Infra-Red Spectra of Nitric Esters

Part 1.—Influence of Inductive Effects of Substituents

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Nitrates of simple primary, secondary and tertiary alcohols can be distinguished by the frequency of the asymmetric stretching NO_2 vibrations, viz., 1632-1630, 1626 and 1621 cm^{-1} respectively. The same band is shifted towards higher frequencies (1675-1640 cm^{-1}) when the position 2 (or 1) is substituted by a negative substituent. The symmetric stretching NO_2 vibrations around 1280 cm^{-1} are not influenced by these structural changes. Only steric factors arising from close-packing around the nitrate group can increase this frequency to 1300 cm^{-1}.

Few papers have been devoted to the study of infra-red spectra of nitric esters,[1-13] and most of them concerned the simplest ester, methyl nitrate. The other papers are of analytical character. Brown [12] and Carrington [13] discussed the structural problems, but no relationship between the infra-red frequencies and molecular structure of nitric esters was found.

The work described here concerns the influence of inductive effects in molecules of nitric esters on the infra-red spectrum of the ONO_2 group.

EXPERIMENTAL

PREPARATION OF NITRIC ESTERS

Nitric esters were prepared by the direct O-nitration of alcohols with excess of concentrated ($d = 1·5$) HNO_3 and ($d = 1·8$) H_2SO_4 (1 : 1 w/w) at -5°C (method A); by the homogeneous reaction of corresponding halides with $AgNO_3$ in acetonitrile (method B); [15] or by the heterogeneous reaction of the halides with $AgNO_3$ in dry ether (method C), and by some other methods (designated with numbers in brackets in table 1). The products, after washing with Na_2CO_3 and $NaHSO_3$ solutions and water, were purified by repeated distillation under reduced pressure.

The purification was carried out until (i) no changes in the infra-red spectra could be detected, (ii) the infra-red bands of impurities (these were traced by their diminishing intensity) were eliminated, (iii) the refractive index n_D^{20} attained a constant value. Compounds fulfilling these requirements were considered to be spectrally pure and subjected to infra-red examination. The list of compounds and their characteristics is given in table 1.

SPECTRAL MEASUREMENTS

A Hilger 800 double-beam recording spectrometer with NaCl prism was used in the 1750-680 cm^{-1} range. The reproducibility was ± 1 cm^{-1} for sharp peaks. The computed spectral slit width changed from 7·7 cm^{-1} at 1700 cm^{-1} to 2·9 cm^{-1} at 750 cm^{-1}.

All samples were examined as capillary films between NaCl plates. Each spectrum was run twice and immediately calibrated with polystyrene film as standard. Two independently prepared samples of each compound were examined. The infra-red absorption frequencies are given in table 2.

TABLE 1

no.	compound	boiling point °C/mm Hg	refractive index n_D^{20}	methods of preparation
I	methyl nitrate	65/760	1·3743 (1·3748 [16])	A
II	ethyl nitrate	87/760	1·3857 (1·3852 [16])	A
III	n-propyl nitrate	25/10	1·3979 (1·3979 [16])	A
IV	isopropyl nitrate	21/10	1·3916 (1·3912 [5])	A(−30°C), C
V	n-butyl nitrate	25/8	1·4063 (1·4063 [16])	A
VI	isobutyl nitrate	25/6	1·4060	A, D
VII	sec-butyl nitrate	22/8	1·4027	A(−30°C), B
VIII	tert-butyl nitrate	22/5	1·4019	A(−40°C)
IX	neopentyl nitrate	28/7	1·4089	A(−20°C)
X	cyclohexyl nitrate	70/4	1·4558	A(−40°C), C
XI	allyl nitrate	50/45	1·4178	A(−40°C), B
XII	benzyl nitrate	83/6	1·5209	B, C
XIII	2-phenylethyl nitrate	96/4	1·5166	C, D
XIV	2-hydroxyethyl nitrate (ethylene glycol mononitrate)	100/1	1·4378	A[1], B
XV	2-chloroethyl nitrate	46/8	1·4439	A,[2]
XVI	2-bromoethyl nitrate	47/7	1·4790	A,[2]
XVII	2-iodoethyl nitrate	75/15	1·5268	A(−40°C),[3]
XVIII	2-cyanoethyl nitrate	88/6	1·4424	A(−10°C)
XIX	acetone cyanohydrin nitrate	51/5	1·4192	A(−20°C)
XX	2-nitroethyl nitrate	74/1	1·4557	A [4]
XXI	2-nitro-2-methyl-propyl nitrate	82/2	1·4458	A
XXII	1,3-dichloro-2-propyl nitrate	174/760	1·4764	A
XXIII	glycidol nitrate	58/12	1·4418	A [5]
XXIV	methanediol (methylene glycol) dinitrate	76/20	1·4303	A [6]
XXV	1,2-ethanediol (ethylene glycol) dinitrate	105/20	1·4473; 1·4454 (25°C); 1·4454 (25°C)[17]	A
XXVI	1,2-propanediol (propylene glycol) dinitrate	92/10	1·4420	A, B
XXVII	1,3-propanediol (trimethylene glycol) dinitrate	74/1	1·4487; 1·4480 (21·2°C); 1·4486 (21·2°C)[18]	A(−25°C)
XXVIII	diethylene glycol dinitrate	130/4	1·4518; 1·4517 [14]	A

