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Chapter 3

Testing the mass-scaling relations in the ($a^3\Pi$) state of $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{16}\text{O}$

Abstract

Electronic spectra of the $a^3\Pi - X^1\Sigma^+$ (0-0) and (1-0) bands of $^{12}\text{C}^{18}\text{O}$, and the (1-0) band of $^{13}\text{C}^{16}\text{O}$ are measured by cavity ring-down spectroscopy in the 200 nm region. The experimental spectra are analyzed using the molecular constants predicted by mass-scaling relations. It is found that the mass-scaling rules for the $a^3\Pi$ state can be used to predict the transition frequencies from $v = 0, J < 8$ in $^{12}\text{C}^{16}\text{O}$ to $v = 1$ and $J < 30$ rovibrational levels in both $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ within the experimental accuracy of 0.2 cm^{-1} .

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3.1 Introduction

The metastable lowest-lying triplet state of CO, $a^3\Pi$, has attracted much interest since the Cameron bands (the spin-forbidden $a^3\Pi - X^1\Sigma^+$ system) were detected in 1926 [42]. Extensive studies on the $a^3\Pi$ state of $^{12}\text{C}^{16}\text{O}$ have been performed in radio-frequency, microwave, infrared, optical and UV studies [10, 43–51]. Also, $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ have been studied using rf, mw and UV spectroscopy [10, 45, 52]. Recently, rotational transitions in metastable CO in its $a^3\Pi$ state have been identified as a sensitive probe to detect a possible time-variation of the proton-to-electron mass ratio, μ , on a laboratory time scale [9].

In our previous work on the UV-frequency metrology on the $a^3\Pi - X^1\Sigma^+$ (0-0) band of CO [10] [Chapter 2], a number of transitions in various isotopologues were measured with an accuracy of 5 MHz. It was found that the transition frequencies in the higher mass isotopologues are well reproduced by scaling

the molecular constants of $^{12}\text{C}^{16}\text{O}$ via the common mass-scaling rules. In this paper, the electronic spectra of the $a^3\Pi - X^1\Sigma^+$ (0-0) and (1-0) bands of $^{12}\text{C}^{18}\text{O}$, and the (1-0) band of $^{13}\text{C}^{16}\text{O}$ have been experimentally recorded for the first time, by cavity ring-down spectroscopy (CRDS) in the 200 nm region. The aim of the present work is to test the common mass-scaling relations specifically in higher rovibrational levels ($v = 1, J \sim 30$) of the $a^3\Pi$ state of CO.

3.2 Experimental setup

The deep-UV spectra of CO are recorded in direct absorption using cavity ring-down spectroscopy (CRDS). Details of the experimental setup have been described in Refs. [75, 76]. Briefly, commercial isotopically-enriched gases (Sigma Aldrich, $^{12}\text{C}^{18}\text{O}$ purity $\sim 95\%$, and $^{13}\text{C}^{16}\text{O}$ purity $\sim 98\%$) are used. A 0.5 micron filter cleans the gas sample from dust and aerosol particles. The gas sample is kept at a stationary pressure of 20 mbar in a 48 cm long gas cell. Tunable deep-UV radiation in the 200 nm region is generated by frequency-tripling the output of a Nd:YAG (532 nm) pumped pulsed dye laser system (Sirah, Cobra Stretch) running near 600 nm at a repetition rate of 10 Hz. The UV light is focused into an optical cavity comprised of two highly reflective mirrors (reflectivity $\sim 99.5\%$ in the 195-210 nm range) mounted via precise alignment tools on opposite sides of the gas cell. The light leaking out of the cavity is detected by a photomultiplier tube (PMT). The PMT signal is subsequently digitized by an oscilloscope (LeCroy 9450, 1 GB sample rate and 350 MHz bandwidth) and the obtained data is analyzed to extract the ring-down time. Typical ring-down times in the present experiment are ~ 200 ns. Ten ring-down times are averaged to reduce the shot-to-shot noise. A full spectrum is obtained by recording the averaged ring-down time as a function of wavelength.

The bandwidth of the UV-radiation after frequency tripling is estimated to be $\sim 0.5 \text{ cm}^{-1}$. Since the laser bandwidth is larger than the Doppler linewidth, estimated to be 0.12 cm^{-1} for CO at room temperature, this may result in non-exponential decay transients of the ring-down signal, and consequently slightly unreliable absorption line intensities in the final experimental spectrum, as discussed by Jongma *et al.* [77]. It is noted that this effect only affects the intensity and does not change absorption line positions. It is relatively small for weak absorptions but may become pronounced in the case of strong absorptions.

The absolute frequency of the fundamental laser is calibrated by recording an iodine absorption spectrum simultaneously with the CRDS signal, using a small fraction ($\sim 5\%$) of the dye laser output split before frequency conversion. Transition frequencies in the CO absorption spectra are obtained by multiplying the dye laser frequency by three. The absolute accuracy of the transition frequencies is estimated to be 0.2 cm^{-1} in the UV-spectrum (for strong and unblended lines it is estimated to be better than 0.1 cm^{-1}).

