

Vibrational spectroscopic and quantum theoretical study of host-guest interactions in clathrates: I. Hofmann type clathrates*

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Hofmann type clathrates are host-guest compounds with the general formula $M(NH_3)_2M'(CN)_4 \cdot 2G$, in which $M(NH_3)_2M'(CN)_4$ is the host lattice and G is benzene, the guest molecule. In previous studies, host-guest interactions have been investigated by analyzing the RT and LNT vibrational (infrared, far infrared and Raman) spectra of these clathrates. All the observed changes in the vibrational spectra of these clathrates are referred to a host-guest interaction originating from weak hydrogen bonding between the ammonia hydrogen atoms from the host lattice and the π electron cloud of the guest (benzene) molecules. In order to obtain an insight into the relative importance of the local crystalline field vs. the anharmonicity effects on the spectroscopic properties of the guest species upon enclathration, as well as to explain the observed band shifts and splittings, several quantum theoretical approaches are proposed.

Keywords: Hofmann clathrates, host-guest interactions, vibrational spectroscopy, vibrational Stark effect, perturbation theory.

INTRODUCTION

Hofmann type clathrates belong to a family of complex compounds composed of two components, a host lattice and guest molecules. They differ from other complex compounds in that the molecules of their components are associated without ordinary chemical bonding. The general formula for Hofmann type clathrates is $M(NH_3)_2M'(CN)_4 \cdot 2G$, where M is an octahedrally coordinated metal (Ni, Mg, Co, Zn, Mn, Cd), M' is a square planar coordinated metal (Ni, Pd or Pt) and G is the guest molecule, usually an aromatic molecule, such as benzene. The structure consists of planar layers containing the metal atoms and the cyanide groups with the NH_3 group protruding above and below these layers. The ammonia groups then define the void wherein the guest molecule resides.

Hofmann type clathrates belong to a tetragonal system, space group $P4/m$ with $Z = 1$. The crystal structure of most of these clathrates has been determined by

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powder X-ray diffraction,¹⁻³ some of them have been determined by single crystal studies⁴⁻⁶ and recently, neutron diffraction data for the structure of $\text{Zn}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{D}_6$ and $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{D}_6$ clathrate have been reported.⁷ The closest contact between the host lattice and the guest molecule is detected between the carbon atom of the benzene molecule and the nitrogen atom from the NH_3 group of the host lattice. This distance is almost always 360 pm,⁴⁻⁷ indicating van der Waals contact.

Apart from the structural studies on these clathrates, extensive spectroscopic (infrared, far infrared and Raman)⁸⁻¹³ studies have been carried out in the last 20 years. The effects of free rotation of the benzene (guest) molecule¹⁴ and the ammonia molecules (host lattice)¹⁵ have been studied by NMR spectroscopy and by inelastic neutron scattering experiments.^{16,17} Theoretical studies regarding the nature of the host-guest interactions, as well as *ab initio* and semiempirical calculations of model subsystems have also been performed.¹⁸⁻²²

The vibrational spectroscopic⁸⁻¹² and NMR^{14,15} measurements, as well as inelastic neutron scattering diffraction experiments^{16,17} have confirmed the existence of a significant host-guest interaction in Hofmann type clathrates. The host-guest interaction detected in Hofmann type clathrates is often referred to as weak hydrogen bonding between the ammonia hydrogen atoms and the π electron cloud of the benzene molecules.⁸⁻¹²

In the spectroscopic experiments, this interaction was most obviously manifested through: (1) frequency shifts and/or changes in the shape of the bands due to the out-of-plane CH bending modes (γ_{CH}) in the guest, benzene molecule,¹² compared to the corresponding values in liquid benzene,²³ and (2) frequency shifts of the symmetric NH_3 deformation vibration (δ_s) in the host lattice, compared to the corresponding frequency of the "empty" clathrates.¹¹

In the last ten years, during our studies of different isomorphous series of Hofmann type clathrates, we have collected a considerable amount of experimental (mainly spectroscopic) data, which provided the basis from which we were able to propose a few quantum mechanical models. These theoretical models gave some insight into various quantum mechanisms, over the spectral behaviour of the guest molecule upon enclathration. The first attempt to explain the splitting of some of the γ_{CH} modes in the benzene molecules at low temperatures was based on a quasi-classical approximation.²⁶ Later, a fully quantum model of the observed splitting was proposed based on the concept of the vibrational Stark effect, including the vibrational angular momentum due to degeneracy.²⁷ The last approach also gave some insight into the relative importance of the local crystalline field vs. anharmonicity effects on the spectroscopic properties of the guest molecules upon enclathration.

In this paper, a combined experimental (infrared and Raman) and theoretical study of the host-guest interaction in Hofmann type clathrates is reported.

