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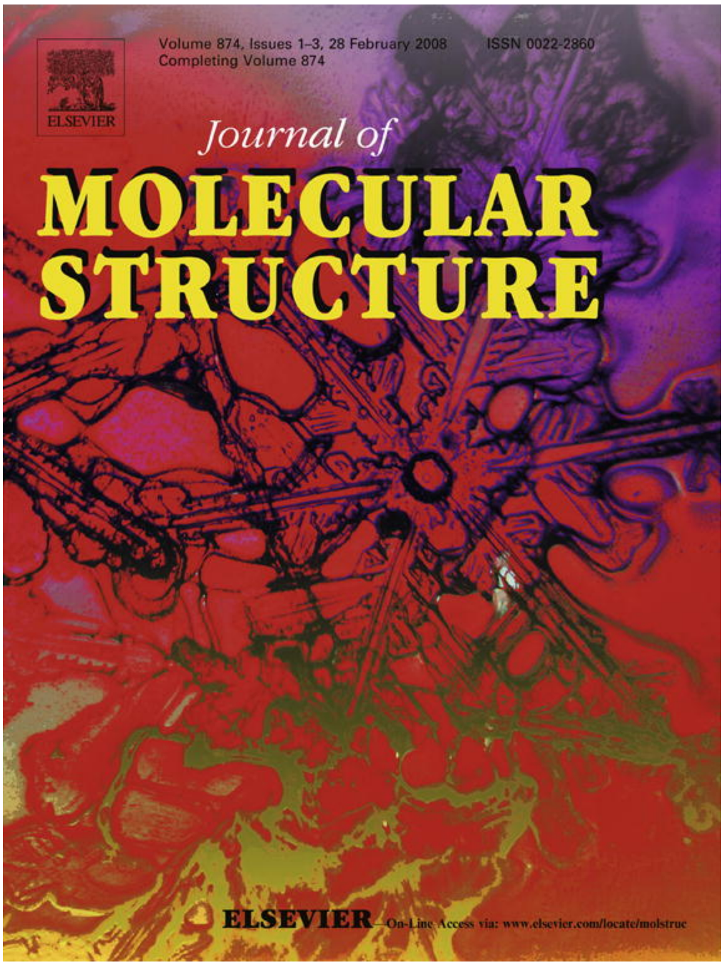
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Vibrational spectra of L-arginine nitrates

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Abstract

Crystals L-arginine·‘HNO_3·$0.5H_2O$ and L-arginine·$2HNO_3$ have been studied by attenuated total reflection Fourier transform infrared (FTIR ATR) and Fourier transform Raman spectroscopy with taking into account their crystal structures.

Keywords: L-Arginine nitrates; FTIR; ATR; Raman spectra

1. Introduction

Intensive research of crystalline salts of L-arginine (L-Arg) as nonlinear optical (NLO) materials is now in progress. The present paper deals with discussion of vibrational spectra of the crystals formed in the system L-Arg + HNO_3 + H_2O. A number of papers devoted to research of this system has been already published [1–7]. Monaco et al. [1] were the first who investigated this system and have obtained L-arginine nitrate in form of fine powder. In Ref. [2] it has been shown that from this system in addition to powdered L-arginine nitrate it is possible to obtain crystalline L-arginine dinitrate L-Arg·$2HNO_3$. Crystal structure of L-Arg·$2HNO_3$ has been determined and IR spectrum registered with nujol was reported. Originally L-Arg·$2HNO_3$ crystals were obtained in form of elongated thin plates $26 \times 5 \times 1$ mm^3 [2] (crystals grown in [7] also had the same habitus $28 \times 8 \times 1$ mm^3), however, later we could grow more bulky crystals with dimensions $20 \times 10 \times 4$ mm^3 [3] and $33 \times 10 \times 5$ mm^3 [4]. In Ref. [4] we could find crystallization conditions of L-arginine nitrate and have determined its crystal structure and composition 2(L-Arg·HNO_3)·H_2O (or L-Arg·HNO_3·$0.5H_2O$). The same IR spectra of crystalline and powdered samples testify that powdered sample is not anhydrous. Ramaswamy et al. [6] carried out detailed vibrational spectroscopic study of L-Arg·$2HNO_3$, however the spectra registered with nujol [2] and KBr pellet [6] are significantly different. It is necessary to reject an assumption that in Refs. [2] and [6] different polymorphs were obtained because of good accordance between unit cell parameters and structures of crystals obtained in [2] and [5,6]. Ramaswamy et al. [6] do not discuss distinctions between IR spectra of [2] and [6]. FTIR spectrum of L-Arg·$2HNO_3$ measured in Ref. [7] also does not coincide with spectrum of [6]. Seemingly the paper [6] was not known to authors of Ref. [7]. Vibrational spectra of L-Arg·$2H_2O$ [8], various salts ofs L-arginine [9–17] as well as spectra of nitrates of other amino acids [18–20] have been published.

