

DFT calculations of Ti-based molecules clustering with Ar for laser-based enrichment of stable isotopes

Production of Sc radionuclides for medical applications

The Scandium (Z=21) element has been identified for its theranostics potential in nuclear medicine thanks to the possible combination of imaging modalities (using ⁴³Sc and ⁴⁴Sc) with radionuclide therapy (using ⁴⁷Sc) [1,2]. However, the efficient production of these isotopes requires to work with enriched Ca (Z=20) or Ti (Z=22) isotopes, which reliable supply is a strategic challenge.

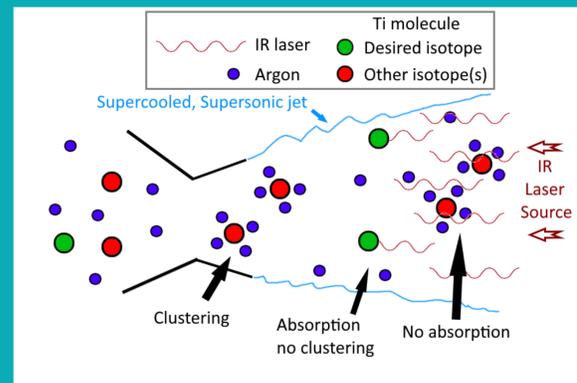
42Ti 208.65 ms ε = 100.00%	43Ti 509 ms ε = 100.00%	44Ti 60.0 y ε = 100.00%	45Ti 184.8 m ε = 100.00%	46Ti STABLE 8.25%	47Ti STABLE 7.44%	48Ti STABLE 73.72%	49Ti STABLE 5.41%	50Ti STABLE 5.18%
41Sc 596.3 ms ε = 100.00%	42Sc 680.70 ms ε = 100.00%	43Sc 3.891 h ε = 100.00%	44Sc 3.97 h ε = 100.00%	45Sc STABLE 100%	46Sc 83.79 d β ⁻ = 100.00%	47Sc 3.3492 d β ⁻ = 100.00%	48Sc 43.67 h β ⁻ = 100.00%	49Sc 57.18 m β ⁻ = 100.00%
40Ca > 3.0E+21 y 96.94% 2ε	41Ca 9.94E4 y ε = 100.00%	42Ca STABLE 0.647%	43Ca STABLE 0.135%	44Ca STABLE 2.09%	45Ca 162.61 d β ⁻ = 100.00%	46Ca > 0.28E+16 y 0.004% 2β ⁻	47Ca 4.536 d β ⁻ = 100.00%	48Ca > 5.8E22 y 0.187% 2β ⁻ = 75.00%

[3]

Radionuclide Half-life Reactions

43Sc	3.89 h	⁴⁰ Ca(α,p) ⁴³ Sc, ⁴² Ca(d,n) ⁴³ Sc, ⁴³ Ca(p,n) ⁴³ Sc, natCa(α,n) ⁴³ Ti→ ⁴³ Sc ⁴⁶ Ti(p,α) ⁴³ Sc
44Sc	3.97 h	⁴⁴ Ca(p,n) ⁴⁴ Sc/ ^{44m} Sc, ⁴⁴ Ca(d,2n) ⁴⁴ Sc/ ^{44m} Sc, natCa(p,xn) ⁴⁴ Sc ⁴⁵ Sc(p,2n) ⁴⁴ Ti→ ⁴⁴ Sc ⁴⁷ Ti(p,α) ⁴⁴ Sc/ ^{44m} Sc
44mSc	58.6 h	⁴⁴ Ca(p,n) ⁴⁴ Sc/ ^{44m} Sc, ⁴⁴ Ca(d,2n) ⁴⁴ Sc/ ^{44m} Sc
47Sc	3.35 d	⁴⁶ Ca(n,γ) ⁴⁷ Ca→ ⁴⁷ Sc, ⁴⁸ Ca(p,2n) ⁴⁷ Sc ⁴⁷ Ti(n,p) ⁴⁷ Sc, ⁴⁸ Ti(γ,p) ⁴⁷ Sc, ⁴⁸ Ti(p,2p) ⁴⁷ Sc, ⁵⁰ Ti(p,α) ⁴⁷ Sc

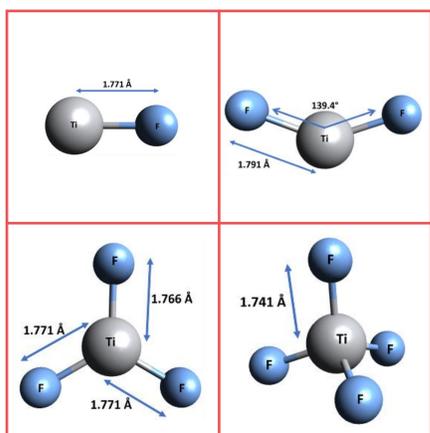
Separation of Isotopes by Laser Assisted Retardation of Condensation



