

## A modified Pinkerton-type helium gas-flow system for high-accuracy data collection at the X3 SUNY synchrotron beamline at NSLS

Lynn Ribaud, Guang Wu, Yuegang Zhang and Philip Coppens\*

SUNY X3 Beamline and Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 1460-3000, USA. Correspondence e-mail: coppens@acsu.buffalo.edu

As the combination of high-intensity synchrotron sources and area detectors allows collection of large data sets in a much shorter time span than previously possible, the use of open helium gas-flow systems is much facilitated. A flow system installed at the SUNY X3 synchrotron beamline at the National Synchrotron Light Source has been used for collection of a number of large data sets at a temperature of  $\sim 16$  K. Instability problems encountered when using a helium cryostat for three-dimensional data collection are eliminated. Details of the equipment, its temperature calibration and a typical result are described.

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### 1. Introduction

Collection of diffraction data at the lowest possible temperatures is highly desirable when high accuracy is required, as in charge density analysis, or in photocrystallographic experiments, in which rapid heat dissipation is essential. In previous work, we have routinely used a Displex cryostat (Graafsma *et al.*, 1991) for cooling. However, the sharp vertical profile of a synchrotron beam may lead to systematic  $\varphi$ -dependent errors caused by slight instabilities of the horizontally mounted cryostat (Volkov *et al.*, 1999). Though the errors can be corrected if many symmetry-equivalent reflections have been measured, their elimination is much to be preferred.

In a recent publication, Hardie *et al.* (1998) described an open-flow helium system for single-crystal X-ray diffraction experiments, which is easy to assemble and convenient to use. The system is based on an APD Heli-tran evaporator (Advanced Research Systems, Allentown, PA, USA) designed for low-temperature ESR experiments. We describe here a modified version of the system, its use at a synchrotron beamline, and calibration of the temperature, both with a thermocouple and through measurement of the strongly temperature-dependent laser-induced fluorescence of a small crystal of a dinuclear Pt complex.

### 2. Description of the system

In the original ESR application, the shield gas in the conduit connecting the Heli-tran evaporator to the sample cavity is an outer stream flowing back from the sample cavity counter to the liquid helium. The outer stream exits at a vent port on the Heli-tran provided for this purpose. A second outer gas stream, originating in the Heli-tran, shields the transfer line from the supply dewar to the Heli-tran and is vented at the supply dewar. In the modification of Hardie *et al.* (1998),

instead of venting the second stream to the atmosphere, it is diverted into the shield-gas vent port on the Heli-tran. The outer stream from the Heli-tran to the sample thus flows in a direction reverse to that of the original design. The authors note that the quartz/aluminium helium-delivery nozzle assembly may be replaced by a single piece constructed entirely of aluminium. Where the original design uses two flow meters (one for the sample shield flow and one for the transfer-line shield flow), in the modified design only one flow meter is used as the stream continues to serve as the sample shield flow as well.

For the instrument installed at the X3A1 station at the SUNY beamline at NSLS, a new delivery nozzle for the Heli-tran was manufactured. It is a simple aluminium tube pressed into an aluminium delivery-nozzle adapter, purchased from Advanced Research Systems. This adapter is the piece to which the sample cryostat would normally be attached. It has 'O' rings to seal the Heli-tran vacuum space. This nozzle is a simplification of the nozzle described by Hardie *et al.* (1998) in which the glassware is replaced by the aluminium tube. Though a nozzle-tip heater was installed, the insulation provided by the heater tape appeared sufficient to prevent condensation; a heating current was not necessary.

As severe space limitations make it necessary to position the supply dewar outside the hutch in which the experiment is performed, a long transfer line with a  $\sim 3$  m flexible section is used. The length of the transfer line necessitates increasing the pressure in the 100 l supply dewar after more than about 70% of the liquid helium has been consumed. Therefore, the pressure-relief valve assembly on the supply dewar adapter was modified by adding an additional relief valve of higher pressure rating. In addition to a valve of 5 psig (1 psig  $\simeq$  6.893 kPa) nominal and a second valve (which can be shut off if required) of 2.5 psig nominal, the ability to close the 5 psig valve and a 14 psig relief valve were added. The 14 psig relief pressure is well below the 45 psig rating of the supply dewar.

