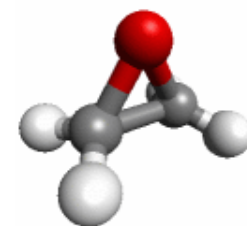


The Cologne Database for Molecular Spectroscopy CDMS

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Brief Description of the Format of the Catalog Entries

Each line in a given catalog entry corresponds to one spectral feature, some of which might be overlapped. The information given for the spectral features is shown below for two lines of H₂C¹⁸O.

Frequency of the line (usually in MHz, can be in cm⁻¹; see below); uncertainty of the line (usually in MHz, can be in cm⁻¹; see below); base 10 logarithm of the integrated intensity at 300 K (in nm²MHz); degree of freedom in the rotational partition function (0 for atoms, 2 for linear molecules, and 3 for non-linear molecules; lower state energy (in cm⁻¹); upper state degeneracy g_{up} ; molecule tag (see below) – a negative value indicates that both line frequency and uncertainty are experimental values; coding of the quantum numbers; and finally the quantum numbers.

```
1872169.0570 0.2000 -1.3865 3 887.6325165 -32503 30327 325 26 324
1872505.7621 0.2374 -2.3388 3 1107.9703 55 32503 30327 622 26 621
```

REMARKS

The line position and its uncertainty are **either** in units of **MHz**, namely if the uncertainty of the line is greater or equal to zero; **or** the units are in **cm⁻¹**, namely if the uncertainty of the line is less or equal to zero !

$$g_{\text{up}} = g_{\text{I}} \times g_{\text{F}};$$

with g_{I} the spin-statistical weight and $g_{\text{F}} = 2F + 1$ the upper state spin-rotational degeneracy.

Note:

Common factors in g_{I} have been divided off frequently. This leads to correspondingly smaller values for the partition function ! See below.

Note:

the degree of freedom in the rotational partition function has been provided because of tradition. It is not needed in any of the calculations or conversions. A linear molecule will only have the value of 2 if exactly 1 value of K or corresponding quantum numbers is permitted (per vibrational state). A molecule with several allowed values of K has an additional degree of freedom and is better considered as a non-linear molecule.

The six digit molecule tag consists of the molecular weight in atomic mass units for the first three digits (here: $2 \times 1 + 12 + 18 = 32$), a 5, and the last two digits are used to differentiate between entries with the same molecular weight.

Note: leading zeros are frequently omitted.

The quantum numbers are given in the following order:

J (or N); K_a and K_c (or $\pm$; K); v ; $F_1 \dots F$

for the upper state followed immediately by those for the lower state (see also below).

- N is the total rotational angular momentum excluding electron and nuclear spins. For singlet molecules, J , the total rotational angular momentum including electron spin, is equal to N .
- K_a and K_c are the projections of N onto the A and C inertial axes, respectively. For symmetric top molecules, only K is needed (instead of K_a and K_c) along with $+$ or $-$, which designate the parity; if redundant, the latter might be omitted. Instead of K , L or I may be used for linear molecules.
- v is a **state number** ! It specifies different vibrational or electronic states. It may also be used to distinguish between different species that have been fit simultaneously. Details on the meaning of the state numbers are given in the documentation !
Note: More than one state number may be needed to designate one vibrational state – this is the case, for example, for a degenerate (e.g. bending) state of a symmetric top molecule !
- $F_1 \dots F$ designate spin quanta. In general, the electron spin S is coupled to the rotational angular momentum first, followed by nuclear spins. In this case $F_1 = J$.

Very Important:

Exactly two characters are available for each quantum number. Therefore, half integer quanta are rounded up ! In addition, upper case characters are used to indicate quantum numbers larger than 99. E. g., A0 is 100, Z9 is 359. Lower case characters are used similarly to signal negative quantum numbers smaller than -9. E. g., a0 is -10, b0 is -20, etc.

Since the program was written for asymmetric top molecules, some of the quantum numbers may be redundant.

Six quantum numbers are available commonly to describe the upper and lower state, respectively. In case more quantum numbers are needed, even if some of them are redundant, the only spin designating quantum numbers are n , F , where n is an [aggregate spin number](#). Please note, however, that more quantum numbers may have been used in some calculations.

