Efficiency of post-Hartree—Fock force field for the interpretation of vibrational spectra of *N,N*-dimethylnitramine

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Harmonic force fields for the molecule of *N,N*-dimethylnitramine were calculated in the RHF/6-31G* and MP2/6-31G** approximations. Scaling of the force fields obtained made it possible to reliably interpret the vibrational spectra of light and perdeuterated compounds reported in the literature. The assignment is confirmed by good reproducibility of experimental isotope shifts upon ^{15}N-amino- and ^{15}N-nitrosubstitution. The frequencies of intramolecular vibrations in far IR and Raman spectra as well as in neutron inelastic scattering spectra for the light and perdeuterated samples of solid *N,N*-dimethylnitramine were identified using the force field calculated with the inclusion of electron correlation (MP2). Although general structures of the force fields calculated in the RHF and MP2 approximations are similar, considerable differences in the force constants of the NO and NN stretching vibrations and especially in the constants of the NO_{str}/NO_{str} and NO_{str}/NN_{str} interactions remain even after scaling the force fields.

Key words: *N,N*-dimethylnitramine, vibrational spectra, quantum-chemical calculation, force field.

Interpretation of vibrational spectra of *N,N*-dimethylnitramine and its D_6-, ^{15}N-nitro, and ^{15}N-amino isotopomers was changed several times as new experimental information became available;[1—9] however, it has not been completed as yet. In particular, the assignment of the frequencies of NN and NC stretching vibrations[2—6] is rather contradictory. The bands in the spectral region below 450 cm^{-1}, characteristic of deformation vibrations of a methyl-substituted amino group and torsional vibrations,[5—8] have no reliable assignment. The lack of reliable experimental data for the low-frequency spectral region can significantly affect the interpretation of the spectra as a whole. The results of numerous studies on normal coordinate analysis[5,6,8,9] indicate the complex character of the vibrations. Contradictory results of numerous attempts of analyzing vibrational spectra of *N,N*-dimethylnitramine and a number of other simplest nitramines suggest that a complete interpretation of these spectral data in the framework of conventional methods is impossible.[1]

A correct choice and assignment of the fundamental frequencies are impossible without preliminary knowledge on the force field. *Ab initio* quantum-chemical calculations are a powerful source of such an information.[10] Typical calculation errors can be effectively compensated for by scaling the force fields in the course of the solution of the inverse spectral problem with refinement of a small set of scaling factors by fitting theoretical vibrational frequencies to the experimental ones.

Our experience on using the force fields calculated by the restricted Hartree—Fock (RHF) method with the 6-31G* basis set and their scaling in the course of interpretation of vibrational spectra of a number of nitro derivatives shows that this approach is highly efficient.[11—13] For three simplest nitramines, $(CH_3)_2NNO_2$, CH_3NHNO_2, and H_2NNO_2, and their isotopomers we obtained a common set of scaling factors, which made it possible not only to reproduce the experimental frequencies in the well-studied spectral regions but also to perform fairly rigorous calculations of modes and distributions of the potential energy of vibrations, and, hence, to assign the bands.[11] Later, the set of recommended scaling factors for the force fields calculated in this approximation was successfully used for the interpretation of the vibrational spectra of the simplest dinitramines $CH_3N(NO_2)_2$ and $HN(NO_2)_2$[12] as well as those of nitrobenzene and its isotopomers,[13] which confirmed a good transferability of the factors obtained.

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They may be widely applied for interpretation of the spectra of more complex derivatives.

Although the use of the results of the RHF/6-31G* calculations[11] made it possible to perform a sufficiently reliable interpretation of the spectra of *N,N*-dimethylnitramine and its isotopomers, the discrepancies between the experimental frequencies and those obtained by scaling sometimes exceeded 20—30 cm^{-1}.

In this work we show that the inclusion of electron correlation into the theoretical force field calculations allows one to eliminate the remaining contradictions. The results of analysis of vibrational spectra of *N,N*-dimethylnitramine and its isotopomers obtained by scaling the force fields calculated in the RHF approximation and at the second-order Møller—Plesset (MP2) level of perturbation theory with inclusion of electron correlation are compared and discussed in detail. We also supplemented the experimental spectra published earlier with far IR and Raman spectra of solid *N,N*-dimethylnitramine.

Experimental

IR spectra were recorded on a Bruker IFS-113 evacuated IR Fourier spectrometer in the frequency range 30—450 cm^{-1} with a resolution of 1 cm^{-1}. Crystalline samples of *N,N*-dimethylnitramine were molded into pellets with adamantane ("chemically pure" grade). Raman spectra of the crystalline phase (20—450 cm^{-1}) were recorded on a Ramanor HG-2S spectrometer equipped with an Ar laser. The following frequencies (ν/cm^{-1}) were detected: 61 s, 98 m, 185 w, 353 s, 425 s (IR); 32 s, 63 sh, 67 m, 163 w, 230 w, 432 m (Raman).

Harmonic force constants in the Cartesian system were obtained for the equilibrium geometric parameters of the molecule of *N,N*-dimethylnitramine[14] from analytical expressions for the second derivatives of the SCF energy in the RHF/6-31G* and MP2/6-31G** approximations using the GAUSSIAN-92 program complex[15] on a Cray XMP-24 computer at the University of Texas at Austin (Austin, Texas). To solve the direct and inverse spectral problems by the scaling procedure, the ANCO and SCALE programs[16,17] were used. The calculated matrices of the force constants were transformed to a complete and nonredundant system of internal coordinates of local symmetry, which meets the criteria for comparability of constants in a series of related molecules. The corresponding sets of internal coordinates have been discussed previously.[18] Individual scaling factors C_i were introduced for the groups of equivalent or similar (in the case of local symmetry) internal coordinates. The modification of quantum-chemical force constants F_{ij}^{theor} was defined as $F_{ij} = (C_iC_j)^{1/2}F_{ij}^{\text{theor}}$.[10]

Results and Discussion

The use of *ab initio* force fields calculated in different approximations for the interpretation of vibrational spectra. The analysis of vibrational spectra of *N,N*-dimethylnitramine and its isotopomers using the force field calculated with inclusion of electron correlation (MP2/6-31G**) and the Hartree—Fock (RHF/6-31G*) force field[11] was carried out by fitting the calculated frequencies to the same set of experimental frequencies. The numbering of the atoms is shown in Fig. 1 and the definition of nonredundant set of internal coordinates of local symmetry is given in Table 1.

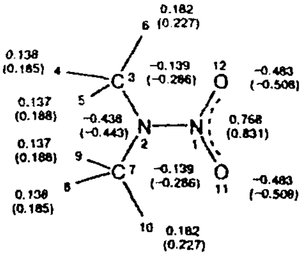

Fig. 1. The equilibrium configuration of the molecule of *N,N*-dimethylnitramine: numbering of the atoms and Mulliken atomic charges calculated for geometric parameters optimized in the MP2/6-31G** approximation (the results of the RHF/6-31G* calculations are given in parentheses).

In the case of RHF approximation, the scaling factors remained nearly unchanged when analyzing a somewhat revised (mostly in the long-wave region) set of experimental frequencies (Table 2). Most of scaling factors for the MP2 force field lie within the range 0.9—1.0. The only exception is the factor corresponding to the NO stretching vibrations, which can be explained by inadequate account of electron correlation in the MP2 method when describing the most unsaturated molecular fragments.

