

Sub-Doppler Laser Spectroscopy of SO₂ Molecule of 30548.0 cm⁻¹ and 31770.0 cm⁻¹ Bands

I. M. Hamada¹, R. Ghazy¹, H. EL-Kashef¹, W. Demtröder²
and G. E. Hassan¹

¹Physics Department, Faculty of Science, Tanta University, Tanta, Egypt

²Physics Department, University Kaiserslautern, Kaiserslautern, Germany

Sub-Doppler excitation spectra of SO₂ molecule of the two bands 30548.0 cm⁻¹ and 31770.0 cm⁻¹ have been measured with the help of the Auto-Scan ring dye laser system, the spectral linewidth was 1.8 GHz when the band 30548.0 cm⁻¹ was measured without skimmer, while the linewidth was 0.15 GHz with the collimating skimmer. The Doppler linewidth was decreased to about 0.2 GHz i.e., six times narrower than before, by the collimation for the 31770.0 cm⁻¹ band. The molecular rotational constants, the centrifugal distortion constants and the moment of inertia of the excited state were calculated. The inertial defects and the valence angle of SO₂ molecule of these bands are tabulated and compared at different conditions.

1. Introduction

The proposal of studying SO₂ molecules is motivated by the air pollution in big cities and also everywhere the prospect of rising concentrations in air atmosphere causes the acid rains and presents threats to the health by inhalation of SO₂ which may cause short term respiratory irritation and on the long term health effects [1].

The absorption bands of sulfur dioxide had been first investigated by Clement [2] in the region 390-260nm by using a spectrograph without high resolution .

Hamada and Merer [3] did an attempt to examine the rotational structure of the SO₂ molecule, to get high resolution absorption spectra of some bands at 334.0, 335.9, 339.5 nm and two bands of SO₂ in the region 300-330 nm [4]. Kullmer and Demtröder [5] surveyed the band spectra of the rotationally

cold SO₂ molecules in a supersonic molecular argon beam seeded with SO₂. They measured the Sub-Doppler rotational spectra of some selected bands with in the spectral range 30300-33000 cm⁻¹, they performed measurements of the **E** band with Sub-Doppler resolution in supersonic beam, they analysed the measured excitation spectra , with linewidths down to 10 MHz.

Bylicki *et al* [6] illustrated the spectral resolution measured with Sub-Doppler laser spectroscopy in cold argon beams, seeded with molecular of metal vapors, they used either LiF or resonant two-photon ionization.

Tajalli *et al* [7] analyzed the Sub-Doppler resonances in the absorption of the laser beam on the frequency of the optical transition in a gas cell.

The transition of ZrN has been studied by Jiang *et al.* using intermodulated laser induced fluorescence spectroscopy, they obtained the Sub-Doppler spectrum at a resolution about 150 MHz [8].

Meyer *et. al.* used the Sub-Doppler laser spectroscopy to show the well-resolved and characteristic hyperfine structures of rovibronic transitions [9]. The study of atmospheric trace gases by Sub-Doppler diode laser spectroscopy has been done by Piccarreta *et al.* They recorded the rotational temperature of about 20k, in a supersonic slit jet expansion. A detailed rotational analysis has been performed yielding band origins and rotational constants. [10].

In this research the spectrum SO₂-molecules in the spectral band 30548 cm⁻¹ and 31770.0 cm⁻¹ were measured and analyzed by using high resolution laser spectroscopy in combinations with the cold molecular beam technique. The rotational molecular constants *A*, *B* and *C* of SO₂ molecules were calculated as a result of the “Least-Squares Fit” of the Hamiltonian operator, these constants are defined as :

$$A = \frac{h}{4\pi C I_A}, \quad (1) \quad B = \frac{h}{4\pi C I_B}, \quad (2) \quad C = \frac{h}{4\pi C I_C}, \quad (3)$$

where *h* is the Plank's constant; *C* is the velocity of light ; *I_A*, *I_B* and *I_C* are the moment of inertia about the axes *A*, *B* and *C* respectively .