Remarks on the Selection Rules and Assignments

Strictly speaking, only the final quantum number F , which includes all effects of rotation etc. as well as electronic and nuclear spins, is a good one; meaning that it has a well-defined an unambiguous meaning. And this holds only in the absence of an electric or magnetic field. Mixing effects mediated by, e. g., vibration-, fine structure- (electronic spin), or hyperfine structure-rotation interaction (nuclear spins) frequently will prevent N , K , v , J , or F_i from being good quantum numbers in general. Of course, in many instances these quantum numbers are reasonably meaningful over a large range of quantum number combinations. Only the selection rule $\Delta F = 0, \pm 1$ holds strictly ! Fine or hyperfine structure effects may cause mixing of levels having different values of N , J , etc., so that $\Delta N = 0, \pm 1$ and $\Delta J = 0, \pm 1$ only hold approximately ! Note: certain hyperfine interactions can cause mixing of *ortho*- and *para*-levels ! E. g. vibration-rotation interaction can cause mixing of different values of K . The strong transitions obey the selection rules $\Delta F = . . . = \Delta J = \Delta N$; for low values of N , other transitions may be comparatively strong.

The projections of the rotational angular momentum onto the a - and c -axes are described by the quantum numbers K_a and K_c . Usually K_c , not K_a , is the more meaningful quantum number for an oblate asymmetric rotor while K_a is more appropriate for a prolate rotor. For that reason, one may find K_p and K_o instead of K_a and K_c , respectively. For rotational levels near the oblate (prolate) limit, i. e. low (high) values of K_a and high (low) values of K_c , it is more useful to use K_c (K_a) as the designated K even if the molecule is a prolate (oblate) rotor !

The ***a*-type** transitions are described by $\Delta K_a = 0 \bmod 2$ and $\Delta K_c = 1 \bmod 2$. Transitions with $\Delta K_a = 0$ are the strongest ones – by far so for a molecule close the the prolate limit, e. g. H₂CO. The ***c*-type** transitions are described analogously: $\Delta K_c = 0 \bmod 2$ and $\Delta K_a = 1 \bmod 2$. Again, transitions with $\Delta K_c = 0$ are the strongest ones – by far so for a molecule close the the oblate limit. Both a - and c -type transitions do not conserve the parity. The ***b*-type** transitions are described by $\Delta K_a = 1 \bmod 2$ and $\Delta K_c = 1 \bmod 2$; these do conserve the parity. And again, transitions with $\Delta K_a = 1$ and $\Delta K_c = 1$ are the strongest ones – by far so for a molecule close the the prolate and oblate limit, respectively. **NOTE:** Mixing effects will cause these selection rules to hold only approximately ! In other words: a molecule with, e. g., only b -type selection rules may have transitions obeying other selection rules in its spectrum in the presence of mixing effects. Moreover, mixing effects may lead to so-called ***x*-type** transitions in the spectrum. These are described by $\Delta K_c = 0 \bmod 2$ and $\Delta K_a = 0 \bmod 2$. Obviously, these transitions are also parity conserving.

The assignment of quantum numbers may seem to be a straightforward issue. While this is true in many simple systems this is **not** the case in general !! Mixing effects are model-dependent, and in extreme cases the assignment of certain levels can be altered based on very small changes in the parameter – even more so if the parameter set is different.

The assignment of, e. g., K quantum numbers is not always unique. To avoid assignment of one quantum number to more than one state, quantum numbers are assigned to levels in the order of increasing ambiguity.

The presence of more than one non-zero spin will cause assignment ambiguities. To minimize these assignment ambiguities, certain rules apply how the various spin-angular momenta are coupled to the rotational angular momentum. Usually, they are coupled in order of decreasing size. **Exception:** one set of equivalent nuclear spin-angular momenta is coupled to the combined spin-rotational angular momentum last. The same applies if two different spin-angular momenta are coupled together before they are coupled to the combined spin-rotational angular momentum. Thus, the electronic spin-angular momentum is usually coupled to the rotation first. **Exception:** if the effects of the nuclear spin-electron spin coupling are larger than the effects caused by the electronic spin alone. This may happen in particular in some radicals with Σ electronic state, e. g. in ¹³CN, the order of the spins is ¹³C, electron, ¹⁴N. Quantum number assignments **always** refer to Hund's case (b). Alternative assignments may be available as non-default in the future.

Comments on the Reliability of the Predictions

The predicted uncertainties of the transition frequencies are model dependent. Therefore, an additional parameter employed in the fit will cause these to increase in general. Basically for the same reason, extrapolations should always be viewed with some caution since these may be affected by spectroscopic parameters that could not be determined thus far. In contrast, interpolations should be reliable in most instances.

