Rydberg States of H_4

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Energies of the 15 lowest Rydberg states of the metastable H_4 cluster have been determined using Koopman's theorem at the equilibrium geometry of the parent ion, H_4^+. To represent the core orbitals of H_4, a 6-31G** basis set has been used at the SCF, MP2, MP4(SDTQ), CI-SD, and CI-SDT levels. The Rydberg orbitals have been modeled using a basis set analogous to that used to model the Rydberg orbitals of H_3 in previous theoretical calculations. To test the validity of the calculations for the H_4 molecule, ab initio calculations were repeated for the Rydberg orbitals of the H_3 molecule at the stable geometry of the H_3^+ core. Predicted transitions were within 2% of the rotational band spectra of H_3 observed by Herzberg. The metastable H_4 cluster formed from charge neutralization of H_4^+ decomposes into two H_2 molecules. Previous calculations have predicted that one of the two H_2 products will be vibrationally hot while the other will be relatively cold and that a large recoil energy of approximately 9 eV is expected for the relative kinetic energy of the two H_2 products. The present work suggests that if Rydberg states are involved in the charge neutralization process, the recoil energy could be reduced due to radiative transitions among the Rydberg states.

Introduction

There has been a great deal of interest in charge neutralization reactions of small ions containing hydrogen, specifically the H_3^+ and H_4^+ ions.[1−3] Rydberg states of H_3 and H_4 may be involved in the overall charge neutralization process.[4−7] Jungen[6] calculated the energies of the 15 lowest lying Rydberg states of H_3. The calculations were performed using a frozen core approximation, solving the one-electron problem in the field of the Hartree−Fock solution for H_3^+. King and Morokuma[4] determined the energies of the same 15 low lying Rydberg states of H_3 using Koopman's theorem with a large Gaussian basis set representing both core and Rydberg orbitals.

Recently, Pan and Borkman[3] performed calculations on the charge neutralization reaction of H_4^+ without consideration of Rydberg states. The positive ion has been shown both computationally[8] and experimentally to be a stable species. It has a planar C_{2v} geometry consisting of an approximately equilateral triangle of three H nuclei with the fourth H bonded to one vertex,[8] as seen in Figure 1. Vibrational analysis of H_4^+ has been carried out using SCF, MP2, and CI calculations.[10] The results show that the triangular portion of the H_4^+ ion contains three strong H−H bonds with high-frequency ring stretching vibrations similar to the H_3^+ ion. The fourth H atom is not as strongly bound, as indicated by the lower frequency of the H_3-H^+ stretching vibration.

The present work calculates the Rydberg state energies of H_4 which are of potential importance in the charge neutralization reactions of H_4^+. Calculations on H_3 Rydberg states are also reported in order to calibrate our methods in a molecule where spectroscopic data are available[5] for comparison.

Computational Methods

Optimization of the H_4^+ ion structure (Figure 1, restricted to C_{2v} symmetry) was performed at the SCF, MP2, MP4(SDTQ), CI-SD, and CI-SDT levels of theory using a 6-31G** basis set to represent the three core electrons. The Rydberg orbitals were modeled at the center of mass of the molecule using a basis set consisting of two s-type functions, eight p-type functions, and four d-type functions (2s8p4d). Each d shell contained six Cartesian d components. Single-point energy calculations were performed on the H_4 molecule at the optimized H_4^+ ion geometry to obtain H_4 energies at each level of theory. The Rydberg orbitals used in the H_4 calculations were modeled using basis sets similar to those used to model the Rydberg orbitals of H_3 by King and Morokuma[4] and Jungen.[6] King and Morokuma[4] tested several different basis sets to represent the core and Rydberg orbitals. Their basis set for the H_3^+ core included four s-type functions and two p-type functions. King and Morokuma's[4] basis set for the Rydberg electron included two s-type functions, eight p-type functions, and seven d-type functions (2s8p7d). Calculations on the H_3^+ ion structure (assuming D_{3h} symmetry)at the SCF, MP2, MP3, and CI-SD levels of theory were done using the same basis set as for the H_4^+ ion for comparison purposes. All calculations were performed using the GAUSSIAN-92 system of programs.[11]

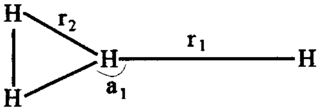

Figure 1. Geometric parameters of the H_4^+ ion. The quantities r_1 and r_2 are H−H bond lengths and a_1 is the indicated H−H−H angle.

