

High-Resolution Infrared and Raman Spectra of the Polycrystalline Sinomenine Hydrochloride

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Abstract. High-resolution infrared and Raman spectra of the polycrystalline sinomenine (SM) hydrochloride have been measured to work out its whole really existing vibrational spectral bands. Except for the hydroxyl stretching modes and IR active bands less than 400 cm^{-1} , most normal modes (about 34) are both IR and Raman active. In addition, 8 Raman bands less than 400 cm^{-1} are tentatively assigned, for the first time to our knowledge, to stretching/bending modes of the aromatic-ring-methoxyls and $(\text{SMH})^+-\text{Cl}^-$ ions, respectively.

1 Introduction

The sinomenine hydrochloride ($\text{C}_{19}\text{H}_{24}\text{NO}_4\text{Cl}$, abbreviated SMHCl) is the hydrochloric acid compound of the sinomenine ($\text{C}_{19}\text{H}_{23}\text{NO}_4$, abbreviated SM), which is a chemical compound possessing important medical values and initially found to exist in traditional Chinese medicinal materials [1-3], and is prone to crystallizing to form the polycrystalline unit. Therefore its vibrational spectral analysis becomes extremely useful, for example, the spectral analysis can be used to analyze the chemical purity and the hydrochlorination level for a given SMHCl sample or the structural modification of the SM derivatives [4-6].

Whereas the SMHCl molecule consists of many vibrational groups, and has many normal lattice vibrational modes [7]. Here, we try to work out the whole really existing vibrational spectral bands of polycrystalline SMHCl with the high-resolution infrared (IR) spectrometer and laser micro-Raman spectroscopy.

2 Experimental methods

The polycrystalline SMHCl with the purity of more than 99 % was purchased from Xi'an Feida biotechnology co., ltd, Xi'an, Shanxi Province, China.

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The IR spectrum of the polycrystalline SMHCl was measured with the Thermo Scientific Nicolet iS50 spectrometer whose resolution is high up to $<0.09\text{ cm}^{-1}$ by using of the general KBr disc technology in the range of $3600\text{--}400\text{ cm}^{-1}$. Raman spectrum was obtained using Thermo Scientific DXR Raman microscope excited by an Nd: YAG laser ($532.0\text{ nm @ }5\text{ mW}$) at a resolution of 1.5 cm^{-1} (900 g/mm) between $3600\text{--}50\text{ cm}^{-1}$. The Raman spectrum was automatically baseline corrected (fluorescence subtracted partly), moderately smoothed and normalized according to the largest counting peak value.

3 Results and discussion

Figures 1–3 show the IR and Raman spectra of the polycrystalline SMHCl in the ranges of $3600\text{--}2800\text{ cm}^{-1}$, $1750\text{--}900\text{ cm}^{-1}$ and $900\text{--}50\text{ cm}^{-1}$, respectively, where blue wavenumbers represent the *both-IR-and-Raman-active* modes whose differences of corresponding wavenumbers are between 10 and -10 cm^{-1} .

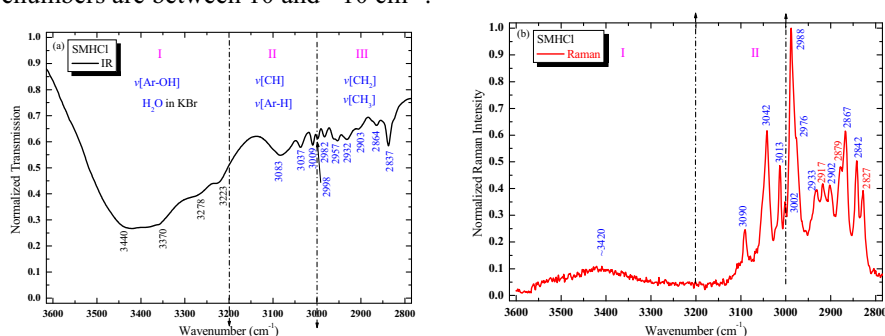


Fig. 1. IR (a) and Raman (b) spectra of the polycrystalline sinomenine hydrochloride (SMHCl, $\text{C}_{19}\text{H}_{24}\text{NO}_4\text{Cl}$) in the range of $3600\text{--}2800\text{ cm}^{-1}$ (the [RH] functional group region).