If a large number of transition frequencies has been measured and is included in a fit the predicted uncertainties can be much smaller than the experimental uncertainties for a large range of quantum numbers. One should keep in mind that these smaller uncertainties are only meaningful if the experimental uncertainties are caused by purely statistical effects. For that matter, the predictions in the CDMS catalog have experimental transition frequencies and uncertainties nerged into the catalog file to indicate a more conservative means.

Recent catalog entries often contain some estimates as to how far the predictions should be reliable. Here "reliable" means that the transition frequencies should be found within three to ten times the predicted uncertainties.

Remarks on the Partition Function

The partition function Q is very important to calculate intensities of molecular lines at a given temperature. In general, only data for the ground vibrational state have been considered in the calculation of Q for a certain species. If excited vibrational states have been taken into account this will be mentioned in the documentation. Usually, individual contributions of the vibrational states are given in the documentation, too, or a link is given to a separate file containing the information.

Spin-statistical weight-ratios have been considered in most instances. **NOTE:** Common factors have been devided off in order to keep Q and g_{up} small. Therefore, it is strongly advizable to compare Q/g_{up} rather than Q from various databases. Non-trivial spin-statistical weight ratios are given explicately in the documentation of a given species. Spin-statistical weight-ratios are the prime reason for Q values of different isotopomers to be quite different on occasion. Other reasons may be that the number of vibrational states considered differ substantially.

In very cold regions of the ISM it may be important to consider *ortho* and *para* states separately. The energy of the lowest rotational or rotation-hyperfine level is 0 by default. The energy of the lowest level for the other spin-modification(s) is usually given in the documentation. Strictly speaking, one should consider Q values for the different spin-modifications separately – at least at low temperatures. We intend to provide this information in the near future.

Some useful equations

Here are some equations the user of the [CDMS](#) catalog may find helpful. They are taken from SUBMILLIMETER, MILLIMETER, AND MICROWAVE SPECTRAL LINE CATALOG by H. M. Pickett, R. L. Poynter, E. A. Cohen, M. L. Delitsky, J. C. Pearson, and H. S. P. Müller; *J. Quant. Spectrosc. Radiat. Transfer* **60** (1998) 883 – 890.

1. The intensity $I(T)$ is calculated according to
$$I(T) = (8\pi^3/3hc) \nu g_l S_g \mu_g^2 (e^{-E''/kT} - e^{-E'/kT})/Q_{rs}(T)$$
with ν and S_g being the line frequency and strength, respectively, μ_g the dipole moment along the molecular g -axis, E'' and E' the lower and upper state energy, respectively, and Q_{rs} the rotation-spin partition function at the temperature T
2. With $I(T)$ in nm² MHz, ν in MHz, and μ_g in D one obtains
$$I(T) = 4.16231 \times 10^{-5} \nu g_l S_g \mu_g^2 (e^{-E''/kT} - e^{-E'/kT})/Q_{rs}(T)$$
3. Or conversely
$$g_l S_g \mu_g^2 = 2.40251 \times 10^4 I(T) Q_{rs}(T) \nu^{-1} (e^{-E''/kT} - e^{-E'/kT})^{-1}$$

Note: While frequently it is straightforward to calculate S_g from $S_g \mu_g^2$ by deviding through the respective μ_g^2 , this is **not always** correct or applicable, for example in cases of strong vibration rotation interaction. Please note also that initially g_l was missing in several equations simply because $g_l = 1$ was used only initially. The value calculated for $S_g \mu_g^2$ is actually $g_l S_g \mu_g^2$.

4. The intensity in nm² MHz is converted to cm⁻¹/(molecule/cm²) by dividing the catalog intensity by
$$2.99792458 \times 10^{18}$$
5. $A = I(T) \nu^2 (Q_{rs}(T)/g_{up}) (e^{-E''/kT} - e^{-E'/kT})^{-1} \times 2.7964 \times 10^{-16} \text{ s}^{-1}$
6. Combined with **2.** one obtains
$$A = 1.16395 \times 10^{-20} \nu^3 g_l S_g \mu_g^2 / g_{up}$$

Note: Numerical problems may occur in eq. 1, 2, 3 and 5 if the frequency ν is small with respect to the lower state energy E'' . It is advisable to take the following expressions into accout:

7. $e^{-E''/kT} - e^{-E'/kT} = e^{-E''/kT} (1 - e^{-(E' - E'')/kT}) = e^{-E''/kT} (1 - e^{-\nu/kT})$
8. With ν/kT much smaller than 1 one obtains
$$1 - e^{-\nu/kT} \approx \nu/kT$$