding lowest order fine structure parameters despite the greater number of parameters determined with respect to Ref. [36]. As a consequence, the predicted uncertainties for the strongest fine and hyperfine components of the *N*=2–1 and 3–2 transitions near 2 and 3 THz are less than 2 and 3 MHz, respectively. It is, of course, advisable to take these

Table 3
Spectroscopic parameters of OH⁺

Parameter	Value ^a (MHz)	Value ^a (cm ⁻¹)
<i>Y₁₀</i> ≈ ω _e	93.514781 (80) × 10 ⁶	3119.3173 (27)
<i>Y₂₀</i> ≈ -ω _e x _e	-2.493092 (58) × 10 ⁶	-83.1606 (19)
<i>Y₃₀</i> ≈ ω _e y _e	31.03593 (166) × 10 ³	1.03525 (55)
<i>Y₄₀</i> ≈ -ω _e z _e	-23.83 (162)	-0.000795 (54)
<i>Y₀₁</i> ≈ <i>B_e</i>	503486.86 (70)	16.794514 (23)
<i>Y₁₁</i> ≈ -α _e	-22435.87 (151)	-0.748380 (50)
<i>Y₂₁</i>	308.28 (55)	0.010283 (18)
<i>Y₃₁</i>	-1.434 (61)	-0.000048 (2)
<i>Y₀₂</i> ≈ - <i>D_e</i>	-58.3607 (128)	-1946.70 (42) × 10 ⁻⁶
<i>Y₁₂</i>	1.4649 (105)	48.87 (35) × 10 ⁻⁶
<i>Y₂₂</i>	7.03 (192) × 10 ⁻³	0.23 (6) × 10 ⁻⁶
<i>Y₀₃</i> ≈ <i>H_e</i>	4.184 (57) × 10 ⁻³	139.6 (19) × 10 ⁻⁹
<i>Y₁₃</i>	-173.3 (288) × 10 ⁻⁶	-5.78 (96) × 10 ⁻⁹
λ ₀₀ ≈ λ _e	64413.2 (38)	2.14859 (13)
λ ₁₀	-340.2 (79)	-0.01135 (26)
λ ₀₁ ≈ λ _D	0.75 (59)	25 (20) × 10 ⁻⁶
γ ₀₀ ≈ γ _e	-4604.23 (108)	-0.153581 (36)
γ ₁₀	142.58 (220)	0.004756 (73)
γ ₂₀	-2.14 (52)	-0.000071 (17)
γ ₀₁ ≈ γ _D	0.789 (36)	26.3 (12) × 10 ⁻⁶
<i>b_F</i>	-74.78 (54)	-0.002494 (18)
<i>C</i>	125.48 (94)	0.004185 (31)

^a Numbers in parentheses are one standard deviation in units of the least significant figures.

predictions with a grain of salt. Nevertheless, it is conceivable that the strongest components of the low- N transitions will be found within three to ten times the predicted uncertainties.

4.2.2. Propynylidyne, $l\text{-C}_3\text{H}$

The linear isomer of the C_3H radical has a regular ${}^2\Pi$ ground state, i.e. the ${}^2\Pi_{1/2}$ spin-state is lower in energy than the ${}^2\Pi_{3/2}$ spin-state, and the spin-orbit parameter A_{SO} is positive. Gottlieb et al. presented a combined study of laboratory data between 80 and 195 GHz and data from astronomical observations near 32.6 GHz [37]. Yamamoto et al. [38] extended these measurements up to 360 GHz and recorded transitions for the lowest ${}^2\Sigma^u$ component of the $\nu_4=1$ CCH bending state which was shifted by strong Renner–Teller interaction from $\sim 600\text{ cm}^{-1}$ to less than 30 cm^{-1} above the lowest rotational level of the ground vibrational state. Moreover, by introducing in the fit Coriolis coupling between the ground and the excited bending state, they were able to use a much smaller set of lambda-doubling parameters: three instead of five despite a larger data set. Very recently, more and greatly improved transition frequencies were obtained near 32.6 GHz through radio-astronomical observations [15]. In the present fit, 30 kHz uncertainty were assumed for the laboratory data because of small residuals in the fits even though 50 kHz were stated in Ref. [37]. Uncertainties of 2 kHz for the frequencies from Ref. [15] appeared to be appropriate by comparison with other observed, very accurately known transition frequencies. In keeping with Ref. [38], the rotational part of the ${}^2\Pi$ ground vibrational state was expressed as

