# THE VIBRATIONAL SPECIES OF MOLECULES IN DISORDERED CRYSTALS : $M(NH_3)_2$ GROUPS AT $C_{4h}$ SYMMETRY SITES

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In a number of $M(NH_3)_2[M'(CN)_4]$ and in the related clathrate compounds, the $M(NH_3)_2^{2+}$ complex ions occupy sites of $C_{4h}$ symmetry. A disorder is obviously present, as the site group of symmetry is not a subgroup of the molecular point group ($D_{3d}$ for the anti-periplanar conformation and $D_{3h}$ for the *syn*-periplanar conformation). A problem exists in such cases, because the results of the unit cell-group analysis cannot be obtained in the standard way. The problem may be overcome, assuming that the molecular symmetry group of the complex is $D_{\infty h}$ – as a consequence of free rotation of the $NH_3$ species.

**Key words :** clathrates, crystal vibrations, dynamic disorder, symmetry, correlations

## INTRODUCTION

Several types of disorder are known to exist [1]. However, two *basic types* might be present in a crystal: a static disorder and a dynamic one [2]. If the disorder is static, then it is most likely that crystal entities are statistically distributed in such a way that the overall high-symmetry structure is preserved. For example, an ordered sublattice of $H_2O$ molecules at $C_{2v}$ sites in a crystallohydrate becomes disordered upon deuteration[*] but the $C_{2v}$ site symmetry as well as the space group symmetry are preserved statistically. On the other hand, free rotation and/or quantum tunnelling (e.g. flipping motion and similar) processes of the structural units are at the origin of the dynamic disorder.

On some occasions, due to the disorder present, the site group symmetry of a crystal entity is not a subgroup of its molecular point group symmetry. It might be of interest to calculate the number and activity of the normal vibrations of these entities in the crystal, in the $k = 0$ approximation. The problem is not a trivial one, since the unit cell group analysis cannot be performed in an ordinary way: the Bhaga-vantam-Venkatarayudu method [3] fails, usually giving non-integer values for the number of particular vibrational species and the correlation method [4] cannot be used at all, since no subgroup-supergroup relationship can be established at all.

In the case of static disorder (i.e. when the structural units have space orientations which are time independent) the molecular point group and the site group may be correlated through their common subgroup ($C_1$ – at least). However, the correlation cannot be easily extended to the point group isomorphic with the factor group of the space group because the average number of the "identical oscillators" is twice (or several times) smaller than the one in an ordered structure. It should also be mentioned that, due to disorder, the translational symmetry of the lattice is destroyed, which means that the selection rules under the $k = 0$ approximation are not operative any more.

If the disorder is dynamic, the correlation between the molecular point group and the site group may be found through a common supergroup (typically an infinite group – $D_{\infty h}$ or $C_{\infty v}$). Due to the free rotation or fast tunnelling motions, the disordered structural units, namely, may be considered as having this high symmetry. The correlation is easily continued to the point group isomorphic with the factor group of the space group. Alternatively, the number and activity of the vibrational modes may be calculated under the $D_{\infty h}$ ($C_{\infty v}$) *molecular* symmetry, allowing then the application of the correlation method in its standard form. The advantages of this latter approach will now be demonstrated.

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[*] The disorder is, in this particular case, both occupational (only part of the $H_2O$ molecules are substituted with HDO) and orientational (the HDO molecules which have only $C_s$ symmetry may take either of the two possible orientations with respect to the $C_2$ axis).

## EXAMPLE: $M(NH_3)_2$ COMPLEX WITH $C_{4h}$ SITE SYMMETRY

The crystal structures of a number of $M(NH_3)_2[M'(CN)_4]$ and $M(NH_3)_2[M'(CN)_4]\cdot 2C_6H_6$ (M = Ni, Co, Zn, Cd ... ; M' = Ni, Pd, Pt) compounds are known [5, 6]. Since the space group is $P4/m$ (i.e. it is symmorphic) and $Z = 1$, the $M(NH_3)_2$ and $[M'(CN)_4]$ complexes both have $4/m$ $(C_{4h})$ symmetry. The point group symmetry of the $M(NH_3)_2$ complex may be $D_{3d}$ (in the *anti*-periplanar conformation) or $D_{3h}$ (in the *syn*-periplanar conformation). Neither of these point groups is a supergroup for the $C_{4h}$ site group. If a free rotation of the $NH_3$ groups around the M–N axis is assumed[*], the molecular point group of the diamminometal(II) complex becomes $D_{\infty h}$. The vibrations of the $M(NH_3)_2$ complex and their symmetry properties have to be evaluated under this infinite point group. Since the molecule is not linear, the easiest way to classify the vibrational modes is by correlation. Generally, the method of ascent of symmetry [7] is the most elegant, but standard correlation tables (Fig. 1) may be used without difficulties [8].

