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$H+H_2$: POTENTIAL-ENERGY SURFACES AND ELASTIC AND INELASTIC SCATTERING*

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I. INTRODUCTION

The $H+H_2$ reaction has long been considered an important prototype for chemical reactions with activation barriers. We have recently reviewed the history of H_3 kinetics, with emphasis on experimental and theoretical studies of the reactive dynamics in the ground electronic state (Truhlar and Wyatt, 1976). The first step in all such calculations is the Born-Oppenheimer approximation, i.e., the assumption of a potential-energy hypersurface (called the potential, the potential surface, or the surface for short). Thus there has been considerable work attempting to obtain this potential surface more accurately, especially by calculating the electronic energy of H_3 but also in some cases by attempting to fit analytic expressions to results of collision experiments. In particular, such work has emphasized the region around the saddle point because this region is thought to be the most important for determining the rate of reaction at low and medium temperatures (less than about 1000°K). This work on the potential surface is reviewed here. We also review theoretical and experimental information about other parts of the ground-state potential surface, about potential surfaces for excited electronic states, about nonreactive dynamics on the ground-state surface, and about the dynamics of processes involving excited electronic states. This review and our previous one cited above, taken together, constitute a review of all work concerned with gas-phase collisions of H with H_2.

II. POTENTIAL-ENERGY SURFACES

A. Ground Electronic State: Saddle Region and Short Range

The first major contribution to understanding the $H+H_2$ reaction was made by London (1929). He presented a formula, without derivation, for the energy of the lowest adiabatic electronic state of H_3 as a function of Coulomb and exchange integrals Q_{ij} and J_{ij} for each pair ij of atoms. These integrals depend on the internuclear separation of that pair. This is the generalization to H_3 of the valence-bond approach that Heitler and London had used to explain the binding energies of H_2 using the potential curve concept, which derives from Born and Oppenheimer's electronically adiabatic separation of the electronic and internuclear motions. The first importance of this formula is that it showed how the energy needed to cause the reaction could be much less than the energy needed to break an H_2 bond. Thus the activation energy of the $H+H_2$ reaction can be understood in terms of internuclear motion governed by one electronically adiabatic potential-energy surface which is the ground-state fixed-nuclei electronic energy of H_3, including internuclear repulsion. Thus future work on the reaction used this Born-Oppenheimer separation and involved the determination of a potential-energy surface as the first step. The second importance is that his formula later served as a basis for many semiempirical potential-energy surfaces that have been used to study the dynamics.

Eyring and Polanyi (1930) used the London formula in a semiempirical way to treat the reaction $H+H_2$, showing that the collinear potential-energy surface as a function of the two nearest-neighbor distances R_1 and R_2 had a saddle point that they correctly interpreted as a crucial factor for determining the energy of activation. The height of this saddle point, with respect to the energy of H infinitely far from H_2, is called the classical barrier height, or, for short, the barrier.

The first published derivation of the London equation was made by Slater (1931), who used valence-bond theory with only the two linearly independent covalent configurations that can be obtained from a basis of one 1*s* hydrogen orbital on each center. Orbital overlap integrals and multiple-exchange integrals were neglected.

The approximations involved in the London formula and the semiempirical way of using it (as developed by Erying and Polanyi) have been critically examined many times (see, e.g., Kassel, 1932; Coolidge and James, 1934; Van Vleck and Sherman, 1935; Hirschfelder et al. 1936, Glasstone et al. 1941, Hirschfelder 1941, Hirschfelder et al., 1954; Aroeste, 1964; Laidler and Polanyi, 1965; Parr and Truhlar, 1971). In particular, Coolidge and James (1934) critically examined these approximations with respect to the cancellation of errors that occurs in the London formula. We should remember their conclusion that the relation of quantum mechanics to the semiempirical method of London, Eyring, and Polanyi (LEP method) is "merely suggestive, rather than justificatory." In spite of this and in spite of London's attitude toward the many uses to which his formula would be put [Hirschfelder (1966), in reminiscing about this, commented, "London told me that he was appalled at the way chemists mangled his formula and still attached his name to the semiempirical results"], the first studies of H_3 reaction dynamics were made possible by the early semiempirical H_3 surfaces. Thus we will examine this work of this period in more detail.

The basis of the LEP method is to realize that the Heitler-London treatment of H_2, with neglect of orbital overlap integrals, expresses the ground-state energy of H_2 as the sum of Q_{ij} and J_{ij}. Thus a Morse curve for H_2 gives a semiempirical value for the sum of these integrals at each distance. Then it was assumed that Q_{ij} is always a constant fraction ρ of this sum. This scheme was originally motivated by examining Sugiura's (1927) calculated values of the integrals. These yielded a roughly constant

ρ of 0.14 at large distances. However, in practice ρ was often treated as an adjustable parameter. It was given various values at various times: 0.10 (Eyring and Polanyi, 1930; Eyring, 1931), 0.00 (Eyring and Polanyi, 1931), 0.14 (Eyring, Gershinowitz, and Sun, 1935), and 0.20 (Hirschfelder, Eyring, and Rosen, 1936). For any value of ρ the method predicts that the lowest-energy reaction path is linear. For low ρ the barrier is symmetric ($R_1 = R_2$) but much too high. As ρ is increased the barrier is lowered. However, for any constant $\rho \gtrsim 0.07$ the symmetric configuration is a local minimum flanked by twin nonsymmetric saddle points. For example (Eyring, 1931), for $\rho = 0.035$ the barrier is symmetric with height 0.91 eV, but for $\rho = 0.10$ the local minimum has a nearest-neighbor distance R_1 of 1.76 a_0 and is 0.49 eV above the energy of $H + H_2$ but the twin saddle points are 0.07 eV higher. Yet Farkas's rate experiments (reviewed in Truhlar and Wyatt, 1976) were interpreted as leading to an activation energy of 0.17 to 0.48 eV and the surfaces with twin saddle points were used for comparison to experiment. It is interesting that if ρ is made an increasing function of R (in accordance with the Heitler-London treatment of H_2), then the basin results from using too high a value at small R; ρ may be large (0.14 or even greater) at large R without making a basin. Such variable-ρ treatments are discussed later in this section.

