Russian Chemical Bulletin, International Edition, Vol. 50, No. 7, pp. 1173—1180, July, 2001

Vibrational spectra of trinitromethane derivatives

V. A. Shlyapochnikov,★ D. V. Levchenkov, and A. B. Kharitonkin

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: shva@ioc.ac.ru

Spectroscopic parameters of trinitromethane derivatives $RC(NO_2)_3$ (R = F, Cl, Br, I, NC, NF_2, N_3) were determined. Vibrational frequencies and modes were calculated and the assignment of experimental spectra was performed. Spectral features due to the mutual influence of the $C(NO_2)_3$ group and other atomic groups and particular atoms were revealed.

Key words: trinitromethane derivatives, *ab initio* quantum-chemical calculations, density functional calculations, force fields, vibrational spectra, normal coordinate analysis.

The problem of mutual influence of atoms and atomic groups in molecules belongs to fundamental chemical problems. Such an influence is most pronounced in the case of particular groups, *e.g.*, the $—C(NO_2)_3$ group. In early studies on α-halo derivatives of trinitromethane and alkyl halides it has been shown that the properties of the Hal atoms in these molecules are significantly different.[1,2] This gave an impetus to further studies on the chemical and physicochemical properties of compounds containing trinitromethyl group.[3,4] Among the physicochemical methods used, considerable attention was given to spectroscopic methods.

However, experimental data available in the literature are sometimes fragmentary despite considerable efforts of researchers. This precludes unambiguous and reliable interpretation of all frequencies of the trinitromethyl group and neighboring atomic groups and establishment of common interrelations between the spectral changes due to the mutual influence of molecular fragments of compounds in question.

The main goals of this work were to rigorously interpret the spectra of trinitromethane derivatives, $RC(NO_2)_3$, based on the potentialities of modern vibrational spectroscopy and to reveal spectral features characterizing mutual influence of the $—C(NO_2)_3$ group and different atoms and atomic groups. In addition, we report and analyze complete experimental spectra of $RC(NO_2)_3$ (R = F, Cl, Br, I, NC, NF_2, N_3) compounds, for which we also performed quantum-chemical calculations of force fields and molecular spectra.*

Experimental

The most part of the experimental spectra of the molecules under study has been reported earlier.[6] A number of complete IR and Raman spectra are first presented in this work. Infrared spectra were recorded on M-80 and IVS-113W spectrometers and Raman spectra were recorded on Ramanor HG-2S and Ramanor U-1000 spectrometers with Ar lasers as excitation sources.

Quantum-chemical calculations of the molecules under study were carried out using the density functional theory (DFT) approach with the B3LYP exchange-correlation functional, 6-311+G(d,p) basis set (as a rule), and GAUSSIAN-94 program package. In some instances, other computational procedures and basis sets were used. Normal coordinate analyses were performed using the NCA program.[7] To provide the possibility of comparing the structural and spectroscopic parameters, quantum-chemical calculations of methane derivatives RCH_3 (R = F, Cl, Br, I, NC, NF_2, N_3) were also performed.

Results and Discussion

The experimental data for all the molecules under study, except for $NCC(NO_2)_3$, the calculated frequencies, and the potential energy distribution (PED) over vibrations are listed in Tables 1—7. Figure 1 presents the diagrams of contributions to the vibrational modes taking several arbitrarily chosen vibrational frequencies of the $FC(NO_2)_3$ molecule as examples. In Fig. 1, the relative values of normalized ($-1 \le x \le +1$) vibrational modes are plotted as ordinates and the chemical bonds and bond angles in the molecule (in an arbitrary way), as abscissas. For clarity, the points on the diagram are connected by lines. This type of graphical presentation of the contributions to vibrational modes seems to be first used. For long, it has been common practice to represent these contributions in the form of huge tables; however, this makes the understanding of the character of intramolecular motions difficult. Presumably, that is why modern spectroscopic studies present no such information.

The experimental IR and Raman spectra of all the trinitromethane derivatives studied are similar*. The most intense IR bands are observed at ~1600, ~1300,

---

* The results of structural studies have been reported earlier.[5]

* Here, we do not consider the results obtained for the $Hg[C(NO_2)_3]$ molecule. Its spectra are also similar to those of the trinitromethane derivatives in question.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1118—1124, July, 2001.