A comparison of *ab initio* force fields calculated in the RHF and MP2 approximations shows that their general structure is independent of the calculation level (Table 3). A change in the sign of off-diagonal force constants is a rare exception and occurs only when the absolute value of the constant does not exceed 0.02 (in corresponding units). At the same time, large differences (first of all, in the force constants of NO and NN stretching vibrations and especially in the constants of interactions between these vibrations, NO str/NO str and NO str/NN str) remain even after scaling the force fields. The effect of electron correlation is significant when the π-electron density considerably contributes to the corresponding chemical bond (NO or NN).

To exclude the effect of the medium from the solution of the inverse spectral problem, the literature data on the gas phase spectra were mostly used. Some bands are shifted noticeably in condensed media.[1] For instance, the $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ frequencies of the stretching vibrations of the nitro group are changed by 30—40 cm^{-1}. We used gas phase IR spectroscopy data[3,4] for 17 of 30 fundamental vibrations of unsubstituted *N,N*-dimethylnitramine (Table 4). The minimization also included 23 experimental frequencies of the perdeuterated derivative, 11 isotope shifts for the ^{15}N-nitro isotopomer, and 19 isotope shifts for the

Table 1. The nonredundant set of internal coordinates of local symmetry for the molecule of *N,N*-dimethylnitramine[a]

No.	Notation	Definition
1	N(1)N(2) str	
2	N(2)C(3) str	
3	N(2)C(7) str	
4	N(1)O(11) str	
5	N(1)O(12) str	
6	N(1)N(2)C(3) bend	
7	N(1)N(2)C(7) bend	
8	C(3)N(2)C(7) bend	
9	NO_2 wag	
10	NO_2 rock	0.7071 (N(2)N(1)O(11) bend) − − 0.7071 (N(2)N(1)O(12) bend)
11	O(11)N(1)O(12) bend	
12	CH_3 s.str (C(3))	0.5774 (C(3)H(4) str) + + 0.5774 (C(3)H(5) str) + + 0.5774 (C(3)H(6) str) −
13	CH_3 s.def (C(3))	− 0.4082 (N(2)C(3)H(4) bend) − − 0.4082 (N(2)C(3)H(5) bend) − − 0.4082 (N(2)C(3)H(6) bend) + + 0.4082 (H(5)C(3)H(6) bend) + + 0.4082 (H(4)C(3)H(6) bend) + + 0.4082 (H(4)C(3)H(5) bend)
14	CH_3 as.str (C(3))	0.8165 (C(3)H(4) str) − − 0.4082 (C(3)H(5) str) − − 0.4082 (C(3)H(6) str)
15	CH_3 as.def (C(3))	0.8165 (H(5)C(3)H(6) bend) − − 0.4082 (H(4)C(3)H(6) bend) − − 0.4082 (H(4)C(3)H(5) bend)
16	CH_3 rock$_\parallel$ (C(3))	0.8165 (N(2)C(3)H(4) bend) − − 0.4082 (N(2)C(3)H(5) bend) − − 0.4082 (N(2)C(3)H(6) bend)
17	CH_3 as.str′ (C(3))	0.7071 (C(3)H(5) str) − − 0.7071 (C(3)H(6) str)
18	CH_3 as.def′ (C(3))	0.7071 (H(4)C(3)H(6) bend) − − 0.7071 (H(4)C(3)H(5) bend)
19	CH_3 rock$_\perp$ (C(3))	0.7071 (N(2)C(3)H(5) bend) − − 0.7071 (N(2)C(3)H(6) bend)
20	CH_3 s.str (C(7))	0.5774 (C(7)H(8) str) + + 0.5774 (C(7)H(9) str) + + 0.5774 (C(7)H(10) str) −
21	CH_3 s.def (C(7))	− 0.4082 (N(2)C(7)H(8) bend) − − 0.4082 (N(2)C(7)H(9) bend) − − 0.4082 (N(2)C(7)H(10) bend) + + 0.4082 (H(9)C(7)H(10) bend) + + 0.4082 (H(8)C(7)H(10)) bend) + + 0.4082 (H(8)C(7)H(9) bend)
22	CH_3 as.str (C(7))	0.8165 (C(7)H(8) str) − − 0.4082 (C(7)H(9) str) − − 0.4082 (C(7)H(10) str)
23	CH_3 as.def (C(7))	0.8165 (H(9)C(7)H(10) bend) − − 0.4082 (H(8)C(7)H(10) bend) − − 0.4082 (H(8)C(7)H(9) bend)
24	CH_3 rock$_\parallel$ (C(7))	0.8165 (N(2)C(7)H(8) bend) − − 0.4082 (N(2)C(7)H(9) bend) − − 0.4082 (N(2)C(7)H(10) bend)
25	CH_3 as.str′ (C(7))	0.7071 (C(7)H(9) str) − − 0.7071 (C(7)H(10) str)
26	CH_3 as.def′ (C(7))	0.7071 (H(8)C(7)H(10) bend) − − 0.7071 (H(8)C(7)H(9) bend)
27	CH_3 rock$_\perp$ (C(7))	0.7071 (N(2)C(7)H(9) bend) − − 0.7071 (N(2)C(7)H(10) bend)
28	NO_2 tors (N(1)N(2))	N(1)—O(12),O(11); N(2)—C(7),C(3)
29	CH_3 tors (N(2)C(3))	N(2)—N(1),C(7); C(3)—H(4),H(5),H(6)
30	CH_3 tors (N(2)C(7))	N(2)—N(1),C(3); C(7)—H(8),H(9),H(10)

[a] The numbering of the atoms is shown in Fig. 1. The notations str, bend, def, wag, rock, tors, s., and as. correspond to stretching, bending for the bond angle, deformation vibration of local symmetry for the methyl group, wagging, rocking, torsional, symmetric, and antisymmetric vibrations, respectively. The torsional coordinate is defined as the sum of the motions in the tetraatomic fragment.

Table 2. Refined values of scaling factors for the force fields of *N,N*-dimethylnitramine calculated in the RHF/6-31G* and MP2/6-31G** approximations[a]

Type of factor	No. of internal coordinate (No., see Table 1)	Value of scaling factor		
		RHF (see Ref.[11])	RHF	MP2
			This work	
NN str	1	0.705	0.685	0.967
NC str	2, 3	0.835	0.835	0.922
NO str	4, 5	0.703	0.705	0.753
ONO bend	11	0.744	0.720	1.005
NO_2 rock	10	0.804	0.812	0.960
NO_2 wag	9	0.711	0.711	0.975
CNC bend	8	0.697	0.695	1.001
NNC bend	6, 7	0.803	0.809	0.963
NO_2 tors	28	0.800	0.800	1.000
CH_3 tors	29, 30	0.800	0.800	0.999
CH str	12, 14, 17, 20, 22, 25	0.817	0.817	0.862
CH_3 s.def	13, 21	0.784	0.788	0.911
CH_3 as.def	15, 18, 23, 26	0.808	0.808	0.897
CH_3 rock	16, 19, 24, 27	0.794	0.810	0.956

[a] See footnote to Table 1.

^{15}N-amino isotopomer (Table 5). The convergence achieved is characterized by mean deviations of 6—7 cm^{-1} (0.7—0.9%) and 9—10 cm^{-1} (~2.5%) for calculations using the MP2 and RHF force fields, respectively.

