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Selective excitation of odd gadolinium isotopes using two-colour photoionisation schemes

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Abstract

Selective excitation of odd isotopes of gadolinium has been carried out using two-colour photoionisation schemes. A new parameter $\eta_{\text{sel-ion}}$ is defined for identifying optimum frequency positions for both excitation steps, where good isotopic selectivity can be achieved without significant sacrifice in the ion yield. The abundance of ^{155}Gd and ^{157}Gd isotopes were theoretically calculated and experimentally verified. All five photoionisation schemes are found to be useful for the selective ionisation of ^{155}Gd and ^{157}Gd isotopes. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Odd isotopes of gadolinium (^{155}Gd and ^{157}Gd) have very high neutron absorption cross-sections and hence they are used as burnable poison in nuclear reactors [1]. Some of the even isotopes such as ^{152}Gd, ^{154}Gd and ^{156}Gd reduce the performance of gadolinium as an effective burnable poison. Very little work has been reported on the selective ionisation of odd isotopes. Guyadec et al. [2] have used a multi-step photoionisation scheme with polarized lasers, where atoms are placed in a uniform magnetic field. A large degree of selectivity has been reported for the odd isotopes. However, utilisation of such photoionisation schemes involving magnetic fields is not viable for large scale separations, due to inherent complexity in the experimental geometry. Santala et al. [3] have used one-photon resonant two-photon ionization schemes, wherein the resonant transition step involves the use of UV photons. The isotope shift of the constituent isotopes is used for obtaining selectivity of odd isotopes. An enrichment of about 45–70% has been obtained for the odd isotopes. More recently, we have used single colour photoionisation experiments within the tunable range of rhodamine-6G dye for selective excitation of ^{155}Gd and ^{157}Gd isotopes using broadband lasers [4]. In single colour photoionisation experiments, ionisation is carried out through a UV laser to satisfy the condition $E_{\lambda_1} + E_{\lambda_i} \geqslant \text{IP}$ (where $E_{\lambda 1}$ is photon energy of the resonance step, E_{λ_i} is photon energy of the non-resonance ionisation step and IP is the ionisation potential of the atom under consideration). Utilisation of a UV laser in the ionisation step results in poor photon economy. Therefore, improvement in the photon utilisation efficiency is required.

In the present paper, we have studied the possibility of using two-colour photoionisation schemes for selective excitation of odd isotopes of gadolinium. The reason for inclusion of an additional resonance step in comparison to our earlier work is multi-fold.

1. The non-resonant ionisation using a UV laser results in poor photon economy due to losses in harmonic generation.
2. Inclusion of an additional resonance transition increases selectivity of the odd isotopes further.
3. The resonance transition within the tunable range of Rhodamine-6G dye (570–610 nm) can be employed for some of the photoionisation schemes. Since copper vapour lasers can be used for pumping Rhodamine-6G dye, the duty cycle can be improved dramatically.

In the present work, five photoionisation schemes were identified for carrying out selective excitation of

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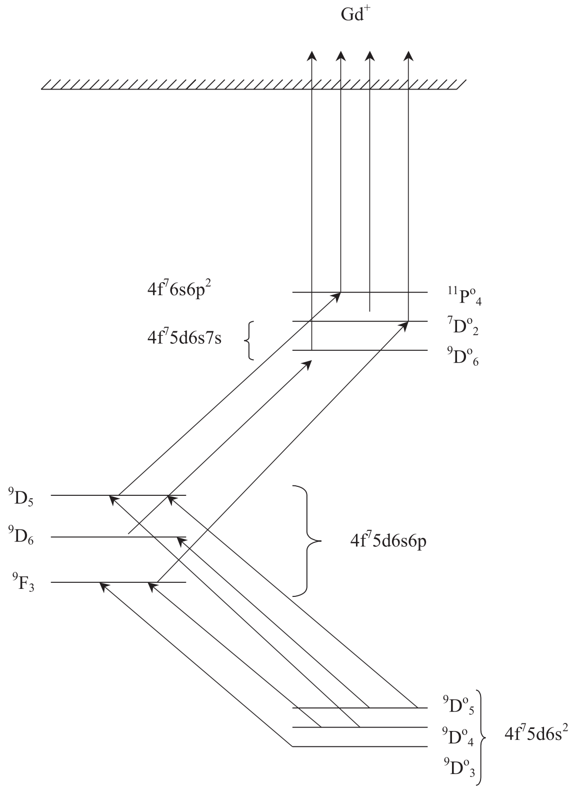

Fig. 1. Schematic of the two-colour photoionisation schemes of gadolinium.

odd isotopes of gadolinium (Fig. 1). Although we have primarily aimed at studying the two colour photoionisation schemes, where both the transitions fall within the tunable region of Rhodamine-6G (viz., Schemes 3, 4 and 5), we have also considered other photoionisation schemes involving other transitions which do not fall within this range.

