6054 *J. Phys. Chem. A* **1997,** *101,* 6054−6062

Stability and Fragmentation of Protonated Helium Dimers from ab Initio Calculations of Their Potential Energy Surfaces

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Received: October 24, 1996; In Final Form: June 2, 1997⊗

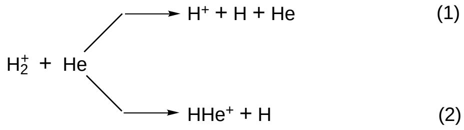
Ab initio calculations are carried out on the helium neutral dimer interacting with a "foreign", ionic probe like H^+. The most stable structure is found to be with the ionic core symmetrically at the center of the two helium atoms, while a less stable configuration is given by the asymmetric linear system with the ion external to the cluster. The nonlinear, C_{2v}, arrangement is also studied and its fragmentation aspects are examined. The three lowest excited electronic states are also presented, and the possible results from cluster excitation and from the ensuing fragmentation patterns are discussed in detail in terms of the species that are expected to be formed, like HeH^+, He_2^+, and He^+ from charge-transfer excitations. The study should help to better understand the breakup dynamics of the larger protonated helium clusters that are currently of interest to experiments and theory.

1. Introduction

Among the many different types of clusters presently under investigation,[1] those formed of ^{4}He atoms are fairly special for at least two reasons. Since He has no triple point and only solidifies at pressures above 25 bar, the clusters of ^{4}He are the only clusters that can become definitely liquid. Furthermore, they represent one of the very few fully quantum systems that are experimentally accessible and can be of well-defined finite dimensions. Thus, several recent theoretical studies predict that, at a given size, ^{4}He clusters will exhibit superfluid behavior,[2,3] and therefore the experimental search of the evidence for such a behavior becomes of great fundamental interest.[4,5]

Several investigations have additionally been directed to the study of the effects that foreign atoms and molecules can have on the properties of helium clusters since experiments have revealed that a sizeable number of such foreign particles can be captured within the helium system and then appear to coagulate to form their own clusters on or within the original He clusters.[6,7] In particular, the use of ionic particles provides an additional element for the study of such systems, since they can be more easily mass selected and their relative stabilities as a function of the cluster size can be analyzed with time-of-flight techniques (and/or) further stimulated by laser excitation before final fragmentation.[8−10]

One of the possible additional ions that has received experimental attention in recent years is the H_2^+ projectile, injected into a drift tube filled with helium gas at a very low temperature.[11−13] From the final drift field dependence of the size distribution for the ensuing cluster ions one can thus obtain information on their relative stabilities, on the possible appearance of "magic numbers" in the sequential behavior as a function of cluster size, and on the likely chromophores located at the core of the cluster ions. In particular, from such experiments it turned out that, surprisingly enough, neither H_2^+ nor $H_2^+He_x$ ions were observed in the drift spectra, and therefore the following fast reactions were considered to be possibly responsible for the disappearance of such ions



Once the H^+ ions are produced, then cluster ions of general formula HHe_n^+ can build up through the three-body collision reactions[12]

$$H^+ + He + He \rightleftharpoons HHe^+ + He \tag{3}$$

$$HHe_{n-1}{}^+ + He + He \rightleftharpoons HHe_n{}^+ + He \tag{4}$$

where a "closed shell" magic number of $n = 13$ was found to correspond to a particularly large stability and to a possible structure of an HHe^+ chromophore centered in a distorted icosahedral structure.[13]

Several microscopic aspects of the above processes, however, still need to be understood, and very little computational modeling of such aspects has been attempted in recent years. In particular, one would like to understand the relative energetics of reaction 1 versus 2 and the corresponding structural features of reaction 3 as the basic process for the cluster growth mechanism surmised by reaction 4. Furthermore, it is also of interest to have some information on the excited electronic states of the possible ionic core and on their perturbation by the additional helium atoms that form the final clusters.

In order to begin to understand at least the structural questions that should be answered, we report in the present work a detailed study of the potential energy curves (PECs) and the potential energy surfaces (PESs) associated with the possible chromophore HeH^+, and with the product of the charge-transfer reaction alternative to reaction 4 that can stop the cluster growth in the above processes.

$$H^+ + He + He \rightleftharpoons He_2{}^+ + H \tag{5}$$

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⊗ Abstract published in *Advance ACS Abstracts,* July 15, 1997.

S1089-5639(96)03320-8 CCC: $14.00

Thus, the excited states of He_2^+ and the full shape of the three-particle system HHe_2^+ could be viewed as the smallest examples of the ionic helium clusters discussed above.

The calculations were carried out at the ab initio level, employing correlated wave functions over a rather broad range of nuclear geometries, and the features of the method employed are briefly described in the following section. Section 3 reports in detail the various outcomes of our calculations, while section 4 summarizes our results and presents our conclusions.

2. The Method of Computation

In the present calculations we have carried out, including electron correlation, studies of potential energy surfaces for a fairly broad range of nuclear geometries associated with the linear symmetric dissociation, linear asymmetric dissociation, and nonlinear, C_{2v} symmetry of the H^+ insertion (or removal) from the He_2 subsystem. The method employed was the multireference single and double excitations with configuration interactions (MRD-CI) method of Buenker and Peyerimhoff,[14] a method that has been used and described by us before,[15−17] and therefore its structural details will not be repeated here again. Suffice it to say, more specifically, that the basis set chosen was the cc-PVTZ (correlation consistent valence triple zeta) suggested earlier by T. H. Dunning.[18] The atomic basis set employed in it was the He:6s2p1d, H:5s2p1d, contracted to He: 3s2p1d, H:3s2p1d, which led to 45 contracted GTO functions for the He_2H^+ system. The total number of MOs used in the CI procedure was 45. No orbitals were excluded or frozen in the excitation process during the CI steps.

Typically, about 46 optimized main configurations were used to generate about 24 000 singly and doubly excited configurations, out of which 15 000 were selected by adopting an energy threshold of 0.2 μhartrees. Using this threshold the CI extrapolation resulted in providing corrections of about 0−6 significant decimal figures in atomic units to the lower roots. A typical value for the number of roots obtained from the Hamiltonian matrix was 5 roots in the case of the $^3A_1$ symmetry near the ground state energy minimum. The fragmentation process was followed out to about 5.0 au for the dissociating coordinate, and several excited states were examined in order to glean some additional information on the possible consequences of electronically exciting the ionic clusters after their formation into the drift tube as discussed before. On the other hand, as we shall discuss below, the quality of our optimized calculations is such that we cannot give quantitative meaning to the higher Rydberg states, which will therefore not be discussed explicitly in the following.