The use of the MP2 force field leads to a good agreement between the calculated and experimental frequencies even without scaling which makes only small changes in the potential energy matrix. In many cases, one can easily correlate the calculated fundamental frequency and other characteristics to the band with nearest frequency in the experimental spectra. Scaling of quantum-chemical force fields resulted in a change in the original ratio of contributions of different vibrations to fundamental frequencies. However, it has almost no effect on the predictions based on quantum-chemical calculations concerning the relative positions of fundamental frequencies (except for frequencies of the deformation vibrations of methyl groups, see Table 4) and the degree of mixing of vibrational modes. The agreement between theoretical intensities, degrees of depolarization, isotope shifts, and experimental data suggests with

Table 3. The force constants of *N*,*N*-dimethylnitramine (in internal coordinates) calculated in the RHF/6-31G* and MP2/6-31G** approximations and obtained by scaling (SQChem) [a]

Notation of force constant	RHF		MP2		Notation of force constant	RHF		MP2	
	Calculations	SQChem	Calculations	SQChem		Calculations	SQChem	Calculations	SQChem
1—1	7.45	5.10	5.84	5.65	6—20, 7—12	0.01	0.01	0.01	0.01
1—2, 1—3	0.28	0.21	0.26	0.25	6—21, 7—13	0.05	0.04	0.04	0.03
1—4, 1—5	1.41	0.98	0.84	0.71	6—24, 7—16	−0.02	−0.02	−0.01	−0.01
1—6, 1—7	1.10	0.82	0.91	0.87	6—27, 7—19	0.04	0.04	0.02	0.02
1—8	0.31	0.22	0.21	0.21	6—29, 7—30	∓0.07	∓0.06	∓0.10	∓0.10
1—9	0.08	0.06	0.08	0.08	6—30, 7—29	∓0.06	∓0.05	∓0.03	∓0.03
1—11	−0.94	−0.66	−0.85	−0.84	8—8	1.02	0.71	0.89	0.89
1—12, 1—20	−0.08	−0.06	−0.08	−0.07	8—9	−0.09	−0.06	−0.06	−0.06
1—13, 1—21	0.04	0.03	0.05	0.05	8—11	0.08	0.06	0.06	0.06
1—14, 1—22	0.06	0.05	0.06	0.05	8—13, 8—21	−0.03	−0.02	−0.03	−0.03
1—15, 1—23	−0.02	−0.01	−0.02	−0.02	8—14, 8—22	−0.09	−0.06	−0.06	−0.06
1—16, 1—24	0.11	0.08	0.09	0.09	8—18, 8—26	−0.02	−0.02	−0.02	−0.01
1—17, 1—25	0.02	0.01	0.01	0.01	8—19, 8—27	−0.03	−0.03	−0.07	−0.07
1—19, 1—27	−0.11	−0.08	−0.11	−0.11	8—29, 8—30	±0.12	±0.09	±0.09	±0.09
1—29, 1—30	∓0.10	∓0.07	∓0.12	∓0.11	9—9	0.81	0.58	0.61	0.59
2—2, 3—3	5.87	4.91	5.46	5.03	9—19, 9—27	0.02	0.02	0.02	0.02
2—3	0.11	0.09	0.06	0.06	10—10	2.01	1.63	1.74	1.67
2—5, 3—4	−0.07	−0.06	0.00	0.00	10—12, 10—20	±0.04	±0.03	±0.03	±0.03
2—6, 3—7	0.44	0.37	0.48	0.46	10—13, 10—21	∓0.03	∓0.02	∓0.02	∓0.02
2—7, 3—6	−0.07	−0.06	−0.03	−0.03	10—14, 10—22	∓0.05	∓0.04	∓0.04	∓0.04
2—8, 3—8	0.27	0.21	0.33	0.32	10—16, 10—24	±0.07	±0.06	±0.07	±0.06
2—9, 3—9	0.02	0.02	0.03	0.03	10—17, 10—25	∓0.04	∓0.03	∓0.04	∓0.04
2—10, 3—10	0.00	0.00	±0.03	±0.03	10—19, 10—27	±0.03	±0.03	±0.03	±0.03
2—11, 3—11	−0.01	−0.01	−0.02	−0.02	10—28	−0.01	−0.01	−0.04	−0.04
2—12, 3—20	0.22	0.18	0.20	0.18	10—29, 10—30	0.08	0.06	0.09	0.09
2—13, 3—21	−0.57	−0.47	−0.52	−0.47	11—11	2.89	2.08	2.39	2.40
2—14, 3—22	−0.10	−0.08	−0.08	−0.07	11—13, 11—21	0.02	0.02	0.02	0.02
2—15, 3—23	0.02	0.02	0.01	0.01	11—14, 11—22	−0.02	−0.02	−0.02	−0.02
2—16, 3—24	−0.04	−0.03	−0.02	−0.02	11—16, 11—24	0.02	0.01	0.01	0.01
2—17, 3—25	0.09	0.07	0.09	0.08	11—17, 11—25	−0.03	−0.02	−0.03	−0.03
2—18, 3—26	−0.02	−0.01	−0.01	−0.01	11—19, 11—27	0.02	0.02	0.03	0.03
2—20, 3—12	−0.02	−0.02	−0.01	−0.01	11—29, 11—30	±0.06	±0.04	±0.06	±0.06
2—22, 3—14	−0.02	−0.02	−0.01	−0.01	12—12, 20—20	60.12	50.00	50.74	40.94
2—25, 3—17	0.01	0.01	0.01	0.01	12—13, 20—21	0.12	0.10	0.11	0.09
2—27, 3—19	−0.04	−0.03	−0.07	−0.06	12—14, 20—22	0.03	0.02	0.03	0.03
2—28, 3—28	∓0.03	∓0.02	∓0.03	∓0.03	12—16, 20—24	0.01	0.01	0.02	0.02
2—29, 3—30	±0.03	±0.03	±0.03	±0.03	12—17, 20—25	−0.14	−0.12	−0.15	−0.13
2—30, 3—29	∓0.04	∓0.03	∓0.04	∓0.04	12—20	0.01	0.01	0.01	0.01
4—4, 5—5	12.90	9.10	11.11	8.36	12—24, 16—20	−0.01	−0.01	−0.01	−0.01
4—5	2.05	1.45	0.32	0.24	13—13, 21—21	0.79	0.62	0.70	0.63
4—6, 5—7	−0.02	−0.01	0.06	0.05	13—21	0.01	0.01	0.01	0.01
4—7, 5—6	−0.13	−0.10	−0.08	−0.07	13—29, 21—30	∓0.01	∓0.01	∓0.01	∓0.01
4—8, 5—8	−0.15	−0.11	−0.10	−0.08	14—14, 22—22	6.00	4.90	5.73	4.94
4—10, 5—10	±0.56	±0.43	±0.57	±0.48	14—15, 22—23	−0.16	−0.13	−0.16	−0.14
4—11, 5—11	0.39	0.28	0.29	0.26	14—16, 22—24	0.08	0.06	0.09	0.08
4—13, 5—21	−0.03	−0.02	−0.03	−0.02	14—17, 22—25	0.11	0.09	0.12	0.10
4—14, 5—22	0.03	0.02	0.02	0.01	14—22	0.02	0.02	0.01	0.01
4—16, 5—24	0.01	0.01	0.02	0.02	14—29, 22—30	∓0.03	∓0.03	∓0.03	∓0.02
4—17, 5—25	0.02	0.01	0.01	0.01	15—15, 23—23	0.68	0.55	0.61	0.55
4—19, 5—27	0.03	0.03	0.03	0.02	15—16, 23—24	−0.04	−0.04	−0.03	−0.02
4—20, 5—12	0.05	0.04	0.02	0.02	15—28, 23—28	∓0.01	∓0.01	∓0.02	∓0.01
4—21, 5—13	−0.06	−0.04	−0.05	−0.04	15—29, 23—30	∓0.02	∓0.01	∓0.02	∓0.02
4—22, 5—14	−0.05	−0.04	−0.04	−0.03	16—16, 24—24	1.00	0.81	0.87	0.83
4—23, 5—15	0.02	0.02	0.02	0.02	16—18, 24—26	−0.01	−0.01	−0.01	−0.01
4—24, 5—16	−0.03	−0.02	−0.04	−0.04	16—24	0.03	0.02	0.02	0.02
4—28, 5—28	0.00	0.00	∓0.04	∓0.04	16—27, 19—24	0.02	0.01	0.02	0.02
4—29, 5—30	±0.02	±0.01	±0.02	±0.01	16—28, 24—28	∓0.02	∓0.01	∓0.02	∓0.02
6—6, 7—7	1.80	1.45	1.59	1.54	16—29, 24—30	0.00	0.00	∓0.01	∓0.01
6—7	−0.03	−0.03	−0.13	−0.12	17—17, 25—25	5.94	4.86	5.65	4.87
6—8, 7—8	0.02	0.01	−0.05	−0.05	17—18, 25—26	−0.16	−0.13	−0.15	−0.13