The asymmetry parameter *K* takes the value :

K = +1 for the case of oblate symmetric top molecules , *K* = -1 in the case of prorate symmetric top molecules and *K* = 0 in case of most asymmetric top molecules, for which

$$B = \frac{A + C}{2} \quad (4)$$

the asymmetry parameter in the case of SO₂ takes the value

$$K = -0.7552, \dots, -0.9416 \quad (5)$$

which means that it can be represented by a near prolate symmetric top. The asymmetry parameter can be changed adiabatically by successive infinitely small changes in its geometry.

2. Experimental Set Up

The excitation energy of the lowest excited state of the SO₂-molecule is 3.2 eV or 26000 cm⁻¹ and more above the electronic ground state. This means that the absorption of the visible spectral range is negligible, whereas in the ultraviolet region the absorption increases.

The Auto-Scan ring dye laser (coherent 699-29) was used to reduce the residual Doppler width below to 10MHz. In addition (LiIO₃) crystal [11-12] was used to double the optical frequency of the dye laser. The position of the doubling crystal was outside the laser cavity. A lens of focal length 100 mm was used to focus the laser beam into the doubling crystal. The power of the single mode-dye-laser was 1mW in wavelength ranges between 605 nm to 645 nm. The power of the doubled laser frequency (UV laser) was about 1mW. The laser induced fluorescence is imaged by a lens system and a concave mirror onto a UV sensitive photomultiplier (EMI6256S) [5].

The wavelength of the dye-laser was measured with high accuracy by a dynamic Michelson wavemeter with relative accuracy about 10⁻⁸cm⁻¹ and the absolute accuracy of about 2 x 10⁻³ cm⁻¹ and by using the dynamic Michelson interferometer [17].

The vacuum system consists of two chambers with about 600mm length. One of the two chambers is the molecular oven chamber and the other one is the chamber where the laser beam cross the molecular beam. Each of the two chambers are pumped with an oil diffusion pump. The large one evacuates. One evacuates the molecular oven chamber with a speed of 5000 L/sec. and the small one evacuates, the interaction chamber, with a speed of 2400 L/sec. Each of these two diffusion pumps are connected with a mechanical pump, the large pump working with a rate of 40 m³/h is connected to the big diffusion pump and the other pre-pump is connected to the small diffusion pump working with a rate of 16 m³/h.

The pressure of the SO₂ gas before the nozzle was between 100 to 350 mbar. The gas under investigation was mixed with argon gas, as a "carrier gas" with a ratio of 95% argon to 5% SO₂. This gas mixture was kept in a cylinder, which was connected directly to the nozzle through a stainless steel tube.

A skimmer was formed by a slit 1.5mm width and 20mm length downstreams of the nozzle. It was placed on a metal wall between the two vacuum chambers.

The wavelength of a spectral line was determined by tuning the dye laser to the center of a molecular line and measuring the laser wavelength with a wavemeter which was controlled by a computer belongs to the Auto-Scan system. The ratio between the fluorescence signal $S_{fi}(\lambda_L)$ and the UV-laser power $P_L(\lambda_L)$ of the frequency doubled laser beam was calculated by the computer. This eliminates changes of the laser power and of the doubling efficiency with the laser wavelength λ_L and allows the correct comparison of the relative line intensities within a spectral run [5].

3. Results and Discussion

In the case of SO₂- molecules there are four different possibilities on one-dimensional representations known as A₁, A₂, B₁ and B₂ as shown in Tables (1) and (2). This representation shows that there are possible symmetry species A₁, A₂, B₁ and B₂ for the eigen wavefunctions $\psi\rangle$. The last column in Table (1) shows the Cartesian coordinates T_x , T_y and T_z transformation and of the rotations R_x , R_y and R_z in the fixed molecular coordinate system a, b and c . C_{2v} is a one dimensional representation of the symmetry group.

Table (1) : SO₂-molecules character.

