



UDC: 535.012

Shavkatjon YORMATOV,
PhD student of SamSU
E-mail: shavkatjonyormatov1710@gmail.com
Abduvakhid JUMABAEV,
DSc, professor of SamSU
Absanov AHMAD,
PhD, associate professor of SamSU
Marjona MUSTAFOYEVA,
Master student of SamSU

PhD Eshonqulov G'.taqrizi asosida

INVESTIGATING ACETONITRILE VIBRATIONS IN PROTIC AND APROTIC MIXTURES

Annotation

Polarized Raman spectroscopy and two-dimensional correlation spectroscopy (2D-COS) were used to study the vibrational behavior of acetonitrile (ACN) in mixtures with dimethyl sulfoxide (DMSO) and water. The Raman non-coincidence effect (NCE) of the $C\equiv N$ stretching mode revealed weak dipole interactions in ACN-DMSO and strong hydrogen bonding in ACN-water. Synchronous and asynchronous 2D-COS spectra showed that ACN vibrations respond differently to solvent concentration changes, with significant spectral shifts in water due to hydrogen bonding. These findings demonstrate how 2D-COS effectively reveals solvent-induced vibrational interactions in molecular systems.

Key words: Acetonitrile, polarized Raman spectroscopy, synchronous 2D-COS, asynchronous 2D-COS, intermolecular interactions.

ИССЛЕДОВАНИЕ КОЛЕБАНИЙ АЦЕТОНИТРИЛА В ПРОТОННЫХ И АПРОТОННЫХ СМЕСЯХ

Аннотация

Поляризованная Раман спектроскопия и двумерная корреляционная спектроскопия (2D-КОС) использовались для изучения колебательных свойств ацетонитрила (АЦН) в смесях с диметилсульфоксид (ДМСО) и водой. Эффект несовпадения частот (ЭНЧ) для валентного колебания $C\equiv N$ показал слабые дипольные взаимодействия в системе АЦН-ДМСО и сильное водородное связывание в системе АЦН-вода. Синхронные и асинхронные 2D-КОС спектры выявили различную реакцию колебаний АЦН на изменения концентрации растворителя, причем в воде наблюдались значительные спектральные сдвиги из-за водородных связей. Эти результаты демонстрируют эффективность 2D-КОС в выявлении раствор-зависимых колебательных взаимодействий в молекулярных системах.

Ключевые слова: Ацетонитрил, поляризованная рамановская спектроскопия, синхронная 2D-КОС, асинхронная 2D-КОС, межмолекулярные взаимодействия.

ASETONITRIL TEBRANISHLARINING PROTİK VA APROTİK ARALASHMALARDAGI TADQIQI

Annotatsiya

Qutblangan Raman spektroskopiyasi va ikki o‘lchamli korrelyatsion spektroskopiya (2D-KOS) yordamida asetonitril (ACN)ning dimetilsulfoksid (DMSO) va suv bilan aralashmalaridagi tebranish xususiyatlari o‘rganildi. $C\equiv N$ valent tebranishi uchun Raman no-moslik effekti (NME) ACN-DMSO tizimida zaif dipol o‘zaro ta’sirlari va ACN-suv tizimida kuchli vodorod bog‘lanishlarini aniqladi. Sinxron va asinxron 2D-KOS spektrlari ACN tebranishlarining erituvchi konsentratsiyasi o‘zgarishiga turlicha javob berishini ko‘rsatdi, suvda esa vodorod bog‘lari sababli sezilarli spektral siljishlar kuzatildi. Ushbu natijalar 2D-KOS metodining erituvchi ta’sirida tebranish o‘zaro ta’sirlarini aniqlashdagi samaradorligini ko‘rsatadi.

Kalit so‘zlar: Asetonitril, Qutblangan Raman spektroskopiyasi, sinxron 2D-KOS, asinxron 2D-KOS, molekulararo ta’sirlar.

