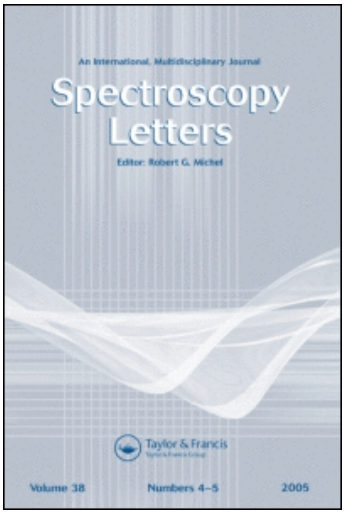

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Zhelyaskov, V. , Georgiev, G. , Nickolov, Zh. and Miteva, M.(1989) 'Raman Temperature Study of 12-Crown-4 Using Fourier Deconvolution of CH Stretching Spectra', Spectroscopy Letters, 22: 1, 15 — 29
To link to this Article: DOI: 10.1080/00387018908053855
URL: http://dx.doi.org/10.1080/00387018908053855

SPECTROSCOPY LETTERS, 22(1), 15-29 (1989)

RAMAN TEMPERATURE STUDY OF 12-CROWN-4 USING FOURIER DECONVOLUTION OF CH STRETCHING SPECTRA

Key words: Crown, Temperature, Raman Spectroscopy, CH Spectra, Fourier Deconvolution, Intramolecular Interaction, Fermi Resonance

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ABSTRACT

The Raman CH stretching spectra of 12C4 in water solution, for temperatures from 5 to 80 ^{o}C, are studied. For the first time, Fourier deconvolution technique is applied to resolve the overlapped components in the corresponding isotropic and anisotropic spectra. The results are treated by means

of a model, explaining the variety of resolved components with a splitting of the unperturbed CH stretching vibration, owing to intramolecular interactions. The temperature behaviour of the coupling constants of these interactions is discussed.

INTRODUCTION

Recently the CH stretching spectra of some crown ethers (12-Crown-4,15-Crown-5 and 18-Crown-6) and their complexes with Li^+, Na^+, K^+ and Cu^{2+} in solution were studied using Fourier deconvolution technique[1]. A model, which explains the variety of components in the resolved spectra by means of a splitting of the unperturbed CH stretching frequency owing to intramolecular and Fermi resonance interactions, was introduced. Using the frequencies of the resolved components in the isotropic and anisotropic spectra, the constants for intramolecular interactions and Fermi resonance as well as all parameters according to the model were calculated for pure crowns and their complexes. It was established that complexation leads to the increase in the frequency of the unperturbed CH stretching vibration owing to the increase in the strain of the crown molecule with complexation. This tendency is most pronounced in the case of Na^+-crown complexes. The interaction constants do not change

significantly with complexation whithin the limits of the estimated error.

It is interesting to be known in what extent the temperature variation affects the interaction constants and all parameters according to the model. That is why in this work the CH Raman stretching spectra of 12-Crown-4 in water solution are studied in the temperature interval 5-80 ^{o}C.

EXPERIMENTAL AND PROCESSING OF THE SPECTRA

The 12-Crown-4 (12C4) was purchased from Merck and used without further purification. Double distilled water was used as a solvent. In comparison with other possible solvents, water is very suitable in this case becouse of both the great solubility of crown in it and relatively small overlapping between the CH stretching vibrations of crown and the low frequency wing of OH stretching vibration exists, which permits us to obtain pure CH stretching spectra after simple digital operations.

Raman spectra were obtained using an optical spectrum analyser OSA 500 (B&M Spectronic). The 514.5 nm line of a Spectra Physics argon ion laser, Model 2020-05, was used for excitation. Data acquisition was performed by means of Apple IIe computer interfaced to the spectrometer. The slit width was chosen to be equal

to the spectral distance between the channels of OSA - 1.4 cm^{-1}, thus determining the accuracy of the data obtained.