The vibrational modes of the $M(NH_3)_2$ complex may be viewed as a set consisting of internal $NH_3$ vibrations, $NH_3$ librations, $NH_3$ hindered translations and hindered translations of the M atom. It should be noted that due to the free rotation around z-axes, two vibrational modes (of $\Sigma_g^-$ and $\Sigma_u^-$ symmetry) connected with $NH_3$ twistings are "lost". Further, the description of two of the $\Pi_g$ modes as $\rho_{as}(NH_3)$ and $\delta_{as}(N{-}M{-}N)^{[**]}$ (cf. Fig. 2b) is mainly a matter of choice. It may be shown, namely, that another set of internal coordinates would also result in two $\Pi_g$ vibrations, which now may be better described as rocking mode of the $M(NH_3)_2$ complex as a whole and $\rho(N{-}M{-}N)$ motion – with respect to stationary positions of the hydrogens. It is the feeling of the authors that the first choice (the one schematically presented in Fig. 2) is in this case more realistic, since the M–N bonds are much weaker compared to the N–H bonds[***].

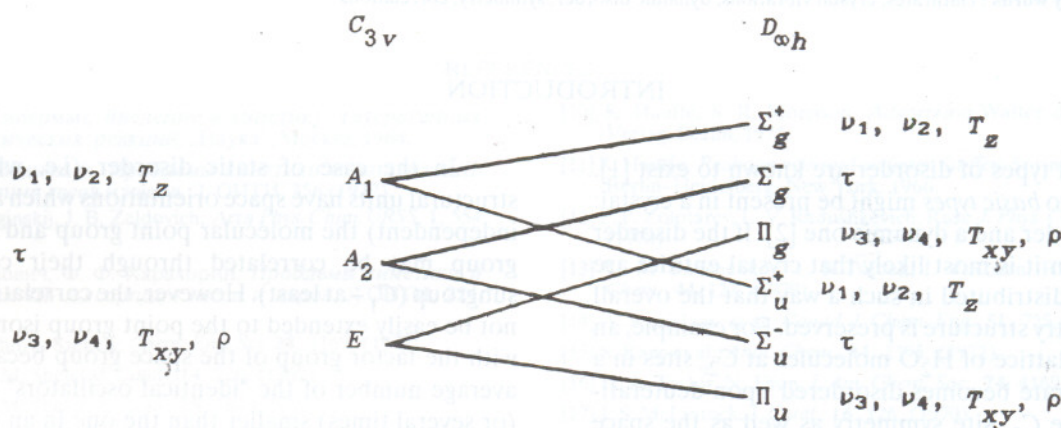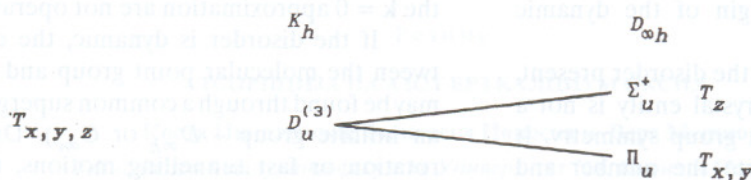$$C_{3v} \qquad\qquad\qquad\qquad D_{\infty h}$$

**Fig. 1a**

**Fig. 1b**

Fig. 1. Symmetry classification of the vibrational modes of the $M(NH_3)_2$ complex: a) vibrations originating from $NH_3$ motions; b) vibrations of the M atoms ($\nu_1, \nu_2, \nu_3$ and $\nu_4$ refer to the internal vibrations of $NH_3$ molecules; $\rho$ and $\tau$ – are $NH_3$ librations and $T$– are hindered translations of either $NH_3$ or M. $\tau$-motions are given only for consistency – otherwise they are "lost" due to the free rotation explicitly assumed. The symmetry of the M-atom, $K_h$, and its irreducible representations may be generated from the direct product of the group of three-dimensional rotations R(3) and the $C_i$ group i.e. $K_h = R(3) \otimes C_i$.