2. Principle

Gadolinium has seven naturally occurring isotopes ^{152}Gd (0.20%), ^{154}Gd (2.15%), ^{155}Gd (14.73%), ^{156}Gd (20.47%), ^{157}Gd (15.68%), ^{158}Gd (24.87%) and ^{160}Gd (21.90%). It is a multi-electron system having a ground state electronic configuration of [Xe]$4f^7 5d6s^2$. Therefore, numerous photoionisation schemes can be formulated for selective ionisation studies. Evaluation of the efficacy of these photoionisation schemes experimentally is not viable because it requires an enormous amount of experimental time and effort. Accordingly, we have developed a spectral simulation method [5] for the theoretical evaluation of the efficacy the photoionisation schemes. Once the most efficient photoionisation schemes are identified, experimental efforts can be focussed on these schemes.

2.1. Selectivity

Isotopic selectivity is defined as the ability to detect the isotope of interest in the presence of other undesired isotopes.

$$S(\omega) = \frac{I_{\mathrm{M1}}(\omega)}{I_{\mathrm{all}}(\omega)}, \tag{1}$$

where $I_{\mathrm{M1}}(\omega)$ is the intensity of the M1 isotope when the laser is tuned to the frequency ω and $I_{\mathrm{all}}(\omega)$ is the intensity of all other isotopes at the same laser frequency ω.

In a multi-step photoionisation process the overall selectivity is defined as

$$S = \prod_{i=1}^{k} S_i, \tag{2}$$

where S is the selectivity of the photoionisation process and S_i is the selectivity of the ith resonance transition and k is the number of resonant transitions involved in the photoionisation scheme.

2.2. Ionisation efficiency (η_{ion})

Ionisation efficiency (η_{ion}) is defined as the ratio of the ion yield of the isotope when the laser is detuned (Δ) from resonance, to the ion yield when the laser is tuned to its resonance frequency.

$$\eta_{\mathrm{ion}} = \frac{I(\Delta)}{I(0)}, \tag{3}$$

where $I(\Delta)$ is the ion yield when the laser is detuned and $I(0)$ is the ion yield when the laser is tuned to the resonance of the isotope.

2.3. Selective ionisation efficiency ($\eta_{sel\text{-}ion}$)

In resonance ionisation spectroscopy, isotopic selectivity of a desired isotope is calculated by estimating the wing contribution of the interfering isotope at the resonance frequency of the isotope of interest. Hence, maximum selectivity can be expected when the laser is tuned to the exact resonance of the isotope of interest. However, in many cases it can be found that the wing contribution of interfering isotopes is of several orders magnitude higher at the resonance than at the detuned positions. Hence, two cases arise:

1. Large selectivity can be obtained by detuning the laser to these detuned positions where wing overlap of the interfering isotopes is small. This results in large selectivity, albeit with a small percentage ionisation of the desired isotope.

A typical plot of ionisation efficiency as a function of laser detuning from the resonance of ^{160}Gd isotope is shown in Fig. 2. It illustrates that if the laser is detuned by about 2000 MHz, then the ionisation efficiency reduces to about ~7.8%. Similarly, if the laser is detuned by about five times the linewidth of the excitation laser (i.e., 6000 MHz), the ionisation efficiency is as small as 0.77%.

2. Alternatively, the laser can be tuned to the exact resonance position of the desired isotope to achieve maximum ionisation. This also results in the ionisation of interferring isotopes, thus leading to poorer selectivity.

In practice one needs to find an optimum frequency position where selectivity is achieved without significant sacrifice in the ion yield. In order to find such optimum frequency positions a new parameter 'selective ionisation efficiency factor' ($\eta_{\text{sel-ion}}$) is defined as

$$\eta_{\text{sel-ion}} = S\eta_{\text{ion}}, \tag{4}$$

where S is the isotope selectivity and η_{ion} is the ionisation efficiency parameter. $\omega_{\text{sel-ion}}$ is defined as the frequency position at which $\eta_{\text{sel-ion}}$ is maximum.

