

Deviation of OH bond in H₂O molecule

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The force constant matrix has been calculated for H₂O molecule in liquid phase under approximation taking into account the possibility of "mixing" different types of its eigen and noneigen normal vibrations belonging to the same irreducible representation of C_{2v} symmetry group.

Проведены расчеты силовой матрицы молекулы H₂O в жидкой фазе в приближении, которое учитывает возможность "смешивания" форм ее собственных и несобственных нормальных колебаний, относящихся к одному и тому же неприводимому представлению группы симметрии C_{2v} .

The force constant matrix of H₂O molecule has been calculated in [1]. To that end, the inverse spectral problem of vibrational spectroscopy was solved. Using the method taking into account both eigen and noneigen normal vibration frequencies, the direction of chemical bond O–H has been found to do not coincide with that of straight line connecting the O and H atomic nuclei. The chemical bond deviation was equal to 6° for H₂O molecule in liquid phase and 2° for that in gas phase. The deviation angle increase from 2° to 6° at gas-liquid phase transition is due to the influence of the nearest surrounding on the molecule. This process is accompanied by changes in normal vibration frequencies and forms.

When solving the inverse vibrational spectral problem in [1], the approximation used did not account for the possibility of "mixing" of eigen and noneigen normal vibrations of H₂O molecule in liquid phase. In this work, an attention is drawn to the fact that for a molecule in a condensed phase, it is impossible to separate strictly eigen vibrations forms from noneigen ones.

Due to the interaction with surrounding, the translational noneigen vibrations of H₂O molecule ω_{tx} , ω_{ty} , ω_{tz} can be accompanied by some deformation of the molecule. Similarly, eigen normal vibrations ω_1 , ω_2 , ω_3 can be accompanied by periodic displace-

ments of the molecule mass center. Both processes can be considered as "mixing" of eigen and noneigen normal vibrations of H₂O molecule in liquid phase. The same situation can take place for noneigen vibrations ω_{rx} , ω_{ry} , ω_{rz} . For calculations, we proceeded from results presented in [1]. The force constant matrices for different isotopic modifications of water were considered to be identical. The parameters of normal vibrations were determined from vibration frequencies of H₂O and D₂O molecules in liquid phase.

The possibility of "mixing" of those normal vibration forms which correspond to the same irreducible representation of the C_{2v} group are here taken into account. Normal vibrations of H₂O molecule and their irreducible representations are listed in the Table 1. It is seen that there are three normal vibrations which are transformed into each of A_1 and B_2 irreducible representations. Consequently, the "mixing" result of different normal vibration forms belonging to one irreducible representation can be represented as a product of the orthogonal matrix 3×3 by the components of basic vectors of the vibrations being mixed.

The basic vectors defining the vibration forms without considering their possible mixing were chosen the same as in the [1] and are presented by the L matrix