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QUANTUM-CHEMICAL CALCULATIONS OF THE STRUCTURE, VIBRATIONAL SPECTRA, AND TORSIONAL AND INVERSION POTENTIALS OF METHYLCARBAMATE

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We present results of ab initio and DFT calculations of the structure, potential functions of the methyl group internal rotation and the amino group inversion, and vibrational frequencies and intensities in IR and Raman spectra of methylcarbamate. The calculations were carried out using different basis sets in the HF, MP2, and DFT/B3LYP approximations. The influence of both the basis set size and the allowance for electronic correlation on peculiarities of the structure of the amino group in methylcarbamate has been analyzed. It is shown that the B3LYP/6-311++G(2d, p) and B3LYP/cc-pVDZ calculations reproduce highly accurately experimental geometric parameters of methylcarbamate. Parameters of torsional and inversion potentials and characteristics of vibrational spectra calculated in different approximations show satisfactory agreement with experimental values.

Keywords: *ab initio and DFT calculations, torsion potential, inversion potential, IR and Raman spectra, methylcarbamate.*

Introduction. Polyurethanes are polymers that contain the urethane group $[-OC(O)NH-]$ in the polymer chain. They are widely used in various branches of industry [1]. They are an essential element of polyurethane foams and foam plastics with high operating specifications [2]. In addition to the urethane with its amide $[-C(O)NH-]$ and ester $[-OC(O)-]$ groups, the polymer also contains hydrocarbon $[-CH_3, -CH_2-]$, ether $[-O-]$, aromatic $[-C_6H_4-]$, and other groups. On one hand the variety of functional groups in the polyurethane chain gives rise to complicated vibrational spectra for these compounds; on the other, it generates intra- and intermolecular bonds of various nature that have a direct influence on the shape and position of spectral bands and lines.

One of the urethanes that is often used to produce polyurethane foams is 4,4'-diphenylmethanebis(methyl)carbamate (DPMC), which contains two urethanes, phenyls, and methyls. The structure, energy characteristics of various conformers, and vibrational spectra of DPMC have been studied only partially [3]. Quantum-chemical calculations of the structure and vibrational spectra of DPMC in the *ab initio* and DFT high-level approximations using expanded basis sets have not been performed. The DPMC molecule contains 41 atoms. Direct calculation of the geometric structure of such an object without high symmetry could turn out to be an exceedingly expensive ordeal. It should be noted that the structure of the DPMC molecule consists of two methylphenylcarbamate molecules bonded through a methylene. Theoretical calculations of the structural parameters and spectral characteristics of simpler urethanes such as methylphenylcarbamate or methylcarbamate enable not only determination of the most suitable approximation and minimization of costs for labor and computer time to find the equilibrium configuration of the complicated polyurethane but also solution of the more important problem of revealing trends in vibrational spectra of the urethane group as a function of its environment (from the simplest urethane methylcarbamate to the complicated polymer chain). We note that methylcarbamate is one of the simplest molecular systems in which two types of internal motion with large

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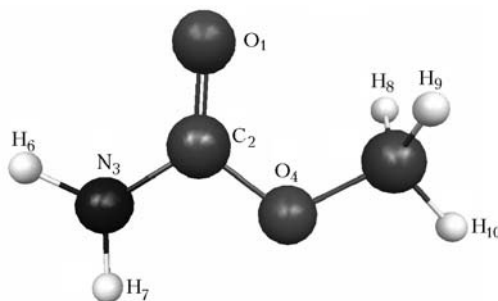


Fig. 1. Equilibrium structure of methylcarbamate.

amplitude are possible. These are inversion tunneling of the NH_2 group and torsion tunneling of the CH_3 group. Therefore, investigation of the spectral and structural characteristics of this molecule is of fundamental interest.

Herein we present results from quantum-chemical *ab initio* and DFT calculations of the molecular structure, torsional and inversion potentials, and vibrational IR and Raman spectra of methylcarbamate.

