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Aspects of Characterizing the Normal Modes of a $(PO_4C_2)^-$ Model by Means of the Potential Energy Distribution

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Summary. In the normal coordinate analysis, potential energy distribution is often used to assist in the assignment of infrared absorption bands to normal modes. Applying this method to a simplified $(PO_4C_2)^-$ model simulating the vibrational behaviour of the phosphate group in DNA, it is shown that normal modes may alter in nature by the influence of external chemical effectors. It is to be emphasized that this circumstance should be taken into consideration whenever the molecules under study are influenced by external interactions.

Keywords. Normal coordinate analysis; Potential energy distribution; Hydrogen bond; Phosphate derivatives.

Aspekte der Charakterisierung der Normalmoden eines $(PO_4C_2)^-$-Modells über die Energieverteilung

Zusammenfassung. Im Rahmen der Normalkoordinatenanalyse wird die Verteilung der potentiellen Energie oft als Hilfsmittel zur Zuordnung von Infrarotabsorptionsbanden zu Normalmoden verwendet. Die Anwendung dieser Methode auf ein vereinfachtes $(PO_4C_2)^-$-Modell zur Simulierung des vibratorischen Verhaltens der Phosphatgruppe der DNA zeigt, daß die Art der Normalmoden durch externe chemische Effektoren beeinflußt werden kann. Es wird betont, daß dieser Umstand immer in Betracht gezogen werden sollte, wenn Moleküle unter dem Einfluß externer Effekte untersucht werden.

Introduction

At present, the methods of vibrational spectroscopy are routinely used as one of the most powerful tools to get information about the interaction between biopolymers and other molecules, *e.g.* water [1]. The interpretation of such vibrational spectra is an everlasting but in many cases complicated task. Normal coordinate analysis is one of the methods suitable to treat intermolecular interactions on a more theoretical basis.

It is well known, for instance, that the wavenumber of the antisymmetric stretching vibration of the PO_2^- moiety of the sugar-phosphate backbone of deoxyribonucleic acid (DNA) is shifted by approximately 20 cm^{-1} to lower wavenumbers when DNA films are brought from the dry to a fully hydrated state. The wavenumber of the corresponding symmetric vibration is changed only little at the same time [2–6]. A very similar behaviour could be proved in presence of adriamycin, an antitumor agent [7]. Nowadays it can be assumed that the molecular mechanism of interaction is determined by the formation of a hydrogen bond between the phosphate group of DNA and water or other molecules, respectively. For this, semi-empirical CNDO/2 molecular orbital calculations have predicted a decrease of the P$\overset{..}{-}$O bond strength and a diminution of the O$\overset{..}{-}$P$\overset{..}{-}$O angle [8].

In order to understand the changes in the vibrational behaviour of DNA during the formation of hydrogen bonds, we have carried out normal coordinate analyses of a simplified $(PO_4C_2)^-$ model. The effect of molecules forming hydrogen bonds on the phosphate group of DNA – which controls biological important changes of conformation – has been simulated by systematic variation of both the P$\overset{..}{-}$O stretching force constants and the O$\overset{..}{-}$P$\overset{..}{-}$O angle. In the following, we will focus on assignment problems appearing in this connection.

Methods

As a geometrical basis for describing the vibrational behaviour of the phosphate group of the sugar-phosphate backbone of DNA, the fragment shown in Fig. 1 has been selected. The structural parameters were taken from *Arnott et al.* [9]. In the normal coordinate analyses, the eigenvalue problems were solved using the program of *Jones* [10] which is based on the GF matrix formalism of *Wilson* [11]. For describing the model vibrations, 20 internal coordinates have been defined (six stretching, eight bending, and six torsional ones). Because of the only 15 normal modes of the model selected, five zero eigenvalues remained which were used as a test for numerical correctness.

As model force field, the *Urey-Bradley* force field for the DNA backbone as proposed by *Lu et al.* [12] was applied. An additional force constant ($f_\tau = 0.093$ aJ·rad^{-2}) was assigned to the torsional motions.