$$E(N) = B[N^2(N+1)^2 - 1] + D[N^2(N+1)^2 - 1]^2 \quad (2a)$$

as is often done for linear molecules in a Π state instead of the more common expression

$$E(N) = BN^2(N+1)^2 + DN^4(N+1)^4 \quad (2b)$$

The resulting spectroscopic parameters are given in Table 4. They are in very good agreement with the previous ones [38]. The very accurate astronomical data greatly improved b_{F} and c for the ground vibrational state, and even more so p and d . The remaining parameters are also somewhat more certain, resulting in correspondingly better predictions. It should be kept in mind that predictions for the ro-vibrational transitions between the ${}^2\Pi$ ground state and the ${}^2\Sigma^u$ excited state are still very uncertain as are the pure rotational transitions that are heavily perturbed by the interaction between the two states.

4.2.3. Bromine monofluoride, BrF

One of the advantages of the SPFIT/SPCAT program suite is that the uncertainties are treated as absolute ones rather than as relative ones. Therefore, the uncertainties of the spectroscopic parameters are *not* normalized to a reduced standard deviation of 1.0. Of course, *ideally*, the reduced

Table 4
Spectroscopic parameters^a of propynylidyne, C_3H

Parameter	$\nu=0$ (${}^2\Pi_r$)
B/MHz	11189.048 (19)
D/kHz	5.1360 (21)
A_{SO}/GHz	432.829 (11)
γ/MHz	-48.40 (48)
p/MHz	-7.0776 (34)
p_{D}/kHz	1.46 (30)
q/MHz	-13.062 (26)
a/MHz	12.361 (95)
b_{F}/MHz	-13.669 (63)
c/MHz	28.181 (203)
d/MHz	16.2579 (28)
$\nu_4=1$ (${}^2\Sigma^u$)	
B/MHz	11212.773 (38)
D/kHz	5.0061 (35)
γ/MHz	-35.452 (40)
$\gamma_{\text{D}}/\text{kHz}$	1.52 (32)
b_{F}/MHz	1.40 (87)
c/MHz	28.50 (108)
$\Delta E^b/\text{GHz}$	610.11 (48)
Interaction term	
G_c^c	-2445.2 (97)

^a Numbers in parentheses are one standard deviation in units of the least significant figures.

^b Energy difference with respect to the average ${}^2\Pi$ state, equals $20.351(16)\text{ cm}^{-1}$; the energy difference between the lowest rotational state of $\nu_4=1$ and the lowest ${}^2\Pi_{1/2}$ rotational state is $27.200(17)\text{ cm}^{-1}$.

^c $G_c=2\beta$. The sign of G_c is not determinable from the fit; we follow the choice from Ref. [38]. However, its sign relative to that of the permanent dipole moment does matter for some very heavily perturbed transitions.

standard deviation of the fit should be 1.0. However, there are several ways to justify very different values. For example, possible systematic errors or a small set of transition frequencies with respect to the number of parameters to be determined may afford values much smaller than 1.0; on the other hand, a spectroscopic term missing in the Hamiltonian easily can result in a value much greater than 1.0. In the **Fitting spectra** section of the CDMS, the effects are demonstrated for CO.

As another example, Müller and Gerry encountered in their work on BrF and IF the problem of having to determine six spectroscopic parameters from six or seven transition frequencies [39]. By constraining the spin–spin coupling constants S and J , they were able to reduce the number of determinable parameters slightly. Nevertheless, because of the still large number of parameters, the reduced standard deviations were between 0.1 and 0.33 for the three different fits. Multiplying the uncertainties with these values would be equivalent to correspondingly smaller uncertainties for the transition frequencies. However, the present fit, which involves considerably more constraints and input data, demonstrates that the estimates of the experimental uncertainties (0.5 kHz mostly) were not too pessimistic, but rather appropriate.

Besides these transitions, the present fit employs microwave and millimeter wave data up to $v=3$ and $J=13$ with uncertainties of 100 and 50 kHz [40,41], respectively, as well as ro-vibrational data up to $v=2-1$ [42,43].

