Interpretation of Vibrational IR Spectrum of Uracil Using Anharmonic Calculation of Frequencies and Intensities in Second-Order Perturbation Theory

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Received May 28, 2009

Abstract—The anharmonic frequencies of fundamental vibrations, overtones, and combination vibrations, as well as the intensities of absorption bands in the IR spectrum of uracil, are calculated. The anharmonic quartic force field and the third-order dipole moment surface calculated by the DFT quantum-mechanical method (B3LYP/6-31+$G(d,p)$) are taken as the initial parameters. The anharmonic frequencies and intensities of vibrations are determined using the second-order perturbation theory in the form of contact transformations. Multiple Fermi resonances and polyads are determined by the diagonalization of a small interaction matrix of vibrations of different types (fundamental, combination, and overtone frequencies). The total experimental IR spectrum of matrix-isolated uracil is interpreted. It is shown that the used method of calculating anharmonic frequencies and intensities can form a basis for anharmonic calculations of vibrations of moderate molecules.

INTRODUCTION

Vibrational spectra of uracil (Ura), the simplest nucleic acid base, have been studied in a large number of theoretical and experimental works. The IR and Raman spectra of gaseous [1], dissolved [2, 3], polycrystalline [4–6], and matrix-isolated [7–15] Ura were measured. In [16–20], the vibrational spectra of Ura were analyzed by semiempirical and ab initio quantum-chemical methods. This analysis showed that calculations using the methods used in these works do not reproduce the band intensities of C=O stretching vibrations and cannot interpret all the experimental absorption bands in the vibrational spectrum of Ura. For example, the authors of [8] attributed the vibrations with the frequencies 1389 and 1525 cm^{-1} to fundamental tones of Ura [8]. However, according to the calculations of [10, 12], these vibrations are not the fundamental vibrations of this molecule. At present, there is no common opinion on the interpretation of the vibrational spectrum of isolated Ura [7–15]. The main reason for the disagreement between the experimental data and theoretical models used is that the spectrum of Ura contains overtones and combination frequencies whose intensities are comparable with the intensities of fundamental vibrations. This is the consequence of the occurrence of Darling–Dennison and Fermi resonances, which leads to the redistribution of intensities between fundamental, combination, and overtone vibrations.

Previously, the authors of [10] attempted to explain the influence of the Fermi resonance on the intensity redistribution of ν(C=O) stretching vibrations using a simplified model. They showed that the intensity of one of the three absorption bands of Ura in the range 1700–1800 cm^{-1}, namely, of the band at 1730 cm^{-1}, considerably increases due to the Fermi resonance between the ν(C=O) stretching vibration and a combination vibration whose shape is determined by changes in the exterior angles formed by the NH and OH bonds. The authors of [14] believe that there are at least nine absorption bands in this range that are caused by Fermi resonances. This fact is confirmed by comparison of the spectra of Ura recorded in different matrices (Kr, Ar, Ne) and analysis of shifts of absorption bands [13].

Clearly, to adequately interpret the experimentally observed frequencies and intensities of the vibrational spectrum of Ura, it is necessary to calculate this spectrum in the anharmonic approximation. It is also should be noted that previous calculations in the approximation of the B3LYP hybrid density functional were performed in [20, 21] without determining the intensities of overtones and combination frequencies.

METHOD OF CALCULATION

The geometric structure of Ura and all its molecular parameters were calculated in the B3LYP approximation with the 6-31+$G(d,p)$ basis set [22]. The quar-
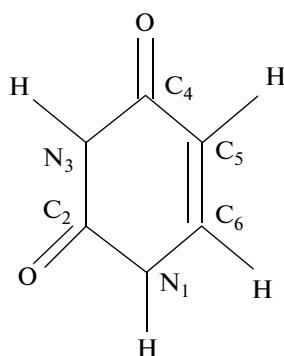
Fig. 1. Molecular diagram of Ura with the enumeration of atoms.

tic force field and cubic surface of the dipole moment were obtained by numerical differentiation of the total energy and electronic matrix elements for the components of the dipole moment with respect to normal coordinates using the following finite-difference formulas [23, 24]:

$$f_{ijr} = [f_{ij}(+\Delta Q_r) - f_{ij}(-\Delta Q_r)]/2\Delta Q_r,$$

$$f_{ijrr} = [f_{ij}(+\Delta Q_r) + f_{ij}(-\Delta Q_r) - 2f_{ij}(0)]/(\Delta Q_r)^2,$$

where ΔQ_r is the increment of the rth normal coordinate, and $f_{ij}(\pm\Delta Q_r)$ and $f_{ij}(0)$ are the quantities in the displaced and equilibrium molecular configurations to be differentiated.

A method for taking into account multiple resonances based on the second-order perturbation theory with an additional numerical diagonalization of the interaction matrix of resonant vibrational states of different types (fundamental tones, overtones, and combination tones) for moderate molecules was previously considered in [25]. In this work, this method is supplemented by the anharmonic calculation of the absorption band intensities, and the vibrational IR spectrum of isolated Ura in the range ~400–3500 cm^{-1} is interpreted.

The anharmonic intensities are calculated based on the approach described in [26]. The theoretical analysis performed makes it possible to clarify the possibility of applying the used scheme of taking into account resonances to the calculations of anharmonic vibrational spectra of polyatomic molecules.

