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**LAMP
SERIES REPORT**
(Laser, Atomic and Molecular Physics)

**LASER RAMAN AND INFRARED SPECTROSCOPIC STUDIES
OF MOLECULAR SYSTEMS:
STRUCTURAL ANALYSIS OF SOME CLATHRATE COMPOUNDS**

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Preface

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LASER RAMAN AND INFRARED SPECTROSCOPIC STUDIES
OF MOLECULAR SYSTEMS:
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ABSTRACT

In this paper the structural analyses of some molecular systems, namely clathrates, depending on the laser Raman and infrared spectroscopic studies are reported.

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1. INTRODUCTION

1.1 Raman effect

Raman scattering is one of the processes resulting from the interaction of radiation with matter. A characteristic feature of Raman scattering is the change in frequency of the scattered light. As distinct from luminescence, where the frequency of the re-emitted radiation is also changed, in Raman scattering the system is not excited for any measurable length of time to a higher energy level.

When incident light quantum $h\nu_0$ collides with a molecule it can either be scattered elastically in which case its energy remains unaltered (Rayleigh scattering) or it can be scattered inelastically in which case it either gives a part of its energy to the molecule or takes energy from it. If the molecule is initially at state $|i\rangle$ with the energy E_i and after interaction with monochromatic radiation of angular frequency ω_0 goes to state $|f\rangle$ with energy E_f , the conservation of energy enables us to write:

$$E_i + h\nu_0 = E_f + h(\omega_0 \pm \omega_{fi}) \quad (1)$$

where; $h\nu_{fi} = E_f - E_i$, and $h(\omega_0 \pm \omega_{fi}) = h\nu_s$, the energy of the scattered photon.

$$\left. \begin{array}{ll} \text{If } E_f = E_i, & \omega_s = \omega_0 \quad (\text{Rayleigh scattering}) \\ E_f > E_i & \omega_s = \omega_0 - \omega_{fi} \quad (\text{Stokes}) \\ E_f < E_i & \omega_s = \omega_0 + \omega_{fi} \quad (\text{anti-Stokes}) \end{array} \right\} \text{Raman scattering}$$

The Raman shifts give directly the energy differences of the system. The Raman lines displaced toward the shorter frequencies are called Stokes lines and those displaced toward the longer frequencies are called anti-Stokes lines.

Such scattering of radiation with change of frequency was first discovered by C.V. Raman and K.S. Krishnan in liquids (1).

Very shortly after the paper of Raman and Krishnan was published, G.S. Landsberg and L.I. Mandelstam (2) in Russia reported the observation of the similar effect in quartz. The effect had been predicted on theoretical grounds in 1923 by A. Smekal (3).

In quantum theory of scattering, the intensity arising from a transition between states $|i\rangle$ and $|f\rangle$, under ordinary conditions of Raman scattering experiments, depends on the polarizability tensor, whose components are given by (4):

$$[\alpha_{xy}]_{fi} = \frac{1}{h} \sum_r \left\{ \frac{[P_y]_{fr} [P_x]_{ri}}{\omega_{rf} + \omega_0} + \frac{[P_x]_{fr} [P_y]_{ri}}{\omega_{ri} - \omega_0} \right\} \quad (2)$$

where $|i\rangle$, $|r\rangle$ and $|f\rangle$ are initial, intermediate and final states of the molecule, respectively; $[P_y]_{fr} = \langle f | p_y | r \rangle$ and here p_y is the vector component of the electric dipole moment operator; $h\nu_0$ = incident photon energy; $h\nu_{rf}$ and $h\nu_{ri}$ are the transition energies between $r \rightarrow f$ and $r \rightarrow i$ states; the summation is over all the states r of the molecule except i or f .

As it is seen in equation 2 that the numerators of the transition polarizability components, $[\alpha_{xy}]_{fi}$, always contain products of components of transition moments of types $[P_x]_{ri}$, involving the initial state and the state r and $[P_y]_{fr}$ involving the final state and the state r . Since these transition moments always occur as products, if the polarizability tensor component is to be non-zero, in the system there must be at least one state r exist which has a non-zero dipole transition moment to both the initial state and the final state.

In figure 1 Raman scattering and infrared absorption processes shown. Although in both cases molecule goes from $|i\rangle$ state to $|f\rangle$ state, the former is a two photon processes.

