CHAPTER I

INTRODUCTION
Atomic isotope shifts in the spectral line of an element having isotopes, provide information of the atom as a whole and thus acts as a link between atomic and nuclear physics. Isotope shifts (IS) in atomic spectra, have been extensively investigated both theoretically and experimentally and has resulted in the formulation of new concepts of electronic interactions. The studies of isotope shifts have provided many valuable information on the structure of the complex atoms [1] as well as the structure of the nuclei [2].

Isotope shift in atomic spectra arises due to two distinctly different effects [3]. The 'mass effect' arises from the difference in nuclear masses of isotopes and results in two types of mass shift. Normal mass shift (NMS) which is due to reduced mass correction, but for a multielectron atom there is an additional coupling effect of the momentum correlation terms leading to specific mass shift (SMS). The NMS in a spectral line is easily calculable but the SMS which is due to correlation between electrons is difficult to evaluate [4]. Since the mass effect (NMS + SMS) is proportional to $1/A^2$, NMS is small in heavy elements however SMS may still be large as it depends on the correlation between the electrons in the configuration of the energy levels. The other effect known as the 'field effect' arises from the electrostatic interaction between the electron charge density at the nucleus and the
nuclear charge distribution of different isotopes. These differences in nuclear charge distribution between the isotopes arise because of the change in the size and shape of the nuclei on addition of neutrons.

The field shift in a spectral line between two isotopes thus depends on, the change in the electronic charge density at the nucleus, $\Delta|\psi(0)|^2_i$, in the transition $i$, as well as on the change in the mean square nuclear charge radii $\Delta \langle r^2 \rangle$, of the isotopes. The study of isotope shift thus can provide information on the electronic configuration of the energy levels of an atom, as well as, on the variation in the nuclear size and shape between different isotopes.

The information obtained from the experimentally observed isotope shift can be thus segregated into two parts: one depending on the electronic structure of the atom and the other on structure of nuclei constituting the atoms.

1.1 Isotope Shifts and Electronic Configuration of Atomic Energy Levels

The magnitude of the field shift for a particular pair of isotopes is proportional to the change in electron charge
density at the nucleus during the transition $\Delta |\psi(0)|^2$, thus a comparison of isotope shifts in different transitions of an element gives a measure of how $\Delta |\psi(0)|^2$ varies between different types of transitions. Those transitions in which the number of s-electron change, have large values of $\Delta |\psi(0)|^2$; so the study of isotope shift in different lines of a spectrum can be a great help in the interpretation of the energy levels involved in the transitions and provide valuable information about the electronic configuration of these energy levels.

On the basis of isotope shift measurements in atomic spectral lines, one can group transition into rather broad categories according to the electronic configurations involved in the transition. These measurements can be correlated with several additional types of electronic configuration and after analysis, one can suggest the electronic configuration of the involved level which have not yet been classified.

In case of complex spectra, because of high density of energy levels, it is sometime difficult to unambiguously give the classification of a spectral line; thus leading to more than one possible classification assigned to a transition. Isotope shift studies eventually enable us to check the energy levels classifications of spectral lines as well suggest possible classification of the unclassified lines. Blaise [5],
Gluck [6], Ross [7] and Ahmad et al [8] have successfully applied the isotope shift studies for understanding the electronic configurations in complex spectra of uranium, tungsten, erbium and neodymium respectively.

When a level has mixed configuration then the isotope shift values are very useful to determine the amount of configuration mixing using the "sharing rule" which was first utilised by Brix and Lindenberger in Gd II [9] and is being successfully utilised even in such complex spectra as those of rare-earths e. g., Ahmad et al [10] and Pushpa et al [11] have applied this rule to confirm configuration mixing in Dy II and Sm II respectively, Villemoes et al [12] have also recently reported configuration mixing in some of the energy levels of Sm II.

