

High resolution spectrum of DyO molecule

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Abstract. Emission spectrum of DyO molecule has been photographed under high resolution in the wavelength region 5000 to 6300 Å. The observed bands have been arranged into three different band systems. The rotational structure in the (0, 0) band of system I is partially resolved and analysed. Isotopic shifts have been calculated for various isotopic molecules and compared with observations. Electronic states involved in the transitions have been discussed.

Keywords. Anharmonicity, molecular orbital; isotopic shift; multiplicity; inter-nuclear distance; vibrational frequency.

1. Introduction

The band spectrum of DyO molecule was first reported by Eder and Valenta (1911) who presented only the wavelength of the observed band heads without any analysis. Piccardi (1941) used a flame source and was able to record nearly 100 bands in the region 4500-6000 Å. He also made a vibrational analysis of some of the bands and assigned six bands to the $\Delta v=0$ sequence with the (0, 0) band head at 5263 Å. Two other sequences corresponding to $\Delta v=\pm 1$ of this system were also observed at 5160 and 5406 Å respectively. Piccardi obtained $w'_e \sim 456 \text{ cm}^{-1}$ and $w''_e \sim 489 \text{ cm}^{-1}$ but the anharmonicity $w_e x_e$ was negative.

Taking into consideration what is known about the spectra of other rare-earth oxides [LaO (Akerlind 1962), CeO (Ames and Barrow 1967), PrO (Shenyavskaya *et al* 1973), GdO (Yadav *et al* 1976) and LuO (Suarez 1970)], it is reasonable to expect that the vibrational frequencies of the electronic states in other rare-earth oxides should lie in the range 700-1000 cm^{-1} . The vibrational frequencies of DyO as determined by Piccardi (1941) are nearly half of this expected value which indicates that the analysis is in serious error.

The infrared absorption spectrum of DyO in an Ar/Ne matrix at 4°K has been studied by Deckok and Weltner Jr (1971). They confirmed the presence of the diatomic oxide by the observation of a strong absorption at 829 cm^{-1} . It is generally observed that the vibrational frequencies of rare-earth oxides in their ground state show a matrix shift of $\sim 30 \text{ cm}^{-1}$ which indicates that the ground-state vibrational frequency of free DyO molecule would be $\sim 860 \text{ cm}^{-1}$.

In the present series of investigations we have photographed the emission spectrum of DyO at moderately high resolution and dispersion. These new observations permit us to correct the earlier analysis by Piccardi (1941) and also to identify some other new systems. The high resolution plates also show incompletely-resolved

rotational structure in some bands from which approximate rotational constants have been calculated. Nature of the molecular states involved in the transition has been tentatively assigned.

2. Experimental details

The spectrum of diatomic dysprosium oxide (DyO) has been excited in a 220 volt DC arc source using pure silver electrodes. The arc current was kept in the range of 2-3 amperes. Commercially available Dy₂O₃ sample (SDS, Bombay) having an estimated purity of 99.9% was used. The spectrum was first recorded on a 1.5 m Bausch and Lomb grating spectrograph. Fresh sample had to be fed several times to maintain proper excitation during the exposure. The final plates were taken on the 10.6 m concave grating spectrograph in the first order (reciprocal dispersion 0.66 Å/mm). Exposure times of the order of 2-5 mins on a smaller instrument and 2-3 hr on a larger instrument were found sufficient to record the spectrum with fairly good intensity on Kodak P1200 plates. The bands lying in the range 5240-5480 Å region were also photographed in the second order of the same grating with a dispersion 0.33 Å/mm and resolution ~ 300000 (i.e. $\Delta 0.02$ Å at 5000 Å). Iron arc lines were used as standard lines for measurement.

3. Correlation diagram and molecular states of DyO Molecule

Dysprosium with atomic number 66 has the following electronic configuration

$$\dots 4f^{10} 6s^2,$$

with 6I_8 as the ground state. The ground state of oxygen is 3P_2 . If we consider molecule formation from neutral atoms the possible molecular states which arise using the separated atom concept are the states with $\Lambda = 7, 6, 5, \dots, 0$ and with resulting total spin $S=3, 2$, and 1.

The energies of the atomic orbitals of Dy and O (separated atoms) and of W (united atom with atomic number 74) are shown in figure 1. It is to be noted that though the energy of $2p$ orbital of free oxygen is slightly higher than that of the $4f$ orbital of Dy in free atomic state (Herman and Skillman 1963) but since the bonding is ionic we have shown the $2p$ orbital of O below the $4f$ orbital of Dy as has been done in the case of PrO (Delaval 1977). Thus the $2p$ orbital of oxygen would be completely filled in the molecule.

