Structural Dynamics of Protonated Methane and Acetylene

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The structural stability of protonated methane (CH_5^+) and acetylene ($C_2H_3^+$) has been investigated with *ab initio* molecular dynamics. In CH_5^+, the hydrogen atoms execute large amplitude pseudorotational motions. The hydrogen migrations are not disturbed by complexation with a hydrogen molecule. In contrast, for $C_2H_3^+$, the three hydrogen atoms permutate cyclically among the end carbon atoms and the bridging position. The theoretical results are consistent with and explain recent spectroscopic observation of these molecules.

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The conventional concept of a stable molecular structure assumes that, despite the possible existence of multiple isomeric forms, there always will be a unique structure that has the lowest energy and can be assigned as the ground-state equilibrium geometry. However, recently, there are strong theoretical and experimental evidences suggesting that the conventional notion of a stable structure may not be applicable to protonated methane (CH_5^+) and acetylene ($C_2H_3^+$) [1]. A thorough state-of-the-art theoretical study on the potential energy surface (PES) of CH_5^+ revealed that the minimum energy structure is best described as a highly distorted CH_3^+ unit strongly bound to a H_2 molecule [2]. However, there are several isomeric structures which are only slightly (<1 kcal mol^{-1}) higher in energy. Moreover, the activation energies for interconversions between these structures are negligibly small once the thermal vibrational energies are included. Recently, experiments on $C_2H_3^+$ using a Coulomb explosion imaging (CEI) [3] technique found that the average structure for this molecule is nonplanar with a proton located on an approximate bridging position but delocalized around (orbiting) the C-C bond. This proposed structure differs substantially from the previous theoretically predicted planar vinyl or planar H-bridged structures. The existence of multiple interconverting isomers with many degrees of freedom makes traditional pointwise quantum mechanical calculations of the potential energy surface very difficult. A more practical approach is to incorporate dynamical effects in the quantum mechanical calculations using the *ab initio* molecular dynamics (AIMD) technique developed by Car and Parrinello [4]. This will be used here to investigate the structure and dynamics of protonated methane acetylene. The results show that, at finite temperature, these molecules have no well defined structures. However, through the evaluation of the vibrational spectra, a direct interpretation of experimental data can be provided.

The AIMD method based on first principles local density functional theory in conjunction with pseudopotentials (PP) and plane-wave basis sets has been applied successfully to the study of the structure and dynamics of many molecular and condensed phase systems [4]. Most often norm-conserving PP were used in the calculations. Unfortunately, there are drawbacks for this potential model. For highly localized orbitals, such as those on first row elements and transition metals, a prohibitively large number of plane waves is required to accurately represent the atomic wave function. To this end, ultrasoft PP proposed by Vanderbilt and co-workers [5,6] were constructed for C and H atoms. All calculations were performed in a face centered cubic cell of size 30 a.u. with a plane-wave energy cutoff of 20 Ry with an effective electron mass of 400 amu and integration time steps of 4–6 a.u. Test calculations on simple hydrocarbons gave very favorable results on both the structure and dynamics. For CH_4, the calculated C-H bond length of 1.112 Å is in reasonable agreement with the experimental value of 1.094 Å. For C_2H_4, the calculated C-H and C-C bond lengths of 1.107 and 1.378 Å, respectively, are to be compared with the observed values of 1.085 and 1.339 Å, respectively. The PP developed here generally overestimate the bond lengths by about 2%–3%, and the calculated vibrational frequencies are about 4%–6% too low.

The calculations on CH_5^+ were started with the energetically unfavorable trigonal bipyramidal structure [2]. Several structures corresponding to local minima and maxima were located and identified with the structures predicted by the conventional *ab initio* quantum mechanical method. After optimization of the electronic wave function and geometry, the system was equilibrated at 300 K. The atomic trajectories for 60 000 time steps (6.4 psec) were then collected for analysis. No drift in the total conserved energy was observed within this time interval.

Analysis of the C-H bonds shows that the H atoms are always attached to the C atom and vibrate with an average bond length of 1.15 Å and an amplitude of ±0.06 Å. Occasionally some H atoms become more

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tightly bound with a bond length of 1.10 Å and a smaller vibrational amplitude of ±0.02 Å. Plots of the interatomic H$\cdots$H distances reveal some very interesting dynamics. For example, in the first 20 000 time steps (Fig. 1), H_1 is farthest away from H_2, but it is closer to the other three H atoms and, momentarily, forms an instantaneous H-H bond with one of them as indicated by the short contact distances of about 1 Å. For the next 20 000 time steps the situation alters. Now H_1 is farthest away from H_3, and a similar sequence of events is repeated for the interactions with the other three H atoms. At 45 000 time steps and beyond, the H_1-H_2 and H_1-H_4 separations are the longest and H_1 interacts mainly with H_3 and H_5. The time averaged structure for CH_5^+ can be recognized as a strongly interacting $CH_3^+(H_2)$ pair. A similar temporal variation of H-H distances is also observed for the other H atoms. It is significant that the instantaneous H$\cdots$H separation varied from 1 to 2.2 Å while the C-H bonds are tightly bound. The exceedingly large amplitude motions are indicative of fluxional H atoms scrambling freely and continuously interchanging their positions on the surface about the C atom. This phenomenon is known as "pseudorotation" and is substantiated from the inspection of the atomic trajectories.

