Reasons for the variability of isotopic ratios of stretching vibration frequencies of H-bonded complexes

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The effect of random resonances and vibration anharmonicity on the isotopic ratios of frequencies for molecules containing hydrogen atoms has been studied. It was found that the "anomalous" frequency dependence of the ν(XH)/ν(XD) isotopic ratio of the stretching vibration frequencies observed for H-bonded systems can be explained in terms of the theory of harmonic vibrations of molecules. The substantial deviation of experimental ν(XH)/ν(XD) from the magnitude equal to the square root of the reciprocal ratio of adjusted masses results from random resonances between the stretching mode of the bridging proton and some other vibration of the system.

Key words: isotopic ratio of vibration frequencies; hydrogen bond; random resonance; vibration mode; unspecific vibrations; anharmonic corrections.

The problem of the isotopic ratio of the frequencies of natural vibrations of a polyatomic system is one of the fundamental problems of the theory of molecular vibrations. Rayleigh has shown as early as in 1899 that an increase in the mass of elements of an oscillating system may only result in a decrease in the frequencies of its natural vibrations.[1] Later, relationships for various combinations of frequency squares for all of the basic vibrations of a molecule have been derived.[2] The most generally employed of these are the so-called rule of products and rule of sums.

The former of these rules states that, in the general case, the ratio between the products of the squares of frequencies of two isotope forms of a molecule is equal to the ratio between the determinants of their kinematic interaction matrices. Hence, the greater the number of vibrations in which the atom being replaced participates, the lower the isotopic ratio of frequencies for each of them. Thus, the isotopic ratio of frequencies is equal to the square root of the reciprocal ratio of the reduced masses only in the case where the vibration is localized in one coordinate both prior to and after the replacement. This condition is only satisfied when the frequency of a given vibration differs dramatically from those of the other vibrations in the system, and its kinematic coupling with them is sufficiently weak.

This situation is most often realized in the stretching vibrations of terminal XH groups. However, even in this case, the isotope substitution may result in the loss of the specific character of the vibrations. If the ν(XD) frequency, after replacement of the H atom by D, is close to the frequency of any of the vibrations in the system, then even a slight kinematic action, which always occurs in real molecules, may be sufficient for resonance to arise. The mixing of vibrations resulting from the resonance leads to substantial changes in their modes and, consequently, to the change of the "normal" value of the ν(XD) frequency by tens or even hundreds of reciprocal centimeters.[3,4] Therefore, a reliable assignment of the bands observed for isotope analogs (which assumes that the modes of vibrations are retained) is only possible when the mass of the atom changes by several percents ($O^{16} \rightarrow O^{18}$ or $C^{12} \rightarrow C^{13}$). When the mass is doubled (which would be most convenient for solving reverse spectral problems), the modes of vibrations may change to such an extent that the unambiguous correlation between the bands of the initial and isotope-substituted molecules would become impossible.[3,4]

In the present work, we have studied the effect of random resonances and anharmonic corrections on the isotopic ratio between the frequencies of vibrations of a molecular system. First of all, it has been important to evaluate quantitatively the variation of frequencies and intensities of the natural harmonic vibrations of individual bonds in a molecule, which results from their resonance. We have chosen a hydrogen cyanide molecule as a convenient object for this study. In this triatomic molecule, the interaction between only two stretching vibrations is allowed in terms of symmetry. The frequency of one of these, ν(C≡N), is ~2100 cm^{-1}. The frequency of the other vibration, ν(C—H), shifts to the same region as a result of deuteration. Consequently, practically sharp resonance arises (caused by the kinematic interaction between the C—D and C≡N

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bonds). We analyzed the process of mixing of two purely harmonic vibrations and its spectral manifestation using this resonance as an example.

For convenience in conducting the analysis, for the calculation of vibration frequencies and intensities for the hydrogen cyanide molecule, the mass of the hydrogen atom (m_H) was monotonically changed (with a spacing of $2^{1/5}$) from 0.5 to 16 spectral masses of hydrogen. With this setting-up of the calculation, an HCN molecule could also be used as an illustrative model in which the mass of the hydrogen atom acts as a parameter that makes it possible to consider all of the characteristics of the bands of resonating vibrations at any remoteness from the point of the sharp resonance. In addition, this approach enabled easy determination of the variation of the ν(CH) frequency resulting from the twofold increase in m_H.