3. Discussion and Results

As mentioned already, the question of clustering helium atoms around a foreign body, either neutral or ionized, requires establishing at the beginning whether such an additional particle (or particles) will be located inside the helium cluster or at the helium cluster on its external region.[9,10] In the present instance one could therefore start to look into the energetics of the above options by examining the presence of the H^+ ion either symmetrically located between the two helium atoms or outside them. In the latter case, of course, the very weak nature of the He_2 bound state[19] will prevent us from initially obtaining such a neutral dimer as a bound isolated system at the level of our computations.[20]

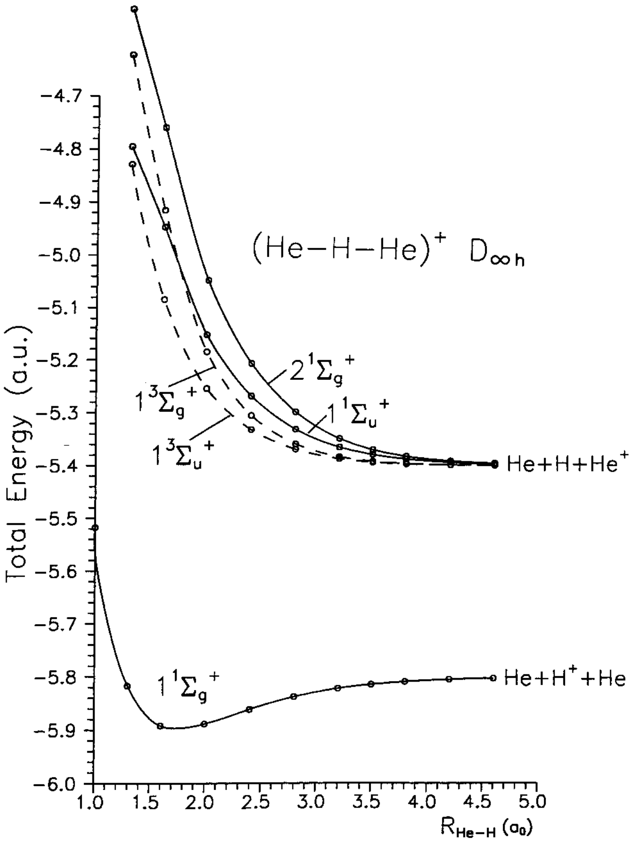

Figure 1. Computed potential energy curves for the symmetric dissociation of $(HeHHe)^+$. The ground electronic state and some of the lower-lying excited states are shown, with the indication of the asymptotic fragments.

3.1. The Linear Symmetric Case. Let us consider, to begin with, the symmetric dissociation of the He_2H^+ cluster where the ion is located, in the "core", i.e. in the middle of the two atoms. The overall symmetry will be $D_{\infty h}$, and the results of the calculations are shown by the potential energy curves of Figure 1, where both singlet and triplet states are reported and where the asymptotic fragments are also indicated.

One clearly sees in the figure the existence of a bound structure where the two helium atoms are located at a distance of about 1.75 a_0 from the ionic core and which has a D_e value of about 2.5 eV with respect to the full fragmentation. As a comparison, the binding energy (D_0) of one He atom to H^+, in the HeH^+ molecule, is 1.84 eV[21] and the equilibrium bond distance is 1.45 a_0, as we shall further discuss below. Its D_e value is 1.98 eV from our calculations.

The next set of excited states, corresponding to the charge-transfer (CT) situation where an ionic helium is now produced asymptotically, is also shown in Figure 1. We clearly see there that all four states, two singlet and two triplet states, are repulsive, and therefore any excitation of the protonated dimer into such excited electronic arrangements will lead to fragmentation with the formation of helium ions. The excitation energy in the Franck−Condon region of the protonated dimer is about 24.3 eV, while the asymptotic energy difference is about 10.98 eV.

In order to analyze more reliably the behavior of the linear system with the ionic core, it is useful to further examine the two asymmetric arrangements that correspond to processes where the sequential removal of one helium atom at the time is examined. The ensuing two-dimensional potential energy surface (PES) is shown in Figure 2, where the region of the cluster minimum energy is clearly visible and where the two

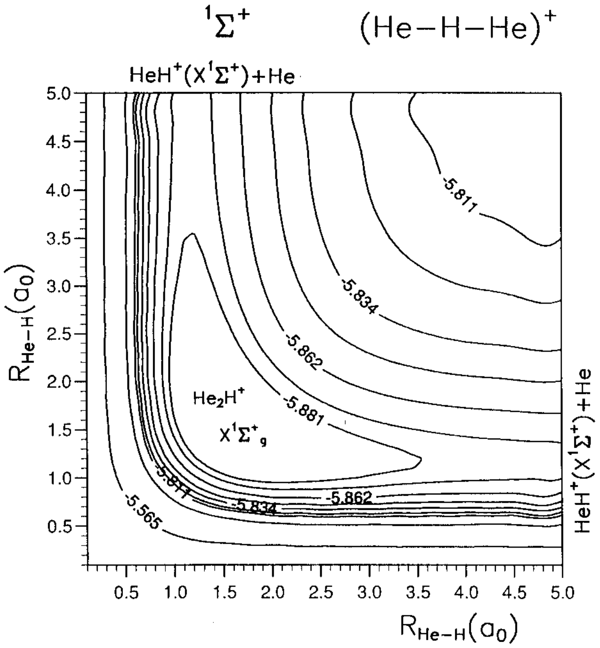

Figure 2. 2D potential energy surface for the ground electronic state of the collinear core-protonated helium dimer. The final channels are also listed in the asymptotic region of the two coordinates.

coordinates are associated with the symmetrical single breakup process

$$He_2H^+(X^1\Sigma_g^+) \rightarrow HeH^+(X^1\Sigma^+) + He(1^1S) \qquad (6)$$

The binding energy of the second helium atom to HeH^+ is about 0.52 eV for all partners in their ground electronic states, as stated in eq 6. The ionic cluster with the H^+ core is therefore shown to be a "true" molecule with rather strong chemical bonds and with the two helium atoms only slightly less bound than in the case of protonated helium. They are also located at a distance only a little larger than in the latter diatomic ion.

It is also interesting to note that, if one carries out calculations starting from the symmetric equilibrium geometry and removing one He atom away from it in any nonlinear direction (C_s configurations), one finds again that the ground electronic state dissociates toward higher energies, while the lower excited states remain fully repulsive. We can thus conclude that the present linear symmetric structure indeed corresponds to a global minimum of this system in its ground electronic state.

