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Interpretation of the vibrational spectra of nitramines on the basis of *ab initio* calculations

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It is shown that, unlike conventional methods of vibrational spectroscopy, the use of *ab initio* harmonic force fields, IR and Raman intensities, and depolarizations makes possible a rigorous interpretation of the experimental spectra of the simplest aliphatic nitramines $(CH_3)_2NNO_2$, CH_3NHNO_2, H_2NNO_2, and their isotopomers. The scale factors, which were introduced for each compound to remove the systematic errors of the SCF MO LCAO calculation by fitting the parameters to the observed frequencies, were mutually adjusted during the solution of the inverse vibrational problem. The set of transferable scale factors established in this work can be used directly to analyze spectra of larger molecules. Some common patterns of the force fields and vibrational spectra of nitramines are discussed.

Key words: nitramines; quantum chemistry; vibrational spectra.

Introduction

By now rather extensive experimental material on vibrational spectra of nitramines has been collected.[1] However, there are still a lot of obscurities in its interpretation. The matter is complicated by the fact that available spectra are obtained, as a rule, in a limited frequency range. In our opinion, even additional experimental data will not allow reliable interpretation of spectra of nitramines of moderate, and much less of high, complexity in terms of traditional empirical methods of vibrational spectroscopy. This pessimistic conclusion is a result of multiple attempts to analyze IR and Raman spectra of the simplest aliphatic nitramines $(CH_3)_2NNO_2$ (**1**), CH_3NHNO_2 (**2**), H_2NNO_2 (**3**), and their isotopomers using calculations of frequencies and modes of normal vibrations.[1]

We performed *ab initio* calculations[2,3] of nitramines **1**—**3** and obtained theoretical estimations of force fields, intensities of transitions in IR and Raman spectra, and depolarizations of Raman bands. This work is devoted to an attempt to use a new approach to the interpretation of the available experimental vibrational spectra on the basis of the aforementioned data.

The main problems in the analysis of spectra of nitramines

The first assignment of frequencies for compounds **1**—**3** was suggested by Davies and Jonathan in 1958 and was based on Raman spectra[4] and their own data on IR absorption spectra[5] (Tables 1—3). Later this interpretation[5] changed its meaning several times as new experimental data were obtained.[6—12] Nevertheless, the bands in the spectral range below 550 cm^{-1}, which is characteristic of deformational vibrations of methyl-substituted amino group and torsional vibrations, still have no reliable assignment. Moreover, they are not always experimentally obtained. The interpretation of frequencies of stretching vibrations ν(NN) and ν(CN) is also rather contradictory.

Additional data, including the spectra of ^{15}N-nitro-, ^{15}N-amino-, and D_6-labeled derivatives, are obtained for compound **1**.[6—8] The proposed assignments of the bands[5,6] show good agreement, whereas the interpretation[7,8] justified by the results of normal coordinate analysis differs considerably from them, mainly concerning the frequencies of stretching vibrations $\nu_{as}(NC_2)$, ν(NN), and $\nu_s(NC_2)$ (see Table 1). For example, the bands at 835—850 cm^{-1}, which are weak in IR spectra but very strong and polarized in Raman spectra of the different phases, were previously assigned[4—6] to the ν(NN) vibration. According to the later studies,[7,8] $\nu_s(NC_2)$ must refer to this range, and either the bands at 980—1010 cm^{-1} of the medium intensity, polarized in the Raman spectrum, or the peaks at 1240—1260 cm^{-1} may be assigned to the ν(NN) vibration. According to the calculation,[7,8] the normal vibrations for the latter two cases show a large degree of mixing with predomination of contributions of ν(NN) and rocking vibrations of methyl groups. It should

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Table 1. Variants of assignment of frequencies (ν/cm^{-1}) of IR and Raman spectra of *N,N*-dimethylnitramine to vibrations of the molecular framework[a]

Assignment	Pellets with KBr		Solid film	Melt	Solutions in CCl_4 (CS_2)		Gaseous phase
	IR [6]	Raman [4–6]	IR[5]	Raman [6]	IR [5,6]	Raman [7,8] [b]	IR [5,6] [c]
$\nu_{as}(NO_2)$	1534 w 1504 s	1524[e](4)	1546 sh 1515 s	—	1527—1534 s, v. s 1519 sh	1528	1561—1566 s, v. s, B
$\nu_s(NO_2)$	1338 s 1298 w	1286(2) w	1345 m 1291 m	—	1305[d] s, v. s	—	1305—1310 s, v. s, A
$\nu_{as}(NC_2)$	1050 w	1103[e](0)	1053 m	—	1129[e] m 1045 w, m	1287—1292	1132[e] w 1038—1052 v. w, w
ν(NN)	849 w 835 w	835—838(12) v. s	837 w	840 v. s; p	843 w	1006 1248—1257	846—849 v. w, w, A
$\nu_s(NC_2)$	1028 w	1016—1024(10) s	1020 m, w	1009 m; p	995—998 m	838—842	980—985 m
$\omega(NO_2)$	762—766[d] m	—	762 m, s	—	764 m	—	770—773 m, C
$r(NO_2)$	622 s	618(7) s	625 m	614 w; dp	610 s	616—619	600, 612 m
δ(ONO)	627 sh			622 s; p		621—626	
δ(CNC)	427 w	417—420(6) m	—	420 m; p	—	417—427	430 m
$t(NC_2)$	350—355[d] w	—	—	—	—	—	—
$\omega(NC_2)$	—	225—228[d]	—	—	—	—	—
$\chi(NO_2)$	173 v. w; 95 w	162—165[d]; 95 w	—	—	—	—	—

[a] ν, δ, ω, r, t, and χ are stretching, bending, wagging, rocking, twisting, and torsional vibrations; sh is shoulder; s, as are symmetric and antisymmetric vibrations; s, m, w are strong, medium, or weak intensities (normalized quantitative estimates of intensities are given in parentheses[4]), v. is very; p and dp are polarized and depolarized bands in the Raman spectrum.

[b] The results of the normal coordinate analysis[9] mainly correspond to the assignment suggested previously.[7,8]

[c] Frequencies of Q-branches or centers of P—R splitting of vibrational-rotational bands and types of contours (A, B, C).

[d] This or analogous assignment has been suggested later.[7,8] [e] See Ref. 5.

be mentioned that the results of the recent normal coordinate analysis agree well with this interpretation.[9]

The interpretation of spectra of compound **2** was refined using the additional data for the parent substance and its ^{15}N-nitro-, D_1-, D_3-, and D_4-isotopomers and the calculations of frequencies and modes of normal vibrations.[6,10] As in the earlier studies,[4,5] the band at 930—950 cm^{-1}, which is weak in the IR spectrum, and strong and polarized in the Raman spectrum, is assigned to the ν(NN) stretching vibration; the band at 1090—1120 cm^{-1}, with the medium intensity in the IR spectrum and strong and polarized in the Raman spectrum is assigned to the ν(CN) vibration (see Table 2). However, the authors of another work[8] suggested the contrary assignment of the same frequencies based on the results of their normal coordinate analysis.

