

Sub-Doppler Laser Spectroscopy of Na₂ in a Cold Molecular Beams

R. Ghazy, I. M. Hamada, W. Demtröder*, H. El-Kashef and
G. E. Hassan

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

* Physics Department, Kaiserslautern University,
Kaiserslautern, Germany.

A collimated, cold and supersonic molecular beam of sodium molecule (Na₂) was constructed to study the rotational constants of sodium molecule. By using the laser induced fluorescence technique, the fluorescence signals were detected. The obtained spectral lines were highly resolved by using the Auto-Scan-ring-dye laser system. The Doppler width of the spectral lines were very narrow i.e. FWHM was very small value down to 10^{-3}cm^{-1} . The results of the rotational constants of Na₂ molecules were fitted by using the least square fitting method. In addition the rotational temperature of Na₂ molecules was determined to be 18K.

1. Introduction:

A single-mode Auto-Scan ring-dye laser had been used to determine the molecular constants of Na₂ molecules, as an example of a diatomic molecule. The Na₂ molecule had been prepared in supersonic, collimated and cold molecular beams. The molecular beam technique is useful to isolate the molecules under investigation from other perturbing factors as much as possible. Furthermore it offers the possibility of reducing the inhomogeneous spectral line broadening caused by Doppler-broadening.

Recently, Reichel *et al.* [1] used the Raman cooling method to cool the cesium atoms in one dimension by using pulses with a square time envelope. Lawall *et al.* [2] reported the first observation of subrecoil laser cooling in three dimensions, where they used the method of velocity selective coherent population trapping. Jones *et al.* [3] used the molecular spectroscopy of the sodium molecule to determine the $Na(3p)$ lifetime and measured the predicted but previously unobserved effect of retardation in the interaction between two atoms. Kulin *et al.* [4] used the laser induced adiabatic passage to

coherently manipulate the atomic wave packets resulting from subrecoil laser cooling in one, two and three dimensions by velocity selective coherent population trapping [5,6].

Collimated molecular beams had been used to reduce the translational or Doppler broadening. This reduction could be achieved by crossing the molecular beam with the laser beam perpendicularly. The internal cooling of the molecules reduces the spectral rotational congestion by cooling the internal degrees of freedom in the peculiar environment of a freely expanding gas jet.

By applying these symmetry operations the electronic energy and consequently the electronic hamiltonian, H_E must be invariant because neither of these operations alters the axially symmetric potential field in which the electrons move, and so cannot alter the energies of the electronic states [7].

As a contribution to the elucidation of the nature of the vibronic bands of Na_2 , Biesheuvel et al. [8] measured the spectra of a number of vibronic bands in the region between 1000 and 1400cm^{-1} by exciting a supersonically cooled beam of Na_2 molecules with a narrow-band : Sapphire ring laser. They also analyzed [9] the fine and hyperfine structure of each rotational transition by using an effective hamiltonian.

Sub-Doppler laser polarization spectroscopy of the photofragments were studied by Vasyutinskii [10]. He–Jiang *et al.* [11] used intermodulated laser induced fluorescence spectroscopy to obtain the Sub Doppler spectrum at a resolution of about 150 MHz.

For a homonuclear molecule the wave equation of the system remains unchanged if the two nuclei are exchanged. This means that, if the coordinates of the first nucleus (x_1, y_1, z_1) are exchanged with those of the second nucleus, (x_2, y_2, z_2) wherever they occur. Therefore, for an exchange of the nuclei the total eigenfunction remains unchanged, which is known as symmetric, or only changes its sign, which is known as antisymmetric. Therefore, for sodium molecules, in case of $\Lambda = 0$, there is no component of the electronic angular momentum along the internuclear axis. For the rotational electronic state Σ_g the even number (positive) rotational levels are symmetric (S) and the odd number (negative) rotational levels are antisymmetric (a) throughout, while for the rotational electronic state Σ_u state, the reverse is the case [12].