It is interesting to note at this point that earlier calculations[22] using the single-determinant SCF-MO approach found the symmetric structure with an equilibrium geometry of 1.75 a_0. On the other hand, large basis set calculations that included correlation effects[23] found an equilibrium geometry with R_{HeH} = 1.747 a_0. Their value for the binding of one He atom was 0.5757 eV. Single-determinant calculations for the first excited state were reported in ref 24 at the equilibrium geometry of the ground state molecule.

3.2. The Linear Asymmetric Arrangement. The situation, on the other hand, becomes different when we examine the energetics of the proton being located "outside" the helium cluster, i.e. the approach of two neutral He atoms to the ionic system. The idea is simply to mimic the possible attachment of H^+ to a helium dimer where the two He atoms are fairly close to each other. In the example shown at the top of Figure 3 we have chosen a He−He distance of 2.1 a_0, while the H^+ distance has been varied from about 0.500 out to 5.0 a_0. Thus, the lowest electronic state shows a minimum in the potential that corresponds essentially to the minimum geometry of HeH^+ (≈1.5 a_0) only slightly perturbed by the extra He atom which is now bound to it by polarization forces but which is not yet located at its lowest possible minimum energy geometry, as we shall see below from the full PES.

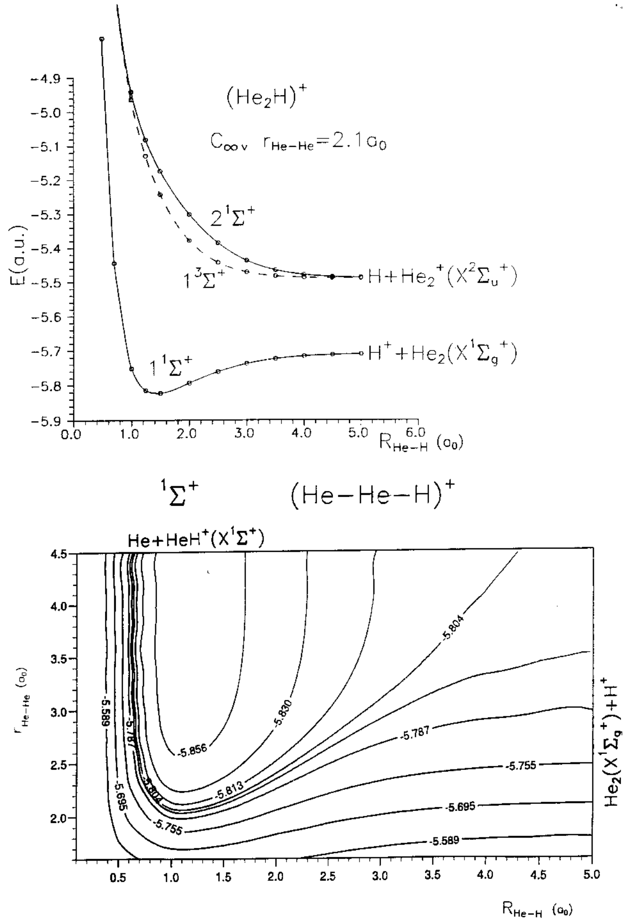

Figure 3. Computed ground electronic state and first two charge-transfer states of the asymmetric linear cluster (top curves of figure). One coordinate, the He−He coordinate, is fixed at 2.1 a_0. The lower part of the figure shows the full PES for the asymmetric linear arrangements, ground electronic state only. The asymptotic products are listed for the R_{HeH} coordinate.

The next two excited electronic states, singlet and triplet, clearly describe a charge-transfer situation whereby a bond-stretched state of He_2^+ is being formed at the fixed 2.1 a_0 relative distance. Its equilibrium distance is given, in fact, by the latest calculations[24] and experimental estimates[25] to be about 2.04 a_0. However, such excited states do not chemically bind the H atom, and therefore both are fully repulsive along the dissociative coordinate which removes the hydrogen atom from the bound ionic core. Thus, one may envisage a situation where the originally formed $HHe^+\cdots He$ cluster could be electronically excited into a bound state of the charge-transfer helium dimer with the subsequent loss of a neutral H atom. The FC excitation energy will be on the order of about 18.0 eV, according to the present calculations.

A more complete view of the ground electronic state is shown in the lower part of Figure 3. We report there the overall shape of the PES for the asymmetric removal of either one H atom, along the R_{HeH} coordinate, or of one He atom, along the r_{HeHe} coordinate. The overall shape of this energy surface naturally confirms the qualitative considerations made from the specific "cut" of it displayed on the upper part of Figure 3: the region of small distances, and of increasingly larger R_{HeH} distances, corresponds to a full fragmentation of the cluster without any evidence of the same type of strongly bound species as that

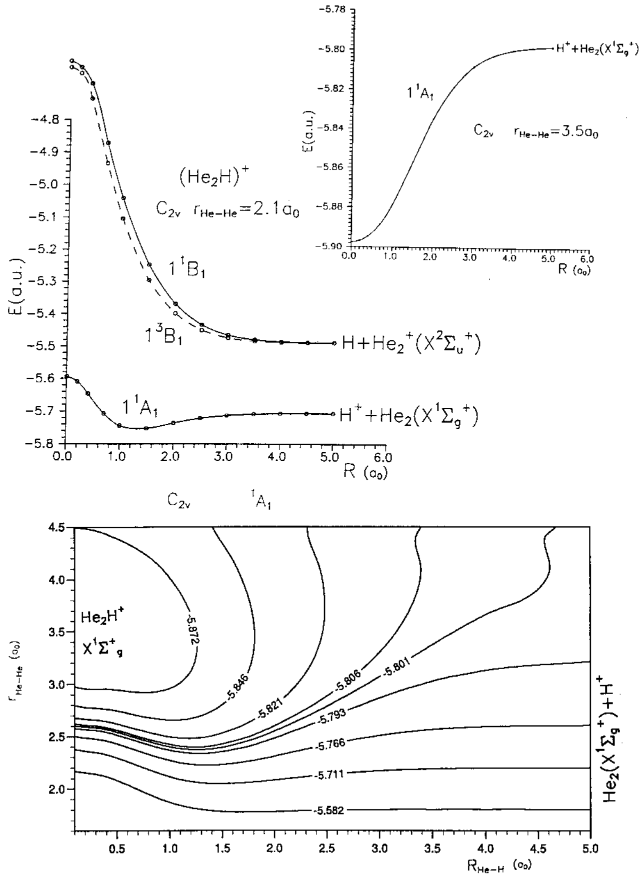

Figure 4. Same as in Figure 3 but for the C_{2v} arrangement. The He−He distance in the curves on the upper part of the figure was kept fixed at 2.1 a_0 and 3.5 a_0, respectively. Both asymptotic products are shown for the full surface in the lower part of the figure.

seen in Figure 2 when the R_{HeH} distance is below 2.0. In other words, the insertion of the ionic hydrogen into the helium dimer and outside the "cluster" only forms weakly bound species which either easily dissociate into three fragments or, by selective removal of one He atom, can be stabilized into the protonated diatomics HeH^+ plus the extra helium: the minimum energy equilibrium geometry of the molecular ion is seen, in fact, along the bottom of the well region and is being only slightly deformed by the additional interaction with the second He atom. At the level of correlation corrections employed in the present work the He_2 dimer obviously is not described as a bound species.