C_{2v}	E	C_2	σ_v	$\sigma_{v'}$	
A_1	1	1	1	1	T_x
A_2	1	1	-1	-1	R_x
B_1	1	-1	-1	1	T_y, R_z
B_2	1	-1	1	-1	T_z, R_y

Table (2) : Symmetry of the rotational levels of the SO₂-molecule.

k_a	k_c	
gerade	gerade	A1
gerade	ungerade	B1
ungerade	gerade	B2
ungerade	ungerade	A2

For asymmetric top molecules, there is a representation on the energy levels given by the quantitative Wang's formula

$$E(J_\tau) = \frac{1}{2}(B+C)J(J+1) + [A - \frac{1}{2}(B+C)]W_\tau \quad (6)$$

where W_τ depends on A, B, C and J in a complicated manner:

$$\tau = K_a - K_c \quad (7)$$

where k_a and k_c [18] are the projection of J on both a and c axes; $k = 0, 1, 2, \dots, J$; and $J = 0, 1, 2, \dots$

For a given J there are $(2J+1)$ different sublevels which are the roots of a secular determinant of degree $(2J+1)$ which can be factorized into a number of determinates of smaller degree leading of these algebraic equations in each case. The degree of these algebraic equations increases linearly with J . The assignments of the measured spectral lines were given as an input file to a Wang program [19] to fit the simulated vibrational spectrum of the SO₂- Molecule. The Wang program performs the refinement of the measured line positions to spectroscopic parameter. Also ,this program can treat arbitrary couplings between several vibrational states since it is using a Watson effective rotational Hamiltonian up to sextic centrifugal distortion terms. Vibrationally (Fermi, Darling-Dennison) couplings are included up to second order. Therefore the combination differences is considered as an exacting test for the correctness of the assignments of the measured spectral lines.

3.1 Spectrum of 30548.0 cm⁻¹:

Figure (1) shows the measured spectrum of 30548.5 cm⁻¹ band with the help of the Auto-Scan ring-dye laser system (CR 699-29). This spectrum was measured in a pure SO₂-molecular beam, with nozzle diameter 80μm, without a skimmer, and at a distance of 15 mm between the nozzle and the interaction point. The spectral linewidth was 1.8GHZ when this band was measured

without a skimmer, while the line width was 0.15GHz with the collimating skimmer, which is very small in comparison with the first scan, this means that the spectral resolution was improved by using the skimmer. This is illustrated in Fig. (2) which shows the same part of the spectrum for these two cases.

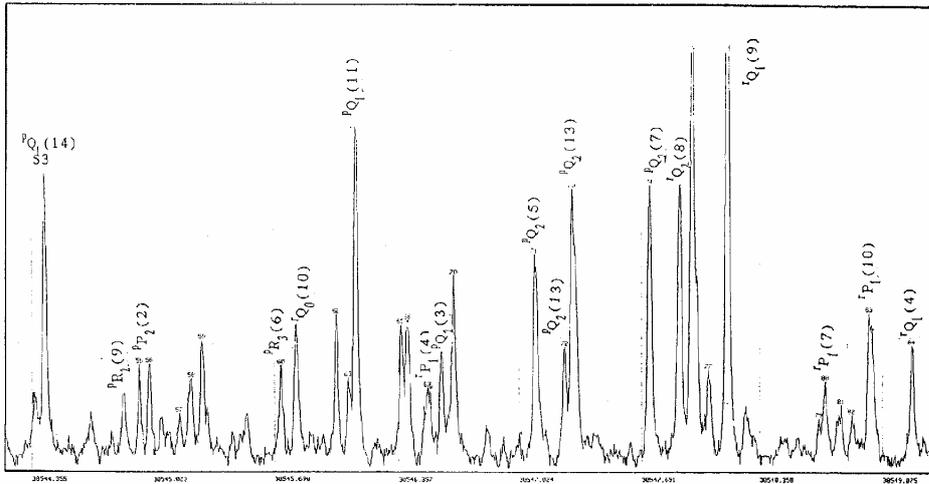


Fig. (1) : Shows the measured spectrum of 30548.0 cm^{-1} band in a pure SO_2 -molecular beam.