RESULTS AND DISCUSSION

The table presents the harmonic frequencies and intensities (ν_h, $I_{IR,h}$) of the IR spectrum of Ura, as well as the anharmonic frequencies and intensities calculated without (ν_a, $I_{IR,a}$) and with (ν_F, $I_{IR,F}$) taking into account the Fermi resonance. In addition, the table indicates exactly which unperturbed fundamental tones, overtones, and combination tones and with which coefficients take part in resultant mixed tones

(polyads). The schematic diagram of the Ura molecule with the enumeration of the ring atoms is presented in Fig. 1.

The calculation shows that seven of the nine out-of-plane vibrations of Ura do not interact with other vibrations, and that the Fermi resonance is observed only for two vibrations, ν_{26} and ν_{25}, which correspond to the displacement of the N_3H and C_2O bonds out of the plane of the pyrimidine ring. In both cases, the fundamental tones resonantly interact with the combination vibrations $\nu_{18} + \nu_{30}$ and $\nu_{19} + \nu_{30}$, and the mutual influence of the vibrations ν_{26} and ($\nu_{18} + \nu_{30}$) can be neglected (the coefficient of interaction is 0.1). Although the shift of resonant frequencies is no more than 1–2 cm^{-1}, the intensity redistribution is ~10–30%. This is related to the fact that the differences between the anharmonic frequencies of the stretching vibrations ν_{26} and ν_{25} and the combination vibrations $\nu_{18} + \nu_{30}$ and $\nu_{19} + \nu_{30}$ are small and equal to 25 and 8 cm^{-1}, respectively. Therefore, as a result of resonance, the intensity of the combination vibrations increases, and the two vibrations $\nu_{18} + \nu_{30}$ and $\nu_{19} + \nu_{30}$ are observed in the experimental spectrum as vibrations with the frequencies 682 and 685 cm^{-1} (Fig. 2).

In the low-frequency range ~300–600 cm^{-1}, there are three Fermi resonances for out-of-plane vibrations, one of which occurs between the fundamental tone ν_{21} and the overtones of the out-of-plane vibrations $2\nu_{30}$ and $2\nu_{29}$, and the remaining two resonances are observed between the fundamental tones ν_{19}, ν_{18} and the combination vibration $\nu_{28} + \nu_{29}$. As a result of the resonance interaction, the frequency of the vibration ν_{21} is shifted toward higher frequencies by 3 cm^{-1}, and the intensity redistribution between the components of the triplet is no more than 5%; therefore, as a result of the resonance interaction, the intensity of the absorption band of the ν_{21} vibration differs little compared to the intensity of the harmonic vibration. In the experimental vibrational spectrum of the isolated Ura molecule, two closely located absorption bands with the frequencies 393 and 401 cm^{-1} correspond to the vibrations ν_{21} and ν_{28} (Fig. 2). The intensity of the combination vibration $\nu_{28} + \nu_{29}$ increases due to the resonance interaction; as a result, this vibration is experimentally observed as a weak absorption band at 557 cm^{-1}.

In contrast, the intensities of the vibrations ν_{17} and ν_{16} decrease due to the resonance intensity redistribution between the components of resonant vibrations. As a result, the vibration ν_{17} becomes so weak that it can hardly be observed in the experimental IR spectrum.

The Fermi resonance between the fundamental vibration ν_{15} and combination vibration $\nu_{27} + \nu_{28}$ is characterized by a close arrangement of the levels; thus, the anharmonic frequencies of the resonant

Experimental and calculated frequencies (ν, cm^{-1}) and intensities (I_{IR}, km/mol) of fundamental and resonant vibrations in the harmonic and anharmonic approximations for the isolated Ura molecule

