IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861. Volume 6, Issue 1 Ver. I (Jan. 2014), PP 29-35
www.iosrjournals.org

Interaction of a tunable laser beam with high-resolution lines of ozone in 4220 – 4226 cm^{-1}

Surajit Bhuyan[1*], Anurup Gohain Barua[2] and Biswa Kr Das[3]
[1,3]*Department of Physics, Lakhimpur Girls' College, North Lakhimpur-787031, India*
[2]*Department of Physics, Gauhati University, Guwahati-781014, India*

***Abstract*: *Interaction of a tunable narrow linewidth-laser beam with the infrared absorption lines of ozone in the region of 4220-4226 cm^{-1} is studied — using the quasi-random model of molecular band absorption. Values of transmittance, computed at intervals of 0.1 cm^{-1}, are obtained for three different absorber thicknesses. The generated absorptance values, which simulate the intensities of the high-resolution absorption lines of ozone, are compared with those generated by the line-by-line (LBL) method.*

Keywords *Line by line method, ozone, quasi–random model, transmittance, tunable laser beam.*

I. Introduction

Ozone is a special form of oxygen, made up of three oxygen atoms. It usually forms when some type of radiation or electrical discharge separates the two atoms in an oxygen molecule (O_2), which can then individually recombine with other oxygen molecules to form ozone (O_3). The ozone layer is a layer in earth's atmosphere which contains relatively high concentrations of ozone (O_3), although it is still very small with regard to ordinary oxygen, and is less than ten parts per million, the average ozone concentration in Earth's atmosphere being only about 0.6 parts per million [1]. Atmospheric optics uses lasers for the remote probing of the atmosphere, including the measurement of traces of pollutant gases, temperature and water vapour concentration. The first precision measurement of ozone in the atmosphere was made using laser remote sensing. The passage of a laser beam through the earth's atmosphere is affected by the atmosphere in many ways. The attenuation and fluctuation of the optical parameters of the penetrating radiation are due to absorption by molecular bands or scattering by atmospheric species. Precise knowledge of spectra of ozone is imperative for accurate measurements involving the propagation of a laser beam through the atmosphere. Infrared spectra of $^{16}O_3$ have been recorded in the 4250 cm^{-1} region with a Fourier transform spectrometer at 0.008 cm^{-1} resolution using white type cell of length 36.16 cm^{-1} filled with 42.8 Torr O_3 [2]. This spectral region corresponds to the $3\upsilon_1 + \upsilon_3$ band and the width of the lines was then 0.01cm^{-1}, due to pressure broadening.

A computer program was developed by Dryson in 1966 to determine the atmospheric transmittance by direct integration (line-by-line) method across the absorption band, using theoretically calculated line position and strength [3]. The LBL algorithm has been used to evaluate the absorption co-efficient to high numerical accuracy [4]. The most accurate theoretical procedure to calculate the absorptance of a vibrational rotational band is probably the line-by-line method or direct integration method [5]. The line-by-line approach provides a mean of direct consideration of the detailed spectral structure of the gases from the microwave to the infrared [6]. The quasi-random model of molecular band absorption is a variant of one of the methods described by Goody and Yung [7]. Infrared transmittances, based on the quasi-random model, have been calculated for H_2O and CO_2 and the results fitted with experimental measurements [8,9]. In this work we consider a tunable laser having line width very narrow in the vicinity of 4220 cm^{-1}. Interaction of this laser beam with nearby absorption lines of ozone is studied with the help of both quasi random model and LBL model.

II. Methods of computation

2.1 Quasi-random model

A detail description of the quasi-random model can be found elsewhere [10]. The quasi-random model characterizes the wing effects accurately, i.e. it takes into account the absorption of spectral lines in as many neighboring intervals as necessary. Each interval Ω, over which the average transmittance is required, is further divided into smaller intervals δ. Each line may be said to be localized within an error defined by the interval size δ. These elementary intervals are chosen small enough to ensure an accurate description of the important band characteristics, yet large enough to simplify the calculations. All the lines falling within a given order of magnitude are subsequently averaged, and each line in each intensity sector is then associated with the appropriate average value. Since the top five intensity sectors in each frequency interval are found to be sufficient to describe the absorptive properties associated with the lines therein. The quasi-random model localizes each line within an error defined by the interval size δ. The transmittance at a frequency ν, as affected by n_p lines within the interval δ_p is computed from the expression