In present communication we report ATR FTIR and Raman spectra of L-Arg·HNO_3·$0.5H_2O$ and L-Arg·$2HNO_3$ and a possible explanation of the above-stated discrepancy is proposed.

2. Experimental

As initial reagents we used L-arginine purchased from “Sigma” Chem. Co., and nitric acid of “chem. pure” grade. Crystals of L-Arg·HNO_3·$0.5H_2O$ and L-Arg·$2HNO_3$ were obtained from aqueous solution as it were described in Ref. [4].

Attenuated total reflection Fourier transform infrared (FT-IR ATR) spectra were registered using Nicolet

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"Nexus" FT-IR spectrometer with ZnSe prism (4000–650 cm^{-1}, Happ–Genzel apodization, single reflection accessory, ATR distortion is corrected, number of scans: 16, resolution: 4 cm^{-1}). Fourier transform Raman spectra were registered using NXP FT-Raman Module of Nicolet 5700 spectrometer (Nd:YVO_4 laser with 976 nm wavelength, Happ–Genzel apodization, resolution: 4 cm^{-1}). Power at the sample in case of L-Arg·HNO_3·0.5H_2O was 0.48 W, number of scans: 256, while in case of L-Arg·2HNO_3 was 0.05 W, number of scans: 1024. Nicolet 5700 spectrometer also was used for registration of FTIR spectra with nujol in the region 650–400 cm^{-1} and with KBr pellet (resolution: 2 cm^{-1}, number of scans: 32).