Vibration	ν_h	$I_{IR,h}$	Interpretation	ν_a	ν_F	Interaction coefficients in polyads	$I_{IR,a}$	$I_{IR,F}$	ν_{exp} [8, 9, 14]	I_{IR}
30 A''	149	0.9	χ	155	155	$[\nu_{30}]$		0.9	–	–
29 A''	167	0.3	χ	167	167	$[\nu_{29}]$		0.3	–	–
21 A'	391	21.3	$\beta(C_2O)$, $\beta(C_4O)$	382	385	$0.98[\nu_{21}]$, $0.16[2\nu_{30}]$, $0.13[2\nu_{29}]$		20.5	393	33
28 A''	395	25.8	χ	398	398	$[\nu_{28}]$		25.8	(401)	(44)
20 A'	516	20.4	γ	515	515	$[\nu_{20}]$		20.4	516	23
19 A'	537	5.7	$\beta(C_2O)$, $\beta(C_4O)$	535	534	$0.98[\nu_{19}]$, $0.19[\nu_{28} + \nu_{29}]$		4.9	537	7
18 A'	562	5.4	γ	552	550	$0.94[\nu_{18}]$, $0.31[\nu_{28} + \nu_{29}]$, $0.12[\nu_{19}]$		6.5	551	25
28 + 29	562			566	569	$0.93[\nu_{28} + \nu_{29}]$, $0.33[\nu_{18}]$, $0.16[\nu_{19}]$	0.8	0.2	557	17
27 A''	562	44.8	$\rho(N_1H)$	567	567	$[\nu_{27}]$		43.7	585 (595)	13 (33)
26 A''	675	88.3	$\rho(N_3H)$	668	666	$0.98[\nu_{26}]$, $0.19[\nu_{19} + \nu_{30}]$, $0.11[\nu_{18} + \nu_{30}]$		82.1	664	100
19 + 30	690			690	691	$0.98[\nu_{19} + \nu_{30}]$, $0.19[\nu_{26}]$	0.1	3.6	682	13
18 + 30	706			707	707	$0.93[\nu_{18} + \nu_{30}]$, $0.34[\nu_{25}]$, $0.11[\nu_{26}]$	0.3	6.6	685	14
25 A''	724	9.9	$\rho(C_2O)$	714	715	$0.94[\nu_{25}]$, $0.34[\nu_{18} + \nu_{30}]$		6.2	719	12
24 A''	743	48.2	$\rho(C_4O)$	749	749	$[\nu_{24}]$		48.2	769	125
17 A'	759	2.9	$Q(CC, CN)$	758	756	$0.94[\nu_{17}]$, $0.27[2\nu_{28}]$, $0.19[\nu_{27} + \nu_{29}]$		2.6	–	–
23 A''	811	55.6	$\rho(C_5H)$, $\rho(C_6H)$	803	803	$[\nu_{23}]$		55.6	806	175
16 A'	958	9.6	Q, γ	947	947	$0.94[\nu_{16}]$, $0.21[\nu_{18} + \nu_{21}]$, $0.18[\nu_{27} + \nu_{28}]$, $0.14[\nu_{24} + \nu_{29}]$		7.8	958	2
22 A''	969	0.5	$\rho(C_5H)$, $\rho(C_6H)$	950	950	$[\nu_{22}]$		0.5	–	–
15 A'	980	6.8	γ	973	961	$0.68[\nu_{15}]$, $0.63[\nu_{27} + \nu_{28}]$, $0.34[\nu_{23} + \nu_{29}]$, $0.14[\nu_{16}]$	5.5	1.0	–	–
27 + 28	957			972	984	$0.71[\nu_{15}]$, $0.67[\nu_{27} + \nu_{28}]$, $0.17[\nu_{23} + \nu_{29}]$	5.5	11.4	963	2
2 × 19	1074			1071	1069	$0.64[2\nu_{19}]$, $0.47[\nu_{18} + \nu_{20}]$, $0.37[\nu_{26} + \nu_{28}]$		1.1	(1070)	
14 A'	1075	6.3	$Q, \beta(C_5H)$	1069	1073	$0.74[2\nu_{19}]$, $0.57[\nu_{14}]$, $0.24[\nu_{26} + \nu_{28}]$, $0.22[\nu_{18} + \nu_{20}]$, $0.10[\nu_{25} + \nu_{28}]$		3.9	1076	14
2 × 27	1125			1139	1141	$2[\nu_{27}]$		17.2	1102	4
24 + 28	1138			1149	1148	$0.98[\nu_{24} + \nu_{28}]$, $0.21[\nu_{13}]$	0.6	2.8	–	–
13 A'	1200	105.3	$Q, \beta(C_5H), \beta(C_6H)$	1172	1171	$0.97[\nu_{13}]$, $0.21[\nu_{24} + \nu_{28}]$		98.9	1186	109
23 + 28	1206			1200	1197	$0.84[\nu_{23} + \nu_{28}]$, $0.53[\nu_{12}]$	0.8	6.6	(1192)	–
12 A'	1233	5.2	$Q, \beta(C_5H)$	1207	1210	$0.84[\nu_{12}]$, $0.53[\nu_{23} + \nu_{28}]$		2.0	1219	4
24 + 27	1305			1320	1317	$0.93[\nu_{24} + \nu_{27}]$, $0.25[\nu_{10}]$, $0.18[2\nu_{26}]$, $0.16[\nu_{17} + \nu_{18}]$	1.1	8.9	1283 (1306)	25
2 × 26	1349			1331	1325	$0.89[2\nu_{26}]$, $0.27[\nu_{11}]$, $0.22[\nu_{16} + \nu_{21}]$, $0.20[\nu_{24} + \nu_{27}]$, $0.13[2\nu_{24}]$		20.1	1314	10
22 + 28	1364			1347	1346	$0.89[\nu_{22} + \nu_{28}]$, $0.40[\nu_{11}]$, $0.13[\nu_{16} + \nu_{21}]$, $0.12[2\nu_{26}]$	0.2	1.9	–	–
11 A'	1385	35.6	$Q, \beta(N_3H), \beta(C_5H)$, $\beta(C_6H)$	1353	1353	$0.77[\nu_{11}]$, $0.44[\nu_{22} + \nu_{28}]$, $0.24[\nu_{15} + \nu_{21}]$, $0.24[\nu_{25} + \nu_{26}]$, $0.18[\nu_{16} + \nu_{21}]$, $0.16[2\nu_{26}]$, $0.14[\nu_{10}]$		8.6	1366	13
15 + 21	1374			1354	1354	$0.96[\nu_{15} + \nu_{21}]$, $0.22[\nu_{11}]$, $0.10[\nu_{10}]$	0.7	8.6		
25 + 26	1399			1383	1382	$0.65[\nu_{25} + \nu_{26}]$, $0.55[\nu_9]$, $0.43[\nu_{10}]$, $0.17[\nu_{11}]$, $0.13[\nu_{24} + \nu_{26}]$, $0.10[2\nu_{26}]$	1.5	29.4	1389	21
10 A'	1407	98.5	$Q, \beta(N_1H), \beta(N_3H)$, $\beta(C_5H)$	1374	1374	$0.78[\nu_{10}]$, $0.34[\nu_{25} + \nu_{26}]$, $0.27[\nu_9]$, $0.21[\nu_{11}]$, $0.21[\nu_{24} + \nu_{27}]$, $0.19[\nu_{24} + \nu_{26}]$, $0.14[\nu_{15} + \nu_{21}]$, $0.13[\nu_{23} + \nu_{27}]$, $0.13[2\nu_{26}]$		68.6	1401	56

Table. (Contd.)

