Mean Life Time of Excited State of $n \rightarrow \pi^*$ Transition of Nitrate Ion in Solution

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The mean life time, T, of the excited state of the $n \rightarrow \pi^*$ transition of the nitrate ion in different solvents has been estimated from a spectrophotometric study. These T values are by a factor of $10^{-3}-10^{-4}$ smaller than computed values for vibration perturbation. The values decrease with increase in the hydrogen bonding power of the solvent. Hydrogen bonding perturbation has been suggested to be the cause of the observed life time of the excited state.

Introduction

The electronic transitions of the nitrate ion have been a subject of both theoretical [1–3] and experimental [4–12] investigations. The mean life time, T, of the excited state of the $n \rightarrow \pi^*$ transition should be infinite and its intensity zero [2] since it is a symmetry forbidden transition. The mechanism due to which it gets observable intensity is a mater of controversy [3, 9]. With a view to investigate the mechanism the present study was undertaken.

In the present paper the mean life times of the excited state of the $n \rightarrow \pi^*$ transition of the nitrate ion have been computed from observed spectra in different solvents. The results are discussed in the light of various possible perturbations of the electronic states.

Mean Life Time of the Excited State

If a molecule is in an excited state, in the absence of an external electromagnetic field, on the average, after a time [13]

$$T = 1/A_{mn} \tag{1}$$

it will emit a photon. T is called the mean life time of the excited state and A_{mn} is Einstein's coefficient given by [13]

$$A_{mn} = \frac{64\,\pi^4\,\tilde{\nu}^3\,e^2}{3\,h}\,D_{mn} = 7.24 \times 10^{10}\,\tilde{\nu}^3\,D_{mn} \tag{2}$$

where $\tilde{\nu}$ is the frequenc of the radiation in cm^{-1} and $e^2 D_{mn}$ is the square of the dipole moment of the transition.

$$D_{mn} = 3.98 \times 10^{-20}\,\frac{1}{\tilde{\nu}} \int \varepsilon(\nu)\,\mathrm{d}\nu\,. \tag{3}$$

$\int \varepsilon(\nu)\,\mathrm{d}\nu$ is the area of the absorption curve, D_{mn} is also related to the oscillator strength, f, given by

$$f = (8\,\pi^2\,m_e\,c\,\tilde{\nu}/3\,h)\,D_{mn} = 1.085 \times 10^{11}\,\tilde{\nu}\,D_{mn}\,,$$
$$\text{and } f = 4.32 \times 10^{-9} \int \varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu}\,. \tag{4}$$

$\tilde{\nu}$ and f values have been determined from absorption measurements. Substituting these values in Eqs. (1) to (4) T values have been computed.

The observed characteristics of the absorption band and the T values of the excited state have been collected in Table 1. The observed T values are much smaller than expected. The intensity (f value) in the forbidden transitions is usually due to the following three causes (l. c. [13, 14]):

(1) Vibration perturbation of the electronic state,
(2) hydrogen bonding, and
(3) solvent-perturbation.

Salt	Solvent	Position		Intensity	Life Time
		$\lambda_{\max}$ mμ	$\tilde{\nu}_{\max}$ cm^{-1}	$f \times 10^5$	$T \times 10^5$ sec
Tetramethyl Ammonium nitrate	Acetonitrile	313	31 949	7.7	1.91
	Ethanol	304	32 895	13.0	1.06
	Water	303	33 003	13.8	1.00
Tetraethyl Ammonium nitrate	Acetonitrile	312	32 051	8.4	1.74
	Ethanol	303	33 003	13.6	1.02
	Water	302	33 112	15.4	0.88

Table 1. Characteristics of the band.

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Vibration Perturbation

The vibration perturbation of the nitrate ion has been studied by STRICKLER and KASHA [3]. The wave function of the nitrate ion, assuming that the Born-Oppenheimer approximation [15] holds is [3]

$$\Psi_{kl}(x\,Q) = \Theta_k(x\,Q)\,\Phi_{kl}(Q) \tag{5}$$

where x represents the coordinates of all the electrons and Q designates the normal coordinates of the nitrate ion. The subscripts k and l enumerate the electronic and vibrational states respectively.

