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Author's Review

## Mode Coupling in Molecular Complexes

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Different dynamical properties of the hydrogen bond and charge transfer complexes are described from the same point of view. An introduction of a coupling parameter responsible for the A—Z and A...B mode interaction in the system A—Z...B (Z is the hydrogen or halogen atom) permits to interpret quantitatively some empirical findings and regularities. They are the A—Z bond length increasing on complexing, the A—Z stretching band shift towards lower frequencies and its linear dependence on the A—Z bond lengthening, the isotopic effects for the A...B and A—H bond lengths and for the A—H stretching frequency, the A—Z vibrational band broadening on complexing in the liquid phase and a dependence between the band halfwidth and the frequency shift. Some relations containing no fitting parameters are established in a good agreement with experiment.

### INTRODUCTION

Many properties of molecular complexes are due to coupling of the inherent modes of the molecules with the »external« ones appearing in the complex formation, e.g. the intermolecular stretching vibrations. Such a coupling has been considered repeatedly (see, e.g. ref. 1, 2). A most clear general formulation of this problem was given in 1957 by Bratos and Hadži<sup>3</sup>. Reviews concerning the later studies were published by Hadži and Bratos<sup>4</sup>, Hoffacker, Marechal and Ratner<sup>5</sup>. It was shown in later papers<sup>6,7</sup> that consistent treating of the mode coupling enables studying from the same point of view certain important structural and dynamical properties of the hydrogen band (HB) complexes.

It has been found experimentally<sup>8-11</sup> that the HB complexes have many features in common with charge transfer (CT) complexes of the  $\sigma$ - $n$  type. The similarity refers to complexes which consist of bases, containing O, N, S or Se atoms, and of Lewis acids involving halogen atoms (e.g. complexes such as 1,4-Dioxide...Br<sub>2</sub>, Quinoline...Jodoform). A three-atom fragment A—Z...B (or A...Z...A) is a common feature of these two kinds of complexes. This fragment seems to be responsible for the most important properties. In the HB case Z is the hydrogen atom and for CT complexes Z is usually a halogen atom. In both cases the complexing is accompanied by A—Z bond lengthening, a low-frequency shift, a broadening and intensification of the  $\nu$ (AZ) vibrational band, etc. The above complexes possess some specific properties as well. E. g.

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the isotopic effects are exhibited by the HB complexes only, where as an appearance of the charge transfer band in the electronic spectra is characteristic of the CT complexes. Nevertheless the dynamic properties of these two kinds of molecular complexes can be treated in terms of the same model.

#### MODEL WITH TWO DEGREES OF FREEDOM

Proceed from the assumption that the fragment A—Z...B plays a dominant role in the dynamics of the complexes considered. The three atoms A, Z, B are assumed to be on a straight line and only two modes — two stretching vibrations of the fragment are taken into account.

Consider the potential energy change for approachment of A—Z and B. If the attraction forces are very weak and the A—Z bond is sufficiently strong the energy minimum will be reached with an unchanging A—Z separation equal to the equilibrium bond length  $r_0$  in the isolated molecule. Such an intermolecular bonding is taken here as very weak (weak Van der Waals complex). In the systems where the interaction between AZ and B becomes sufficiently strong this energy minimum still exists but it will not be absolute since on further rapprochement of AZ and B the A—Z bond stretches the potential energy becoming additionally lower. The absolute energy minimum is reached at the new A—Z bond length  $r_0'$ .

Designate by  $R$  a distance between B and the A—Z molecule center of mass:  $R = r m_A / (m_A + m_Z) + r_{ZB}$  ( $r$  and  $r_{ZB}$  are A—Z and Z...B separations,  $m_A$  and  $m_Z$  are the A and Z atom masses, respectively). Let  $R_0$  and  $R_{00}$  ( $R_0 < R_{00}$ ) be the  $R$  values at the points of the absolute and the relative potential energy minima, respectively. To describe two stretching vibrations of the system introduce the coordinates  $x = r - r_0$  and  $X = R - R_{00}$ . The point  $X = 0$  corresponds to the absolute energy minimum for very weak complexes and to a relative energy minimum for more strong bonding.

