

AN ANALYSIS OF THE VIBRATIONAL LEVELS OF SOME OCTAHEDRAL STRUCTURES

DUŠANKA Ž. OBADOVIĆ^{a)}, SLOBODAN CARIC^{a)} and DRAGOLJUB Lj. MIRJANIĆ^{b)}

^{a)} *Faculty of Sciences, University of Novi Sad, 21000 Novi Sad, Yugoslavia*

^{b)} *Faculty of Technology, University of Banja Luka, 78000 Banja Luka, Yugoslavia*

Received 18 February 1991

UDC 539.2

Original scientific paper

An analysis of the vibrational levels in the Ni(II) octahedral complexes with 1-naphthylacetic acid hydrazide is carried out and the results are compared with those predicted by a simplified theory of vibrational levels in the isolated octahedra which is based on the assumption that the interatomic potentials are of the Lennard-Jones type. A good agreement of the theoretical predictions and the experiment suggests that the forces acting in the analysed octahedral structures are essentially of the Lennard-Jones type.

1. Introduction

The aim of the work was to study experimentally the vibrational levels of the octahedral complexes containing Ni(II) as a central atom, and to test how the experimental results fit a simplified theory of vibrational levels in the octahedral structures.

It should be mentioned that the molecules of the studied compounds are weakly interconnected, so that the intermolecular interactions which would result in formation of zones could be neglected. This assumption was verified experimentally by obtaining the sufficiently sharp bands suggesting an individual behaviour of the molecules, i. e. the possibility of measuring the levels belonging to the inner molecular vibrations.

Apart from this simplification in the theoretical treatment, use is made of an idealization that the octahedral coordination can be replaced by an equivalent coordination of the simple cubic structure and then the vibrations of the central atom in the field of its surroundings are analysed. Such an idealization is acceptable provided the interatomic potentials in the molecule are of the Lennard-Jones type¹⁾, i. e. they are given by the expression:

$$U_{ij} = -\frac{\alpha}{|R_{ij}|^6} + \frac{\beta}{|R_{ij}|^{12}} \quad (1)$$

where R_{ij} denotes the interatomic distance. The corresponding force constants, representing the second derivate of the potential energy along the coordinate, are given by the following law:

$$C_{ij} = \frac{\partial^2 U_{ij}}{\partial R_{ij}^2} \approx -\frac{\alpha}{|R_{ij}|^8} + \frac{\beta}{|R_{ij}|^{14}}. \quad (2)$$

As can be seen, the force constants decrease by the 8th power of ten, which with respect to the interatomic distance in the octahedron gives the following constants:

$$\frac{C(a)}{C\left(\frac{a}{\sqrt{2}}\right)} \approx \frac{1}{16}; \quad \frac{C(a\sqrt{2})}{C\left(\frac{a}{\sqrt{2}}\right)} \approx \frac{1}{256}. \quad (3)$$

Therefore, $C(a)$ and $C(a\sqrt{2})$ can be neglected in comparison to the quantity $C\left(\frac{a}{\sqrt{2}}\right)$ characterizing the motion of the central atom, and the behaviour of the octahedral coordination may be considered as that of the cubic one. Such an approximation ensures an accuracy at the first decimal place.

As we are primarily interested in the energies of vibrational levels, it is not necessary to introduce the normal coordinates and to diagonalize the molecular Hamiltonian. But the informations following from the symmetry of the molecule will be applied. To determine the energy levels, it suffice to use the classical expression for molecular shifts:

$$u_s^\alpha(t) = A_s^\alpha e^{-i\omega t} \quad (4)$$

where $a = (x, y, z)$, $s = 0, 1, 2, \dots, 6$, denotes the number of atom in the molecule (for the central atom $s = 0$) and ω is the frequency of the vibrational level.

The theoretical results thus obtained are in good agreement to the corresponding experimental findings, which confirms the validity of both the approximation used and the supposition that the potentials in the molecules studied are of the Lennard-Jones type.