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[*]    This assumption·may be justified by the fact that the $NH_3$ protons are involved only in weak Van der Waals interactions [6] and therefore there are almost no barriers to the internal rotation.

[**]    Actually, it should be better designated as $\delta_{as}(H_3N{-}M{-}NH_3)$.

[***]   On the other hand, the second choice might be preferable for ethane ($CH_3{-}CH_3$) or a similar covalently bonded molecule.
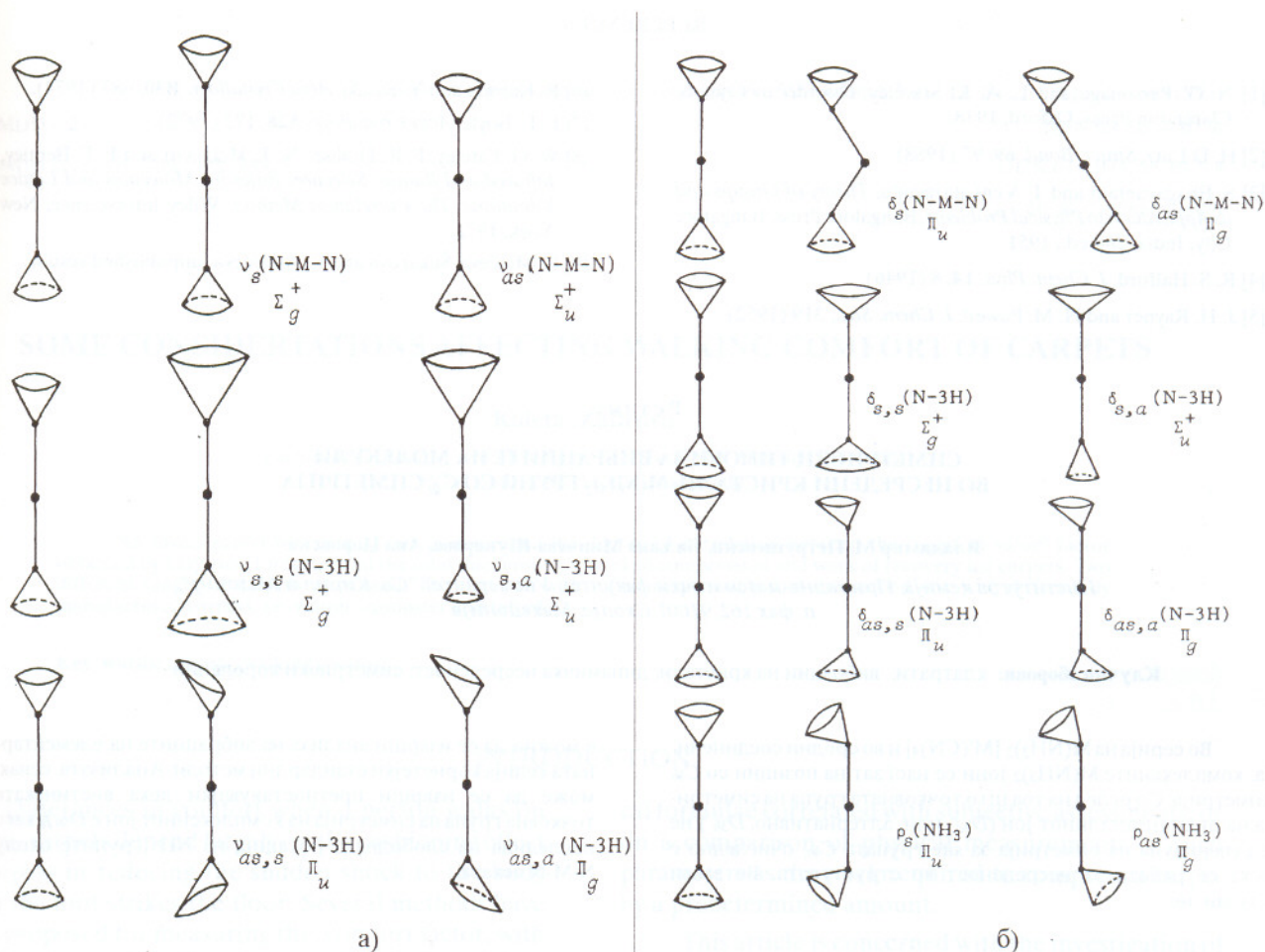
**Fig. 2.** Schematic representation of the vibrational modes of $M(NH_3)_2$ under $D_{\infty h}$ symmetry: a) stretching and b) bending vibrations. The first subscripts – *s* and *as*, denote *symmetric* and *anti-symmetric* vibrations, with respect to the $\sigma_h$ plane; the second subscripts – *s* and *a* are used to denote *synphase* and *antiphase* vibrations of the two $NH_3$ groups. (The cones represent the rotating $NH_3$ molecules. The leftmost part of the figures represents the equilibrium geometry of the complex. Only one component of the degenerate pairs of $\Pi_g$ and $\Pi_u$ symmetry is shown. The $T_{x,y}$ translations of the $NH_3$ molecules are designated as $\delta_s$(N–M–N) and $\delta_{as}$(N–M–N) and the two $T_z$ translations as $\nu_s$(N–M–N) and $\nu_{as}$(N–M–N). Neither hindered translations of the M atom, nor the "lost" $\tau(NH_3)$ librations are shown.)
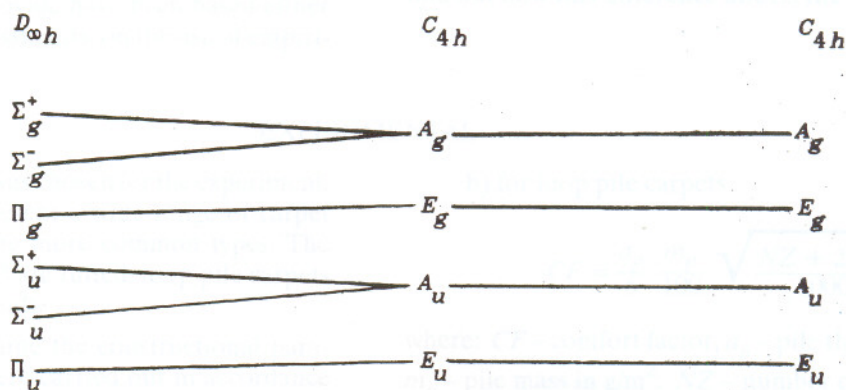