Filling up the molecular orbitals successively in order of increasing energy, we find that out of the 74 electrons in DyO, 48 electrons are accommodated in $1s, 2s; 2p, 3s, 3p, 3d; 4s, 4p, 4d$ and $5s$ atomic orbitals of Dy. Two more electrons are accommodated in the $1s$ orbital of oxygen. Further 14 electrons fill up the two π (6π and 7π) and three σ ($12\sigma, 13\sigma$ and 14σ) orbitals arising from the $5p$ (Dy), $2s$ (O) and $2p$ (O) atomic orbitals. The remaining 10 electrons have to be accommodated in the four molecular orbitals $1\phi, 3\delta, 8\pi$ and 15σ arising from the $4f$ atomic orbitals of Dy.

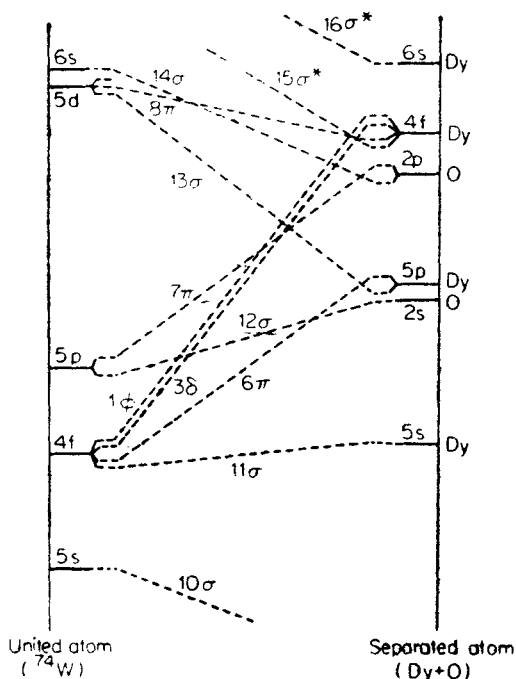


Figure 1. Correlation diagram of DyO

According to Jorgensen (1964) the filling up of orbitals of the $4f$ shell occurs in the order ϕ , δ , π and σ and following the Hund's rule the state with highest multiplicity would lie lowest in energy. We can write for the ground state configuration of DyO as $1\phi^4 3\delta^2 8\pi^2 15\sigma^2$. The highest multiplicity state arising from this configuration is a $^5\Sigma^+$ state.

The 1ϕ and 3δ orbitals correlate with the orbitals of the same symmetry arising from the $4f$ orbitals of the united atom W and have very much lower energy as $R \rightarrow 0$. The 8π orbital can be correlated with the $5d\pi$ orbital of W and increases only slightly in energy in going from $R \rightarrow \infty$ to $R = 0$. The 15σ orbital on the other hand can be correlated only with a $6p\sigma$ orbital of W which is unoccupied in the united atom and hence 15σ is antibonding. It is not necessary that 15σ is the outermost orbital in the molecule. In fact the conclusions of Ackermann *et al* (1976) regarding the relative stability of DyO and DyO⁺ would require that 15σ should lie lower in energy in the molecule as compared to the molecular orbital 3δ and 8π .

The internal rearrangements of the available 10 electrons amongst 1ϕ , 3δ , 8π , 15σ orbitals would give rise to states lying close in energy to the ground state—some of these are

$$\begin{array}{ll}
 \sigma^2\phi^4\delta^4 & \text{--- } 1\Sigma^+, & \sigma^2\phi^4\delta^3\pi & \text{--- } 3\Gamma, \\
 \phi^4\delta^4\pi\sigma & \text{--- } 1\pi, & \phi^4\delta^4\pi^2 & \text{--- } 1\Sigma^+, 3\Sigma^-, 1\Delta.
 \end{array}$$

Some of these singlet and triplet states might be involved in the transitions observed for system II and system III.

4. Description of the spectrum

The spectrum recorded in the region 5000 Å to 6200 Å consists of many red-degraded bands. Most of these are poor in intensity except a few groups which perhaps belong to the (0, 0) sequence of the different band systems. The bands can be grouped into different sequences with intense sequence heads being observed at 5246, 5263, 5348 and 5403 Å respectively.

