Raman spectra and molecular dynamics of R_2NPX_2 (R = Me and Et; X = F, Cl, and Br)

Sh. Sh. Nabiev,* I. I. Ostroukhova, N. V. Revina, and L. P. Sukhanov

State Scientific Center of Russian Federation "Kurchatov Institute",
1 pl. I. V. Kurchatova, 123182 Moscow, Russian Federation.
Fax: 007 (095) 194 1994

The Raman spectra of compounds R_2NPX_2 (R = Me and Et; X = F, Cl, and Br) were studied. The time correlation functions of vibrational and rotational relaxations as well as the characteristic times of these processes were calculated. Conclusions concerning the mechanisms of formation of the contours of the Raman lines with frequencies in the 670—705 cm^{-1} range corresponding to the totally symmetric vibrations of the P—N bond in the R_2NPX_2 molecules were drawn.

Key words: Raman spectrum, frequency of the bond vibration; vibrational and rotational relaxations, correlation function.

Interest in the compounds of the R_2NPX_2 type (R = Me and Et; X = F, Cl, and Br) is due to the presence of two electron-donor atoms, N and P, in these molecules. Monosubstituted halogen phosphines behave as Lewis bases exhibiting a basicity intermediate between those inherent in ethers and free amines. Coordination compounds with such ligands can have the properties of Lewis acids. It was shown previously that a planar configuration of the bonds at the N and P atoms is realized in the R_2NPX_2 molecules, while the P—N bond is shorter than the sum of the covalent radii.[1,2] This fact distinguishes them from other nitrogen compounds with three-coordinated phosphorus, and is evidence for the pπ—dπ interaction between the N and P atoms, which results in acquiring the double bond character by the P—N bond.[1]

It is known that, along with specific structural features of the molecules, the vibrational and rotational relaxation related to the stochastic properties of the medium[3] strongly affect the mechanisms of the physico-chemical processes. Frequencies, shapes, and shifts of the lines in the Raman spectra are among the main sources of information on the relaxation in solutions of organic solvents,[4] ionic systems,[5] and "pure" liquids.[6] Information on the change in the environment of the molecule under study can be obtained using the time correlation functions (TCF) of probabilistic character.[7,8] Such functions can serve as a method of describing the situation when the dynamical quantities are time-correlated. The time correlation functions are usually defined by means of the Fourier transform of the normalized intensity profiles in the spectra of isotropic and anisotropic Raman scattering. It should be noted that although the authors of the overwhelming majority of works dedicated to studying the vibrational and rotational TCF used the contours of lines of Raman scattering corresponding to the vibrations of relatively small molecules,[9—11] there are several publications[12—14] that showed the possibility of obtaining information on the dynamics of large molecules in the condensed phase.

The aim of this work was to study the Raman spectra of compounds Me_2NPX_2 and Et_2NPX_2 (X = F, Cl, and Br) in the range of 100—3000 cm^{-1} and perform the refinement of the frequencies of the Raman lines corresponding to the vibrations of the C_2NPX_2 fragment, their interpretation, and determination of dynamic parameters of these molecules.

Experimental

The Raman spectra of the R_2NPX_2 samples were recorded on an automated Dilor RTI-30 Raman-spectrometer equipped with a triple monochromator. The spectral slit width was periodically monitored with the aid of a low-pressure mercury lamp (λ = 546.1 nm) and kept constant (2.0 cm^{-1}). The LGN-106-M-1 and LGN-503 argon lasers with an output below 1 W were used as the exciting light sources at a wavelength of 514.5 and 488 nm, respectively. A standard 90° geometry for irradiation of the samples was used when recording the polarized and depolarized Raman spectra. The polarization conditions were arbitrarily changed before each subsequent recording of the spectrum. The reproducibility of the frequencies of the maxima of the Raman lines was not worse than 0.3 cm^{-1}. The R_2NPX_2 samples were placed into sealed quartz or transparent fluoroplastic ampules. The temperature of the samples was kept constant (283±2 K) by a water thermostat, primarily in connection with the different values of decomposition temperatures of R_2NPX_2 compounds with different R and X. No decomposition of the R_2NPX_2 samples was observed at the indicated temperature. All procedures connected with preparing the samples were carried out in a dry box under an argon atmosphere. Mathematical processing of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 961—967, May, 1997.