$$T(\nu)=\prod_{i=1}^{5}\left\{(1/\delta)\int_{\delta_p}\exp\left[-\frac{S_i u\alpha/\pi}{(\nu-\nu_i)^2+\alpha^2}\right]d\nu_i\right\}^{n_i} \tag{1}$$

where n_i represents the number of lines within the intensity range i, which itself is characterized by an average intensity S_i, α is the half width at half maximum, u is the absorber thickness, and ν_i refers to the centre of the line. The gases of the atmosphere are usually measured by the unit *atmosphere centimetre* (atm-cm). This measurement unit is used to define an atmospheric gas distributed along a path reduced to a layer at STP, provided the other gases are excluded. The resulting thickness is then expressed in atm-cm, given by $u = cLP$, where c is the fractional concentration of the absorber, L is the path length in cm and P is the pressure in atmosphere.

2.2 Line–by–line model

This method consists of calculating the absorption co-efficient, and then the transmittance, at a large numbers of frequency locations within the spectral range of interest. Since absorption co-efficient is a fast varying function of frequency, it has to be evaluated at very closely spaced locations. The total absorption co-efficient at any frequency location is made up of contributions from a large number of lines in the vicinity of that frequency.

The monochromatic volume absorption coefficient *k* at a frequency ν can be computed as

$$k=\sum_{i=1}^{n} S_i b(\nu,\nu_i) \tag{2}$$

Where b (ν, ν_i) is the Lorentz shape factor defined by

$$b(\nu,\nu_i)=\frac{\alpha/\pi}{(\nu-\nu_i)^2+\alpha^2} \tag{3}$$

The absorptance values are obtained from the expression

$$A=1-T=1-e^{-ku} \tag{4}$$

LBL computation though accurate, have the disadvantage that they require large computation times because a number of function $S_i\, b(\nu,\nu_i)$ in sum may reach tens of thousands.

III. Computation of absorptance

The calculation of the transmittance requires knowledge of the frequency and intensity of each and every spectral line which contributes significantly to the absorption in the frequency range of interest. The manuscript *Line position and intensities of the* $3\upsilon_1+\upsilon_3$ *band of ozone*, Journal of Molecular Spectroscopy 175, 296-302 (1996) is used to get the high resolution infrared lines of ozone in the vicinity of 4220 cm^{-1}. The maximum value is normalized to 0.1, and other values of intensity are taken relative to this. The lines considered are given in TABLE 1 along with the assigned intensities. The half width of the lines is taken as 0.01 cm^{-1}. The entire spectrum in the range 4220– 4226 cm^{-1} is divided into frequency intervals 0.1 cm^{-1} (Ω) wide. Each interval is divided into smaller intervals 0.025 cm^{-1} (δ). Using Simpson's rule of numerical integration, equation (1) is evaluated with the help of a computer program for three different masses per unit area (u): 0.1, 0.5 and 1 atm-cm. First, the transmittance values are calculated at the centers of 0.1 cm^{-1} interval. Transmittances by the wings of lines at the left and right adjacent intervals are also included. The transmittance at the center of an interval is finally obtained as [9]

$$T=T_j\prod_{i\neq j}T_i \tag{5}$$

Next, transmittance values are obtained for another set of frequency intervals whose centers are shifted by half the interval size (0.05 cm^{-1}) from the original positions of the centers of the intervals. This is done in order to minimize the error associated with the occurrence of lines at frequencies near the edges of a given interval. The results for the shifted and un-shifted intervals are averaged, and thus we obtain the average transmittance over a 0.1 cm^{-1} interval.