3. Results and discussion

3.1. Vibrational spectra of 2(L-Arg·HNO_3)·H_2O (L-Arg·HNO_3·0.5H_2O)

Unit cell contains two L-Arg$^+$ cations, two $NO_3{}^-$ anions and one water molecule. Singly charged cation of L-arginine $^+[(H_2N)_2CNH](CH_2)_3CH(NH_3^+)COO^-$ is characterized by protonated $[(H_2N)_2CNH]^+$ guanidyl group, protonated alpha-amino group $NH_3{}^+$ and deprotonated carboxylate group COO^- [4]. IR and Raman spectra of L-Arg·HNO_3·0.5H_2O are shown in Fig. 1, values of wavenumbers are collected in Table 1. Structural data [4] and comparison of IR and Raman spectra allow assigning the characteristic vibrations. High-frequency region contains bands caused by stretching ν(C–H) vibrations of CH and CH_2 groups, ν(N–H) vibrations of NH, NH_2 and $NH_3{}^+$ groups and also stretching ν(O–H) vibrations of water molecule. Characteristic band with peaks at 2879, 2897, 2931 and 2987 cm^{-1} in the Raman spectrum we assign to ν(C–H) vibrations. Respective peaks in the same region can be seen in the IR spectrum. More high-frequency peaks at 3000 ÷ 3407 cm^{-1} in the IR and Raman spectra we assign to ν(N–H) and ν(O–H) vibrations. Wavenumbers of these peaks well correspond to position expected on the basis of structural data [4]. Shoulder at 3404 cm^{-1} in the IR spectrum may be assigned to $\nu(H_2O)$ because it disappeared at dehydration [4]. Singly charged L-arginine cation (L-Arg$^+$) in the IR spectrum has characteristic absorption bands below 1700 cm^{-1} caused by $\nu_{as}(COO^-)$ and also by deformation vibrations of NH_2 and $NH_3{}^+$ groups. Absorption caused by deformation vibration of water molecule also is expected in this region. According to Michael Falk [21] the total range values of $\delta(H_2O)$ for crystalline hydrates is 1582–1721 cm^{-1}, with a mean value 1636 cm^{-1}. The strong band at 1629 cm^{-1} does not disappear at dehydration, but significantly decreases. Therefore it is possible to consider that this band is responsible also for deformation vibration of water molecule. Deformation vibrations of CH_2 groups are shown as more intensive lines in the Raman spectrum. Therefore very strong absorption band at 1397 cm^{-1} probably relates to symmetric stretching vibration of COO^- group. Nitrate ion $NO_3{}^-$ is characterized by $\nu_{as}(NO_3{}^-)$, $\nu_s(NO_3{}^-)$, $\pi(NO_3{}^-)$ and $\delta_{as}(NO_3{}^-)$. It is known that asymmetric $\nu_{as}(NO_3{}^-)$ vibration is shown as very strong absorption band in IR spectrum, while symmetric $\nu_s(NO_3{}^-)$ vibration as very intensive line in Raman spectrum. Very strong absorption band at 1328 cm^{-1} in the IR spectrum we assign to $\nu_{as}(NO_3{}^-)$. Respective peak in the Raman