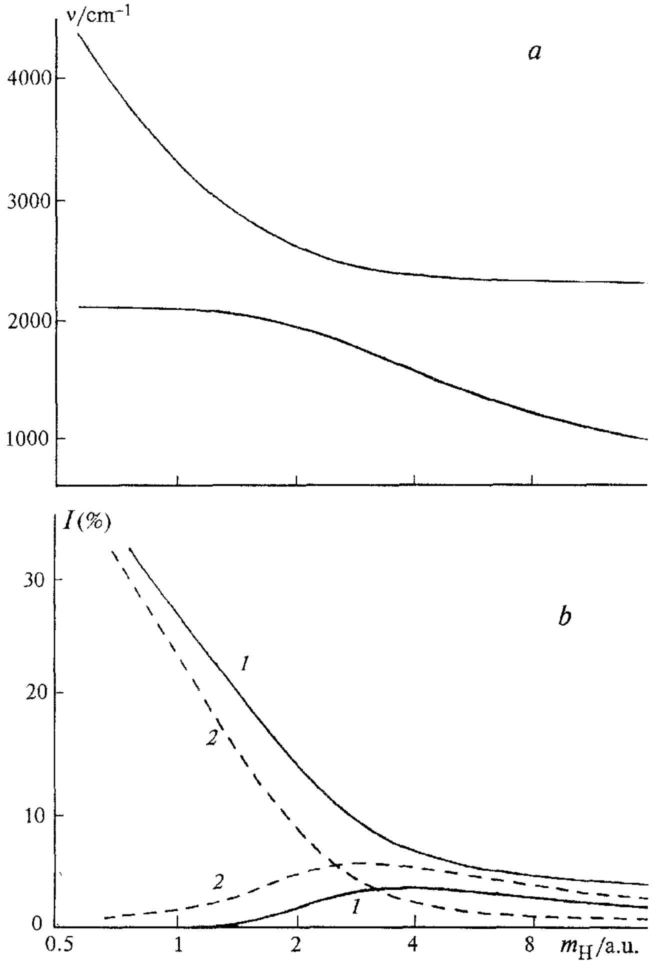

Fig. 1. The dependence of frequencies (*a*) and intensities (*b*) of the bands of stretching vibrations of the model hydrogen cyanide molecule *vs*. the mass of its hydrogen atom at $\partial\mu_{HCN}/\partial q_{CN}$ = −0.33 DÅ^{-1} (*1*) and $\partial\mu_{HCN}/\partial q_{CN}$ = 0.33 DÅ^{-1} (*2*).

Table 1. Frequencies (ν/cm^{-1}) and normalized modes (*q*) of the stretching vibrations of the model hydrogen cyanide molecule

m/a.u.	ν(CH)	*q*CH	*q*CN	ν(CN)	*q*CH	*q*CN
0.544	4630	1.08	−0.13	2088	0.12	0.40
1.088	3297	1.03	−0.14	2082	0.14	0.39
2.176	2588	0.69	−0.28	1913	0.35	0.30
4.352	2357	0.41	−0.38	1541	0.42	0.16
8.704	2301	0.31	−0.40	1194	0.35	0.09
17.408	2281	0.27	−0.41	952	0.28	0.06

The isotopic ratio of the frequencies of harmonic vibrations of the model HCN molecule

The IR spectrum of the HCN molecule was calculated in the harmonic approximation by the known program[5] using the known dynamic[4] and electrooptical[6] parameters. The calculation has shown that the frequencies of both vibrations under consideration decrease monotonically as m_H increases, which is in full agreement with the theory[1–4] (Fig. 1, *a*). The modes of the vibrations undergo drastic changes (Table 1). Actually, in the range of the mass of the H atom from 0.5 to 2, the stretching vibration of the CH bond remains the higher-frequency one; at $2 < m_H < 4$, a substantial mixing of vibrations occurs; and at $m_H > 4$, the lower-frequency vibration of the system corresponds to the vibration of the CH bond. The intensities of the bands of the stretching vibrations determined by their mode also essentially change as m_H increases (Fig. 1, *b*, curves *1*).

The results obtained (see Fig. 1, *a* and Table 1) show that even for this very simple model, for which the full calculation of the vibrational spectrum has been carried out, the isotopic ratio of the frequencies cannot always be unambiguously determined. In fact, in the resonance region, where the coordinate of the C—D bond participates in both resonating vibrations virtually to the same extent, the vibrations of isotope-substituted forms of the molecule are no longer equivalent. In this situation, the notion of the isotopic ratio of frequencies loses its meaning.

The experimental study of the vibrational spectra of isotope analogs of molecules without calculations does not allow one to judge either the mode of vibrations or the occurrence of resonances. Therefore, the assignment of bands is based, as a rule, on their intensities. The latter depend on the modes of vibrations and on the electrooptical parameters (EOP) of the molecule and, in the general case, they can be quite diversified. For example, for the hydrogen cyanide molecule, for which

$$\partial\mu_{HCN}/\partial q_{CH} = 1.08 \text{ DÅ}^{-1},$$

and $\partial\mu_{HCN}/\partial q_{CN} = -0.33 \text{ DÅ}^{-1}$,

the high-frequency vibration is always the most intense (see Fig. 1, *b*, curves *1*). However, it is sufficient to

