Theory of chemical reactions of vibronically excited H_2 ($B\ ^1\Sigma_u^+$). III. Formation of bound excited states of the $(H_2)_2$, $(H_2)_3$, and $(H_2)_5$ clusters

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We present a simple theory of bonding in certain van der Waals clusters and results of configuration-interaction calculations which demonstrate the existence of *bound excited singlet states* of the $(H_2)_2$, $(H_2)_3$, and $(H_2)_5$ clusters. The hypersurfaces of these bound states have minima close to avoided crossings with the lowest $^1A'$ state repulsive hypersurfaces. Similar results are expected for a variety of other clusters. Apart from their importance in the theory and spectroscopy of molecular structure and dynamics, these findings may find application in problems of excitation and energy transfer in liquids and solids, whose properties are supposed to be approximated by large clusters.

I. INTRODUCTION

Aggregates of closed shell, nonreactive atoms or molecules, [e.g., HeH_2, $(H_2)_n$, $(HF)_n$, $(H_2O)_n$ etc.] form clusters which are bound weakly via the long range dispersion forces. The experimental and theoretical study of such van der Waals clusters is of considerable current interest (e.g., Refs. 1–5 and references therein). This is so for two main reasons: Firstly, because such clusters, as well as clusters of metallic atoms (e.g., Refs. 6–9 and references therein) constitute a distinct state of matter which can be isolated and examined experimentally in conditions of low temperatures. Thus, they offer a new and integrated field of research. Secondly, because they are intermediate between the molecular and the liquid or solid phase and, therefore, can be used as basic source of information regarding the rigorous description of atomic and molecular aggregation to form liquids and solids.

Until recently, the theoretical work on van der Waals clusters of closed shell species was confined mainly to the ground state. Numerous studies have dealt with the shallow minima on the repulsive hypersurfaces. A number of reasons for this emphasis exist. For example, (1) Ground state calculations of potential energy surfaces are straight forward by a number of many-electron computational approaches. (2) Due to the young age of this field, there is much work to be done—at the electron correlation level—to deduce reliable information regarding binding mechanisms, conformational stability, and reactivity of clusters in ground states. (3) As is well known, carrying out complete many-electron calculations on a large system is forbidding even with today's computational capabilities. For the ground state, the size of the computations is reduced tremendously by *assuming* the nuclear configurations from known data (e.g., lattices, isolated diatomic or triatomic molecules) or from a few standard geometries (linear, square, tetrahedral, etc.).

The energy surfaces and wave function characteristics of excited states of clusters is essentially *terra incognita*. Weak binding, due to the long range forces, is certainly present. For example, this can be seen in the computations of Römelt *et al.*[10] on the $He + H_2^*$ excited state surfaces, or in the experimental observations via the recently developed low temperature high-resolution spectroscopy.[2]

But apart from this general and nonspecific expectation, important questions remain: Do *chemically bound* excited states exist and, if so, at what geometry? What are their energy hypersurfaces? Their reactivity and decay modes? The extensive computational analysis of Gerhartz *et al.*[11] on the simple H_4 system give an idea of the significance as well as the difficulties present in such questions.

In this paper we make the first predictions for the existence of *bound singlet* excited states in $(H_2)_2$, $(H_2)_3$, and $(H_2)_5$. These predictions are based on a recently proposed simple theory for the formation of stable clusters in excited states[12,13] and are supported by many-electron calculations which include electron correlation and yield reliable energy hypersurfaces at prespecified geometries. This theory has already been used to predict the formation of bound excited singlet states of the noble gas dihydrides MH_2(M = He, Ne, Ar) and of the $(H_2)_2$ dimer, predictions which have been verified computationally at a state-specific Hartree–Fock level[13] or, more accurately, at a configuration–interaction (CI) level for the $(H_2)_2^*$[12] and the HeH_2^*[14] systems. These predictions have provided an explanation of the experimental observations of quenching of the H_2 $^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ line in the presence of H_2 or He.[15–17] After the formation of these excited states, energy must be dissipated via nonadiabatic coupling with the closely lying repulsive ground state. The confirmation of the importance of this decay process awaits the computation of its transition probability.

II. SIMPLE THEORY FOR THE PREDICTION OF BOUND EXCITED STATES OF VAN DER WAALS CLUSTERS AT PRESPECIFIED GEOMETRIES

Chemical binding in excited states of van der Waals clusters has not been determined experimentally yet.

