

Dynamic and Thermodynamic Properties of Crystalline Glycine Polymorphs from Multi-Temperature X-ray Diffraction Data

Thammarat AREE*

Department of Chemistry, Chulalongkorn University, Bangkok 10330, Thailand

Introduction

Glycine having three polymorphs (α , β and γ) at ambient conditions differs in the arrangement of zwitterions in the hydrogen-bonding network and the physical and chemical properties. For insight into the differences in the relative thermodynamic stability of the glycine polymorphs, we apply a novel method of concurrent analysis of multi-temperature atomic displacement parameters (ADPs) [1] to investigate the dynamics of molecules in the crystal and the thermodynamic properties.

Experimental

Synchrotron data to 0.5 Å resolution of the α -polymorph of glycine were collected at 10, 70, 130, 190, 250 and 298 K at KEK Photo Factory, Japan. Prior to data processing with RAPID AUTO, all raw diffraction images were applied for imaging-plate linearity correction. The structures were refined with SHELXL-97, yielding R -factors = 3–5%. Temperature evolution of the ADPs of α -glycine shows normal behaviour although the ADP curves are not completely smooth (Fig. 1). However, the H-atom ADPs are not accurately determined.

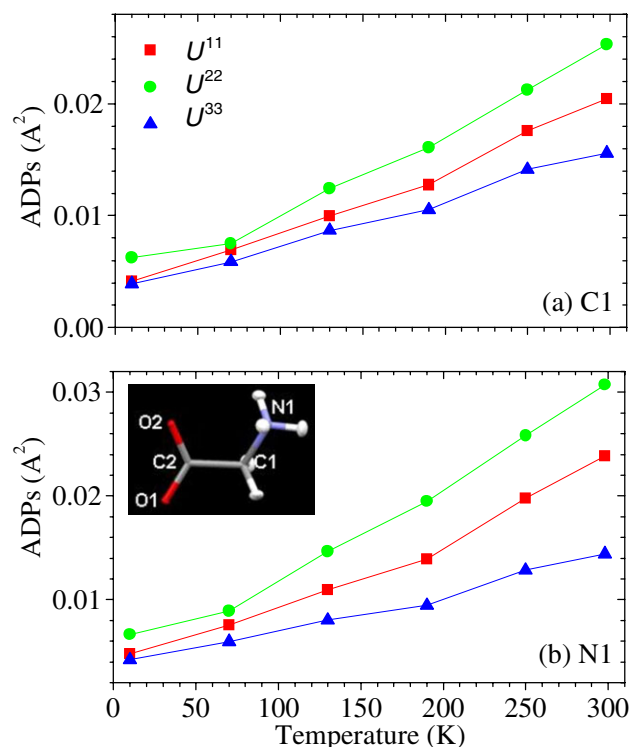


Figure 1. ADPs of (a) C1 and (b) N1 of α -glycine. Standard deviations are $2 \times 10^{-4} \text{ \AA}^2$.

Results and Discussion

The preliminary results of normal mode analysis show that the present best model (rigid body + anharmonic effect accounted for by the Grüneisen constant + internal vibration effect by one epsilon for all atoms) still gives high R -factor, high standard error of Grüneisen constant and the external vibration frequencies (72.4, 82.0, 92.3, 87.2, 118.9 and 191.9 cm^{-1}) in fair agreement with the experimental values (52, 73, 84, 109, 162 and 178 cm^{-1}) [2].

The 24 internal vibration frequencies of zwitterion α -glycine were estimated using ONIOM method and a nine-molecule cluster with the center molecule optimized with high level calculation (B3LYP/6-311+G(2d,p)) hydrogen bonding with eight surrounding molecules frozen at low level calculation (PM3) and found to agree well with those from spectroscopy [3]. The 24 internal and six external vibration frequencies were used together with the molecular Einstein, Debye and Nernst–Lindemann models of specific heat to determine heat capacities C_v and C_p in fair agreement with experimental C_p [4] (Fig. 2). Discrepancy at low temperature (40–80 K) can be improved with good estimate of H-atom ADPs from ONIOM calculation.

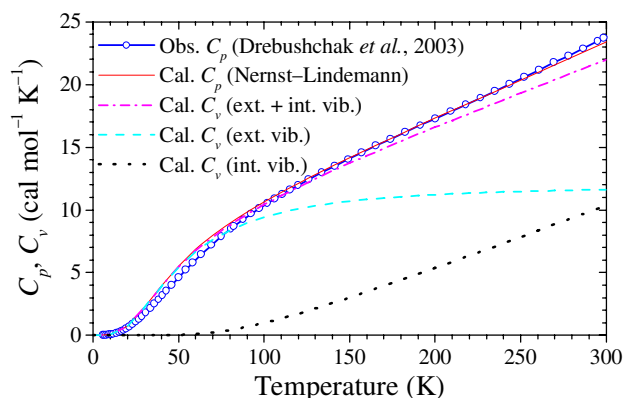


Figure 2. Comparison of C_v , C_p derived from simultaneous analysis of multi-temperature ADPs + ONIOM calculation and C_p from calorimetry [4].

References

- [1] H.-B. Bürgi et al., *Acta Cryst.* A56, 425 (2000).
- [2] K. Machida et al., *Spectrochim. Acta* 33A, 569 (1977).
- [3] M. Kakihana, et al., *Z. Naturforsch.* 43a, 774 (1988).
- [4] V.A. Drebushchak et al., *J. Therm. Anal. Calor.* 74, 109 (2003).

* thammarat.aree@gmail.com