Experimental. Structural, energetic, and spectral characteristics of methylcarbamate were calculated using US [4] and Russian versions [5] of the applied quantum-chemical set GAMESS [6]. The results were displayed using the program MacMolPlt [7]. Calculations were performed using standard basis sets 6-31G, 6-311G, 6-311++G(2d, p), cc-pVDZ, and cc-pVTZ [8] in the Hartree-Fock approximation and with intermediate consideration of electron correlation by the MP2 [9] and DFT methods using the B3LYP hybrid functional [10].

Discussion. *Structure.* Table 1 gives methylcarbamate equilibrium structural parameters that were calculated using basis sets 6-311++G(2d,p), cc-pVDZ, and cc-pVTZ. Figure 1 shows the equilibrium structure.

The calculations showed that consideration of electron correlation is important for establishing the equilibrium geometry of methylcarbamate. Neglect of electron correlation effects causes either placement of the NH_2 group in the plane of the molecular framework (using small basis sets 6-31G and 6-311G) or a small deviation of the amino group from this plane (using expanded basis sets). In this instance the molecular symmetry corresponds either exactly or closely to C_s [because methyl H_8 and H_9 deviate from the $\text{NC}(\text{O})\text{OC}$ plane and are situated symmetrically relative to this plane] whereas the length of the $\text{C}=\text{O}$ double bond is considerably shortened compared with experimental values obtained for analogous compounds (1.219 Å for formamide [11] and 1.220 Å for acetamide [12]). Consideration of electron correlation produces a pyramidal NH_2 group. The maximum deviations from a planar configuration are observed using the MP2 method. For this, the $\text{C}=\text{O}$ bond lengths agree fully with the experimental value whereas the methyl group is shifted relative to its symmetry position and its structure is distorted.

Whether the amino group in methylcarbamate is planar or pyramidal has been discussed for a long time [13–15]. The hypothesis of a pyramidal structure was supported by high-level quantum-chemical calculations [13, 14], the presence of a similar structure for a whole series of analogs [13] (cyanamide, acetamide, urea, etc.), and certain experimental data. Thus, five absorption lines (203.4, 339.8, 397.0, 543.4, and 737.0 cm^{-1}) in the far IR region have been reported [14]. These were assigned to transitions between the ground and three low-lying excited inversion states, thereby confirming the hypothesis about the existence of two equivalent equilibrium positions of the amide hydrogens relative to the $\text{NC}(\text{O})\text{OC}$ plane. However, the lack of a c -component of the dipole-moment vector that was reliably established from an analysis of high-resolution microwave torsion-rotational spectra [15, 16] was a very substantial argument in favor of planar NH_2 . The principal inversion state is located above a rather low potential barrier. The molecular fragment is delocalized. The average value of the corresponding dipole-moment component is equal to zero [13]. A calculation of a system of inversion states [14] confirmed such a point of view. Generalization of the experimental and calculated data confirmed that the "equilibrium" structure, i.e., that corresponding to a minimum of the inversion potential, of the NH_2 group was a pyramidal configuration whereas the structure of the NH_2 group contributing to the energy of the ground state was planar.

Because reliable experimental results for structural parameters of methylcarbamate have not been reported, the rotational constants, which are compared with the experimental values in Table 2, are an important criterion of an adequate reproduction of the geometry. Deviations from the experimental values $\Delta A = A_{\text{ex}} - A_{\text{calc}}$ (ΔB and ΔC were de-