Under low resolution the band heads lying at 5246 Å showed considerable width with perceptible intensity variation over this width (see figure 2a). At higher resolution these band heads have been resolved into several components and some of these heads show measurable rotational structure (figure 2b). The band sequences observed at 5263, 5348 and 5403 Å show single-headed structure.

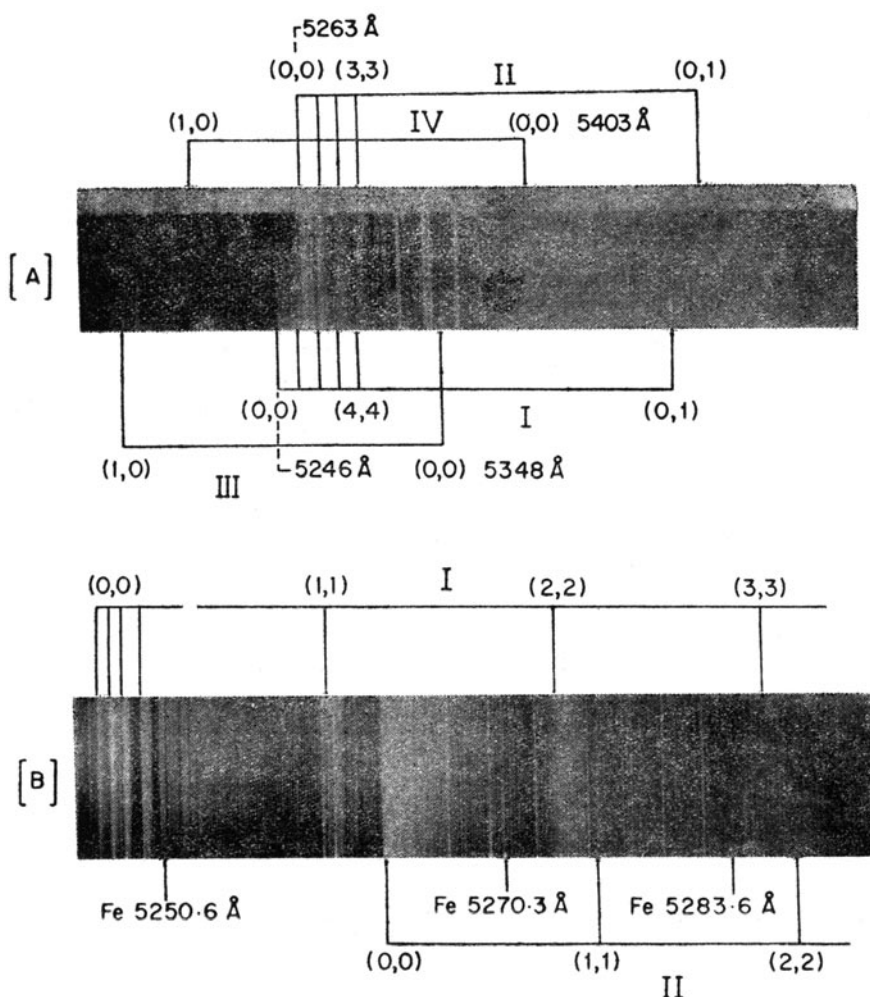


Figure 2. Band spectrum of DyO molecule. [A] Low resolution (1.5 m Bausch & Lomb concave grating spectrograph). [B] High resolution (first order on 10.6 m concave grating spectrograph).

5. Vibrational analysis

It is a general characteristic of the spectra of rare-earth oxides that the vibrational frequency does not change much in going from the ground state to the excited states. Thus the (0, 0) band sequence of any system is expected to be most intense. On this ground we surmised that the intense band head observed at 5246 Å and four other bands showing similar appearance belong to the (0, 0) sequence of system I.

Another sequence of three bands observed at 5487 Å which are relatively weak and diffuse but show a similar many-headed structure has been taken as the (0, 1) sequence. The diffuseness of these bands is probably due to the unresolved isotopic shifts. The sequence corresponding to $\Delta v = +1$ is not observed.

