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COMMENTS

Comment on “Nature of the Chemical Bond in Protonated Methane”

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In their Letter entitled “Nature of the Chemical Bond in Protonated Methane,”[1] Fleming et al. make several statements that do not accurately represent the literature descriptions of earlier studies of CH_5^+. Specifically, the statement that the “... Diffusion Monte Carlo (DMC) calculations show that the C_s(I) structure is populated up to 80% of the simulation”[1] contradicts the results that were reported by us and by Jordan and co-workers.[2−5] Second, Fleming et al. suggest an assignment of the vibrational spectrum of CH_5^+ that contradicts previous assignments of the transitions in the 2400−3200 cm^{-1} region to CH stretching vibrations.[4,6,7] Given the complexity of CH_5^+ and the amount of experimental and theoretical interest in CH_5^+, we wish to correct the statement about localization and rebut the proposed new assignment of the infrared spectrum.

CH_5^+ has three low-lying stationary points, depicted in Figure 1. In their Letter, Fleming et al. state that the DMC calculations of the vibrational ground state wave functions that were calculated by us and by Jordan and co-workers show that as much as 80% of the population is in the C_s(I) structure. Contrary to the discussion ref 1, the value of 80% refers to the fraction of time CH_5^+ is in “C_s-like structures,” which were defined as ones in which one of the H−H distances is smaller than 1.15 Å.[7,8] This definition accounts for the full rotation of the H_2 unit through both C_s stationary points. As the value of the shortest HH distance in the C_{2v} structure is 1.18 Å,[9] this definition also includes excursions toward the C_{2v} saddle point. Further, the reported 80% value was obtained by Padma and Marx and is based on the results of ab initio molecular dynamics (AIMD) and path integral Monte Carlo (PIMC) studies at 300 K, and not from DMC calculations.[7,10] This quantity would have been much smaller had Padma and Marx evaluated the time CH_5^+ resides in a single C_s(I) minimum on the potential surface. The results of DMC, AIMD, and PIMC studies are all in agreement with the description of CH_5^+ in the introduction to ref 1, where CH_5^+ is characterized as being a highly fluxional species, with relatively flat potential surfaces along the two isomerization coordinates.

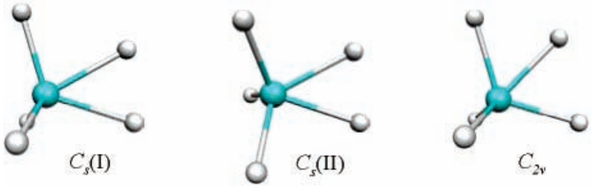

Figure 1. Three low-energy stationary points on the potential surface for CH_5^+.

The second point that we wish to address is the suggestion that the bands in the spectrum at ∼2400 and ∼2700 cm^{-1} could be reassigned to the H_2^+ stretch. Fleming et al. indicate that further analysis would be needed to verify this assignment.[1] We find it troubling that an assignment that disagrees with two sets of independent studies,[4,6,7] both of which were based on vibrational analysis of CH_5^+, was proposed without providing further validation. There are several ways to show that an assignment of the intensity in the 2400−2700 cm^{-1} region of the spectrum cannot be due to H_2^+ vibrational excitation.

The simplest is based on a normal-mode analysis. Analysis of the normal mode vectors shows that four of the five highest frequency normal modes of CH_5^+, calculated at the two stationary points with C_s symmetry, have at least 90% CH stretch character. The fifth has 70% CH stretch character and 30% H_2 stretch character but also has an integrated intensity that is an order of magnitude smaller than that for any of the other modes. Therefore the one high-frequency mode that has any H_2 stretch character is not an important contributor to the structure of the band in the infrared spectrum that extends from 2200 to 3200 cm^{-1}.[6]

The above analysis is admittedly qualitative and based on relatively low-level vibrational calculations. To further investigate this question, we employed two more sophisticated approaches in our studies of CH_5^+. In ref 4, we reported the results of vibrational configuration interaction (VCI) calculations in which the vibrational eigenstates of CH_5^+ were expanded in a self-consistently optimized normal mode basis.[11] Analysis of the states that contribute significant intensity near 2400 and 2700 cm^{-1} show that they all have significant CH stretch character. Similar conclusions were reported by Marx and co-workers.[6,7]

More recently, we used fixed-node DMC simulations to study vibrationally excited states of CH_5^+. In this approach we place a node along the coordinate of interest and calculate the energy of a state with one quantum of excitation in that coordinate.[12] To evaluate the H_2 stretch frequency, we required that the wave function changes sign at a specified value of the shortest H−H distance. The resulting fundamental frequency was 1200 cm^{-1}. Without information about the corresponding intensity of this fundamental, we are not prepared to base an assignment on this frequency. On the other hand, the factor of 2 difference between 1200 cm^{-1} and the 2400 or 2700 cm^{-1} values proposed by Fleming et al. leads us to conclude that excitation of the fundamental in the H_2 stretch is not responsible for the observed intensity near 2400 or 2700 cm^{-1}.

Any of the above three analyses would lead one to conclude that the H_2^+ stretch vibration cannot contribute to the observed

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intensity in the ~2400 or ~2700 cm^{-1} region of the spectrum, as Fleming et al. suggest.[1] Taken together, we find it unlikely that the H_2^+ stretch is responsible for intensity in the 2400 or 2700 cm^{-1} region of the infrared spectrum of CH_5^+.

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