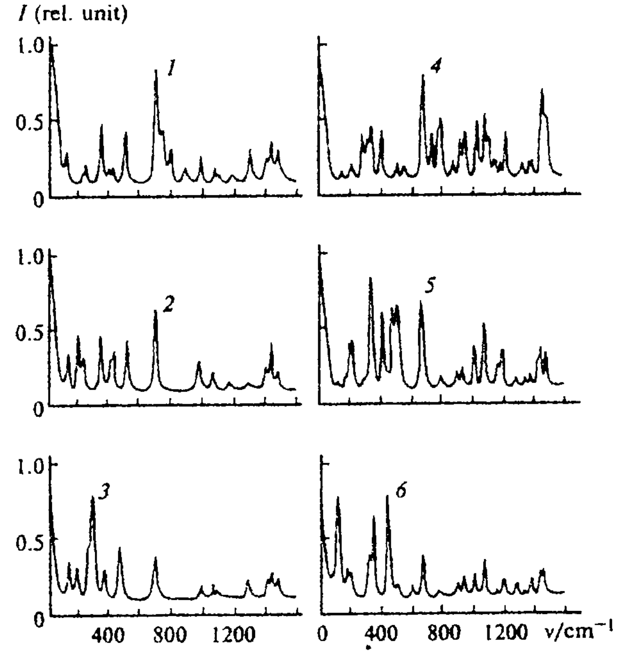

Fig. 1. Raman spectra of compounds R_2NPX_2 in the range of 100—1600 cm^{-1}: *1*, Me_2NPF_2; *2*, Me_2NPCl_2; *3*, Me_2NPBr_2; *4*, Et_2NPF_2; *5*, Et_2NPCl_2; *6*, Et_2NPBr_2.

the Raman spectra was performed on a built-in Apple-IIE computer using special programs. The accuracy of the location of the maxima of the lines and their full widths at half-height in the Raman spectra was ≤1 cm^{-1}.

Results and Discussion

Raman spectra of Me_2NPX_2 and Et_2NPX_2 (X = F, Cl, Br) and their interpretation. There are few published data on the vibrational spectra of the compounds of this class. No assignment of the frequencies was reported in Ref. 15 dedicated to a study of the IR spectrum of Et_2NPF_2. Interpretation of the vibrations of the C_2NP fragment using the vibrational spectra of Me_2NPX_2 (X = F and Cl)[16,17] is contradictory since almost no polarization measurements of the Raman spectra were performed. The vibrational spectra of Et_2NPX_2 (X = F and Cl) were recorded[18] and their interpretation was given. However, the results obtained are ambiguous because of the absence of a control for the cell temperature during recording of the Raman spectra.

The regions of vibrations of the C_2NP and PX_2 fragments in the Raman spectra of compounds R_2NPX_2 we studied are shown in Fig. 1.

Table 1. Experimental frequencies of vibrations in the spectra of Me_2NPX_2 and their assignment

ν/cm^{-1}			Assignment
X = F	X = Cl	X = Br	
2969 sh, dp	2981 w, dp	2971 w, dp	$\nu_{as}(CH_3)$
2939 m, p	2949 m, p	2946 w, p	$\nu_{as}(CH_3)$
2910 m, p	2909 w, p	1916 w, p	$\nu_{as}(CH_3)$
2859 m, p	2846 w, p	2845 w, p	$\nu_s(CH_3)$
2814 m, p	2804 w, p	2799 w, p	$\nu_s(CH_3)$
1488 w, dp	1480 w, dp	1471 w, dp	$\delta(CH_3)$
1443 w, dp	1438 m, dp	1443 w, dp	$\delta(CH_3)$
1417 w, dp	1411 w, dp	1408 w, dp	$\delta(CH_3)$
1306 w, p	1290 vw, p	1280 w, p	$r(CH_3)$ + + $\nu(NP)$ + + $\nu_s(NC_2)$
1189 vw, dp	1176 vw	1170 vw	$r(CH_3)$ + + $\nu_{as}(NC_2)$ + + $\delta(NC_2)$
1102 vw, dp	—	1092 vw	$r(CH_3)$
1071 w, dp	1067 w, dp	1054 w, dp	$r(CH_3)$
991 w, dp	980 w, dp	974 w, dp	$\nu_{as}(PNC_2)$ + + $r(CH_3)$
884 vw, dp	—	—	$\delta(CH_3)$
796 w, p	516 m, p	459 m, p	$\nu_{as}(PX_2)$
740 sh, dp	428 m, dp	365 w, dp	$\nu_{as}(PX_2)$
705 s, p	694 s, p	690 m, p	$\nu_s(PNC_2)$
498 m, p	426 w	—	$\delta(PX_2)$ + + $r(NC_2)$
419 w, p	—	—	$\delta(PX_2)$ + + $\delta(NC_2)$
389 w	400 sh	254 sh	$\delta(PX_2)$ + + $\delta(NC_2)$
338 m, p	338 m, p	277 s, p	$\delta(PX_2)$ + + $r(NC_2)$
235 w	219 m	178 w	$\omega(PX_2)$ + + $r(NC_2)$
217 w	194 m	—	$\delta(PX_2)$ + + $\chi(PN)$
118 w	125 w	126 w	$\chi(PN)$

Note. Notations: p — polarized, dp — depolarized, ν — stretching, δ — bending, r — rocking, ω — wagging, and χ — torsional vibrations.