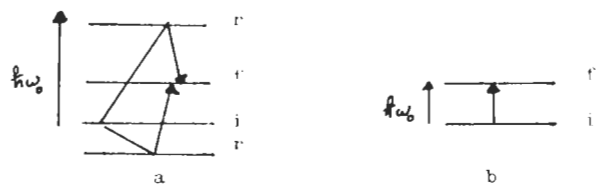


Figure.1. Transition from $|i\rangle$ to $|f\rangle$ state by a) Raman scattering and b) infrared absorption. In normal Raman experiment there is no relation between $h\nu_s$, the energy of the incident photon and $h\nu_0$, the energy of the r states

1.2 Selection rules

1.2.1 Raman spectroscopy

Although we have already seen that existence of at least one level r which has a non-zero dipole transition moment both initial and final states of molecule is necessary condition for the transition polarizability to be non zero, the selection rules however involve only the properties of initial and final states not the properties of the r states.

For a particular transition to be Raman active, at least one of the six tensor components of the type $[\alpha_{xy}]_{fi}$ must be non-zero. It can be shown that $[\alpha_{xy}]_{fi}$ has the same transformation properties as $\langle f|x|i\rangle$. Therefore the general condition for $[\alpha_{xy}]_{fi}$ to be non-zero is that the product $\Psi_f^* xy \Psi_i$ belongs to a representation which contains the totally symmetric species. here Ψ_f and Ψ_i are the time-independent wavefunctions of final and initial states of the molecule, respectively.

For the vibrational Raman spectrum, we have to substitute for Ψ_f and Ψ_i , the vibrational eigenfunctions $\Psi_{v'}$ and $\Psi_{v''}$ of the upper and lower states. Then we can say that a Raman transition between two vibrational level v', v'' is allowed if at least one of the six products of type $\Psi_{v'}^* xy \Psi_{v''}$ is totally sym-

metrical, that is, remains unchanged for all the symmetry operations of the molecule.

For a fundamental vibrational transition, where in the initial state all vibrational quantum numbers are zero and in the final state only the j -th vibrational quantum number has changed to unity, we may write:

$$\langle \Psi_1(Q_j) | xy | \Psi_0(Q_j) \rangle \neq 0 \quad (\text{for Raman activity}) \quad (3)$$

A simple harmonic wavefunction, $\Psi_0(Q_j)$ for the ground state ($v_j=0$), is always totally symmetric; and a simple harmonic wavefunction with $v_j=1$ has the same symmetry species as the normal coordinate Q_j (5). Thus the integral in eq.3 is totally symmetric if the product $Q_j xy$ is totally symmetric. For a non-degenerate fundamental vibration, this condition is satisfied if this vibrational mode has the same symmetry species as one of the six of the six products of type xx, xy, \dots

1.2.2 infrared spectroscopy

The transition moment for IR absorption involves the permanent dipole moment operator, instead of the induced dipole moment operator as in the case of Raman scattering. Therefore the transition probability is proportional to the square of

$$[\vec{p}]_{fi} = \langle f | \vec{p} | i \rangle \quad (4)$$

where \vec{p} is the electric dipole moment operator. It can be shown that the transition moment has the same transformation properties as

$$\langle f|x|i\rangle, \langle f|y|i\rangle \text{ and/or } \langle f|z|i\rangle \quad (5)$$

Thus IR activity of a non-degenerate fundamental vibration Q_j requires, product of the type $Q_j x, Q_j y$ or $Q_j z$ to be totally symmetric. That is the fundamental vibrational modes which are in the the same symmetry species with x, y or z vectors are IR active.

1.3 Mutual exclusion principle

From the Raman and IR selection rules mentioned 1.2.1 and 1.2.2, the following rule, called mutual exclusion principle, can be immediately obtained: For molecules with a center of symmetry, transitions that are allowed in the Raman spectrum are forbidden in the infrared and conversely, transitions that are allowed in the IR spectrum are forbidden in the Raman. On the other words we may also say that in Raman effect only transitions between the states of same symmetry with respect to the center of symmetry (i), can take place ($g \leftrightarrow g$, $u \leftrightarrow u$), however in the infrared, only transitions between the states of opposite symmetry with respect to the center of symmetry are allowed ($g \leftrightarrow u$).

