RESEARCH Revista Mexicana de Física **66** (5) 568–572 SEPTEMBER-OCTOBER 2020

Franck-Condon factors and r-centroids of D-A and D-B band systems of AIO molecule

C. T. Londhe[a] and Hewa Y. Abdullah[b,c,*]
[a] *Department of Physics, Mahatma Gandhi Mahavidyalaya, Ahmedpur- 413515, India.*
[b] *Division of Nuclear Physics, Advanced Institute of Materials Science, Ton Duc Thang University, Ho Chi Minh City, Vietnam.*
[c] *Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Vietnam.*
[*] *e-mail: hewa.abdullah@tdtu.edu.vn*

Received 17 April 2020; accepted 20 May 2020

Franck-Condon factors and r-centroids were computed for the D$^2\Sigma^+$ - A$^2\Pi_i$ and D$^2\Sigma^+$ - B$^2\Sigma^+$ band systems of the aluminum oxide molecule for the $v' = 10$; $v" = 10$ matrix using the method developed by Jarmain and McCallum. The latest Fourier-transform Spectrometer molecular constants of the ground and excited state are used. The intensities of these bands are discussed, and the Franck-Condon factors and r-centroids obey the established relationships.

Keywords: Franck-Condon factors; r-centroids; AlO molecule.

PACS: 33.20.Tp; 33.60.+q; 33.70.Ca DOI: https://doi.org/10.31349/RevMexFis.66.568

1. Introduction

The Franck-Condon factor is an important entity in the diatomic molecular spectra. These factors give an idea about the intensity of a band appearing in a particular band system of a molecule. The Franck-Condon factor is an overlap of the wave-functions of two vibrational states taking part in a transition. In 1966, Krishnamachari *et al.*, [1] observed a new band system of aluminum oxide (AlO) which was D$^2\Sigma^+$ - X$^2\Sigma^+$ falling into the region of 2200- 2800 Å. They used the direct current (DC) arc at low pressure to excite this band system. In the furtherance of these studies, Singh *et al.* [2] reported the rotational constants of D$^2\Sigma^+$ state by analyzing the 2-0, 1-0, 0-0 and 0-1 bands of the D$^2\Sigma^+$ - X$^2\Sigma^+$ transition. The D-X system was reinvestigated again in 1973 by Singh and Saxena [3], who gave the rotational analysis of 11 more bands. In 1985, Singh and Saxena [4] excited AlO and photographed many bands of D$^2\Sigma^+$ - A$^2\Pi$ and C$^2\Pi$ - A$^2\Pi$ intercombination systems of AlO, and the rotational constants of the A$^2\Pi$ state were derived. Rotational perturbations have been observed in the A$^2\Pi$ state. In the present study, the Franck-Condon factors of D-A and D-B band systems will be calculated using the latest molecular constants. These FCF and r-centroids will be added, and new information not reported earlier in the literature.

2. Method of computation

2.1. Franck-Condon factors

The Franck-Condon factor is the square of the integral over the product of the vibrational eigenfunction of the two states involved (the so-called overlap integral). It controls the intensity distribution from band to the band across a system. Franck Condon factors and r-centroids play an important role in finding out the variation of electronic transition moment with internuclear distance [5,6]. The principle based on the electronic jumps is faster compared to the nuclear motion. This principle directs us to see that the bands are intense if the jump from a higher vibrational level to a lower level takes place from either the $r_{\min}$ or $r_{\max}$ position on the potential energy curves' straight to lower level, because then there is a minimum or zero change in position, *i.e.*, $\Delta r (\Delta r = r_{e'} - r_{e''})$ and in momentum is possible. In emission, for one v' value, there are two values of v". The locus of such points on the Deslandres table called the Condon parabola [5]. If the Condon parabola is wide open, then bands of many progressions and sequences appear in a band system. On the other hand, if the Condon parabola is narrow and tends to degenerate in a diagonal line in the Deslandres table along the main sequence, then only the bands of the 0-0 sequence or the 0-1 or 1-0 sequences will hardly appear. The intensity depends on many other factors, such as the probability of transition, the population of the upper state from where the transition is taking place, the line strength or band strength (depending on the rotational line or vibrational band), and the electronic transition moment.

