TOWARDS A NEW ABSOLUTE FREQUENCY REFERENCE GRID IN THE 28 THz RANGE*

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We present a grid of absolute reference frequencies based on CO_2 (or N_2O) lasers locked to saturation peaks of heavy molecules. Frequency differences between OsO_4 peaks corresponding to adjacent CO_2 laser lines from P(12) to P(22) have been measured with 1 kHz accuracy. This set includes one $^{192}OsO_4$ resonance whose absolute frequency is known with the same accuracy. This absolute grid is then used to provide an absolute calibration of the ν_3 band saturation spectrum of SF_6. We also find a 23 kHz average frequency difference between the CO_2 grid and the new OsO_4 grid which we interpret tentatively as a small extrapolation error from the R to the P branch frequencies of CO_2.

1. Introduction

The absolute frequency calibration of high resolution spectra obtained with CO_2 or N_2O laser sources requires a grid of frequency markers of known frequency with respect to the cesium primary standard and for convenient work there should be at least one such frequency reference for each CO_2 or N_2O laser line. Up to now the only available reference lines were those of the corresponding transitions in CO_2 or N_2O themselves [1,2] measured with the saturated fluorescence technique of Freed and Javan [3]. Unfortunately the absolute frequency of most of these resonances is known with an accuracy of 30 kHz only and the reproducibility of these measurements is limited to 5 to 10 kHz in usual conditions because of the difficulty of obtaining these resonances with a narrow width (< 1 MHz) and a high signal-to-noise ratio. On the other hand heavy molecules present a large number of strong and narrow saturation peaks in coincidence with the CO_2 or N_2O laser emission lines over a wide range of frequencies especially since the advent of waveguide CO_2 or N_2O lasers [4,5]. As an example the ν_3 band of OsO_4 covers the region from 940 to 980 cm^{-1} [6] and each CO_2 laser line from P(6) to P(24) and from R(6) to R(24) hits many resonances of various isotopic species [5]. The Q-branch itself can be covered by N_2O laser lines. We have already obtained a linewidth of the order of 3 kHz with this molecule [20] and since the hyperfine structures are either absent or can be well-resolved. we have a potential grid of high quality secondary optical frequency standards [10,5]: 1) When the lasers are locked to OsO_4 peaks the Allan variance [7] of these lasers presently reaches 5×10^{-14} for 10 seconds of integration time and can certainly be substantially improved; 2) owing to the small value of the various possible shifts (curvature shift [8], recoil splitting [9], pressure shift [10] second-order Doppler shift) an absolute accuracy of the order of 10^{-14} is a realistic estimate for the future; 3) finally the absolute frequency of one of the OsO_4 saturation peaks has already been measured with an accuracy of 1 kHz [11]. One can then jump from one OsO_4 line to another corresponding to different CO_2 or N_2O laser lines by direct frequency mixing with a klystron har-