According to Watson [44], several isotopic species of a diatomic molecule AB can be fit together by constraining the Y_{ij} to

$$Y_{ij} = U_{ij} \left(1 + \frac{m_e \Delta_{ij}^A}{M_A} + \frac{m_e \Delta_{ij}^B}{M_B} \right) \mu^{-(i+2j)/2} \quad (3)$$

where U_{ij} is isotope invariant, m_e is the mass of the electron, μ is the reduced mass of AB, M_A is the mass of A, and Δ_{ij}^A is a Born-Oppenheimer breakdown term. In the present case, there are two stable isotopes available for bromine, ^{79}Br and ^{81}Br , with almost equal abundance, but only one for fluorine, namely ^{19}F .

For the hyperfine constants of BrF one has to consider

$$eQq_{ij} \propto Q(\text{Br})\mu^{-(i+2j)/2} \quad (4a)$$

$$C_{ij}(\text{Br}) \propto g_N(\text{Br})\mu^{-(i+2j+2)/2} \quad (4b)$$

$$C_{ij}(\text{F}) \propto \mu^{-(i+2j+2)/2} \quad (4c)$$

$$X_{ij} \propto g_N(\text{Br})\mu^{-(i+2j)/2} \quad (4d)$$

where eQq is the Br nuclear quadrupole coupling constant, Q the nuclear quadrupole moment, C is a nuclear spin-rotation coupling constant, $g_N(\text{Br})$ the Br nuclear magnetic moment, and X stands for the tensorial and scalar nuclear spin-nuclear spin coupling constants S and J , respectively.

The resulting spectroscopic parameters are gathered in Table 5. The Born-Oppenheimer breakdown term Δ_{01}^{Br} has been determined for the first time. Its value of -1.219 ± 0.056 agrees very well with -1.124 ± 0.048 determined recently for BrO [45]. Since fluorine has only one stable isotope, its corresponding value could not be determined. Judged by $\Delta_{01}^{\text{O}} = -1.9630 \pm 0.0039$ for BrO [45], one may expect the true U_{01}/μ to be larger by about 0.5–1.0 MHz than the value given in Table 5. The value of Δ_{10}^{Br} is not determined significantly, but it is of the right order of magnitude.

As the accuracy of the microwave data from Ref. [39] is very high, the two quadrupole coupling constants of ^{79}Br and ^{81}Br were fit independently. The isotopic ratio of 1.1970464 (26) is slightly smaller than the previous value of 1.1970514 (32) [39], but almost three times the combined error smaller than the atomic value of 1.1970568 (15) [46]. On the other hand, the fractional deviation is -8.7×10^{-6} , essentially the same as the contribution of the respective Born-Oppenheimer breakdown term to U_{01}/μ , which is -8.5×10^{-6} . Therefore, it is reasonable to assume that at least part of the deviation of the present quadrupole coupling ratio from the atomic one is due to the breakdown of the Born-Oppenheimer approximation in BrF.

Table 5
Spectroscopic parameters^a of bromine monofluoride, BrF

Parameter	Value
$U_{10}\mu^{-1/2b}$	20083468 (280)
$U_{10}\mu^{-1/2}\Delta_{10}^{\text{Br}}m_e/M_{\text{Br}}$	-345 (283)
$\Delta_{10}^{\text{Br}c}$	-2.40 (197)
Y_{20}	-113889.2 (36)
$U_{01}\mu^{-1b}$	10667.5358 (44)
$U_{01}\mu^{-1}\Delta_{01}^{\text{Br}}m_e/M_{\text{Br}}$	-0.0904 (41)
$\Delta_{01}^{\text{Br}c}$	-1.219 (56)
Y_{11}	-77.8619 (45)
$Y_{21} \times 10^3$	-202.3 (32)
$Y_{31} \times 10^3$	-6.17 (28)
$Y_{02} \times 10^3$	-12.0391 (39)
$Y_{12} \times 10^6$	-54.9 (39)
$Y_{03}^d \times 10^9$	-3.937
$eQq_{00}(^{79}\text{Br})$	1087.36277 (150)
$eQq_{00}(^{81}\text{Br})$	908.37145 (132)
eQq_{10}	-0.94376 (128)
$C_{00}(^{79}\text{Br}) \times 10^3$	88.96 (14)
$C_{10}(^{79}\text{Br}) \times 10^3$	0.46 (13)
$C_{00}(^{19}\text{F}) \times 10^3$	-24.96 (54)
$C_{10}(^{19}\text{F}) \times 10^3$	1.20 (48)
$S_{00} \times 10^3$	-7.116 (173)
$J_{00} \times 10^3$	5.037 (258)

^a Numbers in parentheses are one standard deviation in units of the least significant figures.