It is clear that all components of electric dipole moment \vec{p} , change sign for a reflection at the center of symmetry, whereas the components of the induced dipole moment (therefore, polarizability), which behave as the product of two components of \vec{p} (e.g., xy), remain unchanged. Thus for a fundamental vibrational transition, only the vibrational modes (g) which are symmetric with respect to the center of symmetry can be Raman active and those are antisymmetric (u) with respect to the center of symmetry can be IR active if they also hold the selection rule requirements.

2. STRUCTURAL ANALYSES OF SOME CLATHRATE COMPOUNDS USING

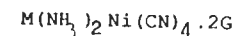
LASER-RAMAN AND INFRARED SPECTROSCOPIES

The structural analysis of the molecular systems using laser Raman and infrared spectra is based on identification of structural units and their symmetry.

Clathrates are molecular compounds that have two components: host lattice and guest molecules. The guest molecules can be trapped

in the holes of the host lattice and in certain conditions, e.g. by evaporation or heating, they may leave the structure. Clathrates are used as molecular traps, as for purification of chemicals and for separation of chemical isomers (6).

The general formula of Hofmann types clathrates (6) is:



where M is a divalent transition metal being in octahedral coordination with two nitrogen atoms of ammonia molecules and four nitrogen atoms of cyanide molecules; Ni(II) is in square planar coordination with four carbon atoms of cyanide molecules; G is the guest molecule. The host lattice consists of two-dimensional polymeric sheets formed from tetracyanonickelate ions $Ni(CN)_4^{2-}$ bridged by coordinating diammine metal(II) cations $M(NH_3)_2^{2+}$. The sheets lie one above the other. Small aromatic molecules like benzene and aniline can be trapped between the sheets and their escape is hindered by the NH_3 molecules which project above and below the sheets (6,7).

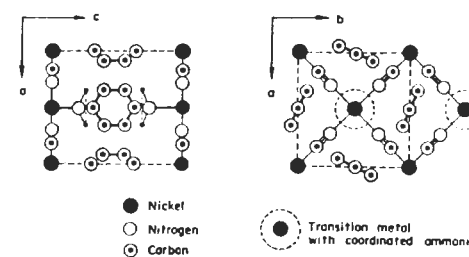


Figure 2 The structure of Hofmann-type clathrates, $M(NH_3)_2 Ni(CN)_4$. The local symmetry around the $Ni(CN)_4$ group is D_{4h} . The z axis is chosen as in the direction of unit cell axis c.

The local symmetry around the Ni atom is D_{4h} (see Fig.1). The character table for the point group D_{4h} is given in Table 1, together with the reducible representations generated from the in-

ternal displacement coordinates of Ni(CN)₄ group: cyanide stretching[$\nu(\text{CN})$], nickel-carbon stretching[$\nu(\text{NiC})$], NiCN angle in-plane bending and out-of plane bending[$\delta(\text{NiCN})$], [$\pi(\text{NiCN})$], respectively.

Any reducible representation (T) can be reduced by some similarity transformations to a completely reduced form (8). If a_j is the number of times the j-th irreducible representation occurs in a reducible representation:

$$a_j = 1/h \sum g_m \chi_j(R_m) \chi(R_m) \quad (6)$$

where h is the order of the point group, g_m is the number of symmetry operations of the m-th class (indicated in the tables by a coefficient before the symbol of the symmetry operation of the the corresponding class), $\chi_j(R_m)$ and $\chi(R_m)$ are the characters of the representation of the symmetry operation R_m in the j-th irreducible and in the reducible representations, respectively (8).

When we apply group theory to Ni(CN)₄ group we find that the vibrations are divided among the symmetry species as follows:

$$\text{Cyanide stretching vibrations, } \nu(\text{CN}) = A_{1g}(\text{R}) + B_{1g}(\text{R}) + E_u(\text{IR})$$

$$\text{Ni-C bond stretching vibrations, } \nu(\text{Ni-C}) = A_{1g}(\text{R}) + B_{1g}(\text{R}) + E_u(\text{IR})$$

$$\text{in-plane angle bending vibration, } \delta(\text{NiCN}) = B_{2g}(\text{R}) + E_u(\text{IR})$$

$$\text{out-of-plane angle bending vibration, } \pi(\text{NiCN}) = A_{2u}(\text{IR}) + B_{2u}(\text{IR}) + E_g(\text{R}).$$