EXPERIMENTAL

The Hofmann type clathrates and their residual host lattices were prepared by previously reported method.²⁴ In order to ensure that the clathrates consist of two benzene molecules, C and H microanalyses were carried out on a COLEMAN C-H analyzer. The powder X-ray diffraction technique was used to check that the clathrates belong to a certain isomorphous series. For this purpose, a JEOL Diffractometer JDX-7E was used (Cu-K α radiation being employed).

The RT and LNT infrared spectra were recorded on a Perkin-Elmer model 580 IR and on a Perkin-Elmer System 2000 FTIR spectrometer from KBr pellets or Nujol mulls. A low-temperature cell, model RIIC VLT-2 was used for the LNT-IR measurements. The RT and LNT Raman spectra were recorded on a Perkin-Elmer NIR FT-Raman spectrometer, model 1700-x using a Nd-YAG laser operating at 1064 nm.

RESULTS AND DISCUSSION

Spectroscopic results

The infrared and Raman spectra of one of the studied clathrates, $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ are shown in Fig. 1. The bands marked with arrows are due to the vibrations of the benzene (guest) molecule. All other bands originate from the vibrational modes of the host lattice.

In our previous spectroscopies studies,^{10–14} evidence for the existence of host-guest interactions in Hofmann type clathrates was obtained from both the vibrational bands of (1) the guest molecules and (2) the host lattice.

1. Vibrational bands of the guest (benzene) molecules

The infrared and Raman spectra of the Hofmann type clathrates (Fig. 1) confirmed that the position of the bands due to the guest molecules remain practically unchanged upon enclathration^{10,12} compared to the corresponding values in liquid benzene.²³ The only exceptions are the bands due to C–H out-of-plane bending modes (γ_{CH}), where two main changes were observed upon enclathration:

- (i) a shift to higher frequencies compared to those of liquid benzene²³ and/or
- (ii) a splitting of some of the γ_{CH} bands at low temperatures.

There are four γ_{CH} benzene vibrations: ν_4 , ν_7 , ν_{11} and ν_{19} . (Hereafter, the notation, intensities and symmetry species are given according to Herzberg²⁵). According to the selection rules of the D_{6h} point group, $\nu_4(A_{2u})$ is IR active and appears (in the spectra of the studied clathrates) as a strong band around 700 cm^{-1} , $\nu_{11}(E_{1g})$ is Raman active and appears in the Raman spectra at around 860 cm^{-1} . The remaining two fundamental modes, $\nu_{19}(E_{2u})$ and $\nu_7(B_{2g})$ are IR and Raman inactive in gaseous benzene.²³ However, due to the lowering of the symmetry, they both appear as weak or very weak bands in the infrared and Raman spectra, respectively (Table I).

- (i) The shift of bands due to the γ_{CH} modes of the enclathrated species

The observed shifts of the γ_{CH} bands to higher frequencies compared to the bands in liquid benzene were in the range of 10–20 cm^{-1} . Shifts to correspondingly

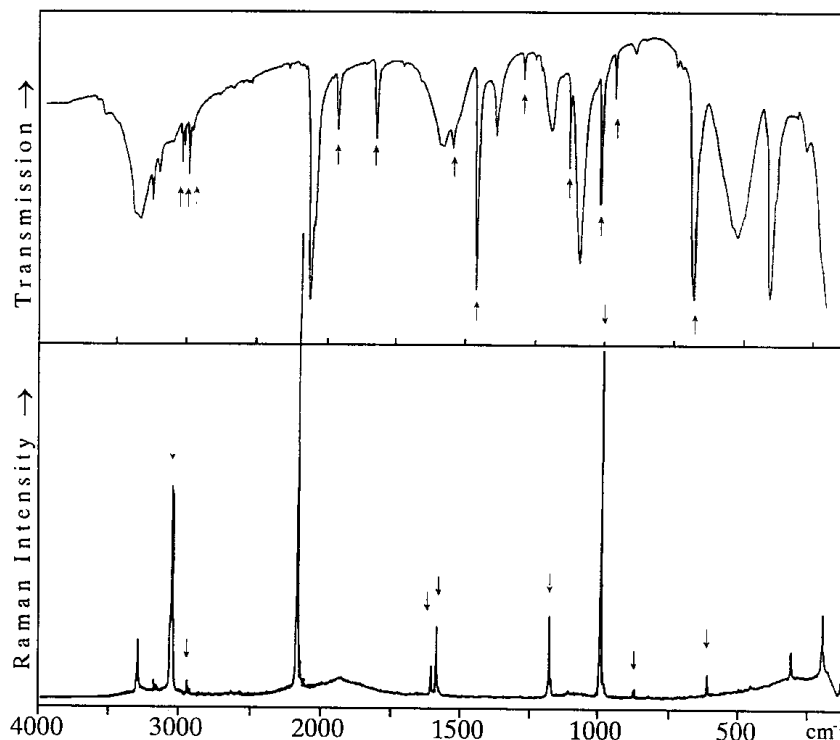


Fig. 1. The infrared (upper) and Raman (lower) spectra of one of the Hofmann type clathrates, $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, at room temperature. (The bands due to the vibration of the guest molecules are marked with arrows.).

higher frequencies (around 30 cm^{-1}) were also observed in the IR spectra of the two combination bands due to the γ_{CH} modes: ($\nu_{11} + \nu_{19}$) and ($\nu_7 + \nu_{19}$), which appear around 1850 cm^{-1} and around 1990 cm^{-1} , respectively (Fig. 1). Additional blue shifts were observed at LNT.

