Potential energy surface and rotational-vibrational dynamics of the $F^{-}-CH_4$ anion complex

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The $F^{-}-CH_4$ anion complex has a single hydrogen-bonded C_{3v} equilibrium structure and our best *ab initio* predictions for its D_e and D_0 values are 2398 ± 12 and 2280 ± 20 cm^{-1}, respectively [1]. We developed a full-dimensional potential energy surface (PES) for $F^{-}-CH_4$ based on a permutationally invariant fit to CCSD(T)/aug-cc-pVTZ energy points [1]. $F^{-}-CH_4$ has been recently used as a precursor in novel photodetachment spectroscopy to investigate the transition state region of the corresponding neutral system. Experiment found a substantially larger splitting (1310 cm^{-1}) in the spectrum of $F^{-}-CH_4$ than the well-known spin-orbit splitting (404 cm^{-1}) of the F atom, in good agreement with our theoretical prediction [2]. We computed the vibrational spectrum of $F^{-}-CH_4$ using the MULTIMODE code and our full-dimensional *ab initio* PES [1]. Experimental data are available in the CH stretching region and the MULTIMODE results [1] are in good agreement with the measured spectrum. Recently we performed reduced-dimensional quantum rotational-vibrational computations for the $F^{-}-CH_4$ and $F^{-}-CH_2D_2$ complexes in a polyspherical coordinate system using the GENIUSH code [3,4] and the *ab initio* PES [5]. A one-dimensional CF stretch, 1D(R_{CF}), a two-dimensional intermolecular bend, 2D(θ, φ), and a three-dimensional intermolecular, 3D(R_{CF}, θ, φ), rigid methane model provided vibrational energies for the low-frequency, large-amplitude modes in good agreement with full-dimensional MCTDH results for $F^{-}–CH_4$. The 2D(θ, φ) and 3D(R_{CF}, θ, φ) four-well computations, describing equally the four possible $CH–F^{-}$ bonds, showed that the ground-state tunneling splitting is less than 0.01 cm^{-1}. For the hydrogen-bonded CH stretching fundamental a local-mode model was found to have almost spectroscopic accuracy [5]. The 2D(θ, φ) and 3D(R_{CF}, θ, φ) rotational–vibrational computations on the T_d-symmetric four-well PES revealed that in most cases $F^{-}–CH_4$ behaves as a semi-rigid C_{3v} symmetric top [5]. For the degenerate intermolecular bending vibrational states substantial splittings of the rigid rotor levels were observed. For $F^{-}–CH_2D_2$ the rotational levels guided the assignment of the vibrational states to either $F^{-}–H$ or $F^{-}–D$ connectivity [5].

[1] G. Czakó, B. J. Braams, J. M. Bowman, *J. Phys. Chem. A* **2008**, *112*, 7466.
[2] M. Cheng, Y. Feng, Y. Du, Q. Zhu, W. Zheng, G. Czakó, J. M. Bowman, *J. Chem. Phys.* **2011**, *134*, 191102.
[3] E. Mátyus, G. Czakó, A. G. Császár, *J. Chem. Phys.* **2009**, *130*, 134112.
[4] C. Fábri, E. Mátyus, A. G. Császár, *J. Chem. Phys.* **2011**, *134*, 074105.
[5] C. Fábri, A. G. Császár, G. Czakó, *J. Phys. Chem. A* **2013**, DOI: 10.1021/jp312160n.