Such a situation of lower stability will also be brought about, as we shall see below, by the nonlinear, external approach of the ion to the helium cluster.

3.3. The Nonlinear Ionic Insertion. We further report on the upper part of Figure 4 the geometric situation in which the C_{2v} arrangement is examined along two specific "cuts" of the full PES also shown in the lower part of the same figure. The potential energy curves help us to start to understand more directly the behavior of the full PES that we will discuss later on. The larger PEC plot corresponds to a fixed distance of the helium dimer of 2.1 a_0, as used before for the asymmetric arrangement of Figure 3. Thus, the shallow minimum shown by the lowest electronic state (1 $^1A_1$) corresponds to a bond-stretched state of HeH^+ with the extra helium atom only weakly bound by polarization forces: this is similar to what we have found for the linear geometry; it only occurs for a different arrangement which now corresponds to the nonlinear attachment of the extra He atom and therefore to a shallower well since the relative distance between the He and H atoms in HeH^+ is now about 1.75 a_0 and corresponds to a vibrationally excited diatomic ion with the extra He weakly bound by polarization forces in a nonlinear arrangement. Hence, as the H^+ atom is removed, the system easily undergoes full dissociation into $H^+ + He + He$, as we have seen happen in the linear asymmetric case of Figure 3. The first electronic excitation into the lowest singlet B state, the 1 $^1B_1$ state, leads once more to a charge-transfer process with detachment of the H atom from the X $^2\Sigma_u^+$ state of He_2^+ formed close to its equilibrium geometry[25] of 2.04 a_0. The full PES, on the other hand, presents now a different picture than that from the asymmetric linear arrangement. The ground electronic state of C_{2v} geometry shows, in fact, that the insertion of the proton into the He dimer produces the most stable arrangement of the ion "into" the cluster, as seen in Figure 2: the $(He{-}HHe)^+$ symmetric structure is formed at an r_{He_2} distance around 3.5 a_0, as expected. We see, in fact, from the inset reporting the PEC behavior for that He_2 distance, that the symmetric insertion leads to a stable linear structure, as shown before in Figures 1 and 2. Thus, one could say that the proton approach causes the distance between helium atoms to increase in order to stabilize the rare gas structure around the H^+ core, while the removal of such a core from the cluster simply causes here the full fragmentation with the positive charge now following the hydrogen core.

3.4. The Excited Electronic States. In order to analyze more reliably the behavior of the excited electronic PES of this system, it is useful to look at the possible final states of the fragments that could be formed following the excitation and the breakup of the initial cluster. We report in Figure 5 the actual results of previous, extensive calculations already reported in the literature which can guide us in the selection of the most likely asymptotic channels obtained from the present evaluation of the excited electronic PES in the various arrangements discussed before.

The lower part of Figure 5 reports the behavior of the electronic states of HeH^+ and those for the neutral HeH system. The results for HeH^+ are taken from ref 26, while those for the neutral diatomics are from ref 27. It is also worth noting from the plotted PEC that we have always added the electronic energy of the third particle in order to refer all the diatomic fragments to the same asymptotic total energies for each of the channels. Thus, the HeH^+ PEC for its ground state (X $^1\Sigma^+$) is reported twice depending on the considered spin state of the additional helium atom which could be formed upon fragmentation considering for the moment only the ground electronic state of helium. We also see from the figure that the full fragmentation of the cluster could arise either from the formation of HeH^+ in its ground state, as discussed before, or from a first group of excited states that allow for the charge to migrate to one of the helium atoms. The formation of either He or H into excited electronic states upon fragmentation, and without charge-transfer effects, can further originate from a third group of either repulsive or bound excited states of HeH^+ and HeH. The calculations indicate the CT process to be about 10.98 eV higher in energy, while the possible fragmentation products into excited electronic states are further located about 9.5 eV still higher in excitation energy.

If one now considers the other fragmentation "cuts", i.e. those that could give rise to helium dimers, either neutral or ionized, then we obtain from existing calculations the set of PEC shown in the upper part of Figure 5. The He_2^+ results for their $^2\Sigma^+$ states are from ref 26, while those for the $^2\Sigma_g^+$ states are taken from refs 27 and 28. The results for the excimer states of the helium dimer are from refs 30 and 31, while the location and classification of the helium atomic states are taken from the

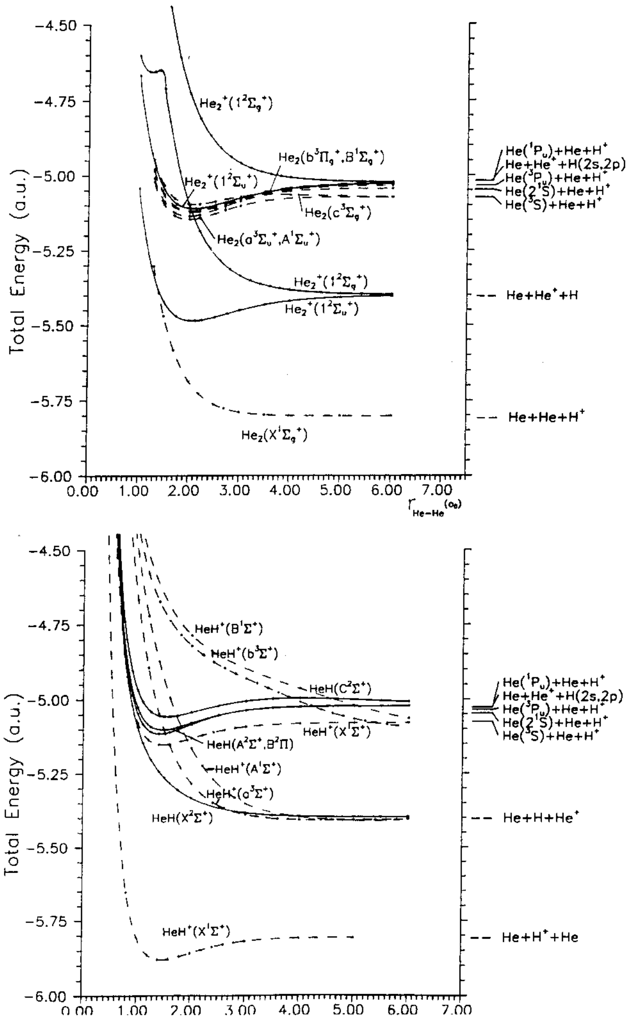

Figure 5. Computed potential energy curves for the ground state and for some of the excited electronic states of the fragmentation products discussed in the present work. The calculations come from the various references listed in the main text.