There are four heads in the (0, 0), (0, 1) and the (1, 2) bands (see also § 6). In the latter cases i.e. in the (0, 1) and (1, 2) bands, these are quite diffuse. But only three heads could be observed in the (1, 1) band. In the remaining bands namely, (2, 2), (3, 3) and (2, 3) only a single band head is observed in each (see table 1). The wave-number separations between the (0, 0) and the (0, 1) bands for all the four components are the same giving a consistent value of $\Delta G''_{1/2}$. Similarly the difference of the

Table 1. Band head positions and their assignments (cm^{-1})

cm^{-1}	$v'-v''$	cm^{-1}	$v'-v''$
19271.04	(1, 0) IV	18501.67	(0, 0) IV
19271.47	(2, 1) IV	18455.44	(1, 1) IV
19165.60	(3, 2) IV	18410.00	(2, 2) IV
19053.58	(0, 0) I	18365.35	(3, 3) IV
19050.98	(0, 0) I	18198.31	(0, 1) I
19048.45	(0, 0) I	18196.48	(0, 1) I
19044.44	(0, 0) I	19193.80	(0, 1) I
19005.60	(1, 1) I	18190.36	(0, 1) I
19003.61	(1, 1) I	18160.39	(1, 2) I
19001.61	(1, 1) I	18158.41	(1, 2) I
18994.24	(0, 0) II	18155.80	(1, 2) I
18958.02	(2, 2) I	18152.51	(1, 2) I
18949.68	(1, 1) II	18134.66	(0, 1) II
18910.87	(3, 3) I	18122.89	(2, 3) I
18905.62	(2, 2) II	18097.44	(1, 2) II

Table 2. Molecular constants of DyO (in cm^{-1})

Constants	System I	System II	System III
w'_e	816.99	821.86	776.71
$w'_e x'_e$	4.84	3.42	3.67
w''_e	865.33	866.92	823.65
$w''_e x''_e$	5.03	3.67	4.40
B'_o	0.3562		
B''_o	0.3642		

wavenumbers of the bands (1, 1) and (0, 1) which represents $\Delta G'_{1/2}$ is nearly the same for the three heads. From the average values of these $\Delta G'_{1/2}$, the vibrational constants have been determined. These are given in table 2.

The sequence of bands with the first head at 5263 Å has been taken to be the (0, 0) sequence of system II. These bands lie quite close to the (1, 1) (2, 2) and (3, 3) bands of system I and show single head. This is the system of bands for which a tentative analysis was proposed earlier by Piccardi (1941). We have assigned the $\Delta v = -1$ of this system as the sequence observed at 5512 Å instead of at 5406 Å as was done by Piccardi (1941). Here also the $\Delta v = 1$ sequence could not be detected. Four bands in $\Delta v = 0$ and two bands in $\Delta v = -1$ sequence have been observed and are given in table 1. The lower-state vibrational frequency is nearly equal to the value of ω_e'' in system I.

The sequence of single-headed and red-degraded bands observed at 5348 Å and 5138 Å have been taken to form the (0, 0) and the (1, 0) sequence of another system. The (1, 0) sequence consists of three bands whereas in the (0, 0) sequence only one namely the (0, 0) band could be observed. The (1, 1) band is masked by a very strong atomic line. Thus only four bands could be observed in this system (system III).

Another sequence of red-degraded and single-headed bands is observed with first sequence head at 5403 Å. A slightly less intense band is observed on the lower wavelength side of this band at a separation of $\sim 14 \text{ cm}^{-1}$. This pattern is not clear in the other bands of this sequence. The (1, 0) band is observed at 5186 Å followed by the other members of the $\Delta v = 1$ sequence. We label this as system IV. Four bands in $\Delta v = 0$ and three bands in $\Delta v = +1$ sequence could be observed in this system. It is found that the lower state frequency of this system is nearly the same as the upper-state vibrational frequency of system II. On this basis we surmise that one of the two combining states in systems II and IV may be common.

Although only $\Delta G'_{1/2}$ could be determined in system III, since the structure and separation of the bands in the $\Delta v = +1$ sequences of systems III and IV are similar, we expect that these two systems might be two sub-systems involving the components of a triplet state. The bands of systems III and IV are given in table 1 and corresponding vibrational constants are given in table 2.

6. Rotational analysis of the (0, 0) band of system I

The only band in which the rotational structure is comparatively well-resolved and free from any overlapping is the band at 5246 Å. This structure is shown in figure 3. At first sight, the structure reveals the presence of a single series of rotational lines with nearly constant intensity. Since the bands are red degraded, the R branches are head-forming and the fact that after head formation, their intensity is too low for observation is exemplified by the observation of a clear gap after the last band head on the longer wavelength side.