TABLE 1. Calculated Equilibrium Structural Parameters of Methylcarbamate

Parameter	6-311++G(2p, d)			cc-pVDZ			cc-pVTZ		
	HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP
O ₁ =C ₂	1.188	1.213	1.209	1.191	1.216	1.213	1.188	1.211	1.209
C ₂ -N ₃	1.354	1.370	1.366	1.357	1.379	1.372	1.351	1.366	1.364
C ₂ -O ₄	1.322	1.357	1.357	1.328	1.363	1.362	1.323	1.354	1.357
O ₄ -C ₅	1.415	1.437	1.436	1.416	1.433	1.433	1.413	1.431	1.433
N ₃ -H ₆	0.992	1.008	1.006	0.998	1.014	1.013	0.989	1.003	1.004
N ₃ -H ₇	0.992	1.008	1.007	0.998	1.014	1.013	0.989	1.003	1.004
C ₅ -H ₈	1.080	1.089	1.089	1.088	1.101	1.100	1.079	1.086	1.089
C ₅ -H ₉	1.080	1.089	1.091	1.088	1.101	1.102	1.079	1.086	1.088
C ₅ -H ₁₀	1.079	1.087	1.088	1.086	1.098	1.098	1.078	1.084	1.086
O ₁ C ₂ N ₃	124.57	125.42	125.29	125.00	125.91	125.65	124.74	125.60	125.52
O ₁ C ₂ O ₄	124.34	124.59	124.64	124.28	124.77	124.63	124.33	124.61	124.63
C ₂ N ₃ H ₆	116.13	114.95	116.37	115.63	113.54	115.39	117.09	115.24	116.99
C ₂ N ₃ H ₇	118.56	117.39	118.38	117.94	115.63	117.61	119.55	117.57	118.90
H ₆ N ₃ H ₇	118.18	117.20	117.98	117.58	115.48	117.16	119.14	117.58	118.50
C ₂ O ₄ C ₅	116.56	113.55	115.06	116.33	113.06	114.59	116.75	113.22	115.09
O ₄ C ₅ H ₈	110.55	110.52	110.75	110.67	110.92	111.09	110.63	110.60	110.54
O ₄ C ₅ H ₉	110.49	110.41	110.29	110.71	111.01	110.76	110.66	110.65	110.90
O ₄ C ₅ H ₁₀	105.71	105.28	105.53	105.73	105.51	105.75	105.87	105.49	105.69
H ₈ C ₅ H ₉	109.40	109.33	109.24	109.14	108.66	108.57	109.19	109.00	108.97
H ₉ C ₅ H ₁₀	110.31	110.63	110.34	110.27	110.36	110.06	110.25	110.58	110.48
H ₈ C ₅ H ₁₀	110.34	110.62	110.64	110.28	110.38	110.60	110.21	110.49	110.25
H ₆ N ₃ C ₂ O ₁	14.86	18.54	15.88	-16.29	-21.73	-17.51	-11.51	-17.61	-13.83
H ₇ N ₃ C ₂ O ₁	164.82	162.53	165.54	-162.97	-158.58	-162.44	-168.22	-163.08	-167.04
N ₃ C ₂ O ₄ C ₅	-177.54	-176.79	-175.91	177.53	176.78	179.02	178.17	177.27	176.50
H ₈ C ₅ O ₄ C ₂	-60.60	-60.84	-55.43	-60.11	-60.02	-52.39	-60.75	-61.48	-64.38
H ₉ C ₅ O ₄ C ₂	60.64	60.25	65.63	61.05	60.89	68.37	60.41	59.41	56.59
H ₁₀ C ₅ O ₄ C ₂	180.00	180.00	-175.20	180.00	180.00	-172.42	180.00	179.03	176.34
Relative energy, [*] kJ/mol	3851.2	1442.6	30.3	4037.5	1939.2	265.3	3804.9	1173.6	0.0

Note. Atomic number corresponds with Fig. 1. Bond lengths in Å; angles, degrees.

^{*}Total energy of methylcarbamate approximated by B3LYP/cc-pVTZ equals -284.4095 arb. units.

terminated analogously) are not given. Calculations using the MP2/6-311++G(2p, d) approximation were performed for two versions of the amino structure, pyramidal and planar (geometry was optimized with "frozen" coordinates for non-planar H₆ and H₇).