Introduction. A useful technique for investigating the nature of polar bonds and differentiating between molecular structures in chemical substance analysis is vibrational spectroscopy [1-2]. Because of its adaptability, it is now essential in many fields, including industrial applications, biochemistry, and chemistry connected to health [3-5]. One of the intriguing aspects of vibrational spectroscopy lies in its ability to uncover subtleties in molecular behavior. For instance, some polar vibrational modes display shifts in their vibration wavenumbers when observed through IR and Raman spectroscopy, reflecting the differing sensitivities of these techniques [6]. Even more fascinating is the discrepancy observed within Raman spectroscopy itself, where the frequencies of certain vibrational modes in isotropic and anisotropic components do not coincide [7-9]. This phenomenon, known as the non-coincidence effect (NCE), provides critical insights into intermolecular interactions, molecular orientations, molecular symmetry and dynamic processes within complex systems. As a result, studying NCEs has become an essential approach for understanding and predicting molecular structures with greater precision, further emphasizing the importance of vibrational spectroscopy in modern science [10-11]. In this paper, we analyzed Raman NCE for the $C\equiv N$ polar bond of acetonitrile (ACN). To date, various intermolecular processes involving this polar bond of ACN have been systematically investigated. The vibrational

wavenumber of the C≡N polar bond, which carries an extremely sensitive environmental probe, depends on the medium's solvation characteristic [12]. The vibrational properties of the C≡N polar bond were also analyzed using Density Functional Theory (DFT) [13]. This analysis explained the mechanism by which the vibrational wavenumber of this triple bond exhibits a blue shift in intermolecular hydrogen bonding. It was found that the triplet bond length is strongly dependent on the H-bond length. It has also been reported that the triple bond strength constant of acetonitrile in aqueous media unexpectedly increases, leading to a blue shift in the corresponding stretching vibration, which is in contrast to the typical consequence of hydrogen bonding in the vibrational wavenumbers of the accepting groups, i.e., a red shift in the wavenumber [14]. The observation of various anomalous effects in the spectral properties of the C≡N polar bond of the ACN molecule necessitates the study of processes involving this bond using more extensive and effective methods. We have studied the nature and strength of intermolecular interaction forces in ACN by determining the Raman NCE of the polar C≡N bond. Studying this effect allows us to understand the formation of molecular systems in ACN and predict their precise geometric structure. Also, in this work, two-dimensional Raman-correlation spectroscopy (2D-COS) analyses of ACN solutions with solvents water, and dimethyl sulfoxide (DMSO), which have different intermolecular interaction natures, were performed. This method is one of the interactive methods for analyzing the spectral properties of vibrational modes in the solution phase [15].

Methods. Polarized and unpolarized Raman spectra of neat acetonitrile and its binary solutions with Water, and DMSO at different concentrations were recorded using a Renishaw Invia Raman spectrometer with a 1200 lines/mm grating. The excitation light source was a Spectrum Stabilized Laser Module with a 532 nm wavelength and 100 mW of power. Raman spectra were acquired at room temperature (298 K) using a Renishaw CCD Camera detector with $\times 100$ objective in a backscattering geometry configuration.

Results and discussions.

Raman non-coincidence effect analysis

The principle of the technique of polarized Raman spectroscopy depends on the mutual orientation of the electric field vectors of light incident on and scattered from a sample. If the field vectors are parallel to each other, a polarized Raman spectrum is formed, and if they are perpendicular to each other, an unpolarized Raman spectrum is formed. Using these spectral results, it is possible to generate isotropic and anisotropic Raman spectra of a vibrating polar bond. Figure 1 shows the isotropic and anisotropic Raman spectra of the C≡N stretching mode of ACN. The peak wavenumber of the isotropic Raman spectrum of the C≡N stretching mode is 2253 cm^{-1} . The wavenumber of the anisotropic component is 2254.4 cm^{-1} . The difference between these wavenumbers is $+1.4 \text{ cm}^{-1}$. The positive splitting of the Raman NCE indicates that the C≡N triplet bonds are arranged antiparallel to each other. Antiparallel ordered triplet bonds generate resonantly coupled dipole couples. These dipole couples are connected by resonant energy transfer. The small value of the Raman NCE indicates that the resonance energy transfer between dipole pairs is very weak. This result indicates that the most sensitive part of the ACN molecule to intermolecular interactions is C≡N. In order to study the intermolecular interaction processes of this triplet bond, Raman spectra of binary mixtures of ACN with DMSO and Water were recorded. Based on the obtained spectral data, two-dimensional synchronous and asynchronous correlation spectra were generated.