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However, it appears that its effect has been observed indirectly in the simplest of them, such as the noble gas dihydrides or the $(H_2)_2$ dimer.[12–17] According to the observations of Akins *et al.*[15] and Fink *et al.*,[16,17] the fluorescence from the $H_2^*\ B\,{}^1\Sigma_u^+$ state in the presence of He or H_2 suffers quenching. In order to interpret the implied energy transfer process, Schaefer *et al.*[18] and later Römelt *et al.*[10] carried out large CI calculations on the $He + H_2^*$ system at a number of geometrical points. Certain negative conclusions were reached but their results did not allow a definitive explanation. The recent theoretical results of Farantos *et al.*[14] and Nicolaides *et al.*[13] have predicted the existence of a *bound* excited singlet state at an avoided crossing with the repulsive ground state. These findings are in accordance with the experimental observations.

Carrying out reliable many-electron calculations on excited states of large van der Waals clusters over thousands of nuclear geometrical points looking for a possible minimum of the hypersurface below certain dissociation limit is, for obvious reasons, unrealistic and intellectually unattractive. For, even for the smallest of such systems, the triatomic HeH_2, the work mentioned above shows that if the hypersurfaces are not mapped out extensively the conclusions may be incomplete.

A more meaningful and realistic approach for the theoretical search of such bound excited states would be one which employs general concepts of symmetry and electronic structure and, through the application of simple rules, allows the prediction of probable stable nuclear configurations which can be verified with a minimum of computational effort. Such a theory is presented below.

We start by recalling two facts:

(1) Due to the increased Coulomb attraction, positive ions of clusters have been found to be bound (e.g., Refs. 4 and 5).

(2) When molecules are excited electronically to singlet states, large charge transfer may occur as a function of rotation or vibration. These situations involve Rydberg-valence configurational mixing and are expected to give rise to large multipole moments. Such cases are the symmetry-breaking "sudden polarization effect" in ethylene (e.g., Ref. 19) or the covalent–ionic switching in $H_2^*\ B\,{}^1\Sigma_u^+$ as a function of the internuclear distance R (20). Thus, as a function of nuclear configuration, we expect to find a geometry for which there exists a "maximum ionicity excited state" (MIES) [e.g., for the $H_2^*\ B\,{}^1\Sigma_u^+$ state, its equilibrium distance is 2.43 a_0[20]—which is the geometry used by Schaefer *et al.*[18]—while its MIES distance is around 4.0 a_0[20]].

The arguments which follow refer to conditions of chemical binding and not to the extremely complicated problem of the multidimensional behavior of the hypersurfaces and the related dynamics.

The lowest singlet excited state of the cluster correlates with an excited singlet atomic or molecular constituent and the remaining part in its ground state. It will be bound if its energy surface has a minimum below the corresponding dissociation limit. Now, suppose the excited singlet molecular constituent AB (A and B are parts of the molecule) has a geometry for which a strong MIES exists (say A^+B^-). Then, starting from the asymptotic region, the system [(cluster − AB) + AB] will want to distort its geometry so that a positive (cluster − AB + A^+) is formed. Depending on symmetry and steric effects determined by the nuclei, as well as overlap effects determined by the electronic characteristics of B^-(e.g., presence of a diffuse Rydberg orbital) the overall cluster may bind at a geometry characterized by two geometries which can be established separately: That of the positive ion (cluster − AB + A^+) and that of the MIES A^+B^-.

It is clear from the above, that the geometrical distortion from the equilibrium position of excited AB to achieve a MIES, is an induced effect, yielding a unique conformation for those AB excited states dissociating into *neutral* species. On the other hand, there are excited singlet states, such as the second ${}^1\Sigma^+$ state of LiF,[21] which become ionic at some point and remain such until dissociation. Although we have not carried out calculations on such species yet, [e.g., on the $(LiF)_2^*$ excited dimer] we expect these excited states to undergo chemical binding with the remaining ground state singlet cluster at a geometry near their (AB) equilibrium position where, due to an avoided crossing with the covalent configuration, strong ionicity appears abruptly.[21]

III. APPLICATION TO $(H_2)_2^*$,$(H_2)_3^*$, and $(H_2)_5^*$. MULTIREFERENCE DOUBLY EXCITED CI CALCULATIONS AND RESULTS

The theory of formation of bound excited singlet states of clusters has already been applied to the noble gas dihydrides HeH_2, NeH_2, and ArH_2.[13] Given the analysis of the binding, it was assumed and was found that state-specific Hartree–Fock calculations are sufficient to predict the existence of such bound states.