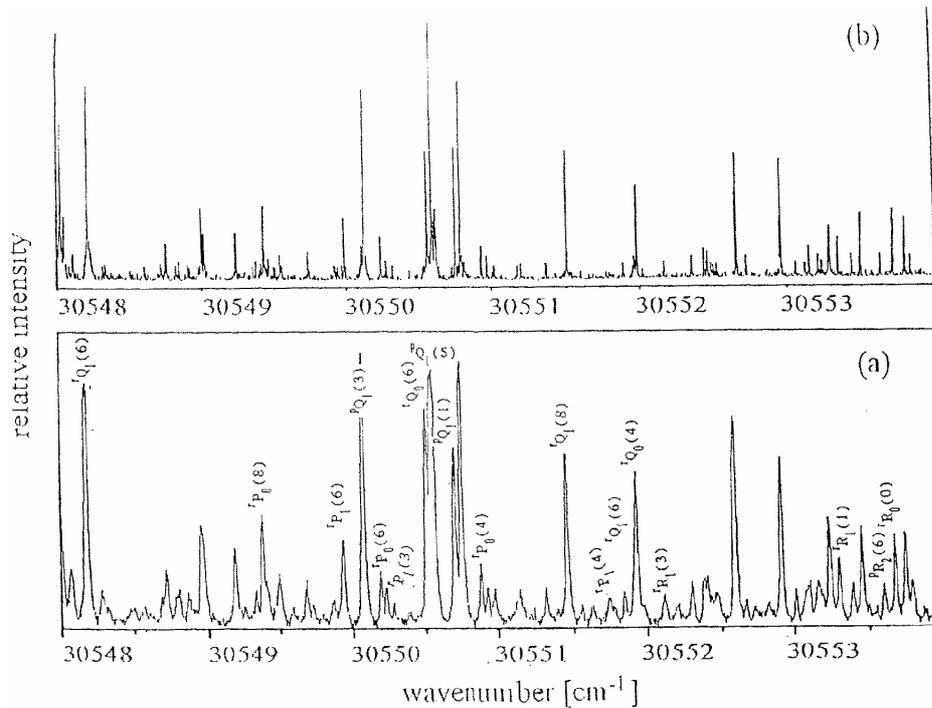


Fig. (2) : Effect of the skimmer on the resolution of 30548.0 cm^{-1} band.

3.2 Spectrum of 31770.0 cm^{-1} Band:

This band was measured with the same parameters as that at 30548.0 cm^{-1} . In addition, this band was measured twice with the following parameters:

Firstly : Pure-molecular beam. A slit skimmer with dimensions 10 mm length and 1 mm width :Nozzle diameter was $200 \mu\text{m}$; Quantum photometer with 30 K ; and distance between nozzle and skimmer 50 mm

Secondly : Cold SO_2 -molecular beam, with 5% of SO_2 -molecular mixed with 95% argon gas as a carrier measured with the same parameters as in the first case but the quantum photometer with 30K and 10K to resolve the peaks which were cut off.

Figure (3) shows the spectrum of the 31770.0 cm^{-1} band which was measured with these experimental parameters. Figure (4) shows the effect of both collimation and the dynamic cooling on the resolution of spectral lines. It also gives a comparison between spectra measured with and without cooling and collimation.