To avoid shutting down the system while changing the supply dewar, a double-necked intermediate holding dewar was purchased. At the expense of a somewhat higher helium consumption rate, this allows refilling of the supply dewar with minimal impact on the operation of the Heli-tran. The holding dewar is a variant of commercially available equipment [Cryofab Inc. (POB 485, Kenilworth, NJ 07033, USA) CSMH-100] and is equipped with an electric pressurizer and a superconducting level indicator. Helium transfer from commercial supply dewars into the holding dewar involves only a small loss of liquid (10 l or less), provided that reasonable care is taken in the process. Much of the loss originates from the necessary venting of the holding dewar prior to the refill transfer and from the unavoidable cooling of the refill transfer line. Care should be taken that other gases are completely purged from the refill transfer line before it is inserted into the double-necked dewar; otherwise ice plugs will develop in the system.

### 3. Temperature calibration

Since a thermocouple positioned in the open gas flow next to the sample creates an undesirable turbulence in the flow, only the control-point thermocouple located in the Heli-tran is available for temperature measurement during data collection. Thus, temperature calibration must be performed in separate experiments.

Calibration with a single crystal of  $\text{TbVO}_4$  at the sample position (phase transition at 33 K; Will *et al.*, 1972) showed the control-point thermocouple to be quite insensitive to the actual sample temperature. The sample temperature is affected by a change in pressure in the holding dewar and especially by a change in the shield flow in the transfer line. Increasing this shield flow diverts more warm helium from flowing to the sample and reduces the temperature.

More detailed calibration was performed both with a thermocouple at the sample position and using the temperature-dependent fluorescence of a complex ion. The X3A1 diffraction station is equipped with spectroscopic instrumentation for sample illumination and sample fluorescence-lifetime measurement (Fullagar *et al.*, 2000). The temperature-dependent fluorescence properties of the potassium salt of the dinuclear platinum complex  $\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4^{4-}$  have been described in detail (Markert *et al.*, 1983). Its phosphorescence originates in a  $6p_z$  to  $5d_{z^2}$  transition to an excited  $^3A_{2u}$  state, which is split by spin-orbit coupling into an  $A_{1u}$  and an  $E_u$  level, with a splitting  $\Delta E = 42 \text{ cm}^{-1}$ . In the green crystals, the lower  $A_{1u}$  level has a lifetime of 4.33 ms, while the lifetime of the higher, thermally populated,  $E_u$  level is only 2.8  $\mu\text{s}$ . The variable Boltzmann distribution over the closely spaced levels leads to a strongly temperature-dependent overall lifetime given by (in  $\mu\text{s}$ )

$$\tau = [1 + 2 \times \exp(-\Delta E/kT)][0.231 \times 10^{-3} + 2 \times 0.350 \times \exp(-\Delta E/kT)^{-1}]. \quad (1)$$

As the potassium salt  $\text{K}_4\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4$  decays over time, we have used the more stable TBA (tetrabutylammonium) salt

for the calibration. The fluorescence properties of the TBA salt were carefully checked with a chromel-gold thermocouple placed at the sample position and were found to be consistent with those reported by Markert *et al.* (1983) within  $\sim 0.5^\circ$ .

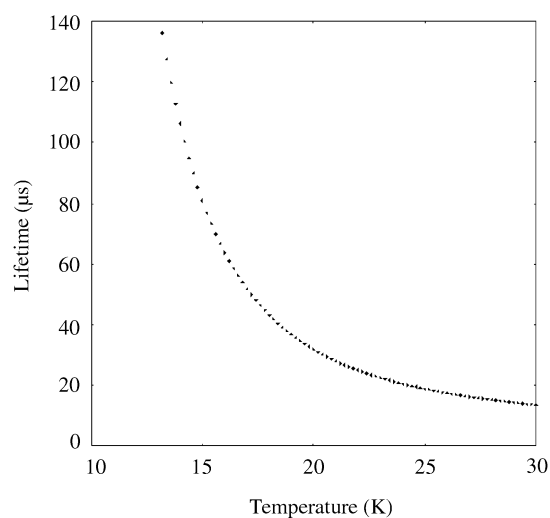
Below about 20 K, the fluorescence lifetime defined by equation (1) varies strongly with temperature (Fig. 1) and thus provides an accurate gauge of the temperature at the sample position. Excited-state lifetimes of a small crystal of  $(\text{TBA})_4(\text{H}_2\text{P}_2\text{O}_5)_4$  were derived by fitting an exponential decay curve to the recorded fluorescence intensities. The corresponding temperatures at different shield flows and settings of the pressure valve are listed in Table 1. In all experiments, the delivery nozzle was located within 3 mm from the sample. As expected, the temperature decreases with increasing flow of the gas through the transfer-line shield, while an increase in pressure in the holding tank leads to a decrease in the temperature reached.

