Vibrational spectroscopy of macrocyclic compounds
with double intramolecular NH···N hydrogen bond

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Abstract

The purpose of this study was to understand the relationship between the vibrational structure and geometry of selected porphyrin-like macrocyclic compounds with double intramolecular hydrogen bonds, in the ground electronic state, by vibrational spectroscopy and computational quantum chemistry methods. The porphyrin, porphycene (constitutional isomer of porphyrin), and dibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene derivatives were selected for the research. The NH···N hydrogen bonds are located in the central part of the macrocycle and the nitrogen atoms form a quadrangular cavity in such systems. The hydrogen atoms of hydrogen bonds can assume either a *trans* or a *cis* configuration, with corresponding nitrogen atoms lying on the diagonal or on the adjacent corners of the cavity, respectively.

Based on a comparison of the vibrational spectra measured by Raman scattering and infrared absorption with the spectra simulated on the basis of quantum-chemical calculations, I assigned a *trans* configuration of the hydrogen atoms in the cavity for 2,3,7,8,12,13,17,18-octaethyl-5,15-diphenylporphyrin, 2,3,7,8,12,13,17,18-octaethyl-5,10-diphenylporphyrin, porphycene, dibenzo[b,i][1,4,8,11]tetraaza[14]annulene, 7,16-dimethyl-dibenzo[b,i][1,4,8,11]tetraaza[14]annulene and 6,8,15,17-tetramethyl-dibenzo[b,i][1,4,8,11]tetraaza[14]annulene. For porphycene and dibenzo[b,i][1,4,8,11]tetraaza[14]annulene I have assigned almost all the normal vibrations for the corresponding bands in the spectra. Moreover, for all tested compounds I assigned a band corresponding to the NH stretching vibration, which is an indicator of the hydrogen bond strength. For porphycene, harmonic quantum chemical calculations predicted a location of this band at about 2800 cm^{-1} and indicated that this band should be the most intense of all in the infrared absorption spectrum, but no such band was observed in that spectral range of the measured spectra. Inspired by this discrepancy, I measured the inelastic neutron scattering spectra as a function of temperature, infrared absorption spectra and Raman scattering in solutions, in low temperature noble gas matrices and in the crystals as a function of temperature, for three different isotopologues of porphycene. I also performed a number of anharmonic quantum chemical calculations and simulations of vibrational spectra. I obtained the assignments for nearly all vibrations in porphycene, including the NH stretching band, by combining the results of measurements with the literature data concerning the fluorescence spectra in low temperature noble gas matrices, in ultracold helium nanodroplets and in supersonic molecular beam, and by comparison with molecular dynamics simulations.

One of the techniques used was the surface-enhanced Raman spectroscopy. The amplification of Raman scattering by plasmons in metallic nanostructures turned out to be so large that it allowed me to register the single molecule Raman spectra of porphycene. Measuring the spatial distribution of the spectra on the nanostructured gold surfaces for the equimolar mixture of the two porphycene isotopologues and observation of the time evolution of it have shown that the spectra come from individual molecules.

As expected, it was noted that the bands corresponding to the vibrations of this type have different position for different tested compounds. I proposed numerical quantum-chemical method involving the observation of structural and spectral changes due to systematic modification of the distance between the heavy atoms involved

in hydrogen bond formation. In this way, I investigated several porphyrin, porphycene, and tetraaza[14]annulene derivatives, significantly differing in hydrogen bond strength from each other. As a result, I received a number of dependencies linking in pairs geometric (bond lengths and angles between them) and spectroscopic parameters (bands positions in the Raman, infrared absorption, and nuclear magnetic resonance spectra). I checked the correctness of the predictions by this method on a group of a porphyrin-like compounds with the geometry of the cavity modified by substituents.