**Fig. 3.** Correlation between the irreducible representations of the $M(NH_3)_2$ molecular point group ($D_{\infty h}$), its site group ($C_{4h}$) and the point group isomorphic with the factor group of the space group of the crystal ($C_{4h}$); only relevant data are given.

Having calculated the number and the symmetry of the $M(NH_3)_2$ vibrational modes, the correlation method is easily applied (cf. Fig. 3).

It should be mentioned, at the end, that the room temperature IR spectra of Hofmann-type clathrates seem to be in good agreement with these group theory considerations [9].

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Резиме

## СИМЕТРИСКИ ТИПОВИ ЗА ВИБРАЦИИТЕ НА МОЛЕКУЛИ ВО НЕСРЕДЕНИ КРИСТАЛИ: $M(NH_3)_2$ ГРУПИ СО $C_{4h}$ СИМЕТРИЈА

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**Клучни зборови:** клатрати; вибрации на кристали; динамичка несреденост; симетриски корелации

Во серија на $M(NH_3)_2$ [M'(CN)_4] и во сродни соединенија, комплексните $M(NH_3)_2$ јони се наоѓаат на позиции со $C_{4h}$ симетрија. Со оглед на тоа што точковната група на симетрија на диаминметалниот јон ($D_{3d}$ или, алтернативно, $D_{3h}$ ) не е супергрупа на симетрија за site-групата $C_{4h}$, очигледно е дека се работи за несреденост во структурата. Во вакви случаи не е можно да се изврши анализа на вибрациите на елементарната ќелија користејќи стандардни методи. Анализата, сепак, може да се изврши претпоставувајќи дека вистинската точковна група на симетрија на комплексниот јон е $D_{\infty h}$ како последица на слободната ротација на $NH_3$ групите околу N-M-N оската.