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High-pressure Raman study on the decomposition of crystalline $Cr(CO)_6$

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Abstract

High-pressure Raman spectra (300–2200 cm^{-1}) of crystalline $Cr(CO)_6$ at room temperature for pressures up to 29.5 GPa have been recorded. A probable second-order phase transition is assigned at ~4.1 GPa. Recorded Raman spectra started to vanish at 20.8 GPa and upon further increase in pressures resulted in complete vanishing at 29.5 GPa. The dv/dp values suggest the breakdown of Dewar–Chatt–Duncanson model for the first time in homoleptic mono carbonyls which has been discussed. Decomposition of $Cr(CO)_6$ leads to the formation of polymeric CO with characteristic sp^2 carbon and (OCO) units for the first time.

1. Introduction

Transition-metal (TM) carbonyl complexes of group VI form an important class of compounds in inorganic and organometallic chemistry. Homoleptic mono metal carbonyls of the general formula $M(CO)_6$ (M = Cr, Mo, W) fall under the category of inorganic molecular crystals [1]. These metal carbonyls are especially known for their catalytic properties [2]. They are used as catalysts in reactions like activating of small molecules in matrix isolation via photolysis [3], as precursors in plasma-enhanced chemical vapor depositions (PECVD), metal-organic chemical vapor deposition (MOCVD), and in chemical vapor depositions (CVD) owing to their ability to form thin films with good adherence on ceramics, glasses, polymers, composite materials fabrication and in metal coatings [4,5].

The pressure sensitivity as an independent variable of these molecular crystals is also a highly interesting area of investigation. Studies involving pressure will throw light on the inter and intra molecular bonding in metal carbonyl crystals leading to phase transitions, polymorphization, polymerization or even decomposition if any, due to the redistribution of electron density [6,7]. Earlier, pressure studies on these systems were performed by Adams et al. Their studies however, showed no phase changes except for the lattice modes for chromium carbonyl up to 5 GPa [1].

Our studies have been focused towards subjecting this family of molecular crystals to higher pressures (>5 GPa) as a part of systematic studies of their behavior under extreme pressure conditions. The principal aim of these studies is to follow and identify any structural changes along the pressure induced regime in the zone of internal modes. This would provide us with information about structural transformations and hence phase transitions if these indeed occur. Further, to the best of our knowledge, no studies subjecting these homoleptic mono carbonyl molecular crystals were beyond the limits of stability have been either performed or reported. We are highly interested in such investigation, which are being undertaken currently and data from these studies will be reported presently.

Here we report the results of the Raman spectra on chromium hexacarbonyl as a function of high external pressures.

2. Experimental

2.1. Material

Chromium carbonyl (purity ⩾98%) was purchased from Sigma–Aldrich Co. and was used as received.

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2.2. Raman spectroscopy

High-pressure Raman studies were conducted at room temperature using a gasketed high-pressure diamond anvil cell (DAC). Typically, the crystalline sample with tiny rub chips was loaded in Mao-Bell-type Diamond anvil cell. Raman spectra were recorded in the back-scattering configuration. The argon ion laser (Ar^+) was used to excite the sample and the laser power was operated at 20 mW. Raman spectra were collected with 10 min exposure by using the high throughput holographic imaging spectrograph with volume transmission grating, holographic notch filter and thermoelectrically cooled CCD detector (Andor) with a resolution of 4 cm^{-1}. The sample was placed in a TS 302 stainless steel gasket hole 70 μm in initial thickness and 200 μm in diameter without a pressure medium. Pressures were determined from the shift of the ruby fluorescence R_1 line [8], excited by the argon ion laser with the wavelength of 514.5 nm. The laser spot on the sample has been so focused that it was close to the ruby chips. This will help us in accounting for the actual pressure on the sample close to the ruby chips and hence the pressure differences will be very minimal [9].

3. Results and discussion

High-pressure Raman studies on metal hexacarbonyls in DAC is an important and extremely useful technique for it provides a very conducive atmosphere [10]. These inorganic molecular crystals crystallize in the orthorhombic system Pnma (D^{16}_{2h}) with site group symmetry (C_s) and with four molecules per unit cell [11]. In this Letter, we report the high-pressure Raman studies of the title compound in the 300–2200 cm^{-1}, as shown in Fig. 1. This provides us with the strong internal Raman active modes of the type shown in Table 1.

