MODERN TENDENCIES IN VIBRATIONAL ANALYSIS OF MOLECULES

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ABSTRACT

The structure of energy spectra of vibrational states for polyatomic molecules depends strongly on the number of discrete vibrational states and their distance from the ground and corresponding dissociation states. Actually it is possible to approximately separate out the harmonic region nearby the bottom of the potential surface (at least for the semirigid molecules), the region nearby the dissociation limit where local modes are of essential importance, and the intermediate region which is characterized by the developed sets of polyads of vibrational states. The report will be mainly connected with this intermediate region [1,2]. The theory of polyads is closely connected with the theory of resonance states. Any polyad is determined as a set of vibrational states characterized by one and the same polyad vector, composed of the so called polyad coefficients, and polyad (secondary) quantum number. The determination of these quantities and their relation to molecular structure is very important for vibrational spectra assignment and interpretation. That is why the polyad structure of vibrational spectra was actively discussed in recent years. The technique most suitable to the polyad description is based on the formalism of creation/annihilation operators and canonical van Vleck perturbation theory [3]. We discuss tendencies of the polyad theory development and some new techniques for solving the problem of polyad structure of vibrational spectra and constituent vibrational states. A very important tendency in molecular vibrational analysis is also connected nowadays with detection and treating resonance states of different types (not necessarily related to the polyads). The method based on canonical perturbation theory is developed for systematic identification of essential resonances. It is suitable for molecules of significant size and complexity as illustrated by several examples of molecules up to ten atoms.

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