The consequences of the predicted basin were discussed by Eyring (1932). First he noted that the predicted basin was so unstable that even if it could be collisionally stabilized it would survive only a few collisions. But the LEP method is approximate and the actual basin might have been deeper. Eyring considered a configuration point representing the instantaneous geometry of the H_3 system. He predicted that it moves very slowly through the first pass and into the shallow basin where it zigzags back and forth before it finds its way out through the second gap. The three atoms would then form a quasimolecule in the "sticky" collision. During this time, if the basin were deeper, the H_3 complex could be stabilized. To understand even the qualitative features of the dynamics it was necessary to have a more reliable calculation of the basic features of the surface. Thus attention was turned to these and we will consider what has been learned from ab initio calculations about the reaction-path part of the surface before returning to the history of the semiempirical work.

The ab initio variation method has also been used to calculate the H_3 energy. The first ab initio calculation on the H_3 potential-energy surface was performed by Coolidge and James (1934). They studied only one geometry (linear symmetric H_3 with $R_1 = 1.7a_0$). They used valence-bond theory with the two configurations mentioned above; for linear symmetric H_3 one may consider instead one symmetry-adapted configuration, which they did. They obtained an energy of -1.72 eV. (We give the energies of all ab initio calculations as binding energies, i.e., the zero of energy is three H atoms infinitely separated; but barriers and other positive energies referring to heights along the reaction path are given with respect to the energy of $H+H_2$.) They also considered several approximations to this result in order to study the justification for semiempirical valence-bond procedures. As mentioned above, they concluded that the approximations needed to obtain the LEP method are so severe that the justification for the latter must be wholly empirical. Their ab initio calculation was soon reproduced by Hirschfelder, Erying, and Rosen (1936), who also showed that at the same level of approximation a much lower energy can be obtained for linear symmetric H_3 by increasing R_1 to $2.0a_0$ where the energy is -3.14 eV. Using the experimental binding energy of H_2, this yields a rigorous upper bound on the classical barrier height of 1.61 eV. This was known to be much too high. It was recognized that a more reasonable approximation is to compare a calculated H_3 energy to an H_2 binding energy calculated at equivalent levels of approximation. Using a Heitler-London wave function for H_2 for comparison with Hirschfelder et al.'s valance-bond result, we obtain an estimate of the saddle-point height of 0.80 eV, still much too large. Hirschfelder et al. (1936) considered three improved approximations for linear symmetric H_3 in which they added ionic configurations with variable coefficients and/or optimized the orbital exponents. While these gave considerably lower energies for H_3, the estimated barrier height was not improved. These calculations are summarized in Table I (for comparison we have corrected the diatomic values Hirschfelder et al. quoted).

Subsequently, further calculations were performed at these same levels of approximation; they predicted that the saddle point is linear and symmetric. First, Hirschfelder et al. (1937) calculated energies for nonsymmetric linear geometries and found that the saddle point for the collinear reaction is symmetric. Stevenson and Hirschfelder (1937) then showed that the energy rose on bending. It is interesting to anticipate a result of the ab initio calculations to be discussed below, i.e., only one ab initio calculation (Conroy and Bruner, 1967) has ever predicted a saddle-point geometry other than linear symmetric. That calculation predicted a narrow shallow basin for linear symmetric geometries which would be far less significant than the broader deeper basins predicted by the early semiempirical calculations, and even that shallow basin disappeared in an improved calculation (Conroy and Bruner, 1967) by the same method. Thus Hirschfelder, Diamond, and Eyring's prediction of a symmetric saddle point has stood the test of time, and the latest calculations (Liu, 1973) have finally

TABLE I

Ab Initio Variational Upper Bound Calculations of the Binding Energy E and Zero-Point Energy $\frac{1}{2}h\nu_s$ for Harmonic Stretching of Linear Symmetric H_3 Along with Estimated Classical Barrier Heights E_b