New experimental data[11] for the parent nitramine **3** and its isotopic species $H_2{}^{15}NNO_2$, D_2NNO_2, and $D_2{}^{15}NNO_2$ in low-temperature Ar- and N_2-matrixes with dilution more than 1 : 1000 are significant for elucidation of specific features and interpretation of their vibrational spectra. It should be remembered that it is very difficult to obtain spectra of nitramine in the gaseous phase due to low vapor pressure and its instability to heating and contact with metals. Therefore, these spectra presently are not registered. Despite considerable weakening of the energetic effect of the medium in inert matrices as compared with the crystalline phase and solutions, which appeared in a large deviation of IR bands (the average difference per one band is[11] ~60 cm^{-1} as compared with condensed phases[4,5,12]), the individual bands exhibit extreme sensitivity to their surroundings in inert matrices as well (see Table 3). Relative shifts of almost half the fundamental bands in two matrices reach 20—30 cm^{-1}.

For the assignment of vibrations[11] the results of *ab initio* SCF calculation of harmonic force field of nitramine in the standard double zeta Huzinaga basis set[13] with polarization functions were used as initial. It is noted[11] that the energetic order and assignment of the predicted frequencies, despite their overestimation, completely correspond to the experiment and the subsequent solution of the inverse vibrational problem. In the course of the solution for 24 frequencies and 24 isotope shifts, 9 diagonal force constants and 12 interaction constants were refined. The significance of their contributions was determined according to the criteria of transferability of valence force field for polyatomic

Table 2. Variants of assignment of frequencies (ν/cm^{-1}) of IR and Raman spectra of *N*-methylnitramine to vibrations of the molecular framework[a,b]

Assignment	Pellets with KBr		Cooled (liquid) film	Solutions			Gaseous phase
				in CCl_4 (C_6H_6)	in H_2O		
	IR[6]	Raman[4,5]	IR[5,6]	IR[5,6]	IR[6]	Raman[6]	IR[6,10] [c]
ν(NH)	—	3219(2)	3276—3308 s, v. s	3370—3416 m, s 3290 s	—	—	3438 w, B
$\nu_{as}(NO_2)$	1579 s	1552(0)	1580—1599 s, v. s 1551—1578 m, v. s	1580—1600 s, v. s	1563 s	—	1614 s, B
t(NNC or NH)	1393 s	—	1395 s	1390 s	1390 s	—	1394 m, B
$\nu_s(NO_2)$	1340 s	1312(1)	1342—1350 s, v. s 1334 s	1326—1334 s, v. s	1331 s	1331 w; p	1332 s, A
ν(CN)	1116 m	—	1118 m, s	1102—1108 m	1124 s	1120 s; p	1092 w
ν(NN)	940 w	946(8)	940—953 v. w, w	928—931 w, m	952 w	940 s; p	928 w
$\omega(NO_2)$	778 w	—	774—776 w, m	778 m	—	—	772 w, C
δ(ONO)	735 w	712(0)	723—734 w	707 w	709 w	709 w	—
$r(NO_2)$	594 w	594(4)	596 m	587—588 w	—	591 w	—
ω(NNC or NH)	—	—	618[d] m	—	—	—	—
δ(NNC)	—	—	—	—	—	320 w	—
$\chi(NO_2)$	—	—	—	—	—	—	—

[a,c] See footnotes[a,c] for Table 1.

[b] The variant of assignment,[8] with the mutual exchange of fundamental frequencies for ν(CN) and ν(NN) vibrations is suggested on the basis of the normal coordinate analysis using the spectra.[6,10]

molecules.[14] The resulting assignment of the spectra of nitramine considerably differs from that proposed previously,[4,5] however, it hardly can be considered more correct, because it is not clear why depolarized lines in the Raman spectrum correspond to the IR bands assigned to the δ(HNH) (1560—1580 cm^{-1}) and $\omega(NH_2)$ (590—630 cm^{-1}) vibrations (see Table 3).

The lack of reliable experimental data for the low-frequency range of vibrational spectra of nitramines **1—3** considerably complicates the interpretation of their spectra as a whole. Therefore, the far IR absorption spectra of these compounds are studied in this work.

Experimental

IR spectra were registered on a Bruker IFS-113 evacuated IR-Fourier-spectrometer in the frequency range of 30—400 cm^{-1} with resolution no more than 1 cm^{-1}. Solid substances were molded into pellets with adamantane (chemically pure). Spectra of solutions in $CHCl_3$ were obtained in a thermostatically controlled cuvette (d = 1.0 mm) with silicon optical windows.

It should be noted that vibrations of the crystalline lattice may also appear in the low-frequency spectral range in addition to intramolecular vibrations. Besides, the previously mentioned[5] substantial changes in positions of the bands and in their intensities for the solid state—solutions in various solvents—gaseous phase transitions (see Tables 1—3) attest to the tendency of molecules **1—3** toward association and complex formation. This is caused by the formation of stable bonds between atoms of polar nitro and amino groups, which is also reflected in the far infrared spectral range.

The following bands are recorded in the spectra of the crystalline phase (ν/cm^{-1}): 61, 98, 185, 353 (**1**); 80, 120, 177, 330 (**2**); and 115, 140, 303, 383 (**3**).

The changes in positions, modes, and intensities of individual bands were observed in solutions. Some frequencies for molecules **1** and **2** agree with those already observed (see Tables 1 and 2). In particular, the bands at 355 cm^{-1} in the IR spectrum of **1** and at 320 cm^{-1} in the Raman spectrum of **2** are assigned to deformations of the amino group, and the bands at 95 cm^{-1} in the IR and Raman spectra of the crystalline phase of **1** are assigned to the torsional vibration of the nitro group.[6] All of the bands obtained for nitramine **3**, as known beforehand, are out of the frequency range of its intramolecular vibrations (see Table 3).

The use of theoretical data for the interpretation of the experiment: a transferable set of scale factors

The data presented above are more evidence that even the use of the theory of small vibrations often does not help to obtain unambiguous interpretation of spectra by traditional empirical methods of analysis in vibrational spectroscopy. The main reason for this is an ambiguity of the solution of the inverse vibrational problem, because the number of refined elements of the matrix of potential energy is much greater, as a rule, than the number of experimental values even when spectra of isotopomers are available. The correct choice and assignment of fundamental frequencies for large molecules are not evident without preliminary knowledge of the force field.

Table 3. Variants of assignment of frequencies (ν/cm^{-1}) of IR and Raman spectra of nitramine[a]

Assignment	Pellets with KBr Raman [4,5 b]	Thin film IR [5]	Solutions in CCl_4, $CH_3C{\equiv}N$ and $C_4H_8O_2$ IR [5]	Matrix isolation	
				in Ar IR [11 b]	in N_2 IR[11]
$\nu_{as}(NH_2)$	—	3426 s	3463—3509 m 3315—3371 m, s	3478.0(2.3)	3474
$\nu_s(NH_2)$	3278(2)	3287 s	3250—3258 s	3359.3(0.6)	3361
$\nu_{as}(NO_2)$	1547(0.5) dp	1546 v. s 1534 v. s	1572—1575 v. s 1567—1570 v. s	1612.8(10.0)	1610.5
$\delta(HNH)$	1642(0)	1613 m	1608 sh	1558.1(1.2)	1581
$\nu_s(NO_2)$	1370(6) p	1379 v. s	1380 v. s 1364 s	1349.6(4.5)	1367.5
$t(NH_2)$	—	—	—	1226.7(2.8)	1238.5
$\nu(NN)$	1050(10) p	1043 m	—	950.9(1.0)	—
$\omega(NO_2)$	—	783 w	785 w	797.9(0.6)	776
$\delta(ONO)$	716(4) p	709 w	727—745 v. w, w	692.5(0.3)	713.5
$\omega(NH_2)$	1176(0.5)	1212 w 1175 s	1211—1227 m, s	628.5(0.7)	587
$r(NO_2)$	598(0.5) dp	596 m	—	484.5(2.3)	—
$\chi(NO_2)$	—	—	—	401.5(0.4)	433.8

[a] See footnote[a] for Table 1.