usual Moore's tables.[32] Here again we see that the charge-transfer fragments correlate with the lowest He_2^+ bound and dissociative states, while the further set of excited electronic states of the fragments mentioned before now correlates with excited states of both He_2^+ and He_2, which correspond in most cases to bound structures of the residual dimer system.

In order to better test the quality of our basis set expansion, we have also carried out some further calculations on the dissociative behavior of the excited states of the HeH^+ system, as examples of some of the states associated with the first group of excitations discussed in Figure 5. This is an important step in order to make sure that we will be able to reliably assign the various asymptotic channels when carrying out the mapping of the excited PES for the various breakup arrangements of the ionic cluster.

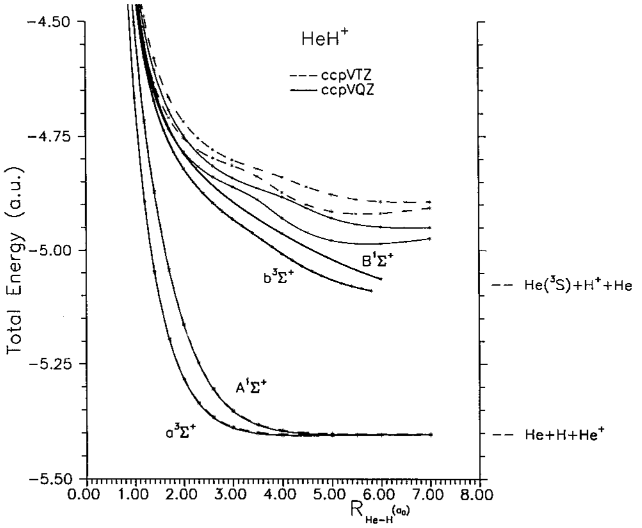

Figure 6. Computed potential energy curves for some excited states of HeH^+. Dashed lines: present calculations with the VTZ basis set discussed in the main text. Solid line present calculations with the larger VQZ basis set also discussed in the main text. Curves with stars and with state labels are earlier calculations from ref 27.

The results of the calculations are presented in Figure 6, where we show the two lowest excited states of HeH^+, the repulsive a $^3\Sigma^+$ and A $^1\Sigma^+$. They both correctly dissociate into the lowest electronic states of the CT channel, as was already shown by the more extensive, earlier calculations[26] reported in Figure 5. Furthermore, the higher excited states that produce the triplet state of helium as one of the asymptotic fragments, located about 8.84 eV above the previous excitation level, are also shown in comparison with earlier results.[27] The previous results are given by the two curves labeled b $^3\Sigma^+$ and B $^1\Sigma^+$ and are shown to lead correctly to the required asymptotes, although no values were available beyond $R_{HeH} \approx 6.0\ a_0$. On the other hand, the present calculations using the valence-triple-zeta (VTZ) basis set discussed in the previous section are shown by the dashed lines and appear to describe the dissociative curves as progressing to the incorrect asymptotic limit. When we improve on the size of the chosen basis, in order to better describe the triplet states of the excited helium atom as the cluster breaks up, and we move to a quadruple-zeta (VQZ) basis (given by He: 7s3p2d1f; H:6s3p2d1f GTOs, contracted to He:4s3p2d1f; H:4s3p2d1f), we obtain a clear improvement for the excited states, as indicated by the unmarked solid curves just below the dashed ones. However, we still seem to have problems in describing the diffuse nature of the helium triplet state and its correct polarization by the core charge at larger internuclear distances. This is due to the lack of Rydberg orbitals being included in our additional basis set expansion since we wanted first to optimize the valence shell correlation. We therefore decided to limit our study to the lower excited states of the relevant PES in order to make sure that our chosen basis set could be trusted in the asymptotic regions and would provide us with the correct behavior of the fragmentation channels involved. In any event, given the range of available laser excitation energies in such experiments,[33] we expect that the lower group of CT states would be the one more directly amenable to detection in time-of-flight observations. It is also worth noting here that the results from the two basis sets described above and those from the earlier calculations[27] all coincide for the lowest curves shown in the figure.

Figure 7 reports the triplet states (left side) and the singlet states (right side) associated with the linear structure containing the ionic core. The lowest two excited states are shown in Figure 7a, while the next higher excited states are reported in Figure 7b. The relevant ground state PES was discussed in Figure 2, and the symmetric dissociation curves were reported already in Figure 1.

One clearly saw from the cuts reported earlier in Figure 1 that the two triplet and two singlet excited states lead to the CT fragments, while the structure of the higher excited states was more complicated, exhibiting various curve crossings and the presence of attractive wells that we did not finally report. The corresponding behavior of the fuller PES of Figure 7 therefore follows this general pattern: the lowest excited PESs,