	H_3			H_2			H_3	
Reference[a]	$R^{\ddagger b}$ (a_0)	E^c (eV)	$\frac{1}{2}h\nu_s$ (eV)	R^d (a_0)	$E^{c,d}$ (eV)	Reference	E_b^e (eV)	Description of H_3 calculation[f] (and one-electron basis[g])
Minimum basis set								
Coolidge and James, 1934	1.7	−1.72						VB: covalent only ($\zeta = 1$)
Hirschfelder, Eyring, and Rosen, 1936	2.0	−2.33		1.64	−3.14	Coulson, 1937	0.80	VB: covalent only ($\zeta = 1$)
	1.89	−2.46		1.41	−3.78	Wang, 1928	1.32	VB: covalent only (ζ opt)
	2.0	−2.65						VB: covalent + ionic: CCI ($\zeta = 1$)
Hirschfelder et al., 1936, 1937	1.84	−2.94	0.20	1.42	−4.02	Weinbaum, 1933	1.08	VB: covalent + ionic: CCI (ζ opt)
Pearson, 1948	1.91	+1.27						MO (not antisymmetrized, ζ opt)
Walsh and Matsen, 1951	2.00	−1.67		1.61	−2.68	Coulson, 1937	1.01	MO ($\zeta = 1$)
	1.82	−1.99		1.38	−3.47	Coulson, 1937	1.48	MO (ζ opt)
Griffing and Vanderslice, 1955	2.0	−1.17			−2.98	Griffing and Vanderslice, 1955	1.81	MO for H_3^- + Koopmans' theorem (ζ opt)
Ransil, 1957	1.95	−1.70		1.61	−2.68	Coulson, 1937	0.98	MO ($\zeta = 1$)
	2.00	−1.78		1.38	−3.47	Coulson, 1937	1.69	MO (ζ opt)
		−2.63						MO: CCI (ζ opt = 1)
		−2.06		1.61	−2.68	Coulson, 1937	0.62	UHF: not spin eigenfunction (ζ not given)
Griffing et al., 1959	1.90	−2.96						MO: CI (ζ opt)
Bradley, 1964	2.05	−2.10		1.61	−2.68	Coulson, 1937	0.56	UHF: not spin eigenfunction ($\zeta = 1$)
	1.91	−2.44	0.120	1.38	−3.47	Coulson, 1937	1.03	UHF: not spin eigenfunction (ζ opt)
	1.91	−2.66						UHF: CI: not spin eigenfunction (ζ opt)
	1.91	−2.68		1.38	−3.47	Coulson, 1937	0.79	spin-projected UHF (ζ opt)
	1.91	−2.88						spin-projected UHF: CI (ζ opt)
Bowen and Linnett, 1966	1.89	−3.04		1.42	−4.02	Weinbaum, 1933	0.98	CCI (outer and middle orbital exponents separately opt)
Shavitt et al., 1968	1.88	−3.01		1.43	−4.02	Weinbaum, 1933	1.01	CI (ζ opt)
Gianinetti et al., 1969	1.91	−3.01		1.44	−4.02	Gianinetti et al., 1969	1.01	CI (ζ opt)
Blustin and Linnett, 1974	1.82	+4.31		1.47	+1.20	Frost, 1967	3.11	MO (GTF: one s shifted off nuclei)

Extended basis set of hydrogen $1s$ orbitals								
Boys et al., 1956; Boys and Shavitt, 1959	1.78	−3.48	0.120	1.42	−4.14	Boys and Shavitt, 1959	0.66	CCI (ETF: two *s*)
Shavitt et al., 1968	1.79	−3.55	0.123	1.41	−4.16	Shavitt et al., 1968	0.61	CCI (ETF: two *s*)
Gianinetti et al., 1969	1.83	−3.47		1.42	−4.16	Gianinetti et al., 1969	0.69	CI (ETF: two *s*)
	1.79	−2.41						MO (ETF: two *s*)
Bacskay and Linnett, 1972	1.79	−3.55			−4.16	Bacskay and Linnett, 1972a	0.61	CCI (ETF: two *s*)
Basis set including polarization functions (or their equivalent)								
Meador, 1958	1.84	−2.48						MO: CI (three hydrogenic is orbitals, two off nuclei; ζ opt)
Kimball and Trulio, 1958	1.93	−3.138						CCI (five equally spaced hydrogenic $1s$ orbitals; ζ opt)
Krauss, 1964	1.7	−2.530						MO (GTF: five *s*, one $p\sigma$)
Hoyland, 1964	1.78	−2.419						CI (six two-center elliptical orbitals with opt parameters)
Edmiston and Krauss, 1965	1.8	−3.891		1.4	−4.600	Edmiston and Krauss, 1965	0.709	PNO: CI (GTF: five *s*, one $p\sigma$, two $p\pi$)
Conroy and Bruner, 1967	1.75	−4.221						Conroy's method
Considine and Hayes, 1967	1.8	−3.050						CI: 52 terms (single-center expansion, 68 orbitals)
Hayes and Parr, 1967	1.8	−3.695						CI: 99 terms (single-center expansion, 85 orbitals)
Michels and Harris, 1968	1.76	−3.543		1.4	−4.191	Michels and Harris, 1968	0.648	CCI (ETF: one *s*, one $2p\sigma$)
Shavitt et al., 1968	1.764	−4.139	0.125	1.402	−4.615	Shavitt et al., 1968	0.476	CCI (ETF: two *s*, one $p\sigma$, one $p\pi$)
Schwartz and Schaad, 1968	1.725	−2.395						MO (twelve floating $1s$ Gaussians)
	1.7	−2.456						MO (eighteen floating $1s$ Gaussians)
Edmiston and Krauss, 1968	1.7	−2.530		1.4	−3.619	Edmiston and Krauss, 1968	1.090	MO (GTF: five *s*, one $p\sigma$, three $p\pi$)
	1.8	−4.064		1.4	−4.647	Edmiston and Krauss, 1968	0.583	PNO: CI (GTF as above)
Ladner and Goddard, 1969	1.765	−3.369		1.4	−4.123	Goddard and Ladner, 1969	0.754	SOGI (ETF: two *s*, one $p\sigma$)
Gianinetti et al., 1969	1.7965	−3.439		1.417	−4.193	Gianinetti et al., 1969	0.754	CI (ETF: one *s*, one $p\sigma$)
	1.795	−3.655		1.423	−4.329	Gianinetti et al., 1969	0.675	CI (ETF: two *s*, one $p\sigma$)
	1.792	−4.008		1.4165	−4.612	Gianinetti et al., 1969	0.604	CI (ETF: two *s*, one $p\sigma$, one $p\pi$)