The potential energy  $U(x, X)$  of a very weak complex in the harmonic approximation is  $(1/2) k_1 x^2 + (1/2) k_2 X^2$ , where  $k_1$  and  $k_2$  are respective force constants. This expression does not account for the  $x$  and  $X$  mode coupling. A simple way to allow for the mode interaction is to introduce to  $U(x, X)$  the term  $k_{12} xX$ , as well as the A—Z bond cubic anharmonicity  $k_1' x^3$ . Then for more strong complexes

$$U(x, X) = (1/2) k_1 x^2 + (1/2) k_2 X^2 + k_{12} xX + k_1' x^3 \quad (k_1' < 0) \quad (1)$$

Due to the coupling term  $k_{12} xX$  the absolute potential minimum position is shifted. The values correspond to it now

$$x_0 = r_0 - r_0', \quad X_0 = R_0 - R_{00} \quad (2)$$

It is readily seen from (1) that for every fixed  $X$  the potential energy minimum is located at points

$$x = -(k_{12}/k_1) X \quad (3)$$

This relation obviously holds for the absolute potential energy minimum as well, i. e.

$$x_0 = -(k_{12}/k_1) X_0 \quad (4)$$

Starting from potential (1) and using adiabatic separation of the variables  $x$  and  $X$  it is possible to solve the Schrödinger equation, finding then the A—Z vibrational frequency and some useful relations which can be directly compared with experiment. It appears that  $X_0$  is the key parameter specifying the mode coupling. Certain physical quantities related to the A—Z...B complex can be expressed in terms of  $X_0$ . The latter is defined as

$$X_0 = -(h/2k_2) (d\nu/dX)_0 = 3h\nu_1 k_{12} k_1' / 2k_1^2 k_2, \nu_1 = (2\pi)^{-1} (k_1/\mu)^{1/2} \quad (5)$$

On the other hand,  $X_0$  is defined also by (2). In (5)  $\mu$  is the A—Z molecule reduced mass,  $h\nu = \varepsilon_1 - \varepsilon_0$ ,  $\varepsilon_1$  and  $\varepsilon_0$  are the energies of the A—Z first excited and ground vibrational states depending on  $X$ . For asymmetrical complexes  $X_0 < 0$ .

An important quantity — the A—Z ground frequency — is

$$\nu = \nu_0 - \Delta\nu_0 - 2h^{-1}k_2 X_0^2 \quad (6)$$

where  $\nu_0$  is the free A—Z vibrational frequency,  $\Delta\nu_0$  is a relatively small frequency shift which is due to  $k_1$  and  $k_1'$  changes. The  $2h^{-1}k_2 X_0^2$  term is most important. Since  $X_0$  depends on  $\mu$  (5), the  $\nu$  (AZ) frequency appears to depend on the Z mass in a nontrivial way.

The potential energy of the charged complexes with very strong »symmetric« bonds of the type (A...Z...A) $^\pm$  (e.g.  $H_5O_2^+$ ,  $F_2H^-$ ,  $(Cl_2I)^-$ , etc.) has an inversion point, and contains only even degrees of  $x$ . For this reason the above equations become to a certain extent modified<sup>6</sup>.

#### STRICT RELATIONS FOR $r_0$ AND $R_0$ BOND LENGTHS AND $\nu$ (AZ) FREQUENCY

Equations (2) and (4—6) yield some strict relations which contain no fitting parameter and are supported by experiment. These relations were originally obtained for HB complexes<sup>6</sup> and can now be partially extended to the CT complexes. Moreover some less strict semiempirical relations for asymmetric HB complexes were found and discussed in<sup>6</sup> (see also<sup>7</sup>). These relations show that the dependences between  $r_0 - r_0$  and  $R_0$  and between  $R_0$  and  $\Delta\nu$  will be quadratic in accordance with experiment.