IV. Results and discussion

Results of the study on the propagation of a 4220 cm^{-1} free electron laser beam through three different path lengths (0.1, 0.5 and 1 atm-cm) of the absorber (atmospheric ozone) are given in TABLE 2 and displayed in the Fig. 2, 3 and 4 for quasi-random-model and line-by-line model. The basic shapes of the absorptance versus frequency curves in the two models have come out to be similar. Because of the consideration of bands instead of lines, variations in quasi-random model values are generally observed to be not as sharp as those in the line-by-line values. The quasi-random curves are relatively smoother as compared to the LBL ones. The prominent absorptance peaks are observed due to the presence of very strong lines near those regions. Thus we see that the experimental data taken for this work agree well with the results. This concludes that the quasi-random model for simulating the intensity distribution by grouping the lines in a given frequency interval works reasonably well — a fact established in recent times for important atmospheric species like nitrogen [11, 12], sulphur dioxide [13] and methane [14].

V. Conclusion

After comparing the results of the quasi-random-model with line-by-line method and experimental results, S. N. Tiwari and N. Mirakhur recommended the use of the quasi-random model for evaluation of the atmospheric radiation [15]. As concluded by Goody and Yung in their monograph [7], in some circumstances the random models might be sufficient, and required less computer time. From the figure it is evident that values obtained from the quasi-random model show reasonably good agreement with those generated from consideration of each line. Hence quasi-random model could be conveniently used in the case involving a large number of lines, for both accuracy and time saving. The frequency dependent absorptive power of molecule is an important topic in atmospheric optics and astrophysics and hence the application prospect of the quasi-random model in atmospheric optics is quite bright. In this work, the broadening of the lines is assumed to be homogeneous, as the rotational lines are observed to be sufficiently fine. Therefore, there is a scope to generalize the model for inhomogeneous broadening as well. Till now, a large number of high resolution absorption spectra of other diatomic and polyatomic molecules have been reported; the present work could easily be extended to these spectra. Temperature and pressure dependence of the linewidth, and consequently of the absorptance, is the aspect that calls for further research.

Acknowledgment

One of the authors Surajit Bhuyan is grateful to the University Grant Commission, India, for the award of a Major Research Project no *F. No 41-890/2012(SR)*and to Dr. M. Pandit, Principal, Lakhimpur Girls' College for his necessary help.

References

[1] http://en.wikipedia.org/wiki/Ozone_layer (accessed 4 December, 2013).

[2] A. Barbe, O. Sulakshina, J. J. Plateaux, Vl. G. Tyuterev and S. Bouazza, Line position and intensities of the $3\vartheta_1 + \vartheta_3$ band of ozone, *Journal of Molecular Spectroscopy 175*, 1996, 296-302.

[3] V.G. Kunde, *Theoretical computations of the outgoing infrared radiance from a planetary atmosphere*, NASA TN-D- 4045, 1967.

[4] L. Sparks, Efficient line-by-line calculation of absorption coefficients to high numerical accuracy, *Journal of Quantitative Spectroscopy & Radiative Transfer*, *57*, 1997, 631–650.

[5] S. N. Tiwari, S. K. Gupta, *Accurate spectral modeling for infrared radiation*, NASA CR-152948, 1977.

[6] B. A. Fomin, Effective interpolation technique for line- by-line calculations of radiation absorption in gases. *Journal of Quantitative Spectroscopy & Radiative Transfer*, *53*, 1995, 663–669.

[7] R.M. Goody, *Atmospheric radiation: theoretical basis* (Ox- ford University Press, New York, 2002).

[8] V.R. Stull, P.J. Wyatt, G.N. Plass, The infrared transmittance of water vapor, *Applied Optics*, *3*, 1964, 229–241.

[9] V.R. Stull, P.J. Wyatt, G.N. Plass, The infrared transmittance of carbon dioxide. *Applied Optics, 3,* 1964, 243–254.

[10] V.R. Stull, P.J. Wyatt, G.N. Plass, Quasi-random model of band absorption, *Journal of Optical Society of America*, *52*, 1962, 1209.

[11] A. Gohain Barua, S.S. Jois, S. Bhuyan, Interaction of a laser beam with the rotational lines of nitrogen in the wavelength region of 5700 Å, *Applied Optics*, *46(23)*, 2007, 5738.

[12] A. Gohain Barua, A.K. Bora, S.S. Jois, Propagation of a 575-nm dye laser beam through nitrogen. *Journal of Atmospheric & Solar Terrestrial Physics*, *68*, 2006, 1330–1333.