(ii) The splitting of bands due to the γ_{CH} modes of the enclathrated species

In our previous studies,^{10,12} a splitting of the weak band assigned to the ν_{19} mode into two components at low temperatures was observed. However, the magnitude of this splitting was different in different Hofmann type clathrates and depended on the nature of the metals M and M' . Thus, in the subseries with M' fixed, the magnitude of the splitting of this band at low temperature increases in the order $\text{Cd} < \text{Mn} < \text{Zn} < \text{Co} < \text{Fe} < \text{Mg} < \text{Ni}$ (Fig. 2 and Table II) while the unit cell volume decreases in the same order (Table II). The mean value of the slope of $\Delta\nu$ vs. $V_{\text{unit cell}}$ obtained from these data is about $-100\text{ cm}^{-1}/\text{nm}^3$ in the three studied isomorphous series of Hofmann type clathrates¹² (Fig. 3).

The most probable explanation for both effects found in the vibrational spectra of these clathrates is an interaction between the guest molecule and the host lattice.

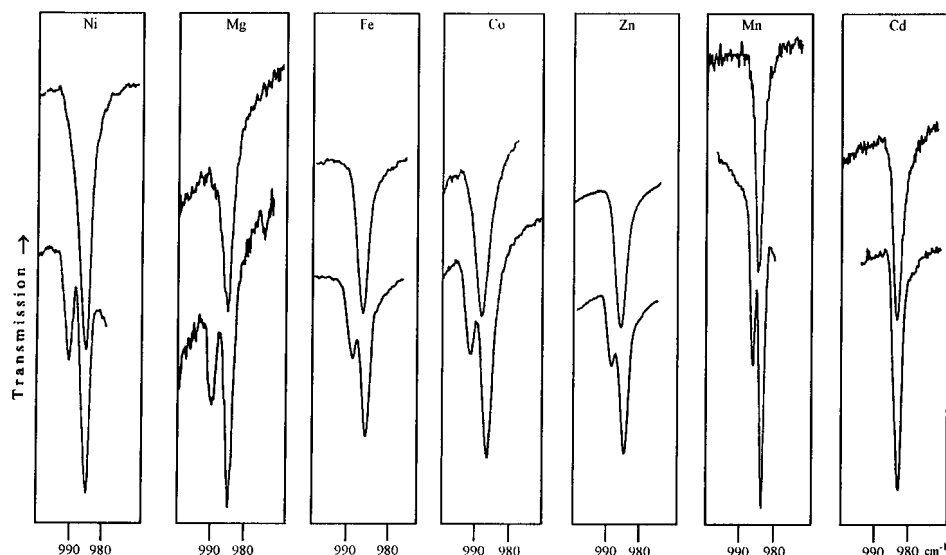


Fig. 2. The CH out-of-plane vibrations in the IR spectra in a series of Hofmann type clathrates: $M(\text{NH}_3)_2\text{Ni}(\text{CH})_4 \cdot 2\text{C}_6\text{H}_6$, where $M = \text{Ni, Mg, Fe, Co, Zn, Mn}$ and Cd . (The upper IR bands were recorded at room temperature and the lower at low temperatures.)

This interaction is obviously not only due to the existence of van der Waals forces, but also to the presence of a weak hydrogen bond between the π electrons of the aromatic guest molecule and the ammonia groups of the host lattice. Further, this interaction is obviously strongly dependent on the volume of the unit cell (Fig. 3), *i.e.*, the effective ionic radii of the octahedrally coordinated metal M attached to the NH_3 groups (R_6) and the square-planar coordinated metal M' attached to the CN groups (R_4).¹² Thus, two correlations for the three studied isomorphous series of Hofmann type clathrates have been made. Firstly, the magnitude of splitting of the band due to the ν_{19} mode at low temperatures was correlated with the effective ionic radii for the octahedrally coordinated metal $M(\text{II})$, R_6 and the square-planar coor-

