Concerning the problem of temperature changes in the intensity of continuous absorption in the spectra of complexes with symmetric H-bond

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The effect of temperature on the spectra of anharmonic vibrations of complexes with symmetric H-bonds was simulated and considered using $H_3O_2^-$ and $H_5O_2^+$ ions as an example. The intensity of continuous absorption observed in the IR spectra of such types of complexes is virtually independent of temperature.

Key words: intensity of vibrational transitions, temperature, symmetric hydrogen bond, continuous absorption.

Changes in the vibrational spectra of liquid and solid molecular systems caused by varying temperature are known to be, as a rule, due to a shift of the equilibrium between different molecular structures present in the system.[1,2] Therefore, the study of the temperature dependence of the IR spectra makes it possible to determine the molecular structure of the system under investigation. Such a type of study was performed for solutions of acids and strong bases.[3–5] A characteristic feature of their spectra is a broad (~3000 cm^{-1}) region of continuous absorption (CA), the contour of which (number, positions, and intensities of individual maxima observed against the background) depends on the composition of the solution. In this case, no appreciable effect of increasing the temperature of the solution by 50—100° on the intensity and shape of the contour of CA of the system was detected.[3–5] More accurate measurements of the CA spectrum, performed for the Cl...H...OSO_2 system at T = 300—340 K, showed[6] that the intensity of the background absorption in the 2100—1200 cm^{-1} region remains unchanged within the accuracy of measurements (±3.5%). At the same time, the peak intensity of several individual bands decreases by 30—40% as temperature increases by 40°.

According to current concepts, the continuous absorption, which is a superposition of several tens and, sometimes, of hundreds of overlapping bands of fundamental and combination modes of complexes with strong (~32 kcal mol^{-1}) symmetric H-bond, is due to the intrinsic properties of these complexes rather than their interaction with the medium.[7] Therefore, changes in the solvation degree of the complexes in solution occurring on varying the temperature must not appreciably affect the shape of the contour and the intensity of CA. Hence, considering this temperature dependence one should analyze the effect of temperature on the spectra of individual complexes with strong H-bonds. To solve this problem, in this work we used the theory of intensities of vibrational transitions in polyatomic molecules.[8,9] This theory makes it possible to take into account (in the harmonic approximation) a) the Boltzmann distribution of the absorption centers over their vibrational levels, b) the contribution of "hot" transitions to the intensities of vibrational bands, c) induced radiation from "hot" levels of vibrational energy of the molecule, and d) dependence of the probability of transition on the quantum number of the vibrational level to which the transition occurs. It follows from this theory that the intensities of the bands of fundamental vibrations of the molecule are independent of temperature. At the same time, the intensities of the overtone bands and those of the second-order combination vibrations slightly increase as temperature increases; in this case, the lower the frequency of considered vibrational transition, the larger is the increase in the intensity.[9]

The populations of different vibrational levels of the molecule are defined not only by temperature, but also by their mutual positions (primarily, by the distance to the zero energy level). The latter is highly dependent on the composition, structure, and dynamic properties of the molecule. Therefore, for a rigorous interpretation of experimental results,[6] the vibrational spectrum of the Cl...H...OSO_2 complex should be calculated at various temperatures.

At the same time, information of general character concerning the temperature dependence of the CA intensity can be obtained by analyzing the temperature effect on the spectra of any molecular systems with strong symmetric H-bonds. The $H_3O_2^-$ and $H_5O_2^+$

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ions, which are the simplest stable hydrates of the hydroxyl ion and proton,[7] are the most appropriate species to be used as such systems. Having similar chemical composition and dynamic properties,[7] these species differ in the number of atoms by about a factor of 1.5.

Results and Discussion

In this work, the IR spectra of the $H_3O_2^-$ and $H_5O_2^+$ ions were calculated in the 4000—0 cm^{-1} region in the temperature interval between 10 and 450 K. The calculations of frequencies and intensities of all vibrational transitions were performed in the anharmonic approximation.[10] Initial data on the geometry, dynamic, and electrooptical parameters of both systems were obtained previously.[11] The calculated values of the coefficients of filling the zero vibrational energy levels of the ions under study at various temperatures are presented in Table 1. As can be seen from this table, the population of the zero level decreases by more than 10% at room temperature even for the $H_3O_2^-$ ion containing only five atoms. The fraction of excited species is approximately doubled on going to the larger $H_5O_2^+$ ion. Only one third of the molecules remains nonexcited at $T = 300$ K in the $(MeO)_2H^-$ ion containing 11 atoms.[11] Thus, considering the intensities of the vibrational bands of polyatomic molecules, one should take into account the "hot" transitions.

The calculations of frequency dependences of the intensities of the second-order vibrational transitions (Fig. 1) using the formulas reported in Ref. 9 showed that appreciable changes in the intensities of the vibrational bands occur only at low temperatures ($T <$ 200 K) and vibration frequencies ($\nu <$ 200 cm^{-1}). The effect in question is rapidly decreased as temperature and frequency increase. For instance, the increase in the temperature from 300 to 500 K at a vibration frequency of 300 cm^{-1} results in an increase in the intensity of transition by 40%, whereas the analogous increase in temperature at a frequency of ~1000 cm^{-1} is followed by an increase in the intensity of the vibrational transition only by 5%.