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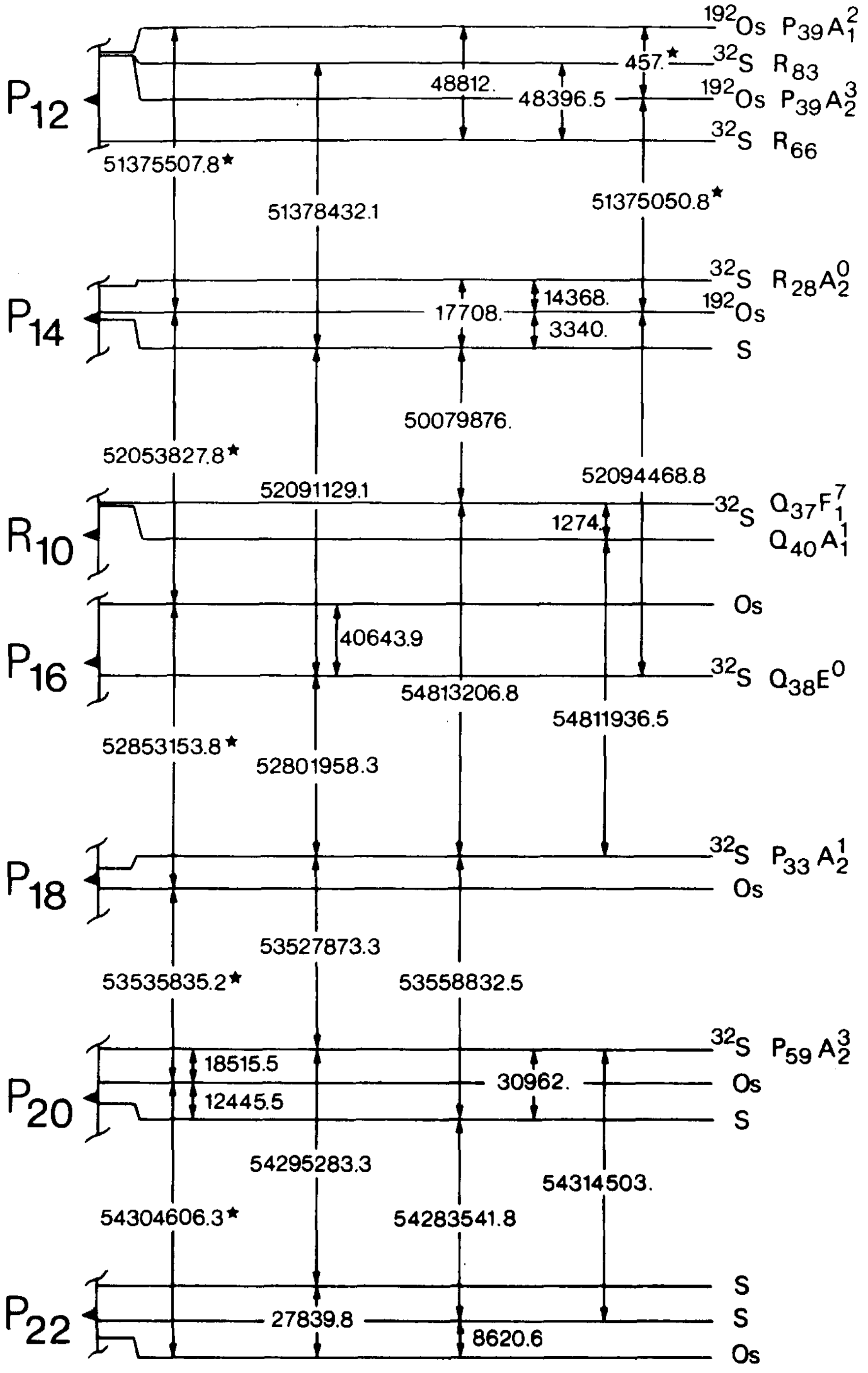

Fig. 1. Grid of OsO_4 frequency markers and frequency differences (in kilohertz) between OsO_4 or SF_6 resonances pertaining to adjacent CO_2 laser tuning ranges. This figure also collects all the known frequency differences connecting OsO_4 and SF_6 lines within each CO_2 laser tuning range as well as the positions of two SF_6 peaks within the tuning range of the R(10) N_2O laser line. Only the measurements between OsO_4 lines, free of hyperfine structures, have a one kilohertz accuracy and are marked with a star.

monic frequency on a point contact MIM diode. In this paper we give preliminary measurements of some frequency differences over a restricted range (264 GHz) to illustrate the possibility of generating such a grid of frequency markers and its potential use for the spectroscopy of other molecules. In the present case we selected the region of special interest for the spectroscopy of the ν_3 band of $^{32}SF_6$ which extends from the P(12) to the P(22) CO_2 lines including the R(10) N_2O line in close coincidence with the P(3) manifold of SF_6 [12].

