

Theoretical calculations on electronic transitions for H_3 , including Rydberg and transition state spectra

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MRD-CI calculations have been carried out on the ground and excited electronic states of H_3 for D_{3h} , $D_{\infty h}$, $C_{\infty v}$, and C_{2v} geometries. Dipole transition moments between the various electronic states have been also obtained at the different geometries calculated. The present work provides accurate theoretical information relevant to the transition state spectroscopy of $H + H_2$ along a collinear path and also along a perpendicular path. In addition, the present work is the first all-electron configuration interaction treatment of the Rydberg states of H_3 , and the results are in excellent agreement with the observed spectra.

I. INTRODUCTION

The H_3 system has been the subject of numerous theoretical and experimental investigations.¹ Early interest in H_3 involved mainly the repulsive ground state, as relevant to the symmetric hydrogen exchange reaction. Interest in the excited states arose from experimental reports of long-lived H_3 species,^{2,3} and in particular since 1979, following the observations of the Rydberg spectra of H_3 ,⁴⁻⁸ which involve transitions between the bound Rydberg states.

Theoretical calculations of H_3 have followed two different approaches, depending on whether the ground state or the Rydberg states were being calculated. For the ground state, emphasis has been placed on accuracy, and calculations by Liu⁹ and Siegbahn and Liu¹⁰ have employed multireference all-electron configuration interaction methods and large atomic orbital (AO) basis sets (Slater-type orbitals by Liu⁹ and Gaussian-type orbitals by Siegbahn and Liu¹⁰), in an effort to produce "chemically" accurate results.¹⁰ The points thus calculated have been fitted by Truhlar and Horowitz¹¹ and the resulting potential (referred to as SLTH) has been widely used and is considered to be the most accurate potential energy surface for any chemical reaction.^{12,13} According to the SLTH potential the ground state of H_3 is repulsive with a saddle point (for the $H + H_2$ reaction) at a $D_{\infty h}$ geometry with closest neighbor distance of 1.757 bohr, and at a barrier of 9.8 kcal/mol with respect to the dissociation limit. Recently, Varandas *et al.*¹³ have carried out new fits to the calculated data in order to obtain analytic representations for the two lowest potentials of H_3 , which undergo a conical intersection at D_{3h} geometries.

Theoretical treatments on the excited states of H_3 have placed emphasis on the calculation of a large number of electronic states, in order to reproduce the observed pattern of the energy levels in the Rydberg spectra of H_3 . These calculations¹⁴⁻¹⁸ made use of single orbital excitations over the H_3^+ core. The first work of this type on H_3 was that of King and Morokuma,¹⁴ who also calculated transition moments for the possible transitions, and this work has been widely used in interpretations of experiments involving the Ryd-

berg states of H_3 .^{5-8,19-22} The frozen-core calculations obtain generally good agreement with the observed spectra on the pattern of the energy levels but the errors in the predicted energy separations between the excited states are of the order of 1000 cm^{-1} . Furthermore, the frozen-core approaches are poor for calculation of the ground state of the neutral, since unlike the Rydberg states, the ground state does not resemble the H_3^+ system.

Recently, the $H + H_2$ system has been the subject of studies in the field of transition state spectroscopy (TSS),²³⁻²⁸ where spectroscopic observations of the transient species between reactants and products are sought. The theoretical work on the TSS of H_3 ^{23,24,26-28} has dealt with absorption from the ground state, $1A'$ to the $1^2A''$ ($2p$) state (where C_s labels are employed). Most of the work has involved the collinear path^{23,26-28} while a 3D treatment has been also carried out.²⁴ The calculated transition state spectra are expected to be sensitive to quantities such as the difference between the ground and excited state potentials (ΔV) and also to the actual variation of the dipole transition moment over the potential energy surfaces, corresponding to a given absorption process. In all the theoretical treatments carried out thus far^{23,24,26-28} the SLTH potential has been employed for the ground state, while for the excited state, model potentials have been used based either on SCF calculations on symmetric linear H_3 structures (for most of the 1D treatments^{23,27,28}) or on diatomics-in-molecules (DIM) calculations (Ref. 26 and for the 3D calculations, Ref. 24). In most of these studies a constant dipole transition moment has been assumed for the absorption from the ground state into the ($2p$) state, throughout the potential energy surface.

Clearly there is a need for more accurate theoretical calculations on the excited states along the reaction path of $H + H_2$ and also for nonlinear geometries, in order to obtain reliable ΔV . Furthermore, since the transition moments with the ground state are also required, it is necessary to carry out a balanced treatment of the ground and the excited states.

Ab initio calculations on the ground and excited states of H_3 have been carried out in the early work of Frenkel²⁹ and

also for C_{2v} geometries by Kulander and Guest.³⁰ Raynor and Hershbach³¹ and also Roach and Kuntz³² have carried out DIM studies on ground and excited states of H₃, for a large number of geometrical arrangements, which at least for the first few states provide helpful qualitative information.

The present work has been undertaken with the aim of producing reliable transition energies and transition moments between the ground and excited states, information which might be useful to investigations of the transition state spectra of H₃. The ground state and the $^2A''(2p)$ states have already been mentioned in connection with the TSS. The $^2A'(2s)$ state is also of interest^{23,24} since it lies very close to the $1^2A''(2p)$ state and it has a large transition moment with the ground state^{14,24} in the molecular regions although zero in the dissociation limit, where the transition ($1s \rightarrow 2s$) is forbidden. Transitions from the ground state to $1^2A''(2p)$ are symmetry forbidden at the linear symmetric geometries ($1^2\Sigma_u^+ \rightarrow 1^2\Pi_u$), at D_{3h} geometries ($1^2E' \rightarrow 1^2A''$), and also at C_{2v} geometries with the base of the triangle larger than the sides ($^2B_2 \rightarrow ^2B_1$). At the dissociation limit the transition is the allowed $1s \rightarrow 2p$ atomic hydrogen transition.

In addition to the above Rydberg states, the first excited state of H₃ is also of interest, because it has a conical intersection with the ground state at D_{3h} geometries and also because it predissociates the $^2A'(2s)$ state and the $J \neq 0$ levels of the $1^2A''(2p)$ state. The lifetime of the $^2A'(2s)$ state has been estimated at < 1 ps from the width of the observed spectra.^{5,33} Similarly, the $J \neq 0$ levels of the $1^2A''(2p)$ state are expected to be short lived, while the lifetime of the $J = 0$ levels of this state has been estimated as 40–100 μ s on the basis of experimental data,²⁰ and it is generally accepted that this state corresponds to the observed metastable H₃ species.^{20,21}

In addition to the calculations aimed at the TSS of H₃, it is of interest to carry out accurate calculations on the Rydberg states at D_{3h} geometries. As mentioned above only frozen-core types of treatments have been devoted to calculations on the Rydberg spectra of H₃. A comparison of the present theoretical results with the observed spectra will serve for an evaluation of the accuracy of the present calculations on the excited states, while a comparison with the accurate calculations of Liu⁹ and Siegbahn and Liu¹⁰ will be appropriate for the ground state results.