Our calculations showed that electron correlation must be considered in order to reproduce the experimental values of the rotational constants. The method of calculation was not in principle important because the calculations using the MP2 approximation and functional B3LYP were practically identical. However, DFT methods were 2–3 times less expensive from the viewpoint of labor and computer time. Rotational constants for pyramidal and planar NH₂ groups calculated using one approximation were not substantially different. Rotational constants obtained using B3LYP/6-311++G(2p, d) and B3LYP/cc-pVTZ approximations gave the best agreement with the experimental values. The structural parameters (Table 1) for these two instances were correlated.

TABLE 2. Rotational Constants of Methylcarbamate

Approximation	A, MHz	ΔA , %	B, MHz	ΔB , %	C, MHz	ΔC , %
HF/6-311++G(2p, d)	11,159.8	4.11	4447.5	1.10	3247.7	2.03
MP2/6-311++G(2p, d)*	10,637.2	-0.77	4399.3	0.02	3179.6	-0.10
MP2/6-311++G(2p, d)**	10,642.6	-0.72	4408.6	0.21	3179.7	-0.10
B3LYP/6-311++G(2p, d)	10,682.7	-0.34	4358.8	-0.92	3161.7	-0.67
HF/cc-pVDZ	11,056.6	3.14	4439.3	0.91	3236.2	1.67
MP2/cc-pVDZ	10,501.4	-2.03	4404.5	0.12	3173.2	-0.30
B3LYP/cc-pVDZ	10,507.8	-1.39	4362.9	-0.82	3155.1	-0.87
HF/cc-pVTZ	11,149.5	4.01	4449.9	1.15	3246.4	1.99
MP2/cc-pVDZ	10,670.7	-0.45	4437.8	0.88	3201.5	0.58
B3LYP/cc-pVTZ	10,678.3	-0.38	4372.9	-0.59	3167.1	-0.50
Experiment [15]	10,719.4	–	4399.1	–	3182.9	–

* Calculation for pyramidal amino group.

** Calculation for planar amino group.

TABLE 3. Parameters (cm^{-1}) of Torsion Potential Function of Methylcarbamate

Approximation	V_3	V_6	V_9	V_{12}	Barrier height
HF/6-311G	229.48	10.57	-0.74	0.34	228.74
HF/6-311G + ZPE	177.80	17.17	6.45	0.16	184.25
HF/6-311++G(2d, p)	404.53	22.18	-0.48	1.06	404.05
HF/6-311++G(2d, p) + ZPE	329.60	26.12	7.17	2.07	336.77
MP2/6-311++G(2d, p)	390.61	19.05	-0.70	0.51	389.91
MP2/6-311++G(2d, p) + ZPE	354.81	61.98	-7.45	-0.48	347.36
HF/cc-pVDZ	386.37	18.61	-1.92	0.30	384.45
HF/cc-pVDZ + ZPE	312.91	25.37	6.28	0.34	319.19
MP2/cc-pVDZ	340.86	30.34	-1.01	0.43	339.85
MP2/cc-pVDZ + ZPE	256.74	76.97	3.73	-2.77	253.97
Experiment [15]	359.141	-0.5845	0	0	359.141

Torsion potential. The potential-energy function for internal rotation of the methyl group in methylcarbamate showed $2\pi/3$ periodicity:

$$V_t(\gamma) = \sum_{n=1} \frac{1}{2} V_{3n} (1 - \cos 3n\gamma), \quad (1)$$

where γ is the angle of internal rotation.

Two terms of series (1) with parameters $V_3 = 359.141 \text{ cm}^{-1}$ and $V_6 = -0.5845 \text{ cm}^{-1}$ were sufficient for an adequate description of the experimental microwave torsion-rotational spectrum [15]. The quantity V_3 was determined by the height of the torsion potential barrier whereas V_6 adjusted its shape.