(*to be continued*)

Table 3 (*continued*)

Notation of force constant	RHF		MP2		Notation of force constant	RHF		MP2	
	Calculations	SQChem	Calculations	SQChem		Calculations	SQChem	Calculations	SQChem
6—9, 7—9	−0.05	−0.04	−0.02	−0.02	17—19, 25—27	0.08	0.07	0.09	0.08
6—10, 7—10	∓0.22	∓0.18	∓0.23	∓0.22	17—28, 25—28	∓0.02	∓0.02	∓0.01	∓0.01
6—11, 7—11	−0.21	−0.16	−0.21	−0.21	17—29, 25—30	∓0.07	∓0.06	∓0.05	∓0.05
6—12, 7—20	−0.02	−0.02	−0.03	−0.03	18—18, 26—26	0.67	0.54	0.60	0.54
6—13, 7—21	−0.03	−0.02	−0.03	−0.03	18—19, 26—27	−0.02	−0.02	−0.02	−0.02
6—14, 7—22	0.12	0.10	0.10	0.09	19—19, 27—27	0.96	0.78	0.84	0.81
6—15, 7—23	0.03	0.03	0.03	0.03	19—28, 27—28	±0.03	±0.02	±0.02	±0.02
6—16, 7—24	0.02	0.02	0.02	0.02	19—29, 27—30	∓0.01	∓0.01	∓0.02	∓0.02
6—17, 7—25	0.07	0.06	0.07	0.06	28—28	0.24	0.20	0.20	0.20
6—19, 7—27	−0.02	−0.01	−0.04	−0.04	29—29, 30—30	0.08	0.06	0.08	0.08

[a] The notations of the force constants correspond to the numbering of internal coordinates in Table 1. The force constants of the stretching vibrations and their interactions are given in mdyn Å^{-1}, the force constants of deformation vibrations and their interactions are given in mdyn Å^{-1}, and the force constants of interactions between the stretching and deformation vibrations are given in mdyn. The force constants, whose absolute values do not exceed 0.01, are not listed.

high probability that the calculated eigenvectors of normal vibrations and potential energy distributions objectively reflect the intramolecular motions in *N*,*N*-dimethylnitramine.

According to MP2 calculations, the stretching vibrations of the C_2NNO_2 frame make an appreciable contribution to the six different frequencies of experimental spectrum of *N*,*N*-dimethylnitramine in the region 800—1600 cm^{-1} (see Table 4). The plots of the contributions of stretching vibrations of all the five bonds of the C_2NNO_2 frame to the modes for these bands are shown in Fig. 2. It is difficult to assign most of the bands to a particular stretching vibration. Only two frequencies (ν_{20} at 1566 cm^{-1} and ν_{24} at ~1300 cm^{-1}), to which the NN bond makes virtually no contribution, can be unambiguously assigned to the A" symmetry type antisymmetric $\nu_{as}(NO_2)$ (very strong in the IR spectrum) and $\nu_{as}(NC_2)$ (weak in the IR and Raman spectra) stretching vibrations of the nitro group and methyl-substituted amino group, respectively. All other vibrations have rather mixed modes.

Considerable difficulties arise when assigning the symmetric $\nu_s(NO_2)$ stretching vibration of the nitro group. Formally, from the viewpoint of conventional consideration of the modes and potential energy distribution (see Fig. 2, Table 4), this vibration can be assigned to either of the two bands, namely, to ν_7 at 1312 cm^{-1}, which is very strong in the IR spectrum and of medium intensity in the Raman spectrum, or to ν_8 at 1242 cm^{-1}, which is of medium intensity in both the IR and Raman spectra and polarized in the Raman spectrum). The nearly equal isotope shifts due to ^{15}N-nitro substitution experimentally observed for both bands are well reproduced (see Table 5) using the MP2 force field (in contrast to the RHF force field). According to calculations, the ν_{11} band at 835 cm^{-1}, which is weak in the IR spectrum but very strong and polarized in the Raman spectrum, corresponds to a totally symmetric normal vibration of the C_2NNO_2 frame, *i.e.*, this band is characterized by synphase changes in the length of all five bonds (see

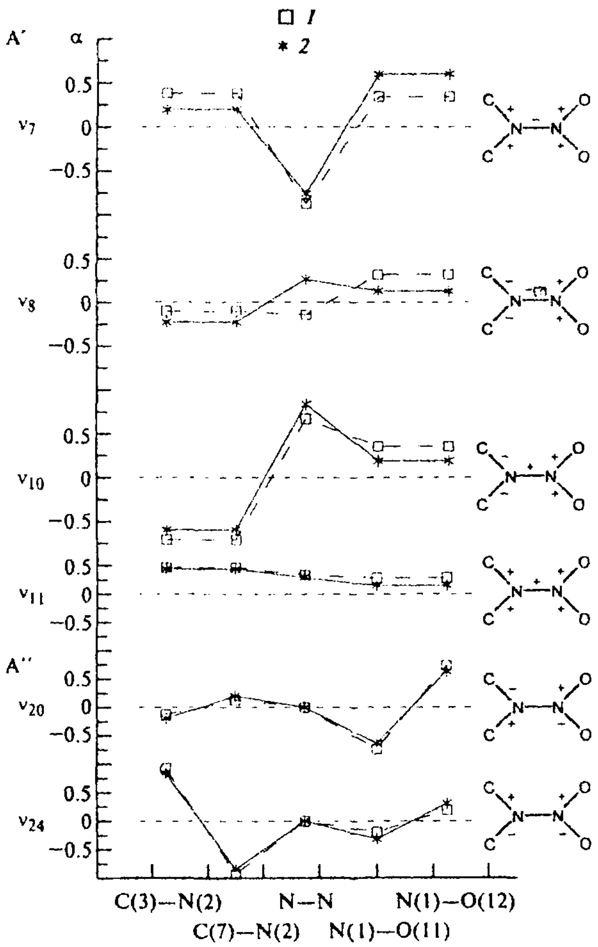

Fig. 2. Plots of distribution of contributions (α) of stretching vibrations of the C_2NNO_2 frame to the modes of certain normal vibrations of *N*,*N*-dimethylnitramine upon scaling of MP2/6-31G** (*1*) and RHF/6-31G* (*2*) force fields. The components corresponding to lengthening and shortening of the bond are indicated by the "plus" and "minus" sign, respectively.

