

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

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### Introduction

Glycine having three polymorphs ( $\alpha$ ,  $\beta$  and  $\gamma$ ) 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  $\alpha$ -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  $\alpha$ -glycine shows normal behaviour although the ADP curves are not completely smooth (Fig. 1). However, the H-atom ADPs are not accurately determined.

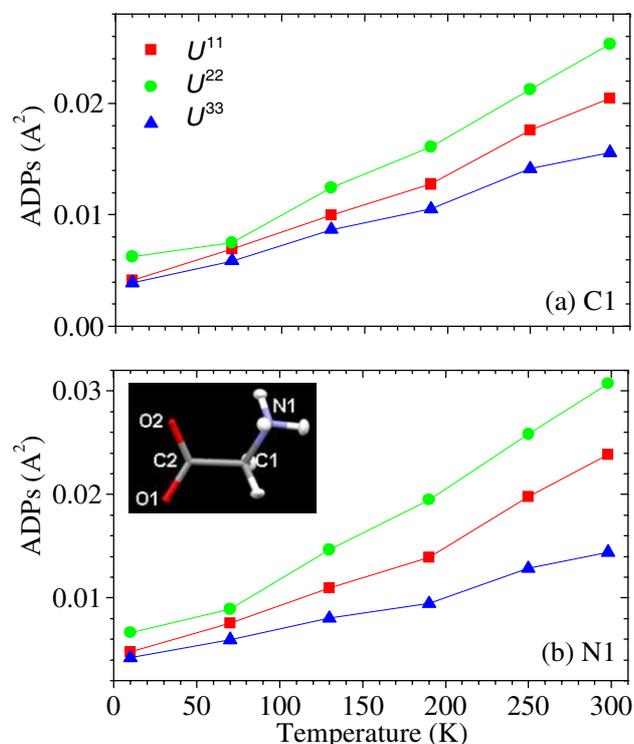


Figure 1. ADPs of (a) C1 and (b) N1 of  $\alpha$ -glycine. Standard deviations are  $2 \times 10^{-4} \text{ \AA}^2$ .

### 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  $191.9 \text{ cm}^{-1}$ ) in fair agreement with the experimental values (52, 73, 84, 109, 162 and  $178 \text{ cm}^{-1}$ ) [2].

The 24 internal vibration frequencies of zwitterion  $\alpha$ -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.

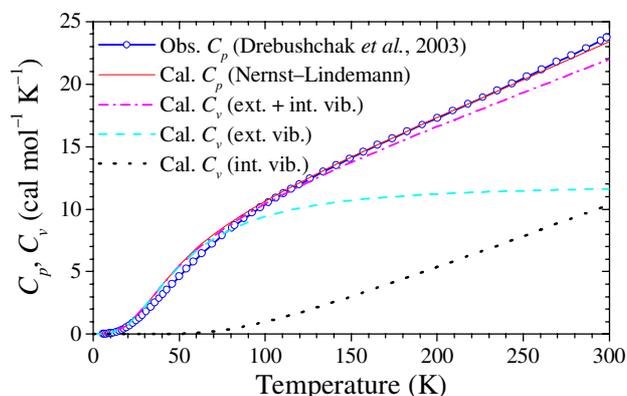


Figure 2. Comparison of  $C_v$ ,  $C_p$  derived from simultaneous analysis of multi-temperature ADPs + ONIOM calculation and  $C_p$  from calorimetry [4].

### References

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