The torsion potential function of methylcarbamate was calculated using basis sets 6-311G, 6-311++G(2d, p), and cc-pVDZ in the Hartree–Fock approximation with intermediate consideration of electron correlation by the MP2 and DFT/B3LYP methods and consideration of the zero-point energy (ZPE) [17]. Calculations were made in 15° steps with frozen torsion angle and optimized geometry over the other internal coordinates. The calculations (Table 3, Fig. 2) showed that the ZPE correction lowered the height of the torsion barrier by an average of 20% and could substantially distort the shape of the potential function. It is noteworthy that the MP2 method should be considered more acceptable

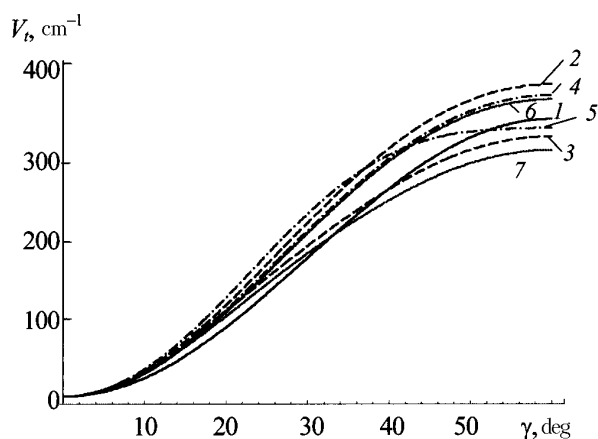


Fig. 2. Methylcarbamate torsion potential functions: experiment [15] (1), calculations by approximation HF/6-311++G(2d, p) (2), HF/6-311++G(2d, p) + ZPE (3), MP2/6-311++G(2d, p) (4), MP2/6-311++G(2d, p) + ZPE (5), HF/cc-pVDZ (6), cc-pVDZ + ZPE (7).

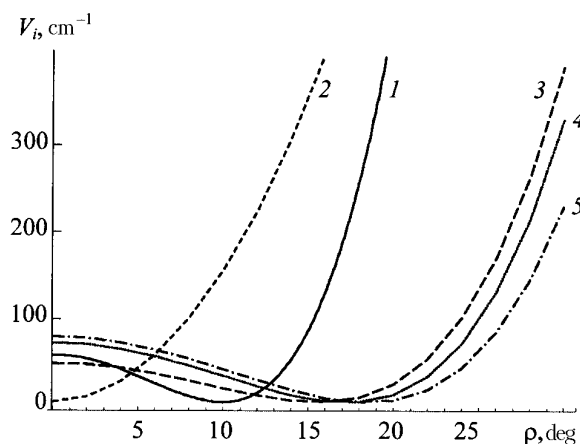


Fig. 3. Methylcarbamate inversion potential functions: experiment [13] (1), calculations by approximation HF/6-311G (2), HF/6-311++G(2d, p) (3), HF/cc-pVDZ (4), B3LYP/cc-pVDZ (5).

for considering electron correlation in calculating the torsion potential. It slightly lowered the height of the potential barrier, in contrast with DFT/B3LYP, which more than halved the height of the torsion barrier.

Thus, the *ab initio* calculation using the MP2/6-311++G(2d, p) approximation and taking into account a ZPE correction reproduced very satisfactorily the height of the torsion barrier (the deviation from the experimental value was +8.6% without the ZPE correction and –3.3% with it). However, the shape of the potential function was considered to be rather inaccurate (Fig. 2).