The line frequencies and their relative intensities in the Raman spectra of Me_2NPX_2 and Et_2NPX_2 are given in Tables 1 and 2, respectively. The assignment of the frequencies in the spectra of Me_2NPF_2 and Me_2NPCl_2 was performed on the basis of calculations[19] using the results of the polarization measurements carried out in this work; in the case of Me_2NPBr_2 the analogy with the fluoro and chloro derivatives was used. The assignment of the frequencies of Et_2NPF_2 was based on the calculations of the normal vibrations of diethylaminodifluorophosphine following the previously described procedure.[18,20] The assignment of the frequencies in the spectra of Et_2NPCl_2 and Et_2NPBr_2 was made by analogy with the fluoro derivative.

As can be seen from the data in Tables 1 and 2, the frequencies of the stretching and bending vibrations of the CH_2 and Me groups lie above 800 cm^{-1}.

In the case of Me_2NPX_2 and Et_2NPX_2 (X = F, Cl, and Br) the assignment of the frequencies of symmetric and antisymmetric vibrations of the C_2N frag-

Table 2. Experimental frequencies of vibrations in the spectra of Et_2NPX_2 and their assignment

ν/cm^{-1}			Assignment
X = F	X = Cl	X = Br	
2973 sh	2977 m	2973 m	$\nu_{as}(CH_3)$
2940 s	2935 s	2939 m	$\nu_{as}(CH_2)$
2915 sh	2897 m	2895 sh	$\nu_s(CH_3)$
2873 s	2872 m	2867 w	$\nu_s(CH_2)$
1480 sh	1480 m	1473 sh	$\delta(CH_3)$
1455 s	1451 m	1451 m	$\delta(CH_3)$
—	1448 sh	1445 m	$\delta(CH_3)$
1387 w	1380 w	1379 w	$\delta(CH_3) + \delta(CH_2)$
1373 w	1345 w	1340 vw	$\delta(CH_2)$
1330 w	1290 w	1283 w	$\delta(CH_2)$
1212 m	1201 m	1202 w	$\delta(CH_2)$
1181 w	1178 sh	1161 vw	$\delta(CH_2)$
1149 w	—	—	$\delta(CH_2)$
—	1105 sh	—	$\delta(CH_3)$
1109 w	—	—	$\delta(CH_3)$
1082 s, p	1976 s, p	1076 m, p	$\nu_s(NC_2)$
1030 m, dp	1022 m, dp	1018 w, dp	$\nu_{as}(NC_2)$
950 m	947 w	947 w	$\nu_{as}(PNC_2) + \delta(CH_3)$
923 m	918 w	914 w	$\nu(CC) + \delta(CH_3)$
873 w	803 w	782 vw	$\delta(CH_3)$
802 m, p	510 s, p	443 s, p	$\nu_s(PX_2) + \delta(CH_2) + \delta(CH_3)$
790 sh, p	486 s, p	420 m, p	$\nu_s(PX_2) + \delta(CH_2) + \delta(CH_3)$
741 m, dp	416 s, dp	347 s, dp	$\nu_{as}(PX_2)$
685 s, p	673 s, p	671 m, p	$\nu_s(PNC_2)$
567 w	608 w	602 w	$\delta(CCN) + \delta(PNC_2)$
517 w	—	501 w	$\omega(PNC_2)$
408 m, p	223 m, dp	125 s, p	$\delta(PX_2) + \delta(NC_2)$
353 sh	—	—	$\delta(PX_2) + \delta(NC_2)$
335 m, p	329 s, p	325 m, p	$\delta(CCN) + \delta(CNC)$
318 sh	304 sh	—	$\delta(PX_2) + r(NC_2)$
288 m, dp	200 m, dp	200 w, dp	$\delta(CCN) + \delta(CNC)$
205 w	193 sh	181 w	$\delta(NPX) + \delta(PNC)$
153 w	130 w	—	$\delta(CNC) + \delta(NPX)$

Note. Notations see in Table 1.

ment taking into account the results of polarization measurements of the Raman spectra is doubtless and confirms the previously made[17,18] assignment. The frequencies of the totally symmetric vibration of the C_2NP fragment for the methyl and ethyl derivatives are nearly equal (705, 694, and 690 cm^{-1} for Me_2NPX_2 and 685, 673, and 671 cm^{-1} for Et_2NPX_2 at X = F, Cl, and Br, respectively). The frequencies of symmetric and antisymmetric vibrations of the PX_2 fragment in the spectra of the methyl derivative are close to corresponding values for the ethyl analog (ν_s 796, 516, and 459 cm^{-1} for Me_2NPX_2 and 802, 510, and 443 cm^{-1} for Et_2NPX_2; ν_{as} 740, 428, and 365 cm^{-1} for Me_2NPX_2, and 741, 414, and 347 cm^{-1} for Et_2NPX_2 at X = F, Cl, and Br, respectively). As we have noted previously,[18] an interesting feature of the Raman spectra of Et_2NPX_2 (contrary to those of Me_2NPX_2) in the region of vibrations of the P—X bond is that the symmetric vibration of the PX_2 fragment appears to be coupled with the symmetric bending vibrations of the CH_2 and Me groups. This results in the appearance of two polarized lines in the Raman spectra (at 802 and 790 cm^{-1} for X = F, at 510 and 486 cm^{-1} for X = Cl, and at 443 and 420 cm^{-1} for X = Br), to which synphase and antiphase deformations of the CH_2 and Me fragments correspond.

