Impurity Absorption Spectroscopy of the Deep Double Donor Sulfur in Isotopically Enriched Silicon

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Introduction

Isotopically enriched Si opens new spectroscopic possibilities by eliminating inhomogeneous broadening.

^{28}Si isotope Enrichment [1]: **99.991 % ^{28}Si**
Sample Purity: $2 \times 10^{12}\,\mathrm{cm}^{-3}$ P; $5 \times 10^{13}\,\mathrm{cm}^{-3}$ B

^{nat}Si isotope distribution: 92.2 % ^{28}Si + 4.7 % ^{29}Si + 3.1 % ^{30}Si

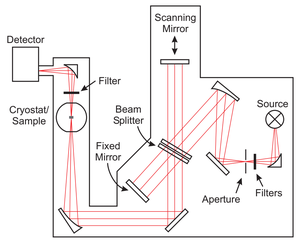
Motivation

- Deep donor S is well studied
- High diffusivity of S in Si
- Several different isotope effects
- Results apply to other chalcogens and deep centres

Experimental Method

Fourier Transform Spectroscopy

- Bomem DA8 Fourier-transform spectrometer.
- Resolution: $0.0024\,\mathrm{cm}^{-1}$ (boxcar truncation), verified to be better than $0.007\,\mathrm{cm}^{-1}$.
- Illumination conditions: Globar, Quartz lamp
- Beam splitters: KBr and CaF_2
- Detectors: HgCdTe, InSb, InAs

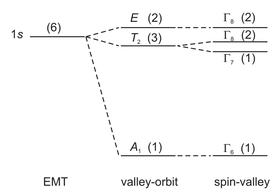


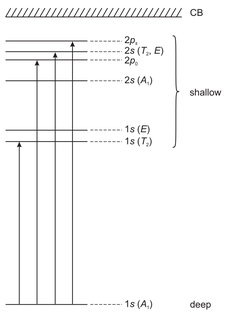
Experimental setup with Fourier-transform interferometer, Cryostat, Detector. The beam path is evacuated.

Sample Preparation

- Si plus sulfur sealed in ampule
- Ampule kept in furnace for 20 h at 1100 °C
- Quench into methanol, polish and etch

Deep Double Donor Sulfur





Valley-orbit splitting of 6-fold degenerate $1s$ ground state together with spin-valley splitting leads to Γ_7, Γ_8 splitting of the $1s(T_2)$ transition.

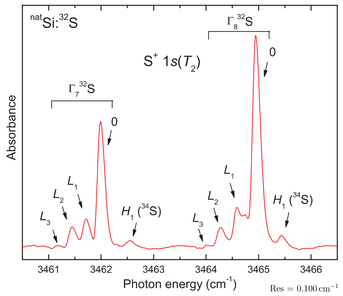
The $1s(A_1) \rightarrow 1s(T_2)$ transition is EMT forbidden, symmetry allowed [2, 3].

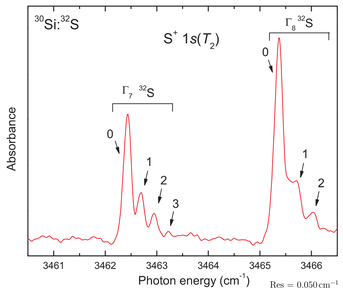
S^+ 1s(T$_2$) in Si

L_i: Si isotope effect
H_1: S isotope effect.

L_i are due to changes in the nearest-neighbour LVM energy of the SSi_4 cluster of the substitutional S atom [4].

The '0'-peak is the result of a S-$^{28}Si_4$ cluster.





'1', '2' and '3' are due to Si isotope effect.

The sattelite pattern is opposite to ^{28}Si due to the 'anti-natural' isotopic compostiton of the ^{30}Si sample (2.5% ^{28}Si, 7.7% ^{29}Si).

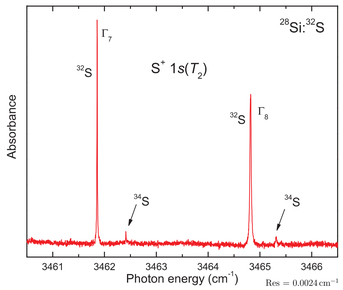
Si isotope enrichment/composition determines the sign for LVM satellite peaks.

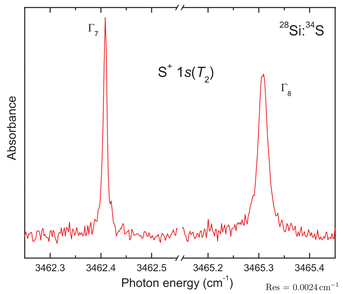
S^+ 1s(T$_2$) in ^{28}Si

The L_i satellites are eliminated.