Table 1. Experimental spectra of $FC(NO_2)_3$ and those calculated by the DFT (B3LYP/6-311+G(d,p)) and MP2 methods

Vibration	Experiment (liquid), ν/cm^{-1}		Calculations		
			B3LYP/6-311+G(d,p)		MP2/
	IR	Raman*	ν/cm^{-1}	PED (%)**	6-31G**, ν/cm^{-1}
1		1631 (2; 0.68)	1695	93 NO	1876
2	1620 vs		1690	89 NO	1876
3			1690	90 NO	1874
4	1355 w	1362 (5; 0.24)	1405	75 NO; 3 CN	1375
5			1344	82 NO	1317
6	1295 vs		1344	77 NO	1317
7		1300 (5; 0.50)	1303	79 CF	1324
8		1024 (4; 0.60)	979	59 CN	1058
9		920 (1; dp)	979	59 CN	1058
10	855 w	859 (15; 0.20)	871	45 ONO; 18 CN; 9 CNO	853
11			818	54 ONO; 13 CNO	793
12	798 vs	800 (1; 0.75)	818	50 ONO; 8 CNO	793
13	710 m		730	19 CF; 21 ρ; 12 τ	723
14			660	27 CN; 6 CNO; 15 ρ; 8 τ	655
15	650 m		660	25 CN; 8 CNO; 7 ρ; 10 τ	655
16		526 (2; 0.24)	521	5 CF; 12 CN; 45 CNO; 6 ρ; 6 τ	527
17			390	52 CN; 19 CNO	417
18		409 (4; 0.75)	390	56 CN; 22 CNO	417
19		365 (2; 0.3)	347	69 CN; 18 CNO	373
20			322	8 CN; 15 FCN; 38 CNO; 16 τ	330
21		325 (2; 0.75)	322	6 CN; 13 FCN; 28 CNO; 18 τ	330
22		243 (1; p)	209	6 CN; 9 CNO; 15 NCN; 20 CNO; 18 τ	218
23			163	54 NCN	172
24		187 (dp)	163	52 NCN	172
25			90	90 τ	79
26			50	91 τ	40
27			50	86 τ	40

* Figures in parentheses denote the intensity and polarization degree or its notation (p for polarized line and dp for depolarized line), respectively.

** Notations ρ and τ stand for the rocking and torsional vibration, respectively.

and ~800 cm^{-1} while the strongest Raman lines are observed at ~1350, ~850, and ~375 cm^{-1}. Their positions vary only slightly on going from one compound to another. With few exceptions, weaker bands are grouped together and these groups follow a regular pattern.

Table 2. Experimental spectra of $ClC(NO_2)_3$ and those calculated by the DFT (B3LYP/6-311+G(d,p)) method

Vibration	Experiment (liquid), ν/cm^{-1}		Calculations	
	IR	Raman**	ν/cm^{-1}	PED (%)*
1			1708	90 NO
2	1630 vs		1708	78 NO
3		1619 (0.72)	1702	93 NO
4		1348 (0.3)	1400	78 NO
5	1278 vs	1285	1341	79 NO
6			1341	75 NO
7		1005 (0.2)	1007	49 CCl; 15 CNO
8	976 w		904	56 CN
9	921 w	930 (0.8)	904	55 CN
10	841 w	848 (0.1)	863	4 CCl; 9 CN
11	701 vs		813	49 ONO; 8 CNO
12			813	50 ONO; 14 CNO
13	645 m		659	35 CCl
14			651	35 CN; 13 CNO; 8 ρ; 8 τ
15			651	31 CN; 11 CNO; 5 ρ
16		437 (0.33)	431	37 CCl; 60 CNO
17			377	53 CN; 24 CNO
18		400 (0.64)	377	53 CN; 30 CNO
19		364 (0.08)	346	72 CN; 15 CNO
20		355 (0.75)	246	37 ClCN; 16 CN; 9 CNO; 13 τ
21			246	25 ClCN; 14 CN; 21 τ
22		207 (0.75)	218	21 NCN; 24 τ; 14 CNO
23		173 (0.83)	168	49 NCN
24			168	44 NCN
25			102	90 τ
26			46	89 τ
27			46	82 τ

* See notes to Table 1.