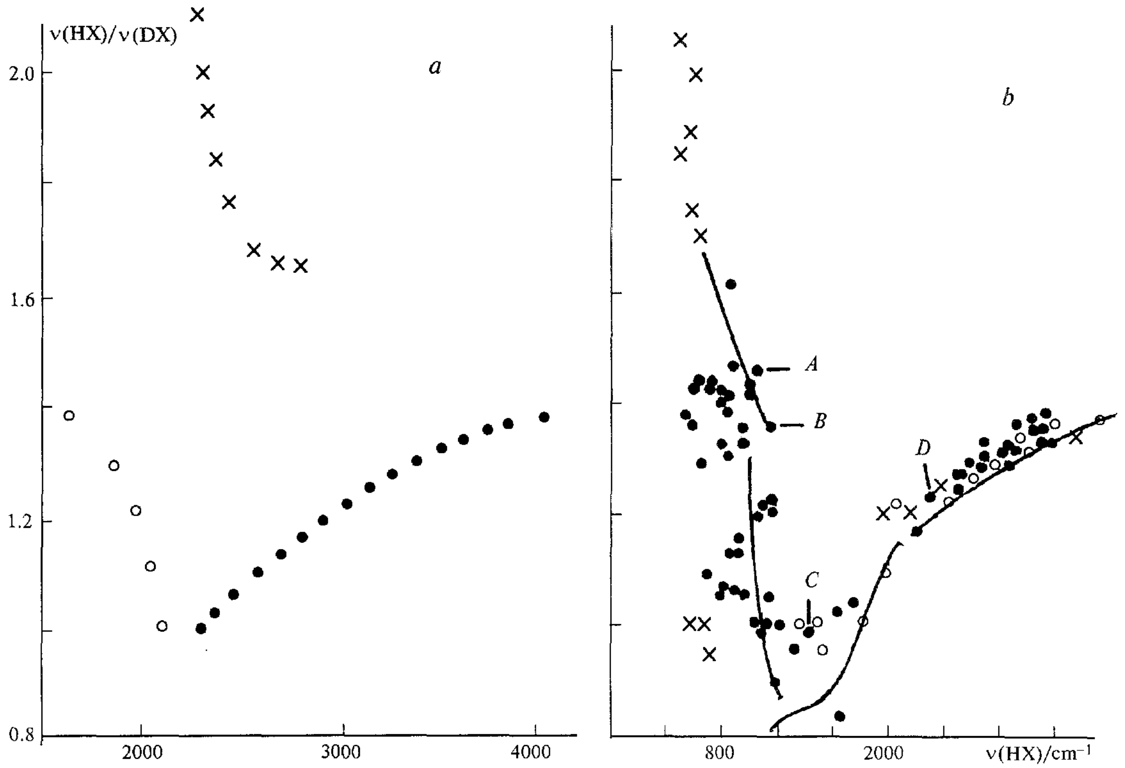

Fig. 2. The dependence of the ν(XH)/ν(XD) isotopic ratio on the frequency of the ν(XH) stretching vibration. *a*) The theoretical curve for resonating harmonic vibrations in the model hydrogen cyanide molecule: both vibrations were chosen from the high-frequency (•) or the low-frequency (o) branch; the ν(XH) vibration was chosen from the high-frequency branch, and ν(XD) was taken from the low-frequency branch (×). *b*) The results of direct spectral measurements: see Ref. 7 (o), Ref. 12 (×), Ref. 13 (•); theoretical curves.[13]

change the sign of one of the EOP

$$(\partial\mu_{\mathrm{HCN}}/\partial q_{\mathrm{CN}} = 0.33\ \mathrm{D\AA^{-1}}),$$

to make the ratio between the intensities of the bands under consideration fundamentally different (see Fig. 1, *b*, dashed lines). Obviously, in various systems, the ratio between the intensities of the bands considered can be quite different. Therefore, in the general case, when one formally juxtaposes the most intense bands in the spectra of the isotope-substituted molecules, one of the following three situations is realized. 1. Both frequencies being compared belong to the high-frequency branch (Fig. 2, *a*, dots). 2. Both frequencies being compared belong to the low-frequency branch (Fig. 2, *a*, rings). 3. The frequency of the protium form of the complex is taken from the high-frequency branch, while that of the deuterium form is taken from the low-frequency branch (Fig. 2, *a*, crosses). The frequency course of the ν(XH)/ν(XD) isotopic ratio has its own specific appearance in each of the above-mentioned cases. In the two former cases, the isotopic ratio decreases monotonically from $2^{1/2}$ to 1 as the region of the resonance is approached. In the latter case, at frequencies close to that of the sharp resonance, the ν(XH)/ν(XD) ratio is substantially greater than $2^{1/2}$.

The analysis carried out for the resonance of two harmonic vibrations allowed the following conclusions to be drawn.

1. As a result of random resonances, the formally calculated isotopic ratio of frequencies may be either greater or smaller than the square root of the ratio between the adjusted masses. The magnitude of the deviation of the isotopic ratio of frequencies from the "normal" value and the spectral region in which this deviation arises are entirely determined by the occasional coincidence of combinations of dynamic and kinematic parameters of each particular molecule. Thus, any attempt to construct the experimental dependence of the isotopic ratios of frequencies of various molecules on a certain vibrational characteristic of the system will inevitably result in an assemblage of points, statistically spread around a certain resonance curve. The magnitude of the spread will be determined by the differences both between the frequencies of sharp resonances and between the potentials of the interaction of resonating vibrations in the set of molecules under consideration.

2. Under certain conditions, the spectrum of the deuterium form of the molecule can exhibit simultaneously two intense peaks; the isotopic frequency ratio for one of them will be higher than the "normal" value, and that for another will be lower than the "normal" value.

3. The degree of influence of the resonance on the isotopic ratio of the vibration frequencies of the molecule can only be estimated based on the calculations. Therefore, determination of the "true" isotopic ratio of frequencies for each particular case may turn out to be a relatively complex and a theoretical, rather than an experimental, problem.

4. In large molecular systems with a great number of vibrations with similar frequencies, more complex resonances simultaneously involving several vibrations are possible.

