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VIBRATIONAL ANHARMONICITY OF THE C-H OUT-OF-PLANE VIBRATIONS IN SOME HOFMANN-TYPE CLATHRATES

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In our previous reports [1,2], we have discussed the host-guest interactions in Hofmann-type clathrates. The motion of the guest (benzene) molecule has been studied through the changes of the frequencies and the shapes of the bands due to CH out-of-plane vibrations. It was found that one of these bands (the one at around 985 cm^{-1}), splits at LNT, the splitting being dependent on the volume of the tetragonal unit cell.

From the recorded FT-IR and Raman spectra of these clathrates, we have made an attempt to calculate some of the anharmonicity coefficients, X_{ij}, for the C-H out-of-plane bending vibrations in $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ and $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ Hofmann type clathrates.

The interaction of the guest (benzene) molecules in these two lattices has been discussed in terms of the calculated anharmonicity constants and the data were compared with the available data for liquid benzene.

1. INTRODUCTION

Hofmann-type clathrates represent a class of inclusion compounds consisting of a host-lattice : diammine-M(II)tetracyano-M'(II) and a guest molecule, enclathrate aromatic compound. Genaral formula : $M(NH_3)_2M'(CN)_4 \cdot 2G$, where M(II) is octahedrally coordinated metal, such as Ni, Zn, Fe, Co, Mn, Cd; M'(II) is square-planar coordinated metal and could be Ni, Pt or Pd; the aromatic compound is usually benzene, thiophene, aniline, *etc.* The crystal structure of these compounds is known [3,4]. The guest molecules (in our case, benzene) are built in the host lattice in the vacancies between the $M(NH_3)_2$ bridges and $M'(CN)_4$ groups. Crystallographic data show that there is no direct chemical bond between the host lattice and guest molecules. This was confirmed by the study of the infrared and Raman spectra of clathrates, the so-called "empty" clathrates and benzene.

In our previous vibrational studies of these compounds [1,2], we discussed the motion of the guest molecule (benzene) by studying the changes of the frequencies and the shape of some of the bands due to the C-H out-of-plane vibrations. We found that both the shape and the frequencies of some of the bands due to C-H out-of-plane bendings are

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strongly dependent on the unit cell volumes [1,2], while the other vibrational modes of benzene showed no changes in either frequencies or band shapes. One of our conclusions for such behaviour of these vibrational modes of benzene was the existence of some kind of host-guest interaction in the Hofmann-type clathrates. The available experimental data, the X-ray diffraction data [3,4], some NMR studies [5] as well as our infared and Raman spectra of these compounds seems to impose the idea that non-bonded proton-proton interactions have a considerable influence on those type of vibrations in which the motions of H atoms are dominant, such as NH_3 rocking vibrations in the host lattice [6] and C-H out-of-plane vibrations in the guest (benzene) molecules [1].

In order to make an estimate of the magnitude of interaction between the guest molecules and the host lattices, the anharmonicity constants, X_{ij}, were calculated using the carefully measured infrared and Raman frequencies for the four C-H out-of-plane fundamentals in benzene and some of their summation bands.

For this purpose we have chosen only two Hofmann-type clathrates : $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (Ni-Ni-Bz) and $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (Cd-Ni-Bz), because previous results indicated very large host-guest interaction in the former and almost no interaction in the last compound [1,2].

2. EXPERIMENTAL

The clathrates were prepared by the methods reported previously [5,7]. The infrared spectra were recorded on Perkin-Elmer 1720 FT-IR spectrophotometer with a maximum resolution of 2 cm^{-1}, while the Raman spectra were recorded with a Spex Ramalog 5M System and exited with a Spectra Physics Ar$^+$ ion laser on the 488 nm line. Raman bands were calibrated with the Ar$^+$ plasma lines and with a neon lamp.

3. RESULTS AND DISCUSSIONS

The Raman spectrum of one of the studied clathrates (Cd-Ni-Bz) and its corresponding infrared spectrum is shown in Fig. 1. The bands due to C-H out-of-plane fundamentals in benzene and some of their combination bands are marked with arrows. Four are C-H out-of-plane fundamentals, two of which are Raman active and two are infrared active. One of the Raman active bands (arround 1005 cm^{-1}) was detected with greater uncertainty then the others [8]. These fundamentals combine in such