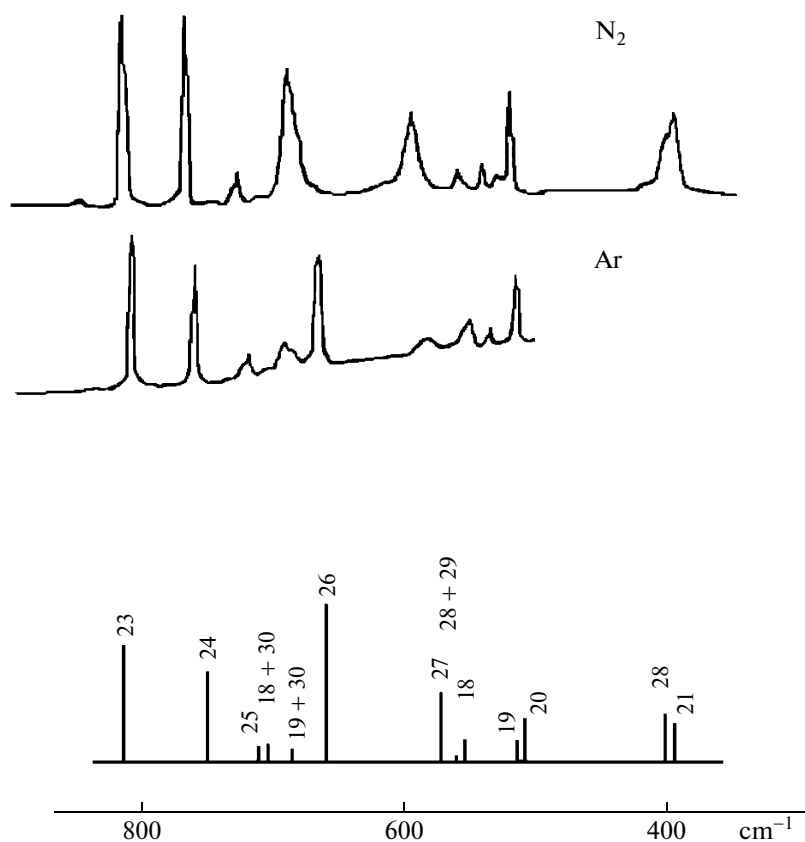| Vibration	ν_h	$I_{IR,h}$	Interpretation	ν_a	ν_F	Interaction coefficients in polyads	$I_{IR,a}$	$I_{IR,F}$	ν_{exp} [8, 9, 14]	I_{IR}
9 A'	1420	14.1	Q, $\beta(N_1H)$, $\beta(N_3H)$	1390	1394	$0.75[\nu_9]$, $0.62[\nu_{25}+\nu_{26}]$, $0.10[\nu_{11}]$, $0.10[2\nu_{25}]$		10.0	–	–
14+21	1475			1450	1448	$0.90[\nu_{14}+\nu_{21}]$, $0.41[\nu_8]$	0.2	11.5	1461	7
8 A'	1502	93.9	Q, $\beta(N_1H)$	1464	1461	$0.66[\nu_8]$, $0.61[\nu_{24}+\nu_{25}]$, $0.39[\nu_{14}+\nu_{21}]$, $0.12[2\nu_{24}]$, $0.12[\nu_{16}+\nu_{18}]$		41.8	(1465) 1473	83
24+25	1467			1465	1468	$0.78[\nu_{24}+\nu_{25}]$, $0.55[\nu_8]$, $0.20[\nu_{14}+\nu_{21}]$, $0.13[2\nu_{24}]$, $0.12[\nu_{16}+\nu_{18}]$	0.3	23.6		
2×24	1498			1503	1506	$0.81[2\nu_{24}]$, $0.45[2\nu_{17}]$, $0.32[\nu_{15}+\nu_{19}]$, $0.13[\nu_8]$, $0.12[\nu_{16}+\nu_{18}]$, $0.18[\nu_8]$, $0.11[2\nu_{26}]$		1.1	–	–
2×17	1542			1515	1519	$0.85[2\nu_{17}]$, $0.45[2\nu_{24}]$, $0.18[\nu_8]$, $0.17[\nu_{23}+\nu_{25}]$		6.3	1525	25
7 A'	1677	60.4	$Q(C_5{=}C_6)$	1641	1643	$0.94[\nu_7]$, $0.18[\nu_{22}+\nu_{25}]$, $0.16[\nu_{14}+\nu_{18}]$, $0.14[\nu_{14}+\nu_{19}]$, $0.12[2\nu_{23}]$		55.3	1644	33
13+20	1720			1686	1684	$0.99[\nu_{13}+\nu_{20}]$, $0.13[\nu_5]$	0.6	11.3	1699	291
16+17	1739			1704	1698	$0.78[\nu_{16}+\nu_{17}]$, $0.47[\nu_{13}+\nu_{19}]$, $0.37[\nu_6]$, $0.15[\nu_{13}+\nu_{18}]$	0.1	138.7	1707	
13+19	1741			1706	1705	$0.82[\nu_{13}+\nu_{19}]$, $0.55[\nu_{16}+\nu_{17}]$	0.03	6.6	1720	
12+20	1753			1722	1720	$0.89[\nu_{12}+\nu_{20}]$, $0.33[\nu_{13}+\nu_{18}]$, $0.19[\nu_6]$, $0.15[\nu_{13}+\nu_{19}]$, $0.14[\nu_{15}+\nu_{17}]$	0.04	16.9		
13+18	1758			1723	1721	$0.87[\nu_{13}+\nu_{18}]$, $0.39[\nu_{12}+\nu_{20}]$, $0.16[\nu_{16}+\nu_{17}]$, $0.15[\nu_6]$, $0.14[\nu_5]$, $0.13[\nu_{13}+\nu_{19}]$	0.1	43.8		