Fig. 2). With equal probability this band can be assigned to either a stretching vibration of the NN bond (*cf.* Refs. 2—4) or a symmetric stretching vibration of the methyl-substituted amino group (*cf.* Refs. 5, 6). An

Table 4. Spectral characteristics calculated in the RHF/6-31G* and MP2/6-31G** approximations and assignment of experimental frequencies for unsubstituted *N,N*-dimethylnitramine[a]

Type of symmetry	No. of vibration	Quantum-chemical calculations						Frequency after scaling, ν/cm^{-1}		Experiment, ν/cm^{-1}	Distribution of the potential energy of vibrations (%)[b]
		ν/cm^{-1}		Intensity			Degree of depolarization,				
				IR, I/km mol^{-1}		Raman, I/Å^4·(amu)$^{-1}$,					
		RHF	MP2	RHF	MP2	RHF	RHF	RHF	MP2		
A′	1	3369	3290	9.6	3.3	65.2	0.67	3045.3	3054.7	3034[c]	56 CH_3 as.str synph 42 CH_3 as.str′ synph
	2	3324	3238	48.2	27.7	91.1	0.38	3004.6	3006.3	2993[c]	43 CH_3 as.str′synph 41 CH_3 as.str synph 16 CH_3 s.str synph
	3	3232	3126	42.4	38.8	180.4	0.05	2921.5	2901.8	2931[d]	82 CH_3 s.str synph 15 CH_3 as.str′ synph
	4	1669	1576	129.0	45.6	9.9	0.51	1495.8	1500.0	1500[c]	80 CH_3 as.def synph 16 CH_3 rock$_{\parallel}$ synph
	5	1636	1554	24.0	10.2	20.6	0.73	1476.0	1477.7	1475[d]	60 CH_3 as.def′ synph 26 CH_3 s.def synph 10 CH_3 rock$_{\perp}$ synph
	6	1657	1526	20.5	33.7	11.8	0.56	1454.3	1451.7	1453[d]	66 CH_3 s.def synph 29 CH_3 as.def′ synph
	7	1550	1391	337.1	270.7	10.5	0.34	1315.6	1311.5	1312[d]	26 NN str 17 CH_3 rock$_{\perp}$ synph 13 NO_2 s.str 7 ONO bend 7 NC_2 s.str 7 CNC bend 7 CH_3 s.def synph 7 CH_3 as.def synph
	8	1421	1302	12.9	2.5	3.3	0.48	1256.1	1231.1	1242[c]	37 CH_3 rock$_{\parallel}$ synph 33 NO_2 s.str 10 ONO bend 7 CH_3 as.def synph
	9	1271	1189	38.8	67.1	5.3	0.75	1142.4	1154.2	1150[c]	59 CH_3 rock$_{\perp}$ synph 21 CH_3 rock$_{\parallel}$ synph 6 CH_3 as.def′ synph
	10	1152	1031	74.6	60.6	2.4	0.24	1002.8	984.1	985[d]	38 NC_2 s.str 20 NO_2 s.str 19 NN str 15 CH_3 rock$_{\parallel}$ synph 7 CH_3 rock$_{\perp}$ synph
	11	948	866	9.9	20.4	12.1	0.23	829.4	830.0	835[c]	33 NC_2 s.str 33 ONO bend 26 NO_2 s.str 8 NN str
	12	911	779	35.6	17.7	0.3	0.74	769.6	768.9	770[d]	95 NO_2 wag 5 NC_2 wag
	13	695	636	6.3	1.5	3.2	0.11	595.0	627.9	612[d]	43 ONO bend 31 NN str 21 NC_2 s.str 5 CNC bend
	14	462	433	4.9	3.5	0.3	0.20	400.6	429.2	430[d,e]	36 CNC bend 34 NC_2 wag 14 CH_3 s.tors 8 NN str
	15	239	244	7.7	14.3	1.4	0.65	211.7	241.7	240[e]	61 NC_2 wag 32 CNC bend 6 CH_3 s.tors
	16	144	169	5.1	3.7	0.1	0.72	125.8	168.8	173[c,e]	80 CH_3 s.tors 18 CNC bend

(*to be continued*)

Table 4 (*continued*)

Type of symmetry	No. of vibration	Quantum-chemical calculations: ν/cm^{-1}		Intensity: IR, I/km mol^{-1}		Intensity: Raman, I/Å$^4 \cdot$(amu)$^{-1}$,	Degree of depolarization,	Frequency after scaling, ν/cm^{-1}		Experiment, ν/cm^{-1}	Distribution of the potential energy of vibrations (%)[b]
		RHF	MP2	RHF	MP2	RHF	RHF	RHF	MP2		
A″	17	365	3288	5.3	1.3	47.9	0.75	3041.7	3052.2	3034[c]	51 CH_3 as.str antiph 46 CH_3 as.str′ antiph
	18	3313	3234	0.0	0.0	20.7	0.75	2995.0	3002.5	2993[c]	47 CH_3 as.str antiph 39 CH_3 as.str′ antiph 14 CH_3 s.str antiph
	19	3226	3122	26.0	17.3	11.5	0.75	2915.5	2898.2	2931[d]	83 CH_3 s.str antiph 15 CH_3 as.str′ antiph
	20	1832	1789	543.1	172.5	0.3	0.75	1562.3	1573.3	1566[d]	84 NO_2 as.str 8 NO_2 rock 5 NC_2 twist
	21	1645	1556	1.5	0.1	11.2	0.75	1477.1	1477.9	1475[d]	85 CH_3 as.def antiph 10 CH_3 rock$_{\parallel}$ antiph
	22	1630	1539	8.4	12.5	7.8	0.75	1465.2	1460.8	1465[d]	88 CH_3 as.def′ antiph 8 CH_3 rock$_{\perp}$ antiph
	23	1591	1482	1.7	1.7	7.0	0.75	1411.6	1413.4	1412[d]	94 CH_3 s.def antiph
	24	1445	1349	0.6	9.2	0.2	0.75	1301.6	1297.5	1298[d]	59 NC_2 as.str 14 CH_3 rock$_{\parallel}$ antiph 8 NC_2 twist 6 NO_2 as.str 6 NO_2 rock
	25	1240	1157	3.3	3.4	5.3	0.75	1116.3	1129.1	1132[d]	76 CH_3 rock$_{\perp}$ antiph 15 CH_3 rock$_{\parallel}$ antiph 7 CH_3 as.def′ antiph
	26	1156	1083	21.5	11.0	1.7	0.75	1044.9	1052.9	1046[d]	56 CH_3 rock$_{\parallel}$ antiph 25 NC_2 as.str 13 CH_3 rock$_{\perp}$ antiph 5 CH_3 as.def antiph
	27	676	619	19.2	5.5	3.2	0.75	606.5	599.6	600[d]	52 NO_2 rock 22 NC_2 twist 16 NC_2 as.str 8 NO_2 as.str
	28	390	371	2.6	1.7	0.3	0.75	351.1	364.2	355[c,e]	58 NC_2 twist 30 NO_2 rock 10 CH_3 as.tors
	29	170	171	0.6	0.5	0.1	0.75	151.9	170.7	173[c,e]	88 CH_3 as.tors 7 NC_2 twist
	30	134	117	0.1	0.0	0.7	0.75	119.5	116.7	120[e]	98 NO_2 tors

[a] See footnote [a] to Table 1; synph and antiph are synphase and antiphase vibration, respectively.

[b] Obtained after scaling the force field calculated in the MP2/6-31G** approximation.

[c] From IR spectra and Raman spectra of powder, solid film, melt, and solutions in CCl_4 or CS_2.[2–6]

[d] From gas phase spectra.[3,4]

[e] Our data on far IR spectra and Raman spectra of powder and frequencies in the Raman spectrum of oriented monocrystal[7] and in neutron inelastic scattering (NIS) experiment.[8]

analogous dilemma arises in connection with the interpretation of the ν_{10} band at 985 cm^{-1} with spectral characteristics similar to those of the ν_{11} band.