Results and Discussion

The H_4^+ ion structure was optimized at the SCF level and at higher levels of theory. The structural parameters for H_4 are defined in Figure 1. The optimized structure and energy at the SCF level are given in Table 1. These results are very similar to results obtained by Pan and Borkman[10] at the SCF level using a different, completely uncontracted basis set containing 5 s functions[12] and 2 p functions.[9] The Rydberg orbital energies of H_4 at the SCF level are shown in Table 2 and were determined using Koopman's theorem. The values calculated in Table 2 represent the virtual orbital energies for the H_4^+ ion. Previous theoretical calculations[4] of H_3 Rydberg states indicated that electron correlation had little effect on these energies. CI-SDT and MP4(SDTQ) calculations were performed for the SCF-optimized structure of the H_4^+ ion. The resulting Rydberg orbital energies differed by less than 0.000 05 Hartrees, indicat-

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TABLE 1: Optimized Geometries and Energies for H_4^+ Calculated at Different Levels of Theory. Bond Lengths r_1 and r_2 Are Given in Angstroms, and the Angle a_1 Is in Degrees. Energies Are Given in Hartrees. The H_4 Neutral Energy Was Calculated at the H_4^+ Energy-Minimum Geometry in Each Case

	SCF	MP2	MP4	CI-SD	CI-SDT
r_1	1.656	1.453	1.389	1.379	1.366
r_2	0.895	0.922	0.936	0.938	0.942
a_1	151.9	153.0	153.5	153.6	153.7
$E(H_4^+)$	−1.8015	−1.8350	−1.8434	−1.8439	− 1.8441
$E(H_4)$	−2.0563	−2.1449	−2.1716	−2.1743	−2.1774

TABLE 2: Rydberg Orbital Energies of H_4 Calculated Using Different Methods. The H_4^+ Ion Core Was Optimized at Each Level of Theory. All Energies Are Given in Hartrees

k	SCF	MP2	MP4(SDTQ)	CI-SD	CI-SDT
1	−0.182 74	−0.178 40	−0.171 64	−0.176 83	−0.182 19
2	−0.165 00	−0.158 43	−0.157 22	−0.155 96	−0.154 71
3	−0.123 49	−0.123 21	−0.123 01	−0.123 02	−0.123 00
4	−0.106 66	−0.100 69	−0.100 34	−0.098 49	−0.096 58
5	−0.076 82	−0.079 81	−0.081 23	−0.081 01	−0.080 82
6	−0.069 43	−0.068 86	−0.067 80	−0.068 69	−0.069 55
7	−0.057 57	−0.057 58	−0.057 52	−0.057 55	−0.057 58
8	−0.057 00	−0.056 54	−0.056 61	−0.056 54	−0.056 47
9	−0.056 50	−0.056 43	−0.056 20	−0.056 20	−0.056 18
10	−0.055 11	−0.055 04	−0.055 00	−0.055 00	−0.054 99
11	−0.053 27	−0.053 19	−0.053 11	−0.053 15	−0.053 18
12	−0.053 24	−0.053 18	−0.053 11	−0.053 14	−0.053 18
13	−0.044 55	−0.043 76	−0.043 81	−0.043 41	−0.043 00
14	−0.038 66	−0.039 77	−0.040 23	−0.040 19	−0.040 16
15	−0.036 58	−0.036 30	−0.035 85	−0.036 19	−0.036 52

TABLE 3: Symmetries and ab Initio Calculated Energies of Rydberg States of H_4 in C_{2v} Symmetry Determined at the CI-SDT Level

k	C_{2v} symmetry	united atom	ϵ_k (Hartrees)	E_k (Hartrees)
1	$1b_2$	$2p_y$	−0.182 19	−2.026 30
2	$1a_1$	2s	−0.154 71	−1.998 82
3	$1b_1$	$2p_x$	−0.123 00	−1.967 11
4	$2a_1$	$3p_z$	−0.096 58	−1.940 69
5	$3a_1$	3s	−0.080 82	−1.924 93
6	$2b_2$	$3p_y$	−0.069 55	−1.913 66
7	$3b_2$	$3d_{yz}$	−0.057 58	−1.901 69
8	$2b_1$	$3d_{xz}$	−0.056 47	−1.900 58
9	$4a_1$	$3d_{z^2}$	−0.056 18	−1.900 29
10	$3b_1$	$3p_x$	−0.054 99	−1.899 10
11	$5a_1$	$3d_{x^2-y^2}$	−0.053 18	−1.897 29
12	$1a_2$	$3d_{xy}$	−0.053 18	−1.897 29
13	$6a_1$	$4p_z$	−0.043 00	−1.887 11
14	$7a_1$	4s	−0.040 16	−1.884 27
15	$4b_2$	$4p_y$	−0.036 52	−1.880 63