We reproduce here strict relations for the A—Z bond length increasing on complexing, which is characteristic both for HB and CT complexes, as well as of the isotopic changes in the  $\nu$  (AH) frequency and in the bond length specific for hydrogen bonds only.

Since the anharmonicity coefficient for the A—Z group usually is negative ( $k_1' < 0$ ) it immediately follows from (4) and (5) that  $x_0 \equiv r_0' - r_0 > 0$ , i. e. the A—Z bond length increases with the complex formation. This effect is known for asymmetric hydrogen bonds, as well as for the  $\sigma - n$  CT complexes. The lengthening is of a  $10^{-2}$  nm order of magnitude in both cases<sup>10,11</sup>.

Using equations (4) and (5)  $X_0$  can be eliminated from (6). A simple relation between the A—H frequency shift  $\Delta\nu \equiv \nu_0 - \nu$  and the A—H bond lengthening will thus be obtained

$$\Delta\nu/\nu_0 = \Delta\nu_0/\nu_0 + c(r_0' - r_0) \quad (7)$$

where

$$c = 3 |k_1'| k_1^{-1} \quad (8)$$

Since  $k_1$  and  $k_1'$  vary but weakly in the series of complexes with the same

A—Z...B fragment, the dependence between  $\Delta\nu$  and  $r_0' - r_0$  must be linear. Note that  $\Delta\nu_0/\nu_0$  is rather small ( $\sim 0.03$ ).

A linear correlation between the  $\nu$ (AH) frequency and the A—H bond length has been repeatedly reported for hydrogen bonds (see, e.g.<sup>11</sup>). Novak<sup>12</sup> found for the O—H...O bonds a proportionality between  $\Delta\nu/\nu_0$  and  $r_0' - r_0$  with a coefficient  $36 \text{ (nm)}^{-1}$  (Figure 1). If typical values  $k_1$  and  $k_1'$  are used

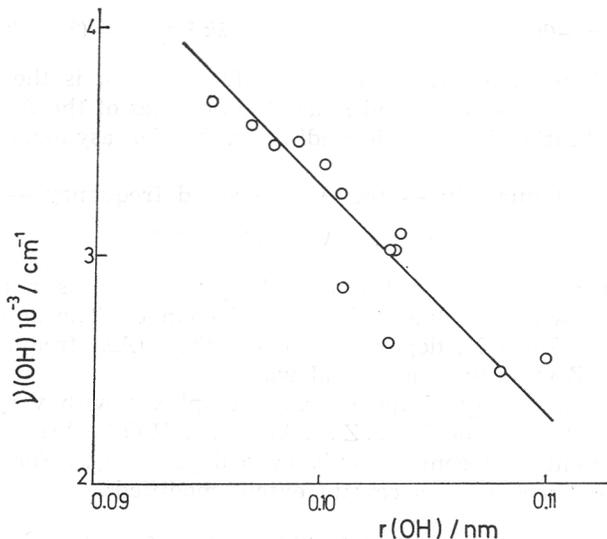


Figure 1. O—H Stretching frequency as a function of the  $r_0'$ (OH) length according to Novak<sup>12</sup>.

( $k_1 = 8 \cdot 10^2 \text{ Jm}^{-2}$ ,  $k_1' = -10^{13} \text{ Jm}^{-3}$ ) almost the same value ( $c = 37 \text{ (nm)}^{-1}$ ) will be obtained according to (8).

The relation (7) will be valid for CT complexes also. Unfortunately the available experimental data are insufficient.

Another strict expression can be obtained for the isotopic frequency ratio  $\nu$ (AH)/ $\nu$ (AD) for asymmetric HB complexes. Using (6) one finds (for derivation see<sup>6</sup>):

$$\nu(\text{AH})/\nu(\text{AD}) = \rho [(c^{1/2} - 1) \nu_0(\text{AH})/\nu(\text{AH}) + 1]^{-1} \quad (9)$$

( $\rho = \mu(\text{D})/\mu(\text{H})$ ). According to (9) for  $\nu(\text{AH}) = \nu_0(\text{AH})$ , i.e. for the free AH group the isotopic ratio is  $c^{1/2}$ , as must be. For  $\nu < \nu_0$ , i.e. for the HB complexes, the ratio is less than  $c^{1/2}$ , as frequently observed in experiment.

