Far IR and Raman vibrational spectra of nitramines

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Vibrational spectra of several nitramines in the long-wave region (50—450 cm^{-1}) were studied. The frequencies of intra- and intermolecular vibrations were separated and a tentative assignment of the frequencies of self-associative complexes was performed.

Key words: nitramines, vibrational spectra, self-associative complexes.

Previously,[1–3] we obtained IR and Raman spectra and analyzed intramolecular vibrations of several of the simplest mono- and dinitramines (NA). The use of a new approach based on scaling of the quantum-chemical force fields in combination with standard procedures of vibrational spectroscopy, *viz.*, comparison of IR and Raman spectra, isotope substitution, and consideration of the intensities and depolarization ratios of the fre-

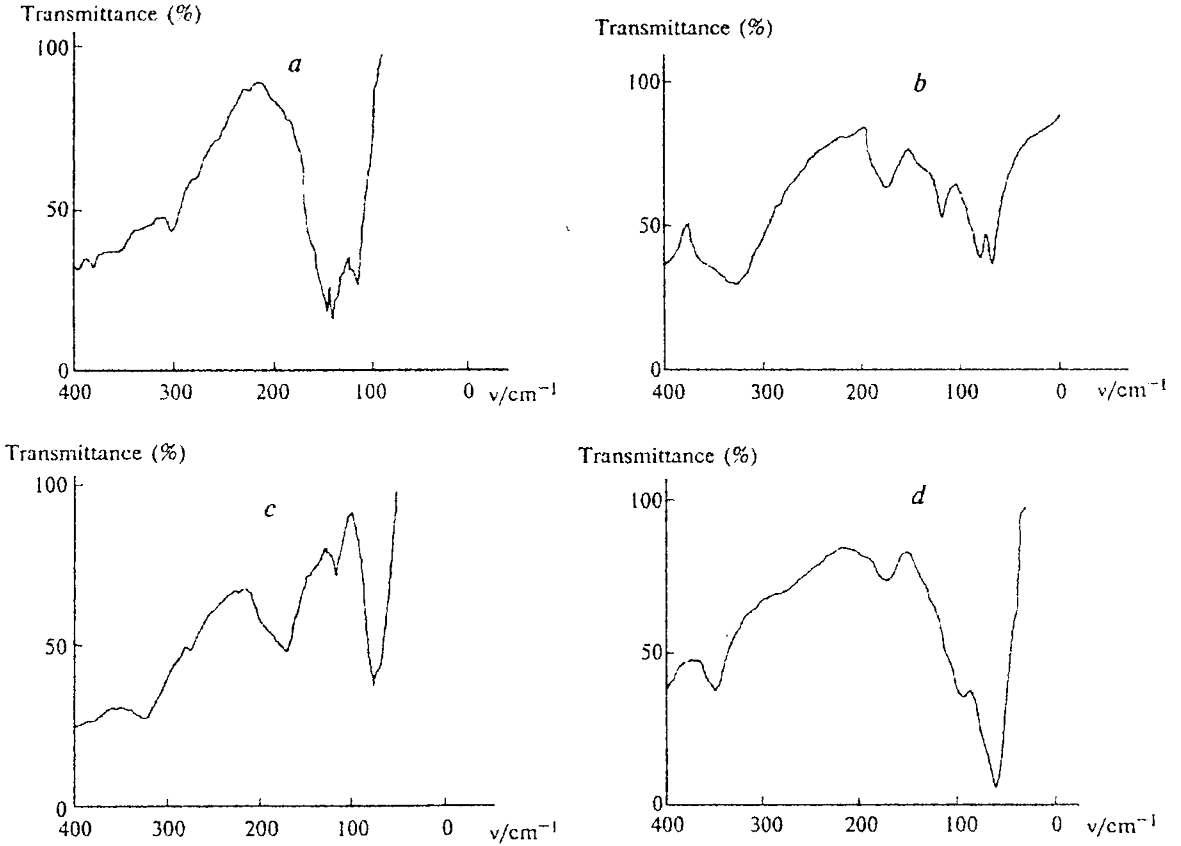

Fig. 1. Far IR spectra of H_2NNO_2 (*a*), CH_3NHNO_2 (*b*), CD_3NDNO_2 (*c*), and $(CH_3)_2NNO_2$ (*d*) in the crystalline state (adamantane pellets).