In emission, the expression is given as:

$$I_{em}^{v'v''} = \left(\frac{64}{3}\right) \pi^4 c N_{v'} \upsilon^4 \bar{R}_{e^2} \left[\int \Psi_{v'} \Psi_{v''} dr\right]^2, \quad (1)$$

where c is the velocity of light, $N_{v'}$ is the number of molecules in the v'^{th} level, υ is the frequency of radiation, $\bar{R}_e$ is the average value of Re (i.e., electronic transition moment), and $\Psi_{v'}$ and $\Psi_{v''}$ are the wave functions of the v' and v" levels, respectively.

In absorption, the expression is given by:

$$I_{abs}^{v'v''} = \left(\frac{8\pi^3}{3hc}\right) I_0 \Delta_x N_{v''} \upsilon \bar{R}_{e^2} \left[\int \Psi_{v'} \Psi_{v''} dr\right]^2, \quad (2)$$

TABLE I. Molecular Constants of $^{27}Al^{16}O$.

STATE	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	r_e	α_e
$D^2\Sigma^+$	40266.7	819.6	5.8	-	0.5652	1.7234	0.0046
$B\ ^2\Sigma^+$	20685.04	870.369	3.651	0.00096	0.608976	1.618	0.00507
$A\ ^2\Pi_i$	5282	728.52	4.888	0.0858/ 0.00387	0.537169	1.7708	0.005002

Note :All constants are in cm^{-1} except r_e, which is in Å and μ, is in amu

TABLE II. Franck-Condon Factors and r-centroids of $D^2\Sigma^+$ - $A\ ^2\Pi_i$ Band System of AlO molecule.

V' V''	0	1	2	3	4	5	6	7	8	9	10
0	**0.7923**	**0.1798**	0.0248	0.0027	0.0003	-	-	-	-	-	-
	1.7503	1.6591	1.5699	1.4812	1.3976						
1	0.1877	**0.4602**	**0.2764**	0.0639	0.0102	0.0014	0.0002	-	-	-	-
	1.8528	1.762	1.6712	1.584	1.4983	1.4188	1.3606				
2	0.0189	**0.3046**	0.2335	**0.3076**	0.1072	0.0231	0.0041	0.0007	0.0002	-	-
	1.9554	1.8633	1.7744	1.6832	1.5977	1.5148	1.439	1.3835	1.3659		
3	0.001	0.0513	**0.3638**	0.0936	**0.2911**	0.146	0.0413	0.0092	0.002	0.0005	0.0002
	2.0618	1.9663	1.8736	1.7893	1.6953	1.6113	1.5309	1.4583	1.4049	1.3846	1.3976
4	-	0.004	0.0917	**0.3782**	0.0218	**0.2441**	0.1735	0.0627	0.0172	0.0044	0.0013
		2.072	1.9774	1.8837	1.815	1.7077	1.6247	1.5464	1.4766	1.4249	1.4022
5	-	0.0001	0.0094	0.1355	**0.3605**	0.0001	0.1822	**0.1854**	0.0847	0.0281	0.0086
		2.2297	2.0823	1.9887	1.8936	2.3324	1.7208	1.638	1.5616	1.4941	1.4436
6	-	-	0.0004	0.0176	0.1787	**0.3219**	0.0119	0.1187	**0.1801**	0.1034	0.0412
			2.2486	2.0927	2.0002	1.9031	1.75	1.7358	1.6516	1.5763	1.5106
7	-	-	-	0.0008	0.0288	0.2184	**0.2721**	0.043	0.0638	**0.1594**	0.1155
				2.2693	2.1033	2.0118	1.9125	1.7769	1.7556	1.6657	1.5907
8	-	-	-	-	0.0015	0.0426	0.2527	**0.2186**	0.0813	0.0244	**0.1275**
					2.2918	2.1141	2.0236	1.9217	1.7876	1.7902	1.6811
9	-	-	-	-	-	0.0024	0.0586	0.2809	0.1672	0.1177	0.0037
						2.3162	2.1253	2.0353	1.9314	1.7934	1.9105
10	-	-	-	-	-	-	0.0035	0.0761	**0.3034**	0.1215	0.1456
							2.3424	2.137	2.0468	1.9428	1.7963