TABLE 1. The character table of D_{4h} point group (8) and reducible representations of Ni(CN)₄ group vibrational modes

D _{4h}	E	2C ₄	C ₂	2C ₂ '	2C ₂ "	2C ₂ "	2C ₂ "	2C ₂ "	2C ₂ "	2C ₂ "	2C ₂ "	2C ₂ "	2C ₂ "	i	
A _{1g}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	xx+yy, zz
A _{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	
A _{2g}	1	1	1	-1	-1	1	-1	-1	1	1	1	1	1	R _z	
A _{2u}	1	1	1	-1	-1	-1	1	1	-1	-1	-1	-1	-1	z	
B _{1g}	1	-1	1	1	-1	1	1	-1	-1	1	1	1	1		xx-yy
B _{1u}	1	-1	1	1	-1	-1	-1	1	1	-1	-1	-1	-1		
B _{2g}	1	-1	1	-1	1	1	-1	1	-1	1	1	1	1		xy
B _{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	-1	-1	-1		
E _g	2	0	-2	0	0	-2	0	0	0	0	0	0	0	2	R _x , R _y (xz, yz)
E _u	2	0	-2	0	0	2	0	0	0	0	0	0	0	-2	x, y
T{ $\nu(\text{CN})$ }	4	0	0	2	0	4	2	0	0	0	0	0	0		
T{ $\nu(\text{NiC})$ }	4	0	0	2	0	4	2	0	0	0	0	0	0		
T{ $\delta(\text{NiCN})$ }	4	0	0	0	2	4	0	2	0	0	0	0	0		
T{ $\pi(\text{NiCN})$ }	4	0	0	-2	0	-4	2	0	0	0	0	0	0		
a{ $\nu(\text{CN})$ [A _{1g}]} = 1/16	(4+2x2+4+2x2)=1														
a{ $\nu(\text{CN})$ [B _{1g}]} = 1/16	(4+2x2+4+2x2)=1														
a{ $\nu(\text{CN})$ [E _u]} = 1/16	(4x2+4x2)=1														
a{ $\nu(\text{NiC})$ [A _{1g}]} = 1/16	(4+2x2+4+2x2)=1														
a{ $\nu(\text{NiC})$ [B _{1g}]} = 1/16	(4+2x2+4+2x2)=1														
a{ $\nu(\text{NiC})$ [E _u]} = 1/16	(4x2+4x2)=1														
a{ $\delta(\text{NiCN})$ [B _{2g}]} = 1,	a{ $\delta(\text{NiCN})$ [E _u]} = 1														
a{ $\pi(\text{NiCN})$ [A _{2u}]} = 1,	a{ $\pi(\text{NiCN})$ [B _{2u}]} = 1, a{ $\pi(\text{NiCN})$ [E _g]} = 1														

Cyanide stretching vibration for free cyanide ion (as diatomic ion) occurs at ca. 2088 cm⁻¹ (9). However these vibrations in Ni(CN)₄²⁻ ion occur at 2128, 2132, 2141 and 2149 cm⁻¹ (an average of say 2140 cm⁻¹) (10). It was found that the upward shift of ca. 50 cm⁻¹ was mainly caused by coupling to the low frequency

M-CN stretching mode (9). In our compounds the $\text{Ni}(\text{CN})_4$ group is further complexed through the nitrogen atoms to the metal. But since the strength of the M-N bond is rather less than that of Ni-C, the shift to expect as a result of mechanical coupling between the M-N and C=N stretching modes must be less than that of Ni-C coupling.

Recently several metal complex hosts have been developed from the two dimensional Hofmann type host lattices, $\text{M}(\text{NH}_3)_2\text{Ni}(\text{CN})_4$, by replacing the ammonia molecules by bidentate ligands (11,12), with the aim of enlarging the range of guest molecules which can be accommodated in the host lattices.