Hence, it follows that the temperature dependence of the continuous absorption is determined by the fraction of the vibrations of higher orders in the absorption in the low-frequency region. In the case of complexes with strong symmetric H-bonds, the most intense are the bands of overtones and combination modes corresponding to simultaneous shifts of the central proton along and across the hydrogen bridge.[11] The frequencies of all such vibrations lie above 1200—1500 cm^{-1}; therefore, there are no reasons to expect any appreciable changes in the intensity of CA for such type complexes. In fact, direct calculations of the integrated intensities of the vibrational transitions in the 1000—4000 cm^{-1} region for the $H_3O_2^-$ and $H_5O_2^+$ ions showed that these intensities increase only by fractions of a per cent as temperature increases from 300 to 340 K.

Table 1. Coefficients of filling the zero vibrational energy levels of the $H_3O_2^-$ and $H_5O_2^+$ ions at various temperatures

Ion	Temperature/K					
	100	200	300	340	400	450
$H_3O_2^-$	1.000	0.977	0.894	0.832	0.765	0.697
$H_5O_2^+$	0.998	0.929	0.758	0.662	0.571	0.491
$(MeO)_2H^-$			0.382[11]			

In conclusion, let us consider changes in the spectrum occurring when an isolated species passes to the condensed phase. In most cases, the structural inhomogeneity of a system caused by thermal fluctuations is known to be rapidly increasing with temperature. It manifests itself as so-called inhomogeneous broadening of all vibrational bands of the spectrum (whereas their integrated intensity remain unchanged). Usually, this broadening (50—100 cm^{-1}) is a determining factor, since it exceeds several times the broadening due to the "hot" transitions and other mechanisms.

From the aforesaid, it follows that the intensity of CA, which is a totality of a large number of completely overlapped bands, is independent of temperature in the case of a condensed phase. At the same time, the peak intensities of the bands (of both fundamental and combination vibrations) standing out against the background will decrease with increasing temperature because of their broadening. Thus, temperature changes in the spectrum of a complex with symmetric H-bond[6] are in complete agreement with the current concept of the nature of this spectrum.

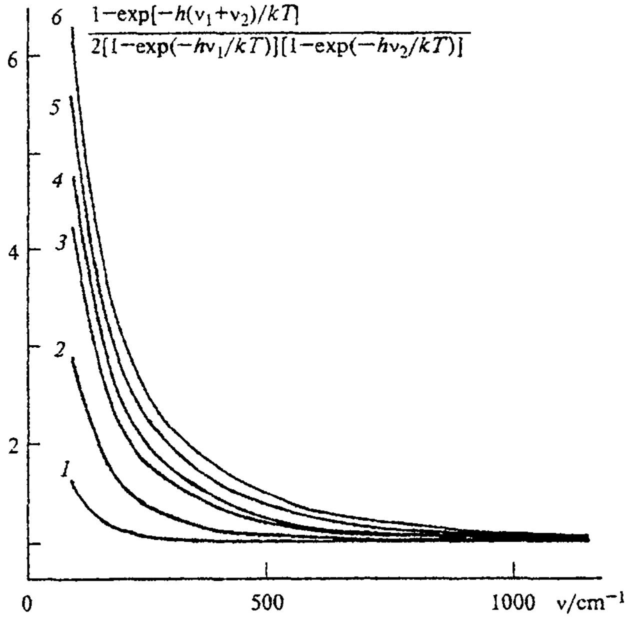

Fig. 1. Frequency dependence of the thermal factor at the absorption coefficient of the second-order vibrational transition at T = 100 (*1*), 200 (*2*), 300 (*3*), 340 (*4*), 400 (*5*), and 450 (*6*) K.

References

1. E. D. Becker, in *Hydrogen Bonding*, Eds. Hadzi and H. W. Thompson, Pergamon Press, London—New York—Paris, 1958, 155.
2. G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, Freeman, San Francisco—London, 1960.
3. G. Zundel, in *The Hydrogen Bond, Recent Developments in Theory and Experiments*, Eds. P. Schuster, G. Zundel, and C. Sandorfy, North Holland, 1976, 687.
4. D. Schioberg and G. Zundel, *Chem. Phys. Lett.*, 1976, **38**, 334.
5. A. Hayd, E. G. Weidemann, and G. Zundel, *J. Chem. Phys.*, 1979, **70**, 86.
6. I. S. Kislina and V. D. Maiorov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1461 [*Russ. Chem. Bull.*, 1997, **46**, 1396 (Engl. Transl.)].
7. G. V. Yukhnevich, E. G. Tarakanova, V. D. Maiorov, and N. B. Librovich, *Usp. Khim.*, 1995, **64**, 963 [*Russ. Chem. Rev.*, 1995, **64**, 901 (Engl. Transl.)].
8. L. A. Gribov, *Teoriya intensivnostei v infrakrasnykh spektrakh mnogoatomnykh molekul* [*Theory of Intensities in the IR Spectra of Polyatomic Molecules*], Izd-vo Akad. Nauk SSSR, Moscow, 1963, 108 pp. (in Russian).
9. M. V. Vol'kenshtein, L. A. Gribov, M. A. El'yashevich, and B. I. Stepanov, *Kolebaniya molekul* [*Molecular Vibrations*], Nauka, Moscow, 1972, 699 pp. (in Russian).
10. A. I. Pavlyuchko, Diss. dokt. khim. nauk [D. Sci. Chem. Thesis], M. V. Lomonosov Moscow State University, Moscow, 1992, 114 pp. (in Russian).
11. G. V. Yukhnevich, E. G. Tarakanova, V. D. Mayorov, and N. B. Librovich, *J. Mol. Struct.*, 1992, 265; 237.

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