A CORRELATION BETWEEN THE INTENSITIES OF VIBRATIONAL OVERTONE TRANSITIONS AND THE REPULSIVE BRANCH OF THE MOLECULAR POTENTIAL

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Energy levels En and overtone n-0 transition intensities of an oscillator with a distorted Morse potential (DMP) and a linear dipole moment function are calculated. The values of (En-E0)/n, when plotted vs n, fall on a straight line very closely for various forms of DMP. A linear least-squares fit to this plot gives the effective anharmonicity parameter, which is then employed to construct an "effective" Morse potential (EMP) for the given DMP. The EMP closely follows the DMP along the most part of the attractive branch and near equilibrium, but in general declines from the DMP in the repulsive region. The EMP intensities systematically either overestimate or underestimate the DMP ones, depending on whether the repulsive branch of the EMP runs over or under the DMP, respectively, and the discrepancies rapidly increase with the overtone number. This effect of the repulsive branch is investigated quantitatively. In particular, the existence of a correlation between the steepness of the repulsive branch of the molecular potential and the rate of the intensity falloff with the overtone number, as predicted by the quasiclassical theory [E.S. Medvedev, J. Chem. Phys. 100, 7192(1994)], is demonstrated conclusively. A semiempirical potential for hydroxyl radical is tested for the occurrence of the effect of the repulsive branch.

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