[1] 2-Hydroxyethyl nitrate was obtained by dissolving ethylene glycol in HNO_3(d = 1·5) at 5°C.[14] The mononitrate was separated from the dinitrate by water extraction.

[2] 2-Chloro- and 2-bromoethyl nitrates were prepared by reacting PCl_3 and PBr_3, respectively, with 2-hydroxyethyl nitrate in chloroform.

[3] 2-Iodoethyl nitrate was prepared by heating 1,2-di-iodoethane and mercuric nitrate in ether.[19]

[4] 2-Nitroethyl nitrate was obtained by the action of N_2O_4 on 2-nitroethanol at 10°C.[20]

[5] Glycidol nitrate was prepared by hydrolysis of both isomeric glycerol dinitrates with 30 % KOH.

[6] Methylene glycol dinitrate was prepared by dissolving paraformaldehyde in conc. H_2SO_4 and adding it to a $H_2SO_4+HNO_3$ mixture at −20°C.[21]

DISCUSSION

$+I$ EFFECT

On comparing the frequencies of a series of primary, secondary and tertiary alkyl nitrates it was found that the $\nu_{as}(NO_2)$ frequency decreases regularly with increasing $+I$ inductive effect of the alkyl. Stepwise substitution of hydrogen atoms with methyl groups in methyl nitrate lowers the frequency by about 5 cm^{-1} for each methyl introduced.

Thus, it is possible to distinguish between primary, secondary and tertiary alkyl nitrates by their $\nu_{as}(NO_2)$ frequencies. The $\nu_s(NO_2)$ frequency in the spectra of