[b] Intensities normalized to the strongest peak (see Refs. 4, 11) are given in parentheses.

Ab initio calculations are a powerful source of additional information, which is sufficient in many cases for the reliable solution of spectral problems.[15] The SCF MO LCAO calculations using double zeta basis sets with polarization functions for well studied molecules yield force constants with accuracy of 10—30 %, and these values are always overestimated. An incompleteness of the basis set used, failure to consider electron correlation, and insufficient harmonic approximation are the main reasons for errors of calculations. All this can be efficiently compensated by scaling the force field in course of the solution of the inverse vibrational problem with refinement of a small number of factors, when theoretical vibrational frequencies are fitted to the experiment.

Moreover, for analogous internal coordinates in similar molecules, the overestimation of force constants obtained by the same method of the quantum chemistry has a quantitatively systematic character and, hence, the scale factors, unlike the force constants themselves, must be well transferable in the series of these molecules. Owing to this, the procedure for the parallel solution of the inverse vibrational problems for the whole totality of objects **1**—**3** with mutual adjustment of values of the obtained scale factors seems to be especially efficient. As scaling is somewhat empirical, remaining uncertainty may be reduced to a minimum by adjusting the theoretical and experimental intensities and depolarization ratios. In order to exclude medium effects, it is desirable to use experimental spectra of the studied substances in the vapor phase. This turned out to be possible for methyl-substituted nitramines **1** and **2**.

Harmonic force constants for molecules **1**—**3** in the Cartesian coordinate system were obtained from analytical second derivatives of the SCF energy by a GAUSSIAN-90 series of programs[16] at the University of Texas (Austin, USA). The equilibrium geometric parameters of molecules **1**—**3** were used, which were optimized by the gradient method at the RHF/6-31G* level and were previously considered.[2] All three molecules are characterized by pyramidal structures of the amino group, and **1** and **3** have C_s symmetry. The matrices of resulting force constants were transformed using the ANCO program[17] into the complete and nonredundant sets of local symmetry internal coordinates, which correspond to requirements of comparison of constants in the series of related molecules. The corresponding sets of internal coordinates were chosen with consideration for previous studies.[11,18]

For solution of the inverse vibrational problem, individual scale factors C_i were introduced for the groups of equivalent or similar (in the case of local symmetry) internal coordinates. The scaling procedure was performed by minimization by the least-squares method of weighted mean square deviations between calculated and observed fundamental frequencies, using the SCAL program,[19] in which the modification of theoretical force constants F_{ij}^{theor} is specified[15] as $F_{ij} = (C_iC_j)^{1/2}F_{ij}^{\text{theor}}$. The total number of scale factors was 14, 16, and 9 for **1**, **2**, and **3**, respectively (Table 4). The use in the analysis of frequencies of isotope-labeled molecules extended the volume of the experimental data by 3—4 times. Thus, the number of varied parameters is much lower than the number of experimental frequencies, the more so as the number of elements of matrices of the potential energy.

A large degree of mixing which corresponds to many normal vibrations of nitramines **1**—**3** (see below) results

Table 4. Refined and transferable scale factors[a]

Type of the factor	1	2	3[b]		Transferable value[c]
			I	II	
NN str	0.705	0.711	0.683	0.689	0.71
NO str	0.703	0.684	0.684	0.685	0.695
CN str	0.835	0.824			0.83
CH str	0.817	0.816			0.815
NH str		0.790	0.790	0.790	0.79
ONO bend	0.744	0.792	0.753	0.797	0.77
CNC bend	0.697				0.70
HNC bend		0.763			0.76
HNH bend			0.718	0.738	0.73
NNC bend	0.803	0.801			0.80
NNH bend		0.802	0.819	0.827	0.82
NO_2 rock	0.804	0.804[d]	0.804[d]	0.804[d]	0.805
NO_2 wag	0.711	0.730	0.720	0.720[d]	0.72
CH_3 s.def	0.784	0.789			0.79
CH_3 as.def	0.808	0.816			0.81
CH_3 rock	0.794	0.799			0.80
NO_2 tors	0.800	0.807	0.800[d]	0.800[d]	0.80
CH_3 tors	0.800	0.800			0.80

[a] Internal coordinates are chosen according to the literature data[11,18] (see text); str is stretching, bend is bending, wag is wagging, rock is rocking, tors is torsional vibrations, def is deformation of methyl group; s is symmetric and as is antisymmetric motions.

[b] The results obtained using fundamental frequencies of IR spectra[11] in Ar- (I) and N_2- (II) matrices.

[c] The factors recommended are the most efficient for the analysis of spectra of the gaseous phase.

[d] Fixed value.

in strong correlations between scale factors and great error in their determination. Therefore, the mutual agreement of scale factors, which are refined for each nitramine **1**—**3**, is substantial for unambiguous interpretation of their vibrational spectra. The recommended united set of well transferable factors (see Table 4) can find wide application for the analysis of spectra of other amino- and nitro-derivatives. The solution of the direct vibrational problem is sufficient for this if analogous *ab initio* force fields are available. The versatility of these factors was confirmed by their successful use in the analysis of the spectra of nitrobenzene and its isotopomers.[20]

The obtained values of scale factors are basically within the range of 0.70—0.85. The smaller values are typical of the stretching vibrations of NN and NO bonds, bending vibrations of CNC, HNC, HNH, and partly ONO angles, and wagging vibration of the NO_2 group. Perhaps this is explained to some extent by large negative charges of the NO_2 group, particularly of its oxygen atoms and of the amino nitrogen atom (Fig. 1), which is connected with the enhanced contribution of the electron correlation for these atoms. In these cases, scaling especially improves the results of the SCF MO LCAO calculations.

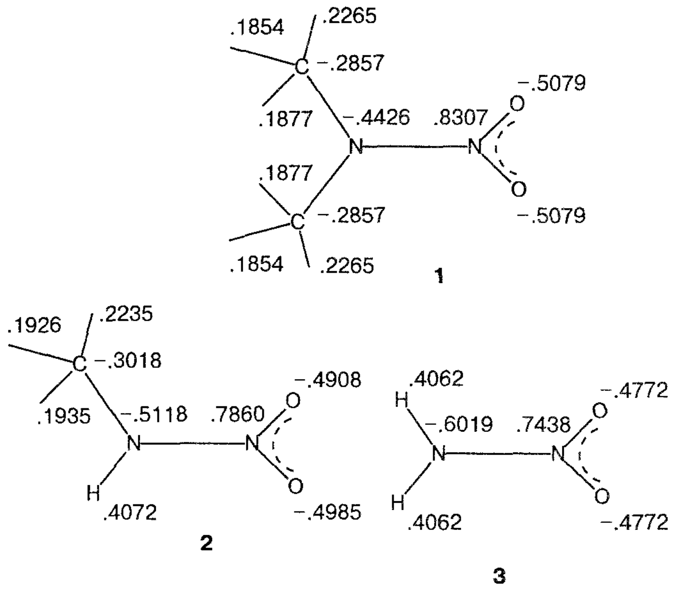

Fig. 1. Mulliken atomic charges for equilibrium forms of *N*,*N*-dimethylnitramine (**1**), *N*-methylnitramine (**2**), and nitramine (**3**).