The isotopic frequency ratio for hydrogen-bonded systems

The dependence of the ν(XH)/ν(XD) ratio on the ν(XH) frequency

In recent years the problem of the isotopic ratio of frequencies in systems involving hydrogen bonds has received increased attention in spectroscopic studies.[7–13] Interest in this problem has been initiated by the results of measurements[7] (see Fig. 2, *b*, rings) which served as a basis for the conclusion about the "anomalous" behavior of the isotopic frequency ratio for the OH group stretching vibration on deuteration. The dependence found[7] was explained[8] by the specific shape of the potential energy surface of systems with H-bonds. In the absence of alternative viewpoints, this explanation has been generally accepted. Therefore, the frequency dependence of the ν(NH)/ν(ND) ratio (see Fig. 2, *b*, crosses) obtained much later[12] has also been interpreted in terms of this ideology.

In a generalization and classification of the results of studies of the isotopic ratios of frequencies for more than a hundred H-bonded systems (see Fig. 2, *b*, dots) the spectral effect being studied was attributed[13] to a specific dynamic property of the X—H...Y linear one-coordinate bridge. In order to achieve a satisfactory agreement of the theoretical dependences with the experimental results, the interval of possible values for the ν(XH) frequencies was to be divided into four regions (see Fig. 2, *b*, solid lines). In each of these, its own mechanism[13] acts, resulting in a nearly linear variation of the ν(XH)/ν(XD) value.

Despite the fact that the sections of the four curves shown in Fig. 2, *b* lie in the regions of the highest concentration of experimental points, the explanation suggested for this effect[13] cannot be taken as wholly convincing. The fact is that three significant questions remain open: 1. What are the primary spectral data which make it possible to exclude the resonance phenomenon from the list of possible reasons for the "anomalous" isotopic ratio of frequencies? 2. How can the very great spread (up to 800 cm^{-1}) in the experimental points (see Fig. 2, *b*) be explained in terms of the model of the one-coordinate bridge with a fixed parameter? 3. What serves as the basis for the selection of the boundaries between the frequency intervals in which each of the four previously suggested[13] mechanisms acts?

Based on the results obtained in the present work, the explanation, which connects the peculiarities in the behavior of the isotopic frequency ratio with the possibility of random resonances between the vibrations with close frequencies, should be considered to be more conclusive. In fact, it can be seen from Fig. 2 that the experimental dependence, which includes virtually all of the data for H-bonded systems known at present, is in full agreement with the theory of resonance of harmonic vibrations.[2–4] This theory accounts for both the frequency dependence of the experimental isotopic ratio of frequencies and the great spread in the ν(XH)/ν(XD) values determined for various systems from the viewpoint of a single mechanism having a clear physical meaning.

It should also be noted that the possibility of a decrease in the frequency of the vibrations of a proton along the hydrogen bridge by up to 500 cm^{-1} has been reported in the literature many times.[12,13] If this is true, then, according to the theory of vibrations,[3,14] the force constants of the bonds of the X—H...Y bridge should be, on the average, ~0.15 mdyne Å^{-1}, *i.e.*, they should be approximately equal to the force constant of the H-bond in liquid water.[14] Since such average values of the force constants of the bonds cannot occur in H-complexes of any strength, the frequency of the stretching vibration of the XH bond of the bridge cannot be less than 1000—1300 cm^{-1}.

This raises the question of whether the stretching vibration frequencies found for systems having natural vibrations with frequencies close to ν(XH) are trustworthy. It has been shown above that the determination of the ratio of frequencies of isotope-substituted molecules may also present great difficulties. Therefore, it seemed necessary to evaluate the validity of the interpretation of bands used[13] in plotting the generalized dependence (see Fig. 2, *b*). For this purpose, of more than a hundred H-bonded complexes, the data for which are presented in Fig. 2, *b*, we have chosen the $H_5O_2^+$ ion and the cyclopropenonediol molecule $C_3O_3H_2$. These two systems were chosen because of their relative simplicity, the difference between their isotopic frequency ratios, and the fact that they had been theoretically investigated. However, the most intriguing feature of these systems is that the ν(XH) stretching frequencies (1050, 1170, 1450, and 2360 cm^{-1})[15–18] and the ν(XH)/ν(XD) ratios (1.46, 1.36, 1.00, and 1.23)[13] attributed to them are found in all of the specific sections of the frequency dependence under consideration (see Fig. 2, *b*, points *A*, *B*, *C*, and *D*, respectively).

Isotopic ratios of vibration frequencies of the $H_5O_2^+$ ion

The $H_5O_2^+$ ion belongs to the class of complexes with a strong symmetrical H-bond in which the stretching

Table 2. Frequencies (ν/cm^{-1}) and normalized modes (q) of some vibrations of the $H_3O_2^-$, $H_5O_2^+$, $(CH_3O)_2H^-$, $(CH_3O)_2H^+$ complexes and their deuterated analogs*