It should be noted that the frequencies of symmetric vibrations of the PX_2 fragment in the spectra of $MePX_2$ (812 and 487 cm^{-1} for X = F and Cl, respectively[21]) are also close to the frequencies of analogous vibrations in the Me_2NPX_2 and Et_2NPX_2 molecules, whereas the frequencies of antisymmetric vibrations of PX_2 in the spectra of the compounds we studied lie 50—70 cm^{-1} lower than the corresponding values for $MePX_2$ (800 and 473 cm^{-1} for X = F and Cl, respectively[21]). It is likely that a shift of the $\nu_{as}(PX_2)$ frequencies for the bromo derivatives should also be expected to be of the same magnitude.

The frequencies of the bending vibrations of the PX_2 fragment in the $MePX_2$ molecules (405 and 278 cm^{-1}, and 237 and 194 cm^{-1} for X = F and Cl, respectively[21]) are also close to the values of the frequencies of the $\delta(PX_2)$ vibrations for Me_2NPX_2 and Et_2NPX_2. It should be noted that, as in the case of the symmetric stretching vibrations $\nu_s(PX_2)$, the bending vibrations of the PX_2 fragment are coupled with the bending and rocking vibrations of the C_2N fragment, and in the case of the methyl derivative also with the torsional vibration of the C_2NP fragment.

Thus, lowered frequencies of the antisymmetric vibration of the PX_2 fragment and of the vibration of the C—N bond in the molecules of the compounds we studied as compared with those of $MePX_2$ and Me_3N [21] are evidence of the weakening of the P—X and C—N bonds both in Me_2NPX_2 and Et_2NPX_2 molecules. This is in agreement with concepts on the increasing of the P—N bond order due to the $p\pi$—$d\pi$ interaction as compared to the C—P and C—N bonds. In the case of bromo derivatives the P—N bond must be longer than in the chloro derivatives in which this bond is, in its turn, lengthened as compared to the fluoro derivatives because of the decreased electronegativity of X, and, as a

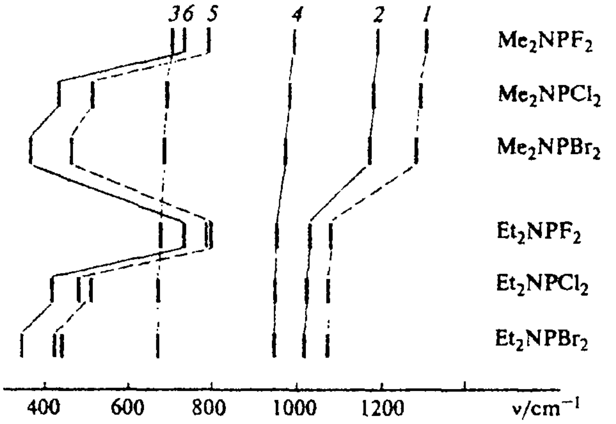

Fig. 2. Dependence of frequencies of stretching vibrations of the C_2NPX_2 fragment on R and X: values of frequencies of symmetric (dashed lines) and antisymmetric (solid lines) vibrations of the C_2N (*1, 2*), C_2NP (*3, 4*), and PX_2 (*5, 6*) fragments are given.

consequence, a weakening of the pπ—dπ interaction for the P—N bond. Ideas on such character of intramolecular interactions are in agreement with the decreasing frequencies of the totally symmetric vibration of the C_2NP fragment on going from X = F to X = Br (from 705 to 690 cm^{-1} in the spectra of Me_2NPX_2 and from 685 to 671 cm^{-1} in the spectra of Et_2NPX_2).

A histogram of the values of the frequencies of the stretching vibrations of the C_2NPX_2 fragment is shown in Fig. 2. As can be seen, the frequency of the vibrations of the P—N bond slightly depends on R and X. This provides reason to consider the vibrations of the C_2NP fragment in the compounds we studied as characteristic ones, which cannot be said about the vibrations of the C_2N fragment.