** Figures in parentheses denote the polarization degree.

The intensity of the Raman line at ~375 cm^{-1} varies over a rather wide range. However, this cannot be detected by visual inspection and is made evident when performing quantitative measurements.[6] Discussing the influence of the trinitromethyl group on the frequencies of the group R and the C—R stretching vibration frequencies requires reliable identification of the corresponding vibrations. In most cases, this can hardly be done using a set of experimental data, since these vibrations are, as a rule, of low intensity. It is only known that the intensities of the C—H stretching bands for the CH_2 and CH_3 groups neighboring to the trinitromethyl group in the IR spectra of polynitroalkanes are nearly an order of magnitude lower than the corresponding parameters for alkanes.[6] A similar decrease in the frequencies of the N_3 group has also been discussed.[8] It seems likely that the decrease in the band intensity is a salient feature of the influence of the

Table 3. Experimental spectra of $BrC(NO_2)_3$ and those calculated by the DFT (B3LYP/6-311+G(d,p), B3LYP/3-21G), and MP2 methods*

Vibration	Experiment (liquid), ν/cm^{-1}		B3LYP/6-311+G(d,p)		B3LYP/3-21G	MP2/3-21G
	IR	Raman	ν/cm^{-1}	PED (%)	ν/cm^{-1}	
1			1687	89 NO	1410	1857
2	1616 vs	1617 (2; 0.82)	1687	88 NO	1410	1854
3			1679	93 NO	1401	1854
4	1348 m	1345 (—; 0.17)	1393	81 NO	1162	1130
5	1290 vs	1290 (3; 0.93)	1334	82 NO	1105	1081
6			1334	82 NO	1105	1081
7	982 m	982 (1; 0.43)	959	37 CBr	955	985
8	921 m	923 (4; 0.91)	893	54 CN	839	871
9	851 m		893	55 CN	839	871
10	840 m	841 (12; 0.12)	856	48 ONO; 18 CNO; 4 CBr	759	750
11	793 vs	790 (1; 0.82)	806	50 ONO; 15 CNO	717	711
12			806	48 ONO; 8 CNO	717	711
13	645 m	640 (2; 0.82)	647	34 CN; 11 CNO; 8 ρ	594	600
14			647	35 CN; 11 CNO; 12 ρ	594	600
15	565 s		628	28 CBr; 18 ρ	575	586
16	445 s	394 (3; —)	374	51 CN; 33 CNO	362	380
17		375 (5; 0.86)	374	55 CN; 29 CNO	362	380
18		345 (20; 0.13)	368	27 CBr; 54 CNO	348	356
19			322	27 CBr; 66 CNO	316	322
20		225 (—; 0.96)	212	11 CN; 15 BrCN; 17 NCN; 8 CNO	207	212
21			212	11 CN; 16 BrCN; 18 NCN; 6 CNO	207	212
22		173 (—; 0.87)	195	21 NCN; 19 CBr; 15 τ	192	198
23			156	32 NCN; 14 CBr; 6 τ	159	162
24			156	34 NCN; 20 CBr; 13 τ	159	162
25		110 (—; 0.97)	105	87 τ	80	56
26			40	93 τ	37	26
27			40	85 τ	37	26

* See notes to Table 1.

Table 4. Experimental spectra of $IC(NO_2)_3$ and those calculated by the DFT (B3LYP/3-21G) and MP2 methods

Vibration	Experiment (solution), ν/cm^{-1}		B3LYP/3-21G		MP2/3-21G, ν/cm^{-1}
	IR	Raman**	ν/cm^{-1}	PED* (%)	
1	1613 vs	1598 m	1404	83 NO	1849
2			1404	95 NO	1845
3			1392	93 NO	1844
4	1350 w	1355 w	1157	72 NO	1128
5	1298 vs	1303 w (0.33)	1100	72 NO	1079
6		1293 m	1100	79 NO	1079
7	950 m	955 w (0.36)	907	34 CI	945
8		859 w	821	58 CN	853
9	839 s	850 s (0.25)	821	59 CN	853
10	786 vs	788 vw	755	9 CN	748
11			713		710
12		650 w	713		710
13	650 m	609 vw	586		597
14	607 w		586		597
15			559		573
16	450 s	428 w	357		378
17		403 w	357		378
18		375 s	330		341
19		313 vs (0.33)	289		297
20		213 m	194		200
21			194		200
22		160 m	175		183
23			146		152
24			146		152
25			83		62
26			38		32
27			38		32

* Due to low accuracy of calculations, the PED values are listed only for relatively high-frequency vibrations.

** Figures in parentheses denote the polarization degree.

trinitromethyl group. This also suggests the necessity of theoretical analysis of the spectra, which is the subject of this study.