Isotope shifts have also revealed very valuable insight and provided information about the screening effects on transition electrons due to other electrons in the atom. Screening ratios can be measured experimentally and compared with the values evaluated theoretically [13]. The agreement between experiment and theory has been usually good which encourage the evaluation of screening factors from the theory [14,15].
1.2 Isotope Shift and Changes in Nuclear Mean-Square Charge Radii $\delta <r^2>$

Field shift, which is predominant in heavy elements ($A \geq 100$) can be factorised into the nuclear part ($\delta <r^2>$) and electronic part ($\Delta |\psi(0)|^2$). By keeping the electronic factor constant, i.e. measuring isotope shift in a particular transition in a chain of isotopes, one can get information on the variation of the nuclear mean-square charge radii, $\delta <r^2>$, between the two isotopes $A$ and $A'$.

On the basis of the systematic studies of isotope shift involving isotopes with nuclear spin $I = 0$, Brix and Kopfermann [13] introduced the concept of 'static' nuclear deformation as with no nuclear spin there is no preferred direction relative for the nucleons for the nuclear deformation. The nuclear deformation, with charge distribution averaged over all directions in space, has the same effect as an increase in nuclear volume and large field isotope shifts occurs when addition of a pair of neutrons brings about the deformation e.g., the sudden jump of isotope shift, observed for $^{150}\text{Sm}$ ($N$, neutron number = 90) on addition of pair of neutrons to $^{150}\text{Sm}$ ($N = 88$), was attributed to large deformation in $^{152}\text{Sm}$ [13]. Now it is an established fact that there is sudden on-set of large nuclear deformation in
N = 88 - 90 region and has been investigated in long isotope chain of stable and radioactive nuclei of rare earths of Ce, Nd, Eu, Gd [2].

1.3 Complexity of Rare-earths Spectra and Contribution of Isotope Shift Studies in the Interpretation of the Spectra

The spectra of rare earth atoms and ions are very complex. Because of the small radii of the 4f orbital, the 4f electrons lie rather close together, consequently, their mutual Coulomb repulsions are quite large. The total energy range covered by the levels of 4f^n is therefore unusually large for a valence subshell - over 12 eV in most cases (4 < n < 10). This is shown in Fig.1.1 for configurations 4f^n 6s^2, which in most cases are the ground configurations of the neutral lanthanides.

The spin-orbit parameter ζ increases much faster with Z than the Coulomb parameters F^K. Thus there is a strong tendency to move from LS coupling in Ce toward moderate jj coupling in Er.

Ionization of neutral lanthanides atom involves ...
Fig. 1.1 Theoretical energy levels of configurations $4f^76s^2$ of neutral lanthanides atoms relative to the center of gravity energy $E_{av}$. The density of levels within each solid block is too great for the levels to be drawn separately.
of one of the 4f electrons, but also removal of the comparatively loosely bound 6s electrons. Hence ionization energies are very low, about 6 eV. That is why many of the levels of ground configurations lie above the lowest ionization limit. Configurations having partially filled subshells in addition to the 4f subshell have more complicated level structures. If the additional unfilled subshells all have \( n > 5 \), then the interactions of these electrons with the 4f electrons are small, and the level structure consists basically of the 4f\(^n\) structure, except with each level of the latter split into several levels as a result of additional small interactions [16].

The binding energies of 4f, 5d, 6s and 6p electrons in neutral lanthanides differ from each other by only a couple of electron-Volts whereas the spread of energies within a configuration is 5 to 10 eV or more. Hence the tendency of overlapping of various configurations is very high. This results in the high density of energy levels, even at energies as low as 2.5 eV above the ground level, and the interpretation of experimental spectra and energy levels is extremely difficult.