Inversion potential. The height of inversion potential barrier V_i of the amino group relative to the NC(O)OC plane in methylcarbamate was $55 \pm 5 \text{ cm}^{-1}$ [14]. Deviations of the amino H atoms from the NC(O)OC plane were $\pm 0.18 \text{ \AA}$ and corresponded to the potential minima. The inversion potential function of methylcarbamate was calculated using basis sets 6-311G, 6-311++G(2d, p), and cc-pVDZ in the Hartree–Fock approximation and with intermediate consideration of electron correlation by the DFT/B3LYP method and with a ZPE correction. Calculations were made in 2° steps with frozen deviation angles ρ for amino H atoms from the NC(O)OC plane and optimized geometry for the other internal coordinates. Figure 3 shows some of the results from the calculations. The experimental potential

TABLE 4. Experimental and Calculated Frequencies (ν , cm^{-1}) and Intensities in IR and Raman Vibrational Spectra of Methylcarbamate

Vibration No.	Assignment (RPE)	Experiment			Calculation using basis cc-pVDZ						
		IR [18]	Raman [19]		MP2	B3LYP					
						I			II		III
		ν	ν	I^a	ν	ν	I_{IR}^b	I_{Raman}^c	ν	I_{IR}^d	ν
1	NH ₂ stretching	3551 m.	3430	18	3762	3701	1.1	63.1	3471	45.5	3575
2	NH ₂ stretching	3435 m.			3622	3561	0.8	110.2	3306	31.9	3433
3	CH ₃ stretching	2998 w.			3242	3145	0.4	73.2	2941	15.7	3039
4	CH ₃ stretching	2957 m.	2970	42	3196	3130	0.7	58.4	2922	25.0	3024
5	CH ₃ stretching	2874 w.	2883	12	3100	3042	0.8	131.2	2862	37.0	2930
6	C=O stretching (79%) and CN (9%)	1747 vs.	1695	25	1874	1831	8.4	3.9	1772	355.6	1830
7	NH ₂ scissors (44% C ₂ N ₃ H ₇ , 28% C ₂ N ₃ H ₆ , 8%H ₇ N ₃ C ₂ O ₁ , 6%H ₆ N ₃ C ₂ O ₁), CN stretching (7%)	1583 s.	1622	20	1617	1577	3.4	3.9	1533	145.7	1533
8	CH ₃ bending	1460 vs.	1477	16	1510	1475	0.1	11.3	1425	4.9	1426
9	CH ₃ bending	1447 sh.			1487	1460	0.6	8.1	1414	27.4	1413
10	CH ₃ bending	1369 m.			1480	1450	0.5	11.5	1401	21.8	1400
11	CN stretchings (28%) and =C–O (18%), HNH bending (20%) and CH ₃ (7% O ₄ C ₅ H ₁₀), C=O swinging (9% O ₁ C ₂ N ₃ , 6% O ₁ C ₂ O ₄)	1345 vs.			1383	1352	8.0	0.2	1314	343.6	1333
12	CH ₃ bending	1195 m.	1205	14	1215	1200	0.4	3.6	1179	18.2	1173
13	CH ₃ bending	1108 m.	1119	24	1188	1175	0.0	3.1	1109	0.9	1141
14	C–O stretchings (57%) and =C–O (10%), NH ₂ swinging (11% C ₂ N ₃ H ₆ , 10% C ₂ N ₃ H ₇), COC bending (7%)	1075 s.	1084	20	1157	1119	2.6	2.4	1097	108.0	1112
15	CN stretchings (28%), C–O (13%), and C=O (11%), NH ₂ bending (26% C ₂ N ₃ H ₇ , 9% C ₂ N ₃ H ₆)	1069 (calc.)			1107	1086	0.1	4.0	1088	2.7	1068
16	=C–O stretchings (51%) and C–O (21%), HNH bending (9%)	880 m.	886	96	896	868	0.7	9.6	873	28.7	859
17	Out-of-plane C ₂ vibration relative to the OON plane	793 m.			786	777	0.6	0.4	755	26.3	777
18	OCO bending (57%) and COC (16%), CN stretching (14%)	702 m.			673	662	0.1	3.9	653	3.1	658
19	NH ₂ twist (28%) H ₇ N ₃ C ₂ O ₁ , 24% H ₆ N ₃ C ₂ O ₁), O=CN bending (35%)	673 m.	673	33	503	498	0.3	2.1	596	10.7	487
20	NH ₂ swinging (33% H ₆ N ₃ C ₂ O ₁ , 11% H ₇ N ₃ C ₂ O ₁ , 6% C ₂ N ₃ H ₇), O=CN bendings (39%) and COC (7%)	520 m.	520	69	439	442	0.1	1.6	555	6.4	432
21	NH ₂ inversion [14]	203.4			488	379	5.6	2.3	537	223.8	368
22	CH ₃ torsion [15]	120.6			180	245	0.0	0.1	343	0.7	234
23	COC bendings (54%), OCO (25%) and O=CN (6%), CH ₃ torsion (9%)	320 s.			301	297	0.3	0.5	313	12.9	293
24	Torsion relative to =C–O bond				155	162	0.3	0.4	187	13.3	161