The attachment of molecules being able to form hydrogen bonds to the phosphate group was simulated in two different ways. Alternatively, the O$\overset{..}{-}$P$\overset{..}{-}$O bond angle was varied between 112° and 117° or the P$\overset{..}{-}$O stretching force constants of either one P$\overset{..}{-}$O bond alone or both together were decreased from 7.459 N·cm^{-1} to 6.459 N·cm^{-1}.

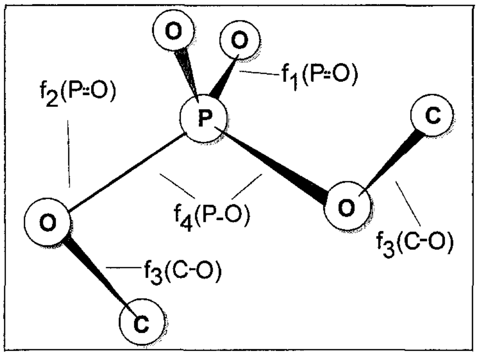

Fig. 1. Structure of the $(PO_4C_2)^-$ model and definition of valence force constants

Results and Discussion

The calculated wavenumbers of the stretching vibrations v_1, v_2, and v_4 are summarized in Tables 1 and 2. In Figs. 2 and 3, the dependences of elements of the potential energy distribution on the force constant $f(P\overset{..}{-}O)$ as well as on the bond angle $\phi(O\overset{..}{-}P\overset{..}{-}O)$ are shown. The stretching vibrations v_3, v_5, and v_6 ($v_{as}(C-O)$, $v_{as}(P\overset{..}{-}O)$, and $v_s(P\overset{..}{-}O)$, respectively) as well as the bending and torsional vibrations of the $(PO_4C_2)^-$ model are not involved because they do not undergo any relevant changes. The calculated stretching frequencis $\tilde{v}_1$, $\tilde{v}_2$, and $\tilde{v}_4$ are represented in Table 1, for a systematic diminution of the $P\overset{..}{-}O$ bond strengths of both $P\overset{..}{-}O$ bonds (case (a)), and for a decrease of the bond strength of only one $P\overset{..}{-}O$ bond (case (b)). It can be seen that v_1 – being an antisymmetric $O\overset{..}{-}P\overset{..}{-}O$ stretching vibration according to its nature – decreases in wavenumber by diminishing the $P\overset{..}{-}O$ stretching force constant as was to be expected (formation of hydrogen bonding) in case (a) more strongly than in case (b). Obviously, v_2 and v_4, show the same tendency.

Looking at the potential energy distribution in dependence on the $P\overset{..}{-}O$ stretching force constants (see Fig. 2), dramatic differences with respect to the change of the nature of the normal vibrations of v_1, v_2, and v_4 are found. Whereas v_1 retains its character in diminishing the $P\overset{..}{-}O$ stretching force constant as being an

Table 1. Calculated wavenumbers of stretching vibrations v_1, v_2, and v_4 of the $(PO_4C_2)^-$ model

$f_1(P\overset{..}{-}O)$	$\tilde{v}_1^a$	$\tilde{v}_2^a$	$\tilde{v}_4^a$	$\tilde{v}_1^b$	$\tilde{v}_2^b$	$\tilde{v}_4^b$
7.459	1207	1118	1081	1211	1114	1080
7.259	1192	1110	1077	1204	1110	1078
7.059	1176	1104	1070	1198	1106	1074
6.859	1161	1100	1062	1193	1102	1069
6.659	1146	1098	1051	1189	1100	1062
6.459	1130	1096	1040	1185	1098	1053

$f_1\,[N\cdot cm^{-1}]$; $\tilde{v}_i$ $[cm^{-1}]$; a for $f_1(P\overset{..}{-}O) = f_2(P\overset{..}{-}O)$ with $\phi(O\overset{..}{-}P\overset{..}{-}O) = 114.00°$; b for $f_2(P\overset{..}{-}O) = 7.459\,N\cdot cm^{-1}$ with $\phi(O\overset{..}{-}P\overset{..}{-}O) = 115.67°$

