THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2006, *110,* 11903−11905
Published on Web 10/10/2006

Nature of the Chemical Bond in Protonated Methane

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Received: August 22, 2006; In Final Form: September 11, 2006

Protonated methane, CH_5^+, is a key reactive intermediate in hydrocarbon chemistry and a borderline case for chemical structure theory, being the simplest example of hypercoordinated carbon. Early quantum mechanical calculations predicted that the properties of this species could not be associated with only one structure, because it presents serious limitations of the Born−Oppenheimer approximation. However, ab initio molecular dynamics and diffusion Monte Carlo calculations showed that the most populated structure could be pictured as a CH_3 tripod linked to a H_2 moiety. Despite this controversy, a model for the chemical bonds involved in this ion still lacks. Here we present a modern valence bond model for the electronic structure of CH_5^+. The chemical bond scheme derived directly from our calculations pictures this ion as $H_3C\cdots H_2^+$. The fluxionality can be seen as the result of a proton transfer between C−H bonds. A new insight on the vibrational bands at ~2400 and ~2700 cm^{-1} is suggested. Our results show that the chemical bond model can be profitably applied to such intriguing systems.

Introduction

Since its first announcement protonated methane,[1] CH_5^+, has been defying theories and pushing experimental techniques to new limits.[2,3] Many different theoretical approaches have been used[4−9] to characterize the structure of this ion, although it was only with the publication of its vibrational spectrum[10] that a link between theory and experiment could be established. Since then, all efforts have turned toward the assignments of the spectrum bands, which hold the essence of the structure of this "chemistry's chameleon".[8]

Early quantum mechanical calculations[4,6] gave a planar potential energy surface that was characterized as there being no molecular structure for this cation. The Born−Oppenheimer approximation (or clamped nuclei approximation) considers the electronic structure to be dependent only on the nuclei position, not on their momenta. For most molecules in their electronic ground states it consists of a meaningful approximation allowing the definition of a potential energy surface that describes the electronic energy of the system as a function of the position of the nuclei. The referent nuclei spatial configuration to minima in the potential energy surfaces is defined as the molecular structure of the system. The flat potential energy surface of the CH_5^+ ion, as a result of the small difference between saddle-points (C_s(II) and C_{2v} in Figure 1) and energy minima (C_s(I) in Figure 1), makes all five protons dynamically identical, which led to the conclusion that an assignment of a molecular structure for this cation without a nuclear dynamics consideration would be incorrect.

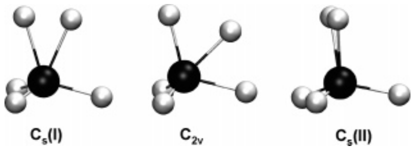

Figure 1. Stationary points of the potential energy surface of CH_5^+.

Despite that, recent ab initio molecular dynamics[7,11,12] and quantum diffusion Monte Carlo calculations[8,13,14] show that the C_s(I) structure is populated up to 80% of the simulation. The close relation between the calculated and the experimental spectra strongly suggests that the molecule can be viewed as a CH_3 tripod linked to a H_2 moiety through a 3-center−2-electron (3c2e) bond.[12,15−18] Because the assignments of vibrational spectrum bands are usually associated with the classical localized picture of chemical bonds that holds the atoms together in a molecule, the lack of a qualitative model for the chemical bonds involved in the conception of this fluxional ion is a major drawback in understanding its vibrational spectrum.