In this study we gave our preliminary laser-Raman and infrared spectroscopic results of $\text{M}(\text{pyz})\text{Ni}(\text{CN})_4$ compounds (13) (where M=Ni or Cd; pyz=pyrazine, $\text{C}_4\text{H}_4\text{N}_2$). Depending on the vibrational spectroscopic study, the structure of these compounds is found to consist of infinite polymeric layers of $[\text{M}-\text{Ni}(\text{CN})_4]_\infty$ analogous to those of Hofmann type clathrates. Bidentate pyrazine molecules form bridges between the metal atoms (M=Ni or Cd) in the adjacent polymeric layers. These host lattices can enclathrate benzene molecules but it is found that aniline can not be trapped in these structures.

3. EXPERIMENTAL METHODS

$\text{M}(\text{pyz})\text{Ni}(\text{CN})_4$ compounds were prepared with a similar method to that used of 4-4'-bipyridyl benzene clathrates (11).

The laser-Raman spectra of the samples were excited using 488.0 nm line of an Ar ion laser and recorded on a Cary 81 spectrometer. The IR spectra were recorded on Nicolet MX-1E FT-IR and Perkin-Elmer 1430 spectrometers.

4. RESULTS AND DISCUSSION

4.1 Vibrational spectra of the polymeric layers

The vibrational wave numbers of $\text{M}(\text{pyz})\text{Ni}(\text{CN})_4$ (M=Ni or Cd) are given in Table 2 together with free $\text{Ni}(\text{CN})_4$ vibrations and those of Hofmann type clathrates for comparison.

If the polymeric sheet consist of a network of square planar $\text{Ni}(\text{CN})_4$ groups bridged by the metal (Ni or Cd) (see Table 1) only four bands: $\nu(\text{CN})$ (E_u), $\nu(\text{NiC})$ (E_u), $\pi(\text{NiCN})$ (A_{2u}) and $\delta(\text{NiCN})$ (E_u) must be observed in the IR spectrum above 400 cm^{-1} . Seven Raman active modes are expected in the same region but generally only two of these $\nu(\text{CN})$ modes (A_{1g} and B_{1g}) are observed in the Raman spectra of these type of complexes since the others are very weak and can not be recognised (9).

TABLE 2 Assignment of the fundamental modes of the tetracyanonickelate group in sodium crystal, $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ and $\text{M}(\text{pyz})\text{Ni}(\text{CN})_4$ compounds* .

Assignment ^a	Na ^a	Cd-NH ₃ ^b	Ni-NH ₃ ^b	Cd-pyz	Ni-pyz
A_{1g} $\nu(\text{CN})$	2149	(2175)	(2177)	(2159) vs	(2193) vs
B_{1g} $\nu(\text{CN})$	2141	(2169)	(2167)	(2145) vs	(2182) vs
E_u $\nu(\text{CN})$	{ 2132 2128	2156	2161	2135 vs	2173 vs
E_u $\nu(\text{NiC})$	543	554	554	545 m	557 m
A_{2u} $\pi(\text{NiCN})$	448	446	460	442 w	460 w
E_u $\delta(\text{NiCN})$	{ 433 421	425	436	422 vs	445 vs

* The values are in cm^{-1} . The bands observed in the Raman spectra are given in parentheses, those observed in the IR spectra are given in without parentheses.
M-NH₃ = $\text{M}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, M-pyz = $\text{M}(\text{pyz})\text{Ni}(\text{CN})_4$ (where M=Ni or Cd). vs=very strong, m=medium, w=weak intense.

^a Taken from ref.10, ^b taken from ref. 7.

The (CN) and (NiCN) vibrational wavenumbers are found to be similar to those of Hofmann type clathrates (7) showing that $[M-Ni(CN)_4]_{\infty}$ layers have been preserved. Since we observed only one $\nu(CN)$ (E_u) band in the IR spectra and the other two $\nu(CN)$ (A_{1g}, B_{1g}) bands in the Raman spectra of the compounds studied we propose a square planar environment around the tetracyanonickelate group.

4.2 Fundamental vibrations of pyrazine molecule

Free pyrazine molecule (see Fig 3) is in D_{2h} point group (14,15). The character table of the D_{2h} point group, together with the reducible representation (Γ_{total}) generated from 30 cartesian coordinates of pyrazine molecule is given in Table 3. As it is given at the bottom of the Table 3, the 24 fundamental vibrations of the molecule are divided among to symmetry species as follows: $5 A_g(R) + B_{1g}(R) + 4 B_{2g}(R) + 2 B_{3g}(R) + 2 A_u$ (in-active) + $4 B_{1u}(IR) + 2 B_{2u}(IR) + 4 B_{3u}(IR)$.