3.3 Results and discussion

Rotationally resolved spectra of the (0-0) and (1-0) bands of $^{12}\text{C}^{18}\text{O}$, at 206 and 199 nm, respectively, are recorded in this work, where 168 transitions with J values up to 32 are assigned in the (0-0) band, and 158 transitions with J values up to 31 are assigned in the (1-0) band. As an example, the experimental spectrum of the (0-0) band of $^{12}\text{C}^{18}\text{O}$ is shown in the upper trace (black) of Fig. 3.1(a). Fig. 3.1(b) shows a zoomed in region of the spectrum, with the reference I_2 spectrum shown as the lowest trace (blue). As high-precision spectroscopy of the (0-0) band of $^{13}\text{C}^{16}\text{O}$ has been performed by de Nijs *et al.* [10][Chapter 2], in the present work, only the (1-0) band at 199 nm is studied, and 139 transitions with J values up to 28 are assigned.

Using the previously reported molecular constants for the $a^3\Pi$ state of $^{12}\text{C}^{16}\text{O}$ and the mass-scaling model that is described in Section VI.B. of Ref. [10] [Chapter 2], the relevant molecular constants for the $a^3\Pi$ state of $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ are calculated, and listed in the second column (scaled) of Table 3.1. These mass-scaled constants are subsequently used in the analysis of the experimental spectra and for testing the mass-scaling model also for higher rovibrational levels in the $a^3\Pi$ state of CO.

Least-squares fits of the experimental spectra are performed using the Hamiltonian for a $^3\Pi-^1\Sigma$ forbidden transition defined in the PGOPHER software [63]. The accurate molecular constants for the $X^1\Sigma^+$ ground state of both $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ are taken from previous laboratory microwave work [53, 78] and fixed in the fits. The mass-scaled molecular constants for the $a^3\Pi$ state, listed in Table 3.1, are set as initial values in the fits. As noted in Ref. [10][Chapter 2], the values of the band origins, T_0 , depend not only on the reduced mass of the molecule but also exhibit an atom dependent energy shift at the GHz level. Similar shifts were observed in the $\text{C}^1\Sigma^+$ and $\text{E}^1\Pi$ states suggesting the discrepancy originates from the ground state, however, the exact source is not yet understood. This finding is confirmed here, therefore, as the first step of a fit, the value of the band origin is set as free parameter, while all other spectroscopic parameters are fixed at the mass-scaled values. The resulting values of T_0 are listed in Table 3.1. This procedure reproduces the experimental spectra well. The standard deviations of the observed-calculated line positions for all three bands are $\sim 0.2 \text{ cm}^{-1}$, of the order of the estimated accuracy for the measured line positions, and shows no increase for higher J values.

To further confirm the validity of the mass-scaling model, fits with the inclusion of T_0 , B , D , A , o , and p as free parameters are performed. Because a fit including the higher-order molecular constants, A_D , γ , λ , and q , results in standard errors much larger than their values these constants are kept fixed at the mass-scaled values. The resulting molecular constants for the $a^3\Pi$ state are shown in the third column (fitted) of Table 3.1. A simulated spectrum of the (0-0) band of $^{12}\text{C}^{18}\text{O}$, using the fitted molecular constants for the $a^3\Pi$ state and a rotational temperature of 300 K, is shown in the lower, red, trace of Fig. 3.1(a). Fig. 3.1(b) shows a zoomed-in region, with $J > 20$, of both experimental and

