THE RIGIDITY OF THE TRIPLY BONDED VAN DER WAALS COMPLEXES AND BIOMOLECULES

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The rigidity of the van der Waals(vdW) complexes were investigated by monitoring the rotational spectra of several dimers of dimethylether(DME) with a small molecule. The FTMW spectrum of the DME monomer exhibits quartet splitting due to the internal rotation of two methyl tops. The vdW bonding, however, effectively reduces the large amplitude motions in the complex and forms a rigid assembly. The rigid assembly formed by the weak triple bonding may be related to that in the biomolecules such as DNA bases or proteins. The FTMW spectrum of the DME dimer [a] exhibited the $A-E$ splitting typical of a one-top molecule: Only one methyl group could exhibit internal rotation, since the three methyl groups among four in DME_2 were hydrogen-bonded. Similarly, the triply bonded vdW complexes DME$\cdots$$F_2C{=}CH_2$, DME$\cdots$$F_2C{=}CFH$ [b], DME$\cdots$OCS, and DME$\cdots$$CO_2$ [c] exhibited the singlet spectrum corresponding to a rigid conformation. Instead, the singly bonded vdW complex DME$\cdots$$H_2O$ [d] is flexible and exhibits not only inversion doublet but also multiplet spectrum due to the internal rotation of the methyl groups. Within an organism, biomolecules such as DNA or enzyme protein maintain their steric conformation with hydrogen bonds, where the identical biomolecules must be exactly the same steric conformation. On the other hand, the smaller binding energy is preferable for their constant repeating of association and dissociation. These conflict properties may be accomplished with the triple vdW bond which can form a rigid assembly with weak intermolecular bond.

[a] Tatamitani, Liu, Shimada, Ogata, Ottaviani, Maris, Caminati, and Alonso, $JACS$, **124**, 2739 (2002).
[b] Tatamitani and Ogata, $JMSpec.$, **222**, 102 (2003).
[c] Newby, Peebles, and Peebles, $JPC\ A$, **108**, 7372 (2004) and $JPC\ A$, **108**, 11234(2004).
[d] Caminati, Dell'Erba, Favero, Maris, Melandri, Ottaviani, Velino, *Spectroscopy in the 21st Century*, p.52, Hayama, Japan (2002).