The curve in Figure 2 is plotted according to relation (9),  $c^{1/2} = [m_{\text{D}}(m_{\text{A}} + m_{\text{H}})/m_{\text{H}}(m_{\text{A}} + m_{\text{D}})]^{1/2}$  taken for the O—H...B systems (1.37). All published experimental data on both the neutral (A—H...B) and the ionic (AH<sup>+</sup>...B<sup>-</sup>) hydrogen bonds are plotted in this Figure<sup>6</sup>. It is important that the relation (9) as well as (7) contains no fitting parameter. The derivation of (9) requires only that the frequency has a quadratic dependence on  $X_0$ . Thus Figure 2 convincingly confirms the model suggested.

An expression similar to (6) for proton vibrational frequency of single-well symmetric hydrogen bonds can also be obtained<sup>6</sup>. In contrast to the asymmetric hydrogen bonds the anharmonicity constant ( $\alpha_2 > 0$ ) comes into the equations with a positive sign, the term  $2h^{-1}k_2 X_0^2$  is relatively small and can

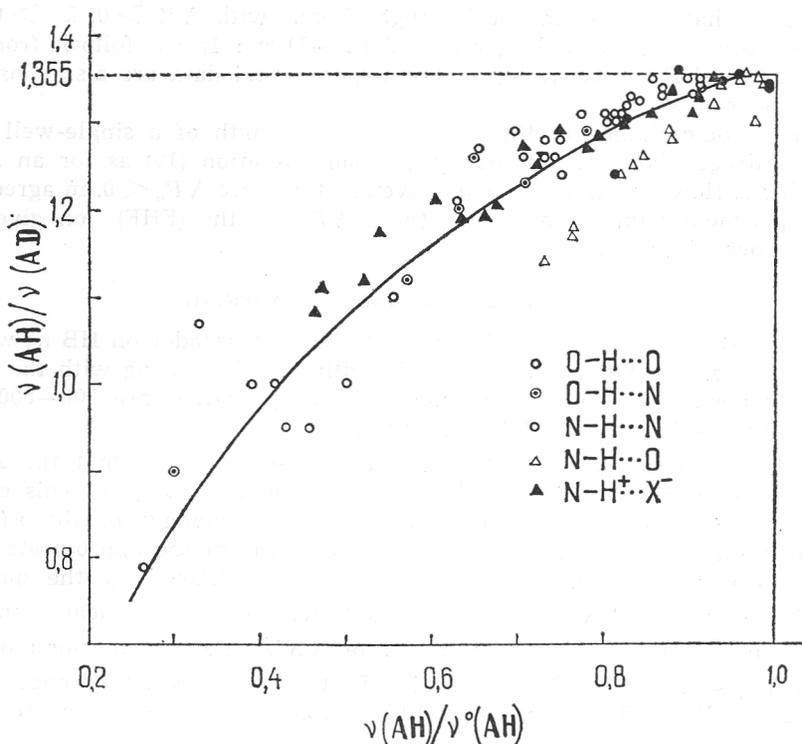


Figure 2. Relation between the  $\nu(\text{AH})/\nu(\text{AD})$  isotopic frequency ratio and  $\nu(\text{AH})/\nu_0(\text{AH})$  (equation (9))

be neglected. For these conditions  $\nu(\text{AH})/\nu(\text{AD}) \approx \rho^{1/2} [1 + 2\kappa_2(\text{AH}) \times (1 - \rho^{1/2})]$ . This expression shows that for symmetric HB complexes the frequency isotopic ratio appears to be higher than  $\rho^{1/2}$  in agreement with experiment for many systems. However there are some other systems for which the quantity  $2h^{-1}k_2 X_0^2$  is probably higher and can not be neglected. In such cases the frequency ratio has to be again lower than  $\rho^{1/2}$ .

