
**LOCAL SURROUNDING, NORMAL VIBRATIONS,
AND STRUCTURE OF ANION NO₂⁻ IN IONIC CRYSTALS****L.A. BULAVIN, V.P. SAKUN, A.V. YAKUNOV**UDC 535.343.2
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We have studied the behavior of the frequencies of intramolecular vibrations and the equilibrium configuration of the nuclear core of anion NO₂⁻ on changes of the temperature and the composition of a matrix and on the electron transition ¹A₁ → ¹B₁ (S₀ → S₁).

1. Introduction

The studies of the connection between the optical properties of the center (atom or molecule) and its internal structure (conformation) are of significant scientific and practical interest. The effect of the local surrounding on an optical center is frequently related to the search for a direct functional connection between the vibration frequency of the center and micro- or macroparameters of the medium [1, 2]. In most cases, the behaviors of various vibrations on a change of conditions of a local surrounding of the center can differ from one another not only quantitatively, but also qualitatively. This induces certain difficulties for the comparison of characteristics of the matrix with the behavior of the totality of all vibrations. One can obtain the important information about the effect of the medium on an optical center, by studying the interrelation between the frequencies of vibrations of a molecule and its conformation [3–5]. A model system convenient for the indicated purposes is a simple molecular anion NO₂⁻ which is characterized by a relatively simple structure, and its optical characteristics are quite sensitive to a change of the local surrounding. A free anion NO₂⁻ (in the ground electronic state ¹A₁) is characterized by the point symmetry C_{2v} and has full-symmetric valence vibration, ν₁, deformational vibration, ν₂, and antisymmetric valence vibration, ν₃. The transition of

the anion into the condensed state is accompanied by the appearance of a perturbation from the side of its nearest surrounding, which defines a change of the corresponding energy spectrum. For example, the frequencies ν₁ and ν₂ in the gaseous phase are, respectively, 1284 and 776 cm⁻¹ [6]. In the crystalline state, their values increase significantly.

Our goal was to study the regularities of both a behavior of the frequencies of intramolecular (normal) vibrations (ν_{*i*}, *i* = 1, 2, 3) and the structure of anion NO₂⁻ on changes of the temperature and the composition of the matrix and on the electron transition ¹A₁ → ¹B₁ (S₀ → S₁). The consideration was carried out by the example of the matrices of crystals of nitrites (MNO₂) and halides (MHal) of alkaline metals. In such matrices, the point symmetry of anion NO₂⁻ is close to the intrinsic symmetry in the free state [7–9].

2. Experimental

The measurement of the spectra of Raman scattering of light (RSL) in polycrystals of NaNO₂ and KNO₂ was performed on a spectrometer DFS-12 on the excitation by a He-Cd laser (λ_{exc} = 441.6 nm, the power W = 80 mW). The error of the determination of a position of the maximum of the Raman scattering (RS) band was less than ± 3 cm⁻¹. By the experimental results, we evaluated the frequencies (in wave numbers) of normal vibrations ν_{*i*} = ν_{*i*}⁰ + χ_{*ii*}, where ν_{*i*}⁰ and χ_{*ii*} are, respectively, the harmonic frequency and the anharmonism constant of the *i*-th vibration (*i* = 1, 2, 3) which are given in the Table together with the literature data of studies of the spectra of RSL, resonance Raman scattering of light (RRSL), infrared

absorption (IRA) and reflection (IRR), and the spectra of photoluminescence (PL) and electron absorption (EA) [7–17] (which are considered most reliable).

3. Method of Calculations

We calculated the conformation characteristics of anion NO_2^- in the approximation of valence forces in molecules with symmetry C_{2v} [18]. The angle $\angle\text{ONO} \equiv 2\alpha$, and the force constants of deformations of both the bond N–O (f_r) and the angle 2α (f_α/l^2) were determined by the formulas

$$4\pi^2\nu_3^2 = \left(1 + \frac{2m_{\text{O}}}{m_{\text{N}}}\sin^2\alpha\right)\frac{f_r}{m_{\text{O}}}, \quad (1)$$