[13] A. Gohain Barua, S. Bhuyan, Interaction of 4 μm laser beam with absorption lines of sulphur dioxide, *Indian Journal of Pure & Applied Physics*, *46(9)*, 2008, 617–620.

[14] A. Gohain Barua, P. Goswami, Interaction of a tunable laser beam with high resolution lines of methane in 9190-9199 cm^{-1}, *Journal of Optics*, *42(1)*, 37-41, 2013.

[15] S. N. Tiwari, N. Mirakhur, *Feasibility of quasi-random band model in evaluating atmospheric radiance*, Final report, Old Dominion University, Norfolk, VA, 1980.

Frequency cm^{-1}	Intensity	Frequency cm^{-1}	Intensity
4220.0370	0.077	4223.0680	0.014
4220.0791	0.020	4223.1814	0.009
4220.2246	0.078	4223.2165	0.060
4220.3787	0.054	4223.2652	0.038
4220.3798	0.014	4223.6997	0.072
4220.4814	0.036	4223.7763	0.030
4220.5402	0.009	4223.9923	0.050
4220.8579	0.064	4224.1098	0.082
4221.0407	0.027	4224.1281	0.094
4221.2063	0.046	4224.1465	0.021
4221.2855	0.073	4224.3764	0.014
4221.4117	0.081	4224.5990	0.063
4221.4585	0.020	4224.6216	0.040
4221.7357	0.014	4224.6502	0.091
4221.8086	0.057	4225.0725	0.075
4221.8727	0.009	4225.1085	0.030
4221.8850	0.082	4225.3235	0.094
4221.8851	0.038	4225.3243	0.086
4222.2684	0.068	4225.3495	0.052
4222.4204	0.029	4225.4548	0.021
4222.4687	0.078	4225.5030	0.100
4222.4827	0.084	4225.6610	0.014
4222.6112	0.048	4225.7381	0.098
4222.8084	0.090	4225.9541	0.041
4222.8144	0.021	4225.9583	0.065
4223.0178	0.088		

TABLE 1: Ozone lines affecting the propagation of 2.4 μm tunable laser beam.

TABLE 2: Absorptance of a 2.4 μm laser beam by atmospheric ozone for three different amounts of absorber thickness.

Frequency cm^{-1}	u = 0.1 atm-cm in		u = 0.5 atm-cm in		u = 1 atm-cm in	
	QRM	LBL	QRM	LBL	QRM	LBL
4220.087	58.28	4.92	67.72	22.30	76.46	39.62
4220.187	58.28	1.90	67.72	9.05	76.46	17.27
4220.287	60.29	0.98	74.68	4.81	84.89	9.39
4220.387	61.65	12.55	78.54	48.85	88.91	73.83
4220.487	61.73	8.70	78.76	36.55	89.14	59.74
4220.587	57.71	0.36	65.78	1.80	73.19	3.56
4220.687	55.40	0.19	55.77	0.94	56.23	1.87
4220.787	55.96	0.49	58.47	2.44	61.38	4.82
4220.887	55.96	2.25	58.47	10.74	61.38	20.33
4220.987	56.23	0.52	59.74	2.57	63.70	5.08
4221.087	56.06	0.65	58.95	3.19	62.27	6.28
4221.187	60.51	3.43	74.98	16.03	84.80	29.49
4221.287	61.01	20.72	76.51	68.67	94.01	90.19
4221.387	60.77	4.01	75.78	18.50	93.63	33.58
4221.487	56.35	1.30	60.26	6.33	84.18	12.25
4221.587	55.66	0.30	57.04	1.47	58.70	2.92
4221.687	55.51	0.51	58.87	2.53	62.12	5.00
4221.787	63.36	3.81	83.43	17.64	93.00	32.17
4221.887	63.24	31.70	83.15	85.13	92.77	97.79
4221.987	63.19	0.54	81.99	2.69	91.74	5.32
4222.087	55.31	0.28	55.31	1.38	55.31	2.73
4222.187	59.54	0.51	71.90	2.50	81.02	4.93
4222.287	59.82	5.01	72.84	22.68	82.26	40.21
4222.387	68.29	1.66	90.88	8.01	97.57	15.38
4222.487	67.42	25.04	89.72	76.33	97.01	94.40
4222.587	67.20	2.79	89.36	13.20	96.80	24.65
4222.687	63.85	0.70	83.29	3.46	95.21	6.80