II. COMPUTATIONAL DETAILS

The MRD-CI method and programs^{34,35} have been employed for the calculations. The AO basis set consisted of the (6s/4s) basis of Huzinaga,³⁶ augmented with two p polarization functions with exponents 0.7 and 0.2 for each H atom. The Rydberg basis was of double-zeta quality (for functions up to 4s) with the following exponents: 0.018 75, 0.0475, 0.005 25, 0.0133, 0.001 387 5, and 0.003 515 for the s set, 0.026 255, 0.0665, 0.005 025, and 0.012 73 for the p and 0.012 75 and 0.026 03 for the d set. These exponents have been obtained by splitting the single-zeta Rydberg basis employed for calculations on Rydberg states of rare-gas hydrides.³⁷ The Rydberg functions were centered on the central H atom in the linear symmetric geometries and in the

center of the triangle for the D_{3h} geometries. For the C_{2v} and $C_{\infty v}$ geometries the Rydberg functions were centered at the midpoint of the distance of the H atom from the center of the H₂ bond.

All the calculations relevant to the TSS of H₃ have been carried out in C_s symmetry, as it is the common symmetry for the different geometries of the H₃ system.

The reference spaces for the CI calculations were determined by carrying out preliminary calculations at different geometries. All configurations with $c^2 > 0.002$ in the CI wave functions have been included in the reference sets. For the calculations on $^2A'$ states the reference space consisted of 54 configurations (which gave rise to 80 configuration functions), the CI space generated involved 35 342 configuration functions and selection of configurations was carried out for the lowest six roots with an energy threshold of 1 μ hartree. For the $^2A''$ calculations the reference space consisted of 36 configurations (52 configuration functions), the generated CI space involved 22 089 configuration functions and selection was carried out with respect to the two lowest root with a threshold of 0.5 μ hartree.

The calculations for the Rydberg spectra of H₃ involved a single D_{3h} geometry with a bond length of 1.64 bohr. These calculations were carried out in C_{2v} symmetry, where 2A_1 and 2B_1 states were obtained. The 2A_1 states correlate with $^2A'_1$ and $^2E'$ states of D_{3h} symmetry, where for the $^2E'$ states 2B_2 states are the partners of the 2A_1 . The 2B_1 states correlate with $^2A''_2$ and with $^2E''$ (along with states of 2A_2 symmetry). The reference space of the 2A_1 calculations consisted of 51 configurations and selection was carried out for the 7 lowest roots with an energy threshold of 0.5 μ hartree. About 5000 configuration functions were selected out of 14 889 generated. For the 2B_1 calculations, 32 reference configurations were employed and selection for the two lowest roots with a 0.1 μ hartree threshold resulted in 4100 selected configuration functions out of 10 623 generated.

Some preliminary calculations on the Rydberg states of H₃ have been also carried out with a single-zeta Rydberg basis³⁷ and also in C_{2v} symmetry. The CI spaces were generated using 52 and 26 reference configurations for the 2A_1 and the 2B_1 states, respectively. All the generated configuration functions (4105 for 2A_1 and 2233 for 2B_1) were included in the calculations of the first seven 2A_1 roots and the first three 2B_1 roots. These calculations were carried out for D_{3h} geometries with different values of the internuclear distances, in order to determine R_e for the Rydberg states. Similar calculations (i.e., along the “breathing” motion of the ring) have been also included in the C_s calculations with the larger basis set mentioned above.

Further details of the calculations shall be presented along with the results in Sec. III.

III. RESULTS AND DISCUSSION

The results of the calculations shall be presented in three sections where in Sec. III A the calculations on the Rydberg spectra of H₃ are discussed while in Secs. III B and III C, the calculated energies and transition moments, respectively, at different geometries are presented.

TABLE I. Calculated energies (in eV) of the excited electronic states of H₃ with respect to the ground state energy,^a at a D_{3h} geometry with bond length of 1.64 bohr.

State	Present work ^b	Present work ^c	Ref. 14
4 ² E'(4p)	4.86	4.86	4.35
3 ² A ₁ '(3d)	4.39	4.35	3.86
1 ² E''(3d)	4.38	4.35	3.86
3 ² E'(3d)	4.33	4.32	3.83
2 ² A ₂ '(3p)	4.30	4.24	3.83
2 ² A ₁ '(3s)	4.27	4.15	3.78
2 ² E'(3p)	3.87	3.82	3.42
1 ² A ₂ '(2p)	2.24	2.25	1.90
1 ² A ₁ '(2s)	2.07	1.96	1.66
1 ² E'(2p)	0.00	0.00	0.00

^aThe calculated ground state energy = -1.553 99 hartree.

^bSplit-Rydberg basis.

^cSingle-zeta Rydberg basis.

A. Calculations related to the Rydberg spectra of H₃

The vertical energies of the first nine excited states of H₃ at a D_{3h} geometry with $R = 1.64$ bohr are given in Table I, relative to the energy of the ground state. The results obtained with both the basis sets employed in the present work are listed in Table I, along with data from the work of King and Morokuma.¹⁴ A comparison of the present large basis results with those of the frozen-core calculations shows that the latter obtain too high an energy for the ground state by about 0.5 eV. The results of the calculations with the single-zeta Rydberg basis differ from those of the split-Rydberg basis by about 0.01 to 0.06 eV (see Table I) for most of the states, except for the (2s) and the (3s) states, where the difference is about 0.11 and 0.12 eV, respectively. Experimental data analogous to the theoretical of Table I exists only for the (2s) state, which is estimated to lie at about 5.05 eV with respect to the ground state dissociation limits of H + H₂, with the ground state estimated at 3.15 eV with respect to the same limits,²¹ so that the experimental 1²E' → 1²A₁' separation of Gellene and Porter²¹ is 1.90 eV. Another estimate of the energy of the 2²A₁'(2s) state with re-

spect to the ground state H + H₂ limit has been given by Watson³⁸ as 5.52 eV. The present calculations with the larger basis set obtained energies of about 3.15 and 5.22 eV for the ground and the (2s) states, respectively, with respect to the energy of H-H₂ with H at 10.0 bohr from H₂. Thus there is excellent agreement with the experimental value on the energy of the ground state while for the energy of the (2s) state the theoretical value of the present work falls between the two previous estimates.^{21,38}

For the energy separations between the excited states themselves, a lot more information is available. In Table II, the theoretical transition energies with respect to the 1²A₂'(2p) state of the present work, along with those of other theoretical work are compared to the experimental T_e values, recently compiled by Watson.³³ As shown in Table II, the theoretical ΔE of the present work obtained with the double-zeta Rydberg basis are within 200 cm⁻¹ of the experimental T_e values, while the frozen-core calculations are generally about 1000 cm⁻¹ off the experimental. The results of the single-zeta basis are not as good as those of the larger basis set, especially for the (2s)-(2p) splitting. Thus calculations with the split Rydberg basis are expected to yield reliable results on the ground and excited states of H₃, more so than calculations with the smaller AO basis set.