We deliberately do not dwell on the accuracy of calculations and do not discuss the mean error, maximum error, *etc.* Experiments were carried out with

Table 5. Experimental spectra of $F_2NC(NO_2)_3$ and those calculated by the DFT (B3LYP/6-311+G(d,p)) method*

Vibration	Experiment, ν/cm^{-1}		Calculations	
	IR	Raman	ν/cm^{-1}	PED (%)
1		1650 w (0.79)	1700	86 NO
2	1625 vs		1691	86 NO
3		1620 w (0.76)	1676	84 NO
4	1342 w	1348 s (0.16)	1396	79 NO
5	1283 vs	1277 m (0.79)	1332	85 NO
6			1330	76 NO
7	1098 vw	1102 w (0.33)	1090	53 CN(F)
8	1035 vw	1035 m (0.67)	999	39 CN(O); 12 NO; 7 CNF
9	972 m	980 w (0.64)	988	34 CN(O); 5 CN(F); 8 NO; 6 CNF
10	920 m	920 w (0.68)	974	13 CN(O); 49 NO
11			905	78 NO
12	847 m	852 vs (0.12)	862	9 CN(O); 4 NO; 9 CNO; 60 ONO
13	808 vs	800 w (dp)	821	55 ONO; 7 CNO
14	797 vs		815	54 ONO; 14 CNO
15		720 vw (0.5)	733	20 CN(F); 13 CNF; 22 ρ
16		651 w	666	25 CN(F); 8 CN(O); 6 NO; 13 ρ
17			652	20 CN(O); 3 CN(F); 6 CNF; 4 NO; 7 τ; 7 ρ
18		550 m (0.5?)	545	20 CN(O); 7 CN(F); 12 CNF; 7 FNF; 12 CNO
19		530 s (0.14)	538	7 CN(O); 3 CN(F); 15 NO; 12 CNF; 10 CNO; 10 FNF; 10 CNO
20		420 m (0.76)	407	38 CN(O); 40 CNO
21		375 w (0.9)	374	18 CN(O); 56 CNO; 6 CNF
22		353 vs (0.35)	338 (?)	47 CN(O); 24 CNO
23			334	54 CN(O); 16 CNF
24			331	40 CN(O); 10 CN(F); 17 CNF
25		223 w (0.9)	223	7 CN(O); 11 N(F)CN(O); 6 ONO; 4 CNF; 7 CNO
26			204	11 NCN; 7 N(F)CN(O); 9 CNO; 9 CNF
27		~184 m (0.81)	198	13 NCN; 10 N(F)CN(O); 7 CNO; 6 CNF; 26 τ
28			170	13 NCN; 10 N(F)CN(O); 7 CNO; 6 CNF
29			153	24 τ; 15 N(F)CN(O); 8 NCN
30			116	15 τ(NO); 73 τ(NF_2)
31		100 w (dp)	95	8 τ(NO); 3 τ(NF_2)
32			61	25 τ(NO)
33			42	89 τ(NO)

* See notes to Table 2.

substances in the condensed phase, while calculations were of course performed for free molecules. It is known that frequency shifts due to transition from the gas phase to the condensed phase can be rather large.[6] We believe that solving the frequency assignment problem does not require precise calculations, since usually frequency shifts in the range up to several tens of cm^{-1} do not lead to significant changes in the contributions to the vibrational modes and, correspondingly, to the PED.

From this points of view, the agreement between theory and experiment (see Tables 1—6, the results of density functional B3LYP/6-311+G(d,p) calculations)* may be thought satisfactory. The maximum difference between the calculated and experimental values (~70 cm^{-1}) was obtained for the antisymmetric NO stretching vibrations in the $BrC(NO_2)_3$ molecule. All other calculated frequencies are in much better agreement with the experimental data. The MP2 method reproduces the experimental values somewhat worse than the DFT approach, since it requires introduction of scale factors of the force field. The results of both MP2 and density functional calculations with the 3-21G basis set were found to be inadequate.

However, this concerns mainly the frequencies of the NO stretching vibrations, whereas all other vibrational frequencies are calculated with reasonable accuracy. Therefore, calculations with the 3-21G basis set in the frequency range below 1300 cm^{-1} are not prohibited (though they should be performed very carefully), which is of great importance in those cases where the use of extended basis sets is impossible (*e.g.*, calculations of the $IC(NO_2)_3$ molecule).

Thus, the results of DFT (B3LYP) calculations of the contributions to vibrational modes and PED allow

---

* Calculations of $ClC(NO_2)_3$ were carried out with the 6-311G(d,p) basis set.

