Theory of chemical reactions of vibronically excited $H_2(B\,^1\Sigma_u^+)$. I. Prediction of a strongly bound excited state of H_4

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The four center H_4 system has been a prototype of quantum chemistry and chemical physics studies.[1-11] Its potential energy surface is repulsive in the ground state. This is the case of polyatomic systems composed of "nonreactive" closed shell singlet molecular fragments: The only kind of binding discovered and studied thus far is due to the long range, van der Waals forces.

There is only scarce reliable knowledge for the excited states of such systems.[12-14] Their multitude and the details of the hypersurfaces present a formidable and laborious many-body problem while the repulsive ground state and lack of information about possible bound excited states constitute difficulties for experimental investigations. In this Communication and in the parallel paper on the noble gas dihydrides,[14] we present a simple theory and its numerical implementation regarding the prediction of bound excited states of some normally nonreactive systems, in prespecified geometries.

The initial chemical interest in the $(H_2)_2$ compound centered around the ground state hypersurface and its relation to the important and puzzling $H_2 + D_2 \rightarrow 2HD$ exchange reaction (e.g., Refs. 1, 2, and 8). Later on, results of extensive configuration interaction calculations on aspects of excited state hypersurfaces were published.[9,10] Although there were limitations as to the quality of the basis sets and the number of configurations considered, these calculations indicated the existence of a bound "excimer state."

Our interest in the H_4 system arose in order to put to test a theoretical model of chemical reactions of vibrationally excited $H_2^* B\,^1\Sigma_u^+$, or of similar maximum ionicity excited states (MIES). This model, which was put forward after the recent discovery of a bound excited state in HeH_2[13] suggests that, in many cases, unbound polyatomic systems can in fact form stable compounds in excited states, in geometries characterized by an avoided crossing with the ground state, if one of the reacting molecules can exist in a MIES. The calculations of this and of the accompanying paper[14] on the noble gas dihydrides are in accordance with this theory.

Theoretical model: When H_2 is excited vibronically to a stretched $H_2^* B\,^1\Sigma_u^+$ state, charge transfer occurs, yielding a MIES at 4.0 a_0.[15] This special state can bind electrostatically and via small overlap effects with nonreactive singlet ground states such as the noble gases[14] or $H_2\,X\,^1\Sigma_g^+$. A singlet excited state for the compound system is formed, whose approximate geometry of minimum energy can be found by considering a three step methodology:

(1) Consideration of the "positive ion complex"; i.e., that part of the molecule which includes the positive ion center of the MIES;

(2) Consideration of the "geometry of maximum ionicity";

(3) Consideration of the overlap and the volume (steric) effects of the molecule added to the MIES.

The application of the above to the $H_2 + H_2^*$ excited potential energy surface takes the following form:

(1) The positive ion complex is H_3^+. This ion is stable in an equilateral trigonal geometry with $r = 1.65\ a_0$.[16] Its electron density is higher in the center than along the bonds[17];

(2) The MIES geometry is the internuclear distance of the "H^+H^-" $B\,^1\Sigma_u^+$ state at 4.0 a_0;[15]

(3) Symmetry considerations then put the "H^-" center above the H_3^+ triangle at an approximate distance of 4.0 a_0. The resulting geometry is trigonal pyramidal—and its stability is verified by many-electron calculations (Fig. 1).

Many electron calculations: The previous analysis shows where the minimum is expected. It is a function of essentially two coordinates: Of r, the side of the triangle, and R, the distance of the fourth H from the center of the triangle.

In order to test these predictions, we have carried out MRD–CI[18] calculations for the ground and first excited singlet state of $^1A'$ symmetry around the anticipated stable geometry.

The important relevant results are presented in Fig. 1, where we plot the H_4 ground and excited singlet surfaces as a function of R and r. The minimum occurs at $R = 3.8\ a_0$, $r = 1.70\ a_0$, where the binding energy with respect to the