Method

We have employed a modern formulation of valence bond theory[19−21] in order to establish a chemical bond scheme for CH_5^+. This modern formulation is known as spin-coupled theory.[22−24] Its theoretical soundness and visual appeal makes it ideal for a well-defined and useful approach to difficult or unusual bonding situations. Theoretical aspects and results for different systems are discussed elsewhere.[25−27] In the spin-coupled theory, the resulting orbitals are a unique outcome of the calculation being associated with a definite physical meaning,[22,23,28] which enables one to associate these orbitals with the classical idea of chemical bonding. The bonds are a result of the overlap between the singly occupied orbitals associated

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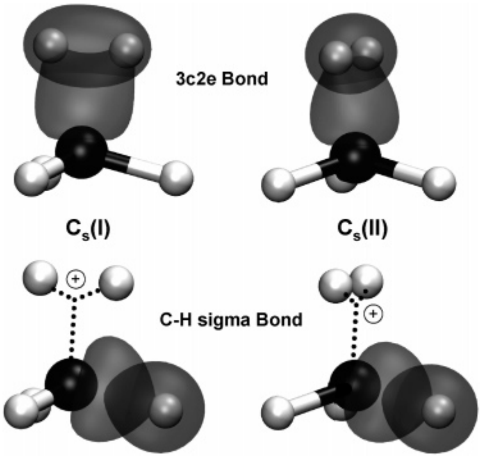

Figure 2. Spin-coupled orbitals for the C_s(I) and C_s(II) structures.

with one spin eigenfunction. The overlap between two orbitals is associated with the amount of space shared by the orbitals. This is the classical model associated with the formation of a chemical bond.[29−31] Thus, the interpretation of a chemical bond scheme is fairly forward from the spin-coupled wave function. It is noteworthy that the localization of the orbitals is not imposed but is the consequence of the variational optimization of the wave function. Therefore, the spin-coupled calculation renders different results when compared to other methods.[18] Apart from molecular orbital schemes where an infinity of orbital sets are associated with a given energy level, the spin-coupled orbitals are biunivocally associated with the electronic energy of the molecular system. The qualitative picture that emerges from the spin-coupled wave function is almost never altered by the inclusion of dynamical correlation.[22,26] On the other hand, a correlated wave function would be necessary for accurate energetic analysis.

Results and Discussion

Our results from the spin-coupled wave function for the CH_5^+ resemble the structure anticipated by Olah in the late 60's.[32] In both C_s(I) and C_s(II) structures the molecule has three 2-center−2-electron chemical bonds between the central carbon atom and three hydrogen atoms (C−H σ bonds in the tripod, Figure 2, bottom). These bonds are much alike the C−H bonds in methane.[33]

However, there is a major difference in the 3c2e scheme. The spin-coupled results show that this bond can be understood as a CH_3 radical linked to a H_2^+ (Figure 2, top). This interpretation is straightforward, once the wave function is governed by the perfect-pairing spin-coupling (Supporting Information, p S4). This simple model accounts for important features of the vibrational spectrum and also accommodates the fluxionality of the cation.

Because the carbon atom is not bound to one or the other hydrogen atom but to both at the same time, there is no particular reason this molecule should remain in the C_s(I) structure. Thus, it is expected to rotate around the bond, as the rotation of CH_3 around the C−C bond in ethane, for example. This is actually confirmed by the energy proximity between this structure and the C_s(II) structure, which corresponds to the transition state for the internal rotation of the H_2^+. The bonds involved in this last structure are very much the same as the ones in the global minima C_s(I) (Figure 2), including the dominating perfect-pairing spin-coupling scheme (Supporting Information, p S6).

When it comes to the intramolecular bond to bond rearrangement process, another manifestation of its fluxionality arises.

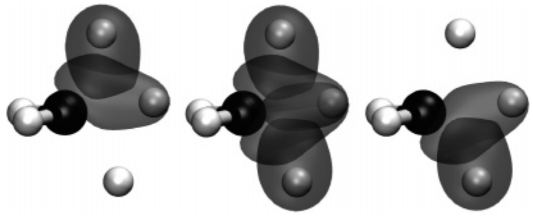

Figure 3. Spin-coupled orbitals for the C_{2v} structure. Left: σ bond between the upper hydrogen and the carbon, distorted by the central proton. Right: σ bond between the lower hydrogen and the carbon, distorted by the central proton. Center: both left and right figures merged.