Configuration 4f\(^n\) 6s and 4f\(^n\) 6p show \( J = \frac{L + S}{2} = J \) coupling. For \( n > 7 \), 4f\(^n\)5d tends toward this type of
coupling because of the increasing value of $\xi_{4f}$. For all configurations of the type $4f^n l_1 (n > 6)$, $J_\perp$ is a quite good quantum number because of the small interaction of the $nl$ electron with the $4f^n$ core, the coupling may be closely $J_\perp J$ (small $l$) or more nearly $J_\perp K$ (large $l$).

The very high density of the energy levels Table 1.1 not only makes their theoretical interpretation difficult, but also greatly complicates even the deduction of the energies of the various levels from the spectra.

Isotope shift studies have played a key role in the interpretation of complex spectra of rare earths, some of the recent studies during last few years are: Nd [17,18,19], Gd [20,21,22], Dy [10,23], Er [24], and Yb [25,26].

1.4 Isotope Shift Studies in Rare Earth Spectra in the Ultraviolet region (3300-3800) Å

Isotope shift studies in rare-earth spectra have been carried out in optical [27], electronic x-ray [28] and muonic region [29]. Most of the earlier measurements in the optical region were carried out using Fabry-Perot interferometer/spectrometer. Measurements in the infrared to
<table>
<thead>
<tr>
<th>Configuration</th>
<th>No. of LS terms</th>
<th>No. of levels</th>
<th>Largest matrix</th>
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<td>1</td>
<td>0</td>
</tr>
<tr>
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<td>1</td>
<td>2</td>
<td>5/2, 7/2</td>
</tr>
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<td>2, 4</td>
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<td>17</td>
<td>41</td>
<td>5/2 - 9/2</td>
</tr>
<tr>
<td>$f^{4}, f^{10}$</td>
<td>47</td>
<td>107</td>
<td>4</td>
</tr>
<tr>
<td>$f^{3}, f^{9}$</td>
<td>73</td>
<td>198</td>
<td>7/2</td>
</tr>
<tr>
<td>$f^{6}, f^{8}$</td>
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<td>295</td>
<td>4</td>
</tr>
<tr>
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<td>119</td>
<td>327</td>
<td>7/2</td>
</tr>
<tr>
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<td>7/2</td>
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<td>7/2</td>
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Table 1.1 Numbers of LS terms and levels of some rare-earth configuration
visible region are being carried out using Fourier Transform spectroscopy [30].

During the last decade high resolution laser spectroscopic techniques like, laser induced fluorescence using atomic beam, two-photon spectroscopy, saturation spectroscopy and polarization spectroscopy using hollow cathode discharge have been used to accurately measure the isotope shifts. But most of the laser based measurements have been restricted to visible region and few measurements exist in ultraviolet region.

The present studies of isotope shift under taken in the region 3300–3900 Å using a Recording Fabry-Perot Spectrometer (REFPOS). Although not as accurate as laser technique, REFPOS covers the spectral range for which neither the commercial Fourier Transform spectoscopy are available nor the laser techniques can be easily used for high resolution studies in the ultraviolet region. The isotope shift studies in the spectra of Nd, Gd, Dy, and Yb in the region 3300–3900 Å are very scanty and have been made earlier mostly with the aluminium coated Fabry-Perot etalons. The present studies undertaken with a pair of broad band multi layer dielectric coated Fabry-Perot etalon has thus provided new data in earlier scanty unexplored ultraviolet region, leading to new
valuable information about the high lying energy levels especially of the singly ionised ions of few of the rare-earths. New information obtained from the present studies are summarised below.