TABLE. 2.—INFRA-RED FREQUENCIES IN cm^{-1}

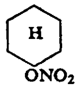
I CH$_3$ONO$_2$	II CH$_2$ONO$_2$ CH$_3$	III CH$_2$ONO$_2$ CH$_2$ CH$_3$	IV CH$_3$ CH—ONO$_2$ CH$_3$	V CH$_2$ONO$_2$ CH$_2$ CH$_2$CH$_3$	VI CH$_2$ONO$_2$ CH—CH$_3$ CH$_3$	VII CH$_3$ CH—ONO$_2$ CH$_2$CH$_3$	VIII CH$_3$ CH$_3$—C—ONO$_2$ CH$_3$	IX CH$_2$ONO$_2$ C(CH$_3$)$_3$	X 	XI CH$_2$ CH CH$_2$ONO$_2$	XII CH$_2$ONO$_2$ Ph	—ONO$_2$ vibrations
1635 (vs)	1630 (vs)	1631 (vs)	1626 (vs)	1632 (vs)	1631 (vs)	1626 (vs)	1621 (vs)	1635 (vs)	1626 (vs)	1638 } (sh) 1632 } (vs)	1633 (vs)	$\nu_{as}(NO_2)$
—	—	—	—	—	—	—	—	—	—	—	—	—
1458 (w)	1481 (vw)	1461 (m)	1471 (w)	1467 (w)	1469 (m)	1464 (m)	1482 (w)	1481 (w)	1464 (m)	1460 (vw)	1497 (w)	
1438 1431 } (m)	1449 (w)	1446 (w)	1456 (vw)	1444 (vw)	1440 (sh)	1453 (sh)	1459 (m)	—	—	1440 1424 } (w)	1458 1436 } (w)	
—	1387 1370 } (m)	1391 (w)	1392 1379 } (m)	1385 (w)	1391 1373 } (w)	1387 (m)	1400 (m)	—	—	—	—	
—	—	1350 (vw)	1353 (vw)	—	—	1360 (w)	1376 (s)	1372 (m)	1369 1355 } (vw)	1359 (w)	1365 (w)	
—	—	1313 (vw)	1334 (vw)	1327 (vw)	1305 (w)	1304 (w)	—	—	1322 (w)	—	—	
1283 (vs)	1283 (vs)	1282 (vs)	1280 (vs)	1282 (vs)	1280 (vs)	1280 (vs)	1301 (vs)	1285 (vs)	1280 (vs)	1295(s) 1280(vs) }	1282 (vs)	$\nu_s(NO_2)$
—	—	1245 (sh)	—	—	—	—	1259 (w)	1265 (w)	1239 (vw)	—	1212 (w)	
1177 (vw)	—	—	1182 (w)	—	—	1176 (vw)	—	1220 (w)	1195 (vw)	—	—	
—	1158 (vw)	—	1144 (w)	—	1160 (vw)	1148 (vw)	1160 (s)	—	1160 (vw)	1158 (vw)	—	
—	1118 (w)	—	1122 (vw)	—	—	1121 (w)	—	—	1121 (vw)	—	—	
—	1091 (w)	1050 (m)	1102 (m)	1053 (w)	1096 (vw)	1093 (vw)	—	—	1093 (vw)	1087 (vw)	1080 (vw)	
—	1011 (s)	1028 (w)	—	1014 (w)	—	1024 (w)	—	1044 (w)	1034 (w)	—	—	
993 (s)	—	976 (s)	—	982 (w)	987 (m)	988 (w)	—	973 (m)	1007 (m)	984 (m)	973 (w)	ν(C—O)
—	—	951 (s)	—	962 (w)	961 (w)	965 (w)	—	943 (vw)	942 (m)	963 (m)	—	
—	912 (s)	918 (w)	936 (w)	932 (w)	929 (vw)	—	931 (m)	924 (wv)	921 (w)	929 (w)	—	
—	905 (s)	894 (sh)	909 (s)	907 (vw)	917 (vw)	896 (s)	—	—	902 (m)	915 902 } (vw)	909 (w)	
863 (s)	863 (s)	868 (s, c)	879 (s)	872 (s, c)	869 (s, c)	867 (vs, c)	876 (vs)	874 (s)	870 (vs)	859 (vs)	862 (s)	ν(O—N)
—	—	—	853 (m)	—	—	—	—	855 (sh)	843 (m)	—	—	
—	—	773 (w)	—	—	—	780 (vw)	780 (w)	—	803 (vw)	—	—	
760 (w)	760 (w)	759 (m)	760 (w)	759 (w)	758 (w)	756 (w)	759 (w)	775 (w)	757 (w)	757 (w)	756 (m)	$\gamma_w(NO_2)$
—	702 (w)	696 (m)	702 (m)	697 (w)	692 (w)	696 (m)	710 (m)	691 (w)	692 (w)	708 (w)	699 (m)	$\delta(NO_2)$

