

Analysis of gold speciation in hydrothermal fluids by Raman spectroscopy: the example of gold chloride solutions

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Study of the frequency of molecular vibrations by Raman spectroscopy allows the study of molecular structure. This technique can be used to study the speciation of fluids at high temperature and pressure by direct observation.

In Au-Cl bearing solutions, a number of parameters are important in controlling complex speciation, such as concentration, chloride content, redox conditions, pH and temperature and pressure. Previous studies (Pan and Wood 1991; Peck *et al.*, 1991) have shown discrepancies in terms of the form and interpretation of Raman spectra.

Effects of pH

The effect of pH on Raman spectra of Au-Cl-OH solutions has been re-evaluated, and although the spectra obtained were rather different from those of Peck *et al.* (1991), we support their conclusion that increasing pH results in complexes in the Au (III) hydrolysis sequence $[\text{AuCl}_x(\text{OH})_{4-x}]^-$, rather than Au(I) complexes as was suggested by Pan and Wood (1991).

A number of new peaks have been identified, and the number of observed peaks for each complex in the hydrolysis series is consistent with the theoretical prediction of Tossell (1996). The observed changes in peaks were very minor, requiring careful use of peak fitting software and consideration of width and relative proportions alongside peak position. For example, although the shift in peak position may be very minor between two complexes, there is likely to be an increase in the peak width and intensity as two unresolvable peaks are interpreted as one.

Effects of chloride concentration

Solutions of the same gold concentration showed very different spectra in the absence and presence of excess chloride. During the pH study the results of

changing pH on the hydrolysis of the Au(III) complex were strongly affected by the chloride concentration. This was particularly clear at low gold concentrations (0.005–0.001 M Au).

Effects of temperature

The effects of temperature were studied on $[\text{AuCl}_4]^-$ solutions from 25–250°C at pressures on the liquid-vapour curve, and significant differences from previous experiments were observed. Solutions were prepared by dissolving $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in distilled water, and gold concentrations were from 0.001 – 0.04M.

Precipitation of gold occurred at high temperatures, along with a fading of the yellow colour of the solution and a decrease in the Raman signal,

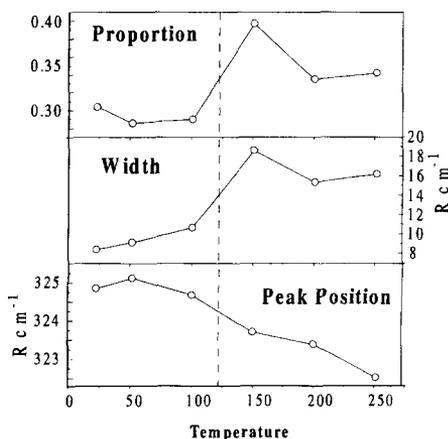


FIG. 1. Changes in the peak parameters for the 323cm^{-1} peak. Gold precipitation shown by dotted line. These data are from a 0.04M Au solution with a liquid:vapour ratio of 1:0.4, but similar changes were seen in all samples.

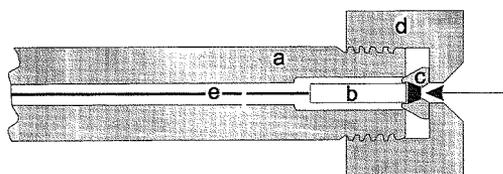


FIG. 2. Schematic illustration of the pressure vessel used for Raman experiments. a: pressure vessel, b: glass sample capsule, c: sapphire window holder, d: closure nut, e: thermocouple. The heavily shaded area represents the window and the arrow represents the Raman laser.

indicating a reduction in the concentration of $[\text{AuCl}_4]^-$ in solution. The temperature of gold precipitation was different in each experimental run, but changes in the peak parameters occurred in all samples at the temperature of precipitation. There was generally a sudden change in the central position of the 347 Rcm^{-1} (A_{1g}) peak, alongside an increase in the width and the relative intensity of the 323 Rcm^{-1} (B_{1g}) peak (Fig. 1). A third Au-Cl stretching peak observed by Pan and Wood (1991) at 332 Rcm^{-1} , and attributed to the formation of $[\text{AuCl}_2]^-$ at temperatures above 100°C , was not observed in this study. The different temperatures of gold precipitation are interpreted as being due to the differences in liquid/vapour proportions, and therefore oxygen fugacity, in the sample charges. Precipitation occurred at lower temperatures in sample charges with smaller vapour bubbles (i.e. lower oxygen fugacities). The stability of Au(III) chloride will be reduced at constant oxygen fugacity as the temperature increases, due to the slope of the solubility contour curves in temperature/ $f\text{O}_2$ space.

Gammons *et al.* (1997) have described the disproportionation of Au(I) chloride to Au(III) chloride plus metallic gold as temperature was decreased (with a change in the solution from colourless to yellow) according to the reaction:



However, in this study gold was formed from Au(III) chloride as the temperature was increased. The associated variation in peak parameters suggests that there is not simply a reduction in the solubility of $[\text{AuCl}_4]^-$ complex, but that some other complex, as yet unidentified, is becoming significant.

Development of a hydrothermal cell for studies to 350°C and 2 kbar

Previous work has been conducted at high temperatures but at pressures dictated by the liquid-vapour

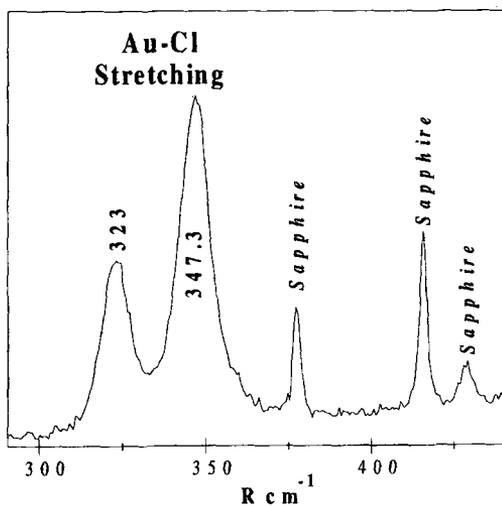


FIG. 3. Raman spectrum of AuCl_4^- in the hydrothermal cell sample chamber, showing the occurrence of sapphire peaks.

curve for the system in question. A hydrothermal cell has been developed at the University of the Witwatersrand to allow Raman spectroscopic analyses under hydrothermal conditions. A conventional cold seal pressure vessel is used, having been modified to accommodate a conical sapphire window at one end (Fig.2). The laser is focused into a glass sample chamber within the pressure vessel. The fluid sample is isolated from all metallic components, allowing a range of systems and concentrations to be studied.

Temperature measurement is via a type K thermocouple, located directly adjacent to the sample capsule, and solid state temperature controller with integral ice point. The pressure-transmitting medium is distilled water, and pressure measurement is by a Bourdon gauge. The cell has been tested to 350°C and 2kbar concurrently. Furnace temperature is controlled by a solid state temperature controller and temperatures at the sample capsule are readily maintained at $\pm 1^\circ\text{C}$ for the duration of an experiment. The laser path length through the fluid is $\approx 1\text{cm}$, sufficient to produce good signal/noise even at low concentrations. The sapphire window introduces a number of peaks into the Raman spectrum (Fig.3) but these are narrow and sharply defined: in practice they provide a useful internal calibration of the peak positions for each analysis.

It is anticipated that this apparatus will allow complete study of the Au-Cl system over the hydrothermal range, allowing a much clearer understanding of how the speciation changes with T and P at a range of pH values.