1.5 Present Isotope Shift Studies in the Spectra of Nd$^+$, Gd, Gd$^+$, Dy, Dy$^+$, Yb and Yb$^+$ in Ultraviolet Region

In the present isotope shift studies, measurements were carried out in the complex spectra of neodymium, gadolinium, dysprosium, and ytterbium with the objective of obtaining information on the electronic configuration of the energy levels of these neutral as well as singly-ionised atoms. On the basis of term shift ($\Delta T$) evaluated for the energy levels existing in literature the configuration assignments of the energy levels have been confirmed in most of the cases and for some levels the assignments have been revised. Configuration mixing have been pointed out on the basis of observed $\Delta T$ values. Theoretical calculations of configuration mixing in case of Dy$^+$ has been verified experimentally using the 'shareing rule'. Crossed-Second-Order effect has been investigated in case of singly-ionised neodymium and gadolinium. Specific mass shifts have been evaluated in some UV lines of Gd II, which enabled to evaluate $\delta\langle r^2 \rangle$ for all the
stable isotopes of Gd including the rare $^{152}\text{Gd}$ which has a natural abundance of 0.2% only.

1.5.1 Isotope Shift in Energy Levels of Singly-Ionised Neodymium (Nd II)

Electronic configurations for many of the known even and odd levels of Nd$^+$ (Nd II) above 28000 cm$^{-1}$ are not known [30]. $\Delta T$ values which could be helpful in the configuration assignments are also scanty for both high lying odd and even energy levels. The strong transitions involving these levels lie mostly in the ultraviolet region and isotope shift data in spectral lines of Nd$^+$ in this region are very scanty. In order to get information on the electronic structure of these high lying energy levels, isotope shift measurements have been carried out in 92 spectral lines in UV region. We have also classified fifteen lines on the basis of isotope shift measured by us. We have also revised the classifications of seven spectral lines of Nd$^+$. The data has been used to evaluate term isotope shifts $\Delta T$ (144-150) for 68 odd and 8 even levels. The configurationed assigned by earlier workers have been mostly confirmed. We have assigned 7 levels to predominant $4f^35d6s$, one level to almost pure $4f^35d6s$ and 6 levels to about 60% $4f^35d6s$ and admixture of $4f^35d^2$ and $4f^46p$. 
4 levels have been assigned to pure $4f^46p$ whereas three levels are assigned to predominant $4f^46p$. The assignment of one level is revised. We have evaluated $\Delta T$ for a level of $4f^36s6p$ configuration for the first time. We have also pointed out that for some of the levels there is difference in $\Delta T$ values evaluated by us and those reported by Blaise et al [30].

1.5.2 Isotope Shift in Energy Levels of Singly-Ionised Ytterbium (Yb II)

Isotope Shifts (IS) measurements in the spectral lines of singly-ionised ytterbium (Yb II) are rather scanty. Earlier Doppler-limited isotope shift measurements were reported in lines at 3694.19 Å (Kerbs and Nelkowski [31], Golovin and Striganov [32] and Chaiko [33]) and in the lines at 2970.56 Å, 3031.11 Å and 3289.37 Å [33]. All the four lines involve the ground state level of $^2S_{1/2}$ of $4f^{14}6s$ configuration: two lines at 3694.19 Å (D$_1$ line) and 3289.37 Å (D$_2$ line) belong to $4f^{14}6p$-$4f^{14}6s$ transitions, whereas the lines at 2970.56 Å, 3031.11 Å belong to $4f^{13}5d6s$-$4f^{14}6s$ transition. The values of isotope shifts for four lines of Yb II at 3289.37 Å, 3669.69 Å, 3694.19 Å and 4180.9 Å involving transition from $4f^{14}6p$ to $4f^{14}6s$ and $4f^{14}7s$ were reported by Ahmad et al [34] where the ratio of isotope shifts in D$_1$ and
D$_2$ was discussed.

Doppler-free laser spectroscopic measurements of isotope shifts have been reported in 3289.94 Å line by Brends and Maleki [35] and in 3694.190 Å line by Pendrill, Gough and Hannaford [36].

We have carried out isotope shift measurements $\Delta \sigma (^{172}\text{Yb} - ^{174}\text{Yb})$ in 57 classified lines of Yb II in the region 3200 - 4600 Å. The Yb II lines at 3401.1010 Å, 4077.276 Å and 4255.765 Å have all been assigned two possible classifications. On the basis of isotope shift values for these lines, we have assigned the correct classifications for these lines. Fawcett and Wilson [37] have the same classification given by us.