Consider now the isotopic change of the equilibrium interatomic separations in HB complexes.

Designate by  $\Delta R_0$  the isotopic change of the A...B bond length:  $\Delta R_0 = R_0(\text{D}) - R_0(\text{H})$ . According to (2),  $R_0 = R_{00} + X_0$ , where  $R_{00}$ , in contrast to  $X_0$ , does not obviously depend on  $\mu$ . Hence

$$\Delta R_0 = X_0(\text{D}) - X_0(\text{H}) = -X_0(\text{H})(1 - \rho^{-1/2}) \quad (10)$$

where  $\rho = \mu(\text{D})/\mu(\text{H})$ . Since  $X_0 < 0$ , it follows from (10) that for asymmetric HB  $\Delta R_0 > 0$ , i.e. the A...B separation becomes larger on deuteration in agreement with experiment. An estimation according to (5) gives the correct order of magnitude  $\Delta R_0 \approx 10^{-3} - 10^{-4}$  nm.

A specific isotopic effect obviously exists also for an equilibrium distance  $r_0'(\text{AH})$ . From (4) and (10) the  $r_0'$  isotopic change is

$$\Delta r_0' \equiv r_0'(\text{AD}) - r_0'(\text{AH}) = -(k_{12}/k_1) \Delta R_0 \quad (11)$$

This means that for asymmetric hydrogen bonds with  $\Delta R_0 > 0$ ,  $k_{12} > 0^6$  the A—H equilibrium length is larger than the A—D one. It also follows from (11) that  $|\Delta r_0'| < \Delta R_0$ , since  $k_{12} < k_1$ . The experimental data are also consistent with these results<sup>6</sup>.

The isotopic change of the equilibrium  $R_0$  length of a single-well symmetric hydrogen bond is defined by the same relation (10) as for an asymmetric bond. However, now  $X_0$  is positive<sup>6</sup>, so that here  $\Delta R_0 < 0$ , in agreement with experimental data. An estimation of  $\Delta R_0$  for the (FHF)<sup>-</sup> ion gives the correct order of magnitude.

#### VIBRATIONAL $\nu$ (AZ) BAND BROADENING

The  $\nu$  (AZ) stretching band is known to become broader on HB as well as on CT complex formation, the band halfwidth ( $\nu_{1/2}$ ) increasing with the intermolecular bond strength<sup>9,11</sup>. The characteristic  $\nu_{1/2}$  values are 200—600 cm<sup>-1</sup> for HB and 10—30 cm<sup>-1</sup> for CT complexes.

A simple reason for the band broadening seems to be that the A...B bond length in the liquid phase is a random function of time. This causes, due to the A...B and A—Z coupling, stochastic changes of the  $\nu$  (A—Z) frequency and, hence, an inhomogeneous broadening of the appropriate band. Insofar as  $\nu$  depends on  $X$ , the halfwidth  $\nu_{1/2}$  is defined by the quantity  $(d\nu/dX)_0 \Delta \bar{X}$ , where  $\Delta \bar{X}$  designates an abbreviation of the mean quadratic deviation of  $X$  from its most probable value  $(\Delta \bar{X}^2)^{1/2}$ . For the harmonic oscillator model  $k_2 \Delta \bar{X}^2/2 = kT/2$  ( $k$  is the Boltzmann constant). Hence  $\nu_{1/2} \sim (d\nu/dX)_0 (kT/k_2)^{1/2}$ . This expression differs from (12) in the numerical coefficient only

$$\nu_{1/2} = (8 \ln 2)^{1/2} (kT/k_2)^{1/2} (d\nu/dX)_0 = (32 \ln 2)^{1/2} (kT k_2)^{1/2} h^{-1} X_0 \quad (12)$$

This equation follows from the more strict Bratos theory<sup>13</sup> and is valid for the Gaussian band shape.