Assuming the nuclei to be fixed in some configuration Q the electronic transition moment between the ground state g and the excited state k is given by

$$M_{\mathrm{gk}}(Q) = \int \Theta_{\mathrm{g}}^*(x,Q)\,M(x)\,\Theta_{\mathrm{k}}(x,Q)\,\mathrm{d}x \tag{6}$$

where $M(x)$ is the electric dipole operator of the electron.

The oscillator strength for the transition g → k, assuming all molecules to be in the ground state is given by [16]

$$f_{\mathrm{g}\to\mathrm{k}} = \frac{8\,\pi^2\,m}{3\,h^2\,e^2}\,E_{\mathrm{g}\to\mathrm{k}}\,|\,\overline{M}_{\mathrm{gk}}\,|^2 \tag{7}$$

where

$$|\,\overline{M}_{\mathrm{gk}}\,|^2 = \int \Phi_{\mathrm{g}0}(Q)\,|\,M_{\mathrm{gk}}(Q)\,|^2\,\Phi_{\mathrm{g}0}(Q)\,\mathrm{d}Q\,. \tag{8}$$

Expanding $M_{\mathrm{gk}}(Q)$ we have

$$\begin{aligned} M_{\mathrm{gk}}(Q) = M_{\mathrm{gk}}(0) &+ \sum_a \left(\frac{\partial M_{\mathrm{gk}}}{\partial Q_a}\right)_0 Q_a \\ &+ \frac{1}{2}\sum_{a,b}\left(\frac{\partial^2 M_{\mathrm{gk}}}{\partial Q_a\,\partial Q_b}\right)_0 (Q_a)\,(Q_b)\,. \end{aligned} \tag{9}$$

Since the n → π^* transition is forbidden the first term is zero. The second term is also zero since there are no vibrations of proper symmetry which could enable the transitions. Hence [3]

$$|\,\overline{M}_{\mathrm{gk}}\,|^2 = \sum_a \sum_{b>a} \left|\left(\frac{\partial^2 M_{\mathrm{gk}}}{\partial Q_a\,\partial Q_b}\right)_0\right|^2 \overline{Q}_a^{\,2}\,\overline{Q}_b^{\,2}. \tag{10}$$

Substituting the estimated value [3] of $|\,\overline{M}_{\mathrm{gk}}\,|^2$; Eqs. (4) to (10) yield $T \sim 4.5 \times 10^{-2}$ sec. This value is much larger than the observed ones (Table 1). So vibration perturbation alone is not sufficient to explain the observed T values.

Hydrogen Bonding

The hydrogen bonding perturbation is similar to that of the vibration perturbation. But there is no symmetry restriction [14]. Since the nitrate ion is symmetrical there is no single vibration which could produce sufficient perturbation. The hydrogen bonding is equivalent to placing a positive charge near the electronic cloud of the nitrate ion and the energy arises due to its interaction with the electron cloud. In many cases, where the vibration perturbations are strong the amounts of the electronic perturbations due to hydrogen bonding and vibration are expected to be of the same order [3]. The observed T values of the n → π^* transition may be attributed mainly to hydrogen bonding. The T values also decrease with the increase in hydrogen bonding power of the solvent (Table 1).

Solvent Perturbation

The oriented solvent dipoles in the case of polar solvents are also expected into disturb the symmetry of the ion, which makes the transition forbidden. Acetonitrile cannot form hydrogen bonds, but it is strongly polar. The solvent perturbation may be the cause of the observed T value in acetonitrile solvent. The T values in the case of acetonitrile are much larger than in ethanol or water, suggesting that the solvent interaction is much smaller than the hydrogen bonding perturbation.

Experimental

The absorption measurements in the region 250 to 360 mμ have been carried out with a UVISPEK spectrophotometer at 25 ± 1 °C. To minimize the effect of the cation, which [17] is proportional zu Z/r, where Z is the charge and r is the radius of the cation, and due to the solubility in organic solvents, tetraalkyl ammonium nitrates for which the values of Z/r are very small, were selected for study. Both tetramethyl ammonium nitrate and tetraethyl ammonium nitrate were prepared starting with reagents of A. R. grade. The solvents acetonitrile and ethanol used were of A. R. grade. For making aqueous solution triply distilled water was used.

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