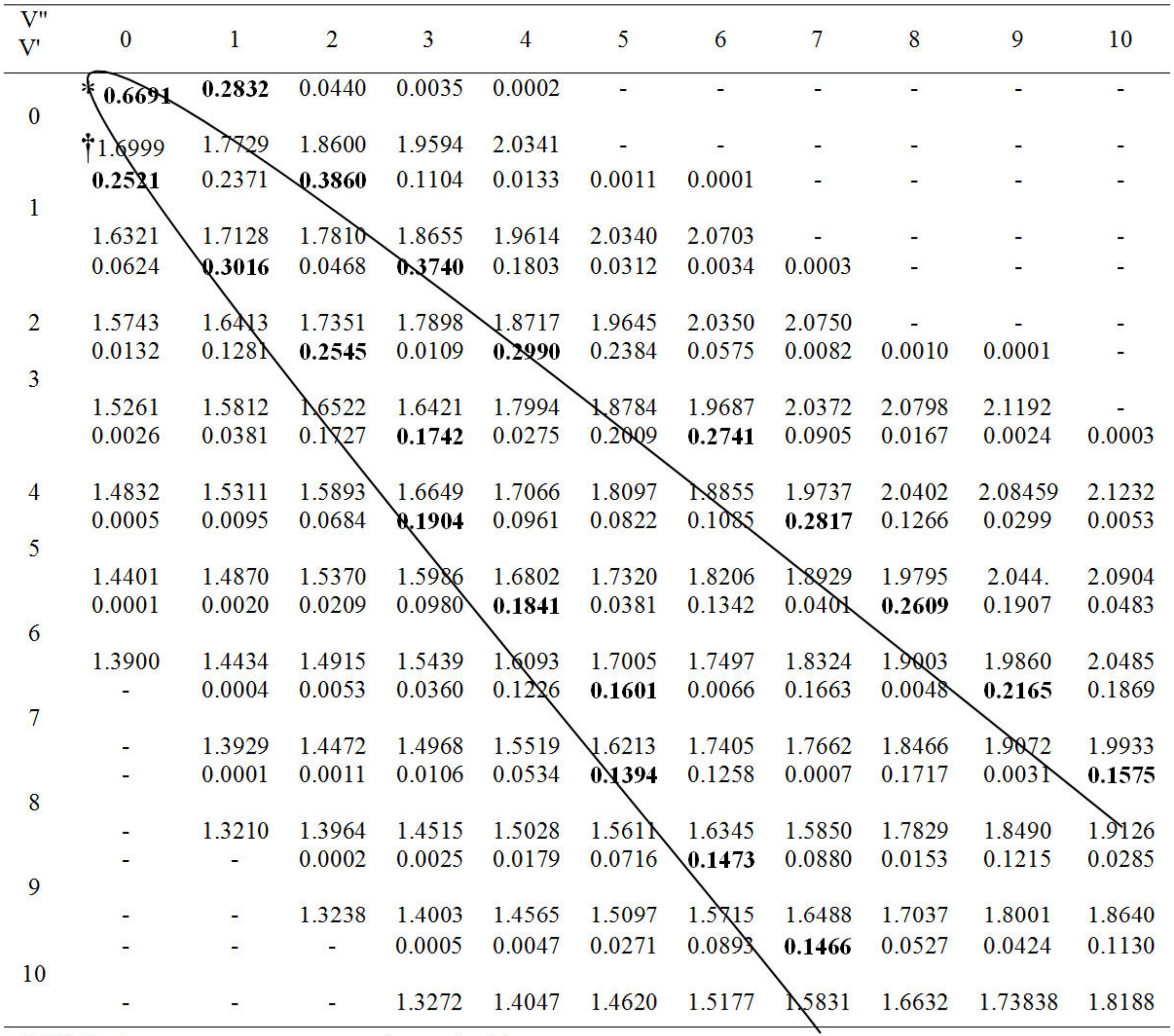
* FC Factor † r-centroids

where h is the Planck's constant, I_0 is the initial intensity, Δx is the thickness of the medium, and $N_{v''}$ is the number of molecules in the v" level. $\bar{R}_e$ and R_e are related to each other by the expression:

$$R_e^{v'v''} = \bar{R}_e \left[\int \Psi_{v'} \Psi_{v''} dr \right]. \qquad (3)$$

The Franck Condon principle, which governs the intensities of the bands based on the assumption that the variation

TABLE III. Franck-Condon Factors and r-centroids of $D^2\Sigma^+$ - $B^2\Sigma^+$ Band System of AlO molecule.



