HIGH-RESOLUTION INFRARED SPECTROSCOPY OF BUTADIENE: TRANS AND GAUCHE ROTAMERS.

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In a search for rotational structure of the gauche rotamer of butadiene, high-resolution (0.002 cm^{-1}) infrared spectra were recorded at a long path length in regions that grew in intensity when the temperature was raised from $0°C$ to $50°C$. These regions were also ones where Huber-Wälchli and Günthard had observed bands for a second, higher energy rotamer, when hot butadiene was frozen in an argon matrix at 4 K.[a] From medium-resolution infrared spectra, DeMaré and coworkers had concluded that a band at 749 cm^{-1} was from the gauche rotamer.[b] Our high-resolution analysis of this largely A-type band indicates it is, however, probably a difference tone [$\nu_{15}(b_g)$ - $\nu_{13}(a_u)$] of the trans rotamer. Attempts to identify other subband series attributable to the gauche rotamer, which is present to only about 5% at room temperature,[c] failed. Much of the searching occurred in the wings of the 525-cm^{-1} band for $\nu_{12}(a_u)$ of the trans rotamer, which has been analyzed for the first time. In addition to rotational transitions associated with the ν_{12} fundamental, the rotational structure in hot bands was also analyzed.

[a] P. Huber-Wälchli, Hs. H. Günthard, *Spectrochim. Acta* **1981**, *37A*, 285.
[b] G. R. DeMaré, Yu. N. Panchenko, J. Vander Auwera, *J. Phys. Chem. A* **1997**, *101*, 3998.
[c] J. Saltiel, D. F. Sears, Jr., A. M. Turek, *J. Phys. Chem. A* **2001**, *105*, 7569.