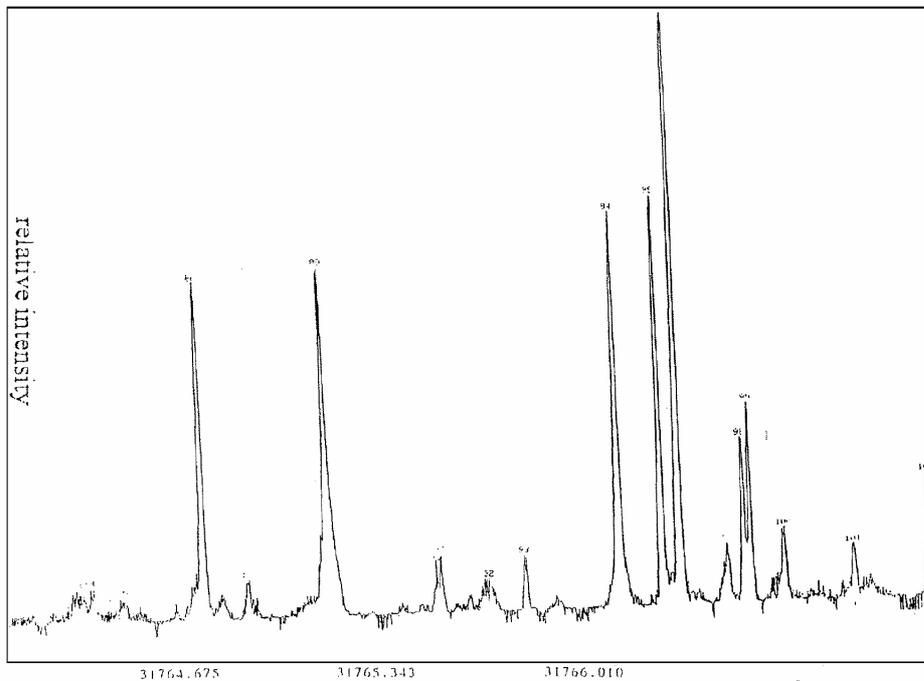


Fig. (3) : The measured spectrum of 31770.0 cm^{-1} band of SO_2 -molecule.

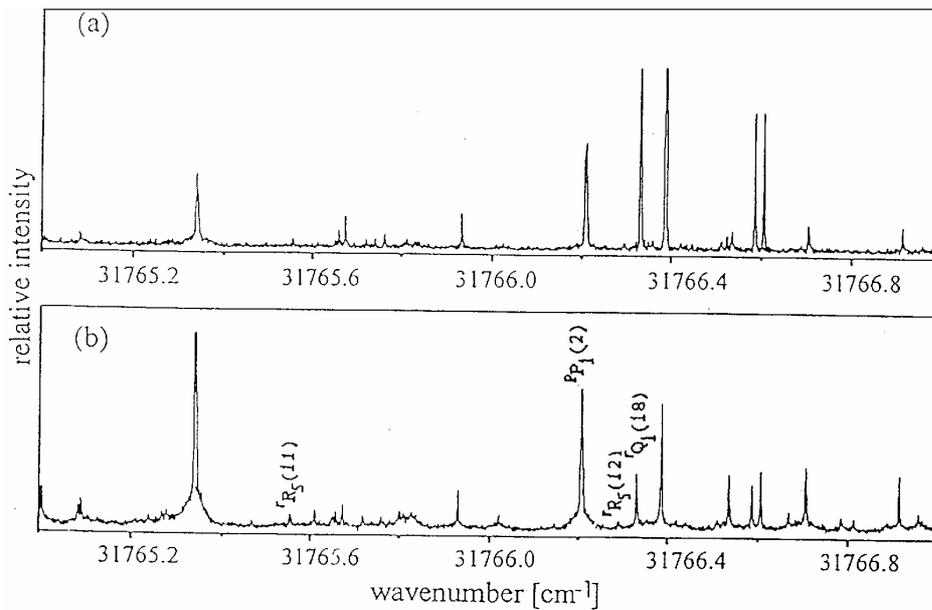


Fig. (4) : Effect of both collimation and the dynamic cooling on the resolution of spectral line.

3.2.1 Lines Assignments of the 31770.0 cm^{-1} Band Without Skimmer

In this case it was difficult to assign some spectral lines because the linewidth was too large due to the low collimation. This collimation was not sufficient to reduce the Doppler width and to resolve overlapping lines. Therefore it was difficult to determine the exact right positions of these lines.

3.2.2 Line Assignments with Collimation

Using the skimmer improved the resolution of spectral lines which partly overlapped in the spectrum obtained in the uncollimated beam. This means that by the collimation the Doppler line width had decreased to about 0.2 GHz. The resolution of the overlapped spectral lines became very high which made it easier assign these lines.

3.2.3 Cooling Effect on the 31770.0 cm^{-1} Band

In this measurement the SO_2 -Molecules were mixed in a percentage of about 5% with argon gas (95%). This seeded beam achieves the dynamic cooling. .

Figure (4) shows the effect of the cooling on the measured spectral lines of the 31770.0 cm^{-1} band. This comparison illustrates that the intensity of some spectral lines is decreased because the rotational temperature becomes lower than that before. As a result the signal to noise ratio becomes higher than in the last spectrum of the same band which was measured in a thermal pure SO_2 molecular beam [20-22].

Rot. Constants and Centrif. Distortion Parameters for State 1:

(KAPPA = -0.9416) [26] (ground State).