However, the effect described does not appear, for example, for the rocking vibration of the NO_2 group. There is even some tendency for the scale factor for this movement in molecules **2** and **3** to exceed 0.85, when it is refined. For **2** this can be caused by substantial correlations with several other scale factors due to the mixed character of normal vibrations. Since reliable data for the low-frequency range of spectra of molecule **2** are scarce (see Table 2), we preferred to fix the factor value for the rocking vibration of its NO_2 group, which is equal to that obtained for **1**. This was a reason for fixing the factors both for analogous and torsional internal coordinates of molecule **3** as well (see Table 4).

Interpretation of experimental frequencies

The scaling procedure as a method for the solution of the inverse vibrational problem[15] needs a preliminary assignment of the vibrational spectrum. For this purpose, analysis of the eigenvectors and of the potential energy distributions for the unscaled theoretical frequencies of molecules **1**—**3** was used. The assignments made are rather conventional, because many normal vibrations show a large degree of mixing, and they reflect, as a rule, only the main contributions.

Generally, nitramines **1**—**3** are characterized by: 1) the existence of several fundamental frequencies with predomination of mixed contributions of NN, NO, and CN (for **1** and **2**) stretching vibrations and of the ONO angle deformation; 2) commensurability of the contributions of the NN stretching vibration to the frequencies assigned to this vibration and to the ones decreased by 400—450 cm^{-1}, *i.e.*, not characteristic of stretching vibrations; and 3) the existence of several fundamentals including mixed contributions of the amino group deformations and of torsional vibrations in molecules **1** and **2** as well.

It is also important to note that CN and NN stretching vibrations in methyl-substituted nitramines **1** and **2** are so strongly mixed with each other that their frequencies, for example, for the CH_3NHNO_2 molecule should be considered as frequencies caused by antisymmetric and symmetric stretching vibrations of the NNC fragment. These vibrations are also mixed to a small extent with rocking vibrations of methyl groups. The calculation attests to some interaction of symmetric stretching vibrations of the NO_2 group and deformations of methyl groups. All stretching vibrations of nitramine **3** are characteristic.

Scaling of force fields for **1—3** resulted in some change in the ratio of contributions of different vibrations to fundamental frequencies. However, this almost did not affect the predictions concerning the relative positions of various fundamental bands (except frequencies of deformational vibrations of methyl groups) and the degree of mixing of the normal modes, which were made in accordance with purely theoretical calculation. There is a good agreement between the theoretical and experimental data (Tables 5—7). This relates both to frequencies and isotope shifts as well as to intensities in IR and Raman spectra and depolarization ratios.

***N,N*-Dimethylnitramine (1).** As already mentioned, spectra of the gaseous phase have priority in the solution of the inverse vibrational problem in our work. The formation of hydrogen bonds in condensed media results in noticeable shifts of some bands. For example, for **1** the frequency of the antisymmetric stretching vibration of the NO_2 group decreases by 30—40 cm^{-1}, and the frequency of its symmetric stretching vibration increases approximately by the same value (see Table 1). For scaling the *ab initio* force field, the data of IR spectra of the gaseous phase[5,6] were used for 18 fundamental vibrations of the parent substance (see Table 5). It should be noted that there are no sufficiently reliable bands for molecule **1** in the spectral range below 150 cm^{-1} The minimization also includes 20 isotope shifts for ^{15}N-amino- and D_6-labeled and 10 shifts for ^{15}N-nitro-labeled **1**. Convergence achieved for compound **1** and its isotopomers is characterized by average deviations from 4 to 9 cm^{-1}.

The main contradiction in the published studies[4—8] of identification of the NN stretching vibration also resulted in differences of assignments of CN stretching vibrations and rocking vibrations of methyl groups, because it concerns the same bands in the frequency range of 850—1250 cm^{-1} (see Table 1). According to our data, the band at ~1000 cm^{-1}, which is the most intense in the considered range of the IR spectrum and polarized in the Raman spectrum (ν_{10}, see Table 5) must correspond to the NN stretching vibration. As previously,[7,8] we assign bands ν_{11} ~850 and ν_{24} ~1300 cm^{-1}, rather weak in the IR spectrum (see Table 5) to $\nu_s(NC_2)$ and $\nu_{as}(NC_2)$. The first of them is very strong and polarized, while the second is very weak and should be depolarized in the Raman spectrum.

The difference between the frequencies of the ONO bending and NO_2 rocking vibrations amounts to only 5—10 cm^{-1} in the experimental spectra, and the shifts of the bands to the high-frequency range on going from the gaseous to condensed phases reach 20 cm^{-1} (see Table 1). IR spectra of the gaseous phase[5,6] are studied insufficiently, and the difference in intensities of bands predicted by the *ab initio* calculation cannot be used for their identification (ν_{13} and ν_{27}, see Table 5). Theoretical frequencies interchanged their positions in the course of the solution of the inverse vibrational problem, and the difference between them turned out to be less than 3 cm^{-1}. But, taking into account possible error of the solution, we cannot insist on this result.

According to the calculation, the band at 185 cm^{-1}, which was obtained by us in the far IR absorption spectrum of the crystalline phase of substance **1**, can be assigned to the wagging vibration of the amino group (ν_{15}, see Table 5). The band at 208 cm^{-1} in the Raman spectrum of crystalline compound **1** can be assigned to the same vibration (see Ref. 4).

Frequencies of torsional vibrations of methyl groups and nitro group in molecule **1** (ν_{16}, ν_{29}, ν_{30} in Table 5) have not yet been determined. It was suggested[6] that one of the bands in spectra of the crystalline phase be assigned to this vibration of the NO_2 group (see Table 1): at 95 cm^{-1} (weak in the IR and Raman spectra) or at 173 cm^{-1} (very weak in the IR spectrum). The line at 162—165 cm^{-1} in the Raman spectrum of the crystalline phase was assigned to the same vibration.

Our calculation showed that the bands at 160—170 cm^{-1} should be assigned to the antisymmetric torsional vibration of methyl groups. The vibration $\chi(NO_2)$ should be observed at *ca.* 120 cm^{-1}, and the band at 107 cm^{-1} in the Raman spectrum of the solution of **1** assigned[7] to the torsional vibration of methyl groups better corresponds to it. For the symmetric torsional vibration of methyl groups, our calculation predicted the frequency at ~125 cm^{-1}, which must not appear in the Raman spectrum. The band with this frequency was not recorded in the experiment. The band at 98 cm^{-1} in the far IR spectrum of the crystalline phase of compound **1** can be conditionally assigned to this vibration.