We have evaluated term shift ($\Delta T$) for 30 even and 19 odd parity levels. Term shift values have been evaluated with reference to 62559.0 cm$^{-1}$ ($J=5/2$), $^2D_{5/2}$ of 4$f^{14}6d$ configuration; as this level has been assigned a percentage purity of 97.5 % 4$f^{14}6d$. We have evaluated $\Delta T$ for 12 levels of 4$f^{13}6s6p$; the $\Delta T$ values lying mostly between 168 mK and 182 mK. For 4$f^{13}5d6p$ configuration, it should be noted that as the percentage of $(^2F_{7/2})(^3F)$ goes down (the contribution of $(^2F_{7/2})(^1D)$ increasing) the values of $\Delta T$ increases.
It has been pointed out that the levels belonging to \((^{2}F_{7/2}) \ (^{3}D_{J})\) have an average \(\Delta T\) value of about 179 mK whereas the levels assigned to \((^{2}F_{7/2}) \ (^{1}D_{J})\) have an average \(\Delta T\) value of 160 mK. This difference in \(\Delta T\) is indicative of different \(\mid \psi(0) \mid^2\) values for the levels belonging to \((^{2}F_{7/2}) \ (^{3}D_{J})\) and \((^{2}F_{7/2}) \ (^{1}D_{J})\). This shows the dependence of \(\Delta T\) values on the multiplicity.

Due to relativistic effects (in high \(Z\) elements) on the \(p_{1/2}\)-wave function, whose small Dirac components of a radial \(s\)-wave function and thus exhibit a nuclear volume effect. Therefore, it is expected that the isotope shifts in transitions \(D_1\) (\(n s^{2}S_{1/2} - np^{2}P_{1/2}\)) and \(D_2\) (\(n s^{2}S_{1/2} - ^{2}P_{3/2}\)) will be different: the field shift in \(D_1\) line will be smaller than in \(D_2\) line. Experimentally we have found that isotope shift in \(D_1\) line is larger than that in \(D_2\) line which is contradictory to expectation. This discrepancy is explained as due to perturbation and slight mixing of configurations in \(^{2}P_{1/2}\) and \(^{2}P_{3/2}\) of \(4f^{14}6p\).

1.5.3 Isotope Shift in Energy Levels of Neutral Gadolinium and Singly Ionised-Gadolinium (Gd I & Gd II)

There are many high lying levels of Gd I which have only
tentative configuration assignments. The transitions from these levels lie mostly in UV region. We have investigated the isotope shifts of spectral lines in ultraviolet region in order to verify the earlier assigned configurations and also to confirm the tentative assignments and to suggest the possible configuration to unassigned levels.

Isotope shift $\Delta \sigma \; (^{156}\text{Gd} - ^{160}\text{Gd})$ has been measured in 70 lines of Gd I spectrum in the range 3290 - 3950 Å. Out of these 70 lines, 15 lines are unclassified in literature and the classifications of these lines have been given by us. $\Delta T \; (156 - 160)$ have been evaluated for the first time for 25 even parity levels of Gd I. Using the present isotope shift data and the earlier data ([38] and references therein). Our $\Delta T$ values confirm the assignments of 13 of these levels to $4f^75d6s6p$ configuration by Blaise et al [39]. 11 levels belong to $4f^75d^26p$ configuration. One level at 34951 cm$^{-1}$ was tentatively assigned to $4f^75d^26p$. We have revised the assignment for this level and suggested that this level may have predominantly $4f^75d6s6p$ configuration. We have also confirmed that the tentative assignments of 6 levels to $4f^85d6s$ is correct except one level at 32563 cm$^{-1}$. We have revised the assignment of this level to $f^7dsp + f^7d^2p$. Three levels have no assignments; out of these one level is assigned to $f^8ds$ and two are assigned to a mixed configuration $f^7dsp +$
$f^7d^2p$. $\Delta T$ values for the seven even levels reported in [39,40,41] have been revised by us.