Table 2. Calculated wavenumbers of stretching vibrations v_1, v_2, and v_4 of the $(PO_4C_2)^-$ model as a function of different bond angles

$\phi(O\overset{..}{-}P\overset{..}{-}O)$	$\tilde{v}_1^a$	$\tilde{v}_2^a$	$\tilde{v}_4^a$	$\tilde{v}_1^b$	$\tilde{v}_2^b$	$\tilde{v}_4^b$
117.00	1215	1111	1079	1202	1104	1072
115.67	1211	1114	1080	1198	1106	1074
114.00	1207	1118	1081	1194	1108	1076
112.00	1201	1123	1082	1189	1112	1077

$\phi(O\overset{..}{-}P\overset{..}{-}O)$ [degree]; $\tilde{v}_i$ $[cm^{-1}]$; a for $f_1(P\overset{..}{-}O) = f_2(P\overset{..}{-}O) = 7.459\,N\cdot cm^{-1}$; b for $f_1(P\overset{..}{-}O) = 7.059\,N\cdot cm^{-1}$ and $f_2(P\overset{..}{-}O) = 7.459\,N\cdot cm^{-1}$

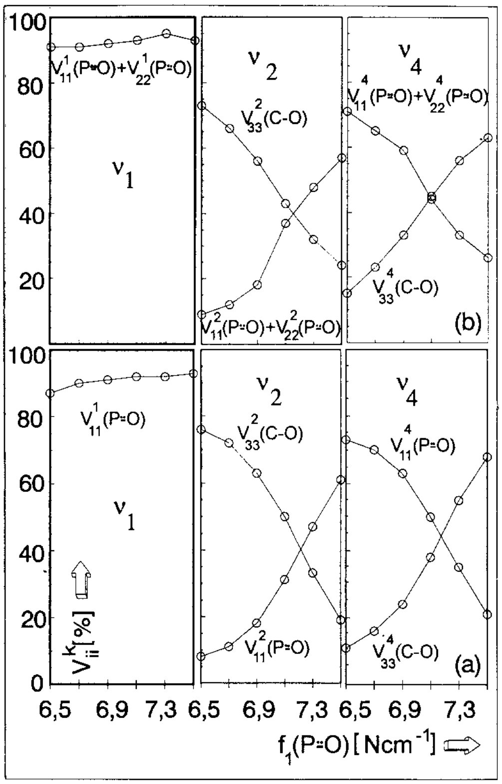

Fig. 2. Main parts of the potential energy distribution V^k_{ii} of the normal modes v_1, v_2, and v_4 of the $(PO_4C_2)^-$ model during the variation of the f_1(P$\doteq$O) valence force constant; (a) for f_1(P$\doteq$O) = f_2(P$\doteq$O), symmetric variation; (b) for f_2 (P$\doteq$O) = 7.459 N·cm^{-1}, asymmetric variation

