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Critical evaluation of measured pure-rotation and rotation-vibration line positions and an experimental dataset of energy levels of $^{12}C^{16}O$ in $X^1\Sigma^+$ state

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ABSTRACT

All available transitions from microwave to visible region (3.8–10 440 cm^{-1}) of the $^{12}C^{16}O$ molecule were collected from the literature and tested using the RITZ computer code. These data have been critically analyzed and used to obtain the most complete and precise set of 2247 experimental energy levels of this molecule covering the 0–67 000 cm^{-1} interval. These levels together with calculated correlation matrix can be used to generate the most precise list of transitions with confidence intervals for astrophysical and atmospheric applications. Comparisons with the HITRAN and GEISA databanks as well as with Goorvitch high-temperature linelist are discussed. A set of corrected HITRAN $^{12}C^{16}O$ transition frequencies together with 99% confidence intervals is presented; it is proposed that this should be employed as a replacement for the current HITRAN database.

1. Introduction

Carbon monoxide is one of the most studied molecules in spectroscopy. During last fifty years the large number of rotation-vibration and pure-rotation line position measurements for $^{12}C^{16}O$ have been performed using different experimental conditions and various techniques including grating, Fourier-transform, Lamb-dip, heterodyne, microwave, and others setups [1–48]. Some data from publications can contain errors caused by improper calibration, presence of foreign gas, pressure shifts, misprints etc. They are not always agreed with each other within experimental accuracies. Up to now most representative set of measured line positions was reported by Coxon and Hajigeorgiou [49], who have collected them from papers [1–22,24–28,30–32,35,38–39,43].

Basic goal of this work is a critical analysis of internal consistency of published data. One reason for such analysis is that there is big difference between calculations based on Dunham coefficients [34] or from the direct potential fit [49] and measurements by Chung et al [46] and Mishra et al [47]. The final result of our study is the most complete and accurate set of $^{12}C^{16}O$ experimental energy levels derived without using any Hamiltonian model. Using this set it is possible to generate a set of transition frequencies free from systematic errors encompassing all vibrational bands. The set can be used also as input data to improve Dunham coefficients [34].

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2. Measured transitions dataset

A set of measured line positions collected form papers [1–33,35–48] was used in our analysis. Most data came from two papers [18,30]. Measured data from [18,30] are available in supplementary data attached to Ref. [49]. In total, a set of 16 307 transitions covering the 3.8–10439.9 cm^{-1} spectral range was collected. Accuracy of the data varies from $1.6\times10^{-8}\,\mathrm{cm}^{-1}$ (500 Hz) [39] to 0.12 cm^{-1} [46]. The highest vibrational band is 41–39 and the highest J value equals to 133 for the 2–1 band. The summary of collected data is given in Tables 1 and 2. Pure rotational data are presented in Table 1. Sources of data are listed in column 1 together with references. Experimental techniques used to measure line positions are given in column 2. Uncertainty of measurements and number of lines N are listed columns 3 and 4. Finally, the extent of measurements is given in columns 5 and 6. Table 2 summarizes rotation-vibration data. Columns 1–3 have the same meaning as for Table 1. Number of lines and extent of measurements for each source are given in columns 5, 7, and 8, respectively. Collected data come from measurements which use different experimental techniques like Microwave (MW), Laser heterodyne (HET), Fourier transform (FT), Cavity ring down (CRD) and others. These data can contain misassigned, badly measured or reported with typos lines. Another issue is possible errors due to improper calibration of some infrared (IR) data or presence in measurements systematic error caused, for instance, by pressure-induced shifts. We shall address all these issues with a method for retrieving experimental energy levels which is presented in the next Section.

3. Method for retrieving experimental energy levels from observed transition frequencies

Transition frequencies are directly observable quantities. On the other hand, energy levels which play an important role in the theoretical modeling and in the creation of calculated linelists are unobservable. Thus, an accurate method for the reduction of observed transition frequencies to energy levels is of major importance in molecular spectroscopy. The relationship between transition frequencies and energy levels of an atom or a molecule is known as a fundamental Rydberg–Ritz combinational principle:

$$\nu_{i\to j}=E_i-E_j \qquad (1)$$

where $\nu_{i\to j}$ is the observed transition frequency, and E_i and E_j are upper and lower energy levels (term values), respectively. The compound quantum number indexes i and j define the spectroscopic assignment of the observed transition frequency $\nu_{i\to j}$. A widely used approach based on this principle is the method of combination differences (CD) [51]. Suppose that we have two transitions with a common upper level $\nu_{i\to j_1}$ and $\nu_{i\to j_2}$, then the difference $\nu_{i\to j_1}-\nu_{i\to j_2}=E_{j_2}-E_{j_1}$ is independent on the upper level. In the same way, pairs of transitions with a common lower level can be used. In a single vibrational band one can take differences between all possible pairs of transitions with

Table 1
Experimental line position data for the $X^1\Sigma^+$ state of $^{12}C^{16}O$ (pure rotational data).