In this section, this theory is applied to clusters of hydrogen molecules, the $(H_2)_2$, $(H_2)_3$, and $(H_2)_5$. This application has two steps: Firstly, we need a methodology for predicting the (approximate) geometry of the singlet bound excited state before a direct calculation. Secondly, we need a computational approach which accounts for electron correlation and yields reliable excited state hypersurfaces.

The proposed methodology goes as follows:

(1) The excited state molecular constituent with which the cluster singlet excited state will correlate asymptotically is $H_2^*\ B\,{}^1\Sigma_u^+$. Its reaction with H_2, $(H_2)_2$, and $(H_2)_4$ is expected to produce the bound excited clusters.

(2) The distance R_0 at which $B\,{}^1\Sigma_u^+$ becomes a MIES is 4.0 a_0.[20]

(3) The positive ion clusters are $(H_2)H^+$, $(H_2)_2H^+$, and $(H_2)_4H^+$. The geometry of $(H_2)H^+$ has been known for some time (e.g., Ref. 22) while the geometries of $(H_2)_2H^+$ and $(H_2)_4H^+$ were determined only recently.[5]

The geometry of the $(H_2)H^+$ system is that of an equilateral triangle with side length of $r = 1.65\ a_0$.[22] Given this

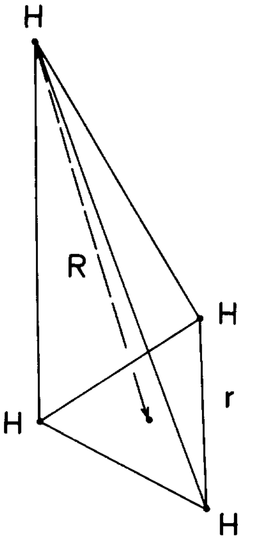

FIG. 1. The geometry used for $(H_2)_2^*$. The quantities R and r were varied in the calculations.

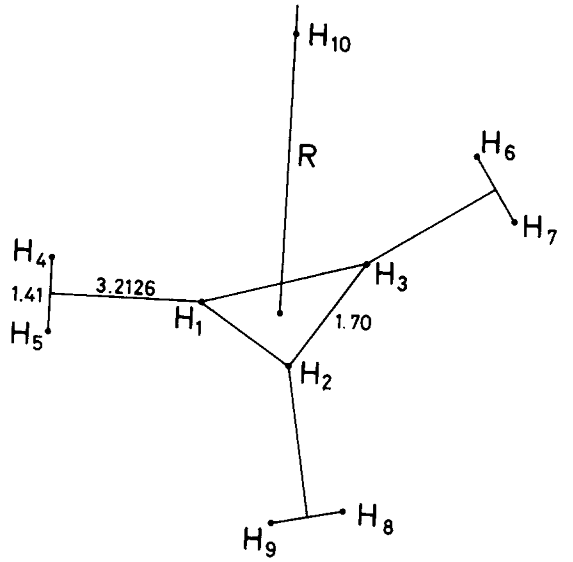

FIG. 3. The geometry of $(H_2)_5^*$, R was varied in the calculations.

configuration, we expect the fourth hydrogen of the $(H_2)_2$ singlet excited state to position itself at about 4.0 a_0 above the center of the triangle (Figs. 1 and 2).

The most stable geometry of the $(H_2)_4H^+$ cluster is what intuitively one might expect: The "nucleus" is the $(H_2)H^+$ system and the three H_2 molecules are bonded directly with each hydrogen of the triangle Ref. 5. Again, our prediction for the configuration of a stable excited state is that where the 10th hydrogen is about 4.0 a_0 above the center of H_3^+ (Fig. 3). Due to the symmetric $H_3^+\cdots H_2$ bonding, the overall attractive potential is expected to be weaker than that of the isolated H_3^+ ion. Thus, the 10th hydrogen is expected to be "floppy", moving in an energy hypersurface which has a flat minimum. Our one dimensional calculations (along the R coordinate) bear this out (Fig. 4) with the computed minimum being at 6.0 bohr. Unlike the situation with the positive ion H_9^+,[5] here we found it necessary to place the three H_2 ligands coplanar with the H_3^+ ring in order to obtain a clear minimum.