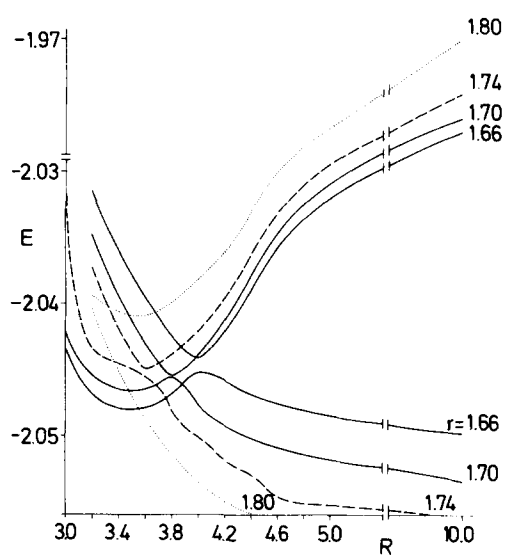

FIG. 1. Potential energy surfaces (in a.u.) for the ground and first excited state of $^1A'$ symmetry of H_4 at the geometry of a trigonal pyramid. R is the distance of the fourth H from the center of the H_3 triangle of side r. At the minimum ($R = 3.8\ a_0$, $r = 1.70\ a_0$), the binding energy of H_4^* with respect to $H_2\,(X\,^1\Sigma_g^+) + H_2^*\,(B\,^1\Sigma_u^+)$ is 3.1 eV.

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TABLE I. Total energies E (in a.u.) and the square of coefficients of the three most important configurations at each 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. At the minimum, $R = 3.8\ a_0$, the two surfaces nearly touch.

$R\ (a_0)$		Ground	Excited
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

exact energy of the separated $H_2 + H_2^*$ system[15] is 3.1 eV. The depth of the minimum with respect to dissociation along the R coordinate (for $R = 10.0\ a_0$, $r = 1.60\ a_0$) is 1.86 eV. At this minimum, the two surfaces almost touch. In fact, there is a volume of configuration space around this minimum where very close avoided crossings occur. This can be seen in the two dimensional Fig. 1. It is reasonable to expect that this hypersurface avoided crossing has implications for the spectroscopy and the photochemistry of the $H_2 + H_2^*$ system[9,11] (e.g., observed[11] quenching of $B\ ^1\Sigma_u^+$).

Table I shows the lower and upper state energies and the square of coefficients of the three most important configurations at three points around the avoided crossing depicted in Fig. 1, for $r = 1.70\ a_0$.

The results of this and the parallel papers on the noble gas dihydrides[13,14] suggest similar situations for many other nonreactive polyatomics or even clusters [e.g., $(H_2)_n$].

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State selection by resonant multiphoton ionization: $N_2^+\ A\ ^2\Pi_u,\ v^+$ [a)]

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In this communication we demonstrate the production of electronically excited, vibrationally state-selected molecular ions by resonant multiphoton ionization via a Rydberg state with an electronically excited ion core. Specifically, it is shown that the dominant ionization pathway for three photon resonant, four photon ionization of N_2 via the $o_3\ ^1\Pi_u$, $v' = 1, 2$ levels leads to the production of $N_2^+\ A\ ^2\Pi_u, v^+ = 1$, 2, respectively. The $o_3\ ^1\Pi_u$ state of N_2 has the electron configuration ... $(1\pi_u)^3(3\sigma_g)^2\ 3s\sigma_g$ and is the lowest member of Worley's third series,[1] which converges to $N_2^+\ A\ ^2\Pi_{1/2u}$. The ionizing transition strongly favors the removal of the outer $3s\sigma_g$ electron leading to the direct production of N_2^+ $A\ ^2\Pi_u$. This is the first experimental evidence in a molecular system showing the degree to which the electronic excitation of the ion core is retained following photoionization of a Rydberg state. Ganz *et al.*[2] recently observed similar effects in the photoionization of Ne $^3D_3$, that is, in all of the transitions that they observed the spin-orbit state of the ion core was preserved.

In addition to preserving the electronic state of the ion core, the $A\ ^2\Pi_u \leftarrow o_3\ ^1\Pi_u$ ionizing transition also preserves the vibrational level of the $o_3\ ^1\Pi_u$ Rydberg state. This is in accord with our calculations for the $A\ ^2\Pi_u,\ v^+ \leftarrow o\ ^1\Pi_u,\ v'$ ionizing transition using Morse potentials for both states[3,4] which give Franck–Condon factors greater than 0.99 for the $v' = v^+$ transition for $v' = 1$ and 2. Although it has been shown previously that multiphoton ionization through certain Rydberg states of NH_3 and NO leads predominantly to electronic ground state, v^+-selected ions,[5] one cannot in general rely on the Franck–Condon principle to predict vibra-

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