$$4\pi^2(\nu_1^2 + \nu_2^2) = \left(1 + \frac{2m_{\text{O}}}{m_{\text{N}}}\cos^2\alpha\right)\frac{f_r}{m_{\text{O}}} + \frac{2}{m_{\text{O}}}\left(1 + \frac{2m_{\text{O}}}{m_{\text{N}}}\sin^2\alpha\right)\frac{f_\alpha}{l^2}, \quad (2)$$

$$16\pi^4\nu_1^2 \cdot \nu_2^2 = 2\left(1 + \frac{2m_{\text{O}}}{m_{\text{N}}}\right)\frac{f_r}{m_{\text{O}}^2} \cdot \frac{f_\alpha}{l^2}, \quad (3)$$

where ν_i is the frequency of the i -th vibration in s^{-1} , m_{O} and m_{N} are, respectively, the masses of atoms of oxygen and nitrogen given in grams and the force constants are taken in dyn/cm . We estimated the equilibrium distance r_{NO} with the help of the empiric Badger relation [19]

$$f_r = 1.86 \times 10^5 (r_{\text{NO}} - 0.68)^{-3}, \quad (4)$$

where the constant f_r is measured in dyn/cm , and r_{NO} in \AA . By using the obtained values of the parameters 2α and r_{NO} , we estimated the area of the equilibrium configuration of the nuclear core of the anion (S) which is proportional to its effective size and is defined by the overlapping of the peripheral regions of electron shells of the anion itself and its nearest neighbors.

4. Results and Their Discussion

It is known that the vibration spectra (RSL, IRR) of crystals LiNO_2 contain a doublet on the neighborhood of the excitation frequency ν_2 (the difference between the components of the doublet $\Delta\nu_2 = 40 \text{ cm}^{-1}$), which is related to the manifestation of two different types of coordination of the routine anion NO_2^- in a crystal lattice [9]. This is confirmed by the difference of the

temperature dependences of the half-widths of separate components of the doublet [20]. Our calculations indicate some distinctions of the conformation characteristics of the mentioned centers which are as follows: $\Delta f_r = 21 \text{ N/m}$, $\Delta(f_\alpha/l^2) = 12 \text{ N/m}$, $\Delta\alpha = 3.5^\circ$, $\Delta r_{\text{NO}} = 0.006 \text{ \AA}$, $\Delta S = 0.0016 \text{ \AA}^2$. In the case of crystal hydrate $\text{LiNO}_2 \cdot \text{H}_2\text{O}$, a similar doublet is not observed [9].

The data presented in the Table show some dispersion in the frequency of the same vibration ($\Delta\nu_i$) which is revealed while using the different methods of registration of the spectrum [RSL (I), IRA (II), IRR, PL (III)] and can exceed the half-width (γ_i) of the relevant vibration bands. For example, the dispersion $\Delta\nu_3^{\text{I,II}} = 4 \text{ cm}^{-1}$ was determined in the spectra of RSL and IRA at $T < 10 \text{ K}$ in the KCl matrix with the half-widths $\gamma_3^{\text{I}} = 2 \text{ cm}^{-1}$ [8] and $\gamma_3^{\text{II}} = 0.4 \text{ cm}^{-1}$ [21]. As a rule, one observes an increase in $\Delta\nu_i$ with γ_i . For example, the most significant difference $\Delta\nu_1^{\text{I,III}} = 9 \text{ cm}^{-1}$ was found for a RbCl crystal at 4.2 K at the corresponding $\gamma_i^{\text{I}} = (4-9) \text{ cm}^{-1}$ [12, 13], whereas $\gamma_i^{\text{I}} = (2-4) \text{ cm}^{-1}$ for crystals KHal at $T = 6 \text{ K}$ [8]. This allows us to assume that the mentioned dispersion is related, to a significant extent, to the difference of the spectral dependences of the inhomogeneous broadening function of an optical band of molecular centers for different methods of its registration. The last assertion is corroborated by the essential difference of the shapes and widths of the vibration band contour according to the indicated methods of registration. For example, at $T \leq 6 \text{ K}$ in crystals MHal, $\gamma_i^{\text{II}} < 1 \text{ cm}^{-1}$ [7, 21], and $\gamma_i^{\text{I}} = (2-10) \text{ cm}^{-1}$ [8, 13]. In liquids and liquid systems, for which the inhomogeneous widening of the optical spectrum is significantly greater than that in crystals, the value of $\Delta\nu_i$ can reach $(20-80) \text{ cm}^{-1}$ [22–24].