Usually conventional quantum mechanical methods are applied to the calculations of harmonic frequencies at equilibrium geometries. In contrast, the vibrational density of states (VDOS) is evaluated from the Fourier transform of the atom velocity autocorrelation function in a molecular dynamics simulation [7]. For a disordered system, all the selection rules are relaxed and the VDOS is directly related to the infrared spectrum [8]. Furthermore, anharmonic effects, which are particularly important for a shallow PES, are explicitly included. The distribution of vibrational modes for CH_5^+ can be divided into two regions (Fig. 2). The high energy band with a peak at 2850 cm^{-1} is associated with C-H stretch modes. The profile of the lower energy vibrations is quite unusual as compared to most free molecules. In particular, the vibrational density of states extends from almost zero frequency to a strong peak at 1330 cm^{-1}. The strong peak is assigned to a H-C-H bend mode. The presence of very low frequency vibrations is a clear signature of diffusive motions corresponding to pseudorotating H atoms with low activation energy barriers.

Despite many attempts, the experimental determination of the vibrational spectrum for CH_5^+ remains elusive [1]. On the other hand, the ion complexes $CH_5^+(X_2)$ can be readily prepared. Recently, an infrared spectrum for $CH_5^+(H_2)$ has been reported [9]. It is unclear if the hydrogen scrambling motions of the CH_5^+ core have been affected by the interactions with H_2. The important question is whether any correlation can be drawn between the two species. *Ab initio* coupled-cluster (CCSD) calculations found a minimum energy structure where the H_2 molecule bound weakly to one of the hydrogen atoms of the CH_5^+ core [9]. The calculated C-H stretching vibrational frequencies are in apparent agreement with the observed results. However, calculations on static minimum energy structures do not provide any information on the dynamical motions of the CH_5^+ core.

AIMD calculations of $CH_5^+(H_2)$ yield a similar picture for the chemical bonding. Within the length of the simulation (5 psec) the H_2 molecule was found to remain closest to and interact with the same H atom of CH_5^+. The mean C$\cdots$(H_2) distance is 2.86 Å. The H_2 molecule is only slightly perturbed from the free state with the bond length elongated by 0.03 Å. These results are in substantial agreement with the CCSD calculations, where the C$\cdots$(H_2) distance is 2.96 Å and the H_2 bond length is 0.004 Å longer than in free H_2. The motions of the hydrogen atoms of the CH_5^+ core are analyzed in the same fashion as described above. The temporal variation

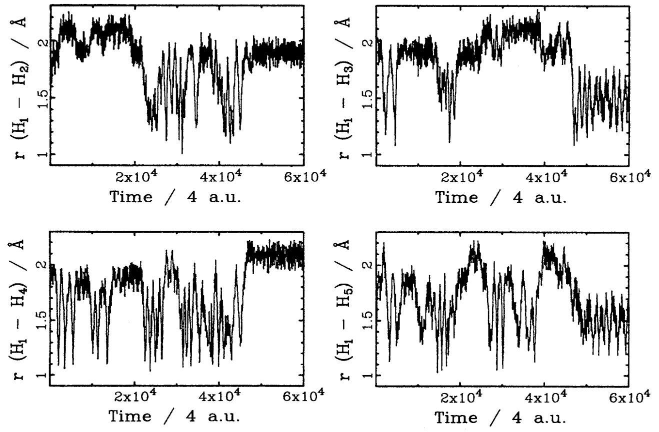

FIG. 1. Temporal variation of H$\cdots$H distances for H_1 in CH_5^+. (1 a.u. = 2.419 × 10^{-17}s.)