As seen from equation (12) the band width of the stretching A—Z vibration in complexes is defined mostly by the same mode coupling parameter  $X_0$  as for the quantities considered above. Eliminating  $X_0$  from the equations (12) and (6) one obtains<sup>14</sup>

$$\nu_{1/2}^2 = \lambda (\Delta \nu - \Delta \nu_0) \quad (13)$$

where

$$\lambda = 16 (\ln 2) kT/h \quad (14)$$

Since  $\Delta \nu_0$  usually vary but weakly from complex to complex it follows from (13) that the squared halfwidth  $\nu_{1/2}^2$  has to be a linear function of  $\Delta \nu$ .

The expression (12) does not take into account the properties of the environment. This effect was taken into account by Sakun<sup>15,16</sup> who introduced into (12) an additional »environmental« factor  $\xi < 1$ . The coefficient  $\lambda$  (14) takes then the form

$$\lambda = 16 \xi (\ln 2) kT/h, \quad \xi < 1. \quad (15)$$

If  $\nu_{1/2}^2$  is plotted against  $\Delta \nu$  for methanol in different solvents, we obtain the pattern drawn by full circles in Figure 3<sup>14,17,18</sup>. Line 1 refers to a certain average value of  $\xi$  specifying the solvents used. Almost all points group in the vicinity of this line.

More demonstrative are the data obtained for various complexes in the same solvent. Such data were published by Detony et al.<sup>19</sup> for adducts of isothiocyanic acid with some oxygen bases in  $\text{CCl}_4$ . These data are also plotted in Figure 3 (open circles). All points lie in the vicinity of line 2.

The dashed line in Figure 3 refers to the Bratos approximation ( $\xi = 1$ ).

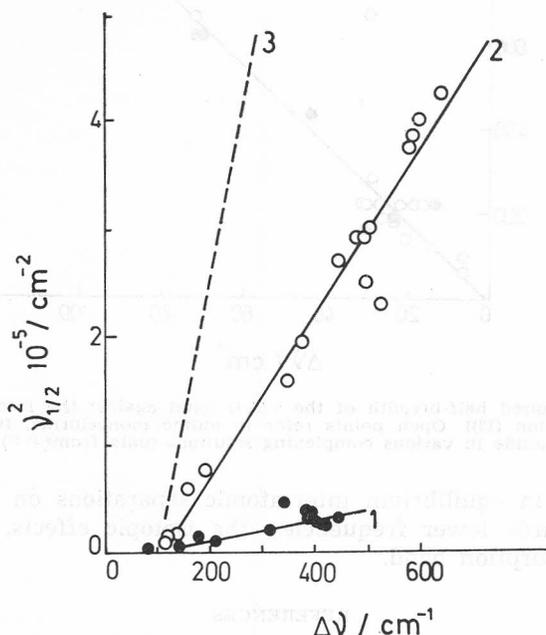


Figure 3. Plot of the squared half-breadth of the  $\nu(\text{AH})$  bond against the frequency shift in the hydrogen bonded complexes (equation (13)). Line 1: methanol in various solvents (data from<sup>11,17,18</sup>); line 2: adducts of isothiocyanic acid with some oxygen bases in  $\text{CCl}_4$  (data from<sup>19</sup>); line 3: according to Bratos expression ( $\xi = 1$ ).

Its slope is approximately 3.5 times that of line 2. Thus the experiments confirm the necessity of introducing the factor  $\xi$  in the  $\lambda$  expression. It seems probable however that the difference in the slopes mentioned is due not only to the environmental effect, but also (and to a higher extent) to the interaction of  $\text{A-Z}$  with the modes of the complex which are not accounted for in the theory suggested.

A direct (linear) dependence between the frequency shift and the halfwidth of the  $\text{A-H}$  stretching IR absorption band of the HB complexes was observed long ago (see, e. g.<sup>11,17-19</sup>), but no theoretical interpretation of it was given.