2. Theoretical analysis of the vibrational levels

The interatomic distances in an octahedral structure are:

$\frac{a}{\sqrt{2}}$ — between the central atom and the atoms at the apexes;

a — between two neighbouring atoms at the apexes;

$a/\sqrt{2}$ — between two atoms at the non-neighbouring apexes.

As has been already pointed out, such an order of the interatomic distances, assuming the Lennard-Jones potentials, indicate that the atomic interactions at the distances a and $a/\sqrt{2}$ can be neglected, as the corresponding force constants decrease by the 8th power of ten.

On the basis of this assumption it suffice to write the equations of the motion of the central atom, which formally corresponds to the replacement of the octahedral structure by the cubic one.

The classical equations for the molecular displacement taking into account the symmetry of the cubic lattice are then:

$$m_0 \ddot{u}_0^x = \frac{c}{2} (u_1^x + u_2^x - 2u_0^x); \quad m \ddot{u}_1^x = \frac{c}{2} (u_0^x - u_1^x); \quad m \ddot{u}_2^x = \frac{c}{2} (u_0^x - u_2^x) \quad (5)$$

$$m_0 \ddot{u}_0^y = \frac{c}{2} (u_3^y + u_4^y - 2u_0^y); \quad m \ddot{u}_3^y = \frac{c}{2} (u_0^y - u_3^y); \quad m \ddot{u}_4^y = \frac{c}{2} (u_0^y - u_4^y) \quad (6)$$

$$m_0 \ddot{u}_0^z = \frac{c}{2} (u_5^z + u_6^z - 2u_0^z); \quad m \ddot{u}_5^z = \frac{c}{2} (u_0^z - u_5^z); \quad m \ddot{u}_6^z = \frac{c}{2} (u_0^z - u_6^z) \quad (7)$$

where u_0^α is the projection of the displacement of the central atom onto one of the axes, while the other quantities in the above equations are the displacement of the atoms surrounding the central atom.

The solution of the above equations will be sought in the form:

$$u_s^\alpha(T) = A_s^\alpha e^{-i\omega t}; \quad \ddot{u}_s^\alpha(t) = -\omega^2 A_s^\alpha e^{-i\omega t} = -u_s^\alpha(t) \omega^2 \quad (8)$$

after which they are reduced to a system of algebraic equations:

$$P(\omega) u_0^x + u_1^x + u_2^x = 0; \quad u_0^x + Q(\omega) u_1^x = 0; \quad u_0^x + Q(\omega) u_2^x = 0 \quad (9)$$

$$P(\omega) u_0^y + u_3^y + u_4^y = 0; \quad u_0^y + Q(\omega) u_3^y = 0; \quad u_0^y + Q(\omega) u_4^y = 0 \quad (10)$$

$$P(\omega) u_0^z + u_5^z + u_6^z = 0; \quad u_0^z + Q(\omega) u_5^z = 0; \quad u_0^z + Q(\omega) u_6^z = 0 \quad (11)$$

where:

$$P(\omega) = 2 \left(\frac{m_0 \omega^2}{c} - 1 \right); \quad Q(\omega) = \frac{2m\omega^2}{c} - 1 \quad (12)$$

(m_0 — is the mass of the central atom and m — of its surroundings).

After equating the determinant of the system of Eqs. (9—11) to zero, the energies of vibrational levels are:

$$E_1 = \hbar\omega_1 = \hbar \sqrt{\frac{c}{2m}} \quad (13)$$

and

$$E_2 = \hbar\omega_2 = \hbar \sqrt{\frac{c}{2m_r}} \quad (14)$$

where m_r is the reduced mass:

$$m_r = \frac{m_0}{1 + \frac{m_0}{2m}}. \quad (15)$$

It is obvious that the energy E_1 is greater than E_2 , because $m_r < 2m$.