4222.787	61.14	5.96	76.42	26.44	90.85	45.90
4222.887	61.93	0.87	78.71	4.28	92.53	8.37
4222.987	58.02	2.93	63.98	13.83	70.82	25.74
4223.087	58.97	1.81	67.88	8.73	76.78	16.69
4223.187	58.12	4.45	64.42	20.37	71.55	36.56
4223.287	55.31	2.59	55.31	12.32	55.31	23.12
4223.387	55.31	0.26	55.31	1.30	55.31	2.58
4223.487	55.31	0.19	55.31	0.93	55.31	1.84
4223.587	59.89	0.31	72.94	1.52	82.18	3.01
4223.687	61.63	8.61	78.18	36.23	88.22	59.34
4223.787	61.63	4.78	78.18	21.70	88.22	38.69
4223.887	60.35	0.44	74.78	2.20	84.91	4.35
4223.987	64.13	12.08	84.05	47.47	93.40	72.41
4224.087	64.34	6.13	84.43	27.12	93.72	46.88
4224.187	61.55	1.77	77.74	8.54	87.69	16.34
4224.287	56.48	0.40	60.62	1.99	65.16	3.94
4224.387	56.23	2.32	59.65	11.08	63.44	20.94
4224.487	60.55	0.47	75.28	2.32	85.34	4.59
4224.587	60.56	9.52	75.33	39.36	85.44	63.23
4224.687	60.56	2.60	75.33	12.32	85.44	23.12
4224.787	56.24	0.36	59.73	1.80	63.67	3.58
4224.887	55.31	0.26	55.31	1.30	55.31	2.59
4224.987	61.75	0.54	78.47	2.68	88.49	5.28
4225.087	61.75	9.16	78.47	38.14	88.49	61.73
4225.187	63.33	0.79	82.54	3.89	92.41	7.62
4225.287	57.66	4.46	65.86	20.41	73.84	36.66
4225.387	63.68	2.94	82.99	13.84	92.53	25.77
4225.487	62.12	9.47	79.02	39.21	88.67	63.04
4225.587	61.79	0.86	78.08	4.23	87.65	8.28
4225.687	56.44	1.94	60.68	9.33	65.35	17.79
4225.787	56.44	1.49	60.68	7.21	65.35	13.90
4225.887	56.30	0.89	60.04	4.38	64.21	8.57
4225.987	55.31	3.39	60.43	15.83	64.93	29.65

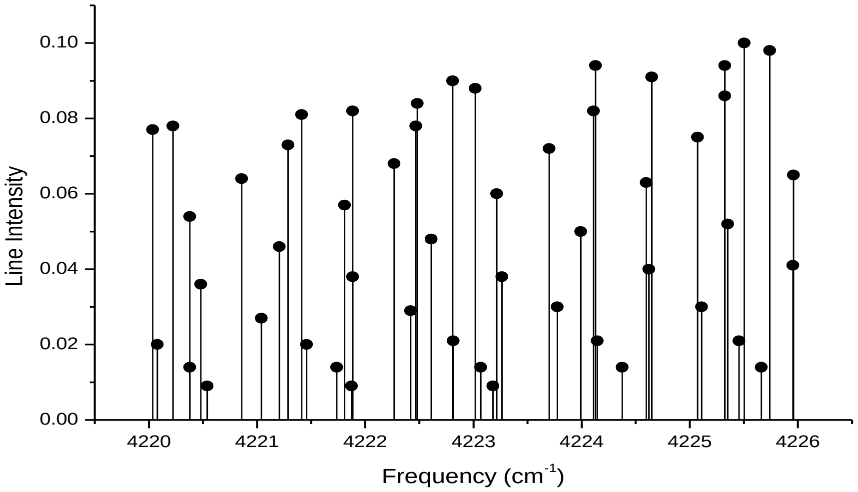

FIGURE 1: High-resolution lines of ozone.