15+17	1760			1730	1729	$0.94[\nu_{15}+\nu_{17}]$, $0.19[\nu_{12}+\nu_{20}]$, $0.17[\nu_6]$, $0.12[\nu_5]$	0.1	13.7		
11+21	1770			1735	1734	$0.93[\nu_{11}+\nu_{21}]$, $0.19[\nu_6]$, $0.18[\nu_{15}+\nu_{17}]$, $0.17[\nu_{12}+\nu_{19}]$, $0.13[\nu_{13}+\nu_{18}]$	0.3	25.0		
12+19	1774			1743	1739	$0.80[\nu_{12}+\nu_{19}]$, $0.37[\nu_6]$, $0.31[\nu_{11}+\nu_{21}]$, $0.18[\nu_{13}+\nu_{18}]$, $0.18[\nu_{15}+\nu_{17}]$, $0.12[\nu_{13}+\nu_{19}]$, $0.12[\nu_{16}+\nu_{17}+\nu_{18}]$		114.9	1733	680
22+23	1780			1751	1750	$0.80[\nu_{22}+\nu_{23}]$, $0.37[\nu_{12}+\nu_{19}]$, $0.35[\nu_6]$, $0.25[\nu_{12}+\nu_{18}]$	2.3	123.9	1758	
12+18	1790			1758	1753	$0.59[\nu_{22}+\nu_{23}]$, $0.50[\nu_{12}+\nu_{18}]$, $0.46[\nu_6]$, $0.36[\nu_{12}+\nu_{19}]$, $0.12[\nu_{13}+\nu_{18}]$, $0.11[\nu_{13}+\nu_{19}]$, $0.10[\nu_{16}+\nu_{17}]$	9.4	158.2	1762	
10+21	1792			1756	1755	$0.97[\nu_{10}+\nu_{21}]$, $0.22[\nu_5]$	0.7	29.2	1774	
6 A'	1774	779.2	$Q(C_4{=}O)$	1742	1762	$0.81[\nu_{12}+\nu_{18}]$, $0.50[\nu_6]$, $0.20[\nu_{12}+\nu_{19}]$, $0.10[\nu_{22}+\nu_{23}]$	9.4	148.4		
5 A'	1807	627.8	$Q(C_2{=}O)$	1773	1776	$0.93[\nu_5]$, $0.24[\nu_{10}+\nu_{21}]$, $0.13[\nu_{13}+\nu_{18}]$, $0.12[\nu_{15}+\nu_{17}]$, $0.11[\nu_{13}+\nu_{20}]$, $0.11[\nu_{12}+\nu_{20}]$		568.4		
7+11	3061				2984	$0.93[\nu_7+\nu_{11}]$, $0.28[\nu_4]$, $0.21[\nu_7+\nu_9]$	0.3	0.6	2970	8
4 A'	3222	2.9	$q(C_6H)$	3081	3082	$0.64[\nu_4]$, $0.64[\nu_7+\nu_9]$, $0.39[\nu_7+\nu_9]$, $0.14[\nu_7+\nu_{11}]$	0.6	0.9	–	–
3 A'	3263	1.1	$q(C_5H)$	3128	3140	$0.68[\nu_3]$, $0.64[\nu_6+\nu_9]$, $0.26[\nu_7+\nu_8]$, $0.24[\nu_4]$, $0.14[\nu_7+\nu_9]$, $0.12[\nu_6+\nu_{11}]$		1.4	3130	4
2 A'	3608	65.8	$q(N_3H)$	3438	3436	$0.98[\nu_2]$, $0.15[2\nu_6]$		60.4	3433	100
2×6	3547			3469	3470	$0.99[2\nu_6]$, $0.15[\nu_2]$		10.2	(3477)	
1 A'	3649	104.5	$q(N_1H)$	3480	3480	ν_1		100.5	3482	166