Thus, the conventional classification of frequencies, when they are correlated with vibrations of certain bonds or atomic groups composed of three or four neighboring atoms, is rather conditional and inefficient, especially in the case of molecular fragments composed of atoms with approximately equal masses and close force constants, like those in nitramines. At the same time, two of the six bands due to the stretching vibrations of the C_2NNO_2 frame, namely, the ν_{11} and ν_{20} bands, which are readily identified by their spectral characteristics, can be assigned to the most symmetric and most antisymmetric modes, respectively (see Fig. 2). Formal classification of other normal vibrations is difficult. It should be noted that our consideration is of conditional character since the contributions of deformation vibrations have not been taken into account; otherwise, the classification would be much more complex (see Table 4).

Table 5. Experimental and theoretical isotope shifts of fundamental frequencies for D_6-, ^{15}N-nitro, and ^{15}N-amino substituted *N*,*N*-dimethylnitramines[a]

Symmetry type	No. of vibration	Assignment	$(CH_3)_2NNO_2$, ν_{exp}/cm^{-1} [b]	Isotope shift, $\Delta\nu$/cm^{-1}								
				$(CD_3)_2NNO_2$			$(CH_3)_2N^{15}NO_2$			$(CH_3)_2{}^{15}NNO_2$		
				Experiment[c]	Scaling		Experiment[c]	Scaling		Experiment[c]	Scaling	
					RHF	MP2		RHF	MP2		RHF	MP2
A′	1	$\nu_{as}(CH_3)$ synph	3034	−770	−783.7	−786.0		0.0	0.0	0	0.0	0.0
	2	$\nu'_{as}(CH_3)$ synph	2993	−755	−780.6	−780.7		0.0	0.0	0	0.0	0.0
	3	$\nu_s(CH_3)$ synph	2931		−817.8	−813.7		0.0	0.0	0	0.0	0.0
	4	$\delta_{as}(CH_3)$ synph	1500	−425	−424.2	−430.9		−0.1	−0.3		−0.9	−1.6
	5	$\delta'_{as}(CH_3)$ synph	1475		−414.6	−420.2		−0.3	−0.8	−2	−0.5	−1.0
	6	$\delta_s(CH_3)$ synph	1453	−360	−355.9	−362.0	−2	−1.9	−1.5		−0.2	−0.4
	7	$\nu_s(NO_2)$	1312	14	13.4	−1.9	−16.5	−21.2	−10.6		−1.7	−11.0
	8	$r_{\parallel}(CH_3)$ synph	1242	−65	−80.2	−63.0	−10	−0.4	−12.2	−8	−13.3	−3.5
	9	$r_{\perp}(CH_3)$ synph	1150		−233.6	−226.4		−0.6	−2.8		−3.4	−3.8
	10	$\nu(NN)$	985	−125	−131.0	−118.7		−2.0	−0.1	−7	−8.7	−8.7
	11	$\nu_s(NC_2)$	835	−60	−51.8	−44.2	−5.5	−5.3	−3.7	−2	−0.8	−0.7
	12	$\omega(NO_2)$	770	−3	−6.5	−6.1	−18.5	−20.0	−19.9	−4	−1.4	−1.5
	13	$\delta(ONO)$	612	−35	−32.2	−34.8		0.0	−0.1	−2	−4.3	−4.6
	14	$\delta(CNC)$	430	−60	−55.3	−63.9		−0.7	−0.8	−1	−0.3	−0.3
	15	$\omega(NC_2)$	240	−30[f]	−27.7	−24.8		−0.1	−0.1	−4	−3.0	−4.3
	16	$\chi_s(CH_3)$	173	−55[f]	−29.7	−44.4		−0.1	0.0		−0.8	−0.2
A″	17	$\nu_{as}(CH_3)$ antiph	3034	−770	−785.0	−788.0		0.0	0.0	0	0.0	0.0
	18	$\nu'_{as}(CH_3)$ antiph	2993	−755	−775.9	−778.5		0.0	0.0	0	0.0	0.0
	19	$\nu_s(CH_3)$ antiph	2931		−818.7	−814.2		0.0	0.0	0	0.0	0.0
	20	$\nu_{as}(NO_2)$	1566		−6.7	−3.4	−30	−33.1	−35.5	−1	−3.5	−1.3
	21	$\delta_{as}(CH_3)$ antiph	1475		−414.5	−419.8	−5	−1.3	−0.7		−0.1	−0.4
	22	$\delta'_{as}(CH_3)$ antiph	1465		−410.2	−411.8	−2	0.0	0.0		−0.2	−0.2
	23	$\delta_s(CH_3)$ antiph	1412	−335	−341.3	−339.4	−3	−0.6	−0.4	−0.5	−0.5	−0.2
	24	$\nu_{as}(NC_2)$	1298	−20	−26.0	−22.1	−3	−1.7	−0.3	−21	−23.5	−25.1
	25	$r_{\perp}(CH_3)$ antiph	1132	−280	−266.7	−267.9		0.0	0.0		−0.1	−0.2
	26	$r_{\parallel}(CH_3)$ antiph	1046	−210	−227.9	−228.4		0.0	0.0	−4	−3.5	−3.1
	27	$r(NO_2)$	600	−30	−25.6	−27.7	−3.5	−2.0	−2.2	−1	−0.8	−1.0
	28	$t(NC_2)$	355	−25	−31.5	−35.4		−0.1	−0.1		−0.6	−0.6
	29	$\chi_{as}(CH_3)$	173	−55[f]	−44.2	−45.1		0.0	0.0		0.0	0.0
	30	$\chi(NO_2)$	120	−20[f]	−4.3	−7.7		0.0	0.0		0.0	0.0

[a] ν, δ, ω, r, t and χ are stretching, bending, wagging, rocking, twisting, and torsional vibrations, respectively; see footnotes to Tables 1 and 4.

[b] See Table 4.

[c] From IR and Raman spectra of powder and solutions in CCl_4 or CS_2 [5,6] (except for the shifts in the low-frequency region).

[d] Averaged shifts from IR spectra of powder and solutions in CCl_4.[4]

[e] From IR and Raman spectra of powder and Raman spectra of solutions in CCl_4 or CS_2.[6]

[f] From Raman spectra of oriented monocrystal[7] and neutron inelastic scattering (NIS) experiment.[8]

In the experimental spectra of *N*,*N*-dimethylnitramine the difference between the frequencies of bending δ(ONO) and rocking $r(NO_2)$ vibrations of the nitro group (ν_{13} and ν_{27}, respectively, see Table 4) is only 5—10 cm^{-1}. The more high-frequency band at 622 cm^{-1}, which is strong and polarized in the Raman spectrum of the melt,[4] corresponds to the first vibration, while the band at 614 cm^{-1}, which is weak and depolarized, corresponds to $r(NO_2)$. The theoretical frequencies changed their positions upon scaling the RHF force field and the difference between them appeared to be ~10 cm^{-1}. However, the use of the MP2 force field eliminates this illusory contradiction.

In the spectral region below 450 cm^{-1} (see Tables 4 and 5) scaling of the MP2 force field made it possible to identify the bands of deformation vibrations of methyl-substituted amino group (ν_{14}, ν_{15}, and ν_{28}) and torsional vibrations of methyl groups and the nitro group (ν_{16}, ν_{29}, and ν_{30}) in the far IR spectra, Raman spectra (our data and see also Ref. 7), and neutron inelastic scattering (NIS) spectra of light and perdeuterated *N*,*N*-dimethylnitramines.[8] For both modifications, theoretical splitting of the frequencies of symmetric ν_{16} and antisymmetric ν_{29} torsional vibrations of the methyl groups decreased from 26 cm^{-1} for the RHF force field to 1—2 cm^{-1} for the MP2 force field, which allowed us to assign the same band observed at 173 cm^{-1} for unsubstituted substance and at 120—125 cm^{-1} for perdeuterated substance to both these fundamental vibrations.