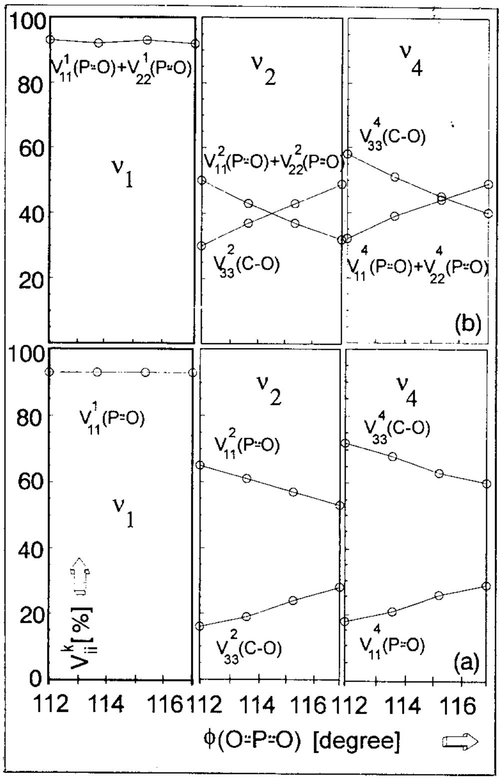

Fig. 3. Main parts of the potential energy distribution V^k_{ii} of the normal modes v_1, v_2, and v_4 of the $(PO_4C_2)^-$ model during the variation of the O$\doteq$P$\doteq$O bond angle; (a) for f_1(P$\doteq$O) = f_2(P$\doteq$O) = 7.459 N·cm^{-1}; (b) for f_1(P$\doteq$O) = 7.059 N·cm^{-1} and f_2(P$\doteq$O) = 7.459 N·cm^{-1}

antisymmetric O∸P∸O stretching vibration, the symmetrical[1] motions v_2 and v_4 change their natures. The higher-frequency vibration v_2 turns from a symmetric O∸P∸O stretching vibration into a symmetric C–O stretching vibration. For v_4, the opposite behaviour was found. Both vibrations are more characteristic in the cases of f_1(P∸O) $= f_2$(P∸O) $= 6.459$ N·cm^{-1} and f_1(P∸O) $= 6.459$ and f_2(P∸O) $=$ 7.459 N·cm^{-1}, respectively, than in the case of f_1(P∸O) $= f_2$(P∸O) $= 7.459$ N·cm^{-1}.

In diminishing the O∸P∸O bond angle (formation of a hydrogen bond), the vibrational frequencies of the antisymmetric O∸P∸O stretching mode decrease in view of a symmetrical (case (a)) as well as an antisymmetrical (case (b)) treatment of both P∸O bonds (see Table 2). At the same time, the vibrational frequencies v_2 and v_4 increase slightly. This "anti-sense" effect in v_1 and v_2 observed upon formation of a hydrogen bond should be the reason for the experimentally obtained vibrational behaviour of DNA in the case of the influence of water mentioned in the introduction. The potential energy distribution obtained when decreasing the O∸P∸O bond angle is shown in Fig. 3. If the P∸O stretching force constants of both P∸O bonds are held fixed at a value of 7.459 N·cm^{-1} (case (a)), the normal vibrations v_2 and v_4 become more and more characteristic for diminishing the O∸P∸O bond angle. However, if one of the two P∸O bonds is remarkably weakened (case (b)), the nature of the normal vibrations v_2 and v_4 in the $(PO_4C_2)^-$ model changes again.

In addition, the above results refer to a problem in connection with the characterization of normal modes. On the one hand, the normal vibrations can be classified according to the symmetry species of the molecular point groups which they belong to and arranged subsequently according to decreasing wavenumbers [13]. On the other hand, the normal vibrations are characterized according to the potential energy distribution [14] and the eigenvectors belonging to them. In this connection, the possibilities to arrange them according to kinetic energy distribution [15] or total energy distribution [16] are of minor importance. Within a normal vibration, all atoms move in phase and with the same frequency. That frequency is equal to the transition frequency in harmonic approximation; according to it, the classification of the normal vibrations can be made. Then, the specific circumstances are decisive for which bonds and angles are stressed within a normal vibration and to which extent. It depends, for example, very strongly on the actual interaction with the surroundings whether the v_2 of the $(PO_4C_2)^-$ model has to be described as the symmetric O∸P∸O or as the symmetric C–O stretching vibration. In any case, it seems to be more realistic to sort the normal vibrations according to their frequencies because of the systematic trend they show in changing systematically the force constants and bond angles (see Tables 1 and 2). In our case, if the normal vibrations are arranged according to the potential energy distribution and the eigenvectors, we get a jump in the frequencies not to be justified. Hence, an external effect, for example hydrogen bonding, can markedly influence the nature of normal vibrations; in a number of cases this can be determinant.

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[1] In this connection it should be noted, that the terms "symmetric" and "antisymmeric" are used as defined by the "in-phase" and out-of-phase" motions, respectively; the $(PO_4C_2)^-$ model itself is out of symmetry.

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