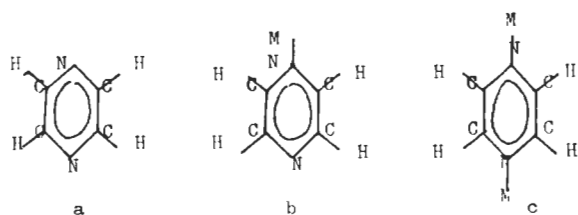


Figure 3 Pyrazine molecule a) free , b) as unidentate ligand and c) as bidentate ligand.

If pyrazine molecule coordinates to a metal as unidentate ligand (see Fig 2 b.) its symmetry drops to C_{2v} but if it coordinates to two identical metal atoms as bidentate ligand its symmetry point group is not altered and be D_{2h} as free molecule. The correlation diagram between C_{2v} and D_{2h} point groups is given in Table 4.

Table 3. The character table of point group D_{2h} (8) and reducible representations of pyrazine molecule

D_{2h}	E	C_2	C_2	C_2	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x yz
A_u	1	1	1	1	-1	-1	-1	-1	in-active
B_{1u}	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x
Ttotal	30	-2	0	0	0	0	10	2	
$a(A_g) = 1/8 (30-2+10+2) = 5$; $a(B_{1g}) = 1/8 (30-2-10-2) = 2$ $a(B_{2g}) = 1/8 (30+2+10-2) = 5$; $a(B_{3g}) = 1/8 (30+2-10+2) = 3$ $a(A_u) = 1/8 (30-2-10-2) = 2$; $a(B_{1u}) = 1/8 (30-2+10+2) = 5$ $a(B_{2u}) = 1/8 (30+2-10+2) = 3$; $a(B_{3u}) = 1/8 (30+2+10-2) = 5$ $T(total) = 5A_g + 2B_{1g} + 5B_{2g} + 3B_{3g} + 2A_u + 5B_{1u} + 3B_{2u} + 5B_{3u}$ $T(vib.) = 5A_g + B_{1g} + 4B_{2g} + 2B_{3g} + 2A_u + 4B_{1u} + 2B_{2u} + 4B_{3u}$									

Table 4 Correlation diagram showing distribution and activity of the normal modes of pyrazine in isolated (or bidentate) and unidentate environments.

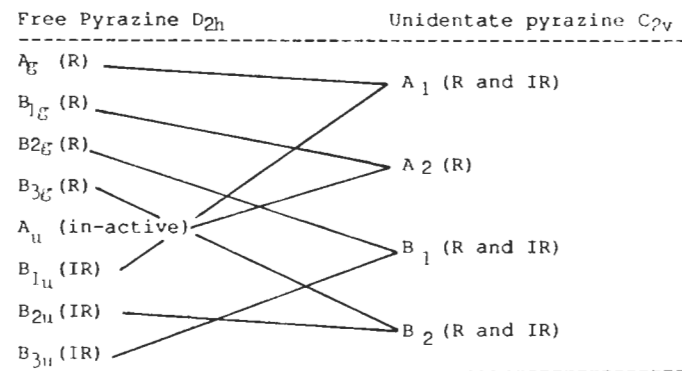


Table 5 Fundamental vibrational wavenumbers of pyrazine in Ni(py₂)Ni(CN)₄ and Cd(py₂)Ni(CN)₄ compounds