2. Experimental Arrangement:

A continuous wave (CW) ring dye laser is a most useful system for biological, medical, scientific and technical applications [13-15] because of the following reasons:

- 1- Wavelength tunability over a wide spectral range;
- 2- Single-frequency radiation source with high spectral power;
- 3- It eliminates several limitations of the standing wave dye laser such as: spatial hole burning, or small output power.

a: It can be pumped harder than a standing wave laser, and can deliver higher single frequency output power due to the higher conversion efficiency in a travelling wave system.

An argon-ion laser (Coherent Radiation) was used with a maximum power of 15 watts (all lines) for pumping of the ring laser (DCM dye) 9 watts were, however sufficient. This gave a dye laser output up to 1 W in a single mode operation. The pumping laser beam is focused into the dye jet by a high reflector broad band mirror (pump mirror).

An etalon Brewster plate and PZT are controlled by a 10-kHz bandwidth frequency servo loop [16] which locks the laser frequency to that of a stable reference interferometer. For optimum laser performance it is necessary to control the thermal lens effects of the jet stream [17-19] to obtain good frequency stability of a single frequency dye laser produced by jitter in the pressure of the mechanical jet pump.

DCM dye (Dicyanoethylene) dissolves in benzylalcohol and ethyleneglycol, was used as a laser active medium, which has a molecular weight 303.36 and the solution possesses sufficient viscosity for a stable jet stream and operated with a nozzle pressure of 6.124 atm. by using a radiant dye nozzle 200 μm and a circulator model (coherent 591 module)[20 & 21].

The signal of the laser induced fluorescence in sodium molecules was measured with the system shown in Fig. (1), which includes the Auto-Scan ring dye laser and the molecular beam system. The laser beam was transported to interaction region with molecular beam by means of an optical fiber with an input coupler between laser beam and the fiber.

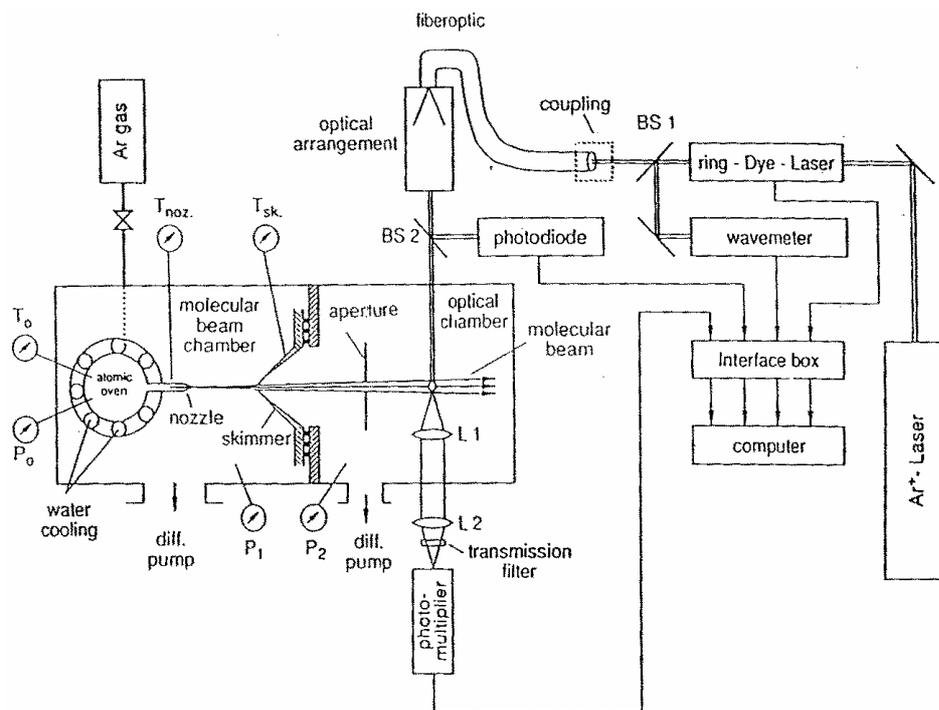


Fig. (1): The experimental arrangement of laser induced fluorescence of Na_2 -molecule .