^b Excluding effects from Δ_{ij}^{F} ; see text.

^c Derived value, unitless.

^d Kept fixed to calculated value from Ref. [40].

The spin-spin coupling constants have been improved somewhat with respect to the previous results [39] while little has changed for the uncertainties of the spin-rotation constants and their vibrational corrections because of correlation effects. Similar to OH^+ , the much more accurate 1–0 transition frequencies greatly improve the predictions for the transitions with small quantum numbers J and v .

4.2.4. Carbon monosulfide, CS

The CS molecule was subjected to spectroscopic investigations very often. Bogey et al. [47,48] and Ahrens and Winnewisser [49] published millimeter and submillimeter data for many isotopomers and many vibrational states. These data was used in the fit with the stated uncertainties. More recently, Kim and Yamamoto [13] published Fourier transform microwave (FTMW) transitions for several isotopomers and up to $v=39$, but almost entirely confined to the 1–0 transitions. The assumed uncertainties were 2 kHz throughout; the internal consistency for lower vibrational states may be somewhat better. At about the same time, Gottlieb et al. [14] obtained very accurate transition frequencies in the millimeter and lower submillimeter region for the ground vibrational state of the main isotopomer and of C^{34}S . Quite remarkable are the smaller uncertainties and residuals for the latter despite its lower abundance by a factor of ~ 23 . Saturation effects for the main isotopomer could be an explanation. Transitions having residuals exceeding 2.5 times their uncertainties

Table 6
Spectroscopic parameters^a of carbon monosulfide, CS

Parameter	Value
$U_{10}\mu^{-1/2}\times 10^{-6}$	38.527064 (34)
$U_{10}\mu^{-1/2}\Delta_{10}^C m_e/M_C$	1339.6 (203)
$U_{10}\mu^{-1/2}\Delta_{10}^S m_e/M_S$	−436.1 (228)
$\Delta_{10}^{C\ b}$	0.7606 (115)
$\Delta_{10}^{S\ b}$	−0.6598 (346)
$Y_{20}\times 10^{-3}$	−194.94197 (174)
Y_{30}	116.23 (34)
Y_{40}	−0.2376 (208)
$U_{01}\mu^{-1}$	24588.1503 (59)
$U_{01}\mu^{-1}\Delta_{01}^C m_e/M_C$	−2.8589 (55)
$U_{01}\mu^{-1}\Delta_{01}^S m_e/M_S$	−1.01022 (143)
$\Delta_{01}^{C\ b}$	−2.5434 (49)
$\Delta_{01}^{S\ b}$	−2.3945 (34)
$U_{11}\mu^{-3/2}$	−177.45608 (114)
$U_{11}\mu^{-3/2}\Delta_{11}^C m_e/M_C\times 10^3$	21.88 (106)
$U_{11}\mu^{-3/2}\Delta_{11}^S m_e/M_S\times 10^3$	3.00 (36)
$\Delta_{11}^{C\ b}$	−2.697 (130)
$\Delta_{11}^{S\ b}$	−0.985 (118)
$Y_{21}\times 10^3$	−27.467 (126)
$Y_{31}\times 10^6$	−757.5 (194)
$Y_{41}\times 10^6$	−3.79 (146)
$Y_{51}\times 10^9$	−903. (56)
$Y_{61}\times 10^9$	12.60 (108)
$Y_{71}\times 10^{12}$	−213.7 (82)
$U_{02}\mu^{-2}\times 10^3$	−40.0607 (102)
$U_{02}\mu^{-2}\Delta_{02}^C m_e/M_C\times 10^6$	9.1 (104)
$U_{02}\mu^{-2}\Delta_{02}^S m_e/M_S\times 10^6$	7.5 (45)
$\Delta_{02}^{C\ b}$	−4.9 (57)
$\Delta_{02}^{S\ b}$	−11.0 (66)
$Y_{12}\times 10^6$	−38.607 (107)
$Y_{22}\times 10^6$	−1.293 (30)
$Y_{32}\times 10^9$	−5.25 (285)
$Y_{03}\times 10^9$	6.861 (71)
$Y_{13}\times 10^9$	−0.6166 (82)
$eQq_{00}({}^{33}\text{S})$	13.0265 (68)
$eQq_{10}({}^{33}\text{S})$	−0.4007 (39)
$eQq_{20}({}^{33}\text{S})\times 10^3$	2.50 (48)
$C({}^{13}\text{C})\times 10^3$	27.02 (59)
$C({}^{33}\text{S})\times 10^3$	17.98 (25)