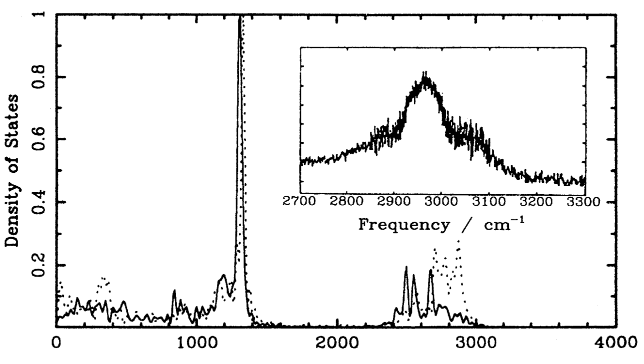

FIG. 2. Vibrational density of states (VDOS) for CH_5^+ (solid line) and $CH_5^+(H_2)$ (dotted line). Experimental infrared spectrum for $CH_5^+(H_2)$ in the C-H stretch region is shown in the inset.

of the H···H distances shows a similar pattern as in the free CH_5^+. Except for the H atom weakly bonded to the H_2 molecule, the average C-H bond distance fluctuates about 1.1 Å with maximum deviation of ±0.05 Å. In the former case, the bond length is slightly longer by 0.01 Å (1.20 Å). In contrast, the H···H distances varied from 1.0 to 2.2 Å indicating that the H atoms are fluxional and vibrate with large amplitudes. Occasionally, two of the H atoms move close enough to form, momentarily, a chemical bond. This description is the same as that for free CH_5^+, where the H atoms undergo fast and continuous interconversions.

The similarity in the dynamical structures is clearly displayed in the computed VDOS shown in Fig. 2. The distributions of the bending and librational vibrations below 1400 cm^{-1}, which reflect the pseudorotation motions, are almost identical. A slight enhancement in the density of states is noted in the calculated low energy bands at 5 and 37 cm^{-1} in $CH_5^+(H_2)$. The largest difference between the VDOS, however, is in the C-H stretching region. The stretch vibrations in $CH_5^+(H_2)$ shift to higher energy by 200 cm^{-1}. Significantly, the three peak profile for the vibrational density distribution for both species remains the same. A three peak band is also observed in the infrared spectrum [9]. The observed peaks at 2859, 2966, and 3053 cm^{-1} correlate very well with the three calculated C-H stretch bands, after scaling up by 6% as described earlier, at 2879, 2954, and 3054 cm^{-1}. The calculated vibrational frequency for the weakly interacting H_2 is 240 cm^{-1} lower than that of the free molecule while the observed shift [9] is 94 cm^{-1}. The structure and the stretching frequencies are in good agreement with those predicted by CCSD calculations on the static structure [9]. The dynamical motions of the protons do not significantly alter the stretching vibrations. The theoretical evidence presented here shows unequivocally that the infrared spectrum of the CH_5^+ core in the H_2 complex is representative of free CH_5^+. The infrared spectrum has also been calculated via the Fourier transform of the dipole moment autocorrelation function. However, the change in the dipole moment for the scrambling motions is much larger than the stretching vibrations. Consequently, the calculated infrared spectrum is dominated by the librational motions and the intensity of the stretching vibrations is too weak and is not sufficiently resolved for direct comparison with experiment. Perhaps, the best experimental signature for a mobile CH_5^+ would be the measurement of the low frequency vibrations.

The structure and dynamics of protonated acetylene has been the subject of special interest [3,10]. *Ab initio* quantum mechanical calculations [11,12] have established that the classical vinyl cation and the nonclassical H-bridged structures are nearly equal in stability. The experimental determination of the equilibrium structure proves to be difficult. Although a bridged structure has been inferred from the analysis of the infrared spectrum [10], there is strong evidence showing that the protons migrate between the apex and the two end equilibrium positions. A recent CEI study [3] further suggests that the bridging proton is delocalized and orbits around the $C=C$ bond.

AIMD calculations revealed the same two nearly degenerate isomers, with the nonclassical structure more stable by 1.2 $kcal\,mol^{-1}$. In the nonclassical structure, the distance of the bridging H to the C atom is 1.328 Å with a C-C bond of 1.240 Å. In the classical structure, the terminal H to C distance is 1.108 Å with a C-C bond of 1.261 Å. The calculated geometries of these isomers are in excellent agreement with previous calculations [11,12]. The results of the dynamics calculations using the temporal evolution of the separations of the three H atoms from the two acetylene C atoms as order parameters are succinctly summarized in Fig. 3. There are large but periodic fluctuations in the C-H distances. The bridging isomer is characterized by two equivalent C-H bonds at 1.27 Å and the vinyl structure by an H atom closer to one of the C (1.11 Å) and further (2.328 Å) from the other. The data collection starts with H_1 bridging at the position and H_2 and H_3 attached to C_a and C_b, respectively. In the ensuing 1000 time steps, H_1 moves towards C_b and away from C_a [Fig. 3(a)]. Simultaneously, H_3 moves away from C_b

