EarlyView publication on wileyonlinelibrary.com
(issue and page numbers not yet assigned;
citable using Digital Object Identifier – **DOI**)

Phys. Status Solidi B, 1–5 (2011) / **DOI** 10.1002/pssb.201046440

www.pss-b.com
basic solid state physics

Temperature-dependent Raman spectroscopy of anilinium chloride near phase transition

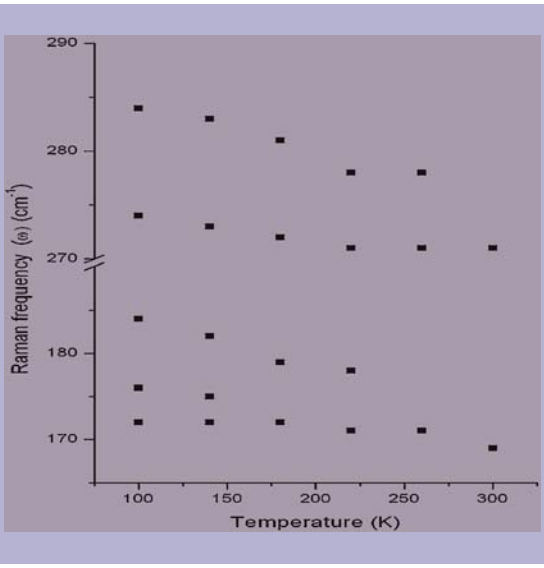
Ashok K. Vishwakarma[1], **Pallavi Ghalsasi**[2], **and Prasanna S. Ghalsasi**[*,1]

[1] Faculty of Science, Department of Chemistry, The M.S. University of Baroda, Vadodara 390002, Gujarat, India
[2] Department of Physics, Indian Institute of Technology, Gandhinagar, Ahmedabad 382424, Gujarat, India

Received 12 August 2010, revised 18 February 2011, accepted 25 February 2011

Keywords anilinium chloride, differential scanning calorimeter, phase transitions, Raman spectroscopy

The existence of various solid phases of organic ammonium halides, due to the presence of hydrogen bonding, has long been established but is limited to alkyl ammonium halides. On the other hand, the presence of such phase transitions was eluded in case of anilinium chloride. In the present work, we have undertaken a systematic temperature dependent Raman spectroscopic study on anilinium chloride, in the range 300–100–350 K. Spectral variation in the low frequency (100–400 cm^{-1}) and high frequency (2500–3700 cm^{-1}) regions around 350 and 260 K shows the signature of the phase transitions in this compound. These phase transitions were reversible in nature. The latter transition is in agreement with DSC measurements.



1 Introduction Ammonium salts have generated a lot of interest due to their common use in synthesis of perovskite (AMX_3 and A_2MX_4) type structured compounds (where A is ammonium salt, M is metal, and X is halide), for semiconducting [1], magnetic [2], ferroic [3], and more recently for multiferroic behavior [4–7]. The existence of various solid phases of the organic ammonium salts has long been established, but mainly alkyl ammonium halides appear to have been studied in any details [8–13]. It is found that in such ionic compounds hydrogen bonding helps in undergoing a series of phase transitions. This is well documented in the form of various studies using heat capacity, single crystal X-ray determination, and infrared spectroscopic techniques. The case of aromatic ammonium halide salts is more complicated due to the presence of increased π–π interaction along with hydrogen bonding interaction. Steed and co-workers [14] have recently pointed out that ionic species generally form low Z' structures where hydrogen bonding, π–π interaction, and ionic nature compete with each other.

In the course of our investigations on the studies of (anilinium)$_2$MCl$_4$, it appeared useful to analyze the vibrational spectra of anilinium chloride [4, 15]. Indeed, these comparatively simple salts represent a model system to study the effect of hydrogen bonding and crystal structure. We report here temperature dependent spectral changes in the internal modes with relation to the probable mechanism of the phase transition. Most of the spectroscopic studies on anilinium salts so far are devoted in the lattice mode region (below 300 cm^{-1}) [16], and finger print regions only. To our

---

[*] Corresponding author: e-mail prasanna.ghalsasi@gmail.com, Phone: +91-265-279-5552, Fax: +91-265-279-5552