From Fig. 1, one can see that the SMHCl sample contains same crystal water which, together with the water in KBr, have produced $\text{O-H}\cdots\text{O}$ hydrogen bond and caused a decreased $\nu[\text{Ar-OH}]$ in the IR spectrum, but the corresponding Raman spectrum is greatly widened because of the laser local heating effect [8]. In the [RH], other than [Ar-OH], functional groups region, all the ten modes found in the IR spectrum have their corresponding Raman ones, which are proved to be really existing and *both IR and Raman active* because of their asymmetry.

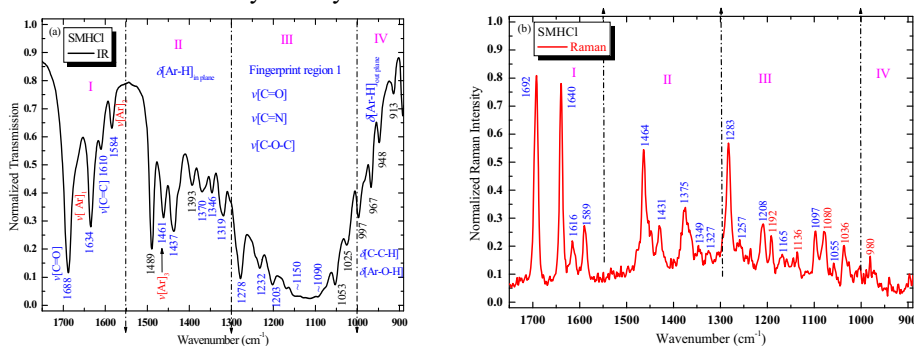


Fig. 2. IR (a) and Raman (b) spectra of the polycrystalline sinomenine hydrochloride (SMHCl, $\text{C}_{19}\text{H}_{24}\text{NO}_4\text{Cl}$) in the range of $1750\text{--}900\text{ cm}^{-1}$ (mostly the functional group region of [CC], [CO], [CN], etc).

From Fig. 2, it can be shown that (1) all the five $\nu[\text{CO}]$, $\nu[\text{CC}]$ and $\nu[\text{Ar}]_{1/2/3}$ modes are *both IR and Raman active*; (2) only few $\delta[\text{Ar-O-H}]$ and $\delta[\text{Ar-H}]_{\text{in/out-of plane}}$ modes are *both IR and Raman active* because of unknown reasons.

In the range of $1300\text{--}600\text{ cm}^{-1}$ fingerprint region, as shown in Figs. 2 and 3, most of stretching modes $\nu[\text{CO}]$, $\nu[\text{CN}]$ and $\nu[\text{COC}]$ and bending modes $\delta[\text{Ar-O-H}]$ and $\delta[\text{Ar-H}]_{\text{in/out-of plane}}$ are both IR and Raman active, but distribute alternately so as to be distinguished with each other very difficultly. According to the comparison with the Raman spectral data of the SM [9], four bands of $308/334/354/374\text{ cm}^{-1}$ and two bands of $92/62\text{ cm}^{-1}$ appear jointly in the Raman spectra of both SM and SMHCl, and can be tentatively, as we add a “?” in Fig. 3, assigned to be the stretching/bending $\nu/\delta[\text{Ar(OMe)}]$ modes of the aromatic rings and OCH_3 methoxyls, respectively. The $106/62\text{ cm}^{-1}$ bands appearing only in the SMHCl Raman spectrum are also assigned tentatively to be the stretching/ bending $\nu/\delta[(\text{SMH})^+\text{Cl}^-]$ modes of the $(\text{SMH})^+$ ion as a whole and Cl^- ion, respectively.