Note. Frequencies numbered according to calculation II (see below), vibrations assigned based on calculation I. Contributions to RPE exceeding 5% are given only for mixed vibrations; m, medium intensity; w, weak; vs, very strong; sh, shoulder, calc, calculated.

^aIntensity in rel. units,

^bIR intensity in $\text{D}^2/(\text{amu} \cdot \text{\AA}^2)$,

^cRaman intensity in $\text{\AA}^4/\text{amu}$,

^dIR intensity in km/mol .

function [14] was recalculated for deviation angles ρ . Figure 3 shows that the calculated heights of the inversion barrier agreed well with the experimental value ($V_i = 45.7 \text{ cm}^{-1}$ using the HF/6-311++G(2d, p) approximation; 69.4, HF/cc-pVDZ; and 77.3, B3LYP/cc-pVDZ). However, the positions of the minima shifted by $6\text{--}8^\circ$ compared with the experimental values. The calculations showed that the ZPE correction was ineffective for calculating the inversion potential because the shape of the potential was significantly distorted.

Vibrational spectra. Vibrational IR and Raman spectra of methylcarbamate have been studied in detail [14–16, 18, 19]. Very different stretching frequencies of the NH_2 and C=O groups have been observed and were explained mainly by the different conditions for recording the spectra. Table 4 lists the frequencies of the fundamental vibrations and the intensities of spectral bands and lines of methylcarbamate corresponding to them [18, 19]. Because the purely torsion transition was not observed in spectra of methylcarbamate, its frequency was determined from microwave spectra [15] as the energy difference of rotational sublevels belonging to the first excited and ground torsion states.

Vibrational IR and Raman spectra of methylcarbamate were calculated by us using a harmonic approximation and basis sets 6-311++G(2d, p), cc-pVDZ, and cc-pVTZ with the Hartree–Fock approximation and intermediate consideration of electron correlation by the MP2 and DFT/B3LYP methods. Table 4 lists some of the results. Calculations using all three basis sets demonstrated approximately identical deviations of vibrational frequencies from the experimental values. Use of basis set cc-pVTZ (with and without considering electron correlation) gave results that differed little from those above and required much more (4–5 times) effort and computer time.

Calculations using the B3LYP/cc-pVDZ approximation were performed in several versions, i.e., with a harmonic approximation (I), with an anharmonic approximation of a quartic force field (QFF) [20] using a vibrational self-consistent field (VSCF) [21] (II), and with a harmonic approximation using a spectroscopic mass of H atoms equal to 1.088 amu [22] (III). Table 4 shows that the calculation using B3LYP/cc-pVDZ with an anharmonic approximation was in general adequate to reproduce the experimental values of the vibrational frequencies and the intensities of methylcarbamate. However, the assignment of vibrations at medium and low frequencies did not always agree with the literature [13, 18]. Thus, it should be noted that our quantum-chemical calculations predicted significant delocalization of the urethane vibrations. Two bands of medium intensity (at 1200 and 1120 cm^{-1}) were assigned [13] to =C-O stretching vibration and NH_2 swinging. The calculations confirmed that both these bands were methyl bending vibrations. Next, the strong band at about 1080 cm^{-1} and the calculated frequency 1069 cm^{-1} were assigned [13] to CH_3 swinging vibrations. According to our calculations, both these frequencies corresponded mostly to mixed vibrations; the first to C-O and =C-O stretchings, NH_2 swinging, and COC bending; the second, CN , C-O , and C=O stretchings and NH_2 bending. The calculated intensities of these bands provided additional arguments in favor of the proposed assignments.