Isotope shift $\Delta \sigma(156-160)$ have been measured in 59 spectral lines of singly ionised gadolinium (Gd II). There are many high odd levels without configuration assignments. Term isotope shift for these energy levels are not also known. We have evaluated $\Delta T(156-160)$ for these levels, which could be helpful in confirming the assignments or suggesting the possible assignment to unassigned energy levels. The even levels belong to $4f^75d6p$, $4f^86s$ and $4f^85d$ configurations. $\Delta T$ for 27 high even parity energy levels have been evaluated; out of which $\Delta T$ values for 5 even levels are being reported for the first time. Our $\Delta T$ values agree with those reported earlier [41]. $\Delta T$ values have been also evaluated for 11 odd levels for the first time; 5 levels being still unassigned. We confirmed the electronic configuration of 5 levels assigned to $4f^86p$. The assignment of one level has been revised on the basis of our $\Delta T$ values. Out of 5 unassigned levels, 2 levels are assigned to $4f^75d6s$ and three levels are assigned to $4f^86p$ configurations.
1.5.4 Isotope Shift in Energy Levels of Dysprosium Atom and Singly-Ionised Dysprosium (Dy I & Dy II)

The spectrum of neutral dysprosium is very complex due to high density of the energy levels. The known energy levels of neutral dysprosium atom (Dy I) above 33,000 cm\(^{-1}\) have no configuration assignments [42]. In order to evaluate \(\Delta T(164-160)\) of these levels, we have measured isotope shift in 48 spectral lines of Dy I spectrum in ultraviolet region. On the basis of measured isotope shift the classification of one line at 3798.7 Å is found to be incorrect. We have evaluated \(\Delta T(\text{\textsuperscript{164}Dy-\text{\textsuperscript{160}Dy})}\) for 32 even parity levels, out of which 20 levels are unassigned. The configurations involved in present investigation are 4f\(^5\)5d6s6p and 4f\(^6\)6s6d. The high even levels having \(\Delta T\) values between (Z-8) mK and (Z+15) mK belong to 4f\(^5\)5d6s6p configuration. One level at 39035 cm\(^{-1}\) has \(\Delta T\) value of (Z-70) mK and may belong to \(f^{10}\)sd configuration. Wyart [43] has theoretically assigned the level at 40005 cm\(^{-1}\) to \(f^{10}\)dsp. But our observed \(\Delta T\) value for this level (Z-41) mK shows that this level does not belong to \(f^{10}\)dsp. So the assignment for the level at 40005 cm\(^{-1}\) is revised. Six high even levels whose \(\Delta T\) values lie between (Z-8) mK and (Z+15) mK have been assigned to \(f^{10}\)dsp.

The known odd parity energy levels of Dy II between
32000-46000 cm$^{-1}$ have no configuration assignments at the present state of theory [44] and it is not easy to assign theoretically these levels. There are 366 odd energy levels of Dy II and Wyart [42] has assigned 117 of these odd levels to 4f$^9$6s$^2$, 4f$^9$5d$^2$ and 4f$^{10}$5d6p on the basis of parametric calculations carried out taking into account the configuration mixing. Experimentally evaluated isotope shift ($\Delta T$) of the energy levels are sensitive probe to check the theoretical composition of the mixed configurations assigned to these levels. Theoretical isotope shift of a level with mixed configuration has been derived by the application of "sharing rule". We have evaluated theoretical values of the term shift ($\Delta T$)$_{\text{theo}}$ for each of the 28 odd levels of Dy II. These values are compared with our experimental values of term shift ($\Delta T$)$_{\text{exp}}$. There is good agreement $\Delta T_{\text{theo}}$ and ($\Delta T$)$_{\text{exp}}$ except for three levels.