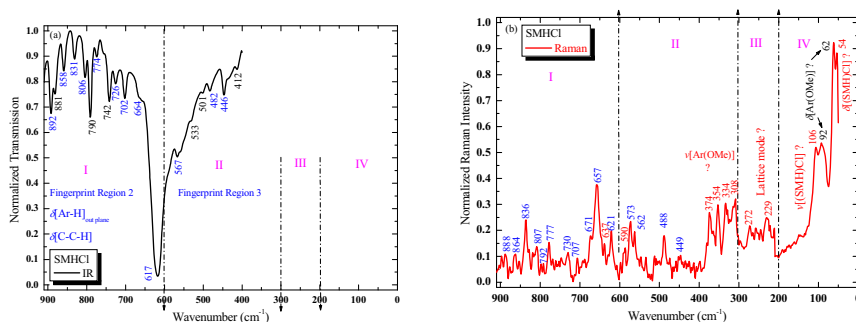


Fig. 3. (a) IR spectrum in the range of $900\text{--}400\text{ cm}^{-1}$ and (b) Raman spectrum in the range of $900\text{--}50\text{ cm}^{-1}$ (mostly *fingerprint* region) of the polycrystalline sinomenine hydrochloride (SMHCl, $\text{C}_{19}\text{H}_{24}\text{NO}_4\text{Cl}$).

4 Summary

We have measured high-resolution infrared and Raman spectra of the polycrystalline SMHCl to find out its whole really existing vibrational spectral bands. Except for the hydroxyl stretching modes $\nu[\text{OH}]$ and IR active bands less than 400 cm^{-1} , most normal vibration modes (about 34) are both IR and Raman active, additional 16 and 14 modes appear only in the IR and Raman spectra, respectively. In the mean while, 8 Raman bands less than 400 cm^{-1} are tentatively assigned to stretching/bending modes of the aromatic-ring-methoxyls and $(\text{SMH})^+\text{--Cl}^-$ ions, respectively. More ideal one-to-one assignment of these IR and Raman bands needs intensive research work on many sinomenine derivatives.

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References

1. X.X. Zhao, C. Peng, H. Zhang, L.P. Qin, *Sinomenium acutum*: A review of chemistry, pharmacology, pharmacokinetics, and clinical use, *Pharmaceutical Biol.* 50 (2012) 1053- 1061.
2. F. Liao, Z.R. Yang, X.H. Lu, X.F. Guo, W.G. Dong, Sinomenine sensitizes gastric cancer cells to 5-fluorouracil *in vitro* and *in vivo*, *Oncol. Lett.* 6 (2013) 1604-1610.
3. T.S. Ma, G. Li, Z.H. Liu, H.J. Yang, G. Huang, L.C. Zhu, Study on purity of sinomenine hydrochloride crystal, *China Pharmaceuticals*, 14 (2005) 26-27 [in Chinese].
4. X.J. Lin, H. Zhang, S.G. Jin, W. Zhang, Preparation and *in vitro* Release of Sinomenine Hydrochloride-loaded Chitosan Nanoparticles, *Chin. J. Exper. Trad. Med. Formulae*, 17 (2011) 22-25 [in Chinese].
5. P. Dou, H. Zhang, W. Zhang, Optimization of Preparation Technology and Investigation of *in vitro* Release Mechanism of Sinomenine Hydrochloride-Polyvinyl Alcohol Microcapsules, *Chin. J. Exper. Trad. Med. Formulae*, 18 (2012) 49-52 [in Chinese].
6. W. Zhang, H.L. Fu, X.Y. Li, H. Zhang, N. Wang, W. Li, X.X. Zhang. Molecularly imprinted polymer doped with Hectorite for selective recognition of sinomenine hydrochloride, *J. Biomater. Sci. - Polymer Ed.* 27(2016): 144-156.
7. T.S. Ma, G. Li, Z.H. Liu, Z.X. Yang, G. Huang, Infrared spectrophotometry of sinomenine hydrochloride, *Central South Pharmacy*, 2 (2004) 108-110 [in Chinese].
8. X.D. Liu, J. Lu, M. Fujihala, D.D. Meng, *et al.* Local Laser Heating Effect on Raman Spectroscopy of β -Co₂(OH)₃Br, *Adv. Mater. Res.* 430-432 (2012) 566-569.
9. Information to be reported.