Fig. 2. Experimental (top) [9] and theoretical (bottom) IR spectra of the isolated Ura molecule in the range 400–800 cm^{-1}. The theoretical spectrum was calculated taking into account Fermi resonances.

vibrations are 973 and 972 cm^{-1}. As a result of the resonance interaction, the levels are split by 23 cm^{-1}, while the intensities are redistributed such that the fundamental tone becomes very weak, whereas the intensity of the long-wavelength component increases almost twofold. Taking into account this redistribution, the experimental absorption band at 963 cm^{-1} should be attributed to the combination vibration $\nu_{27} + \nu_{28}$, rather than to the fundamental vibration ν_{15}, as was previously believed in [8, 9].

The calculation shows that the degree of mixing of the fundamental vibration ν_{14} and overtone $2\nu_{19}$ is approximately the same. The experimental spectrum shows a clearly pronounced doublet in the range 1070–1080 cm^{-1}, whose components have weak intensities, as in the calculation.

According to the calculation, the experimental absorption band at 1102 cm^{-1} is attributed to the overtone $2\nu_{27}$, which corresponds to the displacement of the N_1H bond out of the plane.

The fundamental vibrations ν_{13} and ν_{12} have Fermi resonances with the combination frequencies $\nu_{24} + \nu_{28}$ and $\nu_{23} + \nu_{28}$, whose unperturbed frequencies of anharmonic vibrations differ by 23 and 7 cm^{-1}, respec-

tively. The proximity of the levels and, as a consequence, a considerable interaction of the vibrations ν_{12} and $\nu_{23} + \nu_{28}$ (in contrast to the vibrations ν_{13} and $\nu_{24} + \nu_{28}$) determined both a large change in the frequency (17 cm^{-1} for the pair ν_{13} and $\nu_{23} + \nu_{28}$ and 13 cm^{-1} for the pair ν_{12} and $\nu_{24} + \nu_{28}$) and an increase in the intensity of the combination vibration $\nu_{23} + \nu_{28}$.

The vibrations ν_{10} and ν_{11} are mixed with nine and seven other vibrations (combinations and overtones), which considerably complicates their interpretation. It should be noted that, in the range ~1300–1450 cm^{-1}, anharmonic vibrations are shifted toward lower frequencies by ~30–40 cm^{-1} compared to harmonic vibrations, since their shapes contain changes in the exterior bending angles formed by the NH and CH bonds. As a result, the bands of combination vibrations and overtones are shifted closer to the bands of fundamental vibrations. For example, the difference between the harmonic frequencies of the combination vibration $\nu_{24} + \nu_{27}$ and vibration ν_{10} is 102 cm^{-1}, whereas, in the anharmonic approximation, this difference decreases to 54 cm^{-1}, i.e., by two almost times. The repulsion between closely located levels can lead to an error of ~10 cm^{-1} in calculations of resonant fre-

quencies, which is observed for the vibrations ν_9, ν_{10}, and $\nu_{25} + \nu_{26}$.

The frequencies ν_{11} and $\nu_{15} + \nu_{21}$ differ by only 1 cm^{-1}; therefore, they are not resolved in the experiment and are attributed to the single absorption band at 1366 cm^{-1}.

As a result of the intensity redistribution between the fundamental vibrations ν_9 and ν_{10} and the combination vibration $\nu_{25} + \nu_{26}$, the band of the vibration ν_9, whose intensity is reduced due to the Fermi resonance, cannot be observed in the experimental spectrum, while the combination vibration $\nu_{25} + \nu_{26}$, whose intensity, in contrast, increases many times, was attributed by many authors to fundamental vibrations.

The vibration ν_8 forms a polyad with the combination vibrations $\nu_{14} + \nu_{21}$ and $\nu_{24} + \nu_{25}$. Without taking into account the interaction, the frequencies of the resonant vibrations differed by 14 and 1 cm^{-1}, whereas, with allowance for the interaction, this differences became 13 and 7 cm^{-1}. The proximity of the levels and considerable interaction coefficients determine a substantial intensity redistribution. Both the experimental and the calculated spectra show the splitting of lines in the range of ~1470 cm^{-1}, the most intense of which are referred to as the fundamental vibration ν_8 (Fig. 3).

The interaction of the overtones $2\nu_{24}$ and $2\nu_{17}$ corresponds to the Darling−Dennison resonance. Since the intensity of one of the absorption bands of this doublet is very low (the vibration with the resonant frequency 1506 cm^{-1}), the experimental vibrational spectrum exhibits only one absorption band, which is located at 1525 cm^{-1}, rather than the two components.

The resonance interactions of the vibration ν_7 with other vibrations can be neglected, which is confirmed by the fact that, in the range ~1550−1650 cm^{-1}, the experimental spectrum exhibits only one vibration with a medium intensity and a frequency of 1644 cm^{-1}.

The range ~1700−1800 cm^{-1} is the most complicated to interpret because the number of intense absorption bands in this range considerably exceeds the number of fundamental vibrations. In this case, the character of interactions is analyzed based on the fact that, in polyatomic molecules (including Ura), fundamental and combination tones (or overtones) can simultaneously participate in several Fermi resonances.

Consider the interactions of the fundamental tones ν_5 and ν_6, which correspond to the stretching vibrations $\nu(C_2=O)$ and $\nu(C_4=O)$, with combination vibrations that take into account the occurrence of several Fermi resonances.

Our calculation showed that the fundamental tone ν_6 is at Fermi resonance with the combination vibrations $\nu_{12} + \nu_{18}$, $\nu_{12} + \nu_{19}$, and $\nu_{22} + \nu_{23}$, for which the frequency differences without taking into account the resonance are 16, 9, and 1 cm^{-1}, respectively. Due to the interaction, the frequencies of the combination vibrations $\nu_{12} + \nu_{18}$, $\nu_{12} + \nu_{19}$, and $\nu_{22} + \nu_{23}$ decrease by 4, 1, and 5 cm^{-1}, while the frequency of the resonant fundamental vibration ν_6 increases by 20 cm^{-1}. The resonant interaction led to the redistribution of intensity between the components of the quartet; as a result of which the intensities of all four absorption bands became approximately the same.

Next, the fundamental vibration ν_6 is at resonance with other vibrations, $\nu_{13} + \nu_{18}$, $\nu_{13} + \nu_{19}$, and $\nu_{16} + \nu_{17}$. The calculation shows that the interaction between the fundamental tone ν_6 and the combination vibration $\nu_{16} + \nu_{17}$ is the strongest, which leads to a considerable increase in the intensity of the combination vibration.

In a similar way, three other doublets of bands are formed in the spectrum at the expense of interacting vibrational states. As a result of the resonant interaction of the combination vibration $\nu_{12} + \nu_{19}$ with the fundamental vibration ν_6, the Fermi resonance occurs and two doublets between the fundamental tone and combination vibrations $\nu_{11} + \nu_{21}$ and $\nu_{15} + \nu_{17}$ are formed. Similarly, the interaction of the combination vibration $\nu_{13} + \nu_{18}$ with the ν_6 vibration leads to the formation of the doublet between the fundamental tone and combination vibration $\nu_{12} + \nu_{20}$.