Spectra were measured under paralel and perpendicular polarizations. The base line due to O-H stretching vibrations was subtracted by means of a digital difference method. The isotropic and anisotropic spectra were calculated according to the theory of the Raman scattering and they were corrected accounting for frequency dependence of the Raman intensity[2] All data are corrected for the spectral transmittance of the receiving system. The deconvolution procedure was described in details elsewhere [3-5]

RESULTS

The isotropic (A-C) and anisotropic (E-G) CH stretching spectra of 12C4 in water solution, before and after deconvolution, are presented in Figure 1, for a number of temperatures. Two and three components are observed in the isotropic and in the anisotropic deconvoluted spectra of the crown, respectively. Their frequencies are shown in Table 1.

The positions of the components in the isotropic spectra, Table 1, do not coinside with the positions of the components in the anisotropic spectra, within the

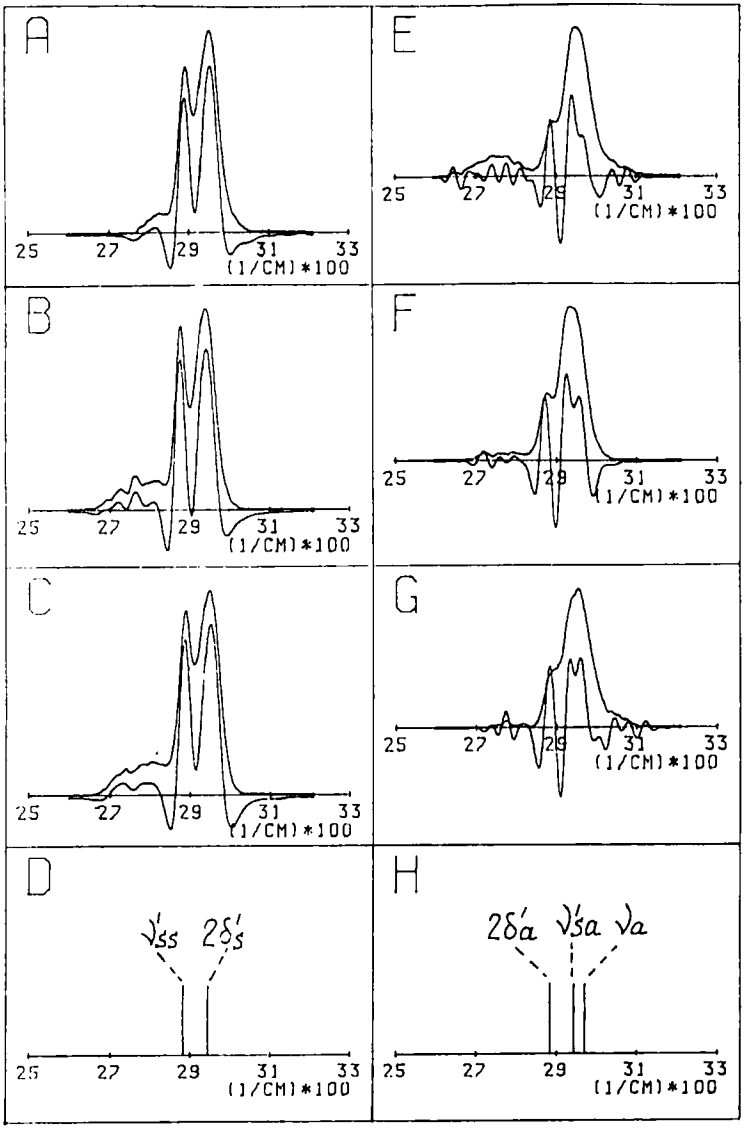

FIG. 1. Isotropic (A-C) and anisotropic (E-G) Raman CH stretching spectra of 12C4, before and after Fourier deconvolution, at various temperatures: (A), (E) 5 °C; (B), (F) 22 °C; (C), (G) 80 °C. Assignment of the isotropic (D) and anisotropic (H) components according to the model.

TABLE 1. Frequencies of the Resolved Components in the CH Spectra of 12C4 for the Investigated Temperatures.