Table 6. Experimental spectra of $N_3C(NO_2)_3$ and those calculated by the DFT (B3LYP/6-311+G(d,p)) method*

Vibration	Experiment, ν/cm^{-1}		Calculations	
	IR	Raman	ν/cm^{-1}	PED (%)
1			2307	83 N(12)N(13); 18 N(1)N(12)
2		1650 m (0.63)	1689	82 NO
3	1635 vs	1620 m (0.71)	1686	94 NO
4	1600 s		1670	93 NO
5			1402	80 NO
6	1353 w	1352 s (0.16)	1379	46 CN (azide); 41 N(1)N(12)
7	1310 vs		1346	80 NO
8		1300 vs (0.62)	1341	79 NO
9	1083 m	1035 vw (dp)	1106	34 CN (azide); 31 N(1)N(12)
10	1017 m	1015 m (0.8)	976	7 CN (azide); 38 CN (nitrile); 17 CN(1)N(12)
11		963 w (0.52)	899	51 CN (nitrile)
12		935 w	863	18 CN; 45 ONO; 8 CNO
13	850 s	855 vs (0.1)	823	8 CNO; 48 ONO
14	809 vs	809 w (0.57)	813	14 CNO; 55 ONO
15		740 w (0.51)	741	14 CN (azide); 13 N(1)N(12); 21 CN(1)N(12); 15 NNN
16		640 w (0.82)	697	9 CN (nitrile); 4 CN(1)N(12); 11 ρ; 6 CNO; 12 $\tau(NO_2)$
17		598 m (0.49)	612	34 CN (nitrile); 9 CNO; 11 τ(NNC); 5 $\tau(NO_2)$
18			598	11 CN (nitrile); 13 CN(1)N(12); 37 NNN
19			529	τ(NNN)
20		465 vs (0.25)	469	11 CN (azide); 34 CNO; 26 NNN
21		410 w (dp)	396	46 CN (nitrile); 35 CNO
22		368 vs (0.32)	354	53 CN (nitro); 13 CNO
23			345	65 CN (nitro)
24			326	27 CNO; 27 τ(NNC)
25			316	27 CN (nitro); 23 CN(1)N(12); 13 NNN
26		225 w (0.41)	215	7 N(1)C(2)N(3); 7 N(3)C(2)N(4); 7 CNO
27		188 m (dp)	177	32 N (nitrile)C(2)N (nitro); 8 CN(1)N(12); 14 τ(NO)
28			167	29 N (nitrile)C(2)N (nitro); 10 τ(NNC)
29			130	57 CN(1)N(12); 14 NNN
30			91	88 τ(NO)
31			74	47 τ(NNC); 27 τ(NO)
32			61	80 τ(NO); 5 τ(NNN)
33			40	92 τ(NO)

* See notes to Table 2.

Table 7. Spectral parameters of trinitroacetonitrile obtained from B3LYP/6-311+G(d,p) calculations

Vibration	ν/cm^{-1}	PED (%)*	Vibration	ν/cm^{-1}	PED (%)*
1	2366	88 NC	16	669	9 CN; 8 NCC; 46 ρ
2	1695	94 NO	17	468	17 CC; 3 CN; 33 CNO; 5 ρ
3	1694	90 NO	18	441	17 CN; 8 NCC; 33 CCN (nitrile)
4	1690	92 NO	19	441	26 CN; 7 NCC; 33 CCN (nitrile)
5	1395	81 NO	20	365	51 CN; 20 CNO; 7 CCN (nitrile)
6	1330	84 NO	21	364	4 CN; 19 CNO; 7 CCN (nitrile)
7	1330	80 NO	22	340	65 CN; 18 CNO
8	1168	54 CC	23	206	27 NCC; 37 NCN; 11 ρ; 6 CNO
9	909	39 CN; 14 NCN; 15 NCC; 10 ρ	24	181	53 NCN; 17 CCN (nitrile)
10	909	36 CN; 14 NCC; 8 NCC; 14 ρ	25	181	54 NCN; 17 CCN (nitrile)
11	866	15 CN; 48 ONO; 8 CNO	26	140	37 NCC; 10 NCN; 33 CCN (nitrile)
12	815	53 ONO; 7 CNO	27	140	38 NCC; 15 NCN; 33 CCN (nitrile)
13	814	48 ONO	28	95	93 τ
14	685	17 CC; 73 ρ	29	49	85 τ
15	670	9 CN; 6 NCC; 59 ρ	30	47	74 τ

* Notations: N denotes the nitrogen atom of nitro group and N (nitrile) denotes the nitrogen atom of nitrile group.