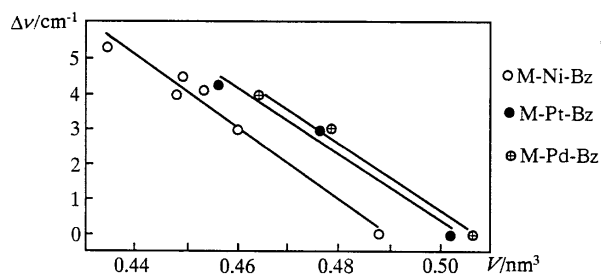


Fig. 3. A plot of $\Delta\nu$ vs. $V_{\text{unit cell}}$ (*cf.* Table II) for three series of Hofmann type clathrates: M-Ni-Bz is $M(\text{NH}_3)_2\text{Ni}(\text{CH})_4 \cdot 2\text{C}_6\text{H}_6$, M-Pt-Bz is $M(\text{NH}_3)_2\text{Pt}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ and M-Pd-Bz is $M(\text{NH}_3)_2\text{Pd}(\text{CH})_4 \cdot 2\text{C}_6\text{H}_6$.

dinated metal M(II), R_4 (Eq. 1), and secondly, the volumes of the tetragonal unit cells were correlated with the effective ionic radii for the octahedrally coordinated metal M(II), R_6 and square-planar coordinated metal M(II), R_4 (Eq. 2). (The values for the effective ionic radii of M and M' were taken from Ref. 28.).

$$\Delta\nu/\text{cm}^{-1} = 20.728 - 171.100 R_6/\text{nm} - 76.687 R_4/\text{nm} \quad (1)$$

(adjusted $r^2 = 0.96$)

$$V/\text{nm}^3 = 0.232 + 1.695 R_6/\text{nm} + 1.837 R_4/\text{nm} \quad (2)$$

(adjusted $r^2 = 0.95$)

TABLE I. The IR and Raman frequencies of the bands due to the γ_{CH} modes of the guest, benzene molecule in the three isomorphous series of Hofmann-type clathrates. Their corresponding unit cell volumes are given in the last column

| Compound | M | ν/cm^{-1} | | | | V/nm^3 |
|----------|----|----------------------|------------------|---------------------|---------------------|-----------------|
| | | $\nu_4^{(a)}$ IR | $\nu_4^{(b)}$ IR | $\nu_{19}^{(a)}$ IR | $\nu_{11}^{(a)}$ IR | |
| M-Ni-Bz | Zn | 706.5 | 706.5 | 985.5 | | 0.453 |
| | Ni | 706.0 | 706.5 | 986.0 | 870.0 | 0.434 |
| | Co | 704.0 | 704.0 | 986.0 | | 0.449 |
| | Mg | 702.0 | 703.0 | 985.0 | | 0.445* |
| | Fe | 702.0 | 703.0 | 984.7 | | 0.448 |
| | Mn | 702.0 | 703.0 | 984.5 | | 0.460 |
| | Cd | 700.0 | 700.0 | 983.5 | 867.0 | 0.488 |
| M-Pd-Bz | Ni | 701.5 | 702.0 | 983.0 | | 0.464 |
| | Co | 701.0 | 701.5 | 983.0 | | 0.471* |
| | Zn | 701.0 | 701.0 | 982.0 | | 0.478 |
| | Mn | 698.0 | 698.5 | 982.0 | | 0.490* |
| | Cd | 698.0 | 699.0 | 981.5 | | 0.506 |
| M-Pt-Bz | Ni | 701.5 | 701.5 | 984.5 | | 0.456 |
| | Zn | 699.0 | 699.0 | 981.5 | | 0.476 |
| | Cd | 696.0 | 696.0 | 981.5 | | 0.502 |

^(a)RT data; ^(b)LT data; IR - infrared data; R - Raman data; * - predicted values on the basis of correlation equations.²

Note that the weak γ_{CH} band due to the ν_7 mode is not listed in this Table since, due to its very weak intensity it could not be assigned with reasonable certainty in the Raman spectra of the studied clathrates

2. Vibrational spectra of the host lattice

For the purpose of studying the vibrational spectra of the host lattice, a series of Hofmann type clathrates partially depleted in benzene was prepared. Thus, the loss of the benzene molecule from the host lattice was followed spectroscopically by the method of the gradual loss of the benzene molecules from the host lattice.

