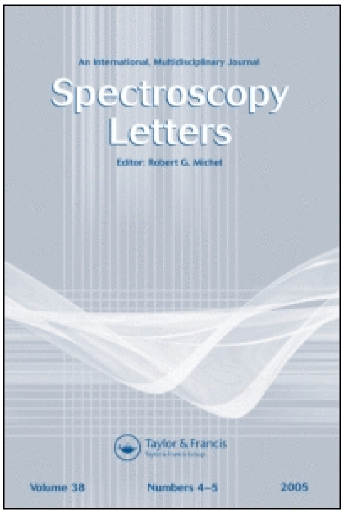

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Formate Ion Internal Vibrations in Lithium Formate Monohydrate (LiX'CO$_2$.X"$_2$0)

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FORMATE ION INTERNAL VIBRATIONS IN LITHIUM FORMATE MONOHYDRATE
($LiX'CO_2.X''_2O$)

Key Words: Lithium formate monohydrate, Formate ion internal vibrations, HCO_2^-/DCO_2^- isotope effect.

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ABSTRACT

The internal fundamentals of the formate ion in lithium formate monohydrate have been investigated for eight isotopically substituted compounds by the aid of Raman spectroscopy. On the basis of the H/D and $^6Li/^7Li$ isotope effects observed for the fundamental bands, it has been concluded that the internal vibrations are not strongly coupled with the external vibrations. The product rule has been applied to the HCO_2^-/DCO_2^- fundamental wavenumbers to discuss an anharmonicity correction for the formate ion internal fundamentals.

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INTRODUCTION

The application of $^{6}Li/^{7}Li$ isotope substitution in lithium compounds is generally very useful in the analysis of the solid state vibrational spectra. This technique is particularly interesting, when combined with the H/D isotope substitution, to study the vibrational mode mixings. In the case of lithium formate monohydrate, the vibrational studies based on the H/D and $^{6}Li/^{7}Li$ band shifts were reported for the external vibrations in the 700 - 200 cm^{-1} region by infrared spectroscopy and in the 300 - 25 cm^{-1} region by Raman spectroscopy.[1,2] From the observed spectral data and the results of the factor group analysis, the seeming degeneracies owing to the weak crystal force field among the sites were considered for many external fundamentals. As a consequence of this complication, the mode mixing between the internal and external modes of vibration could not be discussed in these papers. On the other hand, the single crystal polarized Raman measurements have shown that the correlation field band splitting on the formate ion internal fundamentals was not so clearly observable in lithium formate monohydrate.[3,4]

In the present paper, the formate ion internal vibrations are investigated for eight isotopically substituted lithium formate monohydrates by the use of laser Raman spectroscopy. The isotope product rule is applied to the fundamental wavenumbers to consider an anharmonicity correction.

EXPERIMENTAL

The preparative procedures for the eight isotopically substituted lithium formate monohydrates, $^{6}LiHCO_2.H_2O$, $^{7}LiHCO_2.H_2O$,

$^6LiDCO_2.H_2O$, $^7LiDCO_2.H_2O$, $^6LiHCO_2.D_2O$, $^7LiHCO_2.D_2O$, $^6LiDCO_2.D_2O$ and $^7LiDCO_2.D_2O$, followed the method described elsewhere.[1] The Raman spectra were recorded for polycrystalline compounds using a Cary 82 and Jarrell-Ash 25-300 laser Raman spectrometers equipped with argon ion lasers (514.4 nm) as the excitation source.

RESULTS AND DISCUSSION

Table 1 gives the fundamental wavenumbers of the formate ion internal vibrations. The correlation field band splitting was not clearly observed for any fundamental bands. The spectral data were assigned, on the basis of a C_{2v} symmetry, by comparison with those of related compounds.[5-9]

As seen in Table 1, the formate ion internal fundamentals are not meaningfully affected in their band positions by H_2O/D_2O and $^6Li^+/^7Li^+$ substitutions. This indicates that neither the internal and external modes of vibration of the H_2O/D_2O sites nor the $^6Li^+/^7Li^+$ site translations are strongly mixed with the HCO_2^-/DCO_2^- internal modes. On the other hand, the formate ion internal fundamentals are remarkably isotope shifted by HCO_2^-/DCO_2^- substitution as expected. The band shifts are mainly due to the H/D isotope mass effect in the kinetic energy terms.

To study the vibrational mode mixing between the internal and external modes of the HCO_2^-/DCO_2^- sites, the product rule based on the Wilson's GF matrix method is applied to the fundamental wavenumbers. The observed fundamental wavenumbers are generally used in place of the normal wavenumbers because of the difficulties to determine a complete set of normal wavenumbers of a

TABLE 1

Internal Fundamental Wavenumbers (cm^{-1}) for Formate Ion

		$^6LiHCO_2.H_2O$	$^7LiHCO_2.H_2O$	$^6LiHCO_2.D_2O$	$^7LiHCO_2.D_2O$
$\nu_1(a_1)$	ν C-H	2859	2860	2859	2860
$\nu_2(a_1)$	$\nu_s CO_2$	1371	1373	1371	1372
$\nu_3(a_1)$	δ CO_2	793	793	793	793
$\nu_4(b_1)$	ω C-H	1069	1069	1069	1069
$\nu_5(b_2)$	$\nu_a CO_2$	1588	1588	1588	1588
$\nu_6(b_2)$	ρ C-H	1390	1390	1390	1390