Temperature t^{o}	Isotropic Spectrum		Anisotropic Spectrum		
	1^{-st}	2^{-nd}	1^{-st}	2^{-nd}	3^{-rd}
5	2879	2943	2876	2931	2961
13	2879	2943	2874	2930	2962
22	2878	2943	2873	2927	2958
40	2878	2942	2873	2926	2956
80	2877	2943	2871	2924	2954

limits of the experimental error, ca 1.4 cm^{-1}. So, it can be concluded that five independent components are observed in the spectra. The mutually independent, different frequency shifts of the components with the temperature increase support the last conclusion.

It can be concluded from Table 1, that the temperature increase leads to the decrease in the frequency of the anisotropic components (6 - 7 cm^{-1}) and to some changes in their relative intensities. The positions and relative intensities of the isotropic components do not change within the limits of the experimental error.

DESCRIPTION OF THE MODEL AND ASSIGNMENT OF THE COMPONENTS

Interpretation of the CH stretching region and the designation of the observed components in the literature is controversial[6] . Recently, the complex shape of the OH stretching spectra was interpreted by means of intra-, inter - molecular and Fermi resonance interactions[7,8] . Similar considerations for CH FTIR spectra of cyclobuthene[9] and for Raman spectra of $(CH_3)_4N^+$ in the methyl stretching region[10] were made.

In our previous work, the model which concerns the interactions in and between CH_2 groups in crowns is described. We suppose that three effects are responsible for the splitting of the unperturbed CH stretching vibration ν_u, Fig. 2. The first effect is intramolecular interaction owing to coupling of the two CH oscilators of the CH_2 group. It leads to the splitting of ν_u into symmetric (ν_s) and asymmetric (ν_a) components and V_1 (half the distance Δ_1 between them) is the coupling constant. The second effect is intramolecular interaction owing to a coupling of every two adjacent CH_2 groups in the crown molecule, inter-bond coupling [9]. It leads to the subsequent splitting of ν_s and ν_a into 'in-phase' and 'out-of-phase' vibrations, ν_s into ν_{ss} and ν_{sa} with a coupling constant V_s(V_s is the half of Δ_{2s}) and ν_a into

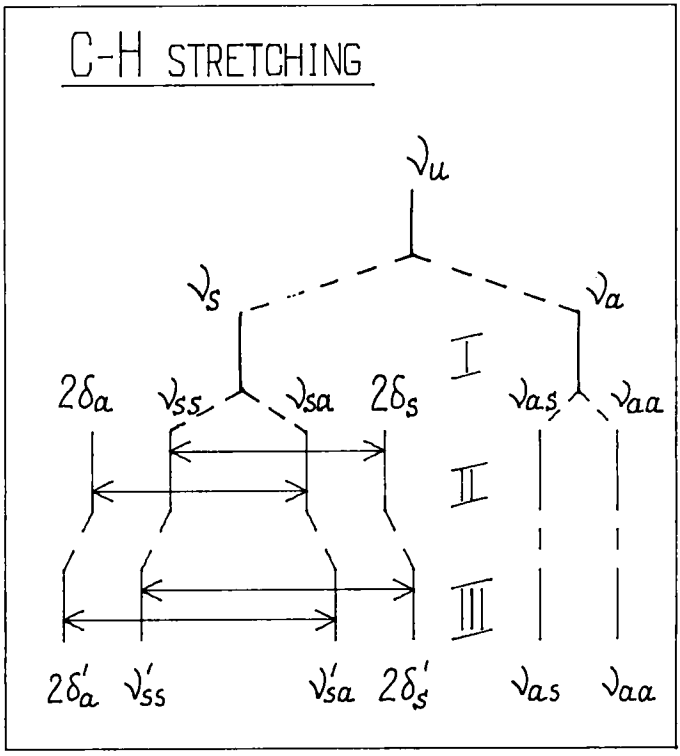

FIG. 2. Model diagram of the processes leading to a splitting of the unperturbed CH stretching vibration. For explanation of the assignments, see text.

ν_{as} and ν_{aa} with a coupling constant V_a (V_a is the half of Δ_{2a}).