$BX = 0.34417379E + 00 \text{ cm}^{-1}$	(FIXED)
$BY = 0.29352650E + 00 \text{ cm}^{-1}$	(FIXED)
$BZ = 0.20273538E + 01 \text{ cm}^{-1}$	(FIXED)
$DJ = 0.22050000E - 06 \text{ cm}^{-1}$	(FIXED)
$DJK = -0.39018700E - 05 \text{ cm}^{-1}$	(FIXED)
$Dk = 0.86399130E - 04 \text{ cm}^{-1}$	(FIXED)
$DJ = 0.56740000E - 07 \text{ cm}^{-1}$	(FIXED)
$DK = 0.84605000E - 06 \text{ cm}^{-1}$	(FIXED)

Rot. Constants and Centrif. Distortion Parameters for State 2:

$BX = 0.349927927E + 00 \text{ cm}^{-1}$	($0.517E - 03$)	($0.648E - 03$)
$BY = 0.285500205E + 00 \text{ cm}^{-1}$	($0.353E - 03$)	($0.161E - 02$)
$BZ = 0.119149185E + 01 \text{ cm}^{-1}$	($0.190E - 02$)	($-.699E - 02$)
$BZ = 0.26387638 E - 06 \text{ cm}^{-1}$	($0.123E - 05$)	($-0.264E - 06$)
$DJK = 0.86624269E - 06 \text{ cm}^{-1}$	($0.130E - 04$)	($0.866E - 06$)
$DK = 0.47352325 E - 04 \text{ cm}^{-1}$	($0.508E - 04$)	($0.474E - 04$)
$DJ = -0.24061577 E - 07 \text{ cm}^{-1}$	($0.743E - 06$)	($-.241E - 07$) = d(J)
$DK = -0.79749012 E - 05 \text{ cm}^{-1}$	($0.172E - 04$)	($-.797E - 05$) = d(K)

Statistics:

Minimum Deviation = $0.65E - 03$
Maximum Deviation = $0.19E + 00$
RMS Deviation = $0.6911E - 01$

Moment of Inertia:

By using the molecular constants shown above it is possible to calculate to the moment of inertia about the principal axes and of the SO₂ molecules.

Taking into account that I_a, I_b and I_c depend on A, B , and C .

The Calculated Moment of Inertia of The Ground State are

$$I_a = 1.380 \times 10^{-46} \text{ Kg} \cdot \text{m}^2$$

$$I_b = 8.128 \times 10^{-46} \text{ Kg} \cdot \text{m}^2; \text{ and}$$

$$I_c = 9.529 \times 10^{-46} \text{ Kg} \cdot \text{m}^2$$

The Calculated Moment of Inertia of the Excited State are

$$I_a = 2.389 \times 10^{-46} \text{ Kg} \cdot \text{m}^2$$

$$I_b = 8.009 \times 10^{-46} \text{ Kg} \cdot \text{m}^2; \text{ and}$$

$$I_c = 9.813 \times 10^{-46} \text{ Kg} \cdot \text{m}^2$$

Inertial defect of molecule:

According to the obtained moments of inertia I_a, I_b and I_c about the principal axes a, b and C respectively of SO₂, it is possible to calculate the inertial defect Δ of the SO₂-molecule which enable us to get more information about the geometry of SO₂-molecule. By using the following equation

$$\Delta = I_c - (I_a + I_b)$$

$$= 0 \quad \text{for a planar molecule ; or}$$

$$\neq 0 \quad \text{for a non-planar molecule.}$$

The different obtained values for both 30548.0 cm^{-1} and 31770.0 cm^{-1} bands are calculated as shown in Table (3).

Table (3) : The obtained values of the inertial defect of SO₂-molecule

Band	Inertial defect (Δ) amu. A ⁰²
1- Ground state	0.021366319
2- 30548.0 cm^{-1}	0.65864391
3- 31770.0 cm^{-1}	-1.000184367

In addition, further information could be obtained about the valence lengths between both S—O and O—O atoms as $r(\text{S—O})$ and $r(\text{O—O})$ respectively.

Valence angle of the molecule:

Furthermore it is possible to determine the valence angle ($2\psi^0$) for each band we calculated. The calculated values of the valence angle are shown in Table (4) in comparison with that of the ground state.

