STRUCTURE AND DYNAMICS OF METHACRYLAMIDE

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Methacrylamide (CH_2=C(CH_3)-$CONH_2$) is formed by an allyl non-polar frame and an amide polar frame connected by a rotatable bond. Despite the relatively reduced size of the molecule, the presence of four nearby functional groups causes complex internal dynamics. The underlying conformational space has been explored by quantum mechanical modeling and surveyed with millimeter-wave rotational spectroscopy using a Stark-modulated free-jet absorption spectrometer, in the 59.6-104 GHz frequency range. According to the relative orientation of the two unsaturated bonds (defined by the dihedral angle τ, C=C-C=O), two conformers were observed, namely s-$trans$ and s-cis. In the s-cis form, the methylene and carbonyl groups lie on the same side and the overall symmetry is C_s ($\tau = 0^\circ$), whereas s-$trans$-methacrylamide consists of two equivalent non-planar minima ($\tau = \pm 151^\circ$), which are enantiomers and are separated by a low energy barrier corresponding to a planar skeletal arrangement ($\tau = 180^\circ$). From relative intensity measurements, s-cis-methacrylamide is estimated to lie 4(2) kJ mol^{-1} above s-$trans$-methacrylamide. The rotational spectra are characterized by a complex hyperfine structure which allowed the determination of the methyl internal rotation barrier and the ^{14}N nuclear quadrupole coupling constants for both conformers. Moreover, the tunneling spliting related to the double minimum potential of s-$trans$-methacrylamide was determined. A one-dimensional flexible model of the vibro-rotational interaction suggests that the corresponding interconversion barrier is about 2.4 kJ mol^{-1} and the first torsional quantum state lies 55 cm^{-1} above the ground state.