The temperature behavior of the optical band of an impurity in the crystal is determined to an essential extent by such two factors as changes of the lattice constant of the matrix and the anharmonic interaction of a local mode of the impurity with vibrations of the matrix. In the above-considered matrices, the total changes of the frequencies ν_i in the temperature range $T = (2-300) \text{ K}$ can differ from one another by magnitude and sign, but they do not exceed $\pm 7 \text{ cm}^{-1}$ (see the Table). For example, as the temperature increases from 15 to 300 K in a KI crystal, the changes of the frequencies are $\Delta\nu_1 = 0$, $\Delta\nu_2 = 1.5 \text{ cm}^{-1}$, $\Delta\nu_3 = 4 \text{ cm}^{-1}$ (see the Table) which correspond to the following changes of the conformation parameters: $\Delta f_r = -4 \text{ N/m}$, $\Delta(f_\alpha/l^2) = 1 \text{ N/m}$, $\Delta\alpha = 0.38^\circ$, $\Delta r_{\text{NO}} = -8 \times 10^{-4} \text{ \AA}$, $\Delta S = 2.76 \times 10^{-3} \text{ \AA}^2$. We note that there exists the correlation in the growth

of both the area S and the lattice constant (d) of the crystal with increase in the temperature. On the whole, the total temperature changes of the absolute values of conformation parameters in the systems under consideration for $T = (2\div 300)$ K are $|\Delta f_r, \Delta(f_\alpha/l^2)| \leq 5$ N/m, $|\Delta\alpha| \leq 0.4^\circ$, $|\Delta r_{\text{NO}}| \leq 0.001$ Å, $|\Delta S| \leq 0.004$ Å².

The Table illustrates the qualitative consistency in variations of all three frequencies in the electron states 1A_1 (ν_i) and 1B_1 (ν'_i) on a change of the composition of the matrix. For example, at 300 K, an increase of the

Frequencies of fundamental vibrations of anion NO_2^- in ionic crystals

Crystal	T, K	Method	ν_1 , cm ⁻¹	ν_2 , cm ⁻¹	ν_3 , cm ⁻¹	Reference
LiNO ₂	300	RSL	1352	872	1273	9
LiNO ₂ ·H ₂ O	300	RSL, IRR*	1350	857	1260*	9
NaNO ₂	300	RSL	1326	827	1232	
	5	RSL	1331	830	1227	
	4.2	EA	1018	632	950**	15
KNO ₂	300	RSL	1322	806	1240	9
	80	RSL	1318	809	1231	
	4.2	EA	1015	616	948**	
CsNO ₂	300	RSL	1317	803	1230	9
NaCl	300	IRA	1348	832	1300	10
	15	IRA	1346	836	1304	7
	4.2	PL	1331	831	–	17
NaBr	300	IRA	1340	824	1279	10
	6	RSL	1327	828	1283	8
	4.2	EA	1020	636	987**	8
KCl	300	RSL, IRA*	1327	811	1287*	8, 10*
	6	RSL	1327	806	1286	8
	2	IRA	1329	805	1290	7
	4.2	PL	1326	804,3	–	12
	4.2	EA	1024	599	974**	8
KBr	300	RSL, IRA*	1317	806	1275*	8, 10*
	6	RSL	1317	800	1274	8
	2	IRA	1318,8	798,5	1276,5	7
	4.2	EA	1011	595	962**	8
KI	300	RSL, IRA*	1309	803	1257*	8, 10*
	12	RSL	1307,5	806,6	1253,2	16
	13	IRA	1308	805	1253	7
	4.2	EA	997	604	947**	8
RbCl	300	IRA	1320	807	1276	10
	5	RSL	1319	799	1280	13
	4.2	PL	1310	801,5	–	12
	4.2	EA	1002	598	965**	12
CsCl	300	IRA	...	806	1271	11
CsBr	300	IRA	...	805	1252	11
	4.2	RRSL, PL*	1314	795,9*	1266	14
	4.2	EA	1015,7	590	959**	14
CsI	300	IRA	...	800	1232	11
	4.2	RRSL, PL*	1301	94,8*	1228	14
	4.2	EA	984.1	620,8	947**	14