In the above equations c denotes the force constant at the distance $\frac{a}{\sqrt{2}}$, i. e.

$$c = c \left(\frac{a}{\sqrt{2}} \right).$$

We shall give here a brief analysis of the obtained results. The molecule under investigation have the O_h group symmetry and consequently they possess 48 symmetry elements²⁾ which are arranged in 10 classes. This means the O_h group possesses 10 irreducible representations. On the other hand, the 7 atoms of the octahedron possess 21 degrees of freedom, 6 of them (the translation and rotation of the molecule as a whole) are omitted in the analysis of vibration levels. Taking into account that there are 15 vibrational degrees of freedom and 10 irreducible representations of the O_h group, 5 energy levels corresponding to the vibrations $1A_{1g}$, $1E_g$, $2F_{1u}$, $1F_{2g}$ and $1F_{2u}$ should be observed. As, for the reasons explained above, the octahedron has been replaced by an equivalent simple cubic structure, on the basis of a similar reasoning only 3 energy levels are obtained, corresponding to the vibrations $2F_{1u}$, $1A_{1g}$ and $1E_g$, one of which has degenerated to zero. The inclusion of the Hamiltonian terms proportional to the Hooke constants $c(a)$ and $c(a/\sqrt{2})$ would lead to the splitting of the observed levels, so that the number of levels would actually be 5. The corrections of this kind have not been car-

ried out. Only an increase of the Hooke constant $c = c(a/\sqrt{2})$ was made in such a way that an approximation was made on the basis of the idea on the Lennard-Jones forces:

$$c\left(\frac{a}{\sqrt{2}}\right) \rightarrow c\left(\frac{a}{\sqrt{2}}\right) + c(a) + c(a\sqrt{2}) = c\left(\frac{a}{\sqrt{2}}\right) \sqrt{1 + \frac{1}{16} + \frac{1}{256}} =$$

$$= 1.0345 c\left(\frac{a}{\sqrt{2}}\right) \equiv c.$$

In testing the model, in expressions (13) and (14) a value of $1.0345 c$ was used instead of $c\left(\frac{a}{\sqrt{2}}\right)$ found in Refs. 3—7.

3. Testing of the model

In order to test the possibility of the practical application of the proposed model, we performed the calculation of IR active vibrational modes of the systems, already studied (Table 1). For the case of $[\text{Co}(\text{NH}_3)_6]^{3+}$ octahedral complex,

TABLE 1.

	$[\text{Co}(\text{NH}_3)_6]^{3+}$				$[\text{Co}(\text{CN}_6)]^{3-}$			$[\text{Fe}(\text{CN}_6)]^{4-}$		$[\text{Fe}(\text{CN}_6)]^{3-}$	
	calc. ³⁾	calc. ⁴⁾	obs. ⁵⁾	our	calc. ⁶⁾	calc. ⁷⁾	our	calc. ⁸⁾	our	calc. ⁷⁾	our
E_{1u} stretching	542	464	464	438	564	565	569	585	584	511	509
$c\left(10^{-8} \frac{\text{N}}{\text{\AA}}\right)$	GVF	UBF			GVF	UBF		UBF		UBF	
	2.00*	1.07			2.063	2.308*		2.428*		1.728	

* The constants was used in our model for vibrational modes calculation
Infrared active vibrational mode of octahedral complexes (10^2 m^{-1}).

the calculations of relevant vibrational modes were performed on the basis of generalized valence force field (GVF) and Urey-Bradley force field (UBF). For the sake of comparison, we have presented the values of the vibrational modes together with our values, which were calculated on the basis of Block force constants³⁾. One can see that our model satisfactory fits into the experimental results of other authors.

4. Experimental results

The IR spectra (KBr pellet) of the Ni(II) complexes and the ligand itself were recorded in the region $200\text{--}4000 \text{ cm}^{-1}$ using a Perkin-Elmer Infracord

spectrophotometer, model 457. The synthesis, spectral and magnetic measurements of the complex described in Ref. 9, suggested an octahedral coordination of the Ni (II). Within this work we analyse the band in the region of lower wavenumbers (below 600 cm^{-1}), which corresponds to the valence vibrations of the Ni (II) and the surrounding atoms.