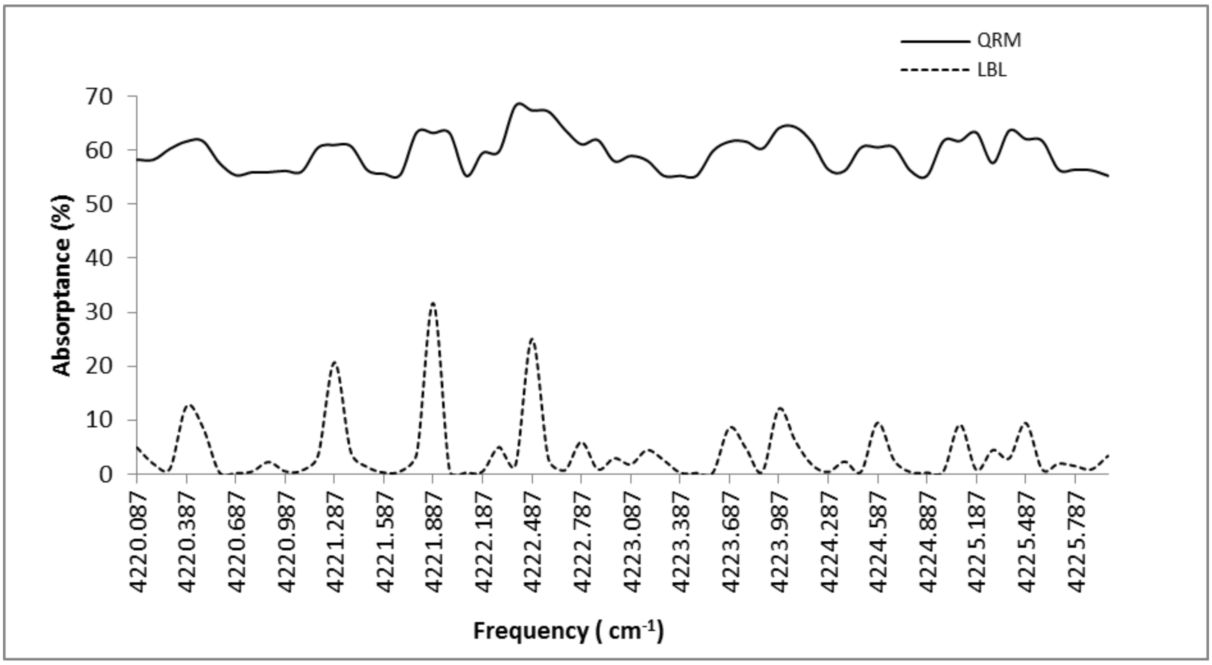

FIGURE 2: Transmission of a 2.4 µm laser beam through 0.1 atm-cm thickness of ozone.

