Physical Chemistry

The use of the hybrid density functional theory (DFT) approach for calculation of vibrational spectra: nitromethane

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The molecular geometry of nitromethane was optimized and its force field and vibrational spectrum were calculated by the BECKE3LYP method. The accuracy of optimization of the geometry of $MeNO_2$ obtained by this method using the 6-311G(d,p) and 6-311++G(d,p) basis sets is not poorer than that obtained at the second-order Møller—Plesset level of perturbation theory (MP2). The vibrational frequencies of nitromethane and its d_1, d_2, and d_3 isotopomers obtained by the BECKE3LYP method are in much better agreement with the experimental data than those calculated at the MP2 level using the same basis set. The average absolute error of calculations performed without the use of any scaling factors is ~2% for frequencies; the maximum deviation is ~4%.

Key words: nitromethane, vibrational spectrum, density functional theory, quantum-chemical calculations.

To interpret the vibrational spectra of organic molecules, the results of calculations of the force fields by quantum-chemical methods are widely used.[1] However, a correction of theoretical vibrational spectra is usually required irrespective of the approximation level, since marked differences are observed between calculated and experimental vibrational frequencies. It is often difficult to separate the procedures used for introducing justified corrections from conventional fitting procedures since the contributions of one or another drawback of the method used to the overall error as well as many factors neglected in the *ab initio* calculations but capable of affecting molecular vibrations can hardly be estimated under experimental conditions. At the same time, incorrect transformation of the theoretical spectrum reduces significantly its value for interpreting and complementing experimental data and its predictive power.

All the aforesaid is entirely true for nitro compounds, because of difficulties in detailed interpretation of most of their experimental vibrational spectra. For this reason, quantum-chemical calculations were used to analyze them in detail. However, all preceding calculations of vibrational spectra of nitro compounds performed by quantum-chemical methods required corrections by using individual scaling factors (~0.7—0.9) for each force constant (or normal coordinate).[2—6] In this work, the potentials of calculating the force field, frequencies, eigenvectors, and intensities of vibrations in the spectra of *C*-nitro compounds by using a comparatively new BECKE3LYP method based on the density functional

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theory (DFT) were estimated taking the nitromethane molecule as an example.

Methods of calculations

In this work, all calculations were performed in the framework of the DFT approximation. This is due mainly to two reasons.

The first reason is the increasing number of publications,[7,8] in which new and ever more sophisticated functionals that work well for a wide variety of small and large molecules are used. The accuracy of DFT methods currently used is, as a rule, as good as that of analogous MP2 calculations. In this case, it is important to take into account the second factor, namely, the computational cost, which increases for DFT methods in the same manner as for SCF calculations (as N^3, where N is the number of nonhydrogen atoms) as the sizes of the molecules increase. The computational cost of high-level *ab initio* approaches increases at least as N^5 (for MP2) or as N^6 (for MP4SDQ or CI), or even as N^7 (for standard CCSD(T) computations).

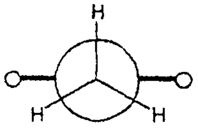
The hybrid BECKE3LYP electron density functional used in our calculations is a combination of the three-parameter unrestricted exchange functional[7] and the unrestricted correlation functional.[9] We believe that this hybrid functional is particularly efficient when optimizing the geometry and calculating vibrational frequencies for compounds of relatively light elements. For 32 molecules composed of elements of the first row of the Periodic table and calculated by the BECKE3LYP/6-311G(d,p) method, the mean absolute deviations of the bond lengths and bond angles are equal to 0.006 Å and 1.6°, respectively, which is much less than for B-LYP or B-VWN density functional methods or for *ab initio* MP2/6-31G(d) and QCISD/6-31G(d) calculations.[10] This is not surprising, since three empirical parameters were optimized on the sample set including these 32 compounds.[7] For vibrational frequencies, the mean absolute deviation from their observed values is equal to 73 cm^{-1}, which is less than that obtained by the QCISD/6-31G(d) method.[10]

The BECKE3LYP method shares the common property of DFT methods, in which they differ advantageously from standard semiempirical approaches; it is nonspecific toward particular molecules. The results of calculations appeared to be good for the number of molecules much larger than 32. For this reason, the BECKE3LYP method is included into the family of combined computational G2M schemes[11] as a method for optimization of geometry and calculation of frequencies. The authors of computational G2M complex used unscaled frequencies of the BECKE3LYP/6-311G(d,p) method. This impelled us to investigate the possibility of using this method for prediction of harmonic vibrational spectra of nitro compounds and in particular that of their simplest representative, nitromethane. All calculations were performed using the GAUSSIAN 94 program.[12]