Table I (continued)

	H_3			H_2			H_3	
Reference[a]	$R^{\ddagger b}$ (a_0)	E^c (eV)	$\frac{1}{2}h\nu_s$ (eV)	R^d (a_0)	$E^{c,d}$ (eV)	Reference	E_b^e (eV)	Description of H_3 calculation[f] (and one-electron basis[g])
Riera and Linnett, 1969	1.800	−3.774	0.122	1.416	−4.482	Riera and Linnett, 1969	0.707	CCI (ETF: one *s*, one *pσ*, one *pπ*)
Riera and Linnett, 1970	1.771	−3.913						CI (basis as above pllus five equally spaced 1*s* Gaussians)
Bacskay and Linnett, 1972	1.79	−2.516						MO (ETF: two *s*; plus two 1*s* Gaussians at bond midpoints)
	1.79	−3.786		1.4148	−4.326	Bacskay and Linnett, 1972a	0.540	CCI (basis as above)
	1.79	−4.128		1.4148	−4.594	Bacskay and Linnett, 1972a	0.466	CCI (basis as above plus twelve off-axial 1*s* Gaussians)
Liu, 1971	1.7, 1.75	−2.578		1.4	−3.635			MO (ETF: four *s*, three *pσ*, two *dσ*, one *fσ*, three *pπ*, three *dπ*, one *fπ*, three *dδ*, one *fδ*)
	1.76	−4.289		1.4	−4.725	Liu, 1971	0.436	PNO: CI (basis as above)
Liu, 1973	1.79	−2.578						MO (ETF: four *s*, three *pσ*, two *dσ*, three *pπ*, one *dπ*, one *dδ*)
	1.80	−3.397						Internal configuration MCSCF (basis as above)
	1.75	−4.296						CI in zero and first order subspaces (basis as above)
	1.757	−4.302	0.127	1.4014	−4.727	Liu, 1973	0.425	Near-complete CI (basis as above)
Exact H_2				1.4008	−4.748	Kolos and Wolniewicz, 1965		

[a] Reference for H_3 calculation. Hiershfelder et al., 1936 refers to Hirschfelder, Eyring, and Rosen, 1936.

[b] Nearest-neighbor distance for which the minimum energy was calculated for this method. In some cases the authors made an extensive search for the saddle-point geometry but in other cases only one or a few geometries were examined.

[c] Zero of energy is 3H; 1 eV = (1/27.2116)a.u.

[d] Internuclear distance and binding energy calculated for H_2 in a calculation comparable to the H_3 calculation (not always available).

[e] Difference of H_2 and H_3 binding energies.

[f] Abbreviations: VB, valence-bond method; MO, molecular orbital (i.e., Hartree-Fock-Roothaan) method; CCI, complete configuration interaction; UHF: unrestricted Hartree-Fock; CI, configuration interaction; PNO, pseudonatural orbitals. These methods and other ab initio methods mentioned in the text are explained in standard references; see, e.g., Krauss (1970) and Schaefer (1972).

[g] ζ, orbital exponent (in a_0^{-1}) of hydrogenic 1*s* orbital when all orbitals have same exponent ($\zeta = 1$ for H); opt, optimized; ETF and GTF, number of one-electron exponential-type basis functions or Gaussia[illegible] basis functions, of each symmetry centered on each nucleus. Optimization of orbital exponents is more important for minimum basis sets than [illegible]xtended basis sets and is not reviewed here for the latter.

established quite firmly that the saddle point on the linear surface is symmetric so that the "Lake Eyring" of the early semiempirical surfaces must be an artifact of the approximations involved.

After these calculations were completed there were no more ab initio calculations of the saddle-point properties until 1951. Since then, however, the interest has been very strong and the results of the calculations have slowly improved. In this process most H_3 calculations have been limited to the linear symmetric configuration in an attempt to calculate the energy of the saddle point. We discuss these ab initio attempts next and then we consider ab initio calculations of other features of the H_3 surface when all three atoms are close: nonsymmetric linear configurations, nonlinear configurations near the saddle point, and equilateral H_3. Then we consider the later semiempirical calculations of surface properties near the reaction path. Finally we consider all kinds of calculations of the very short-range repulsive forces and of the long-range forces and the region of the van der Waals' minimum.

The history of ab initio saddle-point calculations may conveniently be divided into three stages (or "ages" except that the chronology of the stages overlaps to some extent). The first stage involved using minimum-basis sets, that is, three $1s$ functions centered at the nuclei. The second stage involved using more than three spherical basis functions centered at the nuclei. And finally the calculations were performed using more general bases, especially extended basis sets of nuclear-centered functions including polarization functions (e.g., $2p\sigma$ functions in order to better represent the polarization of the charge distribution). The basis sets and results of all the calculations are summarized in Table I and we add only a few comments.