The data were collected by using the coherent Auto-Scan program [22], i.e.,

- Entering the wanted wavelength;
- Wavelength scanning and data storage; and
- System control.

The coherent Auto-Scan system consists of a wavelength meter, interface box, 699-29 control box, and IBM compatible computer. This Auto-Scan system scans over the entire wavelength region covered by the gain medium in steps of 1 MHz. It provides absolute wavelength read out within an accuracy $<4 \times 10^{-7}$, determines the wavelength of the output beam, accepts the wanted wavelength change from the user via the computer, the residual Doppler width could be reduce below 10 MHz

Furthermore it controls the laser cavity length and reference cavity during operation, and it also converts the voltages which come as external input data into a digital representation to be stored in the computer.

3. Results and Discussions:

For illustration of the measured spectra of the Na_2 molecule, a section of the $(2 \leftarrow 0)$ and $(7 \leftarrow 0)$ bands of the $(X^1 \Sigma_u^+) \leftarrow (A^1 \Sigma_g^+)$ system are shown in Figures (2.1a and 2.1b)

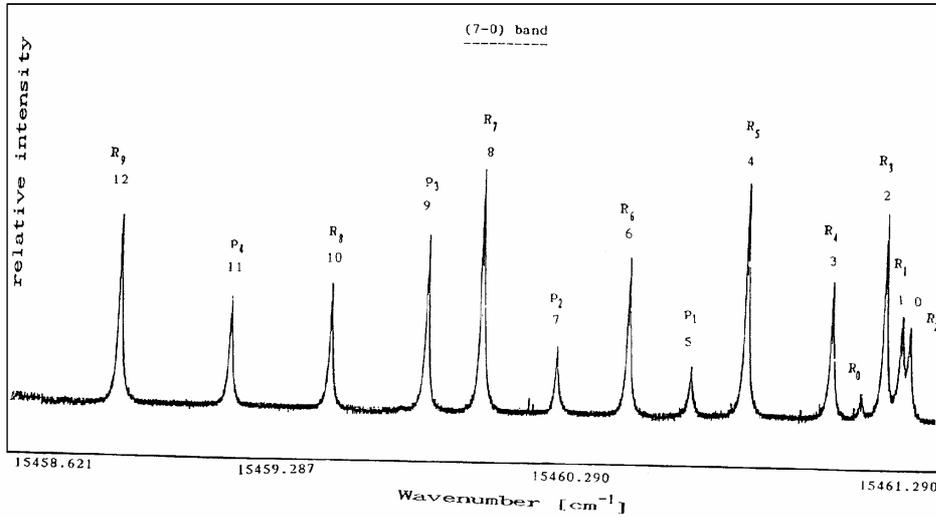


Fig. (2.1a): The measured spectrum of $(2 - 0)$ band

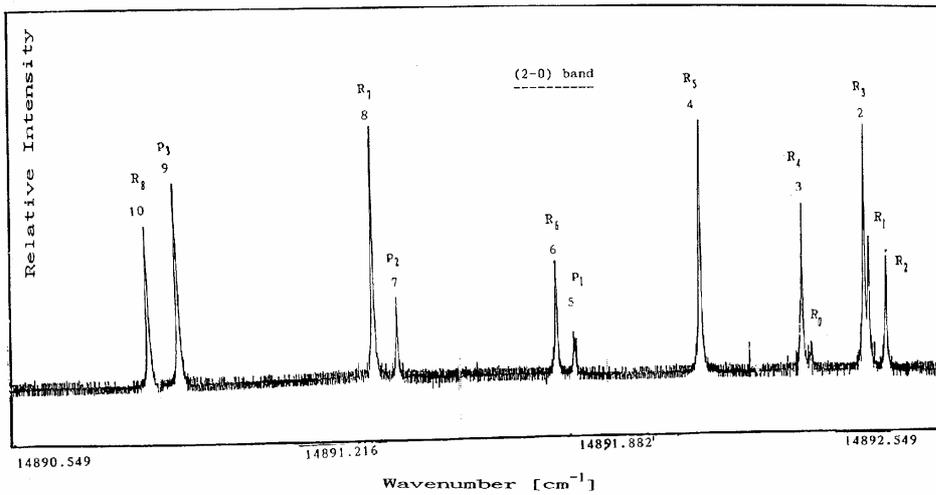


Fig. (2.1b): The measured spectrum of $(7 - 0)$ band

According to the J-assignments of the lines, it is possible to assign the measured spectral lines of the two measured bands as shown in Tables (1) and (2).