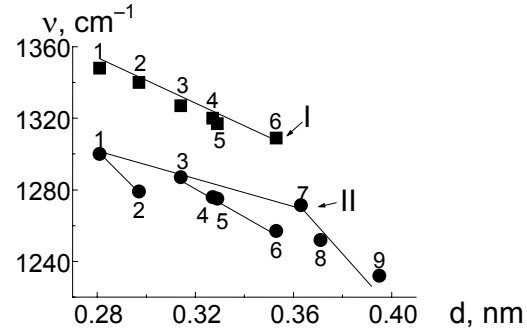


Fig. 1. Frequencies ν_1 (I) and ν_3 (II) of an extrinsic anion NO_2^- versus the lattice constant d of crystals NaCl (1), NaBr (2), KCl (3), RbCl (4), KBr (5), KI (6), CsCl (7), CsBr (8), and CsI (9) at 300 K. Data of the Table are used

lattice constant d of the matrix in the sequence of ions of the base $\text{Li}^+ \rightarrow \text{Na}^+ \rightarrow \text{K}^+ \rightarrow \text{Cs}^+$ or $\text{Cl}^- \rightarrow \text{Br}^- \rightarrow \text{I}^-$ is accompanied by a decrease of ν_i and ν'_i . We note that the almost linear dependence between the parameters ν_1 and d for halides of Na, K, and Rb, as well as between ν_3 and d in the sequences $\text{NaCl} \rightarrow \text{KCl} \rightarrow \text{CsCl}$; $\text{KCl} \rightarrow \text{RbCl} \rightarrow \text{KBr} \rightarrow \text{KI}$, and $\text{CsCl} \rightarrow \text{CsBr} \rightarrow \text{CsI}$ (Fig. 1), is observed at $T = 300$ K in crystals MHal at a nonlinear dependence between ν_2 and d . Thus, the functional interrelation between three frequencies ν_i of intramolecular vibrations and the lattice constant d is complicated. A variation of conditions of a local surrounding of the anion affects slightly the ratio between the frequencies ν_i ($R_{ij} = \nu_i/\nu_j$). For example, $R_{12} = 1.63 \pm 0.02$ in all matrices, and $R_{13} = 1.07 \pm 0.01$ (in MNO_2) and 1.04 ± 0.01 (in MHal). The study of electron-vibration absorption spectra of anion NO_2^- showed that the excitation of an optical electron on the transition $^1A_1 \rightarrow ^1A_1$ is accompanied by a decrease of the vibration frequencies ν_1 and ν_2 by about 30% (Table). We recall that the vibration ν_3 is not active in such a spectrum. In this case, the ratio between the frequencies remains invariable: $R'_{12}(^1B_1) = \nu'_1/\nu'_2 = 1.63 \pm 0.02$. Assuming a practical invariance of the ratio between all three frequencies ν_i in the both electronic states 1A_1 and 1B_1 , we can approximately evaluate the vibration frequency ν'_3 in the state 1A_1 . This will help us to clarify the possible conformational changes of the anion on the excitation of its optical electron (in the Table, they are marked by two asterisks). In addition, the general property of the crystals under consideration consists in the considerable difference between the integral intensities (J_i) of the bands of valence vibrations ν_1 and ν_3 . The performed analysis of the data presented in [7] showed that, the ratio $J_1/J_3 = (1-4)/100$ in the IRA