The calculation of accurate multicenter integrals was for decades a "bottleneck" of ab initio quantum calculations. Thus, for example, the accurate three-center integrals of Hirschfelder and co-workers (Hirschfelder et al., 1936; Hirschfelder and Weygandt, 1938) were used by several subsequent workers (even over 20 years later). Barker et al. (1954) and Barker and Eyring (1954) examined the use of Mulliken's (1949) method for approximating the three-center integrals in terms of two-center Coulombic-type integrals. They performed covalent valence-bond calculations with hydrogen-atom exponents. They found that the energy was raised from −2.33 eV to −2.00 eV. Using this same approximation scheme, Snow and Eyring (1957) found this was decreased to −2.62 eV when the outer orbital exponents and the middle one were optimized separately. Yasumori (1959), Oleari et al. (1961), and Harris et al. (1965) performed additional H_3 calculations using the Mulliken approximation.

Barker and Eyring (1957) also examined a "distance-normalized" approximation to the difficult integrals and obtained an energy of -3.17 eV for the covalent valence-bond wave function when the outer and middle orbital exponents were separately normalized. When this separate optimization of the exponents was finally carried out with correct integrals in a complete-configuration-interaction calculation, the energy lowering was less than 0.1 eV (Bowen and Linnett, 1966). The results using approximate integrals are not included in Table I because of the admittedly serious nature of the approximation. However, the reader should remember that the history of ab initio molecular calculations is filled with examples of calculations containing errors due to inadvertent use of incorrect integral values. No systematic attempt is made here to discuss the accuracy of the integrals involved in all the calculations. Presumably, however, the integrals were all evaluated accurately in calculations carried out within the last 10 years or so. Finally, we should emphasize that progress seen in the successive ab initio calculations reviewed in Table I and below is due not only to the cited efforts of the authors of these calculations but also in many cases to the quantum chemists, including many of these authors but also others, who devised improved methods for integral evaluation and for efficient utilization of computers for large-scale ab initio calculations. These parallel advances interacted strongly with advances in H_3 computations, but it is beyond the scope of the present chapter to discuss them in detail.

The next attempts to use accurate integrals were the ab initio minimum-basis-set molecular orbital calculations of Walsh and Matsen (1951) and Griffing and Vanderslice (1955) and the attempts by Ransil (1957), Meador (1958), and Griffing et al. (1959) to improve these results using configuration interaction based on molecular orbitals and in one case allowing the basis functions to be centered off the nuclei. The molecular orbital method leads to an energy about 0.5 eV higher than the valence-bond method, whereas the configuration-interaction calculations should be equivalent to Hirschfelder, Eyring, and Rosen's (1936) configuration-interaction calculations based on the valence-bond formalism. A complete-configuration-interaction (CCI) calculation is one in which the Hamiltonian is diagonalized in the space of all three-particle functions of the appropriate symmetry that can be formed from the chosen one-electron basis set. Such a result is exact within the restrictions imposed by the one-electron basis and yields the lowest energy that can be obtained with that basis. For three $1s$ functions a CCI consists in general of eight configurations, but for linear symmetric H_3 it may be reduced to four symmetry-adapted configurations. The calculation may be carried out equivalently in either the valence-bond or molecular orbital formalisms or without reference to either. Boys and Shavitt (1959) pointed out that the configuration-interaction wave functions of Walsh and Matsen (1951) and of Meador (1958) include only three of the four linearly independent configurations and that one of these is not a spin eigenfunction. The minimum-basis-set approach was later reexamined by Bradley (1964), Bowen and Linnett (1966), and others. Bowen and Linnett showed that a CCI calculation for a minimum basis set with separately optimized orbital exponents and the best value of R_1 yields an energy of -3.045 eV. This yields a rigorous upper bound of 1.333 eV on the classical barrier height and using the best possible minimum-basis-set calculation on H_2 for comparison yields an estimated barrier of 0.975 eV. Both values are too high to be useful. Rourke and Stewart (1968) showed that Bradley's (1964) minimum-basis-set wave function is not of sufficiently high quality for use with a local-energy method and that variation-method results are expected to be more accurate for this type of wave function.

Even before the configuration-interaction calculations discussed in the preceding paragraph it was very clear that one must go beyond a minimum basis set and Boys et al. (1956) had already done so. Their calculations (Boys et al., 1956; Boys and Shavitt, 1959), the first using an extended basis set, were CCI calculations for two $1s$ exponential-type functions on each nucleus. For linear symmetric geometries this involved 34 symmetry-adapted configurations. They obtained an energy of -3.48 eV and an estimated barrier of 0.66 eV, still much too large. Their result was affected slightly by the method used to calculate some of the difficult integrals. It is now known that the accurate CCI result for this basis with the best value of R_1 and optimization of two (but not four separate) values of the orbital exponents is -3.55 eV (see Table I).

Another extended-basis-set calculation was performed by Kimball and Trulio (1958). They carried out a complete configuration-interaction calculation in the space spanned by five $1s$ exponential functions equally spaced on a line. Their calculated binding energy (-3.138 eV) is of course also lower than any calculated with a minimum-basis set.