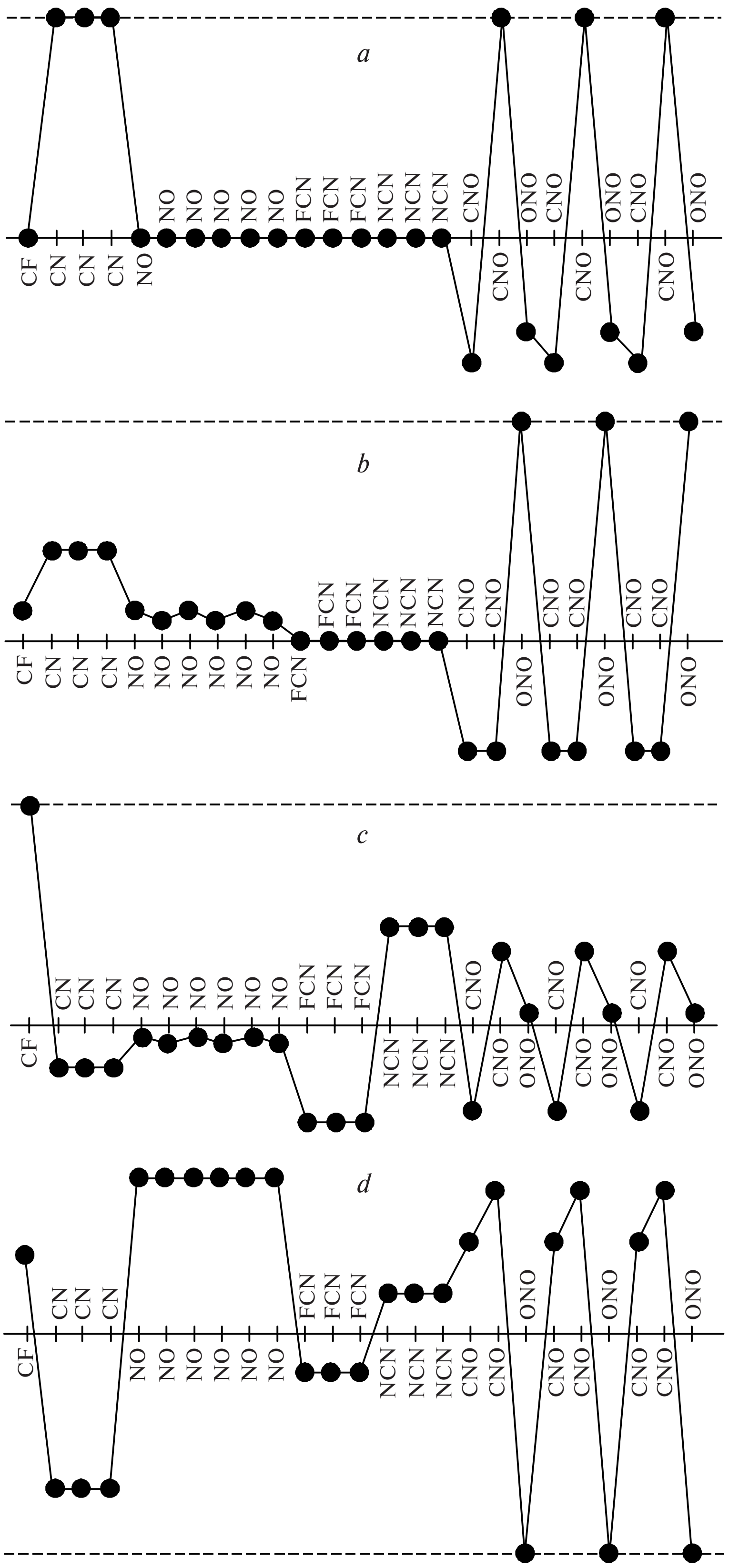

Fig. 1. Diagrams of contributions to vibrational modes of fluorotrinitromethane molecule, calculated for vibrations at ν = 373 (*a*), 871 (*b*), 1303 (*c*), and 1405 cm^{-1} (*d*). The relative values of normalized ($-1 \le x \le +1$) vibrational modes are plotted as ordinates and the chemical bonds and bond angles in the molecule (in an arbitrary way), as abscissas.

interpretation of all vibrational frequencies of the $C(NO_2)_3$ group in the $RC(NO_2)_3$ molecules. All vibrations of this group are rather strongly coupled, which is clearly seen in the diagrams of the contributions to vibrational modes for a number of vibrations of the $FC(NO_2)_3$ molecule (see Fig. 1). On the other hand, many vibrations of the $C(NO_2)_3$ group can be thought to be rather pure. Therefore, they relatively slightly depend on both the molecular symmetry and the nature of the substituent R (see the "PED" columns in Tables 1—7).

