

Molecular Spectra of Sulfur Molecules and Solid Sulfur Allotropes

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Abstract Molecular spectroscopy is one of the most important means to characterize the various species in solid, liquid and gaseous elemental sulfur. In this chapter the vibrational, UV-Vis and mass spectra of sulfur molecules with between 2 and 20 atoms are critically reviewed together with the spectra of liquid sulfur and of solid allotropes including polymeric and high-pressure phases. In particular, low temperature Raman spectroscopy is a suitable technique to identify single species in mixtures. In mass spectra cluster cations with up to 56 atoms have been observed but fragmentation processes cause serious difficulties. The UV-Vis spectra of S₄ are reassigned. The modern XANES spectroscopy has just started to be applied to sulfur allotropes and other sulfur compounds.

Keywords Vibrational spectra · Electronic spectra · Mass spectra · XANES spectra · Photolysis

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List of Abbreviations and Symbols

S_π	Mixture of soluble sulfur rings other than S_8
S_∞	Polymeric sulfur dissolved in liquid sulfur (mixture of very large rings and very long chains)
S_μ	Polymeric insoluble sulfur usually prepared from liquid sulfur
DOS	Density of states
IR	Infrared
FTIR	Fourier transform infrared
LD	Lattice dynamics
MD	Molecular dynamics
Me	Methyl group
STP	Standard temperature-pressure (conditions)
UBFF	Urey-Bradley force field
XANES	X-ray absorption near edge structure

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Introduction

Elemental sulfur is one of the best investigated chemical elements but it represents also one of the most complex systems. The large number of its allotropes (ca. 30 [1]) and their peculiar behavior on melting, vaporization and under pressure made it necessary to investigate this element by as many types of molecular spectroscopy as possible to identify the molecular species present. In this chapter the results of these investigations are reviewed.

Most informative in this context is vibrational spectroscopy since the number of signals observed depends on the molecular size as well as on the symmetry of the molecule and, if it is part of a condensed phase, of its environment. In particular, Raman spectroscopy has contributed much to the elucidation of the various allotropes of elemental sulfur and to the analysis of complex mixtures such as liquid and gaseous sulfur.