The fundamental vibration ν_5 is characterized by the formation of a sextet with the combination vibrations $\nu_{10} + \nu_{21}$, $\nu_{13} + \nu_{18}$, $\nu_{15} + \nu_{17}$, $\nu_{13} + \nu_{20}$, and $\nu_{12} + \nu_{20}$. Because the frequency difference between the resonant vibrations is large, achieving ~50 cm^{-1}, and the interaction coefficients are small; only 10% or less of the intensity of the fundamental tone is redistributed.

In the experimental absorption spectrum of Ura in the range ~1700−1800 cm^{-1}, two or three frequency intervals are commonly distinguished that contain intense absorption bands. These intervals are either ~1700−1720 and ~1730−1770 cm^{-1} or ~1700−1720, ~1720−1740 cm^{-1}, and ~1750−1770 cm^{-1}. The calculation shows that the sum of the absolute intensities of all the absorption bands in this range is 1399 km/mol, which is 70% of the experimental value [8]. Taking into account that the absolute intensities of the absorption bands of Ura measured in different matrices (Kr, Ar, Ne) differ by at least 10% [13], we can state that the experimental and calculated spectra agree well with each other (Figs. 2−4).

The calculation showed that the previously proposed interpretation of the vibrational spectrum of Ura in the range of stretching C=O vibrations is considerably simplified and that this range contains complex (multiple) Fermi resonances.

In this case, it should be noted that, although the intensities of the vibrations ν_5 and ν_6 are very strong and both vibrations lie in the same spectral range,
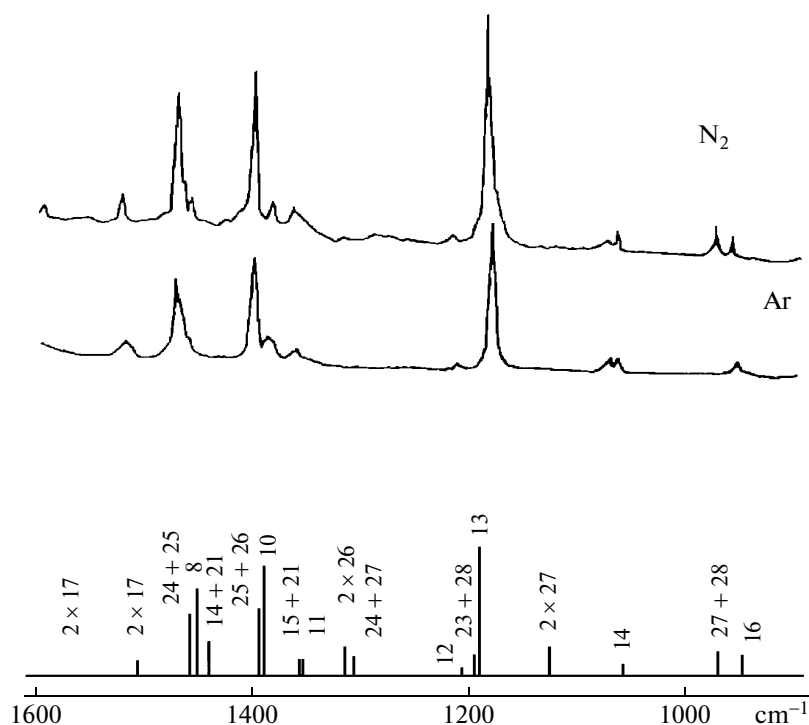
Fig. 3. Experimental (top) [9] and theoretical (bottom) IR spectra of the isolated Ura molecule in the range 900–1500 cm^{-1}. The theoretical spectrum was calculated taking into account Fermi resonances.

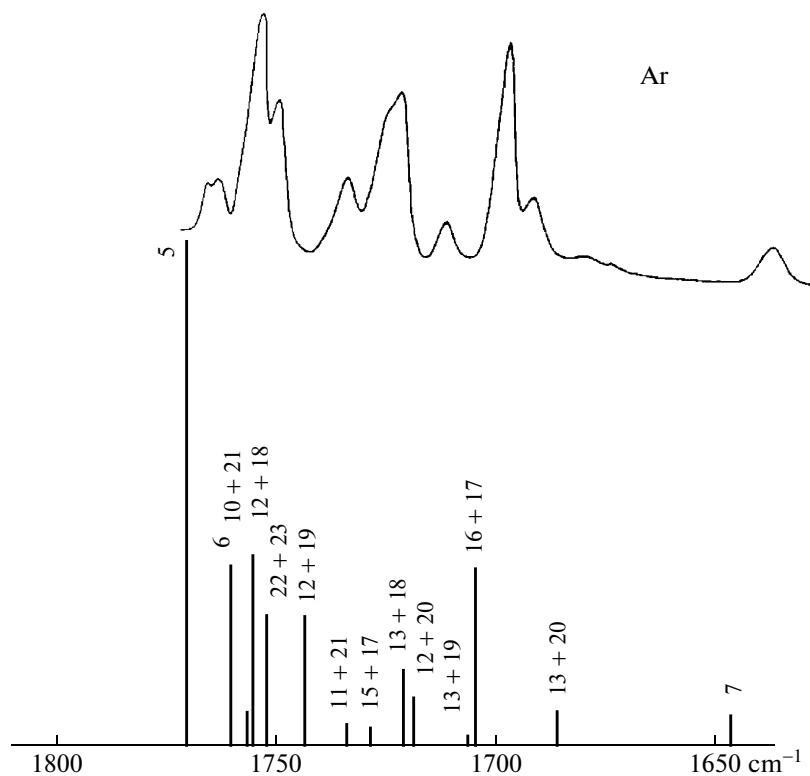**Fig. 4.** Experimental (top) [9] and theoretical (bottom) IR spectra of the isolated Ura molecule in the range 1650–1800 cm^{-1}. Theoretical spectrum was calculated taking into account Fermi resonances.