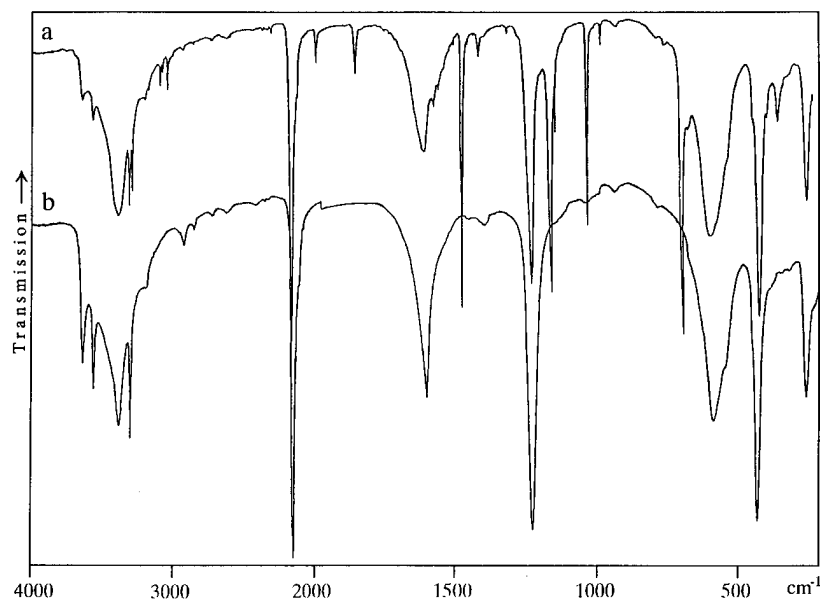


Fig. 4. The RT infrared spectra of one of the Hofmann type clathrates, $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (upper) and the corresponding "empty" clathrate, $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4$ (lower).

The IR spectra of one of the studied clathrates, $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (Ni-Ni-Bz) and its corresponding "empty" clathrate, $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4$ (Ni-Ni) are compared in Fig. 4. From this comparison, it was found that there are two spectral regions in which significant changes can be observed upon enclathration:

- (i) the region of the N–H stretching vibrations; $3400\text{--}3200\text{ cm}^{-1}$, and
 - (ii) the region of the symmetric NH_3 bending vibrations; $1250\text{--}1100\text{ cm}^{-1}$.
- (i) The region of the NH stretching vibration: $\nu_{\text{as}}(\text{NH}_3)$ and $\nu_{\text{s}}(\text{NH}_3)$

The gradual loss of the benzene molecules from the host lattice in one of the studied Hofmann type clathrates, $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, in the region of the N–H stretching vibrations is clearly observed in the infrared spectra presented in Fig. 5a. The band due to the antisymmetric N–H stretching vibration (ν_{as}), a strong and broad band around 3400 cm^{-1} , becomes sharper upon enclathration. Simultaneously, the doublet of weak bands due to symmetric N–H stretching vibrations becomes a singlet. There are at least two reasons for the observed changes in these bands: firstly, removal of the degeneracy of the ν_{as} band and secondly, the host-guest interaction.

- (ii) Region of the symmetric NH_3 deformation vibration (δ_{s}); $1250\text{--}1100\text{ cm}^{-1}$.

The gradual loss of benzene molecules from the host lattice is also clearly observed in the spectral region of the symmetric NH_3 deformation vibration (Fig. 5b). On the other hand, the position of the band due to antisymmetric NH_3 vibrations is practically unchanged (Fig. 5b). The strong doublet between $1200\text{--}1100\text{ cm}^{-1}$ in

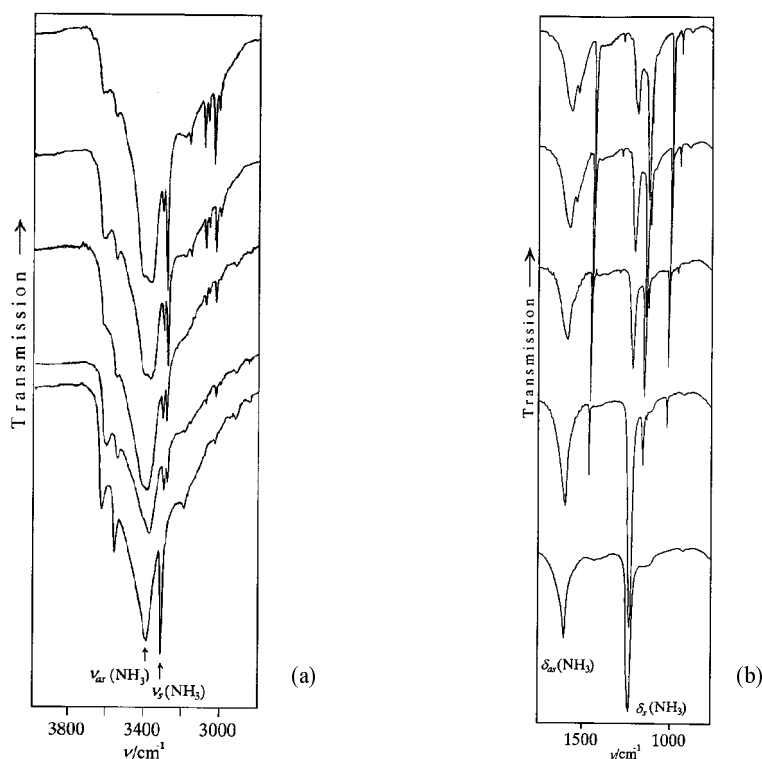


Fig. 5. The RT infrared spectra of the Hofmann type clathrate, $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ partly depleted of benzene, in the region of (a) the N-H stretching vibrations and (b) the NH_3 bending vibrations. The upper and the lower spectra belong to the clathrate and the "empty" clathrate, respectively.

the spectra of the Hofmann type clathrate (Ni-Ni-Bz) becomes a singlet in the spectrum of the "empty" clathrate (Ni-Ni) (Fig. 5b).