Dynamics of molecules R_2NPX_2 (R = Me and Et; X = F, Cl, and Br). The time correlation functions are defined as the Fourier transforms of the isotropic (I_{is}) and anisotropic (I_{anis}) components of the Raman spectrum:

$$G_V(t) = \int \hat{I}_{is}(\nu)\cdot\exp(2\pi ic\nu t)d\nu, \quad (1)$$

$$G_R(t)\cdot G_V(t) = \int \hat{I}_{anis}(\nu)\cdot\exp(2\pi ic\nu t)d\nu. \quad (2)$$

Here G_V and G_R are the vibrational and orientational correlation functions, respectively; t is time; $\hat{I}$ are the intensities normalized as follows:

$$\int_{\infty}^{\infty} \hat{I}(\nu)\cdot d\nu = 1. \quad (3)$$

Components $\hat{I}_{is}(\nu)$ and $\hat{I}_{anis}(\nu)$ are related to the polarized ($I_{\parallel}$) and depolarized ($I_{\perp}$) components by relations

$$\hat{I}_{anis}(\nu) = I_{\perp}(\nu), \quad (4)$$

$$\hat{I}_{is}(\nu) = I_{\parallel}(\nu) - \frac{4}{3}I_{\perp}(\nu). \quad (5)$$

Another characteristic of the processes occurring in the systems in question is the correlation time defined as follows:

$$\tau = \int_0^{\infty} G(t)dt. \quad (6)$$

Unlike the TCF, the correlation time is an integral characteristic of the processes, while τ^{-1} is the rate of disordering of the system.

Vibrational relaxation in liquids is mainly due to the vibrational dephasing. In this case the process of stochastic perturbation of the phase of vibration can be characterized by a vibrational TCF of the form[13]

$$G_V(t) = \exp\{-M_2\tau_v[\tau_v(\exp(-t/\tau)\cdot\nu - 1) + t]\}, \quad (7)$$

where M_2 is the second moment of isotropic component; and τ_v is the time characteristic of the process of the phase perturbation.

Two limiting types of the time dependence of the correlation function are possible depending on the magnitude of the product $\sqrt{M_2}\cdot\tau_v = \xi$.

1. If $\xi \gg 1$, then $G_V(t)$ has the Gaussian form:

$$G_V(t) = \exp[-\pi t^2/(4\tau_V^2)], \quad (8)$$

where τ_V is the time of vibrational relaxation. This is the case of so-called nonhomogeneous line broadening or slow modulation. The mean square of the frequency fluctuation is much larger than τ_v^{-1} and at time ~1 ps (the order of the time of vibrational relaxation) system can be considered a static one.

2. If $\xi \ll 1$, then $G_V(t)$ is exponential:

$$G_V(t) = \exp(-t/\tau_V). \quad (9)$$

This is the case of homogeneous line broadening or fast modulation. The Raman line is broadened due to the motion of neighboring particles.

The rotational relaxation occurs as a result of a hindered rotational motion of the particle caused by its collisions with neighboring molecules. If a change in the orientation of a molecule for the time τ is characterized by the value of the angle of rotation of its molecular axes (θ), then the two limiting mechanisms of rotational motion differing in the time when the molecule is at rest (τ_S) and in motion (τ_F) can be imagined. In the first case reorientation is considered as rotational diffusion: the rotation of the particle by an angle θ consists of a large number of uncorrelated steps. Each of these steps corresponds to the rotation of the particle by an angle ε, and then $\tau_S \ll \tau_F$. In the second case the rotation by an angle θ occurs as the only jump, when $\varepsilon = \theta$, and $\tau_S \gg \tau_F$. No restrictions are imposed on the rotation angles in both mechanisms. According to the author of Ref. 22, one of the fundamental works, the first mechanism (if $\varepsilon \ll \theta$) is characteristic of the rotational motion of large molecules, while the second one is characteristic of the reorientation of small-sized particles.

In addition, one more process, so-called free diffusion, can be described in the framework of the first mechanism. The idea of the possibility of its realization was raised more than 30 years ago.[23] According to this theory, the particle rotates as a free rotator and has its own angular momentum J. At the moments of collisions, the frequency of which is characterized by a certain time τ_j, this angular momentum is changed. There are two limiting cases of the J change as a result of collisions. In the J-diffusion limit both the value and direction of the angular momentum are changed. In the case of M-diffusion only the direction of J is changed, while its value remains unchanged.

If the orientational correlation function for the rotational diffusion has a simple exponential form[24]

$$G_R(t) = \exp(-t/\tau_R), \qquad (10)$$

where τ_R is the time of rotational relaxation, then the expressions for the TCF obtained in the framework of the free diffusion model are fairly complex recurrent formulas,[25] dependent on the symmetry type of the molecule. It should be noted that the following relations[26] are valid at small τ_j values:

$$\tau_j = I/(6k_BT\tau_R) \quad \text{(J-diffusion)}, \qquad (11)$$

$$\tau_j = I/(2k_BT\tau_R) \quad \text{(M-diffusion)}, \qquad (12)$$

where I is the moment of inertia of the molecule, k_B is the Boltzmann constant, and T is temperature.