^a Numbers in parentheses are one standard deviation in units of the least significant figures.

^b Derived value, unitless.

were omitted from the final fit in general. For two transitions from Ref. [14] the small uncertainties were doubled. Also included in the fit were infrared data from Burkholder et al. [50] and Ram et al. [51]. Uncertainties were generally estimated based on the average residuals. In the course of

the study, we obtained an electronic version of the data from Ref. [51]; the uncertainties of the lower vibrational states were very similar to the ones estimated, though somewhat less uniform. For the highest vibrational states the uncertainties were taken as provided from the file. Finally, $\nu=2-0$ transitions for the main isotopomer [52] were used with estimated uncertainties of 0.0007 cm^{-1} .

The resulting spectroscopic parameters are in Table 6. In contrast to most previous studies, hyperfine parameters were determined simultaneously with the remaining parameters. In addition, for two parameters Born-Oppenheimer breakdown parameters have been determined for the first time, namely for $U_{11}/\mu^{3/2}$ and U_{02}/μ^2 ; however, those for the latter had about the right order of magnitude, but were not significantly determined. Vibrational corrections C_{10} to the nuclear spin–rotation coupling parameters were insignificantly determined and were omitted from the final fit. Their absolute values were about 0.1 kHz, which may be of the right order of magnitude. The correction for $C({}^{13}\text{C})$ was negative while that for $C({}^{33}\text{S})$ was positive. Neglect of these corrections should affect the equilibrium spin–rotation parameters no more than about twice the uncertainties in Table 6. In contrast to Ref. [13], Y_{81} was not included in the final fit because it caused all Y_{n1} with $n\geq 4$ to be insignificantly determined and very different from those in Table 6. Moreover, its inclusion had only a minor effect on the standard deviation of the fit. At any rate, these higher order terms should be viewed with some caution.

The Born-Oppenheimer breakdown terms are a very sensitive probe with regard to the agreement of the presently determined spectroscopic parameters with those from previous ones. Table 7 compares those four terms which have been determined in at least one other study. The agreement is reasonable to good, and the deviations may in part be due to the (necessary) neglect of Δ_{11} in previous works.

The combination of very accurate data from several sources and for many vibrational states and isotopomers with less accurate infrared data extending to higher J yield very accurate predictions even for isotopomers that have not been studied in the laboratory. For transitions in the ground vibrational state below 2 THz, the uncertainties are predicted to be below 0.1 MHz.

The data for all four fits are or will be available in the **Fitting spectra** section of the CDMS.

Table 7
Comparison of CS Born-Oppenheimer breakdown terms Δ_{10} and Δ_{01} ^a with those from previous studies

	This work	Ref. [48]	Ref. [51]	Ref. [49]	Ref. [13]
Δ_{10}^C	+0.7606 (115)	–	+0.7477 (138)	–	–
Δ_{10}^S	−0.6598 (346)	–	−0.7229 (419)	–	–
Δ_{01}^C	−2.5434 (49)	−2.586 (25)	−2.5520 (179)	−2.5055 (53)	−2.4738 (43)
Δ_{01}^S	−2.3945 (34)	−2.525 (64)	−2.6832 (481)	−2.342 (14)	−2.2528 (114)

^a Numbers in parentheses are one standard deviation in units of the least significant figures.