Results and Discussion

Optimization of geometry. It is known from published data that the staggered conformation is the most stable conformation of the nitromethane molecule (one C—H bond lies in the plane perpendicular to the plane of heavy atoms), although its energy gain is insignificant (the experimental value of the barrier to internal rotation in the $MeNO_2$ molecule is only 0.006 kcal mol^{-1}).[13] This fact and the results of calculations, according to which all rotamers of nitromethane have nearly the same bond lengths and bond angles,[6] made it possible to assume that conformational transitions have little effect on all vibrational frequencies of nitromethane except for the torsional frequency $\tau(NO_2)$ associated with internal rotation.[14] It is impossible to determine the frequency of this vibration from experimental vibrational spectra, since it is less than 30 cm^{-1}; therefore, we will further use the observed and calculated values of 14 remaining frequencies.

Neglecting conformational effects, we only performed the full geometry optimization of the staggered conformation of the nitromethane molecule (conformation I). The geometric parameters found and their experimental values determined by microwave spectroscopy[13,15,16] are listed in Table 1.



Conformation I

A comparison of the values calculated by the MP2 and BECKE3LYP methods shows that they are in good agreement with the experiment and that their mean absolute deviations are nearly equal to the experimental error. When the 6-311G(d,p) basis set is used in MP2 calculations instead of the 6-31G(d,p) basis set, the bond lengths appear to be much better optimized. In this case, the bond angles well reproduced by calculations in the 6-31G(d,p) basis set remain nearly unchanged. The addition of diffuse functions to the 6-311G(d,p) basis (*i.e.*, the use of the 6-311++G(d,p) basis set) in the BECKE3LYP method mostly affects the

Table 1. Geometric parameters of $MeNO_2$

Parameter	Exp.[a] (gas)	MP2/6-31G(d,p)	MP2/6-311G(d,p)	BECKE3LYP I[b]	BECKE3LYP II[c]
		Bond length/Å			
C—N	1.489	1.487	1.491	1.503	1.504
C—H(1)	1.089	1.086	1.090	1.090	1.090
C—H(2)	1.089	1.083	1.087	1.086	1.086
C—H(3)	1.089	1.083	1.087	1.086	1.086
N—O(1)	1.224	1.241	1.228	1.220	1.221
N—O(2)	1.224	1.241	1.228	1.220	1.221
Mean abs. error		0.009	0.003	0.005	0.005
		Angle/deg			
NCH(1)	107.5	107.1	107.0	106.7	106.5
NCH(2,3)	107.5	107.8	107.9	108.0	108.0
CNO(1)	117.35	117.1	117.0	117.0	117.2
CNO(2)	117.35	117.1	117.0	117.0	117.2
O(1)NO(2)	125.3	125.8	125.9	126.0	125.6
Mean abs. error		0.3	0.4	0.5	0.4

[a] See Refs. 13 and 15 (the error for the bond lengths is equal to ±0.005 Å; that for the bond angles is equal to ±0.5°).
[b] BECKE3LYP/6-311G(d,p).
[c] BECKE3LYP/6-311++G(d,p).

Table 2. Vibrational frequencies of $MeNO_2$ (ν/cm^{-1})

Exp. (gas)[a]		Calculation[b]			
IR	Raman	MP2/6-311G(d,p)	BECKE3LYP I[c]	BECKE3LYP II[d]	Assignment
3080	—	3257 (5.8)	3198 (3.8)	3198 (3.8)	$\nu_a(CH_3)$
3045	—	3232 (6.1)	3167 (4.0)	3166 (4.0)	$\nu'_s(CH_3)$
2974	2972	3123 (5.0)	3076 (3.4)	3075 (3.4)	$\nu_s(CH_3)$
1583	1584	1807 (14.2)	1650 (4.2)	1623 (2.5)	$\nu_a(NO_2)$
1434	—	1504 (4.9)	1478 (3.1)	1476 (2.9)	$\delta'_s(CH_3)$
1410	—	1493 (5.9)	1464 (3.8)	1464 (3.8)	$\delta_a(CH_3)$
1397	1396	1440 (3.1)	1429 (2.3)	1428 (2.2)	$\nu_s(NO_2)$
1380	1380	1430 (3.6)	1401 (1.5)	1400 (1.5)	$\delta_s(CH_3)$
1131	—	1153 (2.0)	1134 (0.3)	1134 (0.3)	$r_\perp(CH_3)$
1096	1094	1134 (3.5)	1108 (1.1)	1111 (1.4)	$r_\parallel(CH_3)$
918	918	953 (3.8)	928 (1.1)	925 (0.8)	$\nu(CN)$
657	657	684 (4.1)	664 (1.1)	661 (0.6)	$\delta(NO_2)$
603	—	606 (0.5)	612 (1.5)	612 (1.5)	$w(NO_2)$
475	475	489 (3.0)	482 (1.5)	482 (1.5)	$r(NO_2)$
Mean error (%)		(4.7)	(2.3)	(2.2)	