Usually, at short times ($\leq 10^{-13}$ s) the particle rotates as a free rotator, and its motion can be described by a TCF of the form[27]

$$G_{FR}(t) = \exp[-(3k_BT/I)t^2]. \qquad (13)$$

With increasing rotation time, the particles endure increasingly more perturbation due to their interaction with the environment, and the TCF begins approaching an exponential form, which corresponds to the conditions of the rotational diffusion.

The knowledge of the τ_j value allows one to estimate the rotation angle ε at the first stage of diffusion assuming that before colliding the molecule rotates as a free rotator with a rate of rotation of $\omega = \sqrt{k_BT/I}$:

$$\varepsilon = \tau_j\omega = \tau_j \cdot \sqrt{k_BT/I}\,. \qquad (14)$$

To find the TCF, we used two procedures:[4] (1) application of the Fourier transform to the experimentally obtained contours of the Raman lines (a discrete Fourier transform); and (2) simulation of the contour of the Raman line by an analytical function with the subsequent use of the Fourier transform. In the second case the profile of the Raman line was assumed to be described by a dispersion curve.

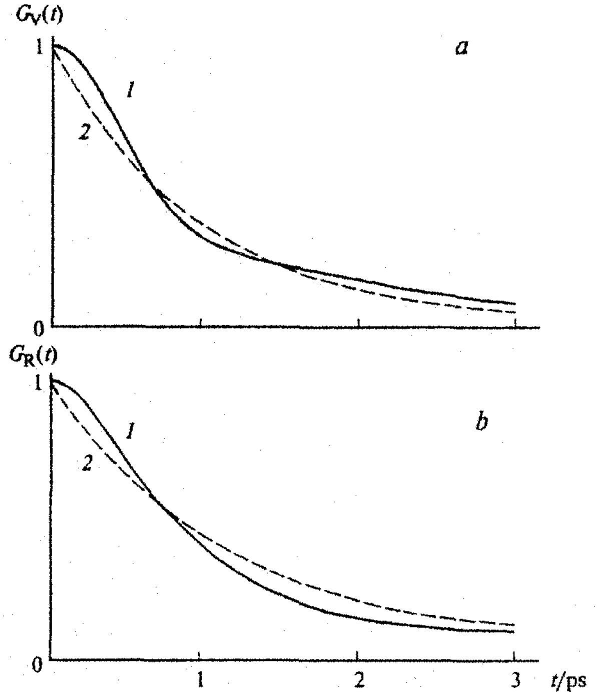

Fig. 3. Vibrational (*a*) and rotational (*b*) TCF calculated using the Fourier transform of the experimental (*1*) and model (*2*) contours of the line of vibration of the P—N bond in Et_2NPCl_2.

As was mentioned above, the calculations of the vibrational and rotational TCF for molecules R_2NPX_2 were carried out using the contours of the Raman lines with frequencies of ~670—705 cm^{-1} corresponding to the totally symmetric vibration of the C_2NP fragment. A characteristic shape of the vibrational and rotational correlation functions is shown in Fig. 3. Calculations of times τ_V and τ_R performed under assumption of the Lorentzian line contour (Table 3) showed that the times of vibrational relaxation τ_V are ~1.0 and ~2.0 ps for Me_2NPX_2 and Et_2NPX_2 respectively, and are virtually independent of the type of X atom. Contrary to τ_V, the τ_R value essentially depends on the nature of X atom and increases in the sequence F (τ_R = 1.3 and 1.9 ps),

Table 3. Parameters of vibrational and rotational relaxation of Me_2NPX_2 and Et_2NPX_2 (X = F, Cl, and Br) molecules at T = 300 K

Molecule	τ_V/ps	τ_R/ps	ε/deg
Me_2NPF_2	0.94±0.10	1.26±0.20	0.96±0.20
Me_2NPCl_2	0.84±0.15	3.18±0.25	1.02±0.20
Me_2NPBr_2	1.09±0.15	4.83±0.30	0.88±0.22
Et_2NPF_2	1.80±0.15	1.93±0.25	0.68±0.21
Et_2NPCl_2	2.12±0.20	4.84±0.30	0.76±0.22
Et_2NPBr_2	2.05±0.20	9.55±0.35	0.71±0.23

Cl (τ_R = 3.2 and 4.8 ps), Br (τ_R = 4.8 and 9.6 ps) for Me_2NPX_2 and Et_2NPX_2, respectively. This is evidence that the processes of vibrational and orientational relaxation nearly equally contribute to shaping the line contour of the totally symmetric vibration of the C_2NP fragment in Me_2NPF_2 and Et_2NPF_2 molecules. At the same time, in the case of Me_2NPX_2 and Et_2NPX_2 (X = Cl and Br) the τ_R value is twice (and more) as much as the τ_V value, *i.e.*, the orientational relaxation can be ignored.