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References

- [1] J. Kawamura, T.R. Hunter, C.-Y.E. Tong, R. Blundell, D.C. Papa, F. Patt, W. Peters, T.L. Wilson, C. Henkel, G. Gol'tsman, E. Gershenzon, *Astron. Astrophys.* 394 (2002) 271–274.
- [2] D.P. Marrone, J. Battat, F. Bensch, R. Blundell, M. Diaz, H. Gibson, T. Hunter, D. Meledin, S. Paine, D.C. Papa, S. Radford, M. Smith, E. Tong, *Astrophys. J.* 612 (2004) 940–945.
- [3] The Cologne Database for Molecular Spectroscopy can be accessed free of charge at <http://www.ph1.uni-koeln.de/vorhersagen/>. An alias is also available: <http://www.cdms.de/>.
- [4] H.S.P. Müller, S. Thorwirth, D.A. Roth, G. Winnewisser, *Astron. Astrophys.* 370 (2001) L49–L52.
- [5] H.S.P. Müller, F. Schlöder, S. Thorwirth, J. Stutzki, G. Winnewisser, in: S. Pfalzner, C. Kramer, C. Straubmeier, A. Heithausen (Eds.), *Proceedings of the Fourth Cologne–Bonn–Zermatt-Symposium 'The Dense Interstellar Medium in Galaxies'*; September 22–26, 2003, Zermatt, Switzerland, Springer, Heidelberg, 2004.
- [6] H.M. Pickett, R.L. Poynter, E.A. Cohen, M.L. Delitsky, J.C. Pearson, H.S.P. Müller, *J. Quant. Spectrosc. Radiat. Transf.* 60 (1998) 883–890.
- [7] H.M. Pickett, *J. Mol. Spectrosc.* 228 (2004) 659–663.
- [8] F. Wyrowski, P. Schilke, S. Thorwirth, K.M. Menten, G. Winnewisser, *Astrophys. J.* 586 (2003) 344–355.
- [9] H.S.P. Müller, E.A. Cohen, D. Christen, *J. Chem. Phys.* 110 (1999) 11865–11875.
- [10] H.S.P. Müller, C.E. Miller, E.A. Cohen, *J. Chem. Phys.* 107 (1997) 8292–8302.
- [11] H.S.P. Müller, E.A. Cohen, *J. Chem. Phys.* 116 (2002) 2407–2416.
- [12] H.S.P. Müller, K. Menten, H. Mäder, *Astron. Astrophys.* 428 (2004) 1019–1026.
- [13] E. Kim, S. Yamamoto, *J. Mol. Spectrosc.* 219 (2003) 296–304.
- [14] C.A. Gottlieb, P.C. Myers, P. Thaddeus, *Astrophys. J.* 588 (2003) 655–661.
- [15] N. Kaifu, M. Ohishi, K. Kawaguchi, S. Saito, S. Yamamoto, T. Miyaji, K. Miyazawa, S.-I. Ishikawa, C. Noumara, S. Harasawa, M. Okuda, H. Suzuki, *Publ. Astron. Soc. Jpn* 56 (2004) 69–173.
- [16] J. Schmid-Burgk, D. Muders, H.S.P. Müller, B. Brubacher-Gatehouse, *Astron. Astrophys.* 419 (2004) 949–964.
- [17] C. Vastel, T.G. Phillips, C. Ceccarelli, J.C. Pearson, *Astrophys. J.* 593 (2003) L97–L100.
- [18] C. Vastel, T.G. Phillips, H. Yoshida, *Astrophys. J.* 606 (2004) L127–L130.
- [19] N. Marcelino, J. Cernicharo, E. Roueff, M. Gerin, R. Mauersberger, *Astrophys. J.*, accepted.
- [20] D.C. Lis, E. Roueff, M. Gerin, T.G. Phillips, L.H. Coudert, F.F.S. van der Tak, P. Schilke, *Astrophys. J.* 571 (2002) L55–L58.
- [21] F.F.S. van der Tak, P. Schilke, H.S.P. Müller, D.C. Lis, T.G. Phillips, M. Gerin, E. Roueff, *Astron. Astrophys.* 388 (2002) L53–L56.
- [22] B. Parise, A. Castets, E. Herbst, E. Caux, C. Ceccarelli, I. Mukhopadhyay, A.G.G.M. Tielens, *Astron. Astrophys.* 416 (2004) 159–163.