We have also observed isotope shifts for some transitions of f$^9$sp - f$^9$ds and f$^9$dp - f$^9$ds types involving high even and low odd energy levels for which $\Delta T$ values have been not reported earlier nor could be evaluated from the present data. Isotope shifts observed in such transitions can throw some light on the percentage compositions of the configurations of these levels.
There are some 240 unassigned levels of Dy II between 30000 and 42000 cm\(^{-1}\). We have evaluated \(\Delta T\) for 65 levels in this region and for most of the levels there is not much variation of \(\Delta T\) values. This could be due to the configuration mixing which is bound to be predominant with such high density of states. On the basis of \(\Delta T\) and also taking intensity of the lines into consideration, we have suggested tentative assignments to some of these levels.

1.5.5 Isotope Shift in Energy Levels of Neutral Ytterbium (Yb I)

Isotope shift \(\Delta \sigma(172-176)\) have been measured in 25 spectral lines of Yb I covering the region 3425-4361 A. One line has been classified by us during the present investigation. We have evaluated \(\Delta T\) values for 8 even parity energy levels for the first time, out of the 14 even levels involved in the present study. These energy levels belong to \(4f^{14}6p^2\), \(4f^{14}6s7d\), \(4f^{13}5d6s6p\), \(4f^{13}6s^26p\) and \(4f^{14}6s9d\) configurations. We have confirmed the earlier reported \(\Delta T\) values by Ahmad et al [45]. We have also evaluated \(\Delta T\) for six high odd levels for the first time. These levels belong to \(4f^{13}5d6s^2\), \(4f^{14}6s10p\), \(4f^{14}6s9f\), \(4f^{13}5d^26s\), \(4f^{14}6s12p\), and \(4f^{13}5d^26s\) configurations. One level at 48701 cm\(^{-1}\) has no
assignment and this level has been assigned by us to 4f^{19}d^2s.

1.5.6 Crossed-Second-Order Effect in Field Shift in $^6$I and $^4$I Terms of 4f$^4$($^5$I)6s Configuration of Nd II and $^8$F and $^6$F Terms of 4f$^8$($^7$F)6s configuration of Gd II

To the first order the mass shift (MS) as well as the field shift (FS), is constant within a pure Russel - Saunders (RS) term of a particular configuration. On this basis the energy levels are grouped according to their term shifts, which enables one to check or assign the electronic configurations to the energy levels. The $\Delta T$ values for different terms of a pure configuration are evaluated relative to a reference level, and, when separated into MS and FS, may show slight difference in MS or FS for different RS terms. This difference has been attributed to the influence of second-order contributions [46].

Crossed-second-order effects in the field shifts manifests in the nl$^N$ns type of configuration where the coupling of the 's' electron to the 1$^N$ core causes the splitting of the RS terms into $^{M+1}L$ and $^{M-1}L$ terms (M being the multiplicity of total angular momentum L of the parent
term resulting from the $I^N$ electrons) [46]. CSO effect leads to different electron charge densities at the nucleus, $|\psi(0)|^2$, for these two terms resulting in different FS values for these terms.

Crossed-second-order effects in the field shift of $^{6}\text{I}$ and $^{4}\text{I}$ terms of $4f^4(5\text{I})6s$ configuration of singly-ionised neodymium has been experimentally evaluated. The CSO-FS difference between the two terms of $nl^nns$ configuration is evaluated by measuring isotope shift in transitions from a common upper level to the levels of these two terms. The experimental value of CSO-FS difference between the two terms, $^{6}\text{I}$ and $^{4}\text{I}$, $[\Delta(\text{FS})]_{\text{CSO}}^{142,150}$ is in good agreement with the theoretically evaluated value. Crossed-second-order effects in the field shift of $^{8}\text{F}$ and $^{6}\text{F}$ terms of $4f^8(7\text{F})6s$ configuration of singly-ionised gadolinium has been experimentally evaluated. CSO-FS difference between the two terms of $^{8}\text{F}$ and $^{6}\text{F}$, $[\Delta(\text{FS})]_{\text{CSO}}^{156,160}$ agree well with theoretical value.