Assignment*	pyrazine solution*		Ni(py ₂)Ni(CN) ₄		Cd(py ₂)Ni(CN) ₄	
	IR	R	IR	R	IR	R
16b, B _{2u} δ _{ring}	418	---	438	---	435	---
16a, A _u δ _{ring}	422	---	485	---	451	---
6a, A _g δ _{ring}	---	600	---	---	---	---
6b, B _{2g} δ _{ring}	---	701	---	704	---	702
4, B _{2g} δ _{ring}	---	756	---	---	---	748
11, B _{3u} δ(CH)	785	---	810	---	796	---
10a, B _{1g} δ(CH)	---	919	---	915	---	913
5, B _{2g} δ(CH)	---	983	---	---	---	---
17a, A ₁ δ(CH)	997	---	---	---	1031	---
1, A _g δ _{ring}	---	1011	---	1038	---	1027
12, B _{1u} δ _{ring}	1019	---	1060	---	1047	---
15, B _{3u} δ(CH)	1061	---	1089	---	1078	---
18a, B _{1u} δ(CH)	1130	---	1132	---	1125	---
14, B _{3u} δ _{ring}	1150	---	1164	---	1157	---
9a, A _{1g} δ(CH)	---	1231	---	---	---	1230
3, B _{2g} δ(CH)	---	1343	---	---	---	1370
19b, B _{3u} δ _{ring}	1412	---	1424	---	1419	---
19a, B _{1u} δ _{ring}	1433	---	1494	---	1481	---
8b, B _{2g} δ _{ring}	---	1524	---	1525	---	1522
8a, A _{1g} δ _{ring}	---	1574	---	1607	---	1587
13, B _{1u} δ(CH)	3011	---	3049	---	3043	---
7b, B _{2g} δ(CH)	---	3040	---	---	---	---
2, A _{1g} δ(CH)	---	3054	---	3081	---	3078
20b, B _{3u} δ(CH)	3061	---	3100	---	3095	---

* Taken from ref. 16, values are in cm⁻¹.

The fundamental vibrational wavenumbers of pyrazine in the IR and Raman spectra of the compounds studied are given in Table 5, together with the vibrational wavenumbers of pyrazine in solution (16). We do not observe any coincidences between the IR and Raman bands of the compounds studied, indicating that pyrazine molecules are centrosymmetric. On the other hand vibrational wavenumbers of the pyrazine molecule in the IR and Raman spectra of the compounds are found notably different than those of free molecule. The shifts are metal dependent. Similar shifts are observed in pyridine (9) and bipyridine (11) complexes and explained by coupling of the internal modes of aromatic molecule with low frequency vibrations, particularly M-N stretching frequency (9,11,19). Therefore depending on the IR and Raman spectroscopic results we propose that the pyrazine molecules bound to metal (M=Ni or Cd) atoms of the adjacent layers of (M-Ni(CN)₄)_∞ as bidentate ligands and form bridges between the layers.

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REFERENCES

1. C.V.Raman and K.S.Krishnan, Nature, 121, 501 (1928).
2. G.S.Landsberg and L.I.Mandelstam, Naturwiss., 16, 557 (1928).
3. A.Smekal, Naturwiss., 11,873 (1923).
4. D.A.Long, " Raman Spectroscopy " McGraw Hill, N.Y. (1977).
5. L.I.Schiff, " Quantum Mechanics " McGraw Hill, N.Y. (1955).
6. M.Hagan, " Clathrate, Inclusion Compounds " Reinhold, N.Y. (1969).

7. S.Akyuz, A.B.Dempster and R.L.Morehouse, Spectrochim. Acta A 30, 1989 (1974).
8. D.Steele, " Theory of Vibrational Spectroscopy " W.B.Saunders company, London (1971).
9. S.Akyuz, A.B.Dempster, R.L.Morehouse and S.Suzuki, J. Molecular struct., 17, 105 (1973).
10. R.L.McCullough, L.H.Jones and G.A.Crosby, Spectrochim. Acta A, 16, 929 (1960).
11. A.Sungur, S.Akyuz and J.E.D.Davies, J. Inclusion Phenomena 5, 491 (1987).
12. T. Hasegawa, S.Nishikiori and T.Iwamoto, J. Inclusion Phenomena, 1, 365 (1984).
13. T.Akyuz, S.Akyuz and J.E.D.Davies, unpublished results.
14. B.J.Bormans, D.de With and F.C.Mijhoff, J. Molecular struct. 42, 121 (1977).
15. G.de With, S. Sharkema and D.Feil, Acta Crystallogr. Sect.B, 32, 3178 (1976).
16. J.F.Arenas J.T.Lopez-Navarrete, J.C.Otero and J.I.Markos J. Chem. Soc. Faraday Trans., 81, 405 (1985).
17. M.Goldstein and W.D.Unsworth, Spectrochim. Acta A, 27, 1055 (1971).
18. J.Metz, O. Schneider and H.Hanack, Spectrochim. Acta A, 38 1265 (1982).
19. S.Suzuki and W.J.Orville-Thomas, J. Molecular Struct. 37, 321 (1977).