TABLE 2.—INFRA-RED FREQUENCIES IN cm^{-1}

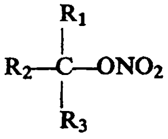
XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXII	XXIII	$-ONO_2$
CH_2ONO_2 │ CH_2Ph	CH_2ONO_2 │ CH_2OH	CH_2ONO_2 │ CH_2Cl	CH_2ONO_2 │ CH_2Br	CH_2ONO_2 │ CH_2I	CH_2ONO_2 │ CH_2CN	CH_3 │ $CH_3—C—CN$ │ CH_3	CH_2ONO_2 │ CH_2NO_2	CH_3 │ $CH_3C—NO_2$ │ CH_2ONO_2	CH_2Cl │ $CH—ONO_2$ │ CH_2Cl	CH_2 │ >O CH │ CH_2ONO_2	vibrations
1631 (vs,c)	1631 (vs)	1652(sh) 1640(vs)	1656(sh) 1641(vs)	1662 1640 (vs)	1660 1643 (vs)	1657 (vs)	1655 1641 (vs)	1653 (vs)	1648 (vs,c)	1638 (vs)	$\nu_{as}(NO_2)$
1500 (w)	—	—	—	—	—	—	1563 1555 (s)	1550 (vs)	—	—	
1469(vw) 1456(w)	1456 (w)	1455 (vw)	1443 (sh)	1460 (sh)	1470 (vw)	1470 (w)	1453 (w)	1470 1460 (m)	—	1458 (vw)	
1438 (vw)	1431 (w)	1434 (w)	1430 (m)	1442 (m,c)	1442 (w)	1441 (vw)	1426 (m)	1428 (vw)	1443 1430 (w)	1430 (w)	
1380 (w)	1396 (vw)	1381 (w)	1377 (w)	1372 (w)	1417 (w)	1395 (w)	1392 (m)	1407 (w)	—	—	
—	1372 (w)	—	—	—	1371 (vw)	1376 (m)	1372 (m)	1377 (s) 1349 (s)	1350 1337 (w)	—	
—	—	1308 (m)	—	—	1336 (vw)	—	—	—	—	1348 (w)	
1282 (vs,c)	1282 (vs)	1280 (vs,c)	1295 1282 1273 (vs)	1295 1281 1262 (vs)	1284 1273 (vs)	1300 (vs)	1284 1278 (vs)	1285 (vs)	1301 1279 1268 (vs)	1285 (vs)	$\nu_s(NO_2)$
—	1235 (vw)	1246 (vw)	1226 (w)	—	1220 (vw)	1232 (w)	1226 (w)	1253 (w)	1250 (sh)	1250 (sh)	
1196 (vw)	—	1196 (vw)	1182 (vw)	1195 (w)	—	1200 (w)	—	1197 (vw)	1214 (w)	—	
—	—	—	—	1177 (w)	—	1141 (m)	—	1162 (w)	1188 (w)	1135 (vw)	
—	—	—	—	—	—	—	1101 (vw)	—	1150 (w)	—	
1086 (vw)	1077 (s)	—	—	—	1074 (vw)	—	—	—	—	1072 (vw)	
1046 1030 (vw)	—	1066 (w)	1055 (m)	1051 (m)	—	—	1041 (m)	1033 (sh)	—	—	
996 (sh)	1022 1006 (w)	1017 (m)	997 (m)	974 (m)	1017 (m)	—	1018 (m)	1019 (m)	1016 1004 (m)	997 (m)	$\nu(C—O)$
978 (w)	—	989 (w)	—	—	989 (w)	—	—	987 (m)		968 (m)	
962 (w)	—	968 (vw)	960 (w)	—	—	949 (vw)	—	—	972 (vw)	950 (vw)	
910 (w)	—	936 (vw)	—	934 (m)	939 (vw)	—	905 (s)	936 (vw)	927 (vw)	909 (w)	
877 (s)	895 (s) 858(m)	880 (s)	875 861 (s,c)	852 (s,c)	893 (s) 845 (s)	897(m) 841(s)	848 (s)	868 860 (s,c)	889(s) 859(s)	860 (s,c)	$\nu(O—N)$
848 (m)	—	841 (s)	828 (m)	—	—	—	—	833 (m)	838 (s)	800 (vw)	
—	—	—	—	802 (w)	—	—	—	—	779 (w)	774 (vw)	
752 (m)	759 (w)	755 (w)	756 (w)	751 (m)	755 (w)	748 (w)	755 (m)	753 (w)	750 (w)	755 (w)	$\gamma_w(NO_2)$
696 (s)	705 (w)	700(w) 675	698 (w)	711(vw) 696	702 (w)	707 (w)	710 (vw)	640 (w)	711 702(w) 686	—	$\delta(NO_2)$