V'' V'	0	1	2	3	4	5	6	7	8	9	10
0	* **0.6691**	**0.2832**	0.0440	0.0035	0.0002	-	-	-	-	-	-
	† 1.6999	1.7729	1.8600	1.9594	2.0341	-	-	-	-	-	-
1	**0.2521**	0.2371	**0.3860**	0.1104	0.0133	0.0011	0.0001	-	-	-	-
	1.6321	1.7128	1.7810	1.8655	1.9614	2.0340	2.0703	-	-	-	-
2	0.0624	**0.3016**	0.0468	**0.3740**	0.1803	0.0312	0.0034	0.0003	-	-	-
	1.5743	1.6413	1.7351	1.7898	1.8717	1.9645	2.0350	2.0750	-	-	-
3	0.0132	0.1281	**0.2545**	0.0109	**0.2990**	0.2384	0.0575	0.0082	0.0010	0.0001	-
	1.5261	1.5812	1.6522	1.6421	1.7994	1.8784	1.9687	2.0372	2.0798	2.1192	-
4	0.0026	0.0381	0.1727	**0.1742**	0.0275	0.2009	**0.2741**	0.0905	0.0167	0.0024	0.0003
	1.4832	1.5311	1.5893	1.6649	1.7066	1.8097	1.8855	1.9737	2.0402	2.08459	2.1232
5	0.0005	0.0095	0.0684	**0.1904**	0.0961	0.0822	0.1085	**0.2817**	0.1266	0.0299	0.0053
	1.4401	1.4870	1.5370	1.5986	1.6802	1.7320	1.8206	1.8929	1.9795	2.044.	2.0904
6	0.0001	0.0020	0.0209	0.0980	**0.1841**	0.0381	0.1342	0.0401	**0.2609**	0.1907	0.0483
	1.3900	1.4434	1.4915	1.5439	1.6093	1.7005	1.7497	1.8324	1.9003	1.9860	2.0485
7	-	0.0004	0.0053	0.0360	0.1226	**0.1601**	0.0066	0.1663	0.0048	**0.2165**	0.1869
	-	1.3929	1.4472	1.4968	1.5519	1.6213	1.7405	1.7662	1.8466	1.9072	1.9933
8	-	0.0001	0.0011	0.0106	0.0534	**0.1394**	0.1258	0.0007	0.1717	0.0031	**0.1575**
	-	1.3210	1.3964	1.4515	1.5028	1.5611	1.6345	1.5850	1.7829	1.8490	1.9126
9	-	-	0.0002	0.0025	0.0179	0.0716	**0.1473**	0.0880	0.0153	0.1215	0.0285
	-	-	1.3238	1.4003	1.4565	1.5097	1.5715	1.6488	1.7037	1.8001	1.8640
10	-	-	-	0.0005	0.0047	0.0271	0.0893	**0.1466**	0.0527	0.0424	0.1130
	-	-	-	1.3272	1.4047	1.4620	1.5177	1.5831	1.6632	1.73838	1.8188

* FC Factor † r-centroids

of $R_e^{v',v''}$ with r, *i.e.*, internuclear separation is slow. The Franck Condon principle also states that the electron jumps in a molecule take place so fast in comparison to the vibrational motion that immediately afterward the nuclei still have very nearly the same relative position and velocity as before the jump. In short, the bands obeying this principle are strong. If the minima of the potential energy curve of the upper electronic state and the lower electronic state lie above one another or $r_e' \sim r_e''$ the 0-0 sequences may likely appear with strong intensities and other sequences like $\Delta v = \pm 1$, etc. may not be seen at all. If $r_e' > r_e''$ or minima of the upper PE curve is displaced slightly with respect to minima of lower PE curve then bands of the same intermediate sequence may be stronger. If $r_e' \gg r_e''$, then the maxima of intensity may lie in the continuum. In the case of emission, there are usually two maxima in v'' progressions because molecule in the upper electronic state can be in any excited vibrational level and jumps can occur from either turning points on PE curve. Details are given in Herzberg [5], and Straughan and Walker [6].