In Table III the calculated frequencies and dipole transition moments for the possible transitions in H₃ are given in the same format as the corresponding data of King and Morokuma.¹⁴ The Einstein coefficient for spontaneous emission may be calculated using the formula

$$A_{nm} = 2.025\,84 \times 10^{-6} (\Delta E)^3 \frac{\sum_{i,k} |R_{n_i m_k}|^2}{d_n}, \quad (1)$$

where ΔE is the transition energy (in cm⁻¹), d_n is the degeneracy of the upper state, $R_{n_i m_k}$ is the dipole transition moment (in atomic units) between the i th partner of the upper state and the k th partner of the lower state. The summation in Eq. (1) is over all the possible combinations between the degenerate partners of the upper state with those of the lower state. The transition moments of Table III correspond to the sum of the squares of the transition moments in Eq. (1),

TABLE II. Comparison of experimental and theoretical energy differences (cm⁻¹) between the 1²A₂'(2p) state and the other Rydberg states of H₃.

State	Exp. T_e ^a	Pres. work ^b	Pres. work ^c	Ref. 14	Ref. 15	Ref. 16	Ref. 17
1 ² A ₁ '(2s)	-1256	-1422	-2346	-1988	-2323	-1936	-2546
1 ² A ₂ '(2p)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2 ² E'(3p)	13 285	13 118	12 628	12 277	11 832	12 179	11 698
2 ² A ₁ '(3s)	16 488	16 307	15 265	15 104	14 728	15 082	14 595
2 ² A ₂ '(3p)	16 879	16 602	16 043	15 511	15 300	15 486	15 166
3 ² E'(3d)	17 120	16 865	16 701	15 521	15 099	15 486	14 990
1 ² E''(3d)	17 403	17 225	16 887	15 751	15 341	15 970	...
3 ² A ₁ '(3d)	17 493	17 302	16 925	15 821	15 413	15 808	...
4 ² E'(4p)	20 889 ^d	21 064	21 059	19 709	19 293	19 760	19 182

^aFrom Ref. 33.

^bSplit-Rydberg basis set.

^cSingle-zeta Rydberg basis set.

^d T_0 value (Ref. 33).

TABLE III. Calculated frequencies (cm⁻¹) and transition moments (atomic units) for the Rydberg transitions in H₃. For each entry the top number is the frequency and the lower number is the square of the dipole transition moment.

Upper state	Lower state				
	1 ² E'(2p)	1 ² A ₁ '(2s)	1 ² A ₂ '(2p)	2 ² E'(3p)	2 ² A ₁ '(3s)
4 ² E'(4p)	39 160 0.002	22 486 1.265	21 064 0.0	7947 0.463	4758 68.230
3 ² A ₁ '(3d)	35 397 0.289	18 724 0.0	17 302 4.552	4184 13.113	995 0.0
1 ² E''(3d)	35 321 1.016	18 647 0.0	17 225 6.736	4108 36.880	918 0.0
3 ² E'(3d)	34 961 2.400	18 287 0.027	16 865 0.0	3748 70.427	558 0.836
2 ² A ₂ '(3p)	34 698 0.0	18 024 2.124	16 602 0.0	3485 0.0	295 51.141
2 ² A ₁ '(3s)	34 402 0.102	17 729 0.0	16 307 0.0	3189 48.948	
2 ² E'(3p)	31 213 0.034	14 540 15.690	13 118 0.0		
1 ² A ₂ '(2p)	18 096 0.0	1422 7.233			
1 ² A ₁ '(2s)	16 674 4.886				

where, as in the previous calculations,¹⁴ only the electronic transition moment is considered at a single geometry without vibrational averaging.

The transition moments reported by King and Morokuma¹⁴ are very close to the values of the present work, within 15% for most transitions, except for the transitions to the ground state where the frozen-core results are different by up to 50% from the values of the present work.

The dipole transition moment calculated for the 1²A₂'(2p) → 1²A₁'(2s) transition when used in conjunction

with the experimental transition energy (of 993 cm⁻¹) in Eq. (1), yields a lifetime of about 70 μs for the 1²A₂'(2p) state. If the value of King and Morokuma for the transition moment is employed the resulting lifetime is about 62 μs. Gellene and Porter have calculated a lifetime of about 87 μs using King and Morokuma's dipole transition moment and an energy difference of about 0.11 eV.²¹ The theoretical values of 70 and 62 μs are both within the range of the experimental value of the lifetime for this state which has been reported as 40–100 μs.²⁰

The radiative lifetime of the 1²A₁'(2s) state is calculated as about 2.16 μs, but this state is not expected to emit since it is rapidly predissociated.

Radiative lifetime for Rydberg states of H₃ other than the (2s) and (2p) states treated above, may be calculated using the data of Table III.

B. Calculations of energies along different paths for the H + H₂ system

The calculations which are to be discussed in this section deal with the spectroscopy of the H + H₂ system, mainly along a collinear path, while a few nonlinear geometries, at 90° and 45° insertion, have been also treated. The C_s point group has been used for all these calculations, as it is the common symmetry in all types of geometries of H₃.

Before the results of these calculations are presented, some calculations of D_{3h} geometries will be discussed, which have been also carried out in the same approach as the above calculations (i.e., in C_s symmetry). The calculated energies of the ground and excited electronic states of H₃ at D_{3h} geometries of different triangle side (R) are listed in Table IV, along with R_e and E_e values derived from these calculations. Experimental R₀ values^{4–8,33} are also included in Table IV as are the R_e values obtained from calculations employing the smaller basis set on the same type of motion.

TABLE IV. Calculated energies (hartree) of the ground and excited states of H₃ at different D_{3h} geometries.

R ^a (bohr)	1 ² E'(2p)	1 ² A ₁ '(2s)	1 ² A ₂ '(2p)	2 ² E'(3p)	2 ² A ₁ '(3s)	1 ² E ₂ '(3d)
1.0	-1.273 81	-1.267 97	-1.244 31	-1.176 35	-1.174 75	-1.169 34
1.2	-1.431 77	-1.405 08	-1.388 45	-1.322 33	-1.316 27	-1.312 39
1.4	-1.511 19	-1.462 42	-1.451 10	-1.387 67	-1.377 50	-1.374 98
1.5	-1.534 05	-1.473 99	-1.464 97	-1.402 93	-1.390 89	-1.388 87
1.6	-1.549 55	-1.478 08	-1.470 47	-1.410 52	-1.396 68	-1.395 15
1.65	-1.555 18	-1.478 00	-1.471 23	-1.412 17	-1.397 43	-1.396 05
1.7	-1.559 53	-1.476 74	-1.470 86	-1.412 43	-1.396 85	-1.395 82
1.8	-1.565 54	-1.471 35	-1.467 12	-1.410 19	-1.393 02	-1.392 37
2.0	-1.569 21	-1.452 74	-1.451 52	-1.397 39	-1.377 56	-1.377 33
2.3	-1.563 13	-1.414 86	-1.417 29	-1.367 50	-1.345 51	-1.342 51
2.6	-1.560 57	-1.349 12	-1.355 20	-1.318 33	-1.290 49	-1.284 58
3.0	-1.535 45	-1.320 30	-1.327 20	-1.300 80	-1.268 14	-1.257 73
E _e	-1.569 29	-1.478 21	-1.471 28	-1.412 46	-1.397 43	-1.396 09
R _e ^b	1.972	1.622	1.658	1.689	1.652	1.664
R _e ^c	1.961	1.600	1.637	1.670	1.633	1.648
R ₀ ^d	...	1.606	1.640	1.682	1.646	1.663

^a R stands for the side of the triangle.