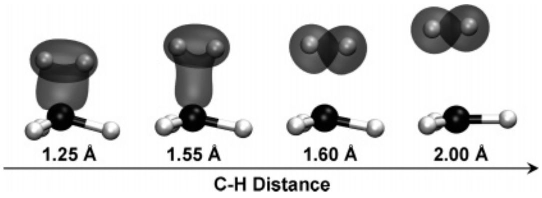

Figure 4. Decomposition curve for CH_5^+. The change of the spin-coupled orbitals for the C_s(I) isomer as a function of the distance between the carbon atom and any of the hydrogen atoms from the H_2^+ moiety.

The spin-coupled results for the C_{2v} structure indicate that it can be seen as a transition structure for the proton transfer between two different C−H σ bonds. In this structure, the 3c2e scheme gives place to two distorted σ bonds with the hydrogen atoms on each side (Figure 3, left and right). The C_{2v} structure is also dominated by the perfect-pairing spin coupling (Supporting Information, p S8). This picture is different from the current view of a 4c4e bond.[34] In the spin-coupled wave function, this 4c4e bond would manifest itself by a deviation from the perfect-pairing scheme, with two different spin-coupling schemes having similar coefficients.

As the H_2^+ (3c2e) bond stretches, the hydrogen atom interacts with the neighboring C−H bond, leading to the rearrangement. The acidity of the H_2^+ moiety accounts for these proton transfers. This H_2^+ acidity also accounts for the acidic nature of CH_5^+, a property broadly used in chemical ionization techniques in mass spectrometry.[35]

Recent studies[12,13] show that the distance distribution of the H−H pair in the H_2^+ moiety lie around 1 Å, which is much closer to the distance for H_2^+ (1.05 Å) than to H_2 (0.74 Å).[36] In both studies, the bands of the spectrum associated with the H_2^+ moiety are $\sim$2400 and $\sim$2700 cm^{-1}. The experimental vibrational frequency for the H_2^+ ion is 2321 cm^{-1}.[36] This may suggest an alternative interpretation of these bands. Instead of C−H stretching bands, these might be assigned as $[H-H]^+$ stretching bands, which would connect our valence bond model to the observed vibrational spectra. However, further analysis is mandatory to establish the validity of the qualitative view advocated here.

One question driven directly by the suggested model is the known decomposition of CH_5^+. When the 3c2e bond breaks, it leads to H_2 and CH_3^+ and not to the CH_3 radical and H_2^+. We calculated the decomposition curve of the ion by driving the H_2^+ moiety away from the tripod. As expected, around 1.55 Å the molecule goes through an electronic rearrangement and the bond scheme of CH_3 radical + H_2^+ gives place to $CH_3^+ + H_2$, giving the expected result, as shown in Figure 4. It is important to note that, throughout the dissociation curve, the same spin-coupling dominates the wave function (Supporting Information).[37] This rules out the possibility of an avoided crossing.

This new insight into the chemical structure of the CH_5^+ opens up new perspectives for the application of valence bond models for fluxional systems. Provided the existence of certain key nuclei arrangements with a substantial residence time, we can approach the fluxionality in a scheme that is known to give directly a meaningful chemical bond picture as a result.

Conclusion

The model proposed here for CH_5^+ is a simple combination of chemical bonds that is coherent with both theory and experimental data achieved so far. It is important to keep the model simple, but complete enough to allow a full interpretation of the observed body of experimental information about this exquisite and challenging ion. The chemical bond model lives on in fluxional systems.

Acknowledgment. We acknowledge Brazilian funding agencies (Propp-UFF, CNPq, FAPERJ and CAPES) for financial support, Dr. Jiabo Li for assistance with the VB2000 package,[24] and Mr. Bruno A. C. Horta and Prof. W. Bruce Kover for comments.

Supporting Information Available: Computational details available include: basis sets, geometries, orbital overlap matrices and spin function weights. This material is available free of charge via the Internet at http://pubs.acs.org.

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