The quantity in the square bracket appearing in Eq. (1) and (2) is known as Franck Condon factor usually denoted by $q_{v'v''}$ and expressed as

$$q_{v'v''} = \left[\int \Psi_{v'} \Psi_{v''} dr\right]^2 . \tag{4}$$

There are different methods of calculating Franck-Condon factors. Expressions are not simple, as the expression for wave-functions $\Psi_{v'}$ and $\Psi_{v''}$ are very complex and sometimes may involve special functions. Chakraborty and Pan [7] have surveyed these methods Sharp [8]. Telle *et al.* [9] have also given the methods to calculate Franck-Condon factors. The comparative study of the FCFs and r-centroids carried out by Nadhem *et al.*, [10,11] and Ramon S. da Silva *et al.*, [12]. In the present study, we used a program developed by Jarmain and McCallum [13,14] to calculate these factors. In this program, the Klein-Dunham series is used to represent the spectroscopic input data, namely, the vibrational and rotational constants. The RKR potential curves are then computed. The Schrödinger wave equation is solved numerically, and the resulting vibronic eigenfunctions are used to calculate the Franck Condon factors and r-centroids [10,11,15].

2.2. r-centroids

Various methods of calculation of r-centroids are described by Jarmain and Nicholls [14]. r-centroids is defined as

$$r_{v',v''} = \frac{\int \Psi_1^{v'}{}_{(r)} r \Psi_1^{v''}{}_{(r)} dr}{\int \Psi_1^{v'}{}_{(r)} \Psi_2^{v''}{}_{(r)} dr}. \qquad (5)$$

Where $\Psi_1^{v'}{}_{(r)}$ and $\Psi_2^{v''}{}_{(r)}$ are the vibrational wave functions of the level v' and v''. If these are normalized, then the denominator of Eq. (5) is equal to unity. The methods for the calculation of r-centroids are described by Jarmain and Nicholls [14], which are (i) direct method, (ii) quadratic equation method, and (iii) difference method. In the present study the direct numerical method is used for the computation of r-centroids.

2.3. Molecular constants

The vibrational and rotational constants of the A$^2\Pi_i$, B$^2\Sigma^+$ and D$^2\Sigma^+$ states are summarized in Table I and are derived from the experimental studies [16-20]. The Franck-Condon factors and r-centroids of the D-A and D-B band systems are computed and presented in Tables II and III, respectively.

3. Results and discussion

The Franck-Condon factors and r-centroids of the band systems B$^2\Sigma^+$ - $X^2\Sigma^+$, C$^2\Pi_r$ - $X^2\Sigma^+$ and C$^2\Pi_r$ -A$^2\Pi_i$ was reported earlier by Londhe *et al*. [21]. The Franck-Condon factors and r-centroids of the D$^2\Sigma^+$ - $X^2\Sigma^+$ system were earlier reported by Smirnov *et al*. [22,23] in 1978. Later, Mummigatti and Jyoti [24] reported the Franck-Condon factors of 42 bands of this system and Reddy *et al*. [25] reported the Franck-Condon factors of 23 bands. In the present study, the Franck-Condon factors and r-centroids of the D$^2\Sigma^+$ - A$^2\Pi_i$ and D$^2\Sigma^+$ - B$^2\Sigma^+$ systems are computed using the constants given by Singh *et al.*, [17,18].

The locus of the strongest band is a parabola called the Condon parabola. The Franck-Condon factors give a measure of the relative band intensities for an electronic transition. The Franck-Condon factors of such bands are shown in bold in Tables II and III. The Δr values, *i.e.*, $r_e' - r_e''$ (where re is the internuclear distance in a particular electronic state), of various transitions can be calculated from Table I. It is clear from this table, the value of Δr of D-B transitions is 0.1164 A^0,so the Condon parabolas must be wider [5]. On the other hand, the value of Δr of the D-A band system is 0.0474 A^0, which is smaller than the previous values of Δr. Therefore, the Condon parabola of the D-A band system is expected to be narrow compared to earlier ones shown in Table II. Only a few bands of the ± 1 sequences appear with appreciable intensity.

4. Conclusion

Franck-Condon factors and r-centroids were computed for the D$^2\Sigma^+$ - A$^2\Pi_i$ and D$^2\Sigma^+$ - B$^2\Sigma^+$ band systems of the AlO molecule. The difference (Δr) in the equilibrium internuclear distances of the upper and lower states of the D-A and D-B band systems are 0.0474 A0 and 0.1164 A0, respectively. Therefore, the Condon parabola of D-A must be narrow in comparison to that of the D-B band system. The bands of the $\Delta v = \pm 1$ sequences appear with maximum intensity.