^b Results of the split-Rydberg basis calculations.

^c Results of the single-zeta Rydberg basis calculations.

^d Experimental values from Refs. 4–8 and 33.

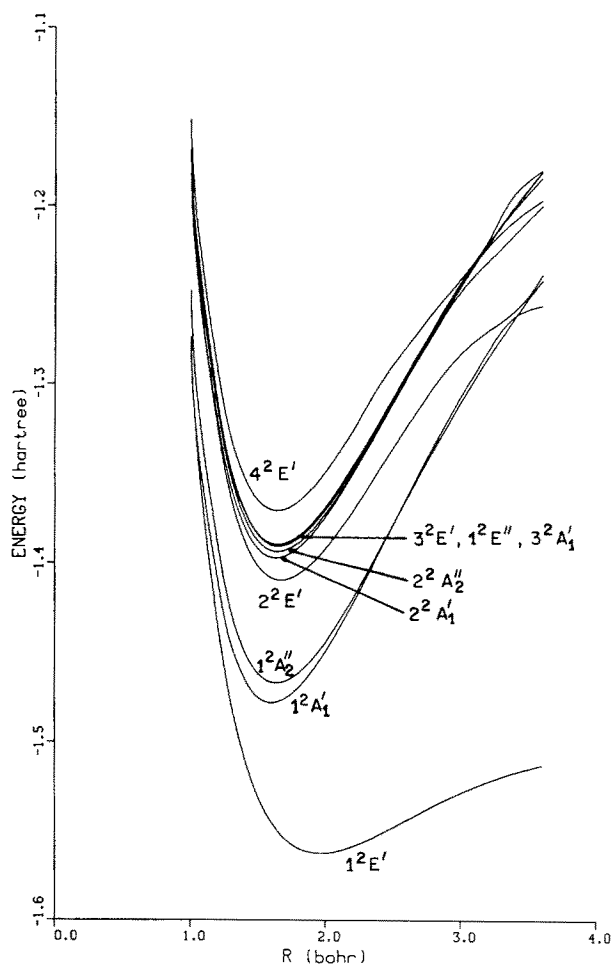


FIG. 1. Potential energy curves of the first ten electronic states of H_3 at D_{3h} geometries.

As shown in Table IV, the theoretical R_e values of the excited states are in good agreement with the corresponding R_0 experimental values. The theoretical values obtained with the smaller basis set also compare well with the experimental. The potential energy curves of the ten electronic states of H_3 treated in the previous section, along the breathing motion of the ring are given in Fig. 1. These curves have been obtained by calculations with the smaller basis set, which appears to lead to good predictions on the geometries of the Rydberg states. Frozen-core calculations¹⁷ also predict correctly the R_e of the Rydberg states. However, DIM calculations³² overestimate the R_e of $1^2A_1'$ by about 0.11 bohr and are very poor for the higher excited states.

The best D_{3h} structure for the ground state is obtained at R of 1.972 bohr at 63.09 kcal/mol above the $H + H_2$ dissociation limit. The DIM calculations also predict the lowest energy D_{3h} geometry at about 2.00 bohr and energy of 63.19 kcal/mol. Similarly, the new fits of the Liu⁹ and Siegbahn and Liu¹⁰ ground state energies, obtained by Varandas *et al.*¹³ also obtained the best ground state D_{3h} structure at R of 1.973 bohr and energy of 63.36 kcal/mol.

The calculations on linear H_3 involved $D_{\infty h}$ geometries and $C_{\infty v}$ geometries. In order to facilitate comparison of the results of the present work with the STO calculations of

Liu,⁹ the geometries have been selected from those calculated by Liu, and for the $C_{\infty v}$ path, approximately along the reaction path for the ground state. The calculated energies are given in Table V. The 2II states have been obtained as both $^2A'$ and $^2A''$ with the two components giving nearly identical results. The first twenty one rows of Table V refer to linear symmetric geometries. The calculated energies for these geometries have been plotted in Fig. 2. As shown in Fig. 2, an avoided crossing exists between $1^2\Sigma_g^+$ and $2^2\Sigma_g^+$ states at R of about 1.70 bohr. This is consistent with the presumed predissociation of the $(2s)$ state by the first excited state of H_3 . Indeed an examination of the character of these states along the symmetric stretch path shows that they are both of mixed valence-Rydberg character and are mainly described by two configurations $1a' \ ^23a'$ (the Rydberg $2s$ configuration) and $2a' \ ^21a'$, which has been associated with the resonance state calculated by Kulander and Guest³⁰ but along the insertion path. Similar results regarding the characters of these two states are obtained along the $C_{\infty v}$ path out to the point with R_1 of 2.30 bohr and R_2 of 1.54 bohr. Beyond this geometry the two states are described by different main configurations. The above considerations show that the $(2s)$ state for collinear geometries has considerable valence character, which will result in large transition moments with the ground state, as will be discussed later.

The ground state saddle point is calculated at $R_1 = R_2 = 1.767$ bohr which is very close to the value obtained by Liu, 1.757 bohr. The barrier at the saddle point, with respect to the energy of a structure with H at 10.0 bohr from H_2 (last entry in Table V), is 9.96 kcal/mol. This is also in very good agreement with the values calculated by Liu⁹ and Siegbahn and Liu¹⁰ of 9.8 and 9.90 kcal/mol, respectively.

At 1.75 bohr (which is close to the saddle point of the SLTH potential¹¹) the present calculations yield a ground state energy of 0.00415 hartree (or 2.61 kcal/mol) above that of Liu.⁹ For symmetrical geometries with smaller bond lengths than 1.75 bohr, the difference between the present energies and those of Liu⁹ increase up to 4.03 kcal/mol at $R_1 = R_2 = 1.3$ bohr. This is due to the well known inadequacies of modest GTO basis sets at short internuclear distances.¹⁰ For larger bond lengths than at the saddle point the difference in the calculated energies decreases down to 0.12 kcal/mol at $R_1 = R_2 = 5.0$ bohr.

For the $C_{\infty v}$ path (see Table VI), corresponding to the collinear $H + H_2$ approach, the present calculations lead to energies which are essentially parallel to those of Liu.⁹ The differences in the calculated energies vary only slightly, from 2.60 kcal/mol at the saddle point to 2.33 kcal/mol at the furthest point with $R_1 = 1.41$ bohr and $R_2 = 4.33$ bohr. Thus a shift of the calculated energies in the present work by about 2.5 kcal/mol would lead to near coincidence of the ground state potential with the SLTH potential along the $C_{\infty v}$ path.