Table (4) : The obtained values of the valence angle of SO₂-molecule. of bands 30548.0 cm⁻¹ and 31 31770 cm⁻¹

Band	Valence angle ($2\psi^0$)
1- Ground state	119.566
1- 30548.0 cm ⁻¹	102.4
2- 31770.0 cm ⁻¹	
Without skimmer	104.12
With skimmer	106.03
With collimation and cooling	106.04

Conclusion:

The fitting which we have done shows that there is a good agreement between lines positions and their intensities for both calculated and observed spectrum. The molecular constants A,B and C of SO₂-molecules were calculated as a result of the "Least-Square's Fit" of the Hamiltonian Operator. These constants are consistent with the literature values [23]. The moment of inertia I_a, I_b and I_c about the principal axes a, b, c and the inertial defects were calculated of both ground and excited states. The valence angle 2ψ of the ground state is larger than that in the excited state, the centrifugal distortion constants $\Delta_j, \Delta_{jk}, \Delta_k, \delta_j$ and δ_k were also calculated.

References:

1. J. W. Winchester, D. L. Johnes and B. I. Mutian, Nuclear Instruments and Methods in Phys. Res. B3, 360 (1984).
2. J. H. Clements, Phys. Rev. 47, 224 (1935).
3. Y. Hamada and J. Merer, Can. J. Phys. 52, 1443 (1974).
4. Y. Hamada and J. Merer, Can. J. Phys. 53, 2555 (1975).
5. R. Kullmer and W. Demtröder, J. Chem. Phys, Vol. 81, 2919 (1984).

6. F. Bylicki; W. Demtroeder.; H. A .Eckel; J. Gress; E. Mehdizadeh; G. Persch; Proceeding Indian Academy of Sciences, *Chemical Sciences*. **103** (2). 211 (1991).
7. H. Tajall; S. Ahmadi; A. ch. Izmailov, *Laser physics* **11**, 12; 1256. (2001).
8. He. Jiang; Ma. Chensheng; GS M. Tong; AS C. Cheung; *J. of Molecular Structure* 480-481, 277 (1999).
9. W. Meyer; M. Keil; A. Kudell; MA. Baig; J. Zhu and W. Demtröder; *J. Chem. Phys. Vol.* 115, no. 6 ; 2590 (2001).
10. L. Piccarreta; AM. Santoro; M. Snels; *The International Society for Optical Engineering* **4070**; 94 (2000).
11. G. D. Hager, S. A. Hanes and M. A. Dreger, *IEEE J. Quant. Electron.* **28**, 2573 (1992).
12. F. R. Nash, J. G. Berman; G. D. Boyed and E. H. Turner, *J. Appl. Phys.*, **40**, no. 13, (1969).
13. G. Nath and S. Hausshi, *Appl. Phys. Lett.*, **14**, no. 5, 154 (1969).
14. D. N. Nikogosyan, *Sov. J. Quant. Elect.*, **7**, No. 1, 1 (1977).
15. J. Donald, W. Harker, G. Linomlm and N. Brnes, *IEEE J. Quant. Electron.* **24**, no. 11, 2231 (1988).
16. R. Eckard, H. Masuda, Y. Far and R. Byer, *IEEE J. Q. Electron.*, **26** no. 5, 922 (1990).
17. S. M. Jafee and W. M. Yen. *Rev. Sci. Instrum.*, **64**, no. 6, 1459 (1993).
18. W. H. Kirchhoff; *J. Mol. Spectroscopy*. **41**, 333(1972).
19. D. Luckhaus, Wang's Program, Private Communication, Kaiserslutern Univ. , Germany.
20. T. Oka and Y. Morino, *J. Mol. Spectrosc.*, Vol. 6, 472 (1962).
21. T. Oka and Y. Morino, *J. Mol. Spectrosc.*, **8**, 9 (1962).
22. J. K. G. Watson, *J. Chem. Phys.*, **46**, no. 5, 1935 (1967).
23. R. Kullmer: Ph.D.thesis, Physics Department, University Kaiserslutern, Kaiserslutern, Germany., (1985).