Reference	Type of measurements	Uncertainty (KHz)	N_s	ν_{min} (MHz)	ν_{max} (MHz)	*RMS1*	RMS2 (KHz)
Winnewisser et al., 1997 [39]	Microwave/Lamb dip[a]	0.5	6	115271.2	691473.1	.17	0.08
Belov et al., 1992 [31]	Microwave[a]	1–2	3	230538.0	461040.8	.56	0.7
Mader et al., 1996 [37]	Microwave[a]	2	1	115271.2	115271.2	.08	0.14
Winnewisser et al., 1985 [19]	Microwave[a]	4–47	5	115271.2	576267.9	.51	8.1
Rosenblum et al., 1958 [2]	Microwave[a]	5	1	115271.2	115271.2	.43	2.1
Belov et al., 1995 [35]	Microwave[a]	5	3	345796.0	1267014.5	.46	2.3
Markov et al., 2002 [44]	Microwave	5	1	576267.9	576267.9	.49	2.5
Gendriesch et al., 2009 [48]	Microwave	5–100	21	226340.3	1938177.8	.09	2.9
Varberg et al., 1992 [32]	Tunable FIR[a]	10–43	26	691473.1	4340138.1	.46	5.1
Evenson, 1995 [36]	Tunable FIR	10–43	22	806651.8	4340138.1	.20	2.8
Bogey et al., 1986 [23]	Microwave	20	31	146403.1	220045.2	$<.01$	0.02
George et al., 1994 [34]	Microwave/Lamb dip[a]	18–136	14	61638754.8	63302467.0	.24	13.5
Wappelhorst et al., 1997 [38]	Sub-Doppler IR[a]	20–136	14	61638754.8	63302467.0	.31	15.5
Gordy & Cowan 1957 [1]	Microwave[a]	30	3	115271.2	345795.9	1.64	49.3
George et al., 1991 [29]	Microwave/Lamb dip[a]	50	1	62546358.3	62546358.3	1.66	83.1
Helminger et al., 1970 [5]	Microwave[a]	60	5	345796.0	806651.7	1.03	7.8
Dixon, 1977 [15]	Microwave[a]	40–60	2	113172.4	114221.7	.14	7.8
Nolt et al., 1987 [25]	FIR absorption[a]	72–140	7	576267.9	3890442.9	.84	92
Pollock et al., 1983 [17]	Heterodyne[a]	70–20000	20	123536339.6	130431270.7	.51	2986
Schneider et al., 1989 [26]	CO laser/Lamb dip[a]	300–3500	140	37695777.7	57902072.9	.17	425
Kildal et al., 1974 [11]	CO laser/heterodyne[a]	2100–10800	22	53337831.5	58670841.0	1.49	7331
Hinz et al., 1987 [24]	CO laser/heterodyne[a]	3000	13	37695777.7	40019664.8	.12	348
Wells et al., 1985 [22]	CO laser/heterodyne[a]	3000	8	38498453.1	40170007.5	.09	281
Schneider et al., 1990 [27]	Heterodyne/IR[a]	3000–5000	25	59811747.5	62394555.0	.25	852
Eng et al., 1974 [10]	CO laser/heterodyne[a]	5000	7	56387992.2	58670841.0	.64	3377
Maki et al., 1990 [28]	IR/heterodyne[a]	3000–10000	2	60214084.9	64593150.8	.61	6061
Sokoloff et al., 1970 [6]	Frequency mixing[a]	55000	1	58024341.0	58024341.0	1.10	60329

For each reference listed in the first column we give type of measurements, uncertainty of measurements, number of transitions *Ns*, measurement range ($\nu_{min}-\nu_{max}$), dimensionless RMS1 and RMS2. RMS1 and RMS2 are defined in Section 4.

[a] Type of measurements is taken from Table 1 Ref. [49].