In the spectral simulation approach the atomic line profile is generated by taking into account the appropriate abundances, isotope shifts of the constituent isotopes, and hyperfine structure in case of the odd isotopes. The atomic line profiles are used for simulation of the excitation spectrum for a given laser linewidth. Isotopic selectivities can be computed using Eq. (1). The

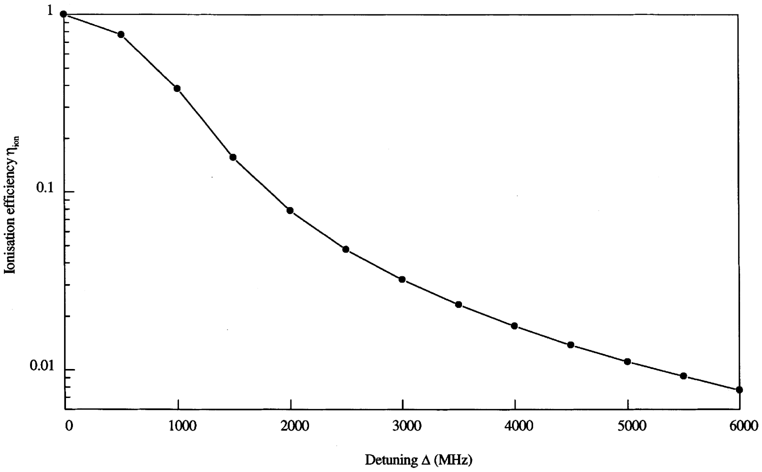

Fig. 2. Computed ionisation efficiency η_{ion} of ^{160}Gd as a function of laser detuning. The laser linewidth and Doppler width are assumed to be 1200 and 800 MHz, respectively.

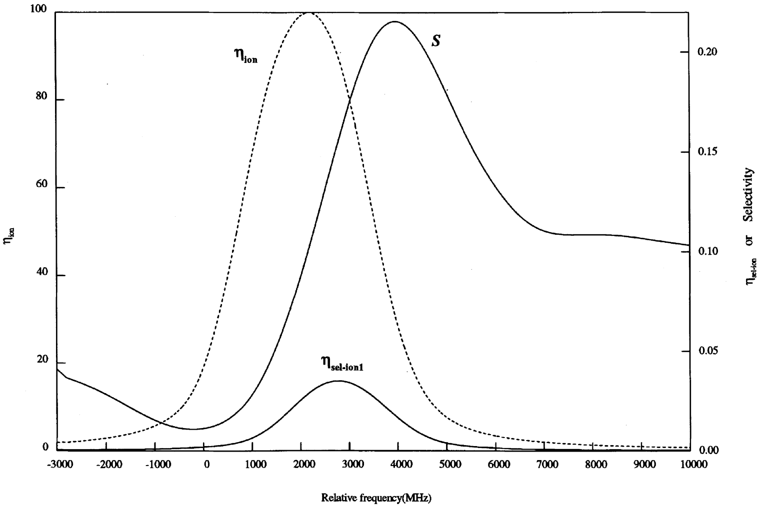

Fig. 3. Ionisation efficiency (η_{ion}), selectivity, and selective ionisation efficiency $\eta_{\text{sel-ion}}$ of odd isotopes as a function of laser detuning for the 585.1629 nm transition.

Table 1
Optimum frequencies for the selective ionisation of ^{155}Gd and ^{157}Gd isotopes utilizing first and second excitation steps

Scheme	First excitation transition		Second excitation transition	
	λ_1 (nm)	$\omega_{\text{sel-ion1}}$ (MHz)	λ_2 (nm)	$\omega_{\text{sel-ion2}}$ (MHz)
1	574.4660	+2136	561.0675	+228
2	585.1537	+2230	561.0675	+92
3	585.6217	+2846	599.1844	−810
4	569.6209	+2270	572.0004	−1008
5	585.1629	+2790	572.0004	−1066

Table 2
Isotope shifts for various transitions relative to the ^{160}Gd isotope

Transition (nm)		Isotope shift (MHz)				
		^{158}Gd	^{157}Gd	^{156}Gd	^{155}Gd	^{154}Gd
First excitation transition	569.6209	−1090	−1910	−2130	−2840	−3510
	574.4660	−1100	−1970	−2170	−2890	−3590
	585.1537	−1100	−2060	−2270	−2950	−3730
	585.1629	−1080	−1990	−2110	−2810	−3490
	585.6217	−1120	−2010	−2200	−2930	−3630
Second excitation transition	561.0675	300	360	690	640	1030
	572.0003	337.5	921	740.9	1182.4	1220.9
	599.1844	502.5	836.6	975.6	964.6	1600.5