A temperature of 15–17 K can be maintained conveniently with a liquid-helium consumption of about  $3 \text{ l h}^{-1}$ .

### 4. Results

The system has been used to collect several large data sets, using a Bruker SMART1000 area detector. Details are summarized in Table 2. Each data set was collected during one or two fills of 11 h each. Merging  $R$  factors, including all measured reflections, are identical to those commonly obtained in room-temperature experiments at the station.

A typical helium-temperature result is the deformation density in the carboxyl plane of L-leucyl-L-alanine tetrahydrate (Görbitz, 1997) shown in Fig. 2(a). Data were collected on a crystal of  $180 \times 80 \times 50 \mu\text{m}$  using two different rotation axes. The resolution in the experimental deformation density map is remarkable, especially in the C–C bond region, which shows a double maximum, which is retained on modeling. Noise levels are satisfactorily low. Some extra detail



**Figure 1** The lifetime of the  $^3A_{2u}$  excited state of  $(\text{H}_2\text{P}_2\text{O}_5)_4^{4-}$  as a function of temperature.

**Table 1**

Temperature calibration based on lifetime measurements of PtPOP as a function of transfer-line shield flow and pressure in the supply dewar.

Pressure (psig)	Shield flow (arbitrary units)	$T_{\text{Heli-tran}}$ (K)	Lifetime ( $\mu\text{s}$ )	$T_{\text{crystal}}$ (K) [equation (1)]
8.5	50	8.8	73.3	15.3
8.5	45	8.8	56.1	16.5
8.5	40	8.7	48.2	17.3
8.5	35	8.7	41.9	18.0
8.5	30	8.7	41.7	18.1
8.0	50	8.7	72.7	15.4
7.0	48	8.6	62.8	15.9
6.0	43	8.7	53.3	16.7
5.0	41	8.7	42.9	17.9
4.0	38	8.6	32.3	19.8

**Table 2**

Data sets collected with the helium gas-flow system ( $\sin \theta/\lambda_{\text{max}} = 1.12 \text{ \AA}^{-1}$ ,  $\lambda = 0.643 \text{ \AA}$ ).

Leu-ala: L-leucyl-L-alanine.4H<sub>2</sub>O. Cu(I)bite: bite = biphenyldiimino dithioether. Clac: ( $\mu_3$ -oxo)-hexakis( $\mu$ -chloroacetato-*O,O'*)-tri( $\mu$ -aqua)-triron(II,III,III) trihydrate.† Mimoun: di( $\mu$ -peroxo)-( $\mu$ -oxo)-( $\mu$ -aqua)-(hexamethyl phosphortriamide)molybdenum(III).† Fe-vanadyl: ( $\mu_3$ -oxo)-hexakis( $\mu$ -pivalato-*O,O'*)-tri( $\mu$ -aqua)-vanadyldiiron(III).† Cr-wheel: octa( $\mu$ -fluoro)-hexadeca( $\mu$ -pivalato-*O,O'*)-octachromium(III).†  $\langle N \rangle$  is the average number of multiple measurements per reflection.