***N*-Methylnitramine (2).** In addition to vibrational spectra of the parent substance **2** (see Table 2), there are experimental data for its D_1-, D_3-, D_4-, and ^{15}N-nitro-labeled derivatives.[6,10] Ten fundamental bands in the frequency range higher than 750 cm^{-1} are obtained in the IR spectrum of the gaseous phase of **2** (see Table 6). The IR spectra of the gaseous phases of two isotopomers of **2** (^{15}N-nitro (10 frequencies) and

Table 5. Experimental and calculated spectral parameters for *N,N*-dimethylnitramine molecule[a]

Symmetry type	№	Experiment [4–8]			Calculation (this work) [b]				
		ν/cm^{-1}		Depolarization ratio	ν/cm^{-1}	Intensity		Depolarization ratio	Potential energy distribution (%)
		IR	Raman			IR /km mol^{-1}	Raman /Å^4 a.m.u.$^{-1}$		
A′	1	3028 w	3034(2)		3045.5	9.6	65.2	0.67	52 CH_3 as.str + 45 CH_3 as.str′
	2	2970[c] sh	2993		3004.8	48.2	91.1	0.38	44 CH_3 as.str + 36 CH_3 as.str′ + + 20 CH_3 s.str
	3	2931[c] m	2946 m		2921.7	42.4	180.4	0.05	77 CH_3 s.str + 19 CH_3 as.str′ + + 4 CH_3 as.str
	4	1492 sh			1494.5	129.0	9.9	0.51	87 CH_3 as.def + 12 CH_3 rock ‖
	5	1475[c] m			1474.9	24.0	20.6	0.73	82 CH_3 as.def′ + 8 CH_3 s.def + + 8 CH_3 rock ⊥
	6	1453[c] m	1452(4)	(dp?)	1451.9	20.5	11.8	0.56	83 CH_3 s.def + 9 CH_3 as.def′ + + 5 NO_2 s.str
	7	1310[c] v. s, A			1319.0	337.1	10.5	0.34	56 NO_2 s.str + 15 NN str + + 12 ONO bend + 10 CH_3 s.def + + 4 CH_3 rock ⊥
	8	1256 m	1252 m	p	1250.6	12.9	3.3	0.48	39 CH_3 rock ‖ + 13 CH_3 rock ⊥ + + 11 NC_2 s.str + 11 NO_2 s.str + + 8 CH_3 as.def + 8 NN str
	9	1132[c] w	1150 w		1132.3	38.8	5.3	0.75	62 CH_3 rock 1 + 26 CH_3 rock ‖ + + 5 CH_3 as.def′
	10	985[c] m	1009 m	p	1004.4	74.6	2.4	0.24	28 NN str + 26 NC_2 s.str + + 18 CH_3 rock ‖ + + 12 CH_3 rock ⊥ + 11 NO_2 s.str
	11	846[c] w, A	840 v. s	0.2	835.2	9.9	12.1	0.23	40 NC_2 s.str + 39 ONO bend + + 14 NO_2 s.str + 6 NN str
	12	770[c] m, C			769.4	35.6	0.3	0.74	97 NO_2 wag
	13	600[c] m	622 s	p	601.7	6.3	3.2	0.11	39 ONO bend + 34 NN str + + 22 NC_2 s.str + 6 CNC bend
	14	(430[c] m)	420 m	p	400.6	4.9	0.3	0.20	40 NC_2 wag + 35 CNC bend + + 10 CH_3 s.tors + 7 NN str
	15	185[d]	208(1)		211.3	7.7	1.4	0.65	52 NC_2 wag + 28 CH_3 s.tors + + 19 CNC bend
	16	98[d]			125.8	5.1	0.1	0.72	62 CH_3 s.tors + 32 CNC bend + + 5 NC_2 wag
A″	17	3028 w	3034(2)		3041.8	5.3	47.9	0.75	53 CH_3 as.str′ + 42 CH_3 as.str + + 5 CH_3 s.str
	18		2993		2995.1	0.0	20.7	0.75	56 CH_3 as.str + 30 CH_3 as.str′ + + 14 CH_3 s.str
	19	2931[c] m	2946(9)		2915.7	26.0	11.5	0.75	81 CH_3 s.str + 17 CH_3 as.str′
	20	1561[c] v. s, B	1528		1559.2	543.1	0.3	0.75	72 NO_2 as.str + 12 NO_2 rock + + 7 NC_2 twist
	21	1475[c] m			1476.3	1.5	11.2	0.75	89 CH_3 as.def + 7 CH_3 rock ‖
	22	1465[c] m	1462		1464.7	8.4	7.8	0.75	92 CH_3 as.def′ + 6 CH_3 rock ⊥
	23	1407[c] m	1406(3)	dp	1408.1	1.7	7.0	0.75	98 CH_3 s.def
	24	1298 w	1292		1298.5	0.6	0.2	0.75	56 NC_2 as.str + 15 CH_3 rock ‖ + + 14 NO_2 as.str + 7 NC_2 twist + + 4 NO_2 rock
	25		1103(0)		1105.9	3.3	5.3	0.75	81 CH_3 rock ⊥ + 12 CH_3 rock ‖ + + 6 CH_3 as.def′
	26	1038[c] w			1037.4	21.5	1.7	0.75	61 CH_3 rock ‖ + 24 NC_2 as.str + + 10 CH_3 rock ⊥ + 4 CH_3 as.def
	27	612[c] m	614 w	dp	604.4	19.4	3.2	0.75	51 NO_2 rock+ 19 NC_2 twist + + 18 NC_2 as.str + 10 NO_2 as.str
	28	350 w			349.7	2.6	0.3	0.75	62 NC_2 twist + 29 NO_2 rock + + 7 CH_3 as.tors
	29	173 v. w	162		151.8	0.6	0.1	0.75	92 CH_3 as.tors + 4 NC_2 twist
	30		107		119.5	0.1	0.7	0.75	98 NO_2 tors

[a] See footnotes[a,c] for Table 1 and footnote[a] for Table 4. [b] Frequencies and potential energy distributions are obtained as a result of scaling. [c] Fundamental frequencies from IR spectra of the gaseous phase.[5,6]

[d] Frequencies of the bands in the far IR spectrum of the crystalline phase (this work).