Krauss (1964) carried out the first calculation including p functions. He used the molecular orbital (SCF) form of wave function and obtained an energy of -2.530 eV. However, a molecular orbital potential surface is not of useful accuracy for H_3. Edmiston and Krauss (1965) then used this basis to carry out their first configuration-interaction calculation. This yielded an energy 0.41 eV lower than obtained by Boys and Shavitt (1959), but the calculated barrier was not improved. This was the first calculation using present state-of-the-art techniques for potential-energy-surface calculations (they used the pseudonatural orbital method); thus it provides a convenient basis for comparison for later calculations. We will abbreviate it

EK1. In a similar but improved calculation, reported later (Edmiston and Krauss, 1968), they obtained an energy 0.17 eV lower than EK1, but by that time Shavitt et al. (1968; see also Karplus 1968) had already reported a result 0.25 eV lower than EK1. Shavitt et al. performed CCI calculations for a double-zeta-plus-polarization basis, which is better than the Gaussian bases of Edmiston and Krauss. This involved 200 symmetry-adapted configurations for linear symmetric geometries. Their calculated barrier was only 0.476 eV. Of special interest are the calculations of Conroy and Bruner (1965, 1967) using a method of Conroy (1964, 1970). They optimized their trial function by minimizing the energy variance functional rather than the usual energy functional. This permits extrapolation of the calculated results to obtain an approximation to the exact energy. This was combined with a new form of trial function explicitly incorporating interelectronic distances and a Monte Carlo-like or Diophantine method for the evaluation of the integrals. First (Conroy and Bruner, 1965) they reported a potential-energy surface for linear H_3 obtained using their extrapolation procedure. Then (Conroy and Bruner, 1967) they made an improved calculation for a greater variety of geometries and reported both upper bounds (see Table I) and extrapolated results (discussed below). A disadvantage of their calculations is the relatively large error in the numerical integration procedure, estimated at ±0.03 to ±0.05 eV. However, they also estimated this to be the overall accuracy of their extrapolated energy surface. Their upper bound energy was 0.33 eV better than the EK1 value.

After their second calculation Edmiston and Krauss concluded "further improvements will come in very small pieces as a result of more configurations, more pseudonatural orbitals, and more Gaussian basis functions." Here and in the discussion of Liu's results, "orbitals" means the linear combinations of basis functions used to construct configurations. Generalizing pseudonatural orbitals to whatever set of orbitals is used in the calculation and the last phrase to "more one-electron basis functions," we now recognize from current experience that this conclusion of Edmiston and Krauss is always true for the last few tenths of eV in large-scale configuration-interaction calculations of potential-energy surfaces.

Several workers (Michels and Harris, 1968; Shavitt et al., 1968; Linnett and Riera, 1969) suggested that, in particular, it would be necessary to add $d\sigma$ basis functions. This was done by Liu, who actually used one-electron bases many times larger than any previous one. In his preliminary report (Liu, 1971) he used the pseudonatural orbital method and obtained an energy 0.40 eV lower than EK1. His second set of calculations (Liu, 1973) differed mainly in the method used to select orbitals and configurations [for the basis set used in the second set of calculations a CCI would involve 14,949 symmetry-adapted configurations, compared to, for example, 35 for the basis of Harris and Michels (1968)]. This involved seven-configuration multiconfiguration self-consistent-field calculations and division of the configuration space into zeroeth-, first-, and second-order parts. The best energy obtained (Liu, 1973) was -4.302 eV, which is 0.41 eV lower than EK1. Comparison to the exact result for H_2 yields a rigorous upper bound to the barrier of only 0.446 eV, lower than all previous calculated values based on upper bound calculations even when those were obtained by subtracting comparable H_2 and H_3 calculations. Comparing Liu's H_3 result to his comparable one for H_2 yields a barrier of only 0.425 eV. Liu estimated the possible errors in his surface in two parts: error due to truncation of the one-electron basis (0.021 to 0.034 eV) and error due to not reaching the CCI limit for this basis set (0.001 eV). His calculated barrier would correspond to an H_3 energy of -4.323 eV and he estimated the actual result cannot be below -4.336 eV. Since he is extrapolating to the exact result from much closer than any previous worker his estimates are preferred over all others. This leads to $-4.323^{+0.021}_{-0.013}$ eV as the bounded energy of the H_3 saddle point, corresponding to a saddle-point height of $0.425^{+0.021}_{-0.013}$ eV. From Liu's arguments one could estimate with less certainty an even more closely bounded result. Thus if we assume that the residual error at the saddle point is at least as large as, but no more than 1.5 times, the residual error in H_2 at the same internuclear distance, then the estimated energy is -4.327 ± 0.005 eV, corresponding to a barrier of 0.420 ± 0.005 eV. For comparison with the kinetics literature, these two sets of bounds can be converted to $9.80^{+0.48}_{-0.30}$ and 9.69 ± 0.12 kcal/mole.

It is interesting to compare these final estimates from Liu's calculations to previous attempts to estimate the energy of the H_3 saddle point on the basis of ab initio calculations. Edmiston and Krauss (1965) improved their first H_3 calculation by including additional configurations in second order and obtained a binding energy of -3.983 eV. They also performed a comparable calculation on H_2. By assuming that the remaining error in the H_3 calculation relative to H_2 is proportional to the ratio of correlation energies, they estimated an H_3 binding energy of -4.23 eV. Conroy and Bruner (1967), in their improved calculation, obtained in extrapolated energy of -4.411 eV. Hayes and Parr (1967) estimated the errors due to angular and radial deficiencies in their 99-term wave function and predicted an exact energy (at $R_1 = 1.8a_0$) of -4.180 eV. Shavitt et al. (1968) assumed the residual error in their H_3 calculation was no more than 1.5 times the residual error in a comparable H_2 calculation, which implies that the energy of H_3 should be no more negative than -4.338 eV. Shavitt (1968) used this ab initio surface with one empirical parameter, a uniform scale factor for the energy profile along the reaction path, to compute transition-state theory rate constants for the isotopic $H+H_2$ reactions. The value of the scale factor that gave best agreement with the high-temperature experimental rates of Westenberg and deHaas was 0.89, implying an H_3 energy of -4.324 eV. After their second calculation, Edmiston and Krauss pointed out that their H_2 calculations at three internuclear distances accounted for 91% of the correlation energy. Thus they assumed that they were accounting for 91% of the correlation energy everywhere. This yielded an estimated binding energy of H_3 of -4.215 eV. Thus the estimates of Shavitt et al. (1968) and Shavitt (1968) agree remarkably well with those of Liu but none of the other estimates fall within even the wider of the bounds given above.