The electronic states of DyO molecule will be of odd multiplicity and the ground state is most probably a $^5\Sigma$ or a high multiplicity sigma state (see § 3). The presence of four heads in the (0, 0) band of system I may be due to several reasons. The most probable one is that in a transition between high multiplicity sigma states the band head appear in pairs [$\text{MnO } (^6\Sigma - ^6\Sigma)$ (Pinchemel and Schamps 1975), $\text{GdO } (^7\Sigma - ^7\Sigma)$

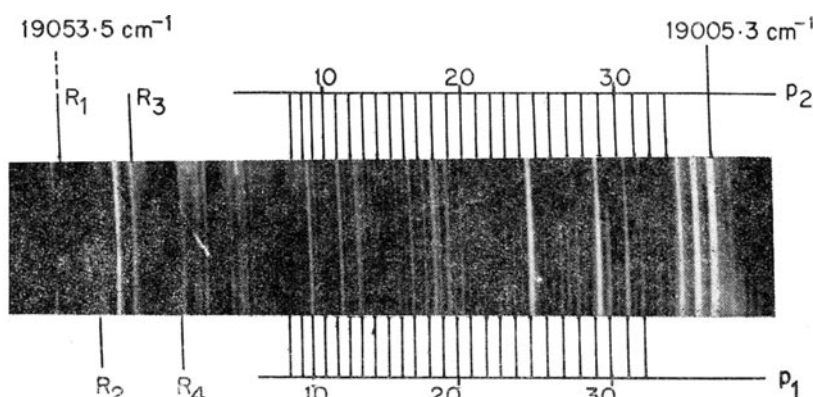


Figure 3. Rotational structure in the (0, 0) band of system I of DyO molecule (2nd order of 10.6 m concave grating spectrograph).

(Yadav *et al* 1980)], and the separation between a pair is so small that they could not be resolved. Similar overlapping is also expected for branch lines.

Assuming the series diverging away from the head to represent a rotational branch, the ΔB value comes out to be $\sim 0.0019 \text{ cm}^{-1}$. For a simple Q branch the coefficients of the terms in (J) and in (J^2) are the same i.e. (ΔB) and if we adjust our running number to such an extent that the numerical coefficient of the linear and the quadratic terms become equal, we find that the band origin must lie very close to the first band head on the shorter wavelength side. Moreover, the running index for the first member of the series in this situation should be as high as 80. Both these results though not impossible are clearly improbable and we conclude that this series of rotational lines form a P branch. This poses another problem which is as follows.

Table 3. Vacuum wavenumbers and J assignments of the rotational lines of the (0, 0) band of system I.

J	P_1	P_2	J	P_1	P_2
7	19035.86	19035.48	27	19015.41	19014.81
8	35.08	34.67	28	14.21	13.62
9	34.32	33.86	29	13.03	12.45
10	33.39	32.96	30	11.81	11.18
11	32.43	31.96	31	10.54	9.86
12	31.54	31.06	32	9.33	8.61
13	30.66	30.11	33	7.99	7.31
14	29.63	29.11	34	6.68	6.00
15	28.63	28.16	35	5.29	4.73
16	27.67	27.25	36	3.95	3.44
17	26.62	26.08	37	2.72	2.04
18	25.57	24.97	38	1.40	19000.74
19	24.45	23.95	39	19000.95	18999.31
20	23.42	22.87			
21	22.32	21.79			
22	21.22	20.65			
23	20.10	19.52			
24	18.94	18.35			
25	17.75	17.79			
26	16.64	16.01			

From the expression for a P branch line we find that the successive separation between the initial members of this series should be of the order of $(B' + B'') \sim 2B''$. Estimating B'' from a graph of the known internuclear distances and total number of electrons for several rare-earth oxides, this value i.e. $2B''$ should be nearly 0.72 cm^{-1} . The observed initial separation between the successive members of the series is only 0.35 cm^{-1} and we are forced to conclude that there are really two series of P branch lines. Taking alternate members of the observed series of lines to belong to each individual P branch, we selected about 30 members of each of the two series and then fitted a quadratic in J by a least squares procedure. We adjusted the J numbering till the constant term and the coefficient of J for the two series comes out to be nearly the same. The J numbering thus obtained (see table 3) would not necessarily be the correct assignment of J values. The numerical coefficients of J and J^2 thus obtained from the two series lead to an estimation of B' and B'' .