Furthermore, by testing with different J-values a good J-assignments from the least-squares-fit the wavenumbers [23] $\nu(\nu', J', \nu'', J'')$ of the assigned lines are recalculated and compared with the experimental values as shown in Tables (1) and (2). The standard deviation (σ_{rms}) of the fit was $\sigma_{\text{rms}} = 0.003 \text{ cm}^{-1}$, the analysis of the measured excitation spectra, with linewidths down to 10 MHz, showed that the Doppler width could be reduces below 10^{-3} cm^{-1} [29]. This means that the mean deviation between the measured and the calculated wavenumbers is about 0.003 cm^{-1} . This correspondings to the experimental accuracy.

Figures (3) and (4) show the fit diagram of the two measured bands ($2 \leftarrow 0$) and ($7 \leftarrow 0$) respectively for both R- and P- branches. On the right side of the diagram the deviations are shown on an expanded scale. In accordance with J-assignments. The measured spectral line positions and the assignments were given as an input file to a home written [22] Fit-program with the least-square-fit-routine program by using a 468- computer in turbo-pascal 6.0.

The two bands of the transition $A^1 \Sigma_u^+ \longrightarrow X^1 \Sigma_g^+$ which were measured in the spectrum, of the sodium molecule, start from a common lower vibrational level $\nu'' = 0$. By using the combination difference method for R- and P-branches outlined by Herzberg [24], which were formulated in Dunham equations [25], the fit shown in Figures (3) and (4.) was obtained. From this fitting we get the ground-state ($X^1 \Sigma_g^+$) rotational constants :

For ($2 \leftarrow 0$) band : Band origin (ν_0) = $14892.1199 \pm 0.0013 \text{ cm}^{-1}$;

Band maximum = $14892.5076 \text{ cm}^{-1}$;

For ($7 \leftarrow 0$) band : Band origin (ν_0) = $15460.9988 \pm 0.0015 \text{ cm}^{-1}$;

Band maximum = $15461.3579 \text{ cm}^{-1}$;

Table (1) : Lines assignments of R- and P- branches for the (0 → 2) band.

J''	R-branch	P-branch
	$\nu_{\text{exp.}} (\text{cm}^{-1})$	$\nu_{\text{exp.}} (\text{cm}^{-1})$
0	14892.3395	
1	14892.4673	14891.8158
2	14892.5068	14891.4209
3	14892.4503	14890.9286
4	14892.3247	14890.3470
5	14892.0920	14889.6772
6	14891.7733	14888.9185
7	14891.3679	14888.0792
8	14890.8554	14887.1405
9	14890.2717	14886.1065
10	14889.5978	14885.0006
11	14888.8271	14883.7997
12	14887.9762	14882.5006
13	14887.0249	14881.1234
14	14885.9887	
15	14884.8628	
16	14883.6313	
17	14882.3480	
18	14880.9598	

Table (2) : Lines assignments of R- and P- branches for the (0 → 7) band.

J''	R-branch	P-branch
	$\nu_{\text{exp.}} (\text{cm}^{-1})$	$\nu_{\text{exp.}} (\text{cm}^{-1})$
0	15461.2083	
1	15461.3528	15461.1158
2	15461.3293	15460.6883
3	15461.2799	15460.2827
4	15460.8539	15459.7866
5	15460.495	15459.1936
6	155460.042	15458.8552
7	15459.4986	15458.1165
8	15458.8570	15457.2873
9	15458.5011	15456.3612
10	15457.7214	
11	15456.8451	

