EXPERIMENTAL INSIGHT ON THE CONFORMATIONAL LANDSCAPE OF THE SF$_6$ DIMER: EVIDENCE FOR THREE CONFORMERS

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The rovibrational spectrum of both parallel and perpendicular bands of the SF$_6$ dimer near the $\nu_3$ band of SF$_6$ monomer was reinvestigated$^b$ using high resolution jet-cooled infrared laser spectroscopy to provide deeper insight on its conformational landscape. Taking advantage of our versatile set-up$^c$, jet-cooled spectra were recorded by combining different geometries of supersonic expansions, SF$_6$ concentrations seeded in a carrier gas and axial distances. Relaxation effects could be evidenced at very low rotational temperature leading to different conformational populations. Three spectral features (noted #1, #2 and #3) belonging to three dimer conformers are unambiguously identified on the grounds of 3 distinct S-S distances derived from the rovibrational analysis of parallel band contours in the 932-935 cm$^{-1}$ range. Symmetry assignment, a priori accessible from the perpendicular band structure of a spherical top dimer, could not be clearly proved. The dependence of such conformational infrared signatures as a function of expansion conditions provides additional information about population dependence and interconversion processes taking place between these three forms predicted to be nearly isoenergetic by theoretical calculations$^d$. Based on experimental considerations, a qualitative picture of the nearly flat potential energy surface of the SF$_6$ dimer is proposed which could explain the dominant presence of #1 and #3 populations in fast/cold axisymmetric expansions and that of #1 and #2 populations in slow/hot planar ones.

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