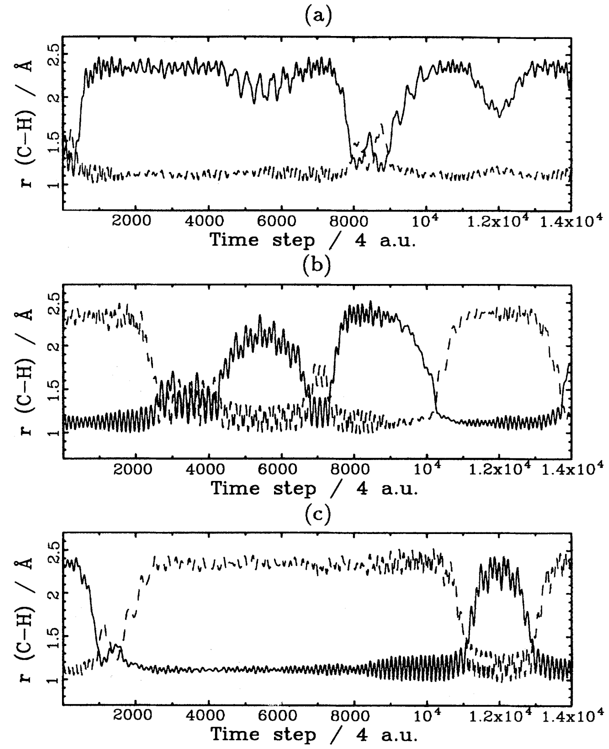

FIG. 3. Temporal variation of C-H bond lengths in $C_2H_3^+$. (a) ——, C_a-H_1; – – –, C_b-H_1. (b) ——, C_a-H_2; – – –, C_b-H_2. (c) ——, C_a-H_3; – – –, C_b-H_3.

and swings towards the middle of the C-C bond on the opposite side [Fig. 3(c)] while H_2 remains attached to C_a. The end result is equivalent to an exchange of H_1 and H_3. The H atoms then vibrate about their mean positions for another 600 time steps. After that, at time step 1600, the bridging H_3 moves towards C_a and H_2 shifts to the bridging position [Figs. 3(b) and 3(c)]. From time steps 7000 to 10 000 a similar exchange between H_1 and H_2 is registered, resulting in H_1 occupying the bridging position. The internal rotation of the protons from one end of the C-C bond via the symmetric bridging position is repeated between H_2 and H_3 at time step 10 400 [Figs. 3(b) and 3(c)]. The orderly proton migration is occasionally disrupted by "recoil" actions as shown in time steps 5000 and 11 700. In both cases, H_1 [Fig. 3(a)] attempted to move towards the central position but was pulled back by C_b. The proton rearrangement is clearly depicted in the snapshots of the molecule in Fig. 4.

The internal rotation model for the motion of the protons in $C_2H_3^+$ in the present calculation has been proposed previously [13,14]. This suggestion is consistent with the experimental observation of splittings in some infrared active C-H stretching vibrational bands. The apparent discrepancy in the structural model deduced by the CEI experiment from conventional spectroscopy may be due to the fact that the protons are not localized on specific sites but undergo large amplitude motions. The migration of the protons coupled with the overall rotation of the molecule may explain the large angular degrees of freedom observed in the CEI experiment [3].

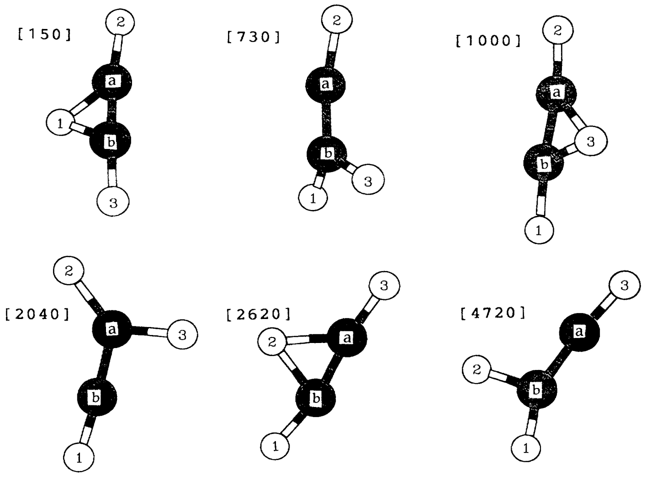

FIG. 4. Sequence of events leading to the cyclic permutation of the H atoms in $C_2H_3^+$. The number in parentheses refers to a snapshot taken at that time step.

The AIMD calculations have been very successful in modeling the structural dynamics of protonated methane and acetylene. The theoretical results provide a powerful means for the interpretation of the experimental observations for the molecules without definite geometries. These results demonstrate the potential for wide applicability of this method in the characterization of fluxional molecules. In view of the extremely shallow PES, the possibility of proton transfer through tunneling is expected to be strongly enhanced. This effect, however, is not included in the present classical dynamics simulation.

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