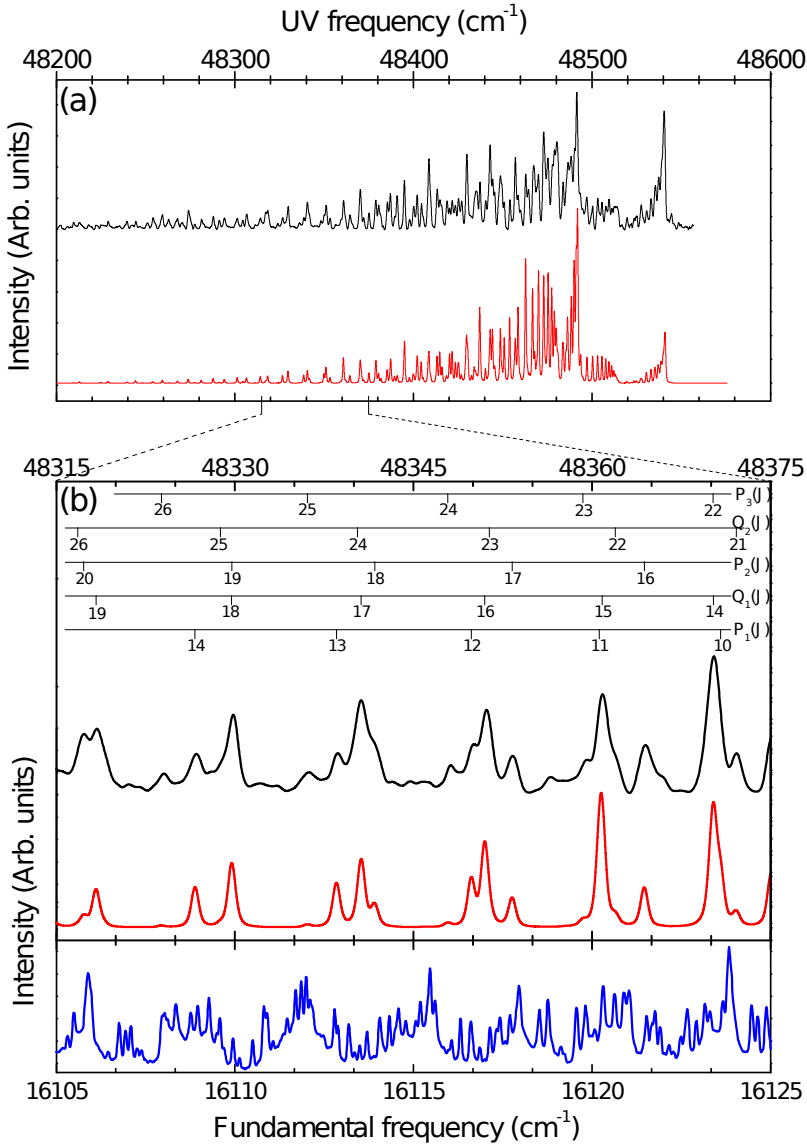


Figure 3.1: In panel (a), the measured, upper trace (black), and simulated, lower trace (red), spectrum of the 0-0 band of the a -X system of $^{12}\text{C}^{18}\text{O}$ are shown. For the simulated spectrum, calculated using PGOPHER [63], the fitted constants found in Table 3.1 and a temperature of 300 K were used. In panel (b), a zoomed in section of the measured and simulated spectra are shown, including the I_2 reference spectrum as the lowest trace (blue). The transitions shown in panel (b) correspond to rotational quantum numbers of $J \sim 20 - 25$.

	Molecular Constant	Scaled (MHz)	Fitted (MHz)
$^{12}\text{C}^{18}\text{O}, v = 0$			
T_0		$1.4533039(5)\cdot 10^9$	$1.4533033(10)\cdot 10^9$
B		48015.57	48018(6)
D		0.1740	0.176(8)
A		1242822	$1.2421(9)\cdot 10^6$
A_D		-10.92	-10.92 ^f
λ		808.40	808.40 ^f
γ		-74.077	-74.077 ^f
o		26044	$2.44(12)\cdot 10^4$
p		148.2	$1.2(6)\cdot 10^2$
q		1.524	1.524 ^f
$^{12}\text{C}^{18}\text{O}, v = 1$			
T_0		$1.5034867(5)\cdot 10^9$	$1.5034874(11)\cdot 10^9$
B		47485.49	47474(7)
D		0.1788	0.160(9)
A		1237759	$1.2361(10)\cdot 10^6$
A_D		-10.92	-10.92 ^f
λ		818.07	818.07 ^f
γ		-71.83	-71.83 ^f
o		25897.3	$2.73(14)\cdot 10^4$
p		143.7	$2.2(8)\cdot 10^2$
q		1.512	1.512 ^f
$^{13}\text{C}^{16}\text{O}, v = 1$			
T_0		$1.5035732(5)\cdot 10^9$	$1.5035727(10)\cdot 10^9$
B		47665.72	47668(9)
D		0.1802	0.181(15)
A		1237743	$1.2393(8)\cdot 10^6$
A_D		-10.96	-10.96 ^f
λ		818.32	818.32 ^f
γ		-72.10	-72.10 ^f
o		25897.5	$2.50(12)\cdot 10^4$
p		144.2	$1.7(8)\cdot 10^2$
q		1.524	1.524 ^f

Table 3.1: The molecular constants for the $a^3\Pi$ state in the $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ isotopologues, for the $v = 0$ and $v = 1$ vibrational states, in MHz. The second column gives the values that are obtained by scaling from the values for $v = 0$, $^{12}\text{C}^{16}\text{O}$ to higher reduced mass and/or vibrational quantum number, using the mass-scaling procedure explained by de Nijs *et al.* [10][Chapter 2]. The value of the band origin is fitted when the other values are fixed, as the value of the band origin cannot be properly mass-scaled. The third column gives the values obtained from a fit to the measured cavity ring-down spectra. The values indicated with an ^f are kept fixed at the mass-scaled value, the others are fitted.

simulated spectra, in the upper, black, and middle, red traces, respectively. This figure shows that the experimental spectrum is well reproduced using the fitted molecular constants.

This work shows that, with an accuracy of 0.2 cm^{-1} , the mass-scaling model reported in Ref. [10][Chapter 2] works well for the $v = 1$ and $J < 30$ rovibrational levels in the $a^3\Pi$ state of both $^{12}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{16}\text{O}$. It should be noted that, although high- J rovibrational levels are observed, the spectral resolution in the present experiment limits the precision of the fitted molecular constants of the $a^3\Pi$ state. A spectroscopic study with a reduced laser bandwidth and Doppler width may yield a further constraint of the molecular constants and test the mass-scaling model at higher precision. The mass-scaling model can be used to predict line positions, limiting the range that needs to be scanned in such an experiment.

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