Energy shift between ^{32}S and ^{34}S centres is visible.

$E_B(^{32}\mathrm{S}) - E_B(^{34}\mathrm{S}) = -0.56\,\mathrm{cm}^{-1}$ confirms previous result for S^+ $1s(T_2)$ [4].





FWHM:
$1s(T_2)$ Γ_7: $0.008\,\mathrm{cm}^{-1}$
$1s(T_2)$ Γ_8: $0.022\,\mathrm{cm}^{-1}$

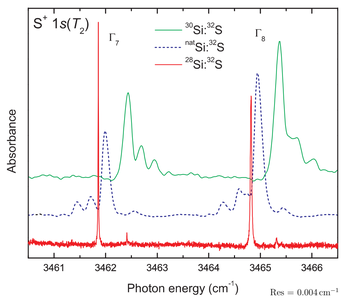
Γ_7 is 100% Lorentzian/ lifetime limited, inhomogeneous isotope broadening is completely removed [5].

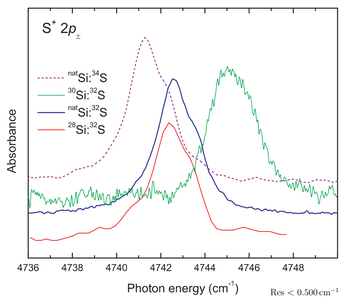
S^+ $1s(T_2)$ Γ_7 is the narrowest donor/acceptor absorption line in silicon to date.
22 × narrower than in previous S spectra [4]; 2 × narrower than in previous P and B spectra [6]

Si- and S-Isotope Shifts

The $1s(T_2)$ Γ_7 line for ^{32}S lies below that of ^{34}S by $0.56\,\mathrm{cm}^{-1}$, confirming the unusual isotope shift for this transition first reported by [4].

Dependence of the binding energy on ϵ_0 and m^* [7] and Si nearest-neighbour effects causes energy shift.





$E_B(^{32}\mathrm{S}) - E_B(^{34}\mathrm{S}) = +1.4\,\mathrm{cm}^{-1}$, confirming the normal sign of the ground state isotope shift [8] also seen for B in Si [5, 7].

Unresolved splitting of S^+ $2p_\pm$ is resolved in selenium (^{28}Si:^{77}Se) [9].

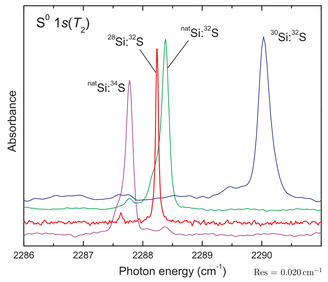
Linewidth is almost entirely lifetime limited.

We confirm an inverted S isotope shift for the S^+ $1s(T_2)$ transition as compared to all other transitions.

S^0 1s(T$_2$)

Host (Si) and impurity (S) isotope shift are present with the normal $E_B(^{32}\mathrm{S}) - E_B(^{34}\mathrm{S}) = +0.61\,\mathrm{cm}^{-1}$ impurity isotope shift.

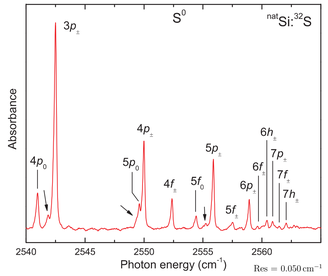
Tails on ^{nat}Si and ^{30}Si samples are seen for S^0 $1s(T_2)$ and p-states, similar to B and P [6]. They are possibly due to unresolved nearest neighbour structure.



S^0 p-states

Arrows indicate absorption lines due to ^{34}S impurity centres.
$E_B(^{32}\mathrm{S}) - E_B(^{34}\mathrm{S}) = +0.64\,\mathrm{cm}^{-1}$ for S^0 $2p_\pm$.

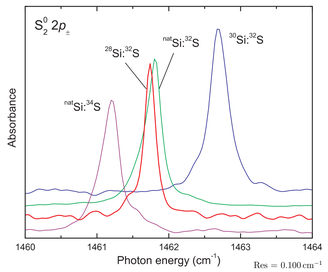
Spectrum shows two more highly excited states than published before [3, 4, 10, 11].



S_2^0 (neutral sulfur pair)

Host (Si) and impurity (S) isotope shift reported for the first time for a S_2^0 transition.

Linewidth improvement for ^{28}Si is not as dramatic here due to lifetime limitations.



Acknowledgments

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