By considering the linear symmetric geometry we may also evaluate the force constant for symmetric stretching of the activated complex. From this one may calculate the zero-point energy $\frac{1}{2}h\nu_s$ of this normal mode in the harmonic approximation. There have been several such calculations and the results are given in Table I. [Harris et al. (1965), whose results are excluded from that table, obtained 0.131 eV.] This quantity, as well as the zero-point energy $\frac{1}{2}h\nu_b$ for a bending normal mode, is important for transition-state theory and the vibrationally adiabatic theory that are discussed elsewhere (Truhlar and Wyatt, 1976).

There has been relatively less attention devoted to geometries other than linear symmetric, but there have been several studies of nonsymmetric linear geometries (Hirschfelder et al., 1937; Boys et al., 1956; Boys and Shavitt, 1959; Conroy and Bruner, 1965, 1967; Edmiston and Krauss, 1968; Shavitt et al., 1968; Goddard and Ladner, 1969; Ladner and Goddard, 1969; Blustin and Linnett, 1975; Liu, 1973). Shavitt et al. (1968) and Liu (1973) have presented accurate analytic fits to their whole collinear surfaces. For use in one-dimensional tunneling corrections to transition-state theory it is of interest to calculate the second derivative at the barrier maximum and express it as the zero-point energy of the upside-down parabola with this force constant. This is called the imaginary zero-point energy of the asymmetric-stretch normal mode of the activated complex, and the few values calculated for it are as follows: $0.084i$ eV by Boys et al. (1956) and Boys and Shavitt (1959), $0.087i$ eV by Harris et al. (1965), $0.090i$ eV and $0.096i$ eV in double-zeta and double-zeta-plus-polarization bases by Shavitt et al. (1968), and $0.094i$ eV by Liu (1973) in his most accurate calculation.

Other important features of the nonsymmetric linear H_3 calculations are the position of the minimum energy path, the energy variation along and near this path, and the description of the bonding changes accompanying movement along this path. Harris et al. (1965), in CCI calculations employing a minimum basis set and the Mulliken approximation, mapped out the approximate position of the minimum energy path through the (R_1, R_2)

plane and the energy variation along it. Their results predicted that the curvature of the minimum energy path was confined to within about $0.4a_0$ of the saddle point and that the full width at half-maximum of the barrier along the curvilinear minimum energy path was about $2.0a_0$. Conroy and Bruner mapped out two complete potential-energy surfaces from their two sets of extrapolated results for the collinear calculation. In their first calculation (Conroy and Bruner, 1965) they found twin unsymmetrical saddle points with $(R_1, R_2) = (1.64a_0, 1.83a_0)$ and energies of -4.479 eV and a shallow symmetric depression with $R_1 = 1.76a_0$ and an energy 0.054 eV higher. These values appear by comparison to Liu's (1973) calculation to be too low by more than their estimated error of ±0.05 eV in integral evaluation. They state that their second calculation (Conroy and Bruner, 1967) led to a linear symmetric saddle point but that calculation gave a barrier which is extremely flat near the top. It appears that their points near the top of the barrier are too widely spaced to judge whether a depression actually exists (Shavitt et al., 1968). Edmiston and Krauss (1968) and Shavitt et al. (1968) found the approximate position of the minimum-energy path through the (R_1, R_2) coordinate system by finding minima along cross sectional cuts almost perpendicular to the reaction path. Edmiston and Krauss did not examine points near enough to the barrier top to judge definitely whether a depression actually exists. The correct way to do this is to find the position of the minimum for linear symmetric geometries and then examine a small displacement along the asymmetric stretch normal mode to see if it is a saddle point or a local minimum. This has only been done by Harris et al. (1965), Shavitt et al. (1968), and Liu (1973). All these workers found that the saddle point was linear symmetric, and there is no longer any serious doubt that this is the case. Liu (1973) also used the method of steepest descents to start at the saddle point and find the accurate position of the whole minimum-energy path in the (R_1, R_2) coordinate system. (This differs from the minimum-energy path in a skewed-axis coordinate system.) The minimum-energy path determined in Liu's linear calculation approaches the equilibrium separation of H_2 much faster than the path of Shavitt et al. (1968). The potential energies along the five most accurate calculated minimum-energy paths at the places where they cross various R_2 = constant lines are compared in Table II (these results were found by interpolation of the published data). In addition, we have followed the suggestion of Shavitt (1968) and in each case scaled the energy profile along the minimum-energy path by a constant determined to make the barrier correct. (For this purpose Liu's barrier is assumed correct.) These results are also shown. First we see that the barriers of Conroy and Bruner (1967) and Edmiston and Krauss (1968) are too flat at the top. We also see that the barrier of Conroy and Bruner is