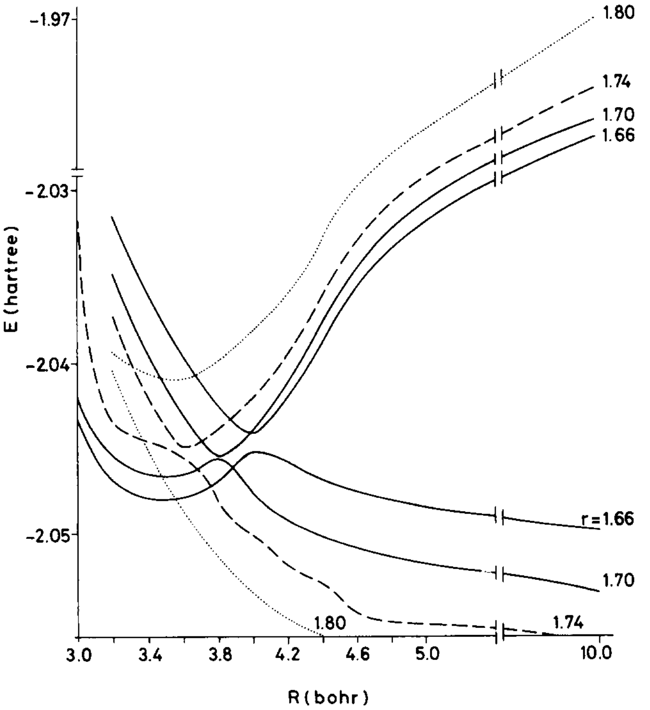

FIG. 2. Potential energy surfaces (in au.) for the ground and first excited state of $^1A'$ symmetry of H_4 at the geometry of a trigonal pyramid. R is the distance of the fourth H from the center of the H_3 triangle of side r. The energies plotted have been obtained using a threshold of 10 μH in the MRD–CI calculations.

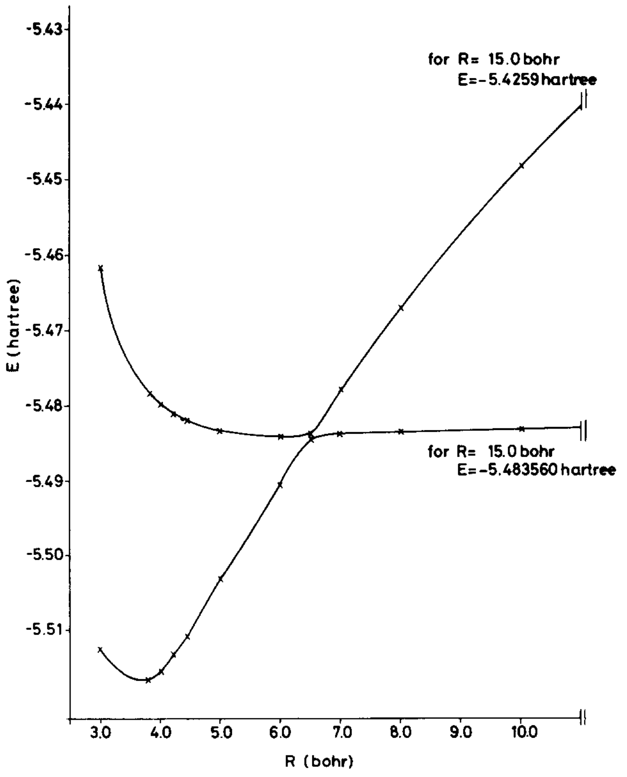

FIG. 4. Potential energy curve for the ground and 2 $^1A'$ excited state of $(H_2)_5$ calculated using the geometry shown in Fig. 3.

According to the calculations of Yamagushi *et al.*[5] and their discussion, the definitive determination of the most stable conformer of the $(H_2)_2H^+$ cluster is still an open question. The energies of the three structures which they considered (see Figs. 2,3, and 4 of their paper) are almost the same. For reasons of computational convenience we adopted the D_{2h} and the C_{2v} conformers of Ref. 5. However, for the C_{2v} case, we placed the ligand H_2 coplanar with the H_3 ring by analogy with the $(H_2)_5$ system. Again, the geometry of the $(H_2)_3$ singlet excited state minimum follows directly from our theory (Figs. 5 and 7).