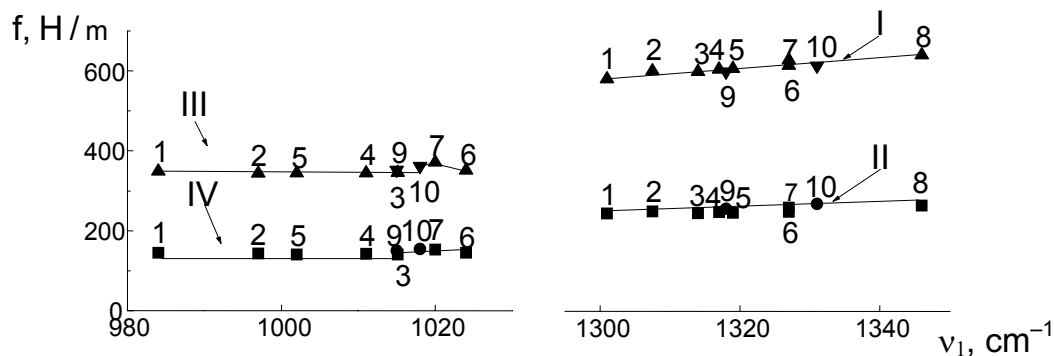


Fig. 2. Relationships between the force constant f_r (I, III), f_α/l^2 (II, IV), and frequency ν_1 of anion NO_2^- in the electron states 1A_1 (I, II) and 1B_1 (III, IV) in crystals CsI (1), KI (2), CsBr (3), KBr (4), RbCl (5), KCl (6), NaBr (7), NaCl (8), KNO_2 (9), NaNO_2 (10) at low temperatures. Calculations are performed by data of the Table

spectrum of crystals KHal-NO_2^- at $T=10$ K; whereas the ratio $J_1/J_3=100/5$ at $T=5$ K in the RSL spectrum of the polycrystal NaNO_2 under study.

According to our calculations, the frequencies ν_i increase with both the force constants f_r and f_α/l^2 (Fig. 2, curves I, II), which can be caused, in our opinion, by a decrease of the effective size of the anion and agrees with a decrease of both the length r_{NO} and the area S of the anion (Fig. 3, curves I–III). In this case, the behavior of the angle 2α is complicated (Fig. 3, curves IV, V). The relative change of the angle, $\delta\alpha$, is more significant than that of the length, δr_{NO} . In crystals MHal , such total relative changes are $\delta\alpha \sim 0.047 > \delta r_{\text{NO}} \sim 0.017$, which agrees with the difference between values of the force constants ($f_r f_\alpha/l^2$). The total changes of the frequencies ν_i on the variation of the composition of the matrix are $\Delta\nu_1 = 51 \text{ cm}^{-1}$, $\Delta\nu_2 = 80$, and $\Delta\nu_3 = 76$. These can be related to such changes of the conformation parameters: $\Delta f_r = 79 \text{ N/m}$, $\Delta(f_\alpha/l^2) = 39 \text{ N/m}$, $\Delta\alpha = 12.2^\circ$, $\Delta r_{\text{NO}} = 0.028 \text{ \AA}$, $\Delta S = 0.047 \text{ \AA}^2$. We indicate the general inequality for the effective size of the anion (area S) in the cases of matrices MNO_2 and MHal , the other conditions being the same (Fig. 3): $S(\text{MNO}_2) > S(\text{MHal})$.

The results of our calculations show that the above-mentioned decrease of the frequencies ν_i on the electron transition $^1A_1 \rightarrow ^1B_1$ corresponds to a decrease of both the force constants f_r and f_α/l^2 (Fig. 2) on the increase of both the length r_{NO} (Fig. 3,a) and the area S (Fig. 3,b), as well as the angle 2α (Fig. 3,c) of the anion, the other conditions being the same. The relative changes of the conformation parameters on the electron transition can be equal to $\Delta\alpha \sim 1.4^\circ$, $\Delta r_{\text{NO}} \sim 0.13 \text{ \AA}$, $\Delta S \sim 0.18 \text{ \AA}^2$. We note that the increase of the relative distance (ΔE) between the combined electron levels

corresponds to a regular decrease of the frequencies ν_i , which is related to the increase of the effective size of the anion. For example, for crystal NaNO_2 , the interrelation between ΔE and ν_1 (both are in cm^{-1}) for various electron states is as follows: $^1A_1(0-1327)$, $^3B_1(18960-1124)$, $^1B_1(25980-1018)$, $^1B_2(\sim 40000-970)$ [25, 26].