TABLE 2.—continued

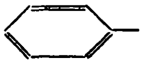
XXIV CH_2ONO_2 $\vert$ ONO_2	XXV CH_2ONO_2 $\vert$ CH_2ONO_2	XXVI CH_3 $\vert$ $CH—ONO_2$ $\vert$ CH_2ONO_2	XXVII CH_2ONO_2 $\vert$ CH_2 $\vert$ CH_2ONO_2	XXVIII $CH_2CH_2ONO_2$ $\vert$ O $\vert$ $CH_2CH_2ONO_2$	$—ONO_2$ vibrations
1675 (vs)	1656 1643 (vs)	1656 1641 (vs)	1634 (vs)	1632 (vs)	$\nu_{as}(NO_2)$
—	—	—	—	—	
—	1456 (vw)	1461 1452 (w)	1472 1449 (w)	1468 1454 (vw)	
1425 (m)	1430 (w)	1428 (vw)	1431 (vw)	1431 (w)	
—	1396 (vw)	—	—	1392 (w)	
—	1372 (w)	—	—	1375 (vw)	
—	—	1308 (w)	1331 (vw)	1362 (vw)	
1283 (vs)	1292 1271 (vs)	1288 1274 (vs)	1278 (vs)	1281 (vs)	$\nu_s(NO_2)$
—	1235 (vw)	1240 (sh)	—	1250 (sh)	
—	—	—	—	—	
—	—	1161 (vw)	—	1138 (s)	
1119 (vw)	1114 (vw)	1115 (vw)	—	—	
—	—	1076 (vw)	—	1094 (vw)	
1018 (m)	1059 (sh)	—	1031 (w)	—	
950 (s)	1040(m) 1004(vw)	1005 (m)	990 (w)	1031 (m)	$\nu(C—O)$
—	—	973 (w)	958 (vw)	—	
—	—	923 (w)	944 (vw)	—	
—	925 (sh)	—	920 (vw)	906 (s)	
840(m) 792(vs)	897(s,c) 860 (sh) 842(s,c)	886(m) 848(s)	859 (s,c)	858 (s)	$\nu(O—N)$
—	—	—	—	—	
—	—	—	—	—	
748 (w)	756 (w)	754 (w)	757 (w)	756 (w)	$\gamma_w(NO_2)$
—	710 (vw)	695 (w)	697 (w)	685 (w)	$\delta(NO_2)$

Band frequencies in cm^{-1}
Intensity: vs, very strong,
s, strong;
m, medium;
w, weak;
vw, very weak;
sh, shoulder; c, composite, barely resolved band.

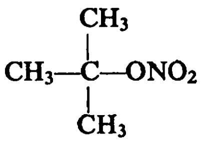
TABLE 3



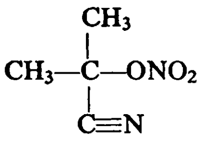
$$R_2—\overset{R_1}{\underset{R_3}{C}}—ONO_2$$

R_1	R_2	R_3	$\nu_{as}(NO_2)$ cm^{-1}	$\nu_s(NO_2)$ cm^{-1}
H	H	H	1635	1283
H	H	CH_3	1630	1283
H	H	C_2H_5	1630	1282
H	H	n-C_3H_7	1632	1282
H	H	i-C_3H_7	1631	1280
H	H	$CH_2{=}CH—$	1632	1280
H	H		1633	1282
H	CH_3	CH_3	1626	1280
H	CH_3	C_2H_5	1626	1280
	cyclohexyl		1626	1280
CH_3	CH_3	CH_3	1621	1301

alkyl nitrates (1283-1280 cm^{-1}) is virtually unaffected by the $+I$ effect. The only exception is tert-butyl nitrate (VII) where $\nu_s(NO_2)$ = 1301 cm^{-1}. We assigned this shift to the steric effect of close-packing of the methyl groups and the nitrate group in the molecule, as can readily be seen from atomic models. To check the suggestion we sought for a molecule approximately isosteric with that of tert-butyl nitrate, but exerting an opposite (i.e., $-I$) inductive effect on its nitrate group. Acetone cyanohydrin nitrate (XIX) is a good example. Its $\nu_s(NO_2)$ frequency is 1300 cm^{-1}, thus proving the influence of steric rather than inductive effects.



$CH_3\text{—}C(CH_3)_2\text{—}ONO_2$ (VII)



$CH_3\text{—}C(CH_3)(C{\equiv}N)\text{—}ONO_2$ (XIX)

	(VII)	(XIX)
$\nu_{as}(NO_2)$	1621 cm^{-1}	1657 cm^{-1}
$\nu_s(NO_2)$	1301 cm^{-1}	1300 cm^{-1}

The spectral data for primary alkyl nitrates show that their $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ frequencies are stationary at 1633-1630 cm^{-1} and 1283-1280 cm^{-1} respectively. On this basis we accept the following " normal " values, to which all shifts are referred:

$$\nu_{as}(NO_2) = 1631\ \text{cm}^{-1};\quad \nu_s(NO_2) = 1281\ \text{cm}^{-1}.$$

$-I$ EFFECT

In the series of glycol nitrates

	XXIV	XXV	XXVII
	$O_2NO\text{—}CH_2\text{—}ONO_2$	$O_2NO\text{—}CH_2\text{—}CH_2\text{—}ONO_2$	$O_2NO\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}ONO_2$
$\nu_{as}(NO_2)$;	1675 cm^{-1}	1656; 1643 cm^{-1}	1634 cm^{-1}
$\nu_s(NO_2)$;	1283 cm^{-1}	1292; 1271 cm^{-1}	1278 cm^{-1}

the $-I$ inductive effect of nitrate groups on each other increases the $\nu_{as}(NO_2)$ frequency. The effect diminishes with introducing additional —CH_2— groups between the nitrate groups, so the $\nu_{as}(NO_2)$ frequency moves towards the normal value of 1631 cm^{-1}.