It is suggested that bending (scissor) vibration of CH_2 is split too, owing to inter-bond coupling [1]. As can be easily evaluated taking into account some typical values for CH_2 bending frequency of crowns [11,12] and overtone ancharmonic constants (10 - 15 cm^{-1})

[10] the overtones of the splitted bending vibration (designated as $2\delta_a$ and $2\delta_s$ in Fig. 2 are situated in the CH stretching region too.

The third effect, Fig. 2, is Fermi resonance between the bending overtones and the components of splitted ν_s vibration in accordance with their symmetry. The symmetry of the components in the two interacting pairs is similar because their origin is similar - a splitting of a symmetric vibration owing to inter-bond coupling. ν_{ss} and $2\delta_s$, with separation Δ_{os} are transformed into ν_{ss}' and $2\delta_s'$ with separation Δ_{3s}; ν_{sa} and $2\delta_a$, with separation Δ_{oa}, are changed into ν_{sa}' and $2\delta_a'$, with separation Δ_{3a}. The Fermi resonance constants of these two proceses are denoted by W_s and W_a, respectively.

In this way the components which could be observed are three symmetric components in the isotropic spectra and three asymmetric components in the anisotropic spectra. It must be noted, that according to the theory of Raman scattering symmetric and asymmetric components appear in the isotropic and anisotropic spectra, respectively. Their correspondence to the five components, observed in our spectra, is shown in Fig. 1D,H. It is assumed that in 12C4 Δ_{2a} is negligibely small [1], as in water [7]. So, $\nu_{as} \equiv \nu_{aa} \equiv \nu_a$. The mutual positions of the symmetric (s) and asymmetric (a)

components after splitting ("s" > "a" or "a" > "s") depends on the sign of the matrix element of the interaction[9] . In our model - diagram, Fig. 2, these designations are chosen to be in accordance with our experimental observations and subsiquent calculations.

The following set of equations apply to this system:

$$2\delta_a' + \nu_{sa}' = 2\delta_a + \nu_{sa} \quad (1)$$

$$2\delta_s' + \nu_{ss}' = 2\delta_s + \nu_{ss} \quad (2)$$

$$2\delta_s - 2\delta_a = d \quad (3)$$

$$\Delta_{3a}^2 = \Delta_{oa}^2 + 4W_a^2 \quad ; \quad \Delta_{3s}^2 = \Delta_{os}^2 + 4W_s^2 \quad (4)$$

$$\frac{\nu_{ss} + \nu_{sa}}{2} = \nu_s \quad ; \quad \frac{\nu_s + \nu_a}{2} = \nu_u \quad (5)$$

$$\Delta_1 = \nu_a - \nu_s \; ; \qquad V = \Delta_1 / 2 \quad (6)$$

$$\Delta_{2s} = \nu_{sa} - \nu_{ss} \; ; \quad V_s = \Delta_{2s} / 2 \quad (7)$$

$$\Delta_{oa} = \nu_{sa} - 2\delta_a \; ; \quad \Delta_{os} = 2\delta_s - \nu_{ss} \quad (8)$$

$$\Delta_{3a} = \nu_{sa}' - 2\delta_a' \; ; \quad \Delta_{3s} = 2\delta_s' - \nu_{ss}' \quad (9)$$

This set of equations can be solved by introducing the following initial conditions. It is assumed that symmetric and asymmetric Fermi resonance constants are equal, $W_s = W_a = W$. The equality of these constants for water is obtained after the solution of similar system of equations [7] . The distance between $2\delta_s$ and $2\delta_a$ - d

is assumed equal to 40 cm^{-1} [1]. The values for intramolecular and Fermi resonance coupling constants as well as for unperturbed frequency ν_u are presented in Table 2.

DISCUSSION

As can be seen in Table 2, the intramolecular constant V_1 and Fermi resonance constant W do not change with the temperature increase. The unsensitivity of V_1 (the splitting Δ_1 respectively) to the temperature variation could be owing to one of the two possible reasons:

-the frequencies of the unperturbed vibrations of the two CH oscilators belonging to CH_2 group do not change with the temperature increase and therefore the exact resonance between them take place for all investigated temperatures;

-the frequencies of the mentioned unperturbed vibrations change in one and the same way with the temperature increase and therefore the condition for an exact resonance is preserved too.