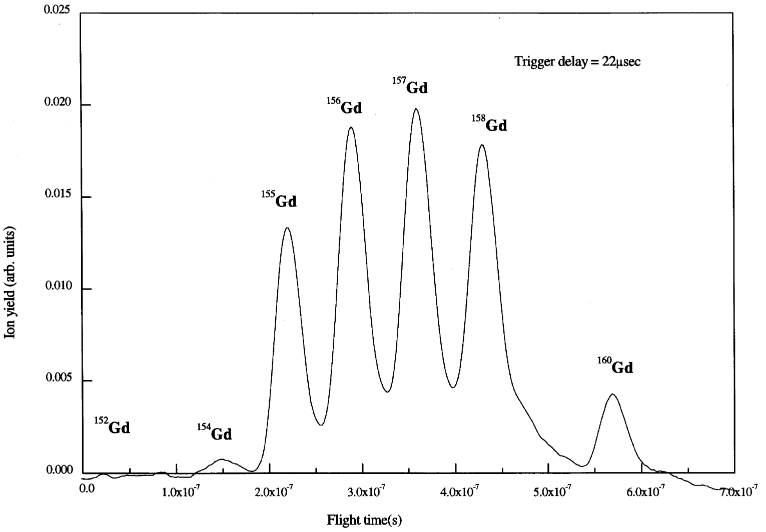

Fig. 4. Time-of-flight mass spectrum recorded by tuning both excitation lasers to their optimum frequency positions of Scheme 1.

details of the calculation of isotopic selectivities using the spectral simulation method for single and multi-step photoionisation can be found elsewhere [6]. A brief description of the method for calculating isotopic selectivities is given below.

In this method, the isotopic selectivity is calculated as a function of laser frequency by incorporating all the atomic and spectral parameters for the first excitation transition. The $\omega_{\text{sel-ion1}}$ (optimum frequency position for the first excitation transition) is identified where selective ionisation of the odd isotopes can be achieved without significant sacrifice in the ion yield. Thus the frequency position ($\omega_{\text{sel-ion}}$) is identified where $\eta_{\text{sel-ion}}$ is maximum. The abundance of all the constituent isotopes is determined at this laser frequency. The optimum laser frequency positions have been calculated for the second excitation transition ($\omega_{\text{sel-ion2}}$) by incorporating the abundances obtained after the first excitation step.

Table 3
Theoretical and experimentally obtained abundances of odd isotopes of gadolinium for two-colour excitation schemes

Scheme	λ_1 (air) (nm)	λ_2 (air) (nm)	Abudance (%) ^{155}Gd		Abudance (%) ^{157}Gd	
			Th.	Expt.	Th.	Expt.
1	574.4660	561.0675	16.2	17.8	27.6	26.5
2	585.1537	561.0675	19.1	21.5	23.7	20.3
3	585.6217	599.1844	27.7	29.0	21.3	23.2
4	569.6209	572.0004	24.7	25.5	20.5	22.4
5	585.1629	572.0004	28.3	27.0	23.9	21.8

Isotopic selectivity, ionisation, and $\eta_{\text{sel-ion}}$ have been plotted in Fig. 3 as a function of laser detuning for the 585.162 nm transition. It can be seen that the isotopic selectivity reaches a maximum value when the laser is tuned to 3970 MHz, where as ionisation of the odd isotopes is maximum at its resonance frequency i.e., 2190 MHz. Therefore, optimum frequency ($\omega_{\text{sel-ion1}}$) for selective excitation is identified as 2790 MHz, where ionisation efficiency is 89.6% relative to the ionisation at resonance (100%). Similarly, the optimum laser frequency positions for both the excitation steps ($\omega_{\text{sel-ion1}}$ and $\omega_{\text{sel-ion2}}$) for all photoionisation schemes have been calculated and tabulated in Table 1. The hyperfine constants *A* and *B* of the odd isotopes for the ground and the two intermediate levels are obtained from [7,8]. The isotope shifts of different second-resonant excitation transitions for the gadolinium isotopes relative to ^{160}Gd were calculated from the results of two-photon Doppler-free spectroscopy by Jia et al. [8]. The isotope shifts for the various first and second excitation transitions are listed in Table 2.

3. Experimental

The details of the experimental setup can be found in [4]. The only difference is that, a tunable dye laser is used in the present study rather than a frequency doubler.