1.5.7 Evaluation of Specific Mass Shift in Gd II

As mentioned earlier the observed isotope shift consists of mass shift and field shift. The mass shift can be separated
into two parts, the normal mass shift (NMS) and the specific mass shift (SMS). In one-electron atomic system, the calculation of the mass shift is straightforward, but for atoms and ions having several electrons the mass shift depends on the total linear momenta of the electrons. In light elements, the observed isotope shift in spectral line can be easily separated into NMS and SMS, as NMS is easily calculable and FS is negligible. Both NMS and SMS are inversely proportional to the square of the mass number A, i.e. $1/A^2$, but SMS may be still large in heavy elements for certain type of transitions in which the correlation between the electrons gets altered during transition. The evaluation of SMS involves a correct treatment of the correlation between the linear momenta of the electrons. Calculations of SMS reported in few specific transitions of some elements have yielded values which are as yet only in qualitative agreement with the experimental values. Even in light elements such as Li, an elaborate treatment yields only values which are in fair agreement with the experimental values. For the heavy elements the calculations are very difficult. Ab initio calculations of SMS have been reported [47] for some transitions in few rare-earth elements.

Evaluation of SMS in heavy elements involves its separation from the FS, as the isotope shift is the sum of the
two (normal mass shift is easily calculable). The separation of SMS from FS is done by the method proposed by King [48] which involves plotting of the isotope shift, in a particular transition \(\lambda_i\) for various pairs of isotopes, against the isotope shift in other transition \(\lambda_j\) for the same pair of isotopes. The plot results in a straight line with the slope giving the ratio of field shift \([FS_i / FS_j]\) and the intercept provides information on the specific mass shift in transition plotted. If the SMS in one of the transition is known then both SMS and FS can be evaluated for the other transition. The SMS has been shown, both theoretically and experimentally, to be negligible in the \((ns - np)\) and \((ns^2 - nsnp)\) type of transitions. Whereas in some transitions, e.g. for the \(f^n - f^{n-1}\) type of transitions, the SMS is theoretically expected to be large. Thus choosing a transition in which SMS is expected to be negligible simplifies the separation of SMS and FS.

Isotope shifts have been measured in four transitions of Gd II using highly enriched stable even - A isotopes (including the rare \(^{152}\)Gd isotope with 0.2 % abundance). All these 4 transitions are of type \(4f^75d6p - 4f^75d6s\) as the SMS was expected to be negligible in the transition. A value of \(\delta<\mathbf{r}^2>_{152,156} = 0.423 \text{ fm}^2\) has been evaluated using the isotope shift data in 3813.97 A line and taking specific mass shift...
\[ \Delta r^2 \] in Stable Gd Isotopes

As mentioned earlier, isotope shift in heavier elements is a composition of mass and field shift. The field shift contains the information about the nucleus as it arises due to the difference in nuclear potential of the isotopes causing differences in the electrostatic interaction between the electrons and the nuclear charge distribution. Thus information on nuclear charge distribution can be extracted from the measured isotope shift by separating SMS and FS via the King plot, as mentioned earlier. The FS values is then used to evaluate the nuclear mean square charge radii \[ \Delta r^2 \] from the field shift.

Isotope shifts involving all the stable even-A isotopes of gadolinium have been studied in four UV transitions of Gd.
II using optical techniques and highly enriched isotopes. In the present studies, the changes in the mean - square nuclear charge radii $\delta \langle r^2 \rangle$ of all even isotopes of $^{^{\text{A}}_{\text{Gd}}}$ (A = 152, 154, 156, 158, 160) have been evaluated, using semi - empirical approach and without restoring to the calibration with the muonic X ray value as reported in [4].
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