As can be seen in Table 2, the frequency of the unperturbed CH oscilator ν_u decreases with temperature increase. From that fact, it can be concluded that probably the second reason is responsible for the temperature behaviour of V_1 In the case of water

TABLE 2. The Values of the Calculated Intramolecular and Fermi Resonance Coupling Constants and the Unperturbed CH Frequency for the Investigated Temperatures. All Data in cm^{-1}.

Temperature (°C)	W	V_1	V_s	ν_u
5	25	29	13	2933
13	26	30	10	2932
22	25	29	10	2929
40	25	29	9	2928
80	25	29	7	2925

solutions of crowns, solute-solute and solute-solvent interactions through CH bonds are negligibely small (CH bonds are absent). Therefore the redistribution of the electron density of the crown molecule owing to temperature increase leads to the equal perturbation of the CH stretching oscilators and to the equal shifts in their frequencies. In contrast, in the case of water[7], the two hydrogen bonds of every water molecule are sligtly different at room temperatures owing to local non-uniformities and the two OH stretching oscilators are not in exact resonance. At temperatures near to the boiling temperature, the strength of the H bonds is negligibly small so the C_{2v} symmetry of water molecule recovers and exact resonance take place, that means the intramolecular splitting increases.

The inter-bond coupling constant V_S shows a tendency to a decrease with the temperature increase. The temperature behaviour of V_S could be explained with the decrease in the interaction between the adjacent CH_2 groups owing to the increase in the internal energy of the crown molecule with the temperature increase. The temperature behaviour of the intermolecular interaction in water[7] is similar but in that case owing to the decrease in the strength of the H bonds with temperature , which leads to the decrease in the interaction between the water molecules.

CONCLUSION

To the best of our knowledge these are the first temperature investigations of CH stretching region of 12C4 in water solution using Fourier deconvolution technique. The temperature behaviour of the coupling constants and the parameters, calculated according to the presented model, are in agreement with the physical ground of the model and justify assumptions made.

ACKNOWLEDGEMENT

This work was done as a part of problem No 261 sponsored by the Bulgarian Ministry of Culture, Science and Education.

REFERENCES

1. V. Zhelyaskov, G. Georgiev, Zh. Nickolov and M. Miteva, Mol. Phys., 1988, submitted for publication

2. D. A. Long, Raman Spectroscopy, McGrow-Hill, New York(1977)

3. J. K. Kauppinen, D. J. Moffat, H. H. Mantsch and D. C. Cameron, Appl. Spectrosc. 35, 271(1981); J. K. Kauppinen, D. J. Moffat, D. C. Cameron and H. H. Mantsch, Appl. Opt., 20, 1866(1981)

4. R. N. Jones and K. Shimokoshi, Appl. Spectrosc., 37, 59(1983); K. Shimokoshi and R. N. Jones, Appl. Spectrosc., 37, 67(1983)

5. G. Georgiev, T. Kalkanjiev and V. Petrov, Spectr. Lett., 16, 753(1983)

6. R. C. Spiker, JR and I. W. Levin, Biochim. Biophys. Acta 388, 61(1975)

7. V. Zhelyaskov, G. Georgiev, Zh. Nickolov, J. Raman Spectrosc., 19, 1988, in press

8. V. Zhelyaskov, G. Georgiev, Zh. Nickolov and M. Miteva, Mol. Phys., 63, 1988, in press

9. J. E. Baggot, H. J. Claset and I. M. Mills, Spectrochim. Acta, 42A, 319(1982)

10. G. Kabish and G. Mobius, Spectrochim. Acta, 38A, 1195(1982)

11. M. Fouassier and JC. Lassegues, J. Chim. Phys., 75, 865(1978), (in french)

12. K. Fukushima and Y. Tamaki, J. Mol. Struct., 162, 157(1987)

Date Received: 08/03/88
Date Accepted: 09/12/88