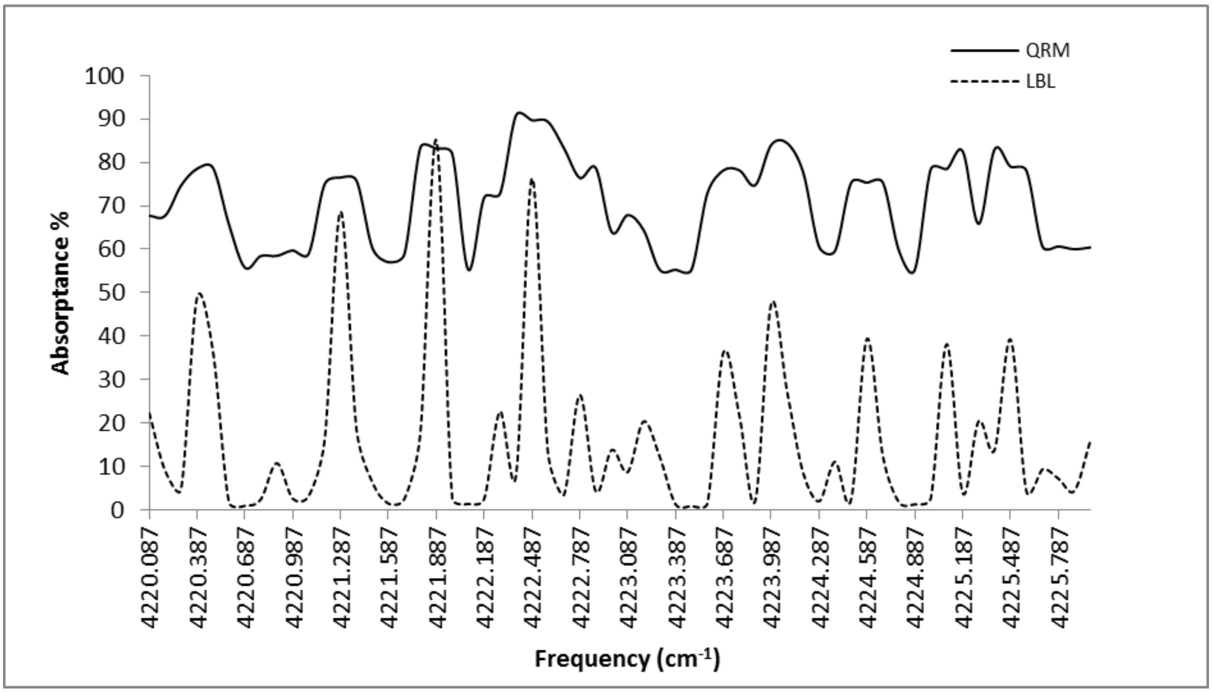

FIGURE 3: Transmission of a 2.4 µm laser beam through 0.5 atm-cm thickness of ozone.

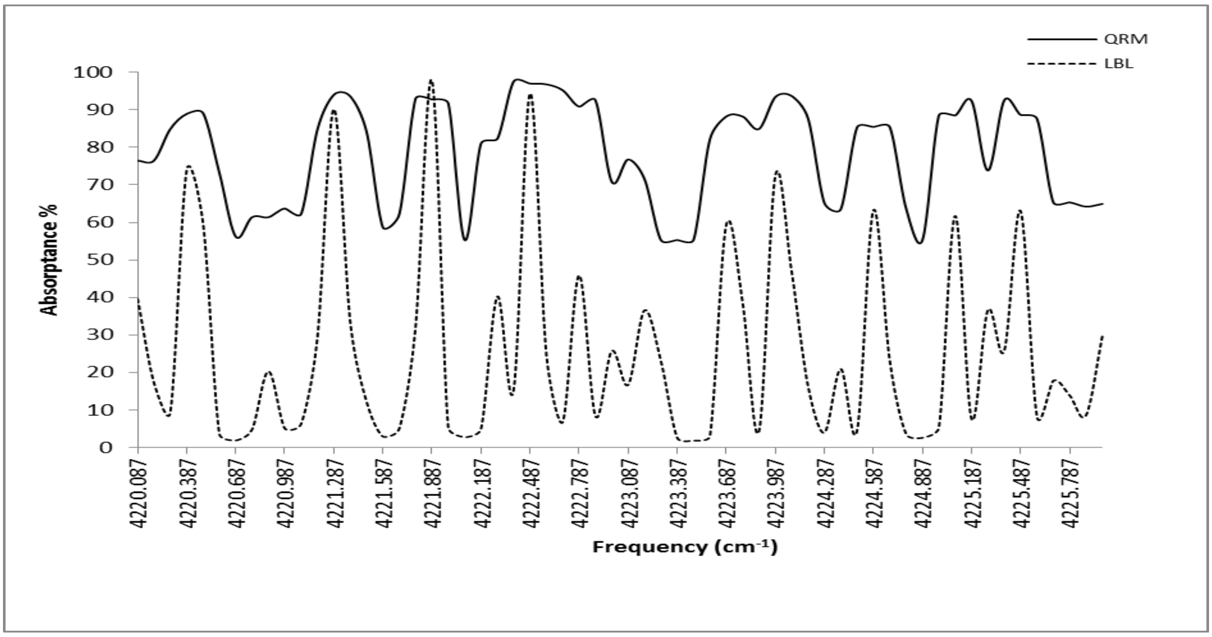

FIGURE 4: Transmission of a 2.4 μm laser beam through 1 atm-cm thickness of ozone.