COMMENTS

Reply to "Comment on 'Nature of the Chemical Bond in Protonated Methane'"

Felipe P. Fleming,[†] André G. H. Barbosa,*[,‡] and Pierre M. Esteves*[,†]

Instituto de Química, Universidade Federal do Rio de Janeiro, Brazil, and Instituto de Química, Universidade Federal Fluminense, Brazil

Received: December 11, 2006 ; In Final Form: February 23, 2007

Hinkle et al. raise two important issues on our work "Nature of the Chemical Bond in Protonated Methane",[1] which we would like to discuss. They are, namely, the inaccuracy of two statements we make in the text and the rebuttal of the assignment proposed to the vibrational bands at 2400 and 2700 cm^{-1}. All of these issues were addressed in a private communication with Prof. Bowman, and we would like to thank him for making the discussion public.

In the third paragraph of our manuscript we say that "...recent ab initio molecular dynamics and quantum diffusion Monte Carlo calculations show that the C_s(I) structure is populated up to 80% of the simulation.", which was criticized by Hinkle et al. for two reasons. Instead of "...C_s(I) structure...", we should have said "...C_s-like structures...", a term proposed by Padma et al.[2] They are absolutely correct in their statement. This was a mistake that we overlooked because we intended to state "C_s-like structures" in the first place. The model we proposed really fit this definition of Padma et al. because the "C_s-like structures" do not depend on a local symmetry, but only on a distance between two protons. Any structure leading to a proton distance in the neighborhood of 1.05 Å (the bond distance of H_2^+)[3] is within the definition of a "C_s-like structure". The fact that in the C_{2v} structure the distance between two protons is 1.18 Å[4] is exactly what we suggest is the driving force for the fluxionality of the species because the C_{2v} structure would be formed by a stretch in the distance between the two protons that form the H_2^+ moiety.

As for the statement that the 80% value was obtained by Padma et al., Hinkle et al. is also correct. But the original sentence stated that the results were "... up to 80%...". As we suggested through a private communication, in their comment Hinkle et al. gave the result of the mentioned analysis and it is 70%. Because we addressed all results in the literature collectively and not separately, the results are up to 80%. This does not strictly mean that DMC affords the 80% result.

The second issue raised by Hinkle et al. is about the assignment proposed by us to the bands at 2400 and 2700 cm^{-1}. It is important to state that we did not carry out any detailed vibrational calculations. Our main concern in this work was the electronic structure of CH_5^+ and the derivation of a model for the chemical structure of this fluxional species. We did perform the analysis of the Hessian of the CASSCF(8,8) wavefunction but only to characterize the resulting structures as minima or as transition states. The thorough treatment given by McCoy and Bowman[4−7] is much more sophisticated than the one we used, and accurate numerical results are expected for the vibrational frequencies.

We would like to thank Hinkle et al. for pointing out the misleading statement in our original work where it is giving the wrong impression that our model concerned only the C_s(I) structure, instead of "C_s-like structures". Finally, we would like to restate that the major concern of our work was the electronic structure of CH_5^+ and its chemical structure.

References and Notes

(1) Fleming, F. P.; Barbosa, A. G. H.; Esteves, P. M. *J. Phys. Chem. A* **2006**, *110*, 11903.

(2) Padma, K. P.; Marx, D. *Phys. Chem. Chem. Phys.* **2006**, *8*, 573.

(3) Linstrom, P. J.; Mallard, W. G. *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; National Institute of Standards and Technology: Gaithersburg, MD, 2005.

(4) Johnson, L. M.; McCoy, A. B. *J. Phys. Chem. A* **2006**, *110*, 8213.

(5) McCoy, A. B. *Int. Rev. Phys. Chem.* **2006**, *25*, 77.

(6) Huang, X.; Johnson, L. M.; Bowman, J. M.; McCoy, A. B. *J. Am. Chem. Soc.* **2006**, *128*, 3478.

(7) Huang, X.; McCoy, A. B.; Bowman, J. M.; Johnson, L. M.; Savage, C.; Dong, F.; Nesbitt, D. J. *Science* **2006**, *311*, 60.

---

* Corresponding authors. E-mail: andre@vm.uff.br; pesteves@iq.ufrj.br.

[†] Universidade Federal do Rio de Janeiro.

[‡] Universidade Federal Fluminense.

10.1021/jp0685131 CCC: $37.00