7. Calculation of isotopic shift

Natural dysprosium consists of the following seven stable isotopes with their percentage abundances given in parentheses ^{156}Dy (0.05%), ^{158}Dy (0.09%), ^{160}Dy (2.29%), ^{161}Dy (18.88%), ^{162}Dy (25.53%), ^{163}Dy (24.97%), ^{164}Dy (28.18%) (Weast 1970). Therefore four isotopic molecules *viz.* ^{161}DyO , ^{162}DyO , ^{163}DyO , ^{164}DyO would contribute significantly to the spectrum, and four isotopic heads should appear in each band with nearly similar intensity.

We have calculated the isotopic shift with reference to the most abundant ^{164}DyO molecule. The calculated shifts for the (0, 0) band of system I are $+0.018 \text{ cm}^{-1}$ (^{161}DyO), $+0.012 \text{ cm}^{-1}$ (^{162}DyO), $+0.0062 \text{ cm}^{-1}$ (^{163}DyO) whereas for the (0, 1)

Table 4. Calculated and observed isotopic heads in the (0, 1) band of system I o DyO (cm^{-1})

Isotope	Calculated	Observed
^{161}DyO	18198.56	18198.65
	18196.73	18196.85
	18194.05	18194.12
	18190.61	18190.63
^{162}DyO	18198.80	18198.95
	18196.97	18196.85
	18194.29	18194.12
	18190.85	18190.89
^{163}DyO	18199.28	18199.35
	18197.21	18197.25
	18194.53	—
	18191.09	18191.15

band the shifts have the magnitudes $+0.729 \text{ cm}^{-1}$, $+0.482 \text{ cm}^{-1}$ and $+0.246 \text{ cm}^{-1}$ respectively.

The calculated isotopic shifts for the (0, 0) band are too low to be resolved but the isotopic heads are clearly visible in the (0, 1) band sequence. The observed isotopic shifts agree well with the calculated shifts and these are given in table 4. Because of the poor intensity and diffuse nature of the bands corresponding to the $\Delta v = +1$ sequence in systems III and IV, we could not mark the isotopic heads.

8. Discussion

The spectra of only a few rare-earth oxides namely CeO, PrO, GdO and LuO (Bacis and Bernard 1973) have been investigated but none of them shows sharp and well-developed band systems. Almost in all the cases only the (0, 0) band sequence shows rotational structure.

The most reliable property of rare-earth mono-oxides is their dissociation energies (Ackerman *et al* 1976; Ames *et al* 1967). Since the rare-earth oxides are ionic in nature and as Gaydon (1968) has shown that for ionic molecules the linear extrapolation gives a lower estimate of D_0 than the actual value, the linear extrapolated value in this case $w_e^2/4w_e x_e = 4.61 \text{ eV}$ is less than the actual value 6.29 eV (Ackerman *et al* 1976).

We have made a comparative study of the rotational constants of TiO, ZrO, CeO; VO, NbO, PrO and FeO, RuO, DyO and have made a graph of r_0 (internuclear distance) versus the total number of electrons (figure 4). The selection of such a group of molecules has been taken in the sense of filling of $3d$, $4d$ and $4f$ shells. The change of internuclear distances with change of electrons are parallel in first two groups of molecules i.e. TiO, ZrO, CeO and VO, NbO and PrO. The r_0 value obtained for DyO fits symmetrically in the third group with only a slight deviation in the third curve at the point corresponding to RuO which is probably due to the fact that Raziunas *et al* (1965) regarded the lower state of this transition in RuO as the ground state but the more recent analysis of Scullman and Thelin (1975) indicates that this is not true. This type of qualitative arguments have been used by Nair and Rai (1967) and Yadav *et al* (1979) in the case of CuI and GaO respectively.

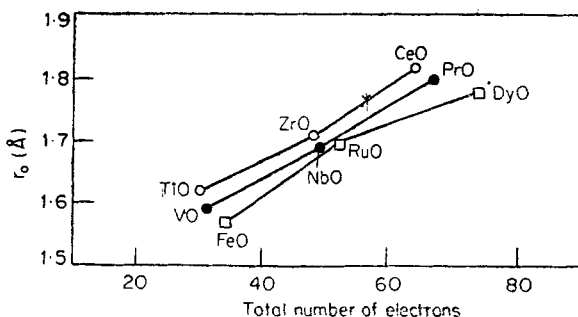


Figure 4. Variation of internuclear distance with number of variations.

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