spectrum we find at 1331 cm^{-1}. The most intensive line in the Raman spectrum at 1048 cm^{-1} relates undoubtedly to $\nu_s(NO_3{}^-)$. Respective narrow band in the IR spectrum we find at 1043 cm^{-1}. Symmetric stretching vibration of ideal $NO_3{}^-$ is inactive in IR absorption spectrum. Weaker, also narrow band at 824 cm^{-1}, we assign to out-of-plane deformation $\pi(NO_3{}^-)$. This mode is Raman inactive for ideal $NO_3{}^-$. Absorption in the region 500 ÷ 600 cm^{-1} may contain also bands caused by deformation vibration of COO^- group and also librational vibrations of water molecule.

3.2. Vibrational spectra of L-Arg·2HNO_3

Asymmetric part of unit cell contains doubly charged L-Arg^{2+} cation and two $NO_3{}^-$ anions [4]. Doubly charged L-Arg^{2+} cation is formed by additional protonation of carboxylate group $^+[(H_2N)_2CNH](CH_2)_3CH(NH_3^+)COOH$. This results in significant variations in hydrogen bonding scheme in comparison with L-Arg$^+$, which is reflected in vibrational spectra. IR and Raman spectra of L-Arg·2HNO_3 are shown in Fig. 2, values of wavenumbers are collected in Table 1. Characteristic band in the Raman spectrum with peaks at 2927, 2957 and 2976 cm^{-1} we assign to stretching ν(C–H) vibrations of CH and CH_2 groups, while more high-frequency bands to stretching ν(N–H) vibrations of NH, NH_2 and NH_3^+ groups. Hydroxyl group forms hydrogen bond with intermediate strength with oxygen atom of one nitrate ion. Stretching ν(OH) vibration is expected near 3000 cm^{-1} on the basis of structural data [4]. Therefore we think that broad band in the IR spectrum with peaks in the region 2833 ÷ 3003 cm^{-1} is overlapping of ν(OH) and ν(C–H) vibrations, while peaks in the region 3071 ÷ 3454 cm^{-1} are caused by ν(N–H) vibrations of NH, NH_2 and $NH_3{}^+$ groups. Two hydrogen bonds formed by $NH_3{}^+$ group are rather strong, while hydrogen bonds formed by guanidyl group are very weak [4]. The presence of strong absorption band at 1739 cm^{-1} is an indication of existence of neutral carboxyl group and hence L-Arg^{2+} cation. Strong peaks in the IR spectrum at 1684, 1655 and 1637 cm^{-1} we assign to deformation $\delta_{as}(NH_3{}^+)$ and $\delta(NH_2)$ vibrations, while band at 1531 cm^{-1} to $\delta_s(NH_3{}^+)$. Respective peaks in the Raman spectrum are comparatively weak. Peaks at 1456 and 1439 cm^{-1} in the Raman spectrum and respective absorption bands in the IR spectrum we assign to deformation vibrations of CH_2 groups. Very strong absorption band with peak at 1317 cm^{-1} we assign to asymmetric stretching vibration of $NO_3{}^-$ anions. In the Raman spectrum in this region we find a line at 1334 cm^{-1}. The most intensive split