In order to substantiate the predictions of this bonding model in $(H_2)_n^*$, we need to apply a general and powerful computational approach which accounts for the details of electron correlation in excited states of systems with long and weak bonds. Such a method is the "multiconfigurational double excitation configuration interaction" (MRD–CI) approach of Buenker and Peyerimhoff.[23] In MRD–CI one has the flexibility of choosing a few configurations contributing the most to the states under examination and using them as a reference multiconfigurational zeroth order vector to perform "singles and doubles CI". Such an approach is necessary for the reliable description of excited states of many molecules (for atomic excited states see, e.g., Ref. 24), where the relative importance of the various configurations changes as a function of geometry.

The AO basis set used was the following: For $(H_2)_2$ and $(H_2)_3$ the 5*s*/3*s* hydrogen set of Dunning[25] was augmented with a *p*-type (exponent 0.7) polarization and an *s*-type (exponent 0.025) diffuse function,[10] while for $(H_2)_5$ the 5*s*/2*s* hydrogen set[26] was employed together with the polarization and diffuse functions.

The calculations were carried out in C_s symmetry for $(H_2)_2$, $(H_2)_5$, and $(H_2)_3$ (with C_{2v} H_5^+) and C_{2v} symmetry for $(H_2)_3$ (with D_{2h} H_5^+). The MOs of the $^1A''$ state [$^1B_1$ for $(H_2)_3$] (with D_{2h} H_5^+) were used in the CI calculations since it was thought that, having been obtained from an SCF, open shell, they would be more appropriate for large values of R. In all cases, enough reference configurations were used to ensure a $\Sigma_n c_{on}^2$ of about 0.95 or more for the reference vectors in the final CI, for all geometries. Configurations were selected on the basis of the contribution to the energy of the first two roots, with a selection threshold T of 10 μH.[23] For $(H_2)_2$, several points were also calculated using $T = 0.1$ μH. This had no appreciable effect on the shapes of the surfaces obtained with $T = 10\,\mu$H. The characteristics of the MRD–CI calculations are given in Table I.

TABLE I. Characteristics of the MRD–CI calculations.

System	Number of reference configurations	Selection threshold (μ H)	Size of secular equation
$(H_2)_2$	15	10	800
$(H_2)_2$	15	0.1	2500
$(H_2)_3$[a]	10	10	2000
$(H_2)_3$[b]	14	10	2500
$(H_2)_5$	11	10	7000

[a] D_{2h} symmetry of $(H_2)_2H^+$.
[b] C_{2v} symmetry of $(H_2)_2H^+$.

Both the ground and the first excited singlet (of the same symmetry as the ground) states were computed. Given the small size of $(H_2)_2$, the side of the triangle r as well as the distance of the fourth hydrogen from the center of the triangle R were varied in order to test whether we find a minimum or a saddle point. The $(H_2)_2$ cluster was the test case for this theory, giving a true minimum near the predicted geometry.[12] Due to computational limitations for the larger $(H_2)_3$ and $(H_2)_5$ systems, only a

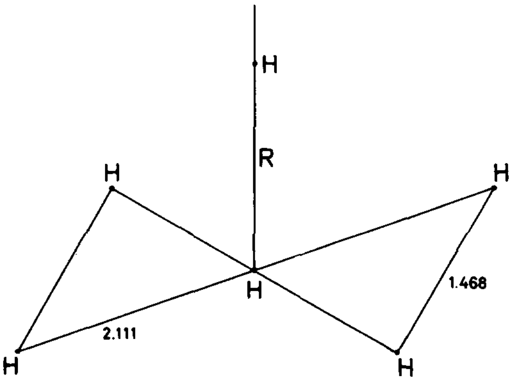

FIG. 5. The geometry of the $(H_2)_3^*$ cluster with D_{2h} geometry of the $(H_2)_2H^+$ moiety and variable R.