In our opinion, an increase in τ_R on going from fluoro derivatives to bromo derivatives of R_2NPX_2 can be explained as follows. The P—N bond order in the C_2NP fragment is decreased as a result of the pπ—dπ interactions with decreasing electronegativity of the X atom. This results in some decrease in the barrier to the internal rotation of the PX_2 group about the P—N bond; the height of the barrier is known[28] only for Me_2NPF_2 (it is about 10 kcal mol^{-1}). At the same time, internal rotations of the methyl and ethyl groups about the C—N bonds are characterized by lower barriers, the heights of which are estimated to be no more than 2 kcal mol^{-1}.[28] Obviously, if the values of these barriers increase with decreasing electronegativity of X atom (it does not contradict previously developed concepts[28]), then the τ_R value should increase as a result. The fact that the τ_V values virtually coincide with τ_R values for Me_2NPF_2 and Et_2NPF_2 is, in our opinion, associated with the structural features of these molecules and, namely, with the highest structural flexibility of fluoro derivatives of R_2NPX_2 as compared with their chloro and bromo derivatives. Therefore the τ_V value (by analogy with the flexible XeF_6 molecule)[29] can, to some extent, be a time characteristic of the intramolecular rearrangements in R_2NPF_2 (0.9±0.1 and 1.8±0.15 ps for R = Me and Et, respectively). It should be noted that the accuracy of indicated values of the times of intramolecular rearrangements in R_2NPF_2 can appear not too high; actually, as was noted above, several vibrations of the C_2NP, C_2N, and PX_2 fragments, as well as those of the CH_2 and Me groups are coupled. This, in turn, can appreciably affect the processes of the energy transfer at collisions and, as a result, have a pronounced effect on the orientational relaxation.

An analysis of the vibrational correlation functions calculated using experimental data, as well as that of TCF obtained in the limiting cases of fast and slow modulation showed that the mechanism of inhomogeneous broadening is mainly realized for Me_2NPX_2 and Et_2NPX_2 at $t \le 0.3$ and 0.4 ps, respectively. The character of broadening begins changing with increasing time, and at $t \ge 2.0$—2.5 ps homogeneous broadening is predominantly observed for compounds R_2NPX_2. This is easily explained by the fact that at relatively long times ($t \ge 1.5$—2.0 ps) the molecular systems under consideration are no more static and the motion of neighboring species mostly contributes to the line broadening.

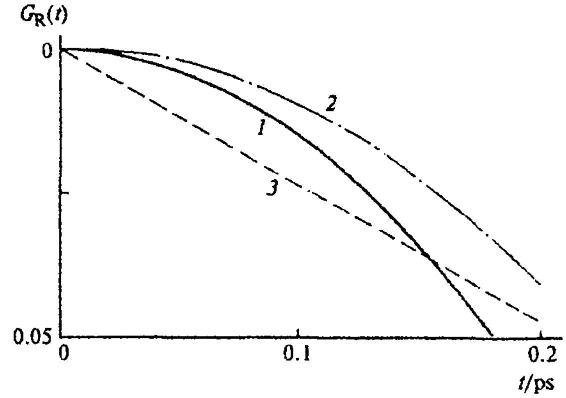

Fig. 4. Rotational TCF $G_R(t)$ for the vibration of the P—N bond in the Et_2NPCl_2 molecule (*1*) and limiting dependences of $G_R(t)$ for the mechanisms of free rotation (*2*) and rotational diffusion (*3*).

A comparison between the rotational correlation functions calculated using the experimental data and the TCF obtained under assumption of the mechanisms of free rotation and rotational diffusion (their characteristic shape is shown in Fig. 4) showed that the molecules in question rotate as free rotators at $t \le 0.03$ ps and $t \le 0.02$ ps for Me_2NPX_2 and Et_2NPX_2, respectively. The character of rotational motion is changed with increasing time, and at $t \ge 0.20$ ps (Me_2NPX_2) and $t \ge 0.15$ ps (Et_2NPX_2) it becomes rotational diffusion. In this case the values of the angle of rotation ε at the first stage of diffusion are ~1.0° and ~0.7° for the methyl and ethyl derivatives, respectively. It should be noted that in all calculations taking into account the rotation of the Me_2NPX_2 and Et_2NPX_2 molecules, the moments of inertia were obtained using the reported[28] values of the geometric parameters of the compounds related to R_2NPX_2: $I(X = F) = 14.2 \cdot 10^{-39}$ and $22.6 \cdot 10^{-39}$ g cm^2, $I(X = Cl) = 26.7 \cdot 10^{-39}$ and $35.1 \cdot 10^{-39}$ g cm^2, $I(X = Br) = 53.0 \cdot 10^{-39}$ and $61.4 \cdot 10^{-39}$ g cm^2 for Me_2NPX_2 and Et_2NPX_2, respectively.

Assuming that the values of the time of cessation of free rotation and of the time characterizing the frequency of collisions with the environment are close, one can conclude that J-diffusion occurs in the systems under study, *i.e.*, the collisions between the R_2NPX_2 molecules are of nonelastic character.