The $\nu_s(NO_2)$ frequency remains stationary around 1280 cm^{-1} if a mean value for the split $\nu_s(NO_2)$ band of ethylene glycol dinitrate is considered (the problem of this band splitting will be discussed in another paper [22]). For methylene glycol dinitrate (XXIV) the $\nu_{as}(NO_2)$ frequency shift is +44 cm^{-1}, while the $\nu_s(NO_2)$ frequency remains close to the normal value.

In diethylene glycol dinitrate

$$O_2NO\text{—}CH_2\text{—}CH_2\text{—}O\text{—}CH_2\text{—}CH_2\text{—}ONO_2, \qquad \text{(XXVIII)}$$

the $-I$ effect of nitrate groups on each other vanishes and both the $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ frequencies reach their normal values (1632 and 1281 cm^{-1}, respectively).

Further examples of the influence of $-I$ effect on the $\nu_{as}(NO_2)$ frequency are afforded by a number of nitrates of the general formula

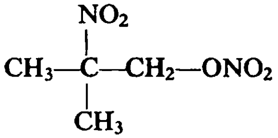
$$X\text{—}CH_2\text{—}CH_2\text{—}ONO_2,$$

	XIV	XV	XVI	XVII	XX	CN
where X =	OH	Cl	Br	I	NO_2	XVIII
$\nu_{as}(NO_2)$	1631	1652	1656	1662	1655	1660 cm^{-1}
		1640	1641	1640	1641	1643 cm^{-1}

While the OH group, which exerts a feeble inductive effect, does not change the frequency, the other substituents cause a shift of +10 to +30 cm^{-1}. However the observation of regular frequency changes with increasing $-I$ effect is not possible due to band splitting, already mentioned with ethylene glycol dinitrate.

High values of ν_{as} (NO$_2$) frequency are also noted in:

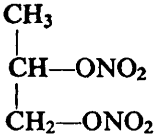
XXI



$$CH_3-\overset{\overset{NO_2}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-ONO_2$$

1653 cm^{-1}

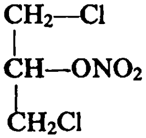
XXV



$$\begin{array}{l} CH_3 \\ | \\ CH-ONO_2 \\ | \\ CH_2-ONO_2 \end{array}$$

1656; 1643 cm^{-1}

XII



$$\begin{array}{l} CH_2-Cl \\ | \\ CH-ONO_2 \\ | \\ CH_2Cl \end{array}$$

1648 cm^{-1}

According to Kumler,[23] nitrates of glycolic acid esters give $\nu_{as}(NO_2)$ = 1656 cm^{-1}. In all the cases, the $\nu_s(NO_2)$ frequency is close to 1281 cm^{-1} (mean values are considered for split bands).

GENERAL CHARACTERISTICS OF THE SPECTRA

Thus, to summarize the above results we list the characteristic frequencies.

$\nu_{as}(NO_2)$	1675-1621 cm^{-1} very strong band ($\varepsilon \approx 1500$)	normal value 1631 cm^{-1}; regular changes due to $+I$ effect (decrease) and $-I$ effect (increase); splitting in X—CH$_2$—CH$_2$—ONO$_2$ systems.
$\nu_s(NO_2)$	1301-1268 cm^{-1} very strong band ($\varepsilon \approx 1000$)	normal value—1281 cm^{-1}; unaffected by either $+I$ effect or $-I$ effect: sensitive to steric effects; band splitting in X—CH$_2$—CH$_2$—ONO$_2$ systems.
ν (C—O)	1050-950 cm^{-1}	bands of variable intensity; no evident rules on relationship between these frequencies and molecular structure were found.
ν (O—N)	895-840 cm^{-1}	
γ_w (NO$_2$)	775-748 cm^{-1}	
δ (NO$_2$)	710-640 cm^{-1}	

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