		$^6LiDCO_2.H_2O$	$^7LiDCO_2.H_2O$	$^6LiDCO_2.D_2O$	$^7LiDCO_2.D_2O$
$\nu_1(a_1)$	ν C-D	2153	2154	2153	2154
$\nu_2(a_1)$	$\nu_s CO_2$	1341	1343	1342	1343
$\nu_3(a_1)$	δ CO_2	788	788	788	788
$\nu_4(b_1)$	ω C-D	913	913	913	913
$\nu_5(b_2)$	$\nu_a CO_2$	1575	1575	1575	1575
$\nu_6(b_2)$	ρ C-D	1029	1029	1029	1029

polyatomic molecule. The product rule is applicable to a single symmetry species. When the vibrational mode mixing between the internal and external modes is not negligible for a symmetry species, the experimental product ratio in question must be different from the theoretical value.

$$\text{RATIO} = \frac{\tilde{\nu}'_1\,\tilde{\nu}'_2 \cdots \tilde{\nu}'_n}{\tilde{\nu}''_1\,\tilde{\nu}''_2 \cdots \tilde{\nu}''_n} = \sqrt{\frac{|G'|\,|F'|}{|G''|\,|F''|}}$$

Since the potential function of a molecule does not change, under the Born-Oppenheimer approximation, by any isotope substitution, the F matrix for the HCO_2^- site vibrations is exactly the same with that for the DCO_2^- site vibrations. In other words, all of the F matrix elements for the formate ion are taken to be $F_D/F_H = 1.000$, even for the H/D-substitution sensitive fundamental modes, in spite of an appreciable anharmonic effect.

$$\text{RATIO} = \sqrt{\frac{|G'|}{|G''|}} \qquad (\text{for } F_D/F_H = 1.000)$$

The product ratios based on a C_{2v} structure are given in Table 2. The experimental ratios for b_1 and b_2 species in Column I agree satisfactorily with the theoretical ratios in Column II, while the experimental ratio for a_1 species is fairly different from the theoretical value. The discrepancy in the a_1 species may be due to the mode mixing with the HCO_2^-/DCO_2^- site external vibrations or to the neglect of an anharmonic effect correction in the use of the observed fundamental wavenumbers. The former explanation is very difficult to be proved experimentally because the HCO_2^-/DCO_2^- site translations are substantially coupled with the H_2O/D_2O site translations.[1,2] However, since the formate ions are situated in general site positions,[10-12] it does not seem reasonable that the mode mixing between the internal and external vibrations occurs for a_1 species only.

Recently, Kidd and Mantsch reported the physical force field of the formate ion in sodium formate.[13] They investigated the anharmonic effect on the observed spectral data by applying the

TABLE 2

Isotope Product Ratios for HCO_2^-/DCO_2^-
(C_{2v} Structure)

	I	II	III
	Obs.	Calc.	Calc.
	$\tilde{\nu}_H/\tilde{\nu}_D$	F_D/F_H=1.000	F_D/F_H=1.026 (η=1)
a_1	1.366	1.398	1.380
b_1	1.171	1.174	1.159
b_2	1.362	1.366	1.349

Donnison's rule.[14] The force constant refinements were studied for the uncorrected and corrected wavenumbers. In the present work, we attribute the anharmonicity correction to the F matrix part of the product rule. According to Shimanouchi and Suzuki, the molecular force field for the H/D-substituted compounds using the fundamental wavenumbers is reasonable in comparison with that from the normal wavenumbers, when the diagonal F matrix elements for the H/D-anharmonicity influenced vibrations are considered independently.[15] They suggested that the correction factor may be $F_D/F_H = 1.026$. The product rule is written as follows:

$$\text{RATIO} = \sqrt{\frac{|G'|}{|G''|}} \times (1.026)^{-\eta/2} \qquad (\text{for } F_D/F_H = 1.026)$$

TABLE 3

Isotope Product Ratios for HCO_2^-/DCO_2^-
(C_1 Structure)

Calc.	$F_D/F_H=1.026$	($\eta=0$)	($F_D/F_H=1.000$)	RATIO =	2.242
		($\eta=1$)			2.185
		($\eta=2$)			2.130
		($\eta=3$)			2.076
Obs.	$\tilde{\nu}_H/\tilde{\nu}_D$			RATIO =	2.179

where η is the number of H/D-anharmonicity influenced vibrations. The calculated product ratios are given in Column III of Table 2. With this anharmonicity correction, the theoretical ratio for a_1 species is closer to the experimental ratio, but the discrepancy is still unsatisfactory. On the other hand, the agreements for b_1 and b_2 species are very reasonable for the uncorrected product rule. Alternately, by considering the symmetry lowering of the formate ion structure in lithium formate monohydrate, the product rules are applied to the C_1 site structure. As seen in Table 3, the theoretical ratio for $\eta = 1$ is comparable with the experimental value.

From the results above mentioned, it is concluded that the formate ion internal fundamental vibrations are not mode mixed with any external vibrations. The anharmonic term is important, to a normal degree, in describing the potential function for the C-H/C-D stretching vibration. Due to the symmetry lowering of the formate ion site in lithium formate monohydrate crystals, the C-H/C-D stretching vibration is slightly mixed with the C-H/C-D bending vibrations which results in a reasonable F matrix correction using the isotope product rule for the C_1 site structure.

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