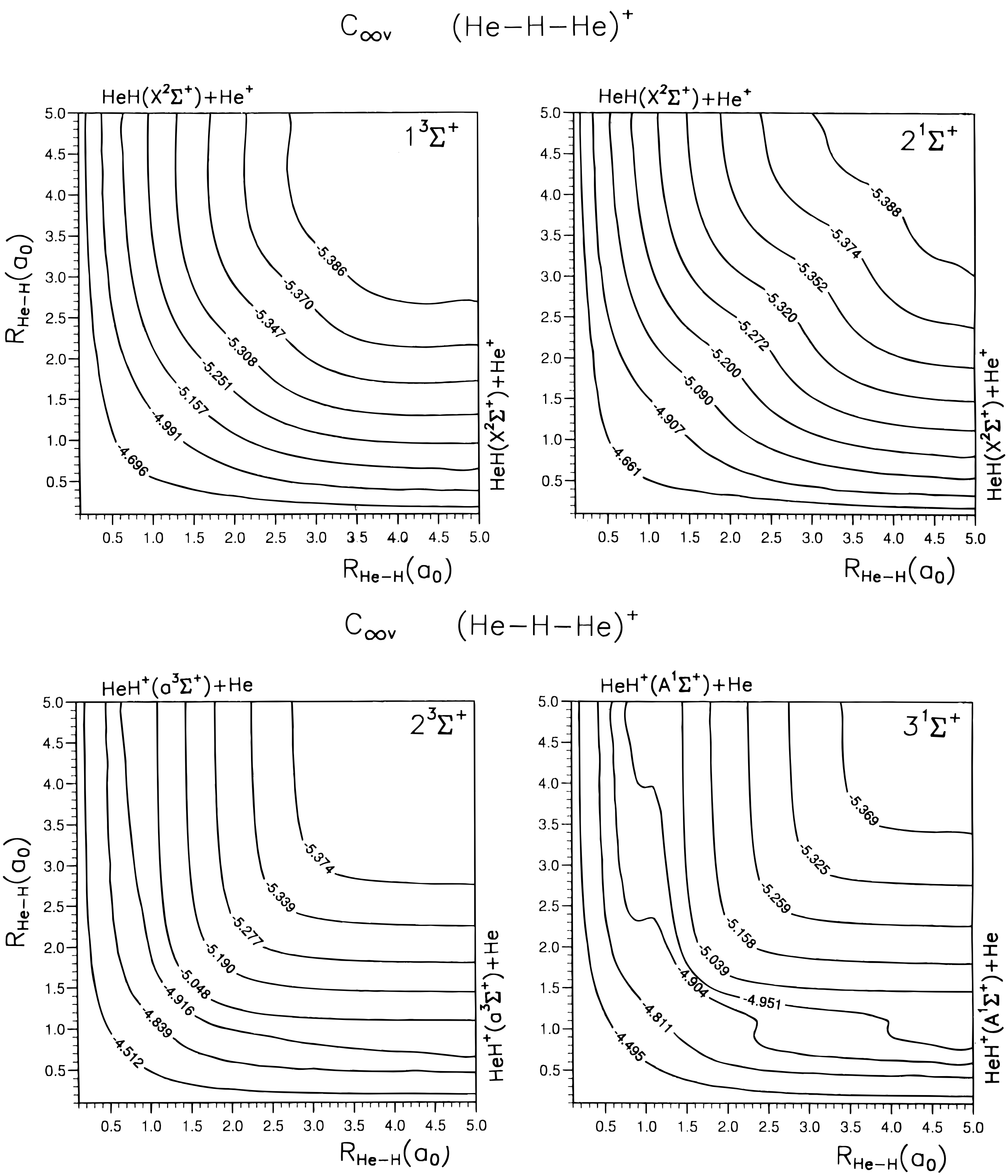

Figure 7. Computed MRD-CI potential energy surfaces for the excited electronic states of the linear $(HeHHe)^+$ arrangement. Left sides: triplet states. Right sides: singlet states. The energies increase from the two states of part a (top) to the states listed in part b (bottom). In both figures the asymptotic fragments are shown for the two coordinates.

singlet and triplet (Figure 7a), correspond to the removal of either of the helium atoms with the transfer of the charge onto the atomic fragment and the formation of the repulsive ground electronic state of HeH, the X $^2\Sigma^+$ state. As one sees in that figure, both surfaces are repulsive in both directions. They lie about 11.15 eV above the ground state asymptotic fragments and about 19 eV above the FC region of the symmetric ionic cluster structure. The next electronically excited states, labeled in Figure 7b the 2 $^3\Sigma^+$ and 3 $^1\Sigma^+$ states, respectively, are also both fully repulsive at all distances and in the region of geometries for the stable trimer of the ground state, the He_2H^+ equilibrium structure of Figures 1 and 2. Their asymptotic channels correspond, symmetrically, to the removal of either of the helium atoms as neutral partners and to the formation of the lowest excited states of the ionic HeH^+ diatomic species: the a $^3\Sigma^+$ and A $^1\Sigma^+$ states, respectively (see also Figure 5). Therefore they are also CT states with respect to the full fragmentation of the symmetric channel in Figure 1 and correspond to the excited equivalent of the asymptotic channels of Figure 2, where the HeH^+ diatomic ion was formed in its