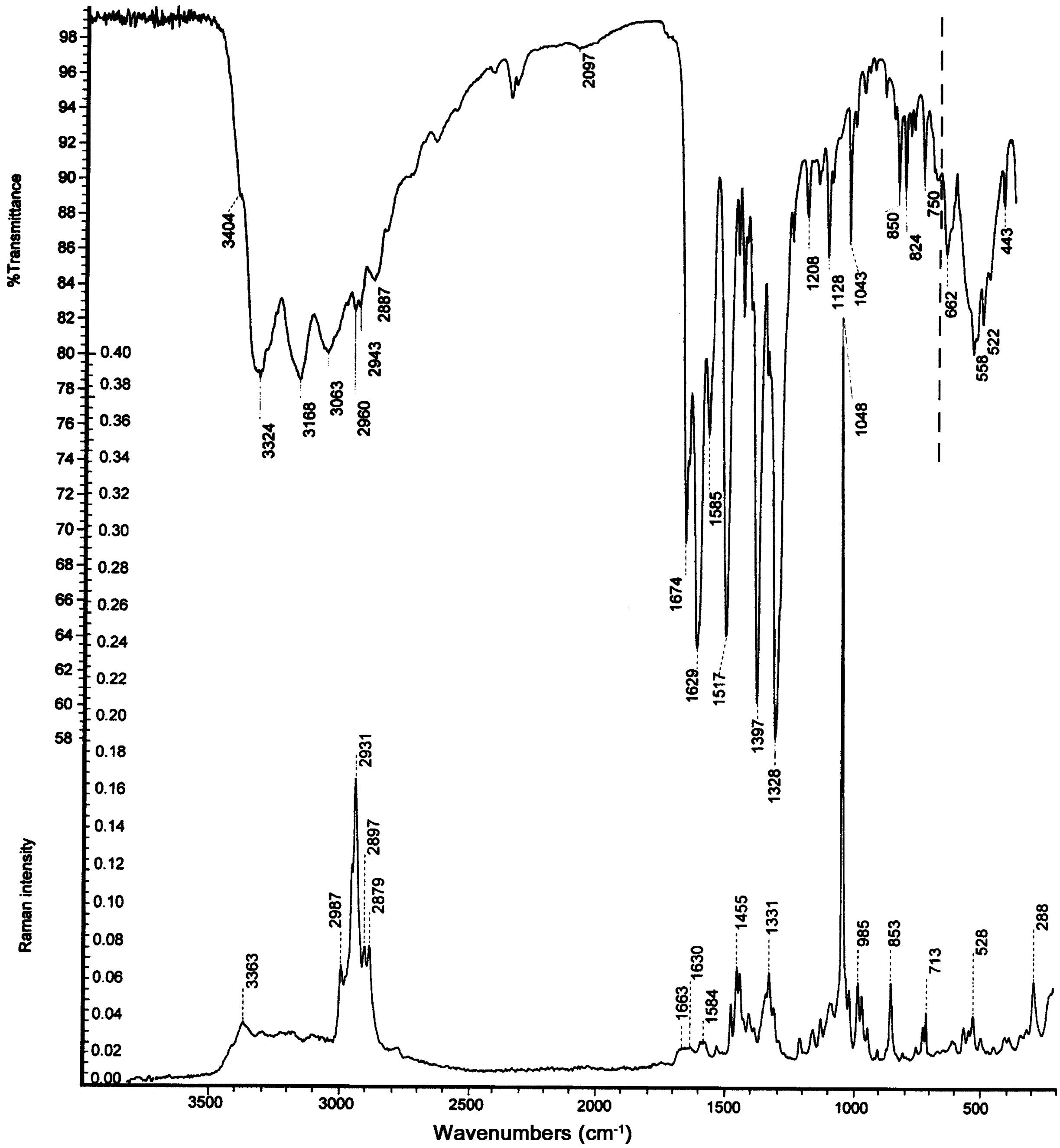

Fig. 1. ATR FTIR and FT Raman spectra of L-Arg·HNO_3·$0.5H_2O$ (spectrum in the region 650 ÷ 400 cm^{-1} was registered with nujol).

line in the Raman spectrum with peaks at 1044 and 1056 cm^{-1} apparently relates to symmetric stretching vibration of nitrate ions. Corresponding bands in the IR spectrum we find as a narrow band at 1039 cm^{-1} and a shoulder at 1052 cm^{-1}. Two nitrate ions in the structure of L-Arg·$2HNO_3$ form significantly different hydrogen bonds [4]. We consider that this can be the reason of splitting. Characteristic narrow $\pi(NO_3^-)$ band in the IR spectrum we find at 822 cm^{-1}. Weak peaks at 727 cm^{-1} and 710 cm^{-1} probably relate to $\delta_{as}(NO_3^-)$. However, CH_2 groups also have absorption in this region (rocking at 720 cm^{-1}). FTIR spectrum of L-Arg·$2HNO_3$ registered (probably with KBr pellet) in Ref. [7] is in good accordance with ATR FTIR spectrum shown in Fig. 2. However, wavenumbers 1112.1 cm^{-1} and 1039.3 cm^{-1} in the spectrum [7] are not indicated in proper places. Peak indicated as 1112.1 cm^{-1} corresponds to peak at 1248 cm^{-1} in our spectrum, while peak indicated as 1039.3 cm^{-1} corresponds to peak at 1111 cm^{-1} in our spectrum. In addition, authors of Ref. [7] assigned to NO_3^- vibrations peaks at 1320.3, 1112.1 and 822.3 cm^{-1}. As it is clear from the above-stated, we do not agree with assignment of the band at 1112.1 $cm^{-1}$to vibration of NO_3^- ion. We mentioned above that IR spectrum shown in Ref. [6] significantly dif-

Table 1
Wavenumbers (cm^{-1}) of absorption peaks and Raman lines of L-Arg·HNO_3·$0.5H_2O$ and L-Arg·$2HNO_3$