These doublets, as suggested in the literature,²⁹ could originate from a Fermi resonance interaction of the NH_3 symmetric deformation vibrations with the overtone of the NH_3 rocking vibration, which appears as a strong and relatively broad band at around 550 cm^{-1} (Fig. 4). However, a detailed analysis of the magnitude of the splitting of these doublets and the ratio of their intensities in all three isomorphous series of Hofmann type clathrates suggested¹¹ that other effects may be responsible for the existence of the doublet. Namely, in all the studied clathrates, a considerable splitting of the IR bands due to $\delta_s(\text{NH}_3)$ modes is observed. The magnitude of this splitting and the ratio of the intensities of these bands varies depending on the metal *M* attached to the ammonia molecules¹¹ and is strongly dependant on the volume of the tetragonal unit cell. Further, this splitting increases with increasing unit cell volume and/or red shift of the $\rho(\text{NH}_3)$ modes. Therefore, the origin of these doublets and their unusual infrared intensity could be understood in terms of strong mechanical (and probably electrical) anharmonicity connected with the motions of the NH_3 molecules which have vibrational, rather than deformational character.

One probable explanation of the behaviour of the vibrational bands due to N–H stretching and NH₃ bending vibrations in Hofmann type clathrates lies in the existence of host-guest interactions.¹¹

Theoretical studies

1. The shift of the bands due to γ_{CH} modes of the enclathrated species

In order to explain the shifts of the bands due to the ν_4 , ν_{19} and ν_{11} modes of the benzene guest molecule in Hofmann type clathrates within a series of structurally similar compounds (as well as the RT-LT shifts), and to judge the relative importance of various factors on the spectroscopic properties of the enclathrated species, a quantum mechanical approach²⁶ was adopted, in the following way.

The γ_{CH} modes of the guest benzene molecules were treated as anharmonic oscillators with a symmetric potential of the type $-U_0 \exp(-aq^2)$, in an *effective local homogeneous electrostatic field* E_L due to the host lattice. Since the lowest energy states (the ground and the first excited states) are of principal interest, expanding the exponential term in a power series, the Hamiltonian of this system takes the form:

$$H = -\frac{h^2}{2m} \frac{d^2}{dq^2} + \frac{m\omega_0^2}{2} q^2 - U_0 - eE_L q - \frac{1}{2} \lambda q^4 + \dots \quad (3)$$

where m is the reduced mass of the normal mode, ω_0 is the harmonic frequency, e its effective charge, U_0 the depth of the potential well, while λ is the quartic force constant (in the previous expression, $m\omega_0^2 = 2aU_0$, while $\lambda = a^2U_0$; also, $\lambda, U_0 > 0$). Truncating the series after the term containing q^4 , the Hamiltonian reduces to:

$$H = H^{(0)} + V$$

where:

$$H^{(0)} = -\frac{h^2}{2m} \frac{d^2}{dq^2} + \frac{m\omega_0^2}{2} q^2 - U_0 - eE_L q \quad (4)$$

and:

$$V = -\frac{1}{2} \lambda q^4$$

Applying the stationary perturbation theory for a non-degenerate case with the perturbation operator V , the following expression is straightforwardly obtained for the wavenumber of the $0 \rightarrow 1$ transition:

$$\nu_{01} = \nu_h - (A + BE_L^2)^{\lambda} \quad (5)$$

In the previous equation,

$$A = \frac{3h}{32\pi^4 c^3 m^2 \nu_h^2}; \quad B = \frac{3e^2}{64\pi^6 c^6 m^3 \nu_h^5} \text{ where } \nu_h \text{ is the harmonic wavenumber.}$$

The obtained formula shows that the frequency of the γ_{CH} modes should decrease as E_L^2 . As the effective local field is expected, in principal, to increase with decreasing temperature (due to the decrease of the unit cell volume), if only electrostatic effects were responsible for the RT-LT band shifts, an opposite trend would be expected to the one experimentally observed. (The experimental results for the discussed modes are summarized in Table I). Lowering the temperature induces a decrease in the quartic force constant λ , implying a more harmonic behavior at LT than at RT. A change in the anharmonicity is thus responsible, within this model, for the observed band shifts. The prediction based on the presented approach is consistent with the results for the C–H stretching vibrations in methyl substituted alkanes, where a decrease of the anharmonicity due to an increase of the steric crowding of the methyl group was observed.³⁰ In the case of enclathrated molecules, the decrease of the unit-cell volume would lead to a similar effect with respect to the steric limitation of the γ_{CH} motions. The smaller amplitude of the oscillations results in a more harmonic behavior of the system. The same consideration also holds for the trend in a series of structurally similar clathrates. Namely, a decrease of the unit cell volume in the presence of only electrostatic effects (unchanged values of λ) within the *effective local homogeneous field* approximation is expected to cause a lowering of the frequencies of the γ_{CH} modes, contrary to most of the experimental observations. Thus, an increased *harmonic* behavior of the γ_{CH} motions with decreasing unit cell volume is responsible for the actual experimental observations. As can be seen from Table I, the predictions of this relatively simple model are in quite good agreement with most of the experimental observations. It should be kept in mind that the present quantum model does not take into account the subtleties of these systems. Further work on the extension of the present model (that would take into account in more detail the effect of the local electrostatic field), based on more precise crystallographic data, is in progress.