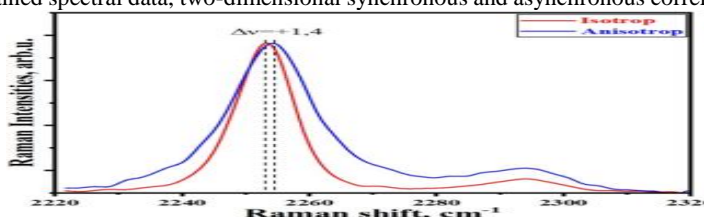


Figure 1. Isotropic and anisotropic Raman spectra of the C≡N stretching mode of ACN.

Two-Dimensional Correlation Spectroscopy analysis

Synchronous and asynchronous 2D-Raman correlation spectra of an ACN and DMSO solution at varying concentrations were obtained (Fig. 2a, b). Synchronous 2D-COS identifies the correlation between two signals occurring simultaneously at the same frequency, revealing how closely different vibrational modes respond to concentration changes. The intensity of the colours in the synchronous spectrum represents the strength of these correlations. Positive correlations, where two modes change in the same direction, are typically shown in warm colours such as red, yellow, or orange. Conversely, anticorrelated modes, which vary in opposite directions, are depicted in cool colours like blue. Asynchronous 2D-COS, on the other hand, highlights phase differences or time lags between vibrational modes by illustrating how signals evolve relative to each other across frequencies or time. The colour intensity in asynchronous spectra provides insight into the interaction sequence of different vibrational modes. When the x-axis signal precedes the y-axis signal, warm colours (e.g., red or orange) appear, indicating dominance. Meanwhile, cool colours (e.g., blue) suggest that the y-axis signal is more prominent than the x-axis signal. It can be seen that a strong signal appears in the synchronous spectrum (Fig.2a). This strong signal corresponds to the fundamental stretching vibration of the C≡N triple bond of ACN, at 2253 cm^{-1} . The dark red central area shows that the shift in this vibrational mode is due to changes in DMSO concentration.

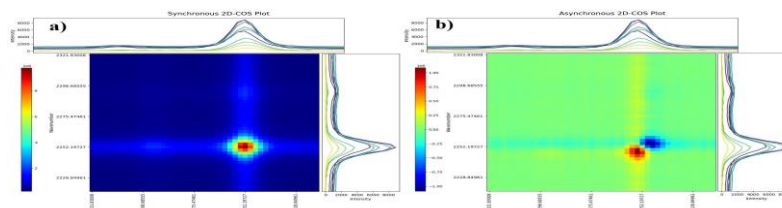


Figure 2. Synchronous (a) and asynchronous (b) 2D Raman correlation spectra of the ACN-DMSO mixture were constructed from the selected concentration range from 1 to 0.05 mole fraction.