A serious contradiction was found for assignments of =C-O and C-O stretchings from the *ab initio* calculations and the literature data [13]. According to the literature [13], the first of these corresponded to 1200 cm^{-1} ; the second, 880 cm^{-1} . Our calculations indicated that both these vibrations were significantly delocalized and that the =C-O vibration with the zero approximation corresponded most likely to 880 cm^{-1} ; the C-O vibration, 1080 cm^{-1} . Examination of the =C-O-C group as a whole correlates 1080 cm^{-1} with an asymmetric vibration; 880 cm^{-1} , a symmetric stretch of this group.

Low-frequency bendings of NH_2 and O=CN also were highly delocalized. A medium band near 790 cm^{-1} was assigned based on the calculations to an out-of-plane vibration of C_2 . Assignment of bands at 700 and 320 cm^{-1} to C=O swinging and COC bending was confirmed by the *ab initio* calculations.

Deviations of calculated frequencies from the experimental values were greatest for the amino inversion vibration and methyl internal rotation. Obviously, this was explained by the specific shape of the inversion and torsion potentials. Therefore, the calculation of the corresponding frequencies and intensities requires a separate examination. It should be emphasized that the given assignments of vibrations were not changed for all completed calculations regardless of the basis set and consideration of electron correlation. It is noteworthy that calculation III (using the spectroscopic mass of the H atom) gave practically the same results as calculation II (with anharmonic approximation) with the exception of the frequency for the C=O stretching vibration. However, calculation III required two orders of magnitude less computer time than calculation II. Because time was one of the determining factors for performing *ab initio* calculations of polyatomic molecular systems, the harmonic approximation B3LYP/cc-pVDZ with the spectroscopic mass should be considered one of the most optimal and effective for modeling the spectral characteristics of urethanes.

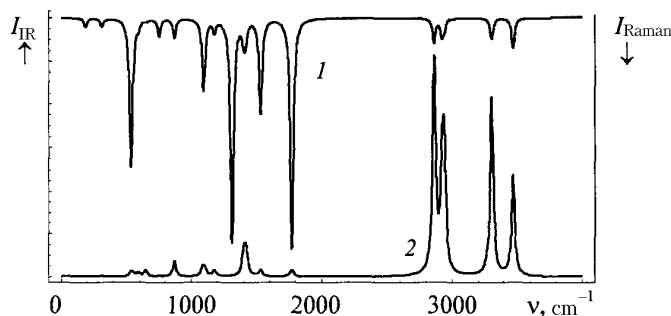


Fig. 4. Methylcarbamate IR (1) and Raman (2) spectra calculated by approximation B3LYP/cc-pVDZ.

Figure 4 shows vibrational IR and Raman spectra of methylcarbamate that were calculated with the B3LYP/cc-pVDZ approximation. Frequencies and intensities of IR absorption bands from calculation II and Raman line intensities from calculation I were used to construct the spectra.

Conclusion. The structure of methylcarbamate was analyzed based on quantum-chemical *ab initio* and DFT calculations. The resulting structural parameters, which adequately reproduced the experimental data, can be used further to determine the structure of more complicated urethanes and polyurethane chains in rigid polyurethane foams. Torsion and inversion potentials of methylcarbamate were calculated. It was shown that the calculation using the MP2/6-311++G(2d, p) approximation and taking into account a ZPE correction predicted highly accurately the height of the potential barrier to internal rotation in methylcabamate. Vibrational IR and Raman spectra of methylcarbamate were calculated using several approximations. The results can be used further to calculate and interpret vibrational spectra of complicated polyurethanes.

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