Ion	Assignment of the vibration	ν_{harm}	ν_H/ν_D	ν_{anh}	ν_H/ν_D	q(O..H)	q(O..H..O)	q(CO..H) q(HO..H)**	q(HCO) q(HOH)**	q(HCH)	q(CO)
$H_3O_2^-$	O..H	1262	1.38	1290	1.41	0.70	1.09	0.81	—	—	—
		(916)		(914)		(0.52)	(0.75)	(0.59)	—	—	—
	H—O..H^A	849	1.52	902	1.53	0.06	—	0.78	—	—	—
		(559)		(588)		(0.09)	—	(0.39)	—	—	—
	O...O	637	0.91	791	1.06	0.16	—	0.10	—	—	—
		(700)		(742)		(−0.15)	—	(0.44)	—	—	—
$H_5O_2^+$	O..H	1388	1.38	1417	1.40	0.80	−0.77	0.25	0.37	—	—
		(1004)		(1011)		(0.56)	(−0.62)	(0.22)	(0.23)	—	—
	H—O..H^A	695	1.42	724	1.43	0.07	—	0.46	0.13	—	—
		(488)		(505)		(0.08)	—	(0.26)	(0.05)	—	—
	O...O	571	0.96	673	1.09	0.16	—	0.08	0.01	—	—
		(598)		(619)		(0.15)	—	(−0.25)	(−0.10)	—	—
$(CH_3O)_2H^-$	O..H	1497	1.38	1515	1.40	0.75	0.06	0.07	0.32	0.42	0.02
		(1083)		(1086)		(0.51)	(0.29)	(0.14)	(0.12)	(0.12)	(0.20)
	H—C—H^E	1465	0.99	1480	1.00	0.67	0.07	0.04	−0.22	0.55	—
		(1479)		(1479)		(0.05)	(0.04)	(0.05)	(−0.40)	(0.68)	—
	H—C—H^A	1397	1.00	1417	1.02	0.13	0.13	0.63	0.48	0.29	—
		(1399)		(1394)		(0.04)	(0.07)	(0.03)	(0.55)	(0.40)	—
$(CH_3O)_2H^+$	H—O..H^B	1650	1.34	1820	1.44	0.23	0.92	−0.44	0.25	−0.05	0.10
		(1231)		(1260)		(0.22)	(0.40)	(−0.15)	(0.24)	(−0.44)	(0.10)
	O..H	1556	1.42	1633	1.48	−0.96	−0.30	0.24	—	0.07	—
		(1100)		(1108)		(0.60)	(0.20)	(0.13)	(−0.08)	(0.05)	—
	H—C—H^A	1485	1.00	1533	1.03	0.19	0.29	0.16	−0.39	0.61	—
		(1481)		(1491)		(−0.04)	(0.01)	(0.01)	(0.38)	(0.68)	—
	H—C—O^B	1123	0.96	1165	0.96	0.01	−0.50	0.21	0.29	−0.49	−0.04
		(1170)		(1210)		(0.11)	(0.49)	(0.25)	(0.17)	(−0.38)	(−0.08)

Note. A is a fully symmetrical vibration, B is an asymmetrical vibration, E is a doubly degenerate vibration.

* The frequencies for the deuterated analogs (ν_D) are given in parentheses.

** The coordinate of the $H_3O_2^-$ and $H_5O_2^+$ complexes.

vibrations are clearly non-specific in terms of mode.[19] To estimate the degree of their unspecificity, we carried out a normal coordinate analysis for four ions of this type (Table 2) using the original program.[20] According to the theory,[2–4] considerable mixing of vibrations of the central proton with vibrations of other atoms of the system (see Table 2) should result in a substantial decrease in the ν(O...H)/ν(O...D) isotopic ratio of frequencies. However, as has been noted above, the values of the isotopic ratio of ν(O...H) vibration frequencies for the $H_5O_2^+$ ion found by different authors, *viz.* ν(O...H)/ν(O...D) = 1.46 (ν(O...H) = 1050 cm^{-1})[15] and ν(O...H)/ν(O...D) = 1.36 (ν(O...H) = 1170 cm^{-1}),[16] are close to the normal value.

The reason for this discrepancy can be understood by calculating frequencies and modes of harmonic vibrations of the $H_5O_2^+$ ion and its isotope-substituted analogs. In order to evaluate the generality of the consideration, an analogous calculation was also carried out for the $H_3O_2^-$ ion having a similar structure. To analyze the results obtained, two features typical of systems with H-bonds are noteworthy. 1. The replacement of the bridging proton by deuterium results in a decrease in the coefficients of the kinematic interaction of several degrees of freedom and, therefore, in a simultaneous decrease in the corresponding vibration frequencies. In this case, the effect of the isotope substitution on the ν(X...H)/ν(X...D) ratio would differ from that in the above-considered example of hydrogen cyanide (were one of the frequencies decreases, while the other remains constant). 2. In the case where the H-bonded complex, in addition to the bridging proton, contains as well other readily replaced hydrogen atoms, the spectral effect of deuteration would be a consequence of the simultaneous change of masses of all of these atoms.

The frequencies and modes of harmonic vibrations of various isotope analogs of the $H_5O_2^+$ and $H_3O_2^-$ ions calculated by the known procedure[5] with the previously reported force field[19] are listed in Table 3. It can be seen that the 1000—1500 cm^{-1} region contains three (for $H_5O_2^+$) or two ($H_3O_2^-$) absorption bands associated with vibrations of the central proton. Notice as well that to obtain the correct experimental ν(O...H)/ν(O...D) value for these ions, one need not carry out the precise assignment of the bands. In fact, it can be seen from Table 3 that in the case of complete deuteration, the isotopic ratios of all of the vibration frequencies of the systems under study are close to 1.4. However, when only the central proton is replaced by deuterium, the ν(X...H)/ν(X...D) values are substantially lower, *viz.* 1.31 ($H_5O_2^+$) and 1.34 ($H_3O_2^-$). In addition, this ratio depends on what isotope form of the ion, H_2OHOH_2(HOHOH) or D_2OHOD_2(DOHOD), was subjected to deuteration (see Table 3).