- A molecule containing the element of interest is introduced in a buffer gas cell.
- The mixture is released through an aperture and the expanding gas jet becomes supersonic, resulting in sudden cooling (to ~15K),

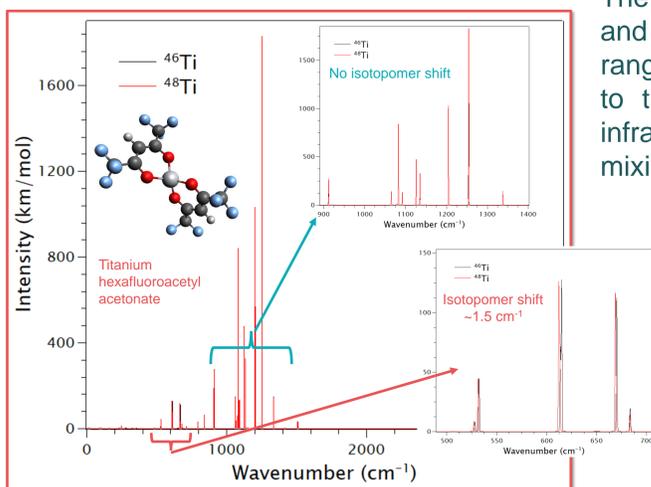
- The buffer gas condensates on the molecules and forms clusters.
- Isotope-selective infrared (IR) excitations of the molecules heats up an isotopomer (molecule containing a specific isotope), preventing clusterization.
- The heavy clusters and clean isotopomer experience different drag forces and can be separated by a skimmer.
- Recycling of the material allows for multiple passages for improved enrichment of the isotope of interest.

The technique has been demonstrated on sulfur [4] but requires specific developments for each new element, especially to identify the appropriate volatile molecule and which IR transitions are most sensitive to isotopomer shifts.



Density Functional Theory (DFT) calculations were performed with the ORCA 5.0 software package [5] using the hybrid PBE0 exchange-correlation functional based on benchmarking on experimental data (bond length, harmonic vibrational frequencies) with TiF₄ [6].

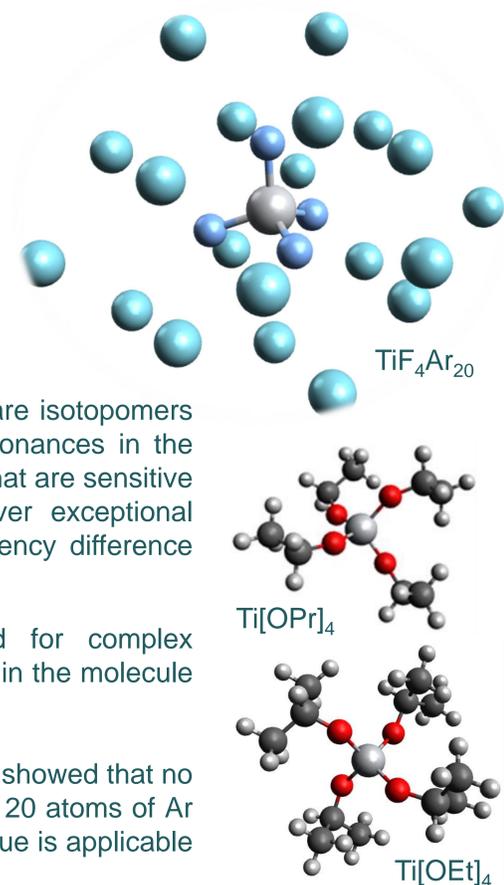
For each molecule, the geometry is first optimized. The harmonic vibrational frequencies are then determined, which are all positive thus confirming that the optimized geometries correspond to true minima in the potential energy surface.



The vibrational spectra are determined for different Ti isotopes to compare isotopomers and identify suitable IR transitions for SILARC. All spectra include resonances in the range 650-850 cm⁻¹, corresponding to a wavelength range of 12-15 μm, that are sensitive to the Ti isotopes. The generation of such photons requires however exceptional infrastructures, such as a free electron laser or a complex laser frequency difference mixing system [7].

Higher frequency/lower wavelength resonances are identified for complex molecules. However, those involved systematically other elements in the molecule and are thus not sensitive to the exchange of Ti isotopes.

The clustering of Ar to TiF₄ is also investigated in this framework. It showed that no clustering is expected at room temperature, while the clustering of 20 atoms of Ar to TiF₄ is still bound at 15K. This suggests that the SILARC technique is applicable for Ti-containing molecules.



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 [4] J.-M. Zellweger, J.-M. Philippoz, P. Melinon, R. Monot, H. van den Bergh. *Isotopically selective condensation and infrared-laser-assisted gas-dynamic isotope separation*. Physical Review Letters **52** (1984) 522-525.
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 [7] E. Boursier, P. Segonds, B. Ménaert, V. Badikov, V. Panyutin, D. Badikov, V. Petrov, B. Boulanger. *Phase-matching directions and refined Sellmeier equations of the monoclinic acentric crystal BaGa₄Se₇*. Optics Letters **41** (2016) 2731.

