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Spectroscopy of interionic interactions in nitrite aqueous solutions

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Correlation has been studied between energy shifts of the vibrational and electron-vibrational absorption bands for $^1A_1 \rightarrow {}^1B_1$ and $^1A_1 \rightarrow {}^1A_2$ transitions of the impurity molecular anion NO_2^- in MNO_2 aqueous solutions (M = Li, Na, K, Cs) with its geometrical size. It is shown that the shortwave shift of the bands is due to decreasing nuclear skeleton area.

Изучена связь между энергетическими сдвигами колебательных и электронно-колебательных полос поглощения переходов $^1A_1 \rightarrow {}^1B_1$ и $^1A_1 \rightarrow {}^1A_2$ примесного аниона NO_2^- в водных растворах MNO_2 (M = Li, Na, K, Cs) и его геометрическими размерами. Показано, что уменьшение площади ядерного остова аниона вызывает коротковолновый сдвиг указанных полос.

The investigation of interionic interactions in aqueous solutions of nitrite salts MNO_2 (M = Li, Na, K, Cs) was the goal of this work. The influence of such interactions on the geometric structure, vibrational and electron-vibrational absorption $^1A_1 \rightarrow {}^1B_1$ and $^1A_1 \rightarrow {}^1A_2$ spectra of the NO_2^- molecular anion (MA) in aqueous solutions has been studied at 4.2 and 300 K.

The NO_2^- molecular anion (C_{2v} symmetry group) exhibits three undegenerate intramolecular vibrations: ν_1 (full symmetric stretching mode), ν_2 (full symmetric bending mode) and ν_3 (asymmetrical stretching mode). Basing on the experimental frequency values ν_1, ν_2, ν_3, the constants of the equilibrium geometric configuration of NO_2^- anion were calculated in the valence forces approach. ν_1 and ν_2 values were taken from [1]. Our calculations are of estimating character.

We used the formulae derived in [2]:

$$4\pi^2\nu_3^2 = \left(1 + \frac{2m_0}{m_N}\sin^2\alpha\right)\frac{f_r}{m_0}, \qquad (1)$$

$$4\pi^2(\nu_1^2 + \nu_2^2) = \left(1 + \frac{2m_0}{m_N}\cos^2\alpha\right)\frac{f_r}{m_0} + \frac{2}{m_0}\left(1 + \frac{2m_0}{m_N}\sin^2\alpha\right)f_\alpha, \qquad (2)$$

$$16\pi^4\nu_1^2\nu_2^2 = 2\left(1 + \frac{2m_0}{m_N}\right)\frac{f_r f_\alpha}{m_0^2}, \qquad (3)$$

where ν_i are expressed in s^{-1}, m_0 and m_N are the masses (in g) of O and N atoms, respectively, f_r and f_α (in dyn/cm) are the force constants characterizing changes in the N–O bond length and the angle ∠ONO (2α), respectively. The estimation of the N–O bond length (r_{NO}) was carried out using the empirical formula of Badger [3]

$$f_r = 1.86 \cdot 10^5 \cdot (r_{NO} - 0.68)^{-3}, \qquad (4)$$

where f_r is in dyn/cm and the N–O bond length r_{NO} in Å. Basing on obtained r_{NO} and 2α values, the area (σ) for the equilibrium configuration of the NO_2^- anion nuclear skeleton was also evaluated.