A comparison of the present results with those of the extensive DIM work of Roach and Kuntz shows that the gross features of the potentials are well reproduced by the DIM calculations but there are some quantitative discrepancies: The DIM results show the ground state saddle point at

TABLE V. Theoretical energies (hartree) of the first six electronic states of linear H₃, for different values of internuclear distances R_1 and R_2 (bohr), of the outer H atoms from the central H atom.

R_1	R_2	$1^2\Sigma^+$	$2^2\Sigma^+$	$3^2\Sigma^+(2s)$	$4^2\Sigma^+$	$1^2\Pi(2p)$	$2^2\Pi$
		$1^2\Sigma_u^+$	$1^2\Sigma_g^+$	$2^2\Sigma_g^+$	$2^2\Sigma_u^+$	$1^2\Pi_u$	$1^2\Pi_g$
1.3	1.3	-1.596 82	-1.399 88	-1.318 71	-1.341 64	-1.386 33	-1.314 21
1.4	1.4	-1.622 49	-1.409 90	-1.331 89	-1.353 99	-1.397 28	-1.325 77
1.5	1.5	-1.639 00	-1.413 49	-1.341 06	-1.359 44	-1.401 43	-1.330 59
1.6	1.6	-1.648 61	-1.413 11	-1.355 44	-1.359 73	-1.400 55	-1.331 51
1.7	1.7	-1.653 21	-1.411 56	-1.376 55	-1.356 51	-1.396 21	-1.328 38
1.75	1.75	-1.653 93	-1.412 41	-1.384 25	-1.353 93	-1.393 08	-1.325 78
1.76	1.76	-1.653 97	-1.412 92	-1.385 33	-1.353 31	-1.392 37	-1.325 25
1.767	1.767	-1.653 98	-1.413 34	-1.385 93	-1.352 87	-1.391 87	-1.324 80
1.77	1.77	-1.653 98	-1.413 55	-1.386 21	-1.352 69	-1.391 65	-1.324 60
1.78	1.78	-1.653 94	-1.414 27	-1.386 85	-1.352 07	-1.390 91	-1.324 00
1.8	1.8	-1.653 80	-1.416 17	-1.387 62	-1.350 74	-1.389 38	-1.322 78
1.9	1.9	-1.651 36	-1.429 24	-1.384 43	-1.343 12	-1.380 79	-1.315 30
2.0	2.0	-1.646 94	-1.443 01	-1.376 64	-1.334 04	-1.370 76	-1.306 67
2.1	2.1	-1.640 85	-1.454 50	-1.367 27	-1.324 19	-1.360 11	-1.297 44
2.2	2.2	-1.633 77	-1.463 87	-1.357 74	-1.313 82	-1.348 98	-1.287 39
2.3	2.3	-1.626 03	-1.471 05	-1.348 09	-1.303 34	-1.337 55	-1.277 41
2.5	2.5	-1.609 31	-1.481 20	-1.331 01	-1.281 71	-1.314 59	-1.257 36
3.0	3.0	-1.569 25	-1.492 63	-1.302 49	-1.232 76	-1.261 89	-1.215 88
3.5	3.5	-1.538 94	-1.496 34	-1.281 32	...	-1.219 49	...
4.0	4.0	-1.519 97	-1.497 99	-1.260 76	...	-1.187 65	...
5.0	5.0	-1.504 47	-1.499 46	-1.224 75	...	-1.148 48	...
1.88	1.68	-1.654 29	-1.411 83	-1.385 30	-1.351 01	-1.389 67	-1.320 76
1.95	1.64	-1.654 67	-1.409 72	-1.384 23	-1.348 80	-1.387 03	-1.318 32
2.02	1.61	-1.655 15	-1.407 49	-1.382 63	-1.345 87	-1.383 65	-1.315 32
2.11	1.58	-1.655 93	-1.404 49	-1.379 84	-1.341 69	-1.378 85	-1.310 80
2.20	1.56	-1.656 73	-1.402 13	-1.376 53	-1.337 24	-1.373 55	-1.306 06
2.30	1.54	-1.657 70	-1.399 31	-1.371 61	-1.332 29	-1.367 61	-1.300 49
2.41	1.52	-1.658 84	-1.395 31	-1.365 90	-1.326 93	-1.361 17	-1.294 48
2.55	1.51	-1.660 14	-1.392 64	-1.358 05	-1.320 10	-1.353 20	-1.287 02
2.69	1.49	-1.661 65	-1.386 80	-1.350 15	-1.313 63	-1.345 66	-1.279 57
2.84	1.48	-1.663 02	-1.382 47	-1.342 13	-1.307 18	-1.337 85	-1.272 31
2.98	1.47	-1.664 17	-1.377 07	-1.335 21	-1.301 58	-1.331 41	-1.265 88
3.19	1.46	-1.665 63	-1.369 62	-1.325 76	-1.293 95	-1.322 47	-1.257 58
3.41	1.45	-1.666 87	-1.361 04	-1.317 57	-1.286 81	-1.314 70	-1.249 98
3.64	1.44	-1.667 88	-1.351 99	-1.310 81	-1.280 39	-1.308 05	-1.243 49
3.87	1.43	-1.668 65	-1.342 96	-1.305 78	-1.275 37	-1.302 86	-1.237 52
4.15	1.42	-1.669 24	-1.332 70	-1.301 34	-1.273 01	-1.298 29	-1.234 18
4.33	1.41	-1.669 51	-1.325 65	-1.299 27	-1.272 98	-1.295 78	-1.230 81
10.0	1.40	-1.669 85	...	-1.294 69	...	-1.294 76	...

1.81 bohr (vs 1.767 bohr of the present work and 1.757 bohr of the SLTH potential). In addition the location and height of the barrier on the potential of the $1^2\Sigma_g^+$ state derived from the avoided crossing with $2^2\Sigma_g^+$, are given as 1.93 bohr and 0.76 eV by the DIM work while the present values are $R = 1.70$ bohr and 0.05 eV for the location and height of the barrier, respectively. Thus, although a qualitative picture may be obtained from the DIM work, quantitative information requires the use of *ab initio* configuration interaction methods.

A comparison is possible between the energies of the $1^2\Pi_u(2p)$ state of the present work with those of Mayne *et al.*,²³ upon which the model potentials for most of the 1D calculations of the transition state spectra of H₃ have been based. As would be expected the absolute differences in the calculated energies are very large (cf. Table V of the present work with Table I of Mayne *et al.*²³) since SCF energies²³ are compared to CI energies. What is perhaps more important is the fact that the difference between the two calculations in-

creases significantly, from about 31.5 kcal/mol at (1.30, 1.30) to 45.4 kcal/mol at (2.50, 2.50).

Although the reaction path of the $H + H_2 \rightarrow H_2 + H$ process is assumed to be collinear,⁹ insertion paths have been found to be important³⁹ when the H atoms are translationally hot, as, e.g., in the recent experimental work of Collins *et al.*,²⁵ where H atoms are produced by photodissociation of H₂S. Mayne *et al.*,²⁴ on the basis of 3D trajectory calculations on the SLTH potential have also found that linear and bent transition state configurations contribute to a comparable extent to the total absorption.