- [23] D. Christen, H.S.P. Müller, *Phys. Chem. Chem. Phys.* 5 (2003) 3600–3605.
- [24] J. Crovisier, D. Bockelée-Morvan, N. Biver, P. Colom, D. Despois, D.C. Lis, *Astron. Astrophys.* 418 (2004) L35–L38.
- [25] S. Thorwirth, F. Wyrowski, P. Schilke, K.M. Menten, S. Brünken, H.S.P. Müller, G. Winnewisser, *Astrophys. J.* 586 (2003) 338–343.
- [26] P. Schilke, C. Comito, S. Thorwirth, *Astrophys. J.* 582 (2003) L101–L104.
- [27] D.M. Mehringer, J.C. Pearson, J. Keene, T.G. Phillips, *Astrophys. J.* 608 (2004) 306–313.
- [28] D.N. Friedel, L.E. Snyder, B.E. Turner, A. Remijan, *Astrophys. J.* 600 (2004) 234–253.
- [29] J. Cernicharo, J.R. Goicoechea, Y. Benilan, *Astrophys. J.* 580 (2002) L157–L160.
- [30] J.M. Hollis, P.R. Jewell, F.J. Lovas, A. Remijan, H. Møllendal, *Astrophys. J.* 610 (2004) L21–L24.
- [31] G.W. Fuchs, U. Fuchs, T.F. Giesen, F. Wyrowski, *Astron. Astrophys.* 426 (2004) 517–521.
- [32] L.E. Snyder, F.J. Lovas, J.M. Hollis, D.N. Friedel, P.R. Jewell, A. Remijan, V.V. Ilyushin, E.A. Alekseev, S.F. Dyubko, *Astrophys. J.* 619 (in press).
- [33] H.M. Pickett, *J. Mol. Spectrosc.* 148 (1991) 371–377.
- [34] J.P. Bekooy, P. Verhoeve, W.L. Meerts, A. Dymanus, *J. Chem. Phys.* 82 (1985) 3868–3869.
- [35] D.-L. Liu, W.-C. Ho, T. Oka, *J. Chem. Phys.* 87 (1987) 2442–2446.
- [36] B.D. Rehfuß, M.-F. Jagod, L.-W. Xu, T. Oka, *J. Mol. Spectrosc.* 151 (1992) 59–70.
- [37] C.A. Gottlieb, E.W. Gottlieb, P. Thaddeus, J.M. Vrtilik, *Astrophys. J.* 303 (1986) 446–450.
- [38] S. Yamamoto, S. Saito, H. Suzuki, S. Deguchi, N. Kaifu, S.-I. Ishikawa, M. Ohishi, *Astrophys. J.* 348 (1990) 363–369.
- [39] H.S.P. Müller, M.C.L. Gerry, *J. Chem. Phys.* 103 (1995) 577–583.
- [40] K.P.R. Nair, J. Hoefl, E. Tiemann, *J. Mol. Spectrosc.* 78 (1979) 506–513.
- [41] R.E. Willis Jr., W.W. Clark III, *J. Chem. Phys.* 72 (1980) 4946–4950.
- [42] K. Nakagawa, K. Horiai, T. Konno, H. Uehara, *J. Mol. Spectrosc.* 131 (1988) 233–240.
- [43] H. Birk, *Z. Naturforsch.* 48a (1993) 581–583.
- [44] J.G.K. Watson, *J. Mol. Spectrosc.* 45 (1973) 99–113.
- [45] B.J. Drouin, C.E. Miller, H.S.P. Müller, E.A. Cohen, *J. Mol. Spectrosc.* 205 (2001) 128–138.
- [46] H.H. Brown, J.G. King, *Phys. Rev.* 142 (1966) 53–59.
- [47] M. Bogey, C. Demuynck, J.L. Destombes, *Chem. Phys. Lett.* 81 (1981) 256–260.
- [48] M. Bogey, C. Demuynck, J.L. Destombes, *J. Mol. Spectrosc.* 95 (1982) 35–42.
- [49] V. Ahrens, G. Winnewisser, *Z. Naturforsch.* 54a (1999) 131–136.
- [50] J.B. Burkholder, E.R. Lovejoy, P.D. Hammer, C.J. Howard, *J. Mol. Spectrosc.* 124 (1987) 450–457.
- [51] R.S. Ram, P.F. Bernath, S.P. Davies, *J. Mol. Spectrosc.* 173 (1995) 146–157.
- [52] R.J. Winkel Jr., S.P. Davies, R. Pecyner, J.W. Brault, *Can. J. Phys.* 62 (1984) 1414–1419.