The map is symmetric, with the highest intensity along the main diagonal line. This means that the ground vibrational mode of ACN changes synchronously with increasing DMSO concentration. The high intensity observed along the diagonal line, however, the weakness of the off-diagonal regions, indicates that the main interaction is due to the vibrational mode of the C≡N bond. This means that there is a significantly variable vibrational coupling between ACN and DMSO. An asynchronous spectrum shows interactions that are delayed by changes in concentration (Fig 2b). This spectrum has two distinct contrasting (red-blue) signals around the wavenumber 2253 cm⁻¹. This situation indicates the presence of a strong correlation, that is, the C≡N vibration of ACN and the effect of DMSO molecules show asynchronous modulation. There are red and blue signals in this region, which reflect different stages of the intermolecular hydrogen bonding effect. Red regions indicate an increase, while blue regions indicate a decrease in intensity, indicating that the vibrational mode is associated with two different transformation processes. The green background means that there is not much phase difference in this system overall; however, there is a clear signal at the center region. This indicates that the vibrational coupling between molecules has a certain phase delay with increasing DMSO concentration. As a general conclusion from the synchronous and asynchronous spectra, it can be said that the stretching vibration of the C≡N bond is strongly reflected in the synchronous spectrum, indicating its important role in ACN-DMSO mixtures. The asynchronous spectrum shows phase delays and, in particular, strong asynchronous changes in the C≡N bond indicate the presence of intermolecular interactions. These results indicate that the ACN-DMSO interactions are mainly modulated by hydrogen bonding effects, which may account for the blue shift of the C≡N vibrations, as opposed to the usual red shift. In the next analysis, 2D-COS was discussed for mixtures with water, which belong to the type of clusters with strong hydrogen bonds, i.e., protic solvents. Such analysis helps to understand how vibrational properties change based on intermolecular hydrogen bonds and solvent effects. Synchronous and asynchronous 2D-Raman correlation spectra of an ACN and water solution at varying concentrations were obtained (Fig. 3a, b). The strongest shift was detected around 2253 cm⁻¹, similar to that observed with DMSO (Fig.3a). The dark red color indicates that this wavenumber is significantly modulated by changes in water concentration. The presence of a dominant signal along the diagonal indicates that the interaction of water on ACN molecules occurs symmetrically. In addition, this may indicate that the Raman intensity increases uniformly across the entire spectrum. This suggests that there are other vibrational changes associated with water concentration. It is possible that the deformation vibrations or low-energy modes of ACN molecules may also change. The asynchronous 2D-COS spectrum has red-blue regions at 2253 cm⁻¹ (Fig.3b). This signal indicates that the C≡N bond is modulated differently with increasing water concentration.

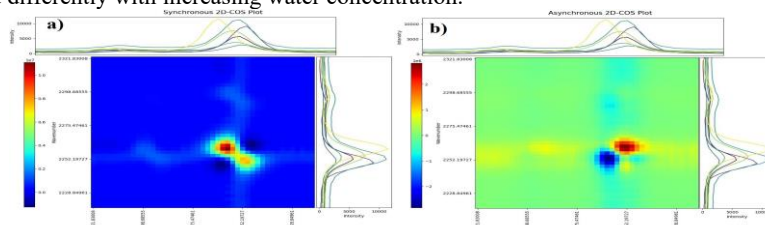


Figure 3. Synchronous (a) and asynchronous (b) 2D Raman correlation spectra of the ACN-Water mixture were constructed from the selected concentration range from 1 to 0.05 mole fraction.

The red and blue colors indicate that the C≡N vibrational state of ACN changes differently with water. This shows that the fundamental mode reacts with a phase delay. The absence of strong off-diagonal signals suggests that although the fundamental vibrations of ACN molecules are changing under the influence of water, there are no other ambiguous bonds. It is likely that ACN molecules do not form strong hydrogen bonds, but rather are dominated by dipole-dipole interactions. In general, ACN-Water mixtures have strong hydrogen bonds and significant spectral changes, while in the ACN-DMSO system, dipole-dipole interactions are dominant and the Raman intensity does not change much.

Conclusions. Polarized Raman spectroscopy and 2D-COS were used to study the intermolecular interactions of ACN with solvents (DMSO and water). The synchronous 2D-COS spectrum showed that the C≡N stretching vibration changed in the same direction with the increase in DMSO concentration, indicating the main interaction in the ACN-DMSO system. The asynchronous spectrum revealed phase delays between the C≡N vibration of ACN and DMSO molecules. In water mixtures, the C≡N stretching vibration showed different behavior with increasing water concentration, suggesting the role of hydrogen bonding. In the ACN-DMSO system, dipole-dipole interactions dominate, with little change in Raman intensity. However, in ACN-water mixtures, strong hydrogen bonds and significant spectral shifts were observed. These results demonstrate the effectiveness of 2D-COS in understanding the vibrational changes and intermolecular interactions in ACN solutions.