The values  $\nu_{1/2}^2$  versus the  $\Delta\nu(\text{AZ})$  stretching frequency shift plotted for iodine monochloride and iodine cyanide in various complexing solutions are shown in Figure 4. The points are seen to group mostly in the vicinity of the straight line. Hence, the quadratic dependence between the band halfwidth and its shift (13) is confirmed for both the HB and the CT complexes.

Summarizing it can be said that the  $\text{A-Z}$  and  $\text{A}\cdots\text{B}$  stretching mode coupling in the fragment  $\text{A-Z}\cdots\text{B}$  in molecular complexes manifests in many characteristic regularities and effects. The coupling parameter  $X_0$

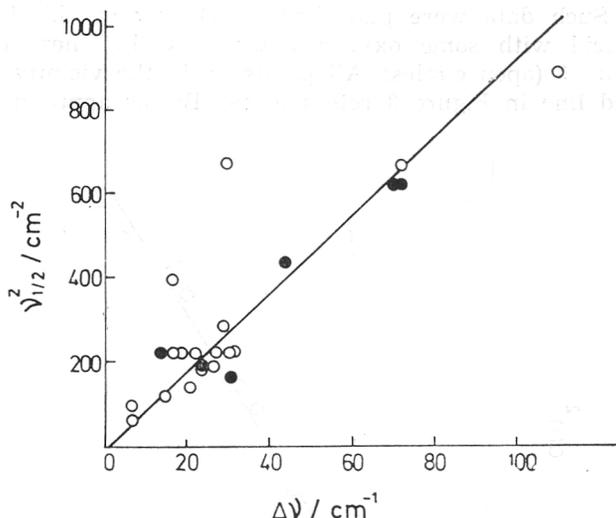


Figure 4. Plot of squared half-breadth of the  $\nu$ (AJ) band against the frequency shift in the CT complexes (equation (13)). Open points refer to iodine monochloride, full points to iodine cyanide in various complexing solutions (data from<sup>8,20,21</sup>).

defines: changes in equilibrium inter-atomic separations on complexing, the  $\nu$ (AZ) shift towards lower frequencies, the isotopic effects, the broadening of the  $\nu$ (AZ) absorption band.

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### IZVLEČEK

#### Nihajne sklopitve v molekulskih kompleksih

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Mnoge lastnosti molekulskih kompleksov so zvezane s sklopitvijo notranjih nihanj molekul z »zunanjsimi« nihanji, ki se pojavijo pri tvorbi kompleksa. Vlogo takih sklopitev so že večkrat obravnavali pri kompleksih z vodikovo vezjo. Po drugi strani pa se izkaže, da imajo kompleksi z vodikovo vezjo in oni s prenosom naboja (tipa  $\sigma$ - $n$ ) mnoge skupne značilnosti. Podobnost je zlasti opazna pri kompleksih, katerih baza vsebuje atome kisika, dušika, žvepla ali selena, Lewisove kiseline pa atom halogena. Pričujoči članek opisuje različne dinamične lastnosti obeh vrst kompleksov z enotnega stališča. Vpeljava sklopitvenega parametra ( $X_n$ ), ki je odgovoren za interakcijo med nihanji  $\nu$  AZ in  $\nu$  A...B v triatomskega sistemu A—Z...B (Z je atom vodika ali halogena) pomaga, da razložimo kvantitativno nekatere empirične najdbe in pravilnosti. To so npr. podaljšanje razdalje vezi A—Z pri kompleksiranju, premik valenčnega traku  $\nu$  AH proti nižjim frekvencam, linearna odvisnost med  $\Delta\nu$  AZ in  $\Delta\nu$  A—Z, izotopski efekti na razdalji A...B in A—H ter na frekvenco  $\nu$  AH, razširjenje traku valenčnega nihanja  $\nu$  AZ pri tvorbi kompleksa v tekoči fazi in odvisnost med polovično širino traku in premikom frekvence. Podano je nekaj relacij, ki ne vsebujejo vsklajevalnih parametrov in so v dobrem skladu z eksperimentom.