Calculations over the full potential energy hypersurfaces of the H₃ system is beyond the scope of the present work. However, some further calculations have been carried out on nonlinear geometries, in order to estimate the variation in the calculated quantities in going from the linear to nonlinear structures. A few points have been calculated at C_{2v} geometries, which are obtained by a motion of the central H atom (starting at the saddle point) away from the line,

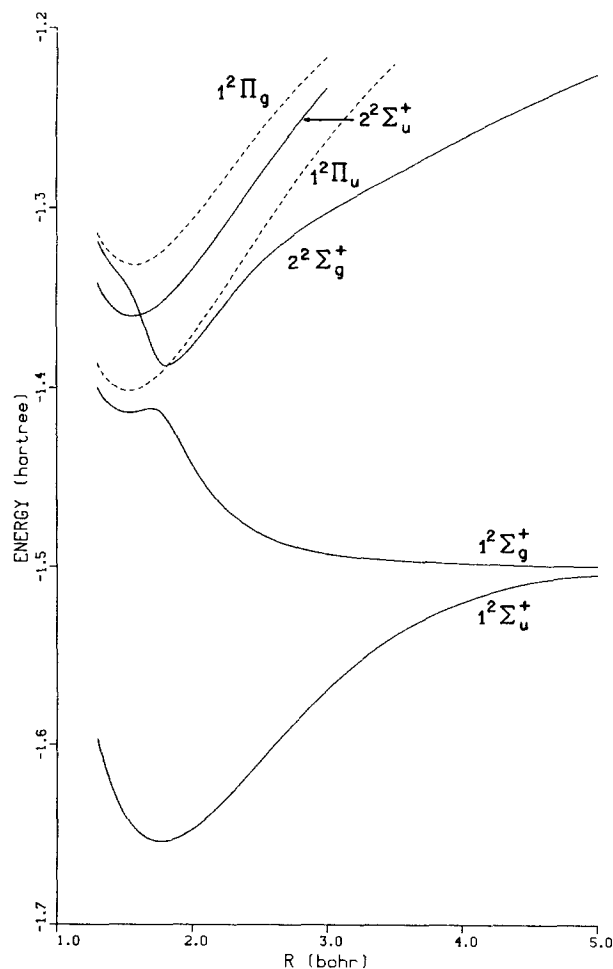


FIG. 2. Potential energy curves of the lowest six electronic state of linear symmetric H_3 .

along a perpendicular path. The ground state, $1^2E'$ at D_{3h} geometries, gives rise to two states, 2^2A_1 and 2^2B_2 at C_{2v} geometries which have a conical intersection at the equilateral triangle structures. Similarly, pairs of states result from the other degenerate Rydberg states of H_3 . The calculated energies at C_{2v} geometries are given in Table VI and Fig. 3, where the expected features of the potentials curves are dis-

played. In addition, in Table VI, the energies calculated at a single point along a 45° insertion path are given.

The character of the $2^2A'(2s)$ state along the 90° path is found to be purely Rydberg, without the valence contribution found at collinear geometries.

Kulander and Guest³⁰ have also carried out calculations of states of H_3 along an insertion path, although a direct comparison with their results is not possible since in the present calculations a path was chosen which goes smoothly from the linear saddle point to the dissociation limits.

C. Calculations of dipole transition moments

The calculated dipole transition matrix elements for the possible transitions between the first four electronic states of H_3 are given in Tables VII, VIII, and IX for the linear symmetric, $C_{\infty v}$, and insertion paths, respectively. The transition moments of interest to the transition state spectroscopy of $H + H_2$, are between the ground state and the $(2s)$ and the $(2p)$ states. These are given in columns four and five of Table VIII, columns three and four of Table IX, and in the third column of Table VII, where the transition to the $(2p)$ state from the ground state is symmetry forbidden. As shown in Tables VII–IX, absorption from the ground state to $2^2A'(2s)$ is everywhere allowed in the geometries calculated and the corresponding transition moments are almost everywhere larger than those calculated for the transition from the ground state to the $2^2A''(2p)$. In addition, the first excited state ($2^2A'$) has appreciable transition moments with the ground state and also with the two excited states of interest, when such transitions are symmetry allowed (see Tables VII–IX).

As mentioned previously, the dissociation limit is obtained by performing a calculation at a geometry where the H atom is at 10.0 bohr away from the H_2 molecule. Such a calculation yields the correct dipole transition moment for the $1s-2p$ transition, obtained as 0.7407 with a corresponding lifetime of 1.6 ns. However, it is not possible to calculate a pure $2s$ state of the atom, because the system does not possess spherical symmetry and mixing of the $2s$ orbital with the σ component of the $2p$ is allowed. As a result at the limit of $R_{H-H_2} = 10$ bohr two nearly degenerate states are obtained with characters $2p-2s$ and $2p+2s$, at about $82\,330\text{ cm}^{-1}$

TABLE VI. Theoretical energies (hartree) of the first eight electronic states of H_3 calculated along the 90° insertion path.

State	(R_{H-H_2}, R_{H_2}) (0.0, 3.534) ^a	(bohr)					
		(0.5, 3.0)	(1.0, 2.5)	(1.7, 1.96)	(3.0, 1.47)	(4.0, 1.42)	(3.0, 1.47) ^b
$1^2A'$	-1.653 98	-1.642 86	-1.623 43	-1.569 37	-1.653 97	-1.666 46	-1.655 53
$2^2A'$	-1.413 34	-1.427 84	-1.476 00	-1.568 94	-1.405 87	-1.339 73	-1.398 82
$3^2A'$	-1.385 93	-1.409 89	-1.439 38	-1.456 93	-1.364 09	-1.319 52	-1.367 26
$4^2A'$	-1.352 87	-1.366 46	-1.389 00	-1.400 40	-1.330 61	-1.300 69	-1.330 76
$5^2A'$...	-1.351 50	-1.374 91	-1.400 47	-1.313 71	-1.286 50	...
$6^2A'$	-1.324 87	-1.339 90	-1.364 63	-1.380 86	-1.308 01	-1.282 98	-1.303 19
$1^2A''$	-1.391 99	-1.409 42	-1.437 66	-1.455 14	-1.367 13	-1.318 75	-1.369 12
$2^2A''$	-1.324 80	-1.338 14	-1.360 68	-1.380 88	-1.297 56	-1.251 59	-1.299 81

^a The saddle point geometry.

^b 45° path.