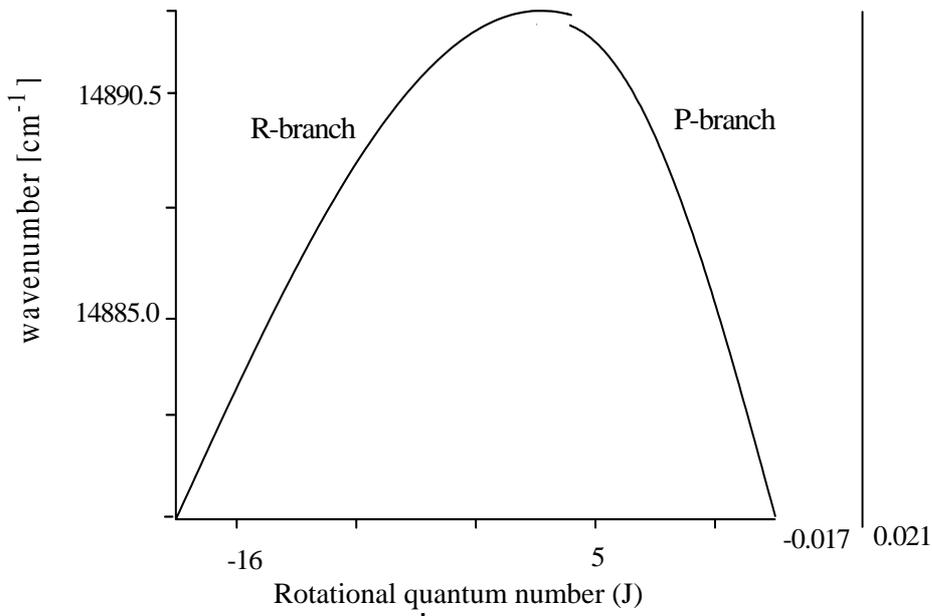


Fig. (3): The fitting of J – assignment of (2 – 0) band.

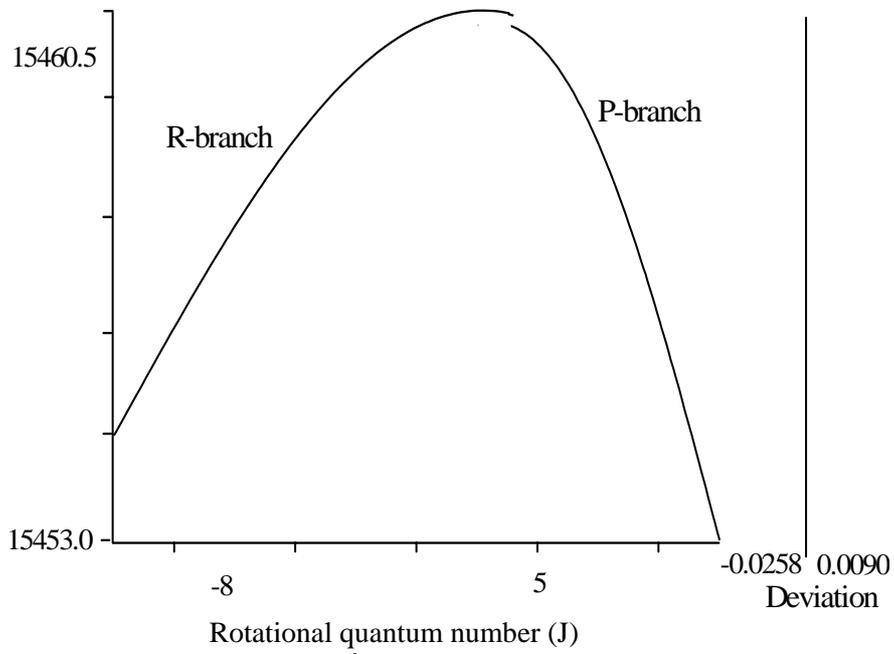


Fig. (4): The fitting of J – assignment of (7 – 0) band

The rotational constants of the ground state are

$$B_v'' = 0.154356628 \text{ cm}^{-1}; \text{ and } v'' = 0;$$

by using this value in equation

$$B_e'' = B_v'' + \alpha_e'' \left(v'' + \frac{1}{2} \right), v'' = 0$$

where

$\alpha_e'' = 0.0008736 \text{ cm}^{-1}$ [26], the constant $B_e'' = 0.154793428 \text{ cm}^{-1}$ could be obtained.