Acknowledgments

The author expresses sincere thanks to Dr. K. Sunanda, Dr. M. D. Saksena, and Dr. M. N. Deo, Bhabha Atomic Research Center, Trombay, Mumbai, and Dr. S. H. Behere, Professor, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad for encouragement and helpful suggestions during this research work.

---

1. S. Krishnamachari, N. Narasimham, and M. Singh, *Canadian J. Phys*. **44** (1966) 2513-2516. `http://dx.doi.org/10.1139/p66-204`
2. M. Singh, *Proc. Indian Acad. Sci. A*, **LXXI** (1970) 82.
3. M. Singh and M. Saksena, *Proceedings of the Indian Academy of Sciences-Section A, Springer* (1973) 139-148. `https://doi.org/10.1007/BF03049515`
4. M. Singh and M. Saksena, *Canadian J. Phys.*. **63** (1985) 1162-1172. `https://doi.org/10.1139/p85-190`
5. G. Herzberg, New York: Van Nostrand Reinhold, 1950, 2nd ed. (1950).
6. B. P. Straughan and M. A. Walker, *Spectroscopy*, **Vol. I to III**, London, Chapman and Hall (1976).
7. B. Chakraborty and Y. Pan, *Appl. Spectros. Rev*. **7** (1973) 283-311. `https://doi.org/10.1080/05704927308055761`
8. C. Sharp, *Astronomy and Astrophysics Supplement Series*. **55** (1984) 33-50.
9. H. Telle and U. Telle, *Comput. Phys. Comm.*. **28** (1982)

1-25. https://doi.org/10.1016/0010-4655(82)90059-5

10. Q. M. Nadhem, Supriya Behere and S. H. Behere, *IOSR-J. Appl. Phys.* **7** (2015) 3-12. https://doi.org/10.9790/4861-07340312

11. Q. M Nadhem, Supriya Behere and S. H. Behere, *Inter. Lett. Chem. Phys. Astronomy* **58** (2015) 90-101. https://doi.org/10.18052/www.scipress.com/ILCPA.58.90

12. Ramon S. da Silva, Maikel Y. Ballester, *Astrophysics and Space Science* **364** (2019) 169. https://doi.org/10.1007/s10509-019-3656-3

13. W. R. Jarmain and J. C. McCallum, *J. Quant. Spectrosc. Radiat. Transfer* **11** (1971) 421.

14. W.R. Jarmain, R.W. Nicholls, *J. Quant. Spectrosc. Radiat. Transfer* **23** (1980) 229-235.

15. M. D. Saksena and K. Sunanda, *Indian J. Physic*. **79** (2005) 409-415

16. K. P. Huber and G. Herzberg, *Constants of diatomic molecules*, Van Nostrand Reinhold Company, New York (1979)

17. M. Singh and M. Saksena, *Canadian J. Phys*. **59** (1981) 955-966. https://doi.org/10.1139/p81-125

18. M. Singh and M. Saksena, *Canadian J. Phys.*. **60** (1982) 1730-1742. https://doi.org/10.1139/p82-233

19. C. T. Londhe, *Studies in molecular spectra*, Ph.D. Thesis (2007)

20. M. Saksena, M. Deo, K. Sunanda, S. Behere, and C. Londhe, *J. Mol. Spectros.*. **247** (2008) 47-56. https://doi.org/10.1016/j.jms.2007.10.002

21. C. T. Londhe, K. Sunanda, M. D. Saksena, and S. H. Behere, *J. Mol. Spectros*. **263** (2010) 178-182. https://doi.org/10.1016/j.jms.2010.07.013

22. A. D. Smirnov, N. E. Kuzmenko, and Y. Y. Kuzyakov, *Journal of Applied Spectroscopy* **28** (1978) 631-632.

23. A. D. Smirnov, N. E. Kuzmenko, and Y. Y. Kuzyakov, *Zh. Prikl. Spektrosk.* **28** (1978) 923-935.

24. V. Mummigattiand B. Jyoti, *Indian J. Phys., B* **53** (1979) 260-261.

25. R. Reddy, Y. N. Ahammed, K. R. Gopal, P. A. Azeem, and S. Anjaneyulu, *Astrophys. Space Sci*. **262** (1998) 223-240. https://doi.org/10.1023/A:1001848028629