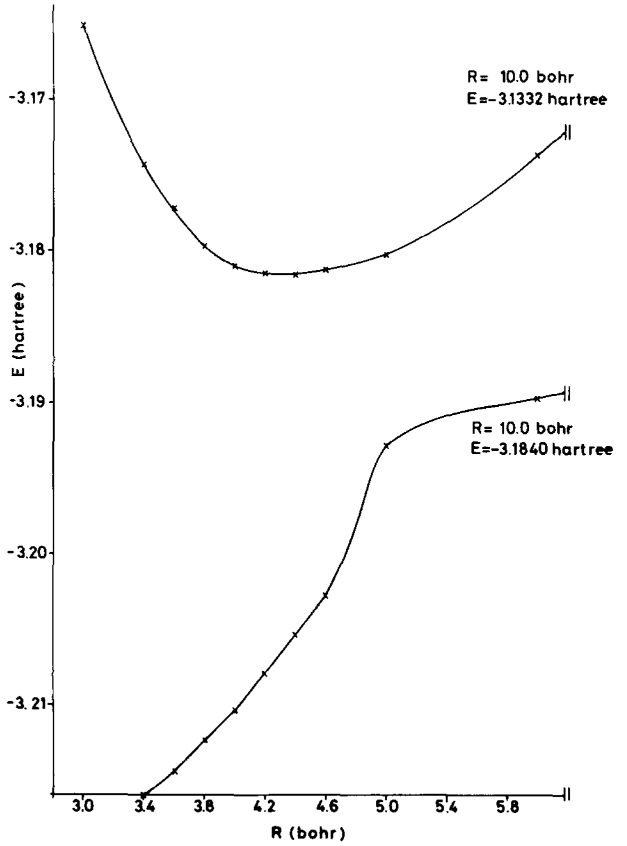

FIG. 6. Potential energy curves for the ground and 2 $^1A_1$ states of $(H_2)_3$ calculated for the geometry given in Fig. 5.

TABLE II. $(H_2)_2$: Total energies,[a] E (in a.u.) and the square of coefficients of the three most important configurations at the avoided crossing for $r = 1.70$ a_0. The configurations $1a'^2 2a'^2$, $1a'^2 2a'3a'$, and $1a'^2 2a'4a'$, are denoted by $2a'$, $3a'$, and $4a'$ for short.

R (a_0)		Ground ($\tilde{X}\ 'A'$)	Excited ($2\ 'A'$)
3.7	E:	−2.046 742	−2.044 816
	$2a'$:	0.789 5	0.000 0
	$3a'$:	0.024 1	0.663 3
	$4a'$:	0.094 3	0.145 4
3.8	E:	−2.046 055	−2.046 010
	$2a'$:	0.772 7	0.033 9
	$3a'$:	0.071 9	0.640 9
	$4a'$:	0.062 7	0.129 5
3.9	E:	−2.047 037	−2.045 189
	$2a'$:	0.000 0	0.774 9
	$3a'$:	0.537 6	0.047 2
	$4a'$:	0.242 0	0.081 4

[a] MRD–CI energies obtained with $T = 1 \times 10^{-7}$ hartree.

few geometrical arrangements were tested which, however, were sufficient to verify our predictions. Again for reasons of computational limitations, the $(H_2)_4$ system was not examined.

The results of our calculations are presented in Figs. 2, 4, 6, and 8 in the form of potential energy curves and in Tables II–V. The tables show the MRD–CI energies of the clusters in the ground and the excited states as well as the square of the coefficients of the most important configurations at the avoided crossings. At the minima, the excited states have mainly Rydberg character in all cases except for the $(H_2)_3$ with D_{2h} H_5^+ which has mainly valence character in the excited singlet state. The calculated minima have depths with respect to dissociation along the coordinate R of about 1.86 eV for $(H_2)_2$, 1.32 eV for $(H_2)_3$ with $D_{2h}(H)_2H$, 1.15 for $(H_2)_3$ with $C_{2v}(H_2)_2H$, and 1.58 eV for $(H_2)_5$. It may

TABLE III. Total energies, E (in hartree) and the square of coefficients of the most important configurations at the avoided crossing for $(H_2)_5$. The geometry is given in Fig. 3.

$R_{(a_0)}$		Ground ($\tilde{X}\ 'A'$)	Excited ($2\ 'A'$)
5.0	E	−5.503 265	−5.483 400
	$1a'^2 2a'^2 3a'^2 4a'^2 1a''^2$	0.730 6	0.000 4
	$1a'^2 2a'^2 3a'^2 1a''^2 4a'5a'$	0.181 4	0.000 7
	$4a'6a'$	0.000 0	0.620 5
	$4a'10a'$	0.011 0	0.014 4
	$4a'11a'$	0.000 2	0.143 9
6.0	E	−5.490 132	5.484 097
	$1a'^2 2a'^2 3a'^2 4a'^2 1a''^2$	0.674 5	0.000 8
	$4a'5a'$	0.234 5	0.000 2
	$4a'6a'$	0.000 8	0.457 2
	$4a'10a'$	0.014 6	0.052 7
	$4a'11a'$	0.000 1	0.233 9
6.5	E	−5.484 136	−5.484 035
	$1a'^2 2a'^2 3a'^2 4a'^2 1a''^2$	0.649 4	0.000 9
	$4a'5a'$	0.261 8	0.000 1
	$4a'6a'$	0.001 7	0.393 3
	$4a'10a'$	0.008 5	0.085 4
	$4a'11a'$	0.000 1	0.264 0
8.0	E	−5.483 734	−5.467 109
	$1a'^2 2a'^2 3a'^2 4a'^2 1a''^2$	0.001 4	0.584 9
	$4a'5a'$	0.002 5	0.325 8
	$4a'6a'$	0.262 4	0.000 0
	$4a'10a'$	0.130 1	0.005 7
	$4a'11a'$	0.321 5	0.001 6