The effects of interactions manifest themselves in the spectra of compounds under study mainly as changes in the parameters of the C—N stretching vibrations (Table 8). However, it should be noted that only one out of the three C—N stretching vibrations (ν(CN)), *viz.*, the high-frequency vibration, can be considered "pure." This is to the greatest extent valid for the $FC(NO_2)_3$ molecule (PED ~60%) and to the least extent valid for $N_3C(NO_2)_3$ (PED ~30%). The other two vibrations ν(CN) are even more strongly coupled, especially the low-frequency vibration. Therefore, attribution of these two vibrations to the C—N stretching vibration is rather conventional. It should also be noted that the spectra of symmetrical molecules (a C_3 symmetry) are characterized by coincidence of two frequencies ν(CN), while those of unsymmetrical $NF_2C(NO_2)_3$ and $N_3C(NO_2)_3$ molecules are characterized by frequency splitting.

As mentioned above, the high-frequency, so-called C—N stretching vibrations are strongly coupled. On the other hand, the diagonal force constant of the C—N bond (F_{CN}) contributes largely to a number of bending vibrations of the molecules under study. For instance, three frequencies of $FC(NO_2)_3$ at 390, 390, and 347 cm^{-1} are characterized by the PED values of 52, 56, and 69% CN, respectively. Therefore, we have the right to interpret these vibrations rather than those lying in the region 800—900 cm^{-1} as the CN "stretching" vibrations. A similar picture is also observed for the spectra of other molecules.

Calculations predict some minor changes in the vibrational frequencies of the $C(NO_2)_3$ group in the series of compounds under study. For instance, the frequency of degenerate, antisymmetric stretching vibration N—O must be higher than that of analogous in-phase vibration for the $BrC(NO_2)_3$ molecule and lower for other molecules ($FC(NO_2)_3$ and $ClC(NO_2)_3$). However, this was not observed experimentally (in the region ~1600 cm^{-1}), which is likely due to overlap of the absorption bands.

The trinitromethyl group was found to have a rather strong effect on the vibrations of the group R and, first of all, on the R—C stretching vibration. These frequencies were also assigned based on the calculated contributions to the vibrational modes and PED values (see Tables 1—7). The calculated frequencies of the $ClC(NO_2)_3$, $BrC(NO_2)_3$, and $IC(NO_2)_3$ molecules correspond to polarized lines of medium intensity in the Raman spectra. According to calculations, the vibrational frequency ν(C—F) of $FC(NO_2)_3$ must lie near 1300 cm^{-1}. However, this spectral region is characteristic of strong vibrations $\nu_s(NO_2)$. Therefore, we failed to single out the ν(C—F) vibration using the set of experimental data. Previously,[4] it was assigned to a Raman line at 1024 cm^{-1}, which has no calculated analogs. Since both B3LYP and MP2 calculations predict the same frequency (~1300 cm^{-1}) for the vibration ν(C—F), we are apt to accept the calculated value.

The frequency ~950 cm^{-1} in the spectrum of the $IC(NO_2)_3$ was assigned to the stretching vibration C—I. Taking into account the accuracy of quantum-chemical calculations of iodotrinitromethane molecule, this assignment should be considered tentative. The stretching vibration C—Hal in the molecules of compounds under study appeared to be relatively pure. The best results were found for the ν(C—F) bond in the $FC(NO_2)_3$ molecule (PED = 79%). For the ν(C—Cl) vibration in $ClC(NO_2)_3$ and ν(C—Br) vibration in $BrC(NO_2)_3$ we obtained that PED = 37%. Calculations also allowed identification of the stretching vibration of the bond nearest to the trinitromethyl group in the $NF_2C(NO_2)_3$, $N_3C(NO_2)_3$, and $NCC(NO_2)_3$ molecules. The corresponding results are compared in Table 9 with the

Table 8. Force constants (F_{CN}) and frequencies (ν) of C—N stretching vibrations in compounds $RC(NO_2)_3$ obtained from B3LYP/6-311+G(d,p) calculations

R	F_{CN}/mdyn Å^{-1}	ν(CN)/cm^{-1}
F	2.66	979, 979, 871
Cl	2.43	904, 904, 853
Br	2.38	893, 893, 853
I*	2.43	853, 853, 748
NF_2	2.43—2.57	999, 988, 974
N_3	2.22—2.77	899, 863, 823
NC	2.355	909, 909, 866

* Calculated in the B3LYP/3-21G approximation.