2. The splitting of bands due to the γ_{CH} modes of the enclathrated species

A quantum mechanical model, based on the concept of the vibrational Stark effect, was also proposed, in order to explain the RT-LT splitting of the ν_{19} mode of the enclathrated benzene molecules. The guest benzene molecule in the electrostatic field generated by the host lattice was treated within the *effective local homogeneous field approximation*.^{26,27} The potential of a polyatomic molecule in a uniform electrostatic field takes the form:

$$V = V_0 + \frac{1}{2} \sum_i m_i \omega_{0i}^2 q_i^2 + \sum_{i \leq j \leq k} k_{ijk} q_i q_j q_k + \sum_{i \leq j \leq k \leq l} k_{ijkl} q_i q_j q_k q_l - \mu \mathbf{E} \quad (6)$$

μ being the dipole moment vector function, \mathbf{E} the electrostatic field vector, while q_i , denotes the i -th normal coordinate with a reduced mass m_i and harmonic frequency ω_{0i} , and k_{ijk} , k_{ijkl} are the cubic and quartic force constants, respectively. Expanding μ in a power series with respect to the normal coordinates gives:

$$\mu = \mu_0 \sum_i \left(\frac{\partial \mu}{\partial q_i} \right)_0 q_i + \frac{1}{2} \sum_i \sum_j \left(\frac{\partial^2 \mu}{\partial q_i \partial q_j} \right)_0 q_i q_j + \dots \quad (7)$$

Including only the first - order terms in q_i the dot product μE takes the form:

$$[\mu_z \mu_y \mu_x] \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = [\mu_{x,0} \mu_{y,0} \mu_{z,0}] \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} + \sum_i \left[\frac{\partial \mu_x}{\partial q_i} \frac{\partial \mu_y}{\partial q_i} \frac{\partial \mu_z}{\partial q_i} \right] q_i \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \quad (8)$$

The dipole moment of the unperturbed (free) benzene molecule is zero, and assuming that the electrostatic field is oriented along the z - axis of the laboratory coordinate system, within the electrical harmonic approximation, the potential takes the form:

$$V = V_0 + \sum_i \left[\frac{1}{2} m_i \omega_{0i}^2 q_i^2 - \left(\frac{\partial \mu_z}{\partial q_i} \right) q_i E_z \right] + \sum_{i \leq j \leq k} k_{ijk} q_i q_j q_k + \sum_{i \leq j \leq k \leq l} k_{ijkl} q_i q_j q_k q_l \quad (9)$$

Treating the last two sums in the previous expression as perturbations, the unperturbed total molecular Hamiltonian becomes diagonal, and the field-dependent vibrational wave function may be factorized:

$$|\Psi_{[n]}(|q\rangle, E_z)\rangle = \prod_i |\Psi_{ni}(q_i, E_z)\rangle \quad (10)$$

where $\{q\} = \{q_1, q_2, \dots, q_N\}$, and $\{n\} = \{n_1, n_2, \dots, n_N\}$.

Since we are particularly interested in the doubly degenerate (E_{2u}) ν_{19} mode of the guest benzene molecule, a more convenient way to write the wave function is:

$$|\Psi_{[n]}(|q\rangle, E_z)\rangle = \left[\prod_i |\Psi_{ni}(q_i, E_z)\rangle \right] |\Psi_a(q_a, E_z)\rangle |\Psi_b(q_b, E_z)\rangle \quad (11)$$

where $|\Psi_a(q_a, E_z)\rangle$ and $|\Psi_b(q_b, E_z)\rangle$ are the wave functions corresponding to the ν_{19} mode components. Application of the stationary perturbation theory with the perturbation operator:

$$H^{(1)} = \sum_{i \leq j \leq k} k_{ijk} q_i q_j q_k + \sum_{i \leq j \leq k \leq l} k_{ijkl} q_i q_j q_k q_l \quad (12)$$

leads to the following expression for the vibrational Stark splitting of the ν_{19} mode components, expressed through wavenumbers:

$$\Delta v_{a,b} = \frac{k_{aabb}^2}{\pi c m^3 \omega_0^5} \left(\frac{\partial \mu_z}{\partial q} \right)_0 E^2 \quad (13)$$

If the vibrational angular momentum is explicitly quantized through the choice of an appropriate basis, the previous expression takes the form:

$$\Delta v_{a,b} = \frac{2k_{aabb}}{m\pi c h^2 \omega_0^3} \left(\frac{\partial \mu_z}{\partial q} \right)_0^2 E^2 \quad (14)$$