TABLE IV. Total energies E (in hartree) and the square of the coefficients of the most important configurations at the avoided crossing for $(H_2)_3$ with C_{2v} geometry for $(H_2)_2H^+$. The geometry is given in Fig. 7.

R (a_0)		Ground ($\tilde{X}\ ^1A'$)	Excited ($2\ ^1A'$)
3.0	E	−3.210 534	−3.162 3
	$1a'^2 2a_1'^2 3a'^2$	0.804 4	0.026 5
	$3a'4a'$	0.076 4	0.734 8
	$3a'5a'$	0.034 3	0.163 2
	$3a'8a'$	0.000 0	0.010 7
4.0	E	−3.212 957	−3.173 640
	$1a'^2 2a'^2 3a'$	0.774 7	0.038 8
	$3a'4a'$	0.126 8	0.072 1
	$3a'5a'$	0.002 5	0.540 4
	$3a'8a'$	0.012 1	0.206 7
4.5	E	−3.207 810	−3.175 503
	$1a'^2 2a'^2 3a'^2$	0.683 0	0.087 3
	$3a'4a'$	0.189 4	0.017 2
	$3a'5a'$	0.033 0	0.652 1
	$3a'8a'$	0.021 3	0.110 5
5.0	E	−3.201 020	−3.175 037
	$1a'^2 2a'^2 3a'^2$	0.596 6	0.148 7
	$3a'4a'$	0.208 0	0.000 1
	$3a'5a'$	0.078 7	0.541 5
	$3a'8a'$	0.048 4	0.178 5
6.0	E	−3.190 381	−3.170 150
	$1a'^2 2a'^2 3a'^2$	0.343 4	0.346 3
	$3a'4a'$	0.200 3	0.047 2
	$3a'5a'$	0.230 5	0.278 6
	$3a'8a'$	0.161 2	0.224 9

TABLE V. Total energies E (in hartree) and the square of coefficients of the most important configurations for $(H_2)_3$, with D_{2h} geometry for $(H)_2H^+$. The geometry is given in Fig. 5.

R (a_0)		Ground ($\tilde{X}\ 'A_1$)	Excited ($2\ 'A_1$)
3.0	E	−3.220 398	−3.165 105
	$1a_1^2 2a_1^2 1b_1^2$	0.789 4	0.019 4
	$2a_1 3a_1$	0.015 7	0.848 3
	$2a_1 4a_1$	0.063 2	0.007 2
4.2	E	−3.207 959	−3.181 415
	$1a_1^2 2a_1^2 1b_1^2$	0.751 9	0.020 5
	$2a_1 3a_1$	0.042 4	0.833 3
	$2a_1 4a_1$	0.133 3	0.038 2
4.4	E	−3.205 461	−3.181 606
	$1a_1^2 2a_1^2 1b_1^2$	0.724 6	0.040 4
	$2a_1 3a_1$	0.077 7	0.796 9
	$2a_1 4a_1$	0.125 1	0.063 2
4.6	E	−3.202 952	−3.181 207
	$1a_1^2 2a_1^2 1b_1^2$	0.690 3	0.066 5
	$2a_1 3a_1$	0.124 4	0.744 0
	$2a_1 4a_1$	0.111 6	0.097 3
6.0	E	−3.189 860	−3.173 876
	$1a_1^2 2a_1^2 1b_1^2$	0.252 2	0.418 4
	$2a_1 3a_1$	0.392 5	0.009 1
	$2a_1 4a_1$	0.278 9	0.516 6