The bands at 120 cm^{-1} in the spectra of light modification and at 100 cm^{-1} in the spectra of the D_6-isotopomer[7,8] were assigned to the ν_{30} torsional vibration of the nitro group. This is in good agreement with the estimate of the frequency of the fundamental torsional transition (115—125 cm^{-1}) we obtained earlier for $(CH_3)_2NNO_2$ on the basis of the solution of the direct one-dimensional problem using quantum-chemical calculations of the potential function of internal rotation.[14] As can be seen in Table 4, the ν_{30} torsional mode is virtually totally pure and, hence, interacts scarcely with the remaining $3N - 7$ internal vibrations. Nevertheless, these interactions, ignored when solving the problem in the one-dimensional approximation, were indirectly taken into account by considering the relaxation of geometric parameters in quantum-chemical calculations of the potential function.

Unlike the ν_{30} torsional vibrations of the nitro group, the $\omega(NC_2)$ wagging-inversion vibration of the methyl-substituted amino group is strongly mixed with the

Table 6. Comparison of the force constants of *N,N*-dimethylnitramine obtained from scaling quantum-chemical force fields and conventional solution of the inverse spectral problem

Internal coordinate	Scaled force constant of the spectral problem (this work)		Force constant from conventional solution of the inverse spectral problem		
	RHF	MP2	See Ref. 5	See Ref. 6	See Ref. 9
			Diagonal constants[a]		
NO str	9.10	8.36	9.42	9.67	9.38
NN str	5.10	5.65	6.70	6.32	6.38
NC str	4.91	5.03	5.01	5.01	5.22
ONO bend	2.08	2.40	(1.30)[b]	(1.24)[b]	(1.20)[b]
NO_2 wag	0.58	0.59	0.32	0.34	0.56
NO_2 rock	1.63	1.67	1.97	1.85	1.80
CNC bend	0.71	0.89	(1.35)[c]	(1.24)[c]	1.23
NNC bend	1.45	1.54	(0.21; 1.36)[d]	(0.18; 1.37)[d]	1.42
NO_2 tors	0.20	0.20	0.09	0.08	0.10
CH_3 tors	0.06	0.08	0.005	0.005	0.01
			Interaction constants[a]		
NO str/NO str	1.45	0.24	1.58	1.73	1.63
NO str/NN str	0.98	0.71	0.80	0.86	0.93
NO str/NC str	0.0	0.01	0.0[e]	0.0[e]	−0.25
	−0.06	0.0			−0.07
NO str/ONO bend	0.28	0.26	(0.45)[b,f]	(0.6)[b,f]	(0.38)[b]
NO str/NO_2 rock	±0.43	±0.48	1.1[f]	1.1[f]	±0.76
NN str/NC str	0.21	0.25	0.64	0.68	0.74
NN str/ONO bend	−0.66	−0.84	(−1.00)[b]	(−0.70)[b]	(−0.76)[b]
NN str/CNC bend	0.22	0.21	(−0.16)[c]	(−0.16)[c]	−0.35
NN str/NNC bend	0.82	0.87	0.0[e]	0.0[e]	0.07
NN str/CH_3 tors	±0.07	±0.11	0.0[e]	0.0[e]	0.0[e]
NC str/ONO bend	−0.01	−0.02	(0.16)[b]	(0.15)[b]	(0.20)[b]
NC str/CNC bend	0.21	0.32	(0.41)[c]	(0.45)[c]	0.57
NC str/NNC bend	0.37	0.46	(0.39)[d]	(0.38)[d]	0.49
	−0.06	−0.03			−0.25
NC str/CH_3 s.str	0.18	0.18	0.0[e]	0.0[e]	0.0[e]
NC str/CH_3 s.def	−0.47	−0.47	−0.66	−0.54	−0.23
CNC bend/ONO bend	0.06	0.06	(0.14)[b,c]	(0.17)[b,c]	0.0[e]
NNC bend/NNC bend	−0.03	−0.12	0.0[e]	0.0[e]	−0.06
NNC bend/ONO bend	−0.16	−0.21	0.0[e]	0.0[e]	(0.08)[b]
NNC bend/NO_2 rock	±0.18	±0.22	(0.43)[d]	(0.40)[d]	±0.24

[a] The force constants of stretching vibrations and their interactions are given in mdyn Å^{-1}, the force constants of deformation vibrations and their interactions are given in mdyn Å^{-1}, constants of interactions between stfetching and deformation vibrations are given in mdyn.

[b] Corresponds to the coordinate of complex scissoring NO_2 sciss vibration $[6^{-1/2}(2\alpha-\beta_1-\beta_2)]$[5,6,9] but not to the ONO bending vibration.

[c] Corresponds to the coordinate of complex scissoring NC_2 sciss vibration $[6^{-1/2}(2\varepsilon_1-\varepsilon_2-\varepsilon_3)]$.[5,6]

[d] Corresponds to coordinates of NC_2 wagging or NC_2 twist $[2^{-1/2}(\varepsilon_2-\varepsilon_3)]$ vibration.[5,6]

[e] Fixed value.

[f] Corresponds to the interaction between the symmetric NO_2 stretching vibration and the NO_2 sciss vibration or to the interaction between the antisymmetric NO_2 stretching vibration and the NO_2 rock vibration.

Table 7. The force constants of stretching vibrations of the simplest nitramines calculated in the RHF/6-31G* and MP2/6-31G** approximations and those obtained by scaling (underlined)

Molecule	Symmetry	Force constant/mdyn $Å^{-1}$										
		RHF/6-31G*						MP2/6-31G**				
		NO str	NO str/ NO str	NN str	NH str	NC str	NCl str	NO str	NO str/ NO str	NN str	NH str	NC str
Primary and secondary amines												
CH_3NHNO_2[a]	C_1	13.08	2.10	7.36	8.28	5.96						
		13.39										
		8.94	1.44	5.23	6.54	4.91						
		9.16										
H_2NNO_2[a]	C_s	13.57	2.18	7.16	8.27			11.66	0.31	5.46	7.50	
		9.21	1.48	4.90	6.53			8.58	0.23	5.72	6.54	
$HNClNO_2$[a]	C_1	13.38	2.20	6.13	8.09		4.97					
		14.47										
		9.10	1.49	4.07	6.35		3.93					
		9.84										
$HN(NO_2)_2$[a]	C_s	13.52	2.20	5.95	8.10			11.87	−0.004	3.40	7.06	
		14.97						11.96				
		8.77	1.43	3.12	6.20			9.22	−0.003	3.47	6.21	
		9.71						9.29				
Tertiary amines												
$(CH_3)_2NNO_2$[b]	C_s	12.90	2.05	7.45		5.87		11.11	0.32	5.84		5.46
		9.10	1.45	5.10		4.91		8.36	0.24	5.65		5.03
CH_3NClNO_2[a]	C_1	13.16	2.19	6.21		5.46	4.79					
		14.06										
		8.95	1.49	4.11		4.52	3.78					
		9.56										
$CH_3N(NO_2)_2$[a]	C_1	13.77	2.25	5.94		5.23						
		14.27										
		14.91	2.30	5.52								
		13.81										
		9.52	1.56	4.22		4.45						
		9.87										
		10.31	1.59	3.93								
		9.55										

[a] See Refs. 20 and 21.