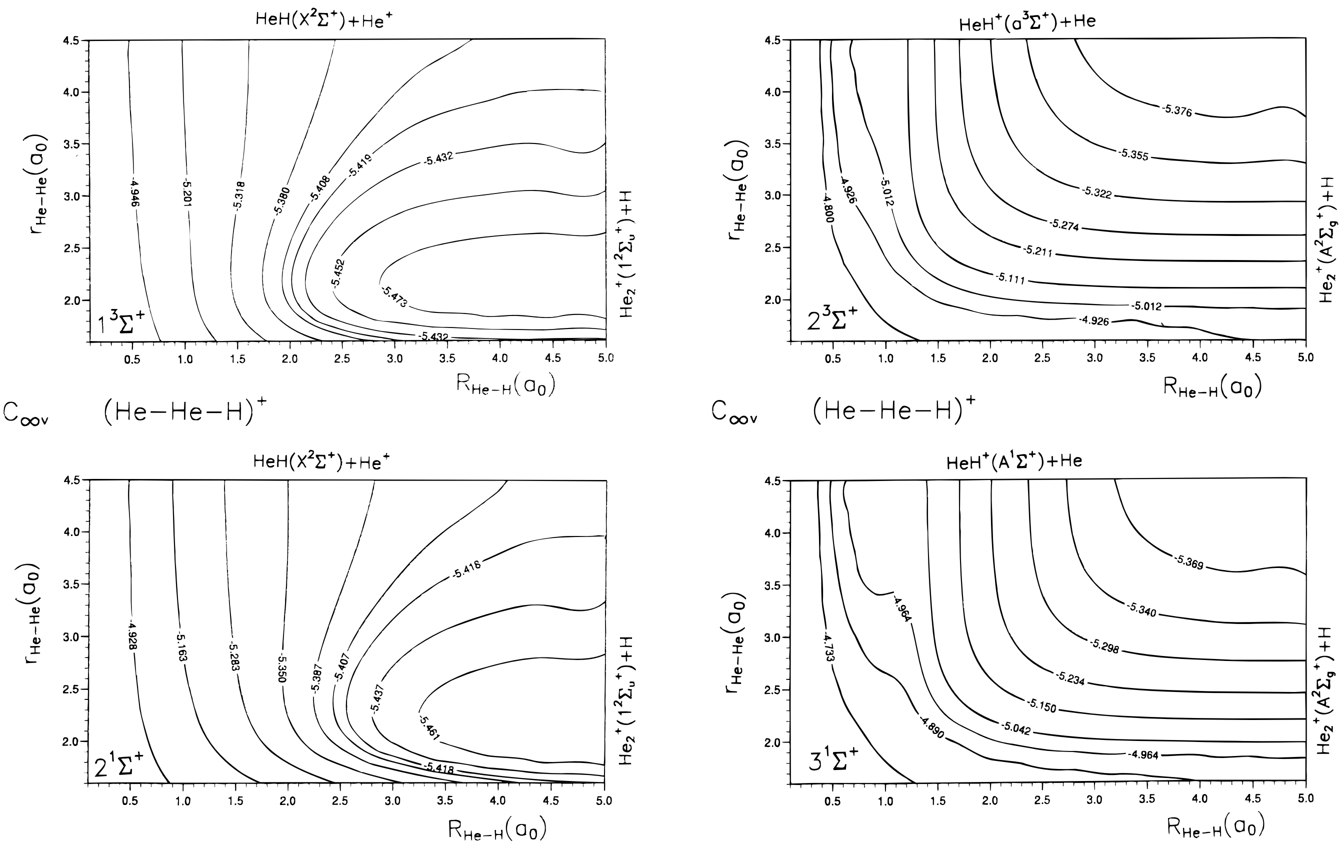

Figure 8. Same as in Figure 7 but for the asymmetric linear arrangements: (a, left) lowest singlet (bottom) and triplet (top) states; (b, right) next higher excited singlet and triplet states, also shown from bottom to top. The vertical asymptotic states refer to the He−He coordinate, while the horizontal states refer to the He−H coordinate. For all the electronic states the asymptotic products for both coordinates are shown.

ground electronic state. In the excited state situation, however, we can obviously have either the singlet or the triplet states of the protonated helium system.

The calculations of Figure 8 report further results for the excited states obtained within the arrangement by which the ionic partner, as discussed before, is brought in from the outside of the cluster and not inside it. Thus, the lowest excited states (singlet and triplet) are shown in Figure 8a, bottom to top. The next higher excited states which also give singlet and triplet configurations are shown in Figure 8b. As in the previous description of the ground electronic state PES of Figure 3, the *x* variable represents the distance between the helium atom and the added proton, while the *y* variable describes the He−He internuclear distance (all values in atomic units).

The two lowest PES, singlet and triplet, now correspond to asymptotic channels where the charge is transferred from the added proton onto the other separating fragment, be it either He_2^+ or He^+. As one sees from the cut shown on the top of Figure 3, the CT complex is repulsive in the region of the ground state of the trimer $HHe^+\cdots He$, a species only weakly bound with respect to either the H^+ removal or to the neutral helium removal with HeH^+ formation. In both its excited singlet and triplet states, therefore, the lowest CT complex can break up either by forming $He_2^+(X\ ^2\Sigma_u^+)$ and the hydrogen atom, which becomes essentially detatched at fairly short distances from the ionic dimer ($x > 3.5\ a_0$), or by forming a dissociating HeH in its ground electronic state ($X^2\Sigma^+$) plus the helium ion in its ground electronic state (^2S). In either case, therefore, the excitation of the weakly bound protonated adduct on the helium dimer breaks up the system by forming either He^+ or He_2^+ ionic fragments. The latter ionic dimer was not formed by adiabatically dissociating the ground electronic state of the same adduct and therefore the CT excitation is seen to bring about different final products.

$$\mathrm{He_2H^+(X\ ^1\Sigma^+)}\begin{cases}\nearrow \begin{cases}\mathrm{He + He + H^+}\\ \mathrm{He + HeH^+(X\ ^1\Sigma^+)}\end{cases} & (7)\\ \xrightarrow{h\nu} \begin{cases}\mathrm{He + He^+ + H}\\ \mathrm{He_2^+(1\ ^2\Sigma_u^+) + H}\end{cases} & (8)\end{cases}$$

The next excited electronic states, singlet and triplet, are seen in Figure 8b to be both fully repulsive at all distances and to give rise to yet another set of final fragments in excited electronic states, depending on the dissociating channel that is being considered. Thus, when one examines the H removal from the adduct, then the corresponding He_2^+ fragment is also moving along a dissociative path since it is being formed in its A $^2\Sigma_g^+$ excited state, and therefore the full fragmentation occurs into He + He^+ + H. When the "internal" dimer coordinate is considered, then the removal of one of the helium atoms leaves behind the HeH^+ system either in its A $^1\Sigma^+$ or its a $^3\Sigma^+$ excited state, which are both repulsive, thus producing the same final products of the full dissociation. In conclusion, the excitation of the weakly stabilized, externally protonated He_2^+ mostly leads to full fragmentation of the cluster, but it could also give rise to the formation of the He_2^+ species by a CT mechanism.

For the sake of completness, we present in Figure 9 the behavior of the lower two excited electronic states for the arrangement where the foreign ion gets inserted into the dimer