Table 6. Experimental and calculated spectral parameters for *N*-methylnitramine molecule[a]

	Experiment [4–6,10]			Calculation (this work)[b]				
№	ν/cm^{-1}		Depolarization ratio	ν/cm^{-1}	Intensity		Depolarization ratio	Potential energy distribution (%)
	IR	Raman			IR /km mol^{-1}	Raman /Å^4 a.m.u.$^{-1}$		
1	3438^c w, B			3435.5	65.3	43.1	0.23	100 NH str
2	3016 w	3032(1)		3031.3	9.1	55.3	0.71	53 CH_3 as.str' + 44 CH_3 as.str
3	2988 w			2994.9	23.2	65.4	0.59	56 CH_3 as.str + 36 CH_3 as.str' + + 8 CH_3 s.str
4	2923 w	2951(6)		2922.6	29.4	105.8	0.04	88 CH_3 s.str + 11 CH_3 as.str'
5	1614^c s, B	1552(0)		1611.5	478.7	0.2	0.74	49 NO_2 as.str + 36 NNC(NH) twist + + 10 NO_2 rock
6	1492^c w			1495.8	85.6	12.2	0.69	85 CH_3 as.def + 10 CH_3 rock ‖
7	1475^c w			1471.2	64.2	16.7	0.69	88 CH_3 as.def' + 8 CH_3 rock ⊥
8	1435^c w	1443 m	0.6	1435.3	146.6	12.2	0.36	81 CH_3 s.def + 6 NO_2 s.str
9	1394^c m, B	1386(2)		1400.0	80.6	3.2	0.75	46 NNC(NH) twist + 34 NO_2 as.str + + 6 CH_3 as.def
10	1332^c s, A	1331 w	p	1340.9	169.9	4.5	0.26	57 NO_2 s.str + 15 ONO bend + + 13 NN str + 9 CH_3 s.def
11	1180 m	1176 w	p	1181.8	7.0	4.6	0.41	52 CH_3 rock ‖ + 19 CN str + + 7 NO_2 as.str + 6 CH_3 as.def
12	1124 s			1126.5	12.5	4.1	0.75	83 CH_3 rock ⊥ + 7 CH_3 rock ‖ + + 6 CH_3 as.def'
13	1092^c w	1117(9)	0.25	1098.0	62.8	2.5	0.13	44 CN str + 23 NN str + +14 NO_2 s.str + 10 NNC(NH) twist + + 7 CH_3 rock ‖
14	928^c w	940 s	0.24	921.8	13.9	7.4	0.16	22 NN str + 22 NO_2 s.str + + 18 ONO bend + 16 CN str + + 13 CH_3 rock ‖
15	772^c w, C			776.1	39.1	0.5	0.46	96 NO_2 wag
16	727 w	712(0)		732.0	57.2	2.8	0.63	42 ONO bend + 21 NNC(NH) wag + + 12 NO_2 rock + 7 CH_3 rock ‖
17	587 w	591 w		578.8	18.2	3.4	0.30	33 NO_2 rock + 22 NN str + + 19 ONO bend + 17 CN str
18	533 w	504(0.5)		530.0	124.8	2.1	0.69	42 NNC(NH) wag + 27 NO_2 tors + + 17 NO_2 rock + 12 NN str
19	330^d	320 w		304.0	9.9	0.6	0.54	66 NNC bend + 21 NO_2 rock + 5 NO_2 tors
20	177^d	227(2)		189.8	0.9	0.7	0.73	72 CH_3 tors + 10 NNC bend + + 10 NNC(NH) wag + 7 NO_2 tors
21	120^d			142.0	1.4	0.4	0.74	56 NO_2 tors + 23 CH_3 tors + + 17 NNC(NH) wag

[a,b,d] See footnotes[a,b,d] for Table 5.

[c] Fundamental frequencies from IR spectra of the gaseous phase.[6,10]

D_3 (7 frequencies)) are also obtained. The absence of reliable information about the low-frequency spectral range (lower than 300 cm^{-1}) is a common disadvantage of these experimental data. Scaling the *ab initio* force field over 19 fundamental frequencies of the parent compound **2** and over 13—15 isotope shifts for each of its isotopic modifications gave a good agreement with the experiment, and average deviations for reproducing frequencies were from 4 to 9 cm^{-1}.

A single, but important, contradiction between different variants of assignment of experimental bands[6,8,10] concerned the interpretation of two bands at ~1100 and ~930 cm^{-1}, weak in the IR spectrum but strong and polarized in the Raman spectrum, for molecule **2** assigned to the CN and NN stretching vibrations (see Table 2). Our calculation confirmed justification of the suggested interpretation[6,10] of the band at 930 cm^{-1} corresponding to the NN stretching vibration. However, the mixed character of this vibration for **2** (ν_{14}, see Table 6) is still higher than for **1**, so that this assignment is rather conditional.

The band of the medium intensity at 618 cm^{-1} in the IR spectrum of the cooled film was assigned[6] to the wagging vibration of the amino group in molecule **2**. However, this interpretation turned out to be wrong. According to our data, a somewhat weaker band at 533 cm^{-1} in the IR spectrum of the liquid film of **2** should be assigned to this vibration (see Ref. 5), which is corroborated by good agreement with spectra of its isotopomers.

Table 7. Experimental and calculated spectral parameters for nitramine molecule[a]

Symmetry type	№	Experiment				Calculation (this work) [b]					
		ν/cm^{-1}			Depolarization ratio	ν/cm^{-1} scaling over		Intensity		Depolarization ratio	Potential energy distribution (%) over spectra I
		IR[11]		Raman[4]				IR /km · mol^{-1}	Raman /Å^4 · a.m.u.$^{-1}$		
		I[c]	II[d]			I	II				
A'	1	3359.3(0.6)	3361	3278(2)		3371.4	3370.7	54.0	58.2	0.11	100 NH_2 s.str
	2	1558.1(1.2)	1581	1547(0.5)	dp	1559.1	1574.7	94.0	2.9	0.49	56 HNH bend + 43 NH_2 wag
	3	1349.6(4.5)	1367.5	1370(6)	p	1364.2	1372.5	258.9	9.0	0.12	65 NO_2 s.str + + 16 NN str + 16 ONO bend
	4	970[e]	980[e]	1050(10)	p	979.2	984.4	17.2	10.6	0.15	48 NN str + 32 NO_2 s.str + + 8 ONO bend
	5	797.9(0.6)	776	—		791.2	796.5	141.3	3.1	0.24	64 NO_2 wag + 14 ONO bend + + 12 HNH bend
	6	692.5(0.3)	713.5	716(4)	p	699.9	709.2	118.9	3.9	0.75	40 ONO bend + 29 NO_2 wag + + 18 NH_2 wag
	7	628.5(0.7)	587	598(0.5)		614.0	620.7	143.4	1.9	0.21	32 NN str + 22 ONO bend + + 21 NH_2 wag + 20 HNH bend
A"	8	3478.0(2.3)	3474	—		3492.8	3492.1	81.5	31.5	0.75	100 NH_2 as.str
	9	1612.8(10.0)	1610.5	1642(0)		1613.3	1616.3	565.0	0.3	0.75	64 NO_2 as.str + + 25 NH_2 twist + + 11 NO_2 rock
	10	1226.7(2.8)	1238.5	1176(0.5)		1221.6	1226.0	105.4	2.3	0.75	67 NH_2 twist + + 33 NO_2 as.str
	11	(587)	587	598(0.5)	dp	572.7	572.9	1.2	1.3	0.75	88 NO_2 rock
	12	401.5(0.4)	433.8	—		420.1	420.2	33.0	1.0	0.75	98 NO_2 tors

[a,b] See footnotes[a,b] for Table 5. [c] In Ar-matrix. [d] In N_2-matrix.
[e] Estimation by the Redlich—Teller product rule.