Compound	Number of reflections collected	Space group	$\langle N \rangle$	Number of unique reflections	$R_{\text{merge}}$ (%)
Leu-ala	102885	$P2_12_12_1$	5.6	14114 ( $>3\sigma$ )	4.8
Cu(I)bite	129993	$P2_12_12_1$	5.5	13630 ( $>3\sigma$ )	5.1
Clac	54414	$P2_1/n$	1.9	29103 ( $>\sigma$ )	2.7
Mimoun	120161	$P2_1/c$	5.5	22029 ( $>\sigma$ )	4.5
Vanadyl	92010	$I4/m$	8.1	11334 ( $>3\sigma$ )	4.4
Cr-wheel	171248	$C2/c$	3.9	43357 ( $>\sigma$ )	3.4

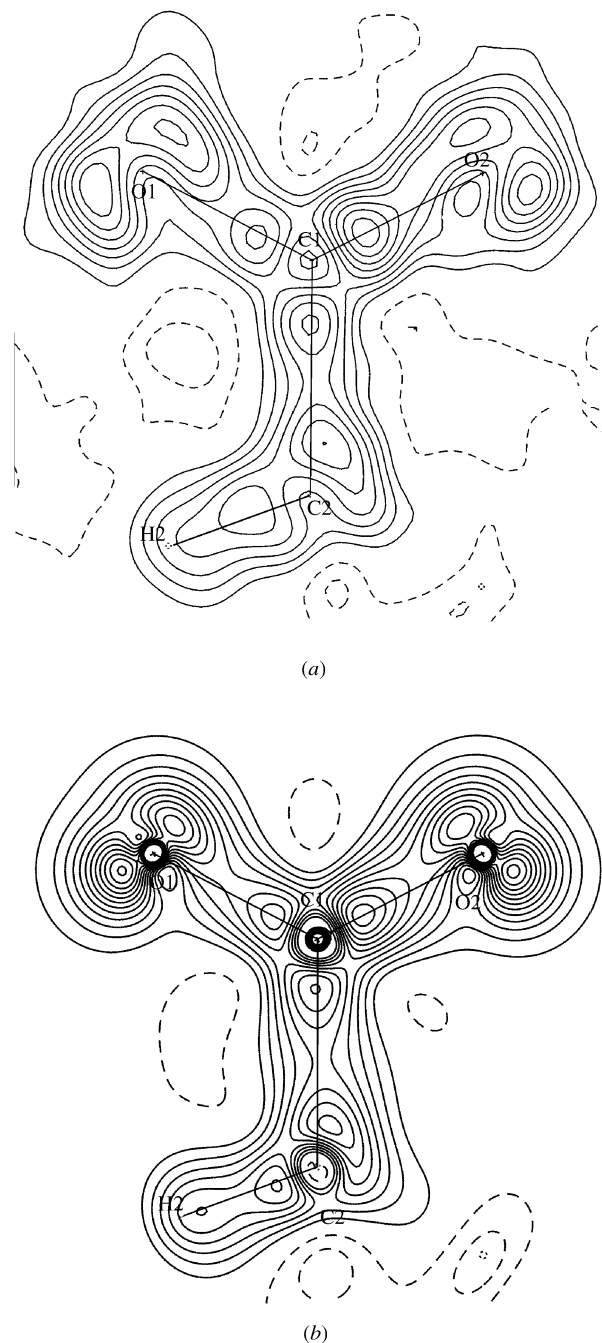
† Data collected by J. Overgaard and F. K. Larsen, Århus University, Århus, Denmark.

is added in the 'static' model map (Fig. 2*b*), indicating that thermal motion can never be completely eliminated and perhaps that at this temperature a higher data cut-off would be desirable even for valence density features. The full study of L-leucyl-L-alanine tetrahydrate will be reported separately.

## 5. Concluding remarks

Open gas systems eliminate stability problems encountered when heavy cryostats are operated in a horizontal orientation at a horizontally polarized synchrotron beam (Volkov *et al.*, 1999). The use of an open gas-flow helium system is now feasible at high-intensity synchrotron sources equipped with area detectors, at which data collection times are minimized.

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**Figure 2**

Deformation density in the plane of the carboxylic group in L-leucyl-L-alanine at 16 K: (a) by Fourier summation of the experimental structure factors, with reference parameters from multipole refinement; (b) model map based on multipole population parameters. The contour interval is  $0.1 \text{ e \AA}^{-3}$ ; negative contours are broken; the zero contour is omitted.  $\sin \theta/\lambda_{\text{max}} = 1.12 \text{ \AA}^{-1}$ ,  $\lambda = 0.643 \text{ \AA}$ .

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