[b] This work.

δ(CNC) bending vibration and symmetric torsional vibration of methyl groups (ν_{15}, ν_{14}, and ν_{16}, respectively, see Table 4). The experimental frequency 240 cm^{-1} assigned to $\omega(NC_2)$ is considerably higher than the estimate of the fundamental frequency of inversion transition ~90 cm^{-1} we obtained earlier on the basis of the solution of the one-dimensional problem.[14] As has been shown in the recent quantum-chemical study of the interaction between the inversion motion of the amino group and the CNC bending vibration in dimethylamine,[19] correct description of the inversion spectrum of this compound involves the use of a two-dimensional model. The inclusion of terms corresponding to the interaction in the Hamiltonian leads to increasing the fundamental frequency of inversion by 30 cm^{-1}. In the case of *N*,*N*-dimethylnitramine, the analogous effect can be one of the reasons for the appreciable difference between the estimates of the inversion frequency based on the solution of the one-dimensional problem and the frequency of the ν_{15} wagging vibration obtained from scaling of quantum-chemical force fields.

***Ab initio* force fields of the simplest nitramines and theoretical estimates of mean amplitudes and shrinkage corrections for internuclear distances.** The above results show the advantages of the use of quantum-chemical force fields and the scaling procedure for the interpretation of vibrational spectra as compared to the widely used conventional empirical approach to the solution of the inverse spectral problem, in which the *á priori* assignment of frequencies is a "restricting" condition. Comparison (Table 6) shows that the conventional force fields obtained by different authors differ from each other as well as from our data not only in the absolute value but often in the sign of constants. Since, as has been shown in this work and our other studies,[11,12,20,21] the use of quantum-chemical force fields scaled by a

Table 8. Experimental (r_a/Å) and theoretical (r_e/Å) internuclear distances, mean amplitudes (u/Å), and shrinkage corrections (($r_\alpha-r_a$)/Å) for the molecule of *N,N*-dimethylnitramine[a,b]

Distance	Experiment[c] (see Ref. 25)		Conventional calculations[6]	Quantum-chemical calculations of geometry and scaled force field (this work)					
				RHF/6-31G*			MP2/6-31G**		
	r_a	u	u	r_e	u	$r_\alpha-r_a$	r_e	u	$r_\alpha-r_a$
C(3)—H(4)				1.0795	0.0778	−0.0594	1.0850	0.0777	−0.0458
C(3)—H(5)	1.115(16)	0.099(17)	0.078	1.0850	0.0786	−0.0690	1.0917	0.0788	−0.0517
C(3)—H(6)				1.0768	0.0775	−0.0637	1.0823	0.0774	−0.0472
N(1)—O(11)	1.225(3)	0.037(3)	0.040	1.1970	0.0403	−0.0063	1.2396	0.0407	−0.0060
N(1)—N(2)	1.383(8)	0.047(20)	0.046	1.3439	0.0521	−0.0026	1.3884	0.0498	−0.0013
N(2)—C(3)	1.463(8)	0.040(6)	0.050	1.4549	0.0493	−0.0105	1.4561	0.0493	−0.0066
N(2)...H(4)				2.0499	0.1050	−0.0309	2.0531	0.1046	−0.0242
N(2)...H(5)	2.014(80)	0.296(100)	0.108	2.1152	0.1030	−0.0503	2.1231	0.1027	−0.0357
N(2)...H(6)				2.0856	0.1039	−0.0433	2.0834	0.1040	−0.0286
N(2)...O(11)	2.199(20)	0.053(11)	0.053	2.1726	0.0570	−0.0057	2.2408	0.0568	−0.0039
O(11)...O(12)	2.224(40)	0.050[d]	0.048	2.1251	0.0503	−0.0106	2.2105	0.0515	−0.0104
N(1)...C(3)	2.412(17)	0.095(14)	0.063	2.3719	0.0645	−0.0018	2.3825	0.0641	−0.0013
C(3)...O(12)	2.551(27)	0.157(35)	0.087	2.5625	0.0961	−0.0039	2.5865	0.0980	−0.0037
C(3)...C(7)	2.625(22)	0.065(18)	0.062	2.5228	0.0923	−0.0031	2.4978	0.0807	−0.0041
C(3)...O(11)	3.513(8)	0.064(7)	0.063	3.4537	0.0671	0.0003	3.4945	0.0683	0.0005

[a] The physical meaning of geometric parameters r_a and r_α determined by the gas-phase electron diffraction method and their relationship with the equilibrium values of r_e were considered previously.[26]

[b] In both cases (conventional and using quantum-chemical force fields) the u and $r_\alpha-r_a$ values were calculated for the temperature at which the electron diffraction experiment was performed (343 K), taking no account of nonlinear terms of the relation between nuclear displacements in the Cartesian coordinates and internal coordinates.[24,27]

[c] Gas-phase electron diffraction data (planar C_{2v} model), T = 343 K.

[d] Fixed parameter.

unified set of transferable factors leads to the adequate reproducibility of experimental vibrational frequencies of a number of the simplest nitramines, we are sure that they are preferred.

Changes in force constants in the series of related molecules must reflect changes in their electronic structure to a considerably greater extent than frequency shifts in vibrational spectra, which are often dependent on the degree of mixing of normal vibrations. The force constants of stretching vibrations in the simplest nitramines obtained from our quantum-chemical calculations are listed in Table 7. Tendencies for the force constant of the NO stretching vibration to successively increase and for the force constant of the NN stretching vibration to synchronously decrease are observed as the effective electronegativity of substituents at the amine nitrogen atom increases. This tendency cannot be changed by the scaling procedure because of the good transferability of scaling factors.[20,21] It can be considered as a manifestation of a general regularity of weakening of the p—π-conjugation between amino and nitro groups with increasing electronegativity of substituents at the amine nitrogen atom. Tendencies reflecting this regularity are also manifested in changes in calculated geometric parameters and barriers to internal rotation and inversion in the simplest nitramines.[12,14,22,23]

One useful application of data on the force field is in the calculation of mean amplitudes (u) and shrinkage corrections ($r_\alpha-r_a$) for internuclear distances in the molecule used in the analysis of electron diffraction data.[24] The values of these parameters obtained for *N,N*-dimethylnitramine from electron diffraction experiments,[25] using the conventional solution of the inverse spectral problem,[6] and in this work using scaled quantum-chemical force fields, are compared in Table 8. There is no agreement between these results, which is caused by experimental errors in the electron diffraction study and distinctions in the force fields used and in the interpretation of vibrational spectra (first of all, bands in the low-frequency region). The mean amplitudes calculated[6] for the N—N bond and the distances between carbon atoms of methyl groups and between each of these atoms and the nearest oxygen atom of the nitro group (the C(3)...C(7) and C(3)...O(12) distances, respectively); which are dependent on inversion motion in the amino fragment, differ appreciably from our data. Calculations using quantum-chemical RHF and MP2 force fields scaled using the same set of experimental frequencies result on the whole in close values of mean amplitudes. However, in this case the maximum deviation obtained for the u(C(3)...C(7)) mean amplitude exceeds 0.01 Å as well. This difference as well as inadequate reproducibility of experimental frequencies of deformation vibrations of the amino group upon scaling of the RHF force field (ν_{14} and ν_{15}, see Table 4) can be associated mainly with the somewhat worse quality of the Hartree—Fock force field as compared to the MP2 force field. Most of the $r_\alpha-r_a$ corrections calculated using the MP2 force field have considerably smaller absolute values than those calculated using the RHF force field.

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