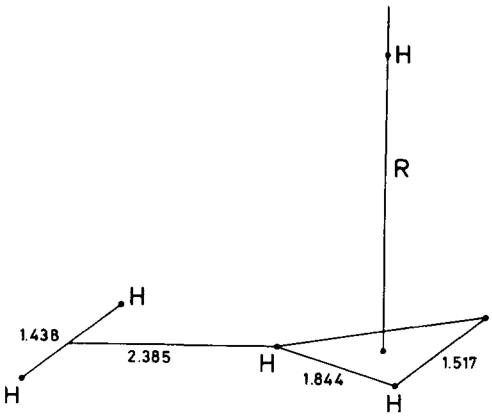

FIG. 7. The geometry of $(H_2)_3$ with C_{2v} $(H_2)_2H^+$ moiety and variable R.

also be noted that of the two conformers considered for $(H_2)_3$, the one with D_{2h} $(H_2)_2H^+$ is more favorable for the excited state.

These results constitute the essential information as regards the goal of this work. Future calculations and analyses could deal with the range of applicability of this theory to other systems, detailed mappings of the wave functions and hypersurfaces of excited states of clusters and their possible relation to bulk properties.

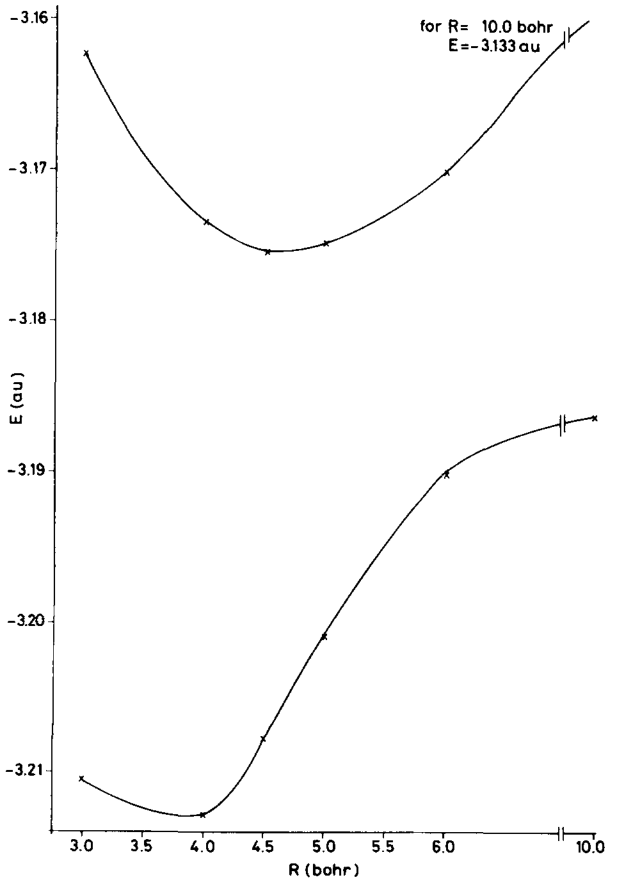

FIG. 8. Potential energy curves for the ground and 2 $^1A'$ states of $(H_2)_3$ with C_{2v} $(H_2)H^+$ moiety.

IV. CONCLUSION

A simple theory of formation of bound singlet excited states of van der Waals clusters was presented and was supported by configuration–interaction calculations on the $(H_2)_2$, $(H_2)_3$, and $(H_2)_5$ clusters. The minima of the excited state hypersurfaces are found at surfaces of avoided crossings—with the lowest $^1A'$ state—of small gap, where the wave functions acquire mainly a Rydberg character. The essential topological similarity of these clusters is reflected on the potential energy hypersurfaces (Figs. 1–8).

Apart from their expected importance in spectroscopy (e.g., see Refs. 16 and 17 for quenching of the fluorescence of H_2^* $B\ ^1\Sigma_u^+$ in the presence of H_2) these low lying bound singlet excited states may play an important role in chemical or photochemical reactions in the gaseous, liquid or solid state phase (e.g., see Ref. 11 for the simplest model system $H_2 + H_2$).

The present proposal is not restricted to the $(H_2)_n$ clusters (e.g., see Ref. 13 for results on the noble gas dihydrides). For one thing, using the H_2 $B\ ^1\Sigma_u^+$ state as the MIES, a number of protonated clusters could be examined [e.g., $(H_2O)_n$ H^+]. Furthermore, a systematic study of the wavefunction characteristics and multipole moments variation of low lying molecular excited states as a function of geometry may reveal a number of MIES which can have a similar behavior to that of H_2 $B\ ^1\Sigma_u^+$.

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