[a] See Ref. 6. [b] The error (%) calculated using the formula $100\% \cdot (\nu_{calc} - \nu_{exp})/\nu_{exp}$, where ν_{exp} is the frequency in the IR spectrum, is given in parentheses. [c] BECKE3LYP/6-311G(d,p). [d] BECKE3LYP/6-311++G(d,p).

length of the N—O bond ($\Delta r \geq 0.001$ Å), making it closer to the experimental value.

Vibrational frequencies. In Table 2, the vibrational frequencies of $MeNO_2$ calculated by different methods are compared with their experimental values obtained from the Raman and IR spectra of $MeNO_2$ in the gas phase.[6,17,18] It follows from the data presented that an appreciable correction of the frequencies calculated by the MP2/6-311G(d,p) method is required. The large mean error (4.7%) and first of all its very wide scatter (from 0.5 to 14.2%) require several different scaling factors to be introduced. The results of BECKE3LYP calculations of the vibrational spectrum using the same basis set are much better. Actually, the spread of errors is narrowed down to 4%, and the mean error is only 2.3%. The largest error is equal to 4.2% and refers, as in the preceding calculations, to the antisymmetric stretching NO_2 vibration ($\nu_a(NO_2)$). The error of calculation of this frequency can be decreased by adding diffuse functions (*i.e.*, by using the 6-311++G(d,p) basis set). This expansion of the basis set affects pronouncedly only the $\nu_a(NO_2)$, which is in agreement with the above mentioned fact that it only affects the geometry of the NO_2 group.

The calculated and experimental frequencies of three isotopomers of nitromethane are presented in Table 3. The assignments we proposed on the basis of the analysis of the eigenvectors of the vibrations and their intensities in the IR spectrum are in agreement with those made earlier for the observed absorption bands. Only BECKE3LYP/6-311G(d,p) frequencies were calculated for deuterated analogs of $MeNO_2$, since this method appeared to be reasonably good for nitromethane itself. The best agreement between the theoretical and experi-

Table 3. Vibrational frequencies (ν) of nitromethane isotopomers

ν/cm^{-1}											
CH_2DNO_2				CHD_2NO_2				CD_3NO_2			
Exp. (gas)[a]		Calculation[b]	Assignment	Exp. (gas)[a]		Calculation[b]	Assignment	Exp. (gas),[c]	Calculation[b]	Assignment	
IR	Raman			IR	Raman			IR			
3071	—	3178	$\nu_a(CH_2)$	3029	3029	3163	$\nu_s(CH)$	2315	2378	$\nu_a(CD_3)$	
3002	3004	3107	$\nu_s(CH_2)$	2300	—	2358	$\nu_a(CD_2)$	2283	2348	$\nu'_s(CD_3)$	
2266	2267	2316	$\nu_s(CD)$	2194	2195	2248	$\nu_s(CD_2)$	2194	2202	$\nu_s(CD_3)$	
1578	1578	1645	$\nu_a(NO_2)$	1574	1572	1645	$\nu_a(NO_2)$	1572	1641	$\nu_a(NO_2)$	
1426	1415	1454	$\delta(CH_2)$	1388	1388	1424	$\nu_s(NO_2)$	1388	1423	$\nu_s(NO_2)$	
1387	1388	1422	$\nu_s(NO_2)$	1283	1283	1314	$\delta_\parallel(CD)$	1081	1090	$\delta_s(CD_3)$	
1288	1287	1315	$w(CH_2)$	1264	—	1297	$\delta_\perp(CH)$	—	1063	$\delta'_s(CD_3)$	
1258	1258	1296	$r(CH_2)$	1057	1060	1066	$\nu_s(CD_2)$	—	1059	$\delta_a(CD_3)$	
1068	—	1082	$\delta_\perp(CD)$	988	985	990	$w(CD_2)$	943	949	$r_\perp(CD_3)$	
957	957	956	$\delta_\parallel(CD)$	895	894	904	$\nu(CN)$	894	908	$\nu(CN)$	
898	898	905	$\nu(CN)$	888	—	934	$r(CD_2)$	883	885	$r_\parallel(CD_3)$	
651	651	648	$\delta(NO_2)$	640	640	644	$\delta(NO_2)$	625	628	$\delta(NO_2)$	
579	—	602	$w(NO_2)$	559	559	553	$w(NO_2)$	542	547	$w(NO_2)$	
454	454	456	$r(NO_2)$	443	443	451	$r(NO_2)$	426	433	$r(NO_2)$	
Maximum error (%)[d]		4.3				5.2			4.4		
Mean error (%)		2.2				2.3			1.6		

