IR DISSOCIATION OF WEAKLY BOUND VAN DER WAALS COMPLEXES: \((\text{SF}_6)_n\), \((\text{SiF}_4)_n\), \((\text{SiH}_4)_n\), \((\text{C}_2\text{H}_4)_n\), \((n=2, 3)\) IN THE 9-11 \(\mu\text{m}\) RANGE

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ABSTRACT. Small \((\text{SF}_6)_n\), \((\text{SiF}_4)_n\), \((\text{SiH}_4)_n\), \((\text{C}_2\text{H}_4)_n\), \((n=2, 3)\) clusters have been produced in a molecular beam. \text{SF}_6 and \text{SiF}_4 dimer dissociation spectra were measured and spectral features due to clusters containing different S and Si isotopes could be resolved. The contribution of trimers could be estimated in case of \text{SF}_6. Dissociation spectra of small \text{SiH}_4 clusters were measured for the first time in the frequency range 880 \(\text{cm}^{-1}\) - 940 \(\text{cm}^{-1}\). In the dissociation spectra of ethylene clusters van der Waals modes coupled with the out of plane \(\nu_7\) \text{C}_2\text{H}_4 vibration have been observed for the dimer, and a long predissociation lifetime (15 ns) has been inferred from the observed narrow (FWHM = 10 MHz) rotational lines.

1. INTRODUCTION

IR predissociation experiments on small clusters can provide information about the formation of the clusters, about the dissociation process itself and sometimes about the structure of the studied complexes. Clusters are usually produced in a nozzle expansion by properly selecting the nozzle diameter, the source pressure and temperature. The cluster formation process can be manipulated by using various seeding gases with different concentration. In order to produce small clusters, a combination of small nozzle diameter, high source pressure and very diluted gas mixtures is required.

The formed complex can be excited by IR (laser) radiation of suitable frequency, which is usually close to the frequency of a vibrational mode of the monomer species. For weakly bound systems the energy of the excited complex exceeds by far their binding energy, thus the IR excitation originates the cluster bond rupture after a fast intramolecular relaxation. From the spectral linewidth of the IR absorption

the lifetime of the excited complex can be calculated.

In the dissociation process the cluster fragments are scattered out of the supersonic beam. The fragments can be detected in order to obtain information about the energy partition in the dissociation. The IR cluster dissociation cross-section can be obtained by measuring the attenuation of the beam signal. The IR dissociation spectrum is recorded monitoring the beam attenuation as a function of the laser frequency. This spectrum can give some insight in the structure of the complex. We measured the dissociation spectra for clusters of SF₆, SiF₄, SiH₄ and C₂H₄.

2. EXPERIMENTAL

2.1 The apparatus

The molecular beam apparatus consisting of three differentially pumped sections, is sketched in Fig. 1. In the first chamber the molecular beam is produced, in the second chamber it is crossed by the radiation from a CW CO₂ laser. The laser with a cavity length of 1.95 m can be operated single-mode with ¹²CO₂, ¹³CO₂ and N₂0, providing more than 250 laser lines between 880 and 1100 cm⁻¹. The long time power stability is better than 1%, the frequency stability better than 1 MHz. A piezoelectric translator, mounted on the laser grating, allows a 75 MHz fine tuning of the laser frequency within each laser line. The laser beam is gently focused to a spot of 0.8 mm diameter on the molecular beam axis. The distance between laserset and the detector (bolometer) is 400 mm. As bolometer serves - on a substrate of sapphire (2 mm x 5 mm) - a doped Ge detector of 1 mm x 1 mm (Infrared Laboratories) typically operated at 4.2 K. The N.E.P. at 4.2 K is 0.5·10⁻¹³ WHz⁻¹/², the responsivity 5·10⁴ V/W and the response time 2.5 ms. During the measurements the response time increases due to cryofrost, (condensation of molecules on the cold detector surface). The bolometer is well shielded from external sources of heat radiation by screens at temperatures of 77 K and 4.2 K and from the laser straylight by several screens between laser and detector.

Figure 1. Experimental set-up.