Taking into account the atoms of the first coordination sphere around Ni (II), the complexes under study can be divided into three groups, containing NNNNOO, NNNOOO and NNNOOO. As 1-naphtylacetic acid hydrazide (L) behaves as a bidentate ligand, it can be expected that in the case of bis-ligand complexes, four sites of the first coordination sphere are occupied by the oxygen atoms of the CO and nitrogen atoms of the NH_2 group, respectively. The remaining two sites in the case of the $\text{NiL}_2(\text{NCS})_2$ complex are occupied by the NCS groups, so that the surroundings around the Ni (II) is of the type NNNNOO¹⁰⁻¹²). The complexes $\text{NiL}_2(\text{OAc})_2$ and $\text{NiL}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, the acetate and sulphate groups are coordinated through the oxygen atom, forming a surroundings of the type NNNOOO¹²⁻¹⁴). In the tris (ligand) complexes, $\text{NiL}_3 \cdot X \cdot m\text{H}_2\text{O}$ ($X = \text{Cl}, \text{Br}, \text{I}, 1/2\text{SO}_4$; $m = 2$ or 4) all 6 sites of the first coordination sphere are occupied by the N and O of the bidentate ligand (the surroundings of the type NNNNOO), whereas the halogens, sulphate group, as well as the water molecules are outside the first coordination sphere.

The position of valence vibration bands of the Ni (II) and surrounding atoms were determined according to Eqs. (13) and (14). The values of force constants were taken from the literature for similar molecules¹⁵⁻¹⁷). On the basis of these values, those IR bands were identified that can be ascribed to the vibrations of this type.

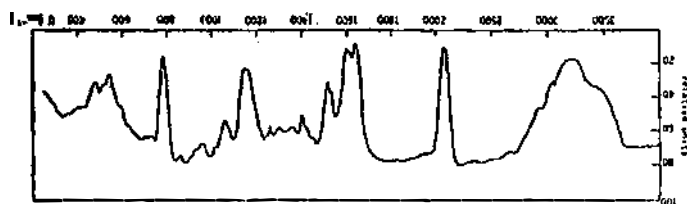


Fig. 1. IR spectrum of $\text{NiL}_2(\text{NCS})_2$

In Fig. 1 is presented a part of the spectrum of the $\text{NiL}_2(\text{NCS})_2$ complex. The bands at 545 and 475 cm^{-1} correspond to the valence vibrations of the Ni-N and Ni-O, respectively; the N and O belonging to the bidentate ligand. On the other hand, the band at 505 cm^{-1} may be ascribed to the Ni-N valence vibration, the N atom being the one of the NCS group.

The obtained values of frequencies of valence vibrations served as the basis for calculation of the force constants presented in Table 2.

5. Conclusion

The values for c , given in the Table 2 are determined using the formula (13) and (14), where the frequencies were taken from our experiment.

A comparison of the above experimental results and the findings of other authors for similar structures¹⁵⁻¹⁷⁾ showed an agreement within the limits of variation of the relevant parameters for the structures studied.

TABLE 2.

Complex	ν_{exp} (cm^{-1})	Ni-O c (10^2 N/m^2)	ν_{exp} (cm^{-1})	Ni-N c (10^2 N/m^2)
$\text{NiL}_2(\text{NCS})_2$	475	2.06	545 505(NCS)	2.45 16.38
$\text{NiL}_2(\text{OAc})_2$	485	2.41	550	2.41
$\text{NiL}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$	490	2.18	550	2.41
$\text{NiL}_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	485	2.14	545	2.45
$\text{NiL}_3\text{Br}_2 \cdot 2\text{H}_2\text{O}$	490	2.18	545	2.45
$\text{NiL}_3\text{I}_2 \cdot 2\text{H}_2\text{O}$	485	2.14	545	2.45
$\text{NiL}_3\text{SO}_4 \cdot 4\text{H}_2\text{O}$	490	2.18	550	2.41

Frequencies of valence vibrations, force constants and the vibrational energies in octahedral Ni (II) complexes.