During the fully symmetrical vibration of the hydrogen bridge of the $H_5O_2^+$ ion (ν^H(O...O) = 571 cm^{-1}) and the fully symmetrical vibration of the H—O...H angle (ν(HO...H) = 693 cm^{-1}) resonating with it, the central proton remains at rest. Therefore, the replacement of this proton by deuterium does not result in a change in the frequencies of the above-mentioned vibrations. However, when the peripheral hydrogen atoms are replaced by deuterium, the frequencies of the ν^H(O...O) and ν(HO...H) natural vibrations decrease to 488 and 593 cm^{-1}. This variation results not only from the increase in the masses of the H atoms (this would afford the following values: ν(HO...H) = 512 cm^{-1} and ν^H(O...O) = 542 cm^{-1}), but also from the increase in the resonance of these vibrations. Due to the increase in the resonance, the ν^D(O...O) frequency increases to 593 cm^{-1} (this is now the high-frequency vibration), while the ν(DO...H) frequency decreases to 488 cm^{-1} (this vibration becomes the low-frequency one). Therefore, the formal determination of the isotopic frequency ratio for the ν^H(O...O) vibration affords 0.96, instead of 1.05; and for the ν(HO...H) vibration, the result is 1.42, instead of 1.35 (see Table 3).

For lack of the information on the presence of the resonance in the system, both vibrations, ν(HO...H) and ν(DO...D), would be assigned to the high-frequency branch, while ν^H(O...O) and ν^D(O...O) would be assigned to the low-frequency branch, and the isotopic ratios would be 1.17 and 1.16 (see Table 3). It is of interest that the frequencies of the corresponding vibrations of the $H_3O_2^-$ ion behave in a similar way, when the peripheral hydrogen atoms are replaced by deuterium (see Table 3). These peculiarities of the behavior of isotopic frequency ratios for the $H_5O_2^+$ and $H_3O_2^-$ ions will be observed as well in the Raman spectra.

Table 3. The isotopic ratios of vibration frequencies for the $H_5O_2^+$ and $H_3O_2^-$ ions

Ion	Assignment of the vibration	ν(HHH)	$\frac{\nu(HHH)}{\nu(HDH)}$	$\frac{\nu(DHD)}{\nu(DDD)}$	$\frac{\nu(HHH)}{\nu(DDD)}$
$H_5O_2^+$	H—O..H	801	1.00	1.00	1.35
	H—O..H	693	1.00	1.00	1.42/1.17*
	O...O	571	1.00	1.00	0.96/1.16*
	H—O..H	1435	1.26	1.32	1.39
	O..H	1383	1.31	1.21	1.38
	O..H..O	1042	1.33	1.33	1.37
	H—O..H	436	1.10	1.06	1.37
	O..H..O	428	1.11	1.06	1.41
$H_3O_2^-$	H—O	3392	1.00	1.00	1.37
	H—O..H	849	1.00	1.00	1.21/1.52*
	O...O	637	1.00	1.00	1.14/0.91*
	H—O	3392	1.00	1.00	1.37
	O..H..O	1562	1.30	1.36	1.40
	O..H	1262	1.34	1.34	1.38
	O..H..O	873	1.39	1.39	1.39
	H—O..H	501	1.12	1.06	1.38

* The values obtained at various variants of the interpretation of the spectrum of the deutero analog.

Thus, the experimentally determined isotopic ratios of frequencies for the $H_5O_2^+$ and $H_3O_2^-$ ions, close to 1.4, result from the simultaneous replacement of the central and peripheral hydrogen atoms. The correct determination of the ν(X...H)/ν(X...D) ratio for these ions is possible when only the central proton is replaced by deuterium. Therefore, in experimental studies of systems containing several readily substituted hydrogen atoms, the true isotopic ratio of the frequencies of vibrations of the bridging proton can be obtained only in the case where these vibrations are specific in mode.

Isotopic ratios of vibration frequencies of the $C_3H_2O_3$ molecule

The unit cell structure of the molecular crystal of cyclopropenonediol is unknown.[17,18] It is assumed that planar $C_3H_2O_3$ molecules are arranged in layers. In each of the layers, the carbonyl oxygen atom of one molecule forms two H-bonds with the OH groups of two other molecules. On the basis of the experimentally recorded absorption and Raman spectra of crystalline cyclopropenonediol[17] and the results of the calculation[18] of natural vibrations of the $C_3H_2O_3$ molecule, it has been concluded[17,18] that the frequencies of two OH vibrations of this molecule are substantially different (2360 and 1516 cm^{-1}), and their isotopic ratios amount to 1.26 and 1.00, respectively.[17,18]