unlike vibration ν_6, vibration ν_5 interacts with a considerably smaller number of combination vibrations and overtones. Clearly, the reason for the disagreement between the experimental and calculated intensities of the vibration ν_5 is an insufficiently high accuracy of the used quantum-mechanical method of calculation, which overestimates the frequency of this mode by 30 cm^{-1}.

In the range of stretching vibrations of the CH and NH bonds, resonances between fundamental tones, combination tones, and overtones do not cause significant intensity redistributions. On the whole, we can state that the theoretical and experimental spectra in the range ~3000−3500 cm^{-1} agree well with each other.

CONCLUSIONS

According to our calculations, interactions between vibrations should be considered taking into account multiple Fermi resonances, i.e., the participation of fundamental and combination tones (or overtones) in several Fermi resonances.

Our calculation showed that only eight of the 30 fundamental vibrations of Ura (seven out-of-plane vibrations and one in-plane vibration) do not interact with other vibrations.

Taking into account multiple resonances leads to a noticeable spectral manifestation of combination vibrations and overtones, whose intensities in the anharmonic approximation are comparable with the intensities of fundamental vibrations in the harmonic approximation. The resonant interaction manifests itself the most strongly in interactions of combination tones and overtones with the very intense fundamental tone of the stretching ν(C=O) vibration of Ura.

Thus, the application of the second-order perturbation theory to the calculation of anharmonic frequencies and intensities of the isolated Ura molecule and taking into account multiple resonances allowed us to achieve good agreement between the experimental and calculated spectra of this molecule and to interpret its total IR spectrum.

REFERENCES

1. L. Harsanyi and P. Csaszar, Acta Chim. Hung. **113**, 257 (1983).
2. R. C. Lord and G. J. Thomas, Spectrochim. Acta, A **23**, 2551 (1967).
3. A. Aamouche, M. Ghomi, C. Coulombeau, et al., J. Phys. Chem. **100**, 5224 (1996).
4. H. Susi and J. S. Ard, Spectrochim. Acta, A **27**, 1549 (1971).
5. J. Florian and V. Hrouda, Spectrohim. Acta. A **49**, 921 (1993).
6. M. J. Wojcik, J. Mol. Struct. **219**, 305 (1990).
7. A. J. Barnes, M. A. Stuckey, and L. Le Gall, Spectrohim. Acta. A **40**, 419 (1984).
8. M. Szczesniak, M. J. Nowak, H. Rostkowska, et al., J. Am. Chem. Soc. **105**, 5969 (1983).
9. S. Chin, I. Scott, K. Szczepaniak, and W. B. Person, J. Am. Chem. Soc. **106**, 3415 (1984).
10. M. J. Wóicik, H. Rostkowska, K. Szczepaniak, and W. B. Person, Spectrohim. Acta. A **45**, 499 (1989).
11. M. J. Nowak, J. Mol. Struct. **193**, 35 (1989).
12. M. Graindourze, T. Grootaers, J. Smets, et al., J. Mol. Struct. **243**, 37 (1991).
13. A. Yu. Ivanov, A. M. Plokhotnichenko, E. D. Radchenko, G. G. Sheina, and Yu. P. Blagoi, J. Mol. Struct. **372**, 91 (1995).
14. M. Maltese, S. Passerini, S. Nunziante-Cesaro, et al., J. Mol. Struct. **116**, 49 (1984).
15. E. D. Radchenko, A. M. Plokhotnichenko, G. G. Sheina, and Yu. P. Blagoǐ, Biofizika **2**, 923 (1983).
16. W. D. Bowman and T. G. Spiro, J. Chem. Phys. **73**, 5482 (1980).
17. M. Ghomi, R. Letellier, E. Taillandier, et al., J. Raman Spectrosc., No. 17, 249 (1986).
18. W. L. Peticolas, D. P. Strommen, and V. Lakshminarayanan, J. Chem. Phys. **73**, 4185 (1980).
19. Y. Nishimura, M. Tsuboi, S. Kato, and K. Morokuma, J. Am. Chem. Soc. **103**, 1354 (1981).
20. V. Barone, G. Festa, A. Grandi, et al., Chem. Phys. Lett. **388**, 279 (2004).
21. P. M. Él'kin, M. A. Érman, and O. V. Pulin, Zh. Prikl. Spektrosk. **73**, 431 (2006).
22. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., *Gaussian 03* (Gaussian Inc, Pittsburgh, 2003).
23. S. Dressler and W. Thiel, Chem. Phys. Lett. **273**, 71 (1997).
24. R. Burcl, S. Carter, and N. C. Handy, Chem. Phys. Lett. **380**, 237 (2003).
25. S. V. Krasnoshchekov and N. F. Stepanov, Zh. Fiz. Khim. **82**, 680 (2008).
26. A. Willetts, N. C. Handy, W. H. Green, and D. Jayatilaka, J. Phys. Chem. **94**, 5608 (1990).

Translated by V. Rogovoi