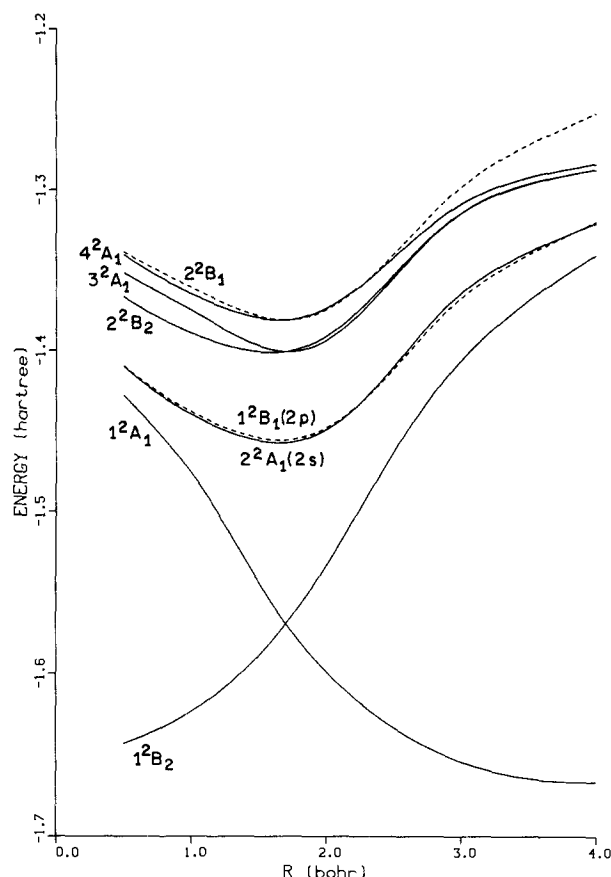


FIG. 3. Calculated energies of electronic states of H₃ along a 90° insertion path. R stands for the distance of H from the midpoint of the H₂ bond, solid lines represent $^2A'$ (2A_1 and 2B_2) states and dashed lines represent $^2A''$ (2B_1) states.

above the ground state limit (with the experimental $1s-2s$ transition energy at $822\,59\text{ cm}^{-1}$ ⁴⁰). These states being mixed $s-p$ have nonzero dipole transition moments with the ground state. Such symmetry-breaking problems giving erroneous charge distributions at the atomic dissociation limits have also been noted in connection with calculations of van der Waals compounds of Ne.⁴¹

Given that the above problem exists at the dissociation limit, the range of validity of the transition moment calcula-

tions connecting the ground and the ($2s$) states must be examined. At geometries near the saddle point, where the system is interacting, the calculated transition moments are expected to be reliable. For intermediate distances, from 3.0 to 4.33 bohr (see Tables V and VIII), the calculated moments involving the ($2s$) state might be overestimated, although at such geometries the degeneracy of the two p - s states, which has been found at the dissociation limit, does not exist.

In previous theoretical work on the TSS of H₃, the dipole transition moment has been either assumed constant or has been represented by a model function.²³ The transition state spectra have been predicted on the basis of classical trajectory calculations on the ground state potential,^{23,24} on the basis of time-dependent quantum mechanical calculations for the motion of the nuclei on the ground state potential²⁶ and also on the basis of the overlap between the bound levels of the upper state [always assumed to be the $1^2A''$ ($2p$) state] and the vibrational continuum of the ground state. It is evident that the spectra obtained in the above studies²³⁻²⁸ will be significantly modified if the actual transition moments calculated for the $1^2A' \rightarrow 1^2A''$ ($2p$) process are introduced in the calculations of the spectra. It is instructive to consider the variation of the oscillator strength for the above absorption, as a function of the transition energy. Such a plot is given in Fig. 4. As shown in Fig. 4, the oscillator strength is essentially zero at transition energies lower than about $60\,000\text{ cm}^{-1}$, and it gains intensity at large transition energies, corresponding to large distances of H from H₂. This is in support of the conclusions of Mayne *et al.*,²³ that observations of absorption into the $1^2A''$ ($2p$) state would require conditions of low energy collisions.

Also marked in Fig. 4 are points corresponding to the perpendicular insertion path, and also a single point on the 45° insertion path. As shown the largest oscillator strengths are calculated for the perpendicular path with the 45° point at intermediate magnitude between the collinear and perpendicular paths. It might also be noted that although there are some small differences in the magnitudes, the variation of the oscillator strength with transition energy appears to be of the same type, for all angles of approach of H + H₂.

A plot of the oscillator strength for the absorption from the ground state to the $^2A'$ ($2s$) is given in Fig. 5. It should be

TABLE VII. Dipole transition moments (atomic units) calculated at symmetric linear H₃ geometries.

$R(\text{bohr})$	$1^2\Sigma_u^+ \rightarrow 1^2\Sigma_g^+$	$1^2\Sigma_u^+ \rightarrow 2^2\Sigma_g^+$	$1^2\Sigma_g^+ \rightarrow 1^2\Pi_u$	$2^2\Sigma_g^+ \rightarrow 1^2\Pi_u$
1.7	0.7941	0.5233	2.2391	1.8204
1.767	0.5524	0.8386	1.6714	2.2764
1.8	0.3826	0.9567	1.2902	2.4818
1.9	0.0147	1.1032	0.5266	2.6896
2.0	0.1377	1.1663	0.2477	2.6669
2.1	0.2062	1.2366	0.1294	2.6000
2.2	0.2370	1.3198	0.0623	2.5094
2.3	0.2490	1.4262	0.0260	2.3790
2.5	0.2420	1.6715	0.0162	1.9982
3.0	0.1566	2.0123	0.0715	0.9401
3.5	0.0751	1.9261	0.1022	0.5037
4.0	0.0297	1.7046	0.1348	0.3484
5.0	0.0039	1.2268	0.2541	0.3166

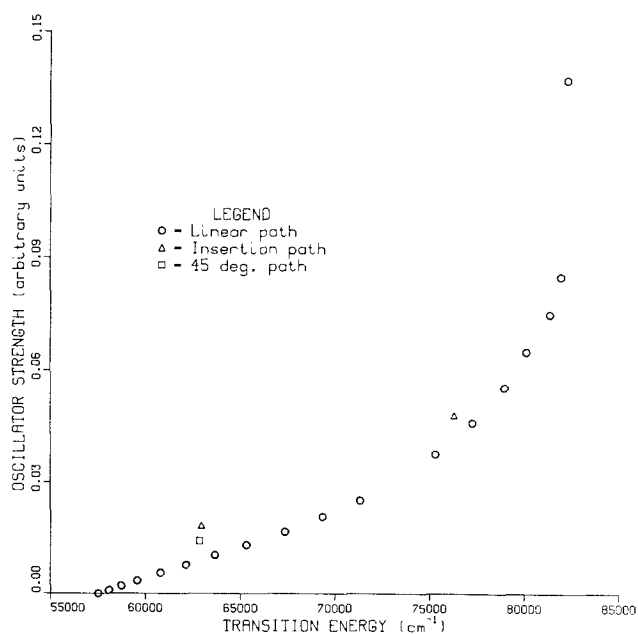
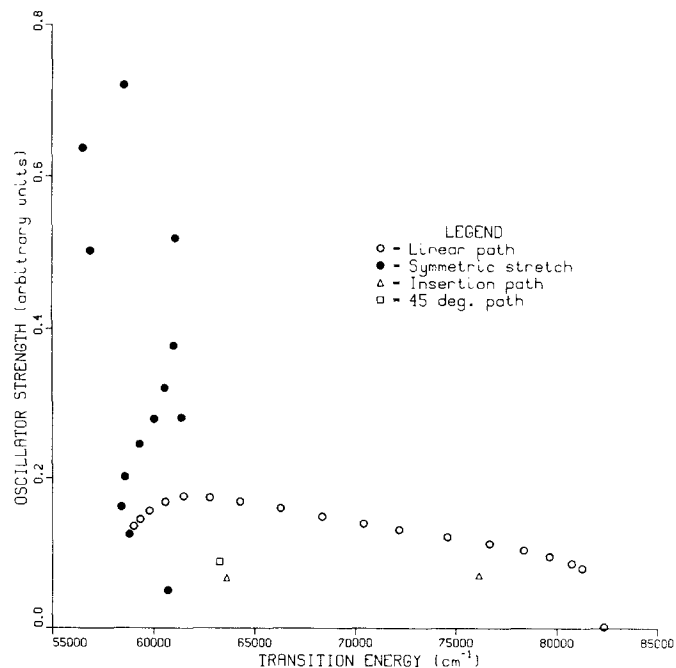
TABLE VIII. Dipole transition moments (atomic units) calculated along the collinear $H + H_2$ path.