TABLE 4: Rydberg Orbital Energies of the H_3 Molecule Calculated Using Different Methods. The H_3^+ Ion Core Was Optimized in D_{3h} Symmetry. All Energies Are Given in Hartrees

k	SCF	MP2	MP3	CI-SD
1	−0.197 47	−0.197 97	−0.199 80	−0.198 61
2	−0.135 80	−0.135 65	−0.135 09	−0.135 45
3	−0.127 29	−0.127 25	−0.127 10	−0.127 20
4	−0.071 20	−0.071 26	−0.071 48	−0.071 34
5	−0.058 04	−0.058 00	−0.057 84	−0.057 94
6	−0.056 46	−0.056 45	−0.056 40	−0.056 43
7	−0.055 85	−0.055 86	−0.055 88	−0.055 87
8	−0.054 71	−0.054 71	−0.054 71	−0.055 86
9	−0.054 40	−0.054 39	−0.054 38	−0.054 71
10	−0.037 27	−0.037 29	−0.037 37	−0.037 32

TABLE 5: Radiative Transitions Predicted at Different Levels of Theory for the H_3 Molecule. The H_3^+ Ion Core Was Optimized at Each Level of Theory. All Energies Are Given in Electronvolts

transition	SCF	MP2	MP3	CI-SD	expt[5]
$3p(e')-2s(a_1')$	1.76	1.75	1.73	1.74	1.75
$3p(a_2'')-2s(a_1')$	2.16	2.16	2.14	2.15	2.21

ing that electron correlation has a minimal effect on the Rydberg states of H_4 as long as the core geometry is frozen.

The H_4^+ ion was also geometry optimized using correlated methods including MP2, MP4(SDTQ), CI-SD, and CI-SDT. The calculated geometries and energies are shown in Table 1. Comparing the SCF and correlated methods, one sees in Table 1 that the distance between the H_3 triangle and the fourth H atom (r_1 in Figure 1) decreased by about 0.2−0.3 Å. The distance r_2 in Figure 1 increased by about 0.03−0.05 Å when correlation was added. The bond angle a_l was little changed. Each correlated method led to different Rydberg orbital energies. The values of the Rydberg orbital energies $k = 1-15$ for each method are given in Table 2. Since there are no experimental values known for the H_4^+ ion geometry, the CI-SDT calculated geometry was assumed to be the most accurate.

Table 3 shows the symmetries and energies of the $k = 1-15$ Rydberg states of H_4 calculated at the CI-SDT level. The estimated total energies given in Table 1 result from Koopman's theorem,

$$E_k = E_{core} + \epsilon_k$$

where the ϵ_k values represent the virtual orbital energies for the H_4^+ ion (Table 2) and E_{core} is the energy of the H_4^+ ion given in Table 1.

To further test the validity of the calculations for the H_4 cluster, ab initio molecular orbital studies were conducted on the Rydberg orbitals of the H_3 cluster at the minimum energy geometry of the H_3^+ core. Koopman's theorem was used to estimate the Rydberg orbital energies. Using the 6-3 l G** basis for the core and a 2s8p4d basis for the Rydberg orbitals at the SCF level, 99.8% of the predicted Hartree−Fock limit for H_3 was reached, and our predicted Rydberg transitions for the H_3 cluster were within 2% of values obtained from the rotational band spectra observed by Herzberg.[5]

The H_3^+ ion was also geometry optimized using correlated methods to act as a benchmark for the H_4 calculations. Optimizations were performed at the MP2, MP3, and CI-SD methods. Each correlated method led to different Rydberg orbital energies, as was the case for the H_4 molecule. The values for Rydberg orbital energies $k = 1-10$ for each method are given in Table 4. Optimization at correlated levels changes the minimum energy geometry. This changes the absolute values of the Rydberg orbital energies. This topic is discussed in more detail later.