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quencies, made it possible to assign the intramolecular vibrations.

Several frequencies in the spectra of NA change appreciably on going from the gas phase and diluted solutions to condensed phases, which is interpreted as a consequence of intermolecular interactions.[4] To identify the frequencies of self-associative NA complexes, directly characterizing the intermolecular interactions, in this work we studied the far IR spectra of condensed phases of several simplest NA (including some of those for which detailed investigations of intramolecular vibrations were performed previously).

Experimental

The compounds under study were synthesized following the previously described procedures.[5—7]

The far IR spectra were recorded on a Bruker IFS-113v vacuum Fourier spectrometer in the frequency range 50—450 cm^{-1} with a resolution of less than 1 cm^{-1} and the Raman spectra were recorded on a Ramanor HG-2S spectrometer equipped with an Ar laser as excitation source.

To obtain far IR spectra of the substances, crystalline specimens were molded into pellets with adamantane ("chemically pure" grade) of thickness 3—4 mm. Adamantane is a more convenient matrix as compared to widely used Nujol and low-density polyethylene,[8] since no absorption bands of pure adamantane are observed in the spectral region under consideration. However, because of its volatility, the pellets with the substances were first placed in polyethylene and then in Teflon bags before recording the spectra (these materials have intrinsic absorption bands at 72 and 202 cm^{-1}, respectively). The analysis of these two types of far IR spectra made it possible to reliably determine the absorption bands corresponding to the vibrations of NA molecules.

The far IR spectra of solutions were recorded in thermostatted cuvettes of variable thickness (1 mm as usual) with silicon windows. Benzene, toluene, and chloroform were used as solvents, since non-polar solvents traditionally used for recording far IR spectra appeared to be unsuitable in the case

Table 1. Vibrational frequencies (ν/cm^{-1}) in the 430—25 cm^{-1} region of condensed phases of nitramines obtained experimentally and from scaling of the quantum-chemical force fields

Molecule	Experiment (this work)			Calculations[1—3]		Assignment
	Phase state	IR spectrum	Raman spectrum	RHF/6-31G*	MP2/6-31G**	
H_2NNO_2	Cryst.	383 v.w		420.2	398.6	τ(NN)
		303 w				
		170 m				$\nu_{complex}$ (?)
		145 m.br, 115 m	124 m, 89 s			$\nu_{complex}$
CH_3NHNO_2	Cryst.	340 m.br	340 w	304.0		δ(NNC)
			200 w	189.8		τ(CN)
		177 m.br				$\nu_{complex}$ (?)
			164 w	142.0		τ(NN)
		80 s	108 m, 80 s			$\nu_{complex}$
		67 s	65 w			σ
CD_3NDNO_2	Cryst.	329 w, 202 m		275.3		δ(NNC)
		177 w				$\nu_{complex}$ (?)
				154.9		τ(NN)
		122 s		117.2		τ(CN)
		81 s				$\nu_{complex}$
$(CH_3)_2NNO_2$	Cryst.	353 m		351.1	364.2	t(NC_2)
			230 w	211.7	241.7	ω(NC_2)
		185 w				$\nu_{complex}$ (?)
			163 v.w	151.9	170.7	τ_{as}(CN)
				125.8	168.8	τ_s(CN)
				119.5	116.7	τ(NN)
		98 m				$\nu_{complex}$
		61 s	67 m, 63 m			σ
$CH_3N(NO_2)_2$	Liquid	371		361.0		t(NC)
		264	264 s	267.5		δ(NNN)
		244	245 v.w	232.9		ω(NC)
		211		200.8		τ(CN)
		112, 91	153 w, 124 m, 108 m, 99 m			$\nu_{complex}$ $\nu_{complex}$
		78	77 s	72.9		τ_{as}(NN)
				29.2		τ_s(NN)

Note: δ, ω, t, and τ are internal bending, wagging, twisting, and torsional vibrations, respectively; $\nu_{complex}$ is the vibration of self-associative complex; s, as are symmetric and antisymmetric vibrations, respectively; s, m, w are strong, medium, and weak intensities, respectively; and σ designates crystal lattice vibrations.