REFERENCES

1. J.X. Cheng, X.S. Xie, "Vibrational spectroscopic imaging of living systems: An emerging platform for biology and medicine," *Science*, 350(6264), (2015). <https://doi.org/10.1126/science.aaa8870>
2. G.J. Thomas Jr., "Raman spectroscopy of protein and nucleic acid assemblies," *Annu. Rev. Biophys. Biomol. Struct.*, 28, 1-27 (1999). <https://doi.org/10.1146/annurev.biophys.28.1.1>
3. W.H. Su, D.W. Sun, "Fourier Transform Infrared and Raman and Hyperspectral Imaging Techniques for Quality Determinations of Powdery Foods: A Review," *Compr. Rev. Food Sci. Food Saf.*, 17(1), 104–122 (2018). <https://doi.org/10.1111/1541-4337.12314>
4. Z. Movasaghi, S. Rehman, I.U. Rehman, "Raman spectroscopy of biological tissues," *Appl. Spectrosc. Rev.*, 42, 493-541 (2007). <https://doi.org/10.1080/05704920701551530>
5. J.B. Wu, M.L. Lin, X. Cong, H.N. Liu, P.H. Tan, "Raman spectroscopy of graphene-based materials and its applications in related devices," *Chem. Soc. Rev.*, 47(5), 1822–1873 (2018). <https://doi.org/10.1039/C6CS00915H>
6. G. Fini, P. Mirone, B. Fortunat, "Evidence for Short-Range Orientation Effects in Dipolar Aprotic Liquids from Vibrational Spectroscopy: 1. Ethylene and Propylene Carbonates," *J. Chem. Soc., Faraday Trans.*, 69(8), 1243–1248 (1973). <http://dx.doi.org/10.1039/f29736901243>

7. D.E. Logan, "The non-coincidence effect in the Raman spectra of polar liquids," *Chem. Phys.*, 103, 215–225 (1986). [https://doi.org/10.1016/0301-0104\(86\)80022-2](https://doi.org/10.1016/0301-0104(86)80022-2)
8. H. Torii, "Approximate theories of the Raman non-coincidence effect: a critical evaluation in the case of liquid acetone," *J. Mol. Struct. THEOCHEM.*, 311, 199-203 (1994). [https://doi.org/10.1016/S0166-1280\(09\)80057-2](https://doi.org/10.1016/S0166-1280(09)80057-2)
9. P. Mirone, G. Fini, "Local order and vibrational coupling in solutions of polar molecules," *J. Chem. Phys.*, 71, 2241–2243 (1979). <https://doi.org/10.1063/1.438557>
10. Z. Wang, Y. Han, Q. Peng, C. Jiang, H. Wang, "The intermolecular interactions of methanol diluted in protic and aprotic solvent probed by polarized Raman spectroscopy and HNMR," *J. Mol. Liq.*, 387, 122658 (2023). <https://doi.org/10.1016/j.molliq.2023.122658>
11. A. Jumabaev, U. Holikulov, S. Yormatov, T. G. Devi, "Influence of Dielectric Environments on Raman Non-Coincidence Effects in the C=O Stretching and NH₂ Bending Modes of Formamide," *Vibr. Spectrosc.*, 103767 (2025). <https://doi.org/10.1016/j.vibspec.2025.103767>
12. H.C. Garcia, L.F. de Oliveira, B.G. Nicolau, M.C. Ribeiro, "Raman spectra of acetonitrile in imidazolium ionic liquids," *J. Raman Spectrosc.*, 41(12), 1720-1724 (2010). <https://doi.org/10.1002/jrs.2628>
13. J.M. Alía, H.G. Edwards, "Vibrational spectroscopic properties of hydrogen bonded acetonitrile studied by DFT," *J. Phys. Chem. A*, 109(35), 7977-7987 (2005). <https://doi.org/10.1021/jp051892y>
14. F. Muniz-Miranda, A. Pedone, M.C. Menziani, "Blueshift of the C≡N stretching vibration of acetonitrile in solution: computational and experimental study," *J. Comput. Chem.*, 45(28), 2352-2359 (2024). <https://doi.org/10.1002/jcc.27452>
15. Y. Park, S. Jin, I. Noda, Y. M. Jung, "Continuing progress in the field of two-dimensional correlation spectroscopy (2D-COS), Part I: Yesterday and today," *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.*, 281, 121573 (2022). <https://doi.org/10.1016/j.saa.2022.121573>