The obtained rotational constants of the excited state are

$$B_v' = 0.108163495; \quad \text{and}$$

$$B_e' = 0.112531495.$$

It was possible to obtain the moment of inertia (I_e) and the intermolecular distance (r_e) in the equilibrium position of the molecule (minimum of the potential curve) for both ($X^1 \Sigma_g^+$) state and $A^1 \Sigma_g^+$ state according to the equations

$$B_e = (h/8\pi^2 c I_e); \text{ and } I_e = \mu r_e^2$$

where $\mu = \frac{1}{2}m$ is the reduced mass of the Na_2 -Molecule; $m = 23 \text{ amu}$.

These results are shown in Table (3) as a comparison with the literatures.

The number of molecules $N_i(J)$ in the rotational level J of the lowest vibrational level at the temperature T is proportional to

$$N_i(J) \propto (2J+1) \exp(-BJ(J+1)hc/KT)$$

The relative intensity distribution of the lines in the rotational band is expected by the product of the rotational population distribution $N(J)$ in the ground state and the Hönl-London factors [12] as :

$$I(J) \propto \left(\frac{2}{Q_r} \right) \cdot g_I \cdot S_I \cdot \exp\left(\frac{-J(J+1)}{Q_r} \right)$$

where $Q_r = kT_{rot} / (hcB)$

k : Boltzmann's constant;

h : Plank's constant;

c : Velocity of light; and

$g_1 = 2(I + 1)$ Statistical weight of the nuclear spins

The Hönl-London-Factor S_1 for $A | \Sigma_g \longrightarrow X | \Sigma_g$ transition is

$$S_1 = J'' + 1 \quad \text{for} \quad R\text{-branch;}$$

and $S_1 = J'' + 1$ for P -branch.

For J_1 and J_2 the rotational temperatures for R - and P - branch were calculated in the final form by using Dunham equations [25], we reach to the following equation :

$$T_{rot} = \frac{(J_1(J_1 + 1) - J_2(J_2 + 1))hcB}{\ln((2J_1 + 1)I(J_2)) / ((2J_2 + 1)I(J_1))}$$

The rotational temperature of the Na_2 -molecule calculated from this equation was 18 K.

4. Conclusion:

Using a collimated cold molecular beam it was possible to reduce the Doppler width of the lines in the Na_2 spectra. It was shown that both the cooling and the collimation are essential to allow the complete resolution of the spectral lines with linewidths down to 10^{-3}cm^{-1} .

The assign of the spectral lines was performed with the method of combination differences. The least-square-fits show a low rms deviation of 0.08cm^{-1} . The rotational constants of sodium molecule were calculated for the ground and excited states, the assignments of the observed spectral lines are made according to the selection rules for both the P- and R- branches, and the rotational temperature of the sodium molecule was obtained as 18K.

Table (3) : The obtained molecular constants of sodium molecules and its comparison with the literatures.

Mol. Constant	Present Work	Literature
1: $X^1 \Sigma_g^+$		
$B_e''(\text{cm}^{-1})$	$0.15479 \pm 6.784\text{E-}5$	0.15485 [27]; 0.154641 [28]
$I_e''(\text{kg.m}^2)$	1.80715E-45	1.15098E-45 [27]; 1.80893 [28]
$r_e''(\text{A}^\circ)$	3.06754	3.07745 [27]; 3.07773 [28]
2: $A^1 \Sigma_g^+$		
$B_e'(\text{cm}^{-1})$	$0.11253 \pm 6.091\text{E-}5$	0.11092[28]; 0.11078 [24]
$I_e'(\text{Kg.m}^2)$	2.48584E-45	2.52198E-45 [28]; 2.5251E-45[24]
$r_e'(\text{A}^\circ)$	3.59774	3.63403 [28]; 3.63628 [24]

References:

1. J. Reichel, M. B. Dahan, F. Bardou, E. Peik, S.Rand, C. Salmen and C. Cohen, 12th Internatinal Conf. of Laser Spectroscopy, 11-16 June, Italy, (1995).
2. J. Lawall, S. Kulin, B. Saubamea, N. Bigelow, M. Leduce, C. Cohen, 12th Jnt. Conf. of Laser Spectroscopy, 11-16 June, Italy, (1995).
3. M. Jones, P. Julienne, P. Lett, W. Philip, E. Tiesinga, and C. Williams, *Europhysics Letters*, **35**, JSS: 2,85(1996).
4. S. Kulin, B. Saubamea, E. Peik, J. Lawall, T. Hijmans and C. Cohen, *Physical Review Lett.* **78**, ISS: 22, 4185(1997).
5. W. Philips, C. Ekstrom, W. Golding, S. Rolston, Proceeding of the 5th symposium on frequency standards and Metrology, USA (1997).
6. W. Philips, 14th International Conf. on Atomic Phys., 3, July-5A4g., (1994).
7. G. W. King, "*Spectroscopy and Molecular Structure*", Holt, Rinehart and Winston, Inc. (1964).
8. C. A. Biesheuvel ; J. Bulhuis ; MHM Janssen ; S. Stolte ; J. G. Snijders; *Journal of Chemical Physics.* **109**, (22), 9701 (1998).

9. C. A. Biesheuvel; J. Bulthuis ; M.H.M. Janssen; S. Stolte ; J. G. Snijers; *Journal of Chemical Physics*. **112**, (8), 3633 (2000).
10. Vasyutinskii; Zhurnal; Teckhnicheskoi ; *Fizik* **69**, (9), 41 (1999).
11. He. Jiang; Ma. Chensheng ; Gs. M. Tong; As. C. Cheung; *Journal of Molecular Structure*. **480-481**, 277 (1999).
12. G. Herzberg : *Spectra of Diatomic Molecules*, vol.1, Van Nostrand Reinhold Company Inc. Neatherlands, (1950).
13. S. M. Jarrett and J. F. Young: *Optics letters*, **4**, (6), 176 (1979).
14. K. H. Drexhage: "Dye Lasers", Chapter 4: Edited by F. P. Schafer (Springer, Berlin, (1973).
15. G. Nair, *Progress in Quantum Electronics*, **7**, 153 (1982).
16. Cohernt: CR 699-29 Auto Scan Operator Manual (1985).
17. H. W. Koginic, E. P. Ippen, A. Dienes, and C. V. Shnak, *IEEE J. Quant. Electron*, **QE-8** 373(1972).
18. B. Wellegehausen, L. Laepple and H. Welling: *Appl. Phys.*, **6**, 335 (1975).
19. Teschke, J. R. Whinnery, and A. Dienes, *IEEE J. Quant. Electron.*, **QE-12**, 513 (1976).
20. P. R. Hammond: Laser dye DCM, Its special properties, *Optics Comm.*, **29**, 331(1979).
21. U. Brackmann, *Lambdachrome "Laser dyes"*, *Lambdaphysik GmbH*, D-3400 Gottingen, W. Germany (1986).
22. V. Boutel, Doktor Arbeit, Fachbereich Physik, Uni. Kaiserslutern, Kaiserslutern, Deutschland (1991).
23. D. L. Albritton, A. L. Schmeltekopf, and R. N. Zare: *Modern Research*, vol. II edited by K. N. Rao, Academic Press, (1976).
24. G. Herzberg: *Constants of diatomic molecules*, vol. IV, Litton Educational publishing Inc. (1979).
25. J. L. Dunham: *Phys. Rev.*, **41**, 721 (1932).
26. V. Bossel, *Entropie*, **42**, 12 (1971)
27. W. Demtröder, M.Mclintock and R. N. Zare; *J.Chem. Phys.*, **51**, (12), 54 95 (1969).
28. Babaky and K. Hussein. *Can. J. Phys.*, **67**, 912 (1989).
29. Kullmer, and W. Dem troder; *J. Chem. Phys.* **81**(7), 2919 (1984).