The connection between the frequencies ν_i and the relevant conformation parameters, which is established by us, is of importance on the analysis of the temperature behavior of the optical spectrum structure, in particular, on the consideration of the inhomogeneous or homogeneous broadening of the vibration bands. On the whole, the low-temperature optical spectrum of the molecular centers under consideration is characterized by a quite small inhomogeneous widening. At low temperatures ($T \leq 10$ K), the half-widths of activation bands in the vibration and electron-vibration spectra are $\gamma \sim (0.1-10) \text{ cm}^{-1}$ [7, 8, 14, 16, 27]. We have revealed a correlation between the temperature behavior of the half-width γ_i of the vibration bands and the area S which is proportional to the radius of the first coordination sphere (r_1) of anion NO_2^- . This assertion is based on the comparison of the corresponding data on the RSL spectra for single crystals of NaNO_2 and MHal-NO_2^- , for which the above-presented inequality for the parameter S holds true. Specific features of the inhomogeneous broadening of an optical band are usually considered at low temperatures. In this case, the contribution of the homogeneous broadening to the summary contour of the band is minimized, and the value of γ_i is independent of T and is practically determined by the inhomogeneous broadening. At $\Delta T = (4.2-10) \text{ K}$, the values of γ_1 , γ_2 , and γ_3 of the bands of the TO-component of the spectrum in a single crystal NaNO_2 are, respectively, 1.1, 0.1, and 1.2 cm^{-1} [27] and are significantly less