Single crystal studies have led to the assignment of most of the IR and Raman modes. Our current assignments are based on those reported by Adams and Taylor [12]. Since the specimen under investigation is a polycrystalline sample, we cannot precisely assign the observed modes based on the combination of the single-crystal studies [9]. However, the observed Raman modes in our studies can be safely designated to the internal modes due to the region of current interest and are shown in Table 1.

Further, the only IR active mode is also shown in Table 1. This is the only IR active mode ν_6, which becomes allowed as a weak feature in the Raman studies [12]. The inclusion of this feature further helps in following the high-pressure phase along with the Raman active modes. Table 1, also shows the values for pressure dependences dν/dp.

Fig. 2 shows the typical frequency vs. pressure correlation plots for the ν(MC) and δ(MCO) modes. Raman spectra were collected *in situ* at room temperature and elevated pressures, up to 26.7 GPa. The correlation plot in Fig. 2 shows the trend of the vibrational frequencies in response to the high external pressures. All these bands show change in intensity and vanish at elevated pressure. This is a commonly observed phenomenon as it is known that pressure affects the Raman intensities via changes in bond polarizabilities [10]. Further all the bands in Fig. 2 show blue shifts. The discussion pertaining to the blue shifts of all the observed Raman peaks is deferred to a later section

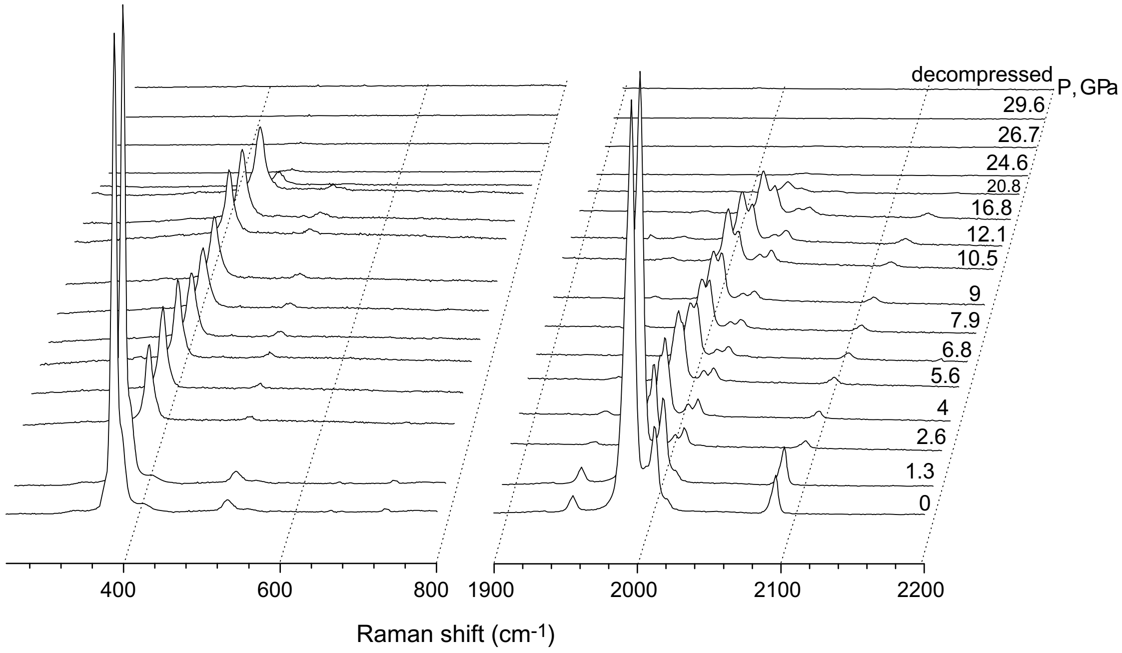

Fig. 1. Representative Raman spectra of $Cr(CO)_6$ at ambient conditions and at high-pressures. Spectra are recorded from ambient to 29.6 GPa and then decompressed to ambient pressure. For clarity the diamond first-order peak has not been included.