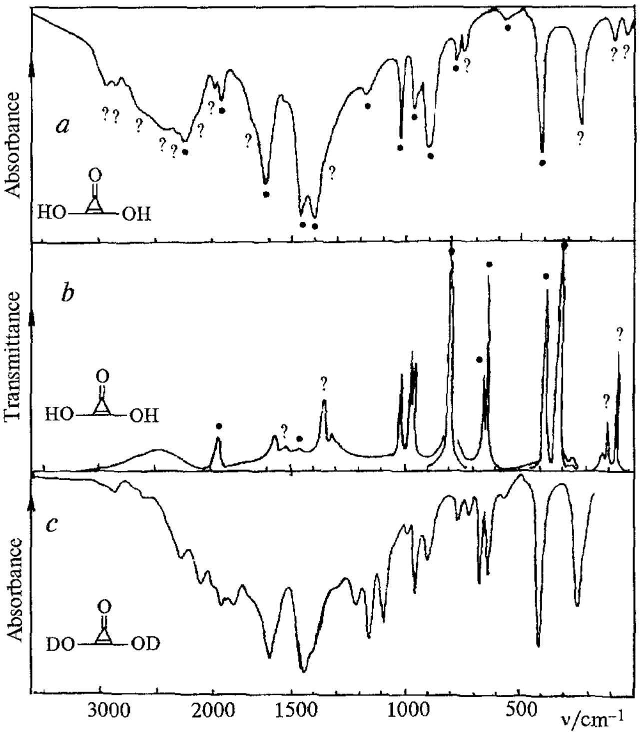

Fig. 3. The IR absorption (*a*) and Raman (*b*) spectra[17] of crystalline cyclopropenonediol and the IR absorption spectrum of its deuterated analog (*c*).

Let us analyze whether the spectra recorded[17] and the calculation carried out[18] allow one to draw conclusions concerning the frequencies of the OH vibrations of the $C_3H_2O_3$ molecule and their isotopic ratios. We consider initially the experimental data. The IR spectrum of the crystalline cyclopropenonediol has no peculiarities (Fig. 3, *a*). The frequency range between 3000 and 40 cm^{-1} is uniformly filled with more or less intense absorption bands. As a result of deuteration (Fig. 3, *c*), the whole broad absorption region shifts somewhat to lower frequencies. However, the bands corresponding to equivalent vibrations cannot be identified from the spectral profile. A consideration of the Raman spectrum (Fig. 3, *b*) is also unhelpful. Therefore, experimental determination of the ν(OH) stretching frequencies and their isotopic ratio for the crystalline cyclopropenonediol is impossible.

The spectrum of an individual $C_3H_2O_3$ molecule was calculated[18] using the force constants found by semiempirical quantum-chemical calculations. The calculated stretching frequencies of the two OH groups, $\nu(OH_1)$ and $\nu(OH_2)$, were found to be identical (2833 cm^{-1}) and their isotopic ratios were found to be 1.38. The disagreement with the experiment amounted to 473 and 1317 cm^{-1}. The frequencies of deformations of the OH groups, δ(OH), γ(OH), and γ(OD), were also calculated with a substantial error (100—400 cm^{-1}). Apart from the low accuracy of the calculations, the fact that they allowed us to describe only some of the bands observed (they are marked with dots in Fig. 3, *a*) is also unsatisfactory. Many bands, including some intense bands, remained uninterpreted (they are marked with question marks in Fig. 3, *a*).

Thus, the experimental results[17] and the data of calculations for a separate $C_3H_2O_3$ molecule (see Ref. 18) do not allow one to determine properly the ν(OH)/ν(OD) value and, therefore, do not give grounds to speak of an anomalous isotopic ratio of frequencies in crystalline cyclopropenonediol.

The effect of the anharmonicity of vibrations of hydrogen-bonded systems on the isotopic ratio of frequencies

For completeness of this study, we should consider the problem of how the isotopic frequency ratio for H-bonded systems is affected by the anharmonicity of their vibrations. An anharmonic calculation of the IR spectra of twelve complexes with weak H-bonds[21] has shown that the vibrations of these bonds have virtually harmonic character in all cases, since the displacements of heavy atoms are slight. The anharmonic corrections to the ν(OH) stretching frequencies are 70—180 cm^{-1}, and there is no correlation between a correction magnitude and the strength of the H-bond. The results presented indicate that even in the case in which the anharmonic corrections do not decrease on going to the deuterium-substituted complexes, the variations of the isotope frequency ratios caused by them (~3 %) will not exceed the experimental error.

Of particular interest for us was the evaluation of the magnitudes of anharmonic corrections and the extent to which they influence the isotopic frequency ratios in the systems with strong H-bonds. For this purpose, we calculated the frequencies of anharmonic vibrations for four complexes with symmetrical hydrogen bridges: $H_5O_2^+$, $H_3O_2^-$, and $(CH_3OH)_2H^+$ $(CH_3O)_2H^-$, and for their analogs deuterated at the OH groups according to the procedure described and tested previously.[19] The enthalpies of formation of these complexes are ~30 kcal mol^{-1}.

