EXPERIMENTAL INSIGHT ON THE CONFORMATIONAL LANDSCAPE OF THE SF_6 DIMER: EVIDENCE FOR THREE CONFORMERS

PIERRE ASSELIN, *Department of Chemistry, MONARIS, CNRS, UMR 8233, Sorbonne Universités, UPMC Univ Paris 06, Paris, France*; ALEXEY POTAPOV[a], , *Laboratory Astrophysics Group of the Max Planck Institute for Astronomy at the Friedrich Schiller University, Jena, Germany*; VINCENT BOUDON, *Laboratoire ICB, CNRS/Université de Bourgogne, DIJON, France*; LAURENT BRUEL, *CEA Marcoule, DEN, Bagnols-sur-Cèze, FRANCE*; MARC-ANDRÉ GAVEAU, MICHEL MONS, *CEA Saclay, LIDYL, Gif-sur-Yvette, France*.

The rovibrational spectrum of both parallel and perpendicular bands of the SF_6 dimer near the ν_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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