Thus, a detailed investigation of the Raman spectra of the R_2NPX_2 compounds, as well as that of the contours of the lines corresponding to the vibrations of the P—N bond allowed us to find a number of characteristic features in the behavior of molecules of these substances in the condensed state. These features are related to the structure and character of intramolecular interactions, which makes it possible to predict the behavior of the R_2NPX_2 compounds in various chemical reactions with organic and inorganic compounds.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-34250).

References

1. W. Gordy and R. Cook, *Microwave Molecular Spectra*, Wiley, New York, 1970, 549 pp.
2. *Molecular Structure by Diffraction Methods*, Eds. G. A. Sim and L. E. Sutton, The Chemical Society, London, 1974, **2**, 513 pp.
3. W. R. Rotschild, *Dynamics of Molecular Liquids*, Wiley, New York, 1984, 417 pp.
4. Sh. Sh. Nabiev and I. I. Ostroukhova, *Spectrochim. Acta*, 1993, **49A**, 1527.
5. S. A. Kirillov, in *Dinamicheskie svoistva molekul i kondensirovannykh sistem* [*Dynamic Properties of Molecules and Condensed Systems*], Ed. A. N. Lazarev, Nauka, Leningrad, 1988, 190 pp. (in Russian).
6. J. Griffiths, in *Molecular Spectra and Structure*, Ed. J. Durig, Elsevier, New York, 1977, **6**, 273.
7. D. W. Oxtoby, *Adv. Chem. Phys.*, 1979, **40**, 1.
8. J. Lascombe, M. Bernard, P. Caloine, and J. Devaure, *Molecular Motions in Liquids*, Ed. J. Lascombe, Dordrecht, Reidel, 1974, 387.
9. J. Yarwood, R. Arndt, and G. Doge, *Chem. Phys.*, 1977, **25**, 387.
10. N. S. Golubev, N. D. Orlova, and L. A. Platonova, *Pis'ma Zh. Eksp. Teor. Fiz.*, 1982, **35**, No. 2, 65 [*JETP Lett.*, 1982, **35** (Engl. Transl.)].
11. *Molekulyarnaya kriospektroskopiya* [*Molecular Cryospectroscopy*], Ed. M. O. Bulanin, Saint-Petersburg University Publishing House, Saint-Petersburg, 1993, 300 pp. (in Russian).
12. B. J. Bulkin and K. Brezinsky, *J. Chem. Phys.*, 1978, **69**, 15.
13. W. G. Rothschild, *J. Chem. Phys.*, 1976, **65**, 455.
14. T. Kato, *J. Chem. Phys.*, 1989, **90**, 2951.
15. R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 415.
16. M. A. Fleming and R. C. Taylor, *Spectrochim. Acta*, 1965, **21**, 1189.
17. J. R. Durig and J. Casper, *J. Cryst. Molec. Struct.*, 1972, **2**, 1.
18. Sh. Sh. Nabiev, V. P. Novikov, V. D. Klimov, T. M. Kuznetsova, and L. D. Shustov, *Zh. Prikl. Spektrosk.*, 1987, **46**, 493 [*J. Appl. Spectr.*, 1987, **46** (Engl. Transl.)].
19. S. A. Katsyuba and R. R. Shagidullin, *Zh. Obshch. Khim.*, 1984, **54**, 694 [*J. Gen. Chem. USSR*, 1984, **54** (Engl. Transl.)].
20. V. P. Novikov and A. I. Malyshev, *Zh. Prikl. Spektrosk.*, 1980, **33**, 545 [*J. Appl. Spectr.*, 1980, **33** (Engl. Transl.)].
21. J. R. Durig, A. E. Stanley, and M. R. Jolilian, *J. Raman Spectr.*, 1981, **10**, 44.
22. Ya. I. Frenkel', *Kineticheskaya teoriya zhidkostei* [*Kinetic Theory of Liquids*], Nauka, Leningrad, 1975, 592 pp. (in Russian).
23. R. G. Gordon, *J. Chem. Phys.*, 1966, **44**, 1830.
24. P. Debye, *Polar Molecules*, Dover, New York, 1945, 312 pp.
25. R. E. D. McClung, *J. Chem. Phys.*, 1971, **55**, 3459.
26. P. S. Habbard, *Phys. Rev.*, 1974, **A6**, 2421.
27. W. A. Steele, *J. Chem. Phys.*, 1971, **56**, 1456.
28. L. V. Vilkov, V. S. Mastryukov, and N. I. Sadova, *Opredelenie geometricheskogo stroeniya svobodnykh molekul* [*Determination of Geometric Structure of Free Molecules*], Khimiya, Leningrad, 1978, 223 pp. (in Russian).
29. Sh. Sh. Nabiev, *Vysokochist. Veshchestva*, 1993, 138 [*High-Purity Substances*, 1993 (Engl. Transl.)].

Received December 25, 1996;
in revised form March 4, 1993