[a] See Ref. 6. [b] Using the BECKE3LYP/6-311G(d,p)//BECKE3LYP/6-311G(d,p) method for conformation **I**. [c] See Ref. 17. [d] The error was calculated using the formula $100\% \cdot (\nu_{calc} - \nu_{exp})/\nu_{exp}$, where ν_{exp} is the frequency in the IR spectrum.

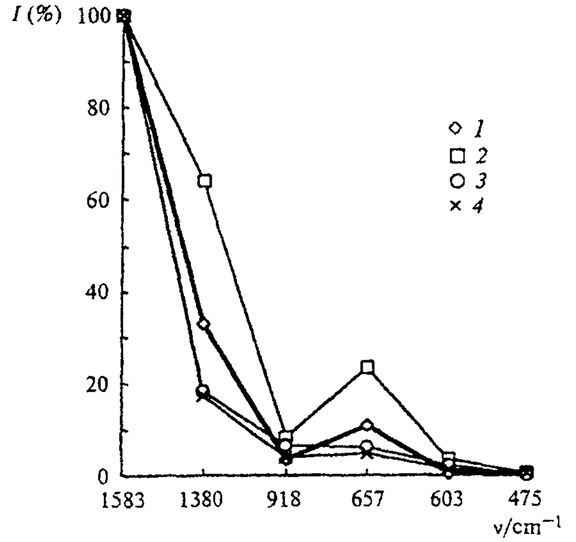


Fig. 1. Intensities of several bands in the IR spectrum of MeNO$_2$: experiment (*1*), calculations by the MP2/6-31G(d,p) (*2*), BECKE3LYP/6-311G(d,p) (*3*), and BECKE3LYP/6-311++G(d,p) (*4*) methods, respectively.

mental data on vibrational frequencies is observed for CD$_3$NO$_2$ (the mean absolute error is equal to 1.6%); as in the case of MeNO$_2$, the largest error (4.4%) falls on the ν_a(NO$_2$). The imperfectly deuterated isotopomers also obey the regularities established.

Agreement between the experimental and calculated values of the intensities of absorption bands in the IR spectra is also a significant indicator of the correctness of the force field. The relative intensities of the bands in the IR spectrum of MeNO$_2$ are presented in Fig. 1. Taking the intensity of the most active vibration (ν = 1583 cm^{-1}) as 100%, one can compare the observed and calculated values.[19] As can be seen, the BECKE3LYP results are as a whole closer to the experiment than the MP2 results. The relative overestimation of the values obtained by the MP2 method can most likely be explained by the significant underestimation of the intensity of the antisymmetric NO$_2$ vibration. As was shown above, this is just the vibration on which the largest error of the MP2 calculations of frequencies (14.2%) falls. Taking this fact into account, the MP2 method reproduces somewhat better the ratio of intensities of the five remaining vibrations presented in Fig. 1. At the same time, the general picture is better reproduced by the BECKE3LYP/6-311++G(d,p) method, which changes the ratio of intensities of the stretching C—N vibration at 918 cm^{-1} and deformation δ(NO$_2$) vibration at 657 cm^{-1} in the right direction as compared to calculations in the 6-311G(d,p) basis set.

Thus, the frequencies of the d$_0$-, d$_1$-, d$_2$-, and d$_3$-isotopomers of nitromethane calculated by the BECKE3LYP/6-311G(d,p) method are in good agreement with those observed in the Raman and IR spectra for the gas phase, which makes it possible to correctly assign the absorption bands. The mean error of determination of geometric parameters using the above method lies within the limits of experimental error, while that of frequency determination is equal to ~2% for the frequencies of all isotopomers. Therefore, it is believed that the BECKE3LYP method might appear to be convenient as a method of calculations of vibrational spectra of *C*-nitro compounds that requires no correction (*i.e.*, that uses no scaling factors). Naturally, the conclusion drawn for one compound is a tentative conclusion and must be confirmed by calculations on more objects.

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