It follows from the derived expressions that the ratio of the $\Delta\nu_{a,b}$ values for two structurally similar clathrates is equal to the square of the ratio of the effective local electrostatic fields at the particular enclathration sites. Further, the vibrational Stark splitting of the ν_{19} mode components increases with the square of the field strength. This is in line with the experimental observation.^{10–13} The splitting of this mode increases with decreasing temperature, *i.e.*, with decreasing unit cell volume for a particular clathrate. On the other hand, for a series of isostructural Hofmann type clathrates, the splitting increases also with decreasing unit cell volume. A good correlation between the observed ν_{19} mode splitting and the unit cell volume of the members of the mentioned series of compounds has been found.^{10–13} Since in both the mentioned cases the local field is expected to increase, the presented approach is capable of modeling successfully the system under consideration.

TABLE II. The measured splittings of the ν_{19} mode components, the corresponding unit cell volumes, and the estimated relative field strengths (with respect to the member with the smallest measured splitting) in the three isomorphous series of Hofmann type clathrates

| Compound ^(a) | $\Delta\nu_{a,b}/\text{cm}^{-1(b)}$ | V/nm^3 | Rel. field ^(b) |
|-------------------------|-------------------------------------|-----------------|---------------------------|
| Ni-Ni-Bz | 5.3 | 0.434 | 1.3292 |
| Mg-Ni-Bz | 4.5 | 0.444 | 1.2247 |
| Fe-Ni-Bz | 4.0 | 0.448 | 1.1547 |
| Co-Ni-Bz | 4.3 | 0.449 | 1.1972 |
| Zn-Ni-Bz | 4.1 | 0.453 | 1.1690 |
| Mn-Ni-Bz | 3.0 | 0.460 | 1.0000 |
| Cd-Ni-Bz | 0.0 | 0.488 | |
| Ni-Pd-Bz | 4.0 | 0.464 | 1.5811 |
| Co-Pd-Bz | 3.5 | 0.471 | 1.4790 |
| Zn-Pd-Bz | 3.0 | 0.478 | 1.3693 |
| Mn-Pd-Bz | 1.6 | 0.490 | 1.0000 |
| Cd-Pd-Bz | 0.0 | 0.506 | |
| Ni-Pt-Bz | 4.3 | 0.456 | 1.1972 |
| Zn-Pt-Bz | 3.0 | 0.476 | 1.0000 |
| Cd-Pt-Bz | 0.0 | 0.502 | |

^(a) $\text{M-M'-Bz} \equiv \text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$; ^(b)LNT values

The splittings of the ν_{19} mode in the studied series of structurally similar Hofmann type clathrates (measured at LT) are presented in Table II, together with the relative field strengths at the enclathration sites estimated by the presented model (both representations lead to the same values). The benzene guest molecules may thus serve as a probe for "measuring" the local field strengths in this series of inclusion compounds.

Attempts to apply the presented approach to the host crystalline lattices are currently in progress.

CONCLUSIONS

In this work, an attempt to summarize all the experimental and theoretical results obtained in our, nearly a decade long, study of Hofmann type clathrate has been made. Therefore, only the main aspects of the vibrational and theoretical findings have been presented here. More details can be found in our published papers.^{10–13,26,27}

ИЗВОД

ВИБРАЦИОНО-СПЕКТРОСКОПСКА И КВАНТНО-ТЕОРИЈСКА ИСПИТИВАЊА ИНТЕРАКЦИЈА ДОМАЋИН – ГОСТ У КЛАТРАТИМА: I. КЛАТРАТИ ХОФМАНОВОГ ТИПА

БИЉАНА МИНЧЕВА-ШУКАРОВА, ЛИЛЈАНА АНДРЕЕВА, ЉУПЧО ПЕЈОВ и
ВЛАДИМИР ПЕТРУШЕВСКИ

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Клатрати Хофмановог типа су једињења типа домаћин-гост, са општом формулом $M(NH_3)_2M'(CN)_4 \cdot 2G$. $M(NH_3)_2M'(CN)_4$ је решетка домаћина, а G је гост (бензен). У претходним радовима, интеракције домаћин – гост код ових клатрата су биле испитиване анализом собно- и нискотемпературних вибрационих спектра (инфрацрвених и раманских). Све запажене промене у вибрационим спектрима су приписане интеракцијама домаћин – гост. Сматра се да су ове интеракције узроковане слабом водоничном везом између амонијачних протона решетке домаћина и π -електронског облика молекула бензена. Ради добијања бољег увида у релативну важност ефеката локалног кристалног поља (у односу на ефекте због анхармоничности) на спектроскопске особине госта приликом уклапања у решетку клатрата и, такође, да би објаснили померање и цепање трака у спектрима, примењени су различити квантно-теоријски модели.

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