

## SPECTROSCOPIC CHARACTERIZATION OF THE ELUSIVE *GAUCHE*-ISOPRENE BY HIGH RESOLUTION MICROWAVE SPECTROSCOPY

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The microwave spectrum of isoprene has been investigated in a cryogenic (4-7 K) He buffer gas cell (12-26.5 GHz) and in a room temperature waveguide (8.7-26.5 GHz). Rotation about the single C-C bond converts the lower-energy *trans* rotamer to the higher-energy *gauche*-conformer *via* an unstable, planar, *cis* transition state. As in butadiene, it is counterintuitive that *gauche* is more stable than *cis* because it has long been believed that planarity is required for  $\pi$  electron delocalization, a factor that often imparts greater stability. In standard jet experiments, observation of the higher-energy *gauche* conformer has proven challenging. However in the buffer gas cell, collisions with cold He result in rapid but gentle conformational cooling, allowing for straightforward observation of the *gauche*-isoprene rotamer. The rotational spectrum of *gauche* is complex owing to the combined effects of rotational line splitting ( $0^+ / 0^-$  from *gauche-gauche* inversion) and A/E splitting of the methyl rotor. On the basis of new theoretical calculations, steric hindrance of methyl rotation is predicted to be lower in the *gauche* than in the *trans* conformer ( $V_3$  barrier approximately  $653\text{ cm}^{-1}$  or  $7.8\text{ kJ/mol}$ ). In addition to the on-going spectroscopic analysis, efforts are now underway to better characterize the energetics of C-C bond rotation in isoprene, with the goal of ultimately understanding the factors that result in the greater stability of the *gauche* relative to the *cis* isoprene rotamer.