Table 9. Diagonal force constants (F) and frequencies (ν) of stretching vibrations C—R in the $RC(NO_2)_3$ and RCH_3 molecules

R	F_{CR}/mdyn Å^{-1}			ν(CR)/cm^{-1}		
	$RC(NO_2)_3$	RCH_3	ΔF	$RC(NO_2)_3$	RCH_3	Δν
F	7.20	5.39	1.81	1303	1034	269
Cl	3.85	3.25	0.60	1007	714	293
Br	3.08	2.56	0.41	959	576	383
I*	2.57	2.19	0.38	907	512	395
NF_2	3.78	4.42	−0.64	1090	1043	47
N_3	6.13	4.60	1.53	1106	915	191
CN	5.62	5.29	0.38	1168	929	239

* The estimates for ICH_3 and $IC(NO_2)_3$ were obtained from B3LYP/3-21G calculations.

results of calculations for the RCH_3 molecules. The experimental spectra of the latter were taken from Ref. 9.

Comparison of the frequencies of stretching vibrations C—R in the R—CH_3 and R—$C(NO_2)_3$ molecules shows that the trinitromethyl group causes a substantial increase (up to ~400 cm^{-1}) in the frequency ν(C—R). This is due to changes in the structural parameters of the molecules, first of all to shortening of the C—R bonds. The only exception is the $NF_2C(NO_2)_3$ molecule. Here, the C—N bond in the CNF_2 group is longer than in the NF_2CH_3 group, but the N—F bond lengths are appreciably different. The F_{C-R} constants behave analogously (see Table 9). The F_{C-F} values change to the greatest extent (from 5.39 to 7.20) on going from FCH_3 to $FC(NO_2)_3$.

Thus, the main effect of the interaction between the trinitromethyl group and other neighboring atomic groups and particular atoms is an increase in the force constant of the C—R bond. Comparison of the frequencies of the C—R stretching vibrations in methane and trinitromethane derivatives allows construction of a tabulated dependence (see Table 9), which can be used for tentative estimation of positions of the ν(C—R) bands in the spectra of compounds containing the trinitromethyl group. For instance, the C—Hg stretching vibrations in $Hg[C(NO_2)_3]$ molecule must lie in the region 800—900 cm^{-1}.

This work was supported in part by the Russian Foundation for Basic Research (Project No. 97-03-33712a).

References

1. S. S. Novikov, V. V. Sevost′yanova, and A. A. Fainzil′berg, *Usp. khimii*, 1962, **31**, 1417 [*Russ. Chem. Rev.*, 1962, **31** (Engl. Transl.)].
2. A. N. Shidlovskaya, Ya. K. Syrkin, S. S. Novikov, A. A. Fainzil′berg, V. V. Sevost′yanova, and V. I. Gulevskaya, *Dokl. Akad. Nauk SSSR* [*Dokl. Chem.*], 1960, **132**, 1376 (in Russian).
3. N. I. Sadova, L. V. Vilkov, and T. I. Anfimova, *Zh. Strukt. Khim.*, 1972, **13**, 763 [*J. Struct. Chem. (USSR)*, 1972, **13** (Engl. Transl.)].
4. S. S. Novikov, G. A. Shvekhgeimer, V. V. Sevost′yanova, and V. A. Shlyapochnikov, *Khimiya alifaticheskikh i alitsiklicheskikh nitrosoedinenii* [*Chemistry of Aliphatic and Alicyclic Nitro Compounds*], Khimiya, Moscow, 1974, 347 (in Russian).
5. D. V. Levchenkov, A. B. Kharitonkin, and V. A. Shlyapochnikov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 368 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 385].
6. V. A. Shlyapochnikov, *Kolebatel′nye spektry alifaticheskikh nitrosoedinenii* [*Vibrational Spectra of Aliphatic Nitro Compounds*], Nauka, Moscow, 1989, 136 pp. (in Russian).
7. V. A. Sipachev, *J. Mol. Struct.*, 1985, **121**, 143.
8. G. Kh. Khisamutdinov, V. I. Slovetskii, Yu. M. Golub, S. A. Shevelev, and A. A. Fainzil′berg, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 338 [*Russ. Chem. Bull.*, 1997, **46**, 324 (Engl. Transl.)].
9. L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, *Kolebatel′nye spektry mnogoatomnykh molekul* [*Vibrational Spectra of Polyatomic Molecules*], Nauka, Moscow, 1970, 559 pp. (in Russian).

Received November 2, 2000;
in revised form December 25, 2000