Table 2. Experimental frequencies (v/cm^{-1}) in the far IR and Raman spectra of condensed phases of nitramines

Molecule	Liquid or solution in $CHCl_3$ [a]		Crystalline phase (adamantane pellets)		Tentative assignment[b]
	IR	Raman	IR	Raman	
$(C_2H_5)_2NNO_2$	348 s	335 w			
	300 w				
	275 w				
		125 m			$\nu_{complex}$
	80 s				$\nu_{complex}$
$(NCC_2H_4)_2NNO_2$			379 m		
	337 m		343 m		
	313 m				
	295 w		298 m		
	187 s		200 s		$\nu_{complex}$
	187 s		182 s		$\nu_{complex}$
			125 s		$\nu_{complex}$
	90 s				$\nu_{complex}$
			70 s		σ
			60 s		
$CH_2(NHNO_2)_2$			377 m.w		
			166 m		
			132 s.br		$\nu_{complex}$
			107 s.br		$\nu_{complex}$
			83 s		$\nu_{complex}$
			55 m.br		σ
$CH_2(NNO_2CH_3)_2$			360 s	359 s	
			313 w		
			259 m	263 m	$\nu_{complex}$
			100 s	90 sh	
			60 s	69 s	σ
				30 m	
				19 m	
$(CH_2NHNO_2)_2$			363 m		
			352 m	335 v.w	
			323 s	308 w	
			250 w		
			147 m	164 w	$\nu_{complex}$
			120 sh	130 m	$\nu_{complex}$
			100 s	107 m	$\nu_{complex}$
				87 v.w	$\nu_{complex}$
			68 m	42 m	σ
$(CH_2NNO_2CH_3)_2$			350 m		
			325 m	335 w	
			280 w	286 m	
			145 w	162 w	
			105 s	93 s	$\nu_{complex}$
				65 sh	
			58 m	58 s	σ
				32 m	

[a] Both IR and Raman spectra were obtained for liquid $(C_2H_5)_2NNO_2$, whereas only IR spectrum of solution in $CHCl_3$ was obtained for $(NCC_2H_4)_2NNO_2$.

[b] See note to Table 1.

of NA. The final experimental data were the differences between the spectra of solutions and those of pure solvents. The results obtained are listed in Tables 1, 2 and shown in Figs. 1 and 2.

Results and Discussion

As follows from the analysis of vibrational spectra of the simplest NA based on scaling of the quantum-chemical force fields,[1-3] the frequencies of bending vibrations of the amino group lie in the high-frequency range (higher than 200 cm^{-1}) of the spectral region considered (see Table 1).

The frequencies of crystal lattices are localized mainly below 75 cm^{-1}. It is in this spectral region that a decrease in the number of bands is usually observed on going from crystal to solution (see Fig. 2).

Changes in the frequencies of torsional vibrations in the series of simplest nitramines are shown in Fig. 3.

It can be assumed that only frequencies of intramolecular torsional vibrations and those of self-associative complexes lie in the spectral region 75—200 cm^{-1}. The latter can be tentatively assigned by comparing the experimental far IR spectra. There are several bands in the spectra of nitramines whose positions and shape are likely dependent on the phase state. The IR spectra containing one or two strong very broad absorption bands in the region ~100 cm^{-1}, to which strong lines in the Raman spectra usually correspond (see Tables 1 and 2), are characteristic of the crystalline phase of NA. For instance, two broad bands with maxima at 115 and 140 cm^{-1} are observed in the far IR spectrum of crystalline nitramide H_2NNO_2. An intense band with the maximum at ~200 cm^{-1} and halfwidth up to 70 cm^{-1} appears in the spectrum on dissolution of H_2NNO_2 in $CHCl_3$. This band becomes more intense and even broader and its maximum is shifted to 230 cm^{-1} as the nitramide concentration in solution increases. Similar effects accompanying phase transitions were also observed in spectra of other NA. However, the broad band in the IR spectrum of nitramide $(N{\equiv}CCH_2CH_2)NNO_2$ is shifted from 125 cm^{-1} to 90 cm^{-1} on going from the crystalline form to the solution in chloroform (Table 2, Fig. 2), *i.e.*, in contrast to the spectra of nitramide H_2NNO_2, in this case the frequencies are shifted towards the lower frequency region.