L-Arg·HNO_3·$0.5H_2O$		Assignment	L-Arg·$2HNO_3$		Assignment
IR	Raman		IR	Raman	
3404sh	3407sh	ν(OH) H_2O	3454	3457	ν(NH)
3324	3363;3321	ν(NH)	3373sh	3360	NH, NH_2, NH_3^+
3297sh	3297	NH,	3352sh;3326	3252;3230	
3261sh	3288;3217	NH_2,	3268;3221	3171	
3168	3183;3172	NH_3^+	3171		
3063	3093;3057		3157;3151		
	3037		3071		
			3003		
2992sh	2987	ν(CH)	2982		ν(CH)
2960	2944;2931	CH, CH_2	2951	2976	CH,
2943	2897		2924	2957	CH_2
2887	2879		2904	2927	ν(OH)
2843sh			2880	2897sh	COOH
			2833	2890sh	
				2862sh	
2743sh	2768	Overtones	2784;2765	2772	Overtones
2652		Combinational	2702; 2644	2738	Combinational
2573			2573		
2428			2489		
2097			2055		
			1739	1736	ν(C=O)COOH
1674	1672	$\nu_{as}(COO^-)$			
1662sh	1663	$\delta_{as}(NH_3{}^+)$	1684	1677	$\delta_{as}(NH_3{}^+)$
	1651;1641	$\delta(NH_2)$	1655	1650	$\delta(NH_2)$
1629	1630	$\delta(H_2O)$	1637;1621sh	1631sh	
1585	1591;1584		1586sh	1580	
	1575	$\delta(NH_2)$			
1517	1530	$\delta_s(NH_3{}^+)$	1531		$\delta_s(NH_3{}^+)$
1473	1477	$\delta(CH_2)$	1467		$\delta(CH_2)$
1453	1455		1453	1456	
1441sh	1443		1420	1439	
1423sh	1429				
1397	1409	$\nu_s(COO^-)$			
1361	1388	$\omega(CH_2)$	1400	1389	$\omega(CH_2)$
1351sh	1343	$\tau(CH_2)$	1385	1361	$\tau(CH_2)$
1328	1331	$\nu_{as}(NO_3{}^-)$	1317	1334	$\nu_{as}(NO_3{}^-)$
1312sh;1265	1313;1296		1294		
			1248	1259	ν(C–OH)
1208	1211		1225		
1165;1157sh	1162	$\rho(NH_3{}^+)$	1172	1173	$\rho(NH_3{}^+)$
1128;1111	1132	$\rho(NH_2)$	1111	1116sh	$\rho(NH_2)$
1084sh	1095;1090	ν(C–N)	1082	1085	ν(C–N)
1043	1048	$\nu_s(NO_3{}^-)$	1052sh;1039	1056;1044	$\nu_s(NO_3{}^-)$
1020	1020				
986	985				
966	969		955	959	γ(OH)
943	946		918	918	COOH
902	906		891		
868;850	869;853		858	866	
824		$\pi(NO_3{}^-)$	822	830	$\pi(NO_3{}^-)$
802;788	805				
750	753		758;741	761;745sh	
	725		727	731	$\rho(CH_2)$
709;694	713	$\delta_{as}(NO_3{}^-)$	710	714	$\delta_{as}(NO_3{}^-)$
662	608	$\delta(COO^-)$	657;584	657;626	
558;545	565;544	$\nu_L(H_2O)$	540		
522	528		534;517	535	
497	498		471		
443	447;402		426	429;404	
	386;288			335;311	

ν- stretching, δ-deformation scissoring, ω-wagging, τ-twisting, π- out-of-plane deformation, ρ-rocking, γ- out-of-plane bending, ν_L- librational, s-symmetric, as-asymmetric, sh-shoulder.