Although reliable experimental frequencies were not obtained[4—6,10] for torsional vibrations of CH_3- and NO_2-groups in molecule **2**, the contributions of these vibrations to adjacent bands with strongly mixed modes made it possible to predict their fundamental frequencies (ν_{20} and ν_{21}, see Table 6). Our calculated frequencies agree well with the newly obtained experimental frequencies: 177 and 120 cm^{-1} in the far IR absorption spectrum of the crystalline phase of **2**. At the same time, they differ considerably from those calculated by the traditional method[8] not only in value, but also in the relative positions ($\chi(NO_2)$ = 158 and $\chi(CH_3)$ = 112 cm^{-1}). Our calculation also allowed us to improve the interpretation of individual bands in spectra of isotopomers of **2**.

Nitramine (3). The absence of experimental spectra for the gaseous sample of **3** (see Table 3) makes the analysis in terms of the used approach difficult. However, as was discussed above, this absence is compensated to some extent by IR spectra of the parent substance **3** and its ^{15}N-amino- and D_2-labeled derivatives in inert matrices.[11] Scaling the *ab initio* force field for **3** is performed by the spectra in two variants: for the Ar-matrix (24 frequencies and 22 isotope shifts, including the data for three isotopomers) and for the N_2-matrix (24 frequencies, including the data for the D_2-labeled derivative). The achieved agreement with the experiment is characterized by average deviations for frequencies, which are 9—14 and 10 cm^{-1} for two variants under consideration. The results of the solution of the inverse vibrational problem are presented in Table 7.

The main contradictions between the previous variants of interpretation of IR and Raman spectra of molecule **3**, as seen from Table 3, concern assignments as follows: 1) frequencies of the antisymmetric stretching $\nu_{as}(NO_2)$ and bending δ(HNH) vibrations, 2) external deformations of the amino group $\omega(NH_2)$ and $t(NH_2)$, and 3) the rocking vibration of the nitro group $r(NO_2)$. In the first case, our calculation confirms the assignment suggested in Ref. 11 and the good correspondence to the experiment of intensities of IR and Raman bands (ν_2 and ν_9, see Table 7) can serve as an important additional argument. The ν_2 band in the Raman spectrum was considered as depolarized due to its weak intensity.[4] However, it is polarized, according to our calculation, but its calculated depolarization ratio is sufficiently high (0.49).

The assignment of the amino group deformations $\omega(NH_2)$ and $t(NH_2)$ (ν_7 and ν_{10}, see Table 7) suggested in Ref. 11 were also confirmed as a whole. However, according to our data, both $\omega(NH_2)$ (ν_7, see Table 7) and $r(NO_2)$, the rocking vibration of the nitro group (ν_{11}, see Table 7) can be related to the band at 587 cm^{-1} of the IR spectrum of molecule **3** in the

N_2-matrix. Previously no band in this spectrum was assigned to the rocking vibration.[11] The frequency of the band assigned to $r(NO_2)$ by authors of Ref. 11 in the IR spectrum of **3** in the Ar-matrix is too low (484.5 cm^{-1}, see Tables 3 and 7). The origin of the latter band is associated either with matrix effects or with the presence of some admixtures. This problem should be additionally studied.

It should be mentioned that according to our calculation, the intensity of the IR band of the NO_2 group rocking vibration must be very weak, and the band may not always be observed in the experiment. The weak depolarized band at 598 cm^{-1} in the Raman spectrum was assigned to this vibration,[4,5] which agrees well with our results. At the same time, according to the calculation, the difference between the ν_7 and ν_{11} frequencies must be comparable with matrix shifts observed, and one somewhat broadened band in the Raman spectrum could correspond wholly to these vibrations.

It is likely that matrix effects noticeably change the intensity and the frequency of the NN stretching vibration (ν_4, see Table 7). The bands of this vibration were not observed at all in IR spectra of molecule **3** and its D_2-labeled derivative in the N_2-matrix, and in the Ar-matrix spectra their frequencies (950.9 and 948 cm^{-1}) differ much less than predicted by the calculation. The estimation of the ν_4 frequency by the Redlich—Teller product rule gives 970 and 980 cm^{-1} for **3** in Ar- and N_2-matrices, respectively. The use of these values considerably improved the general agreement between the calculation and the experiment.

Scaled quantum chemical force fields of nitramines

From our viewpoint, the presented results demonstrate significantly greater efficiency of the use of *ab initio* force fields and scaling procedure in the analysis of vibrational spectra as compared with traditional methods. Validity of *ab initio* force fields and reliability of the scaling procedure are confirmed by extensive experience.[15] This makes the comparison of the force constants for nitramines **1**—**3** between each other and with experimental data[8,9,11] justified (Tables 8 and 9).

First of all let us note that there are no substantial distinctions in the general structure of matrices of the potential energies, which are characterized by large values (>0.2 in the corresponding units) of some off-diagonal constants related to the internal coordinates of nitro or amino groups. The largest constants mainly involve interactions between the coordinates of stretching vibrations of adjacent bonds with each other and with some deformation coordinates. The stretching vibration of the central NN bond interacts with vibrations of both groups. There are no large interactions between coordinates in different groups.

Table 8. Main force constants of the N—NO_2 moiety in simplest nitramines[a]

Internal coordinates	$(CH_3)_2NNO_2$			CH_3NHNO_2		H_2NNO_2[b]	
	This work	See Ref. 8	See Ref. 9	This work	See Ref. 8	This work	See Ref. 11
			Diagonal force constants				
NO str	9.07	9.67	9.38	8.94; 9.16	9.90	9.28	9.57(68)
NN str	5.25	6.32	6.38	5.23	6.74	4.91	6.27(96)
NO_2 wag	0.58	0.34	0.56	0.57	0.36	0.55	0.60(4)
ONO bend	2.15	(1.24)[c]	(1.20)[c]	2.19	(1.44)[c]	2.11	2.15(12)
NO_2 rock	1.62	1.85	1.80	1.45	1.81	1.36	2.13(21)
NO_2 tors	0.195	0.084	0.10	0.208	0.032	0.175	0.163(7)
			Force constants of interactions				
NO str/NO str	1.44	1.73	1.63	1.44	1.05	1.49	0.82(66)
NO str/NN str	0.99	0.86	0.93	0.97; 0.89	0.98	0.84	0.61(20)
NO str/ ONO bend	0.28	(0.6)[c,d]	(0.38)[c]	0.20; 0.25	(0.52)[c,d]	0.21	0.0[e]
NO str/NO_2 rock	±0.42	1.1[d]	±0.76	±0.46	1.07[d]	±0.47	1.06(54)
NN str/ONO bend	−0.68	(−0.07)[c]	(−0.76)[c]	−0.59	(−0.75)[c]	−0.52	−0.84(14)
NO_2 wag/ONO bend	0.001	0.0[e]	0.0[e]	−0.004	0.0[e]	−0.004	0.23(5)

[a] Force constants of stretching vibrations and their interactions are expressed in mdyn $Å^{-1}$, deformations and their interactions are expressed in mdyn $Å^{-1}$, and interactions between stretching vibrations and deformations are expressed in mdyn.

[b] Standard deviations of the least-squares method are given in parentheses.

[c] Corresponds to the coordinate of the complicated scissoring NO_2 vibration $[6^{-1/2}(2\alpha - \beta_1 - \beta_2)]$, and not bending ONO vibration.

[d] Corresponds to the interaction of the symmetric stretching NO_2 vibration with NO_2 scissoring vibration or antisymmetric stretching NO_2 vibration with rocking NO_2 vibration.