A simplified theory of vibrational levels in the octahedral structures can be formulated assuming the octahedral coordination is equivalent to that of a simple cubic one, and thus, the interatomic potentials are of Lennard-Jones type.

A good agreement of the simplified theory to the experimental results indicates that the forces playing a predominant role in the analysed octahedral structures are, most probably, those of the Lennard-Jones type.

References

- 1) J. E. Lennard-Jones, A. E. Ingram, *Proc. Roy. Soc. (London)* **A107** (1925) 636;
- 2) L. O. Landau and E. M. Lifshitch, *Quantum Mechanics*, Nauka, Moscow (1974) (in Russian) pp. 423, 427, 460;
- 3) H. Block, *Trans. Faraday Soc.*, **55** (1959) 867;
- 4) T. Shimanouchi and I. Nakagawa, *Spectrochim. Acta* **18** (1962) 89;
- 5) T. E. Haas and R. J. Hall, *Spectrochim. Acta* **22** (1966) 988;
- 6) L. H. Jones, *J. Chem. Phys.* **41** (1964) 856;
- 7) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta* **18** (1962) 101;
- 8) D. Bloor, *J. Chem. Phys.* **41** (1964) 2573;
- 9) S. Yu. Chundak, V. M. Leovac, D. Ž. Obadović and D. M. Petrović, *Transition Met. Chem.* **11** (1986) 312;
- 10) Yu. Ya. Kharitonov, R. I. Machkoshvili, N. B. Generalova, R. N. Shchelikhov, *Zh. neorg. khim.* **20** (1975) 965;
- 11) Yu. Ya. Kharitonov, R. I. Machkoshvili, N. B. Generalova, *Zh. neorg. khim.* **19** (1974) 1564;

- 12) Yu. Ya. Kharitonov, R. I. Machkhoshvili, D. R. Metreveli, N. I. Pirtskhalava, *Koord. khim.* **3** (1977) 1060;
- 13) R. I. Machkhoshvili, D. P. Metreveli, G. Sh. Mitashvili, R. N. Schelikov, *Zh. neorg. khim.* **29** (1984) 2019;
- 14) P. N. Biswas, M. K. Dasgupta, S. Mitra and N. R. Chaudhuri, *J. Coord. Chem.* **11** (1982) 225;
- 15) A. F. Zanoli and G. Peyornel, *Spectrochim. Acta* **40A** (1984) 597;
- 16) K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compound*, Interscience, New York (1970);
- 17) G. Herzberg, *Spectra of Diatomic Molecules*, D. Van Nostrend Company, New York (1950).

ANALIZA VIBRACIONIH NIVOVA NEKIH OKTAEDARSKIH STRUKTURA

DUŠANKA Ž. OBADOVIĆ^{a)}, SLOBODAN CARIC^{a)} i DRAGOLJUB LJ. MIRJANIĆ^{b)}

^{a)} *Prirodno-matematički fakultet, 21000 Novi Sad*

^{b)} *Tehnološki fakultet, 78000 Banja Luka*

UDK 539.2

Originalni znanstveni rad

Analizirani su vibracioni nivoi oktaedarskih kompleksa Ni(II) pomoću predložene pojednostavljene teorije vibracionih nivoa u izolovanim oktaedrima uz pretpostavku da je međuatomski potencijal Lennard-Jonesovog tipa. Dobro slaganje predložene teorije i eksperimenta sugerira da su sile, koje egzistiraju u analiziranim oktaedarskim strukturama, uglavnom Lennard-Jonesovog tipa.