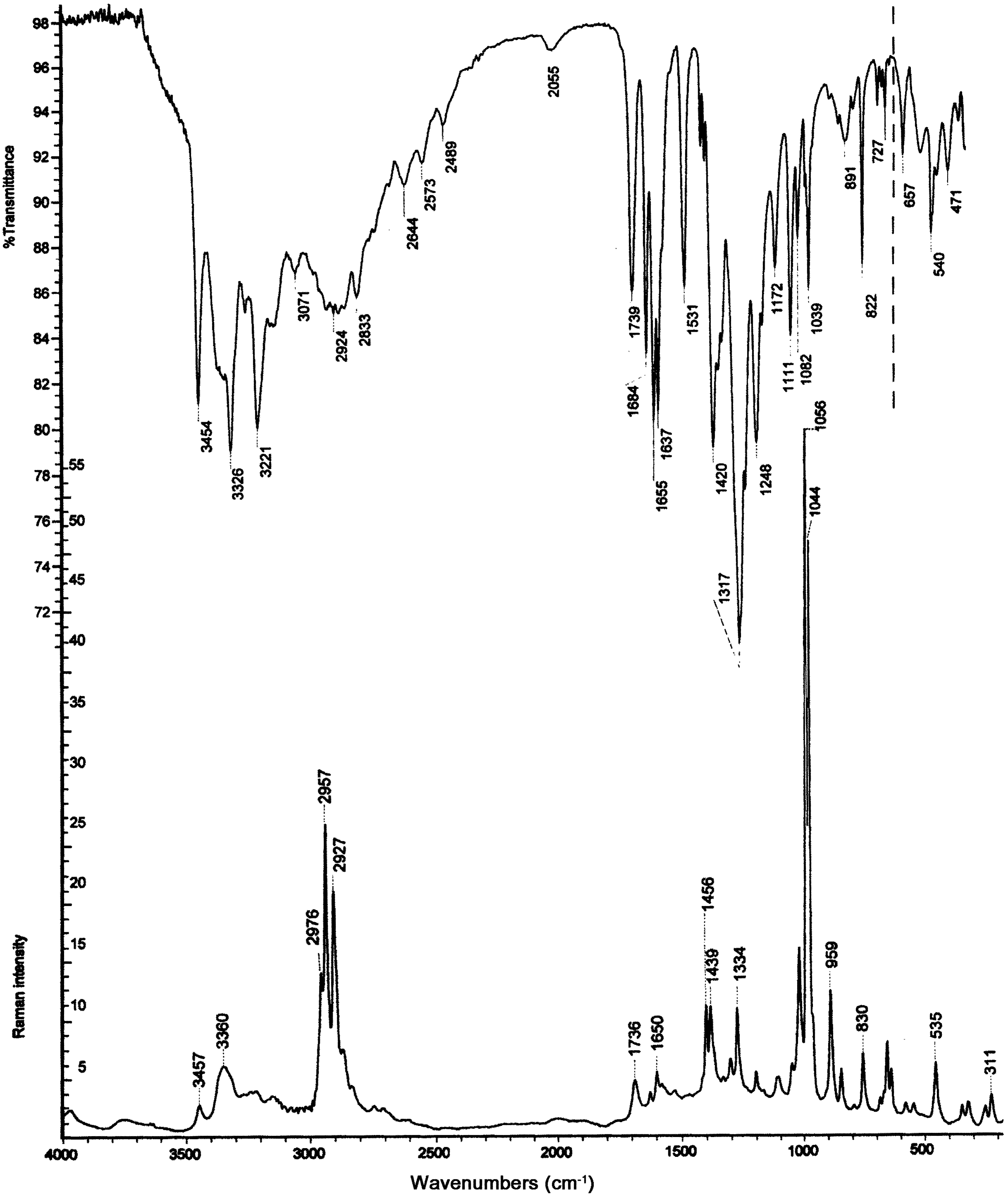

Fig. 2. ATR FTIR and FT Raman spectra of L-Arg·$2HNO_3$(spectrum in the region 650 ÷ 400 cm^{-1} was registered with nujol).

fers from the spectrum registered in nujol [2], while ATR FTIR spectrum (Fig. 2) is in good accordance with spectrum in nujol. We consider that probable reason for this discrepancy is decomposition and ionic exchange during preparation of KBr pellet. Moreover, authors [6] emphasize that the "mixture was then pressed under vacuum at very high pressure". The possibility of such distortion was demonstrated recently one more time in Ref. [22]. We tried to reproduce the spectrum of [6] by preparing KBr pellet under high pressure. However, registered spectrum differs from both spectra in Fig. 2 and that shown in [6], which at least indicates that by applying high pressure during preparation of KBr pellet, IR spectrum of L-Arg·$2HNO_3$ can be significantly distorted. In addition, symmetric stretching vibration of NO_3^- ions in the Raman spectrum appears as single line at 1046 cm^{-1}(see Fig. 3 and Table 2 in [6]) instead of split line with peaks at 1044 cm^{-1} and 1056 cm^{-1} (Fig. 2).

4. Conclusion

Two crystals from the system L-arginine + HNO_3 + H_2O, namely, 2(L-Arg·HNO_3).H_2O (or L-Arg·HNO_3·0.5H_2O) and L-Arg·2HNO_3 are studied by vibrational spectroscopy. Discrepancy of the spectrum of L-Arg·2HNO_3 with earlier published one can be caused by partial ionic exchange and decomposition of the sample at preparation of KBr pellet under high pressure.

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