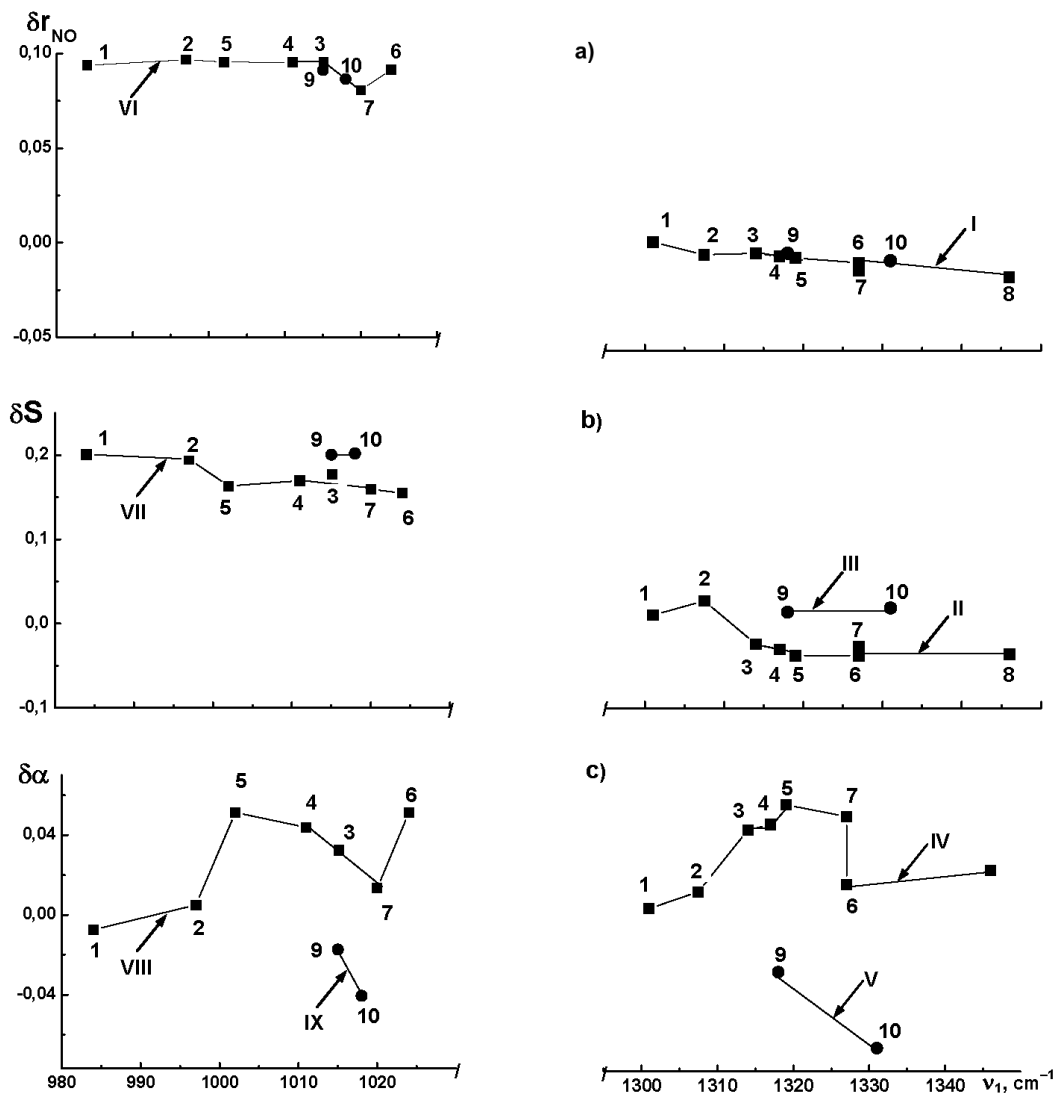


Fig. 3. Relationships between the relative change $\delta\Phi = (\Phi - \Phi_0)/\Phi_0$, where $\Phi = r_{NO}$ (a), S (b), α (c), $\Phi_0 = \Phi_{CsI}$ in the electron state 1A_1 , and the frequency ν_1 in the electron states 1A_1 (I-V) and 1B_1 (VI-X) of anion NO_2^- in crystals CsI (1), KI (2), CsBr (3), KBr (4), RbCl (5), KCl (6), NaBr (7), NaCl (8), KNO_2 (9), $NaNO_2$ (10) at low temperatures. Calculations are performed by data of the Table

than those in alkaline-halide single crystals, $\gamma_i = (2-9) \text{ cm}^{-1}$ [8, 13, 14]. We have observed also a considerable difference in the temperature-induced broadenings for the indicated bands, which determines a homogeneous widening of the spectrum. For example, as T increases from 4.2 to 80 K, the summary increase in the half-widths of RS bands is $\Delta\gamma_i(NaNO_2) = (0.05-1.6) \text{ cm}^{-1}$ [27] $< \Delta\gamma_i(MHal) = (2-47) \text{ cm}^{-1}$ [8]. The last inequality should be related to the enhancement of the anharmonic interaction of local vibrations of the center NO_2^- with phonons of the matrix with decrease in the area S ,

which corresponds to an increase in the overlapping of peripheral regions of the shells of the center and its nearest surrounding.

5. Conclusions

The experiment performed by us, analysis of literature data, and results of our calculations indicate the regular connection between the parameter of a position structure of the matrix (lattice constant d , radius r_1), frequencies of intramolecular vibrations ν_i , and the conformation

parameters (force constants f_r and f_α/l^2 , equilibrium distance r_{NO} , and area S) of anion NO_2^- . It is established that a change of the local surrounding of an anion and the excitation of its optical electron on the transition in the lowest excited state ${}^1A_1 \rightarrow {}^1B_1$ are accompanied by a change of parameters of the equilibrium configuration of the anion. Such summary changes can be as large as $\Delta f_r = 250 \text{ N/m}$, $\Delta(f_\alpha/l^2) = 110 \text{ N/m}$, $\Delta\alpha = 12^\circ$, $\Delta r_{\text{NO}} = 0.13 \text{ \AA}$, $\Delta S = 0.18 \text{ \AA}^2$. Especially significant conformational changes are observed on the excitation of the optical electron of the anion. An increase in the size of the anion with the relative energy ΔE between the relevant combining electron levels causes the enhancement of the effect of perturbation of the local surrounding of this anion, which is of certain interest for the studies of the radiation resistance of materials. We have established the connection between the radius r_1 , which is related to the overlapping of peripheral regions of the electron shells of anion NO_2^- and its nearest neighbors, and the value of inhomogeneous or homogeneous broadening of its vibration bands. The difference of the frequencies ν_i of the same vibration obtained by using different methods of registration of the spectrum can be used as a criterion of the inhomogeneity of optical centers by their spectroscopic characteristics. Such estimations are topical, in the first turn, at room temperature, when the correct separation of the contributions of the homogeneous and inhomogeneous broadenings of an optical band meets difficulties.

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ЛОКАЛЬНЕ ОТОЧЕННЯ, НОРМАЛЬНІ КОЛИВАННЯ ТА БУДОВА АНІОНА NO_2^- В ЮННИХ КРИСТАЛАХ

Л.А. Булавін, В.П. Сакун, А.В. Якунов

Резюме

Досліджено поведінку частот внутрішньомолекулярних коливань та рівноважної конфігурації ядерного кістяка аніона NO_2^- при зміні температури, складу матриці та електронному переході ${}^1A_1 \rightarrow {}^1B_1$ ($S_0 \rightarrow S_1$).