[e] Fixed value.

Table 9. Main force constants of amino moieties in simplest nitramines[a]

Internal coordinates	$(CH_3)_2NNO_2$ This work	$(CH_3)_2NNO_2$ See Ref. 8	$(CH_3)_2NNO_2$ See Ref. 9	CH_3NHNO_2 This work	CH_3NHNO_2 See Ref. 8	H_2NNO_2[b] This work	H_2NNO_2[b] See Ref. 11
Diagonal force constants							
NN str	5.25	6.32	6.38	5.23	6.74	4.91	6.27(96)
CN str	4.90	5.01	5.22	4.91	4.37	—	—
NH str	—	—	—	6.54	6.58	6.53	6.22(15)
NNC bend	1.44	(0.18; 1.37)[c]	1.42	1.09	(0.79;	—	—
NNH bend	—	—	—	0.83	0.56;	0.77	0.80(4)
CNC (HNC, HNH) bend	0.71	(1.24)[d]	1.23	0.48	0.15)[e]	0.41	0.51(13)
Force constants of interactions							
NN str/CN str	0.22	0.68	0.74	0.18	0.59	—	—
NN str/NH str	—	—	—	0.01	0.0[f]	0.0	2.10(66)
NN str/NNC bend	0.83	0.0[f]	0.07	0.69		—	—
NN str/NNH bend	—	—	—	0.57	(−0.32)[e]	0.50	0.42(8)
NN str/CNC (HNC, HNH) bend	0.22	(−0.16)[d]	−0.35	0.25		0.22	−0.30(21)
CN str/NO str	−0.06; 0.0	0.0[f]	−0.25; −0.07	−0.05;−0.01	0.0[f]	—	—
CN (NH) str/NNC (NNH) bend	−0.05;0.36	(0.38)[c]	−0.25; 0.49	−0.34; 0.15		0.05; 0.12	−0.13(8)
CN str/CNC (HNC) bend	0.21	(0.45)[d]	0.57	0.20	(0.03; 0.23)[e]	—	—
CN str/CH_3 s.def.	−0.46	−0.54	−0.23	−0.45	−0.43	—	—
NH str/NH str	—	—	—	—	—	−0.04	−0.26(16)
NH str/HNH bend	—	—	—	—		0.11	−0.66(22)
NNC (NNH) bend/NO_2 rock	±0.17	(0.04)[c]	±0.24	0.03; 0.09	(−0.34;−0.02)[e]	±0.13	0.22(5)

[a] See footnote[a] for Table 8.

[b] Standard deviations of the least-squares method are given in parentheses.

[c] Correspond to the coordinates of wagging NC_2 vibration or rocking NC_2 vibration $[2^{-1/2}(\varepsilon_2 - \varepsilon_3)]$.

[d] Corresponds to the coordinates of the complicated scissoring NC_2 vibration $[6^{-1/2}(2\varepsilon_1 - \varepsilon_2 - \varepsilon_3)]$.

[e] Correspond to the internal coordinates of scissoring CNN vibration $[6^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3)]$, rocking NH vibration $[2^{-1/2}(\alpha_2 - \alpha_3)]$, or wagging NH vibration.

[f] Fixed value.

The comparison shows that empirical matrices of the potential energy for molecules **1**—**3** are qualitatively worse than ours, because they have no analogous structural similarity. Force constants obtained by different authors for the same molecules sometimes differ by 1.5—2 and more times, and values of some of them completely contradict our data. Many of the off-diagonal constants are too large or have the opposite sign as compared with the scaled *ab initio* values. Since the latter result in quite adequate reproduction of experimental frequencies of nitramines **1**—**3** and their isotope shifts, we are sure that the force fields obtained are preferable.

The comparison of force constants is rather indicative of the characteristics of the change in the electronic structure in the series of **1**—**2**—**3** as the total electronegativity of substituents at the amino nitrogen atom increases. As seen from Tables 8 and 9, variation in the majority of force constants on going from **1** to **3** is systematic. There is a tendency toward an increase in the force constant for the NO stretching vibration and toward decrease in the constants for the NN stretching vibration and torsional vibration of the NO_2 group. This correlates with inverse changes in the NO and NN bond lengths[2] and additionally demonstrates a tendency for the conjugation between amino and nitro groups to decrease successively along this series of compounds.

General regularities of vibrational spectra of nitramines

The changes in the electronic structures of nitramines must appear as shifts of fundamental frequencies, although the problem can be complicated by the large degree of mixing of many normal vibrations discussed above. The dependences of the vibrational frequencies of the N—NO_2 moiety on the total Mulliken charge of the nitro group are presented in Fig. 2.

Unlike NN stretching vibrations, NO stretching vibrations in nitramines belong to the most characteristic modes. Nevertheless, one can mention for the **1**—**2**—**3** series both a successive increase in the $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ frequencies and a tendency to a decrease in the ν(NN) frequency, which agrees well with the expected change in conjugation. The shifts of frequencies of the nitro group deformations behave rather regularly as well.

As a rule, the vibrations of the N—NO_2 moiety in molecules **1**—**3** are sufficiently characteristic with re-

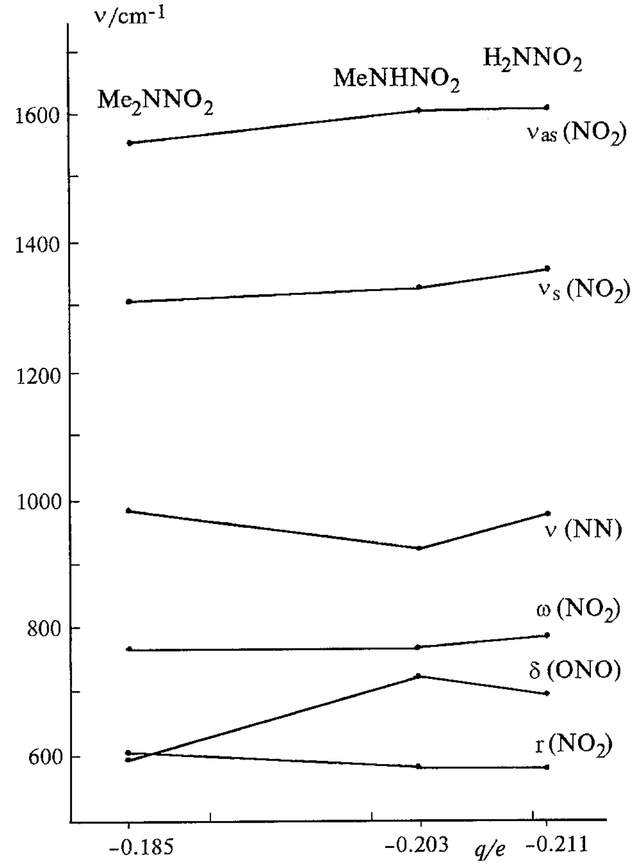

Fig. 2. Dependences of the vibrational frequencies of the N—NO_2 moiety on the total Mulliken charge of the nitro group (see Fig. 1).

spect to frequency and the bands move within a rather narrow range up to about 50—60 cm^{-1}, except for the lines of the strongly mixed δ(ONO) bending vibrations, which shift in the range of ~130 cm^{-1}.

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