For multi-step photoionisation, it is necessary to have good spatial overlap of both the excitation lasers. In order to ensure a good spatial overlap both dye lasers are tuned to the resonance of the exciation transitions. By varying the spatial overlap of both the dye lasers, and monitoring the ionisation of the photoions, effective overlap is ensured. The atoms excited by the lasers are ionised by a non-resonant ionization step by photons from the second excitation laser. The pulse energies of both lasers were appropriately minimised to reduce saturation broadening and to avoid multi-photon ionisation (MPI) of the atoms.

4. Results and discussion

First, the excitation lasers were tuned to the resonance frequencies of the first and second excitation transitions of the photoionisation scheme. The resonance frequency of ^{160}Gd isotope was identified by scanning the dye laser at a scan rate of 0.00005 nm/s while monitoring the ion yield of the isotope. After identifying the resonance of ^{160}Gd isotope, both the dye lasers are detuned to their optimum frequency positions

Table 4
Thermal neutron absorption properties of natural, and mixture 1 and mixture 2

Isotope	$\sigma_{\gamma,n}$ (barns)	Natural isotopic mixture		Mixture 1[a] (single-colour photoionisation scheme)		Mixture 2[a] (two-colour photoionisation scheme)	
		Abundance (%)	σ_{nat} (barns)	Abundance (%)	σ_1 (barns)	Abundance (%)	σ_2 (barns)
^{152}Gd	735	0.2	1.47	0	0	0	0
^{153}Gd	36 000	0	0	0	0	0	0
^{154}Gd	85	2.15	1.83	1.0	0.85	1.0	0.85
^{155}Gd	60 900	14.73	8970.6	20.0	12 180.0	17.8	10 840
^{156}Gd	1.5	20.47	0.3	32.4	0.49	25.1	0.37
^{157}Gd	254 000	15.68	39 827.2	24.3	61 722	26.5	67 310
^{158}Gd	2.2	24.87	0.6	19.5	0.43	23.7	0.52
^{160}Gd	0.8	21.90	0.2	3.0	0.02	5.7	0.04
Total			48 800		73 900		78 152

[a] Mixture 1 abundances obtained after single colour excitation (Ref. [4]).

[a] Mixture 2 abundances obtained after two-colour excitation (present work).

($\omega_{\text{sel-ion1}}$ and $\omega_{\text{sel-ion2}}$) deduced from theoretical calculations. Subsequently, the time-of-flight mass spectrum of the isotopes is recorded (Fig. 4). The abundance of the constituent isotopes is computed after deconvoluting the time of flight spectrum. The results are listed in Table 3. It can be seen from Table 3 that abundance of the odd isotopes obtained experimentally are in good agreement with the theoretically predicted values. The overall abundance of the odd isotopes can be raised to 40–52%. The abundance of the unwanted isotopes can be limited to ~50%, in which the abundance of the ^{156}Gd is about ~25%. Although the abundance of ^{156}Gd is large, the performance of the enriched gadolinium isotopic mixture as burnable poison is not ruined, because the ^{156}Gd isotope has a thermal neutron absorption cross-section of 1.5 barns. The abundance of the unwanted isotopes such as ^{152}Gd and ^{154}Gd is further reduced as a result of selectivity of the second resonance transition. The microscopic capture cross-section of a typical isotopic mixture obtained using the two-colour photoionisation scheme is 78152 barns which is ~1.6 times larger than the capture cross-section for natural gadolinium (Table 4).

5. Conclusion

We have studied five photoionisation schemes for obtaining selective excitation of odd isotopes of gadolinium. Optimum detuned frequency positions for the first and second excitation steps have been theoretically determined using the spectral simulation method. The abundances of odd isotopes are determined by detuning the lasers to these optimum frequency positions. For all two-color photoionisation schemes studied, experimental abundances were in excellent agreement with the theoretical values. The two-colour photoionisation schemes studied can increase the abundance of odd isotopes up to ~52%, apart from complete removal of unwanted isotopes such as ^{152}Gd.

The isotope shifts of the second excitation transitions were small in comparison to the first excitation transitions. Therefore, utilisation of broadband lasers for the second excitation step would not significantly improve selectivities. Despite the smaller selectivities, these multistep photoionisation schemes are attractive because they improve the photon utilisation efficiencies. In particular, photoionisation Schemes 3, 4 and 5 are of importance since both the excitation transitions involve Rhodamine-6G dye lasers. These can be pumped by high repetition-rate copper vapour lasers thereby increasing photon economy.

Several photoionisation schemes can be formulated for gadolinium because it has a rich spectrum. The primary handicap at present is the limited spectroscopic data, such as hyperfine structure and isotope shift of the higher excited transitions. This also highlights the need for more extensive work on these aspects, and we are presently working in this area.

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