Herzberg observed an emission spectrum of H_3 which was interpreted as being due to transitions between Rydberg states. Two transitions were analyzed at 7100 Å (1.75 eV) and at 5600 Å (2.21 eV), as shown in Table 5. These transitions were assigned to $3p(e') \rightarrow 2s(a_1')$ and $3p(a_2'') \rightarrow 2s(a_1')$, respectively. The orbital symmetries designated here correspond to the assumption of an H_3^+ core with D_{3h} symmetry. For the corresponding transitions in the H_4 molecule, it is assumed that the H_4^+ core has C_{2v} symmetry. If we assume that the analogous transitions occur in H_4 as occur in H_3, the two strong transitions observed by Herzberg[5] would correspond to three transitions in the H_4 molecule because the p_x and p_y orbitals are no longer degenerate in C_{2v} symmetry. The p_z orbital in H_3 is perpendicular to the plane of the molecule, thus giving it A_2'' symmetry. In the H_4 molecule, the p_z orbital lies in the plane

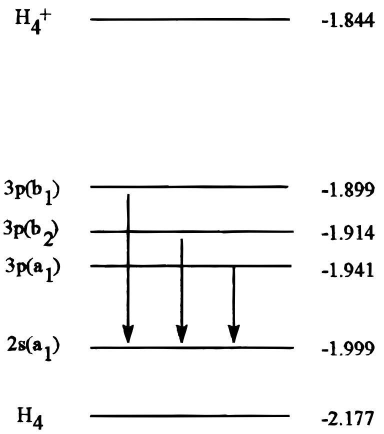

Figure 2. Relative energy diagram for H_4 indicating possible Rydberg transitions. Energies are given in Hartrees. The vertical arrows represent expected radiative transitions calculated at the CI-SDT level.

TABLE 6: Possible Radiative Transitions for the H_4 Molecule Predicted at Different Levels of Theory. The H_4^+ Ion Core Was Optimized at Each Level of Theory. All Energies Are Given in Electronvolts

transition	SCF	MP2	MP4	CI-SD	CI-SDT
3p(a_1)−2s(a_1)	1.59	1.57	1.55	1.56	1.58
3p(b_2)−2s(a_1)	2.60	2.44	2.43	2.37	2.32
3p(b_1)−2s(a_1)	2.99	2.81	2.78	2.75	2.71

of the molecule along the C_2 axis, giving it A_1 symmetry in the C_{2v} point group. The three Rydberg transitions in H_4, corresponding to the two transitions observed in H_3, are therefore 3p(a_1) → 2s(a_1), 3p(b_2) → 2s(a_1), and 3p(b_1) → 2s(a_1) with CI-SDT energies of 1.58, 2.32, and 2.71 eV, as seen in Figure 2 and Table 6.

It was mentioned previously that electron correlation has a minimal effect on the Rydberg orbital energies as long as the core geometry is frozen. Within each frozen core, at all levels of theory, the Rydberg orbital energies differed by an amount less than 0.000 05 Hartrees. But, it can clearly be seen in Tables 2 and 3 that the Rydberg orbital energies changed by as much as 0.3 eV when correlated methods were used and structural optimization was performed which changed the geometry of the core. This was true for both the H_3 molecule and the H_4 molecule.

Table 5 shows the transitions observed by Herzberg,[5] calculated using different levels of theory. The core was optimized at each level of theory indicated in the table. Analogous transitions for the H_4 molecule can be seen in Table 6. Again, the core structure was optimized at each level of theory. In the case of the H_4 molecule, the predicted radiative transitions differed by less than 0.3 eV for all levels of theory. The Rydberg orbital energies themselves differed from each other for the various levels of theory by about the same amount as seen in Tables 2 and 3. The tentative conclusion is that accurate predictions of Rydberg transition energies in H_3 and H_4 require use of precise values of the ion core structural parameters. The use of a correlated wave function to describe the Rydberg electron is not necessary.

The decomposition of metastable H_4 formed from the charge neutralization reaction of the H_4^+ ion has been studied previously.[3] The metastable H_4 cluster was predicted to decompose from the Franck−Condon geometry into two H_2 molecules. The results suggested that one of the H_2 product molecules would be vibrationally hot (3−4 eV) while the other would be relatively cold. A large recoil energy, on the order of 9 eV, was predicted for the relative kinetic energy of the two H_2 products. If there was loss of energy due to radiative transitions among the Rydberg states accompanying charge neutralization, it is possible that both H_2 product molecules might be vibrationally cold and/or that the recoil energy predicted previously would be smaller.

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