Taking into account the results of previous quantum-chemical calculations, the above experimental data suggest that the broad bands in the far IR spectra of NA, whose positions are appreciably shifted on dissolution and dependent on concentration, correspond to self-

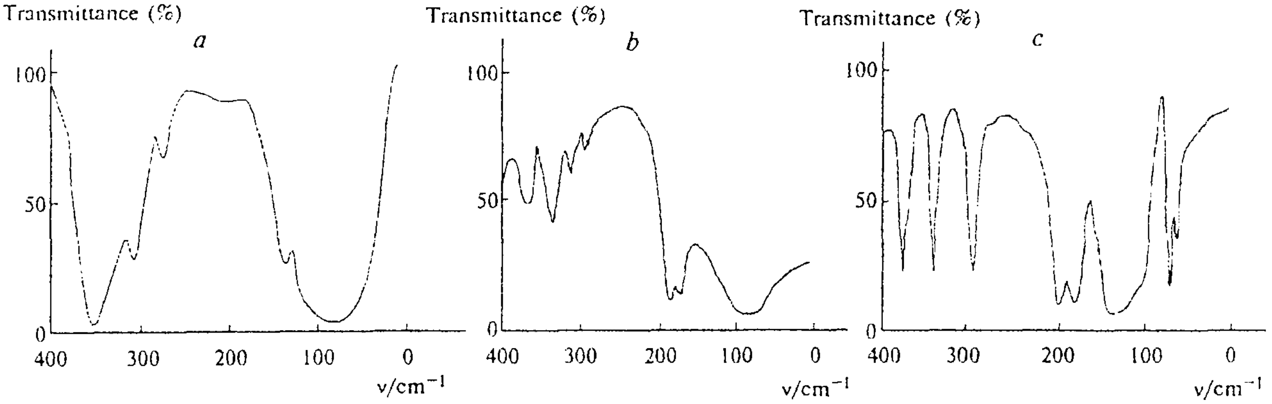

Fig. 2. Far IR spectra of $(C_2H_5)_2NNO_2$ in the liquid phase (*a*) and $(NCC_2H_4)_2NNO_2$: a solution in $CHCl_3$ (*b*), and in the crystalline state (adamantane pellets) (*c*).

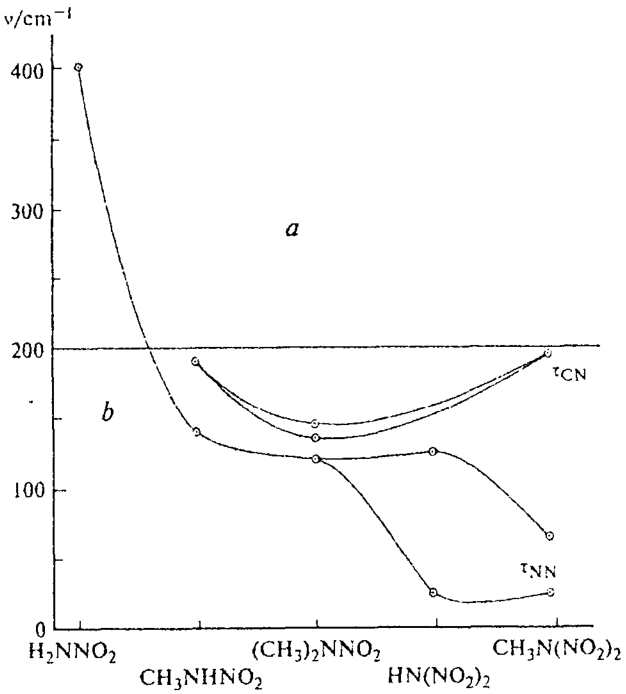

Fig. 3. Diagrams of changes in the frequencies of torsional vibrations of nitro groups (τ_{NN}) and methyl groups (τ_{CN}) obtained for the simplest nitramines after scaling of the quantum-chemical force fields; *a*, region of bending vibrations, and *b*, region of torsional vibrations.

associative complexes rather than to the intramolecular vibrations. Analogous bands are also characteristic of the spectra of *C*-nitro compounds in the liquid phase, though they lie in the lower frequency region (*e.g.*, at 80 cm^{-1} and at 50 cm^{-1} in the spectra of nitromethane CH_3NO_2 [6] and nitrobenzene $C_6H_5NO_2$,[9,10] respectively).

Our assignment of the frequencies of vibrations of self-associative complexes (see Tables 1 and 2) should be considered as tentative. In this case the possibility of the formation of associates of different structure and composition must be taken into account, which requires a detailed complex investigation using other physico-chemical methods.

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