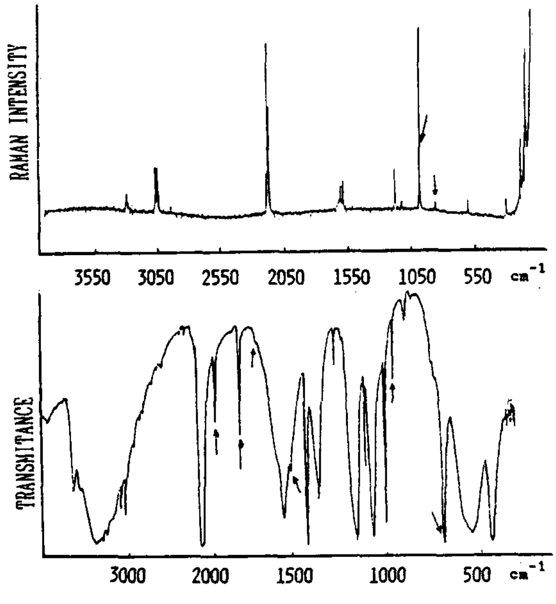

Fig. 1. Raman (upper) and IR (lower) spectra of Cd-Ni-Bz at RT.

Table 1. Calculated anharmonicity constants for some Hofmann type clathrates (frequencies measured at RT).

	Ni-Ni-Bz		Cd-Ni-Bz		Liquid**	
Mode*	ν/cm^{1}	$X_{i,j}$/cm^{1}	ν/cm^{1}	$X_{i,j}$/cm^{1}	ν/cm^{1}	$X_{i,j}$/cm^{1}
ν_4	706.0	-	701.5	-	673	
ν_{11}	870.0	-	868.0	-	849	
ν_{19}	986.5	-	984.0	-	975	-
ν_7	1004.0	-	1005.0	-	995	-
$\nu_4 + \nu_{11}$	1577.5	+1.5	1568.0	-1.5	1528.0	+6.0
$\nu_4 + \nu_{19}$	-	-	-	-	1636.0	-12.0
$\nu_4 + \nu_7$	1703.5	-7.0	1701.5	-5.0	1659.0	-9.0
$\nu_{11} + \nu_{19}$	1854.5	-2.0	1848.0	-4.0	1815.0	-9.0
$\nu_7 + \nu_{11}$	-	-	-	-	1838.0	-6.0
$\nu_7 + \nu_{19}$	1993.5	+3.0	1988.0	-1.0	1960.0	-10.0

* - Herzberg's [9] numbering of the vibrations of benzene. ν_7, ν_{11}, $\nu_4 + \nu_{19}$ and $\nu_7 + \nu_{11}$ are Raman active modes (under the unit cell group approximation [8])

** - Frequencies for fundamental vibrations are taken from Ref. 10 and those for combination bands are taken from Ref. 11.

way that there are six possible second order transitions due to summation bands, four of which are infrared and two Raman active (under the unit cell group approximation [8]). All four infrared active summation bands were detected in the infrared spectrum (Fig. 1), while the corresponding bands in the Raman spectrum have not been observed.

The calculated anharmonicity constants are given in Table 1. The zero-order frequencies could not be obtained due to lack of experimental data (most of the other second order transitions were overlapped by some more intensive bands from the clathrate). In the last column of Table 1, the corresponding anharmonicity constants for liquid benzene are given for comparison.

The calculated anharmonicity constants, for both studied clathrates are approximately the same (although not all of them have been obtained). The main difference is in the different signs of the two combination bands ($\nu_4+\nu_{11}$ and $\nu_7+\nu_{19}$) in the two studied clathrates (see Table 1). Since the frequencies of these two combination modes are obtained with great certainty, the corresponding calculated anharmonicity constants can be regarded as fairly accurate.

In spite of the fact that on the basis of these results one could not judge the relative magnitude of the host-guest interaction in the studied clathrates, some tentative conclusions can be derived : some of the summation bands involving the

C-H out-of plane vibrations in the enclathrate benzene molecules show different signs of the anharmonicity constants which may indicate different host-guest interaction in the two clathrates. In Ni-Ni-Bz, which is known to have the smallest volume of the unit cell [2], two of the four calculated anharmonicity constants have positive values, while in Cd-Ni-Bz, with the largest volume of the unit cell, all anharmonicity constants have negative values.

On the other hand, relatively large values for the anharmonicity constants in liquid benzene indicate larger interaction compared to that in clathrates which is to be expected in view of the fact that in liquid benzene the molecules are more densely packed then in the clathrates.

The above results for the anharmonicity constants can be regarded as a first attempt to make an estimate of the magnitude of the interaction between the host lattice and the guest molecule in Hofmann-type clathrates. In order to make further conclusions on this type of interaction more precise measurements are needed, in the first place on the second order transition bands in different type of clathrates.

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