R_1^a	R_2^a	$1^2\Sigma^+ \rightarrow 2^2\Sigma^+$	$1^2\Sigma^+ \rightarrow 3^2\Sigma^+$	$1^2\Sigma^+ \rightarrow 1^2\Pi$	$2^2\Sigma^+ \rightarrow 3^2\Sigma^+$	$2^2\Sigma^+ \rightarrow 1^2\Pi$	$3^2\Sigma^+ \rightarrow 1^2\Pi$
1.767	1.767	0.5524	0.8386	0.0	0.0	1.6714	2.2764
1.88	1.68	0.4977	0.8717	0.0711	0.0714	1.5759	2.3176
1.95	1.64	0.4375	0.8980	0.1087	0.1474	1.4691	2.3650
2.02	1.61	0.3531	0.9283	0.1397	0.2559	1.3133	2.4420
2.11	1.58	0.2296	0.9565	0.1737	0.4191	1.0740	2.5406
2.20	1.56	0.0977	0.9698	0.2027	0.5762	0.8067	2.6253
2.30	1.54	0.0167	0.9554	0.2319	0.7133	0.5281	2.7010
2.41	1.52	0.1165	0.9296	0.2572	0.8085	0.3210	2.7054
2.55	1.51	0.2006	0.8918	0.2855	0.8716	0.0875	2.7175
2.69	1.49	0.2488	0.8472	0.3140	0.8975	0.0529	2.7065
2.84	1.48	0.2790	0.8085	0.3412	0.8925	0.1634	2.6823
2.98	1.47	0.2912	0.7751	0.3662	0.8733	0.2369	2.6632
3.19	1.46	0.2945	0.7330	0.4051	0.8222	0.3156	2.6306
3.41	1.45	0.2854	0.6959	0.4421	0.7475	0.3655	2.5898
3.64	1.44	0.2688	0.6605	0.4804	0.6535	0.4011	2.5431
3.87	1.43	0.2480	0.6276	0.5199	0.5534	0.4198	2.4893
4.15	1.42	0.2209	0.5929	0.5616	0.4413	0.4453	2.4453
4.33	1.41	0.2043	0.5694	0.5853	0.3695	0.4710	2.4303

^a R_1 and R_2 stand for the distance of the outer H atoms from the central H atom.

TABLE IX. Dipole transition moments (atomic units) calculated along the insertion path.

R_{H-H_2}, R_H	$1^2A' \rightarrow 2^2A'$	$1^2A' \rightarrow 3^2A'$	$1^2A' \rightarrow 1^2A''$	$2^2A' \rightarrow 1^2A''$	$3^2A' \rightarrow 1^2A''$
0.5,3.0	0.7786	0.5317	0.0	1.8185	1.9188
1.0,2.5	0.5781	0.8689	0.0	0.8001	2.5715
1.7,1.96	0.000	1.2736	0.0014	0.0	2.7020
3.0,1.47	0.1623	0.5883	0.3105	0.0	2.8584
4.0,1.42	0.3080	0.5523	0.4549	0.0	2.5822
3.0,1.47 ^a	0.3073	0.6784	0.2723	0.5896	2.7613

^a 45° point.FIG. 4. Calculated oscillator strengths for the $1^2A' \rightarrow 1^2A''$ ($2p$) absorption at different transition energies.FIG. 5. Calculated oscillator strengths for the $1^2A' \rightarrow 2^2A'$ ($2s$) absorption at different transition energies.

noted that the scale of Fig. 5 is larger by a factor of 5 than that of Fig. 4. It is obvious that the absorption to this state would occur at lower transition energies, between 55 000 and 60 000 cm⁻¹ and the largest oscillator strengths are obtained from the symmetrical geometrical distortions with respects to the saddle point (solid circles in Fig. 5). Thus transition spectra involving the ²A'(2s) state would be especially strong, for the higher energy collisions, which would take the H + H₂ system near the saddle point geometries. As shown in Fig. 5, in this case the nonlinear geometries have lower magnitude oscillator strengths, as was expected from the differences in the valence contribution to the character of the (2s) state between the linear and nonlinear structures.

A consideration of the plots in Figs. 4 and 5 (taking into account the scale factor difference) shows that almost everywhere (except at the dissociation limits) the absorption to the ²A'(2s) state is predicted to be considerably stronger than the absorption to the ²A''(2p) state. As noted previously the (2s) state is rapidly predissociated but the time domain of the experiments investigating the spectroscopy of the transition state is probably sufficiently short^{23,24} to make observations of absorption into the ²A'(2s) state.

IV. CONCLUSIONS

Ab initio configuration-interaction calculations have been presented for the ground and excited electronic states of H₃ at different molecular geometries. The results of the present calculations on the excited states are in good agreement with the observed Rydberg spectra of H₃,⁴⁻⁸ while the calculated energies for the ground state lie on a surface essentially parallel to the SLTH potential.⁹⁻¹¹

Dipole transition moments have been presented for the absorption processes from the ground state to the ²A'(2s) and to the ²A''(2p) states, and also for the other possible transitions between the first four electronic states of H₃. On the basis of the calculated oscillator strengths for different transition energies two types of transition state spectra are predicted: One type, corresponding to absorption to the (2p) state, would show intensity at high frequencies, near the atomic 1s-2p frequency and no appreciable intensity at frequencies lower than about 70 000 cm⁻¹. The other type of spectrum, corresponding to the (2s) absorption, is predicted to show high intensity at lower frequencies which would involve transitions from H₃ geometries near the saddle point. Furthermore, absorption into the (2s) state is predicted to be stronger than that to the (2p) state everywhere, except at the dissociation limits. The previously predicted transition state spectra of H₃,^{23,24,26-28} display intensity maxima at both low and high frequencies and thus they give a composite picture of the spectra indicated by the present results. The present data on the energies and the transition moments might lead to more accurate predictions when employed in treatments such as the previous^{23,24,26-28} for the calculation of the transition state spectra.

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