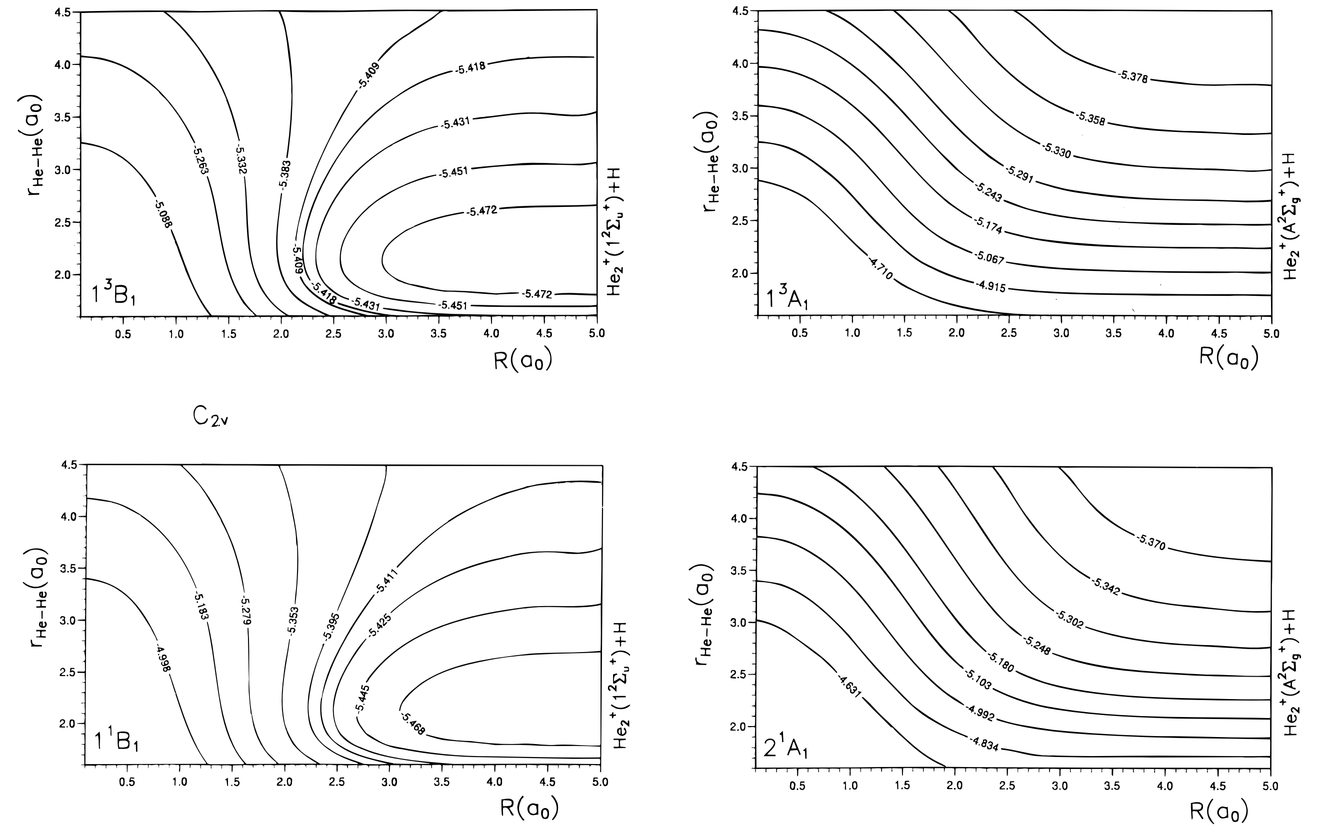

Figure 9. Same as in Figure 8 but for the C_{2v} arrangements: (a, left) 1 $^1B_1$ and 1 $^3B_1$ states; (b, right) next higher singlet and triplet states. The asymptotic states listed refer to the R_{HHe_2}, or x, coordinate for each PES.

cluster along the C_{2v}, perpendicular direction. As discussed before, and as shown in Figure 4, the ground electronic state has an absolute minimum at the full insertion arrangement, whereby the two helium atoms separate to accommodate the ionic core in the linear symmetric structure. On the other hand, the cluster is dissociating along an attractive, long-range surface cut when the H^+ is removed and a series of temporary, weakly bound complexes can be formed with the HeH^+ core and the additional helium atom attached to it. The excited electronic states, both triplet and singlet, that are the closest to the ground state are shown in the two diagrams of Figure 9a. The removal of the H atom leads now to the formation of CT species where He_2^+ is formed in its (X $^2\Sigma_u^+$) ground electronic state. At the same time, the removal of one of the helium atoms leads to repulsive configurations of the HeH^+ system in its singlet and triplet Σ^+ states, and therefore it leads to full fragmentation of the ionic clusters when the He−He distance is stretched beyond the equilibrium distance of the isolated dimer ion and the H atom has not been removed as yet.

The next higher electronic states, both singlet and triplet, are reported in Figure 9b and appear to be fully repulsive along both coordinates. The removal of the H atom leads to the formation of an excited electronic state of He_2^+, the A $^2\Sigma_g^+$ state, which is a repulsive state. At the same time, the removal of one of the helium atoms leads to the dissociative, repulsive states of HeH^+ that eventually cause the full fragmentation of the ionic cluster.

4. Summary and Conclusions

In the present work we have examined the shape of the lowest potential energy surfaces that can help us to model the relative energetics and the optimal geometries of small helium clusters containing a "foreign" ion. Specifically, we have carried out MRD-CI calculations of the interactions within a protonated helium dimer over a broad range of relative geometries and for three representative orientations corresponding to "external" proton addition to the cluster and to H^+ insertions into the cluster from linear and nonlinear approaches. We have also examined the possible excited electronic states of such ionic clusters and the different fragmentation products that could be formed after the breakup process.

In spite of the simplicity of the system being studied, several aspects of the results are likely to be useful also for the larger systems, which we are currently further analyzing.[34]

(i) The symmetric insertion of the ion core provides the most stable structure and the most strongly bound configuration for the protonated dimer.

(ii) The location of the ion outside the cluster (asymmetric linear arrangement) only gives rise to an HeH^+ core with an extra atom weakly bound by polarization forces. Thus, in this instance the ionic core structure appears to be the most logical and most stable arrangement of the system.

(iii) According to the initial structure of the cluster, either linear symmetric or asymmetric (linear and nonlinear), the fragmentation paths along the ground electronic states invariably lead to fragments where the residual charge remains on the proton, and therefore only neutral atomic helium is produced.

(iv) The lowest electronic excitation, on the other hand, leads to the formation of charge-transfer (CT) states whereby the positive charge is relocated, depending on the arrangement examined, either on He_2^+ or on He^+, species that can exist in stable bound states. In the linear arrangements He^+ can also be formed together with a dissociative HeH(X $^2\Sigma^+$) state.

(v) The analysis of the next higher excited electronic states indicates the presence of two types of PESs: one rather close to the first excited level and that, for all orientations examined, behaves essentially in the same way as the latter; that is, it gives rise to CT states, either atomic (He^+) or molecular (HeH^+ and

He_2^+). A further higher group of electronically excited surfaces that dissociate into electronically excited helium atoms or into bound excimer states of He_2 is also surmised by our calculations.

The variety of possible fragmentation products after electronic excitation, even for a simple system as the present one, indicates that it may be of interest to further use H^+ as a foreign, inserted ion into helium clusters and to observe more closely the behavior of such small ionic clusters in terms of relative time-of-flight stability and of relative excitation probabilities into different products. Such results would complement the existing findings from drift-tube experiments and would further spur calculations of larger aggregates.[34]

Acknowledgment. The financial support of the Italian National Research Council (CNR) and of the Italian Ministry of Universities and Research (MURST) is gratefully acknowledged. One of us (F.S.) thanks the E.U. for the award of a Fellowship to the University of Rome, under Contract No. ERB-CHBG-CT930346, where this work was completed. F.A.G. also thanks Professor Peter Toennies for various useful discussions and for the warm hospitality in his laboratory in Göttingen during the summer of 1996.

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