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On the Third Fundamental Band of Li^+ Translational Vibration in Lithium Hydrogen Oxalate Monohydrate

Short Communication

Yoshiyuki Hase[a,*] and **Marcia L. A. Temperini**[b]

[a] Instituto de Química, Universidade Estadual de Campinas,
13100 Campinas, SP, Brasil
[b] Instituto de Química, Universidade de São Paulo,
01000 São Paulo, SP, Brasil

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The third Li^+ translational mode of lattice vibration of lithium hydrogen oxalate monohydrate has been assigned to the band at about 383/360 cm^{-1} taking the characteristic $^6Li/^7Li$ isotope band shifts into consideration.

(Keywords: Lithium hydrogen oxalate monohydrate; Vibrational spectral data; Li^+ *translational vibration; Isotope effects)*

Über die Zuordnung einer der drei translatorischen Li^+*-Moden in Lithiumhydrogenoxalat-Monohydrat (Kurze Mitteilung)*

Es wurden die IR-Spektren der Li- und H-isotopen Lithiumhydrogenoxalat-Monohydrate bei 100 K und 300 K gemessen. Einer der drei translatorischen Moden wird einer Bande zugeordnet, die bei Berücksichtigung der $^6Li/^7Li$ Isotopenverschiebung bei 383/360 cm^{-1} auftritt.

Since lithium hydrogen oxalate monohydrate, $LiXC_2O_4 \cdot X_2O$, where $X = H$ and D, cystallizes in a triclinic lattice of space group P 1 (C_1^1) containing one formula unit in an unit cell[1,2], the Li^+ site is situated in crystallographically general position, and accordingly three fundamental bands of lattice vibration with respect to the Li^+ site translation are expected in vibrational spectroscopy. Previously, on the basis of the isotope band shifts among $^6LiHC_2O_4 \cdot H_2O$, $^7LiHC_2O_4 \cdot H_2O$, and $^7LiDC_2O_4 \cdot D_2O$, *Villepin* and *Novak* assigned, reasonably, two $^6Li/^7Li$-sensitive bands at about 450/425 and 300/290 cm^{-1} as the Li^+ lattice vibrations[3]. However, the assignment for the ^{6}Li/^{7}Li-sensitive bands, according to *Villepin* and *Novak*, at about 383/350 and 360/336 cm^{-1}, as a result of vibrational mode coupling between the COO group wagging and the remaining Li$^+$ translational vibrations, may be questionable since the appearances of these bands are not very consistent among the observed spectra.

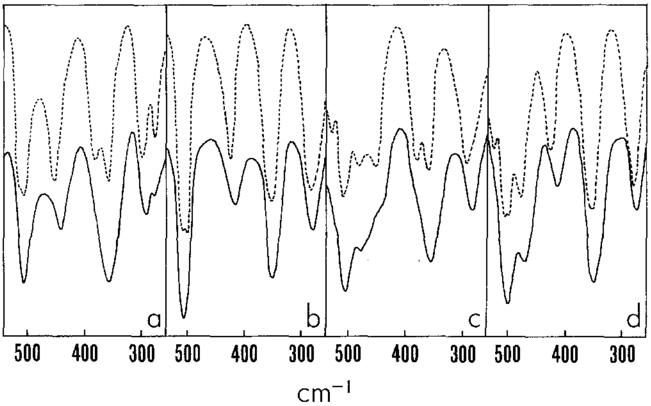

Fig. 1. Infrared spectra (from 540 to 260 cm^{-1}) measured at 300 K (———) and 100 K (------) of ^{6}LiHC$_2$O$_4$·H$_2$O, ^{7}LiHC$_2$O$_4$·H$_2$O, ^{6}LiDC$_2$O$_4$·D$_2$O, and ^{7}LiDC$_2$O$_4$·D$_2$O

Fig. 1 shows the infrared spectra, from 540 to 260 cm^{-1}, measured for ^{6}LiHC$_2$O$_4$·H$_2$O, ^{7}LiHC$_2$O$_4$·H$_2$O, ^{6}LiDC$_2$O$_4$·D$_2$O, and ^{7}LiDC$_2$O$_4$·D$_2$O at 300 and 100 K. The observed infrared and *Raman* spectral data in the region of the Li$^+$ translational lattice vibrations are listed in Table 1.

At first it should be noted that the infrared band at 336 cm^{-1}, observed for ^{7}LiHC$_2$O$_4$·H$_2$O at 300 K by *Villepin* and *Novak*[3], is never found in our any measurements. On the other hand, the low-temperature infrared band at 383 cm^{-1} of ^{6}LiHC$_2$O$_4$·H$_2$O, which is absent in the spectral data for ^{7}LiHC$_2$O$_4$·H$_2$O and ^{7}LiDC$_2$O$_4$·H$_2$O, is also clearly observed for ^{6}LiDC$_2$O$_4$·D$_2$O. The infrared intense band at about 360 cm^{-1} is found for all four isotopically substituted salts without any characteristic H/D and/or ^{6}Li/^{7}Li isotope band shifts, and consequently assigned as one of the XC$_2$O$_4^-$ site internal vibrations. Here the band at about 383 cm^{-1} is attributable to the third Li$^+$ translational vibration of the ^{6}Li-salts. The corresponding band of the ^{7}Li-salts is shifted by the ordinary mass effect to the 360 cm^{-1} region and accidentally degenerated with the internal vibration. Taking into account the wavenumber differences between the

Table 1. *Observed wavenumbers (in* cm^{-1}*) for* $LiXC_2O_4 \cdot X_2O$

$^{6}LiHC_2O_4 \cdot H_2O$			$^{7}LiHC_2O_4 \cdot H_2O$			
IR 300 K	IR 100 K	*Raman* 300 K	IR 300 K	IR 100 K	*Raman* 300 K	
444 m	456 s	445 vw	420 m	432 s	423 vw	T′ Li^+
357 s	384 s		355 s	360 s		T′ Li^+
	361 s	362 vw			357 vw	
293 m	303 s		278 m	290 s		T′ Li^+
$^{6}LiDC_2O_4 \cdot D_2O$			$^{7}LiDC_2O_4 \cdot D_2O$			
IR 300 K	IR 100 K	*Raman* 300 K	IR 300 K	IR 100 K	*Raman* 300 K	
440 m	453 m	444 vw	416 m	428 s	418 vw	T′ Li^+
358 s	382 s		354 s	357 s		T′ Li^+
	362 s	360 vw			357 vw	
286 m	295 s		277 m	285 s		T′ Li^+

Li^+ lattice vibrations at 300 and 100 K, the Li^+ band in question at room temperature is expected in the 360 cm^{-1} region and the accidental degeneracy can also be considered.

Experimental

The four isotopically substituted salts of $LiXC_2O_4 \cdot X_2O$ were prepared by the usual method described in[4].

The infrared spectra were measured at 300 and 100 K as Nujol mulls on a Perkin-Elmer IR 180 spectrophotometer. The spectral resolution for most measurements was typically 2 cm^{-1}. The *Raman* spectra were measured at 300 K, on a Cary 82 laser *Raman* spectrometer equipped with a Spectra Physics 165 argon ion laser (514.5 nm) as the excitation source. The *Raman* spectral resolution was typically 5 cm^{-1} in the Li^+ lattice mode region.

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