Table 2 presents data on the vibrations accompanied by the greatest deformations of the O...H...O bridge as an example. Analysis and generalization of the information obtained in the calculations led us to the following inferences. The corrections to the frequencies of various vibrations caused by the dynamic anharmonicity vary from 0 to 185 cm^{-1} for all of the complexes considered. Their relative magnitude can be as high as 39 %. The values for these corrections obtained by averaging them over all of the vibrations of all of the complexes amount to 54 and 18 cm^{-1} for the protium and deuterium forms, respectively. However, for some symmetrical (A) and asymmetrical (B) vibrations such as ν^A(O...O), ν^B(O...H...O), ν^B(HO...H), and ν^B(CO...H), the anharmonic corrections are 2—3-fold higher (100—200 cm^{-1}). When these corrections are taken into account, the isotopic ratio of frequencies changes by no more than 10 %. The average values of the anharmonic corrections to the frequencies of the stretching vibrations of the central proton for the protium and deuterium forms (40 and 5 cm^{-1}, respectively) are substantially less than the values obtained by averaging over all of the vibrations. They cause changes in the isotopic ratio of frequencies of about 2 %, *i.e.*, they are within the accuracy of the measurements.

* * *

The experimentally found dependence of the isotopic ratio of frequencies of the stretching vibrations of H-bonded systems on the ν(XH) value may be explained in terms of the theory of harmonic vibrations of molecules. The great deviation of the ν(XH)/ν(XD) value from 1.4 results from a random resonance between the stretching vibration of the bridging proton and some other vibration in the system.

When this resonance arises, the notion "isotopic ratio of the frequencies of equivalent vibrations" loses its initial meaning. In this case, the correct assignment of the bands recorded in the IR and Raman spectra can only be based on the results of normal coordinate analysis for the system under consideration.

In the systems containing several hydrogen atoms which can be easily replaced, the unambiguous experimental determination of the isotopic ratio of vibration frequencies of the bridging proton is only possible in the case in which its vibrations are specific in form. Otherwise, the calculation of the vibration frequencies for the isotope analog of the system studied, in which only the bridging proton is replaced by hydrogen, is needed.

Anharmonicity of the vibrations of complexes with strong and weak hydrogen bonds has no noticeable effect on their isotopic frequency ratios.

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References

1. Lord Rayleigh, *Scientific Papers*, Cambridge University Press, 1899, **1**, 562.
2. M. V. Vol'kenshtein, M. A. El'yashevich, and B. I. Stepanov, *Kolebaniya molekul* [*Vibrations of Molecules*], Gostekhizdat, Moscow, 1949, **1** (in Russian).
3. M. V. Vol'kenshtein, L. A. Gribov, M. A. El'yashevich, and B. I. Stepanov, *Kolebaniya molekul* [*Vibrations of Molecules*], Nauka, Moscow, 1972, 699 pp. (in Russian).
4. L. A. Gribov, *Vvedenie v molekulyarnuyu spektroskopiyu* [*Introduction to Molecular Spectroscopy*], Nauka, Moscow, 1976, 399 pp.(in Russian).
5. L. A. Gribov and V. A. Dement'ev, *Metody i algoritmy vychislenii v teorii kolebatel'nykh spektrov molekul* [*Methods and Algorithms of Calculations in the Theory of Vibrational Spectra of Molecules*], Nauka, Moscow, 1981, 356 pp. (in Russian).
6. L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, *Kolebatel'nye spektry mnogoatomnykh molekul* [*Vibrational Spectra of Polyatomic Molecules*], Nauka, Moscow, 1970, 559 pp. (in Russian).
7. A. Novak, *Struct. Bonding*, 1974, **18**, 177.
8. N. D. Sokolov and V. A. Savel'ev, *Chem. Phys.*, 1977, **22**, 383.
9. M. Ichikava, *Chem. Phys. Lett.*, 1981, **79**, 583.
10. J. Emsley, *Struct. Bonding (Berlin)*, 1984, **57**, 147.
11. A. V. Iogansen and M. Sh. Rozenberg, *Zh. Strukt. Khim.*, 1986, **27**, 53 [*J. Struct. Chem.*, 1986, **27** (Engl. Transl)].
12. E. Grech, Z. Malarski, and L. Sobczyk, *Chem. Phys. Lett.*, 1986, **128**, 259.
13. N. D. Sokolov, M. V. Vener, and V. A. Savel'ev, *J. Mol. Struct.*, 1990, **222**, 365.
14. G. V. Yukhnevich, *Infrakrasnaya spektroskopiya vody* [*Infrared Spectroscopy of Water*], Nauka, Moscow, 1973, 208 pp. (in Russian).
15. G. Pieotin, J. Roziere, J. Potier, and A. Potier, *Adv. Mol. Relax. Processes*, 1975, **7**, 177.
16. N. B. Librovich, B. P. Sakun, and N. D. Sokolov, *Chem. Phys.*, 1979, **39**, 351.
17. A. Lautié, M.-F. Lautié, and A. Novak, *Canad. J. Chem.*, 1985, **63**, 1394.
18. A. Lautié, M.-F. Lautié, and A. Novak, *J. Mol. Struct.*, 1986, **142**, 29.
19. G. V. Yukhnevich, E. G. Tarakanova, V. D. Mayorov, and N. B. Librovich, *J. Mol. Struct.*, 1992, **265**, 237.
20. A. I. Pavlyuchko, Sc. D. (Chem.) Thesis, Moscow Univ., Moscow, 1992, 114 pp.
21. L. A. Gribov, T. T. Merzlyak, and I. S. Perelygin, *Zh. Prikl. Spektrosk.*, 1981, **35**, 688 [*J. Appl. Spectrosc.*, 1981, **35** (Engl. Transl.)].

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