

Quantum-Mechanical Analysis of Intensity Distribution in Resonance Raman and Two-Photon Absorption Spectra of Nucleic Acid Base Pairs

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This study continues the investigation of the resonance Raman (RR) and two-photon absorption (TPA) spectra of nucleic acids by direct calculations of the intensity distribution with the quantum-mechanical method [1] for the adiabatic model in the Herzberg-Teller approximation. In [1] it is suggested that one- and two-photon absorption spectra as well as luminescence and Raman resonance spectra of polyatomic molecules be described using a single approach, in line with the similarity of their physical nature. In one-photon absorption spectra the Herzberg-Teller effect may be quantitatively described with confidence using the procedure [2]. Extension of this procedure to RR and TPA spectra allows one to calculate vibronic coupling and evaluate the relative intensities of lines in these spectra using the same set of initial data. Inclusion of the vibronic term makes it possible to explain the presence of lines corresponding to one-quantum nontotally symmetric vibrations, their odd overtones and combinations. In this study, the method of direct quantum-mechanical calculations is applied to the calculation of the RR and TPA spectra of adenine-thymine (A-T), adenine-uracil (A-U) and guanine-cytosine (G-C) base pairs.

It is shown that the basic features of the intensity distribution in the spectra can be explained only by taking into account the vibronic mixing of electronic states and the contribution to the components of the scattering tensor from excited electronic states located close to the resonance state. Furthermore, it should be noted that the influence of a particular excited electronic state on the intensity distribution in RR spectrum depends not only on the closeness of this state to the resonance state, but also on such factors as the character of the vibronic interaction and the oscillator strength of the corresponding transition. The calculated results agree satisfactorily with experimental RR spectra of A-T, A-U and G-C [3] excited by laser radiation at 266, 240, 218 and 200 nm. The comparative analysis of vibration mode activity was made. A common feature of these spectra is the redistribution of intensity between the bands of two vibrations in passing from the RR spectra corresponding to the resonance with the first two $\pi\text{-}\pi^*$ transitions to the spectra corresponding to the resonance with the third and fourth $\pi\text{-}\pi^*$ transitions. This feature, which was reflected in our calculations, can be explained by the complexity of intramolecular interactions and by marked changes in the geometrical parameters due to the electronic excitation.

The direct quantum-mechanical calculations of the relative intensities of lines in the TPA spectra of A-T and A-U in the region of the second transition and of G-C in the region of the first $\pi\text{-}\pi^*$ transition were also performed. Previously, the method [1] was applied to the description of the RR and TPA spectra of adenine, thymine, uracil and guanine [4-5]. The general and specific features of the intensity distribution in the RR and TPA spectra of nucleic acid base pairs A-T, A-U, G-C and single molecules (adenine, thymine, guanine and cytosine) are compared and discussed.

[1] T. Burova, Zh. Strukt. Khim. 38 (1997) 248-254.

[2] M. Kovner, M. Prijutov, Dokl. Akad. Nauk SSSR 204 (1972) 634-636.

[3] S. Fodor, T. Spiro, J. Amer. Chem. Soc. 108 (1986) 3198-3205.

[4] T. Burova, G. Ten, V. Kucherova, Optics and spectroscopy 95 (2003) 25-29.

[5] T. Burova, G. Ten, V. Kucherova, Optics and spectroscopy 97 (2004) 1-4.