Ideal-Gas Thermodynamic Properties of Urea

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Ideal-gas thermodynamic properties of urea computed using experimental vibrational spectrum from matrix-isolated urea sample [1] and assuming C_{2v} symmetry were found in good agreement with entropy data observed experimentally [2]. The reported low-frequency absorption band of 227 cm^{-1} assigned to NH_2 group inversion and mainly responsible for the observed agreement, however, is not confirmed by the subsequent microwave study and quantum-chemical calculations at the MP2/6-311^{++}G** level [3]. Non-planar stereoisomers of urea with C_2 and C_s symmetry were identified. The lowest vibrational frequency for the most stable (C_2) structure was predicted to be 385 cm^{-1}, much higher than obtained in matrix isolation experiments. In this report, we present new quantum chemical calculations and detailed statistical-mechanical analysis aimed to reconcile the experimental and theoretical findings. A particular consideration is given to suggested anharminicity effects [3] of NH_2 inversion modes.

References

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