TABLE II

Energies (in eV) Along Minimum-Energy Path in (R_1, R_2) Coordinates System for Given Values of R_2 (Where R_1 and R_2 Are the Interatomic Separations of the Two Nearest Neighbors)

Case	1	2	3	4	5	1	2	3	4
calculation	Conroy and Bruner,	Edmiston and Krauss,	Edmiston and Krauss,	Shavitt et al.,	Liu,				
$R_2(a_0)$	1967[a]	1968[b]	1968[a]	1968[b]	1973[b]	Scaled	Scaled	Scaled	Scaled
Saddle point	0.34	0.58	0.53	0.48	0.42	0.42	0.42	0.42	0.42
1.9	0.33[c]	0.59[c]	0.55[c]	0.46	0.41	0.42[c]	0.43[c]	0.44[c]	0.41
2.2	0.28	0.54	0.53	0.40	0.34	0.36	0.39	0.43	0.35
2.6	0.16	0.38	0.37	0.28	0.23	0.20	0.28	0.30	0.25
3.0	0.05	0.23	0.22	0.17	0.14	0.06	0.17	0.18	0.16
3.4				0.10	0.07				0.09

[a] Extrapolated surface, relative to experimental energy of $H+H_2$.

[b] Upperbound surface, relative to calculated energy of $H+H_2$.

[c] These values are slightly uncertain because of the insufficient number of points calculated in this neighborhood.

too low at $R_2 > 3.0a_0$; that is, their interaction energy goes below 0.1 eV (and even below 0.0 eV) much too close to the saddle point. However, the scaled barrier of Shavitt et al. (1968) is in very good agreement with the barrier of Liu (1973).

Recently, Baskin et al. (1974), Blustin and Linnett (1974), and McCullough and Silver (1975) have pointed out that the correct minimum-energy path through the (R_1, R_2) plane cannot be obtained by considering the minima along cuts parallel to the axes. This is implicit in all the work discussed above and is also mentioned explicitly in an article discussed below (Truhlar and Kuppermann, 1971).

Weston (1959) and Shavitt (1968) pointed out that for tunneling corrections to transition-state theory one needs the minimum-energy path not in the (R_1, R_2) coordinate system but in normal-mode coordinate systems in which the axes are scaled and skewed so that the reduced mass is the same for motion in any direction. Of course, such a coordinate system depends on the ratios of the isotopic masses of the nuclei. Shavitt replotted the (R_1, R_2)-minimum-energy path in such a coordinate system for the equal-mass case. Choosing the scaling so the reduced mass is $\frac{2}{3}$ the mass of H showed that reaction-path curvature is non-negligible within $0.4a_0$ of the saddle point and the fullwidth at half-maximum of the barrier is about $1.8a_0$. Truhlar and Kuppermann (1971) determined the actual minimum energy path in this coordinate system for the surface of Shavitt et al. (1968). In addition, they developed an analytic approximation [based on the rotated-Morse-curve method of Wall and Porter (1962)] to the whole collinear surface following Shavitt's (1968) suggestions for scaling and found that the minimum-energy path for this surface in normal-coordinate space for the equal-mass case (Truhlar and Kuppermann, 1972). This surface is called the scaled SSMK or the Truhlar-Kuppermann surface.

Goddard and Ladner (1969, 1971; Ladner and Goddard, 1969; Goddard, 1972) provided a quantum-mechanical orbital picture of the reaction by using the best possible wave function for which the orbitals have an independent particle interpretation, that is, are eigenfunctions of one-electron Hamiltonians corresponding to the nuclear attraction and the nonlocal field of electrons in the other two orbitals. This was called the spin-coupling optimized group operator (SOGI) method. It provides a picture of the reaction in which the orbitals of the reactants gradually delocalize over all three centers, then relocalize to form product states. This orbital picture was used as a basis for a general theory (the orbital phase continuity principle) of orbital phase relationships accompanying bonding changes in reactions. It is a generalization of the valence-bond method and has certain conceptual advantages over the Woodward-Hoffman approach, which has been successfully applied to many molecule-molecule reactions. According to the latter, the $H+H_2$ reaction might be considered thermally forbidden [see, e.g., the orbital correlation diagram given by Hoffman (1968)], but the Woodward-Hoffman rules are actually not very useful for considering the reactivity of open-shell atoms, like H, with molecules. Of course, a quantitative understanding of the energetic changes along the reaction path requires a detailed consideration of the changes in the correlation energy (defined as the difference between the exact energy and that calculated from a molecular orbital or group-operator wave function) accompanying the reaction. This question, however, is closely tied to the question of completeness of the basis set since final convergence of the energy calculations requires simultaneous improvement of both. Several authors have discussed these problems (see, e.g., Edmiston and Krauss, 1965, 1968; Michels and Harris, 1968; Gianinetti et al., 1969; Linnett and Riera, 1969; Liu, 1971, 1973).

There has been very little work on nonlinear geometries. Stevenson and Hirschfelder (1937) evaluated $\frac{1}{2}h\nu_b$ (defined above) by taking derivatives of the energy expression with respect to bond angle. They obtained 0.059, 0.069, 0.052, and 0.067 eV in the four approximations considered by Hirschfelder et al. (1936) in the order they are listed in Table I. Thus their results were roughly the same as the value of 0.056 eV obtained by the semiempirical method of Eyring and Polanyi with $\rho=0.20$. Boys et al. (1956) and Boys and Shavitt (1959) calculated a value of 0.059 eV; however, since this value is based on a nonlinear geometry with a 40° bond angle, the value is