E1

ROTATIONAL ENERGY SURFACES OF MOLECULES EXHIBITING INTERNAL ROTATION

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The concept of a rotational energy surface, as introduced by Harter and Patterson[1] and elaborated by others, will be briefly reviewed. (Such surfaces represent one aspect of the application of methods from classical mechanics, modified by semi-classical quantization, to the treatment of higher excited states of quantum systems, where the correspondence principle should be applicable.) Rotational energy surfaces constructed for torsional levels below the top of the barrier in acetaldehyde, an asymmetric top molecule with a symmetric top internal rotor, will then be described, paying particular attention to their stationary points, separatrices and catastrophe histories as a function of J. The concept of the "best" quantization axis for the molecule-fixed component of the total angular momentum will be examined from a classical point of view, and attempts to use these ideas for labeling eigenvectors obtained from a large matrix diagonalization will be discussed.

1. W. G. Harter and C. W. Patterson, J. Chem. Phys. 80, 4241 (1984).

E2

THE MICROWAVE SPECTRUM OF THE ANILINE–WATER VAN DER WAALS COMPLEX

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Hydrogen bonded complexes are of considerable interest since they may serve as prototypes of larger systems found in the theory of liquids, bio–molecules, and many other fields. There are several types of hydrogen bonds, e.g. O–H...O as in the water dimer[1] or in the phenol–water complex[2], or N...H–O as in ammonia–water[3]. All of them show up a (almost) linear equilibrium structure.

We studied the aniline–water complex by means of a pulsed molecular beam microwave Fourier transform spectrometer. The complex can be described in terms of a centrifugal distorted rotor with the rotational constants A = 3161.49(42) MHz, B = 1114.4722(18) MHz, and C = 1070.9828(18) MHz. The planar moments $\frac{1}{2}(I_{aa}+I_{cc}-I_{bb})$ of aniline and water agree within 0.7 uÅ^2 which indicates that the water molecule is located in the ac–plane of the aniline monomer. Consequently, the μ_b dipole moment component should be zero which is consistent with the fact that very strong a–type lines but no b–type lines could be observed. Assuming a linear N...H–O bond two possibilities remain for the position of the water proton not involved in the hydrogen bond. Either the hydrogen is directed towards the amino protons or away from them. Only in the latter conformation the dipole moments of water and aniline are almost parallel and result in a dipole moment for aniline–water consisting of a almost pure μ_a component which explains the absence of c–type transitions in the spectrum.

[1] T. R. Dyke, K. M. Mack, and J. S. Muenter, J. Chem. Phys. 66, 498 (1977).

[2] recently studied in our group.

[3] T. Herbine and T. R. Dyke, J. Chem. Phys. 83, 3768 (1985).