2. Experimental set-up and measurement procedure

These experiments were performed with the saturation spectrometer described in [5]. The two low-pressure lasers oscillating on adjacent CO_2 (or N_2O) lines were locked to OsO_4 (or SF_6) saturation peaks using third-derivative servo-loops. We used a rather large pressure (a few 10^{-4} Torr) in the absorption cell both to reduce curvature-induced shifts and to optimize the signal-to-noise ratio. A typical peak-to-peak width of the order of 30 kHz resulted from the combined effects of pressure, saturation and modulation broadening. Under these conditions the magnetic hyperfine structures of the SF_6 lines [13,5] are not resolved and yield an additional broadening. For example the hyperfine structure of A_2 lines extends over 60 kHz. Also the hyperfine mixing of vibration–rotation states gives even more complicated structures [14]. Differential saturation among these unresolved components limits the accuracy of SF_6 measurements to a few kilohertz. For this reason only the OsO_4 lines can be considered as accurately defined and measured. A point contact tungsten-nickel MIM diode receives simultaneously the beams from the two CO_2 lasers and the signal from an X band klystron whose 5th harmonic is generated by the diode. This experimental set-up yields a beat note with 25 to 30 dB signal-to-noise ratio in a 100 kHz bandwidth and enables one to measure the frequency difference ν_{diff} between the adjacent CO_2 lines as:

$$\nu_{\mathrm{diff}} = 5\nu_X \pm \nu_{\mathrm{beat}},$$

where ν_X and ν_{beat} are respectively the X band klystron frequency and the measured beat frequency lying in the 40–100 MHz region. The beat note is observed on a spectrum analyser (HP 8553 B–8552 B) following a 32 dB gain and 3 dB noise-figure preamplifier. A tracking generator (HP 8443 A) operating in the "restore signal" mode is used to count the beat note frequency with an external counter. The X band klystron is phase-locked to the nth harmonic of a quartz crystal oscillator and directly counted by a microwave counter (HP 5345 A + frequency converter 5255A) whose time base was calibrated against a cesium beam frequency standard. The two counting processes (beat note and klystron) are synchronized in order to cancel out the effects of the X band klystron frequency instabilities on the precision of the measurement. With such an apparatus and experimental procedure, the accuracy was limited only by the laser instabilities and counter time base frequency drift.

3. Results and discussion

The resulting grid of measured frequencies is displayed on the figure where the measurements between OsO_4 lines (marked with a star) are given with a one kilohertz uncertainty estimated both from the statistical reproducibility and by permutations of the two lasers. Even though hyperfine structures limit the accuracy of the SF_6 grid to some unknown fraction of these structures (~ 3 kHz depending upon the symmetry of the structures) it is interesting to note that the internal consistency of the SF_6 and OsO_4 measurements is always better than 3 kHz and that the total frequency difference between the extreme lines of OsO_4 differs only by 500 Hz over the 264 GHz going through either grid. On the P(20) CO_2 laser line the P(59) $A_2^3 SF_6$ line should be preferred to the other SF_6 line as a reference peak because of a close component on the high frequency side of the latter resonance with pulling effects which could amount to 10 kHz. The N_2O laser measurements have less accuracy (~6 kHz) owing to a degraded signal-to-noise ratio and wider lines. From the measured frequency differences and the absolute frequency measurement of the $^{192}OsO_4$ line in coincidence with the P(14) CO_2 line we can assign absolute frequencies to each resonance in the figure using the shortest pathways through the OsO_4 reference grid. These frequencies are given in table 1. All these lines have been measured in the past with respect to the

Table 1
Absolute frequencies (kHz) of the various resonances considered in this work referenced to the measurement of the OsO_4 line reported in [11] and absolute frequencies of three OsO_4 peaks with respect to CO_2 using the absolute CO_2 frequencies tabulated in [1]

Laser line	Molecule	Resonance assignment	Absolute frequency (reference $^{192}OsO_4$ [11])	Frequency distance to CO_2	Absolute frequency (reference CO_2 [1])	Difference
CO_2 P(12)	$^{192}OsO_4$	P(39) A_1^2	28516052446.3			
	$^{32}SF_6$	R(83)$E^1+F_1^2+A_1^0$	28516052030.8			
	$^{192}OsO_4$	P(39) A_2^3	28516051989.3	25328	28516051966.2	23.1
	$^{32}SF_6$	R(66)$A_1^0+F_1^0+F_2^0+A_2^0$	28516003634.3			
CO_2 P(14)	$^{32}SF_6$	R(28) A_2^0	28464691306.5			
	$^{192}OsO_4$	? hot line	28464676938.5	3215	28464676914.2	24.3
	SF_6	?	28464673598.5			
N_2O R(10)	$^{32}SF_6$	Q(37) F_1^7	28414593720			
	$^{32}SF_6$	Q(40) A_1^1	28414592446			
CO_2 P(16)	OsO_4	?	28412623110.7			
	$^{32}SF_6$	Q(38) E^0	28412582468.6			
CO_2 P(18)	$^{32}SF_6$	P(33) A_2^1	28359780510.3			
	OsO_4	?	28359769956.9			
CO_2 P(20)	$^{32}SF_6$	P(59) A_2^3	28306252637.2			
	OsO_4	?	28306234121.7			
	SF_6	?	28306221676.2			
CO_2 P(22)	SF_6	?	28251957355.2			
	SF_6	?	28251938136.0			
	OsO_4	?	28251929515.4	−12150	28251929495	20.4

CO_2 saturated fluorescence peaks [5,15]. The comparison between the two sets of absolute frequencies reveals an average difference of the order of 30 kHz. To investigate this discrepancy we have repeated some of the measurements with respect to CO_2 in an external saturated fluorescence cell filled with a 40 mTorr pressure and illuminated by a one watt-laser beam with an improved optical isolation between the laser and the CO_2 cell. The results of these measurements are given in the 5th column of table 1 with a 3 kHz standard deviation. The frequency difference P(12)–P(22) which can be inferred from these results and the OsO_4 grid differs by only 2.7 kHz from the corresponding difference in reference [1] but there still is a systematic shift of the order of 23 kHz between both sets of absolute values. This shift could have two origins: first, the lack of intrinsic reproducibility in the realization of the CO_2 standard; second, the possibility of a small error introduced in the extrapolation of absolute frequencies from the R to the P branch of CO_2 through the theoretical fit of frequency differences performed by the authors of [1].

A good general agreement exists on the value for R(30) of CO_2 [16]

$$\nu_{R(30)} = 29442483321.7 \text{ kHz} \pm 5.1 \text{ kHz} \quad (1\sigma).$$

The missing direct link between R(30) and P(14) has been established at the LPTF through a beat between two CO_2 lasers respectively locked to the R(30) and P(14) CO_2 peaks, an HCN 337 μm laser and the second harmonic of a 43.5 GHz klystron [17]:

$\nu_{R(30)} - \nu_{P(14)} = 977809598.4 \pm 4$ kHz (1σ)

yielding the following absolute value for P(14) of CO_2:

$\nu_{P(14)} = 28464673723 \pm 7$ kHz (1σ),

which is 23.8 kHz higher than the value given in [1] and in very good agreement with the above systematic shift. It is therefore tempting to suggest that both shifts have the same origin and that the CO_2 frequencies in the P branch have to be reanalyzed and perhaps up-shifted by ~ 23 kHz. In any case this demonstrates the present limitations of the tabulated CO_2 markers. We should also point out that the measurement of P(14) combined with the measurement of OsO_4 with respect to CO_2 gives an independent determination of the absolute frequency of the OsO_4 line:

$\nu_{OsO_4} = 28464676938 \pm 8$ kHz (1σ),

where standard deviations have been added quadratically.

Other more direct measurements of the absolute frequency of any of the OsO_4 lines are necessary to confirm the absolute position of the new grid which is presently entirely fixed, at the kilohertz level of accuracy, by the measurement reported in [11]. This new grid can be easily extended from 940 to 980 cm^{-1} with OsO_4, from 900 to 940 cm^{-1} with RuO_4 [18] and from 860 to 900 cm^{-1} with XeO_4 [19] using N_2O and the various isotopic species of CO_2 in conventional or waveguide lasers. Other molecules with similar advantages (high mass, free of hyperfine structures, small pressure shifts) should be searched for and are likely to be found for the 9–10 μm spectral range, but already the three tetroxides can serve, through the use of combinations of CO_2 laser frequencies, to generate reference frequency markers for a good portion of the infrared where high quality saturation peaks are not available.

Our measurements are to be considered as a feasibility demonstration which is still far from the accuracy level that one may reasonably hope to reach in the future from the linewidth and the stability and accuracy figures, quoted in the introduction of this paper for lasers slaved to saturation peaks of heavy molecules. But, in view of the amount of effort and time involved in such high precision measurements, we have preferred to present these partial and preliminary results (at the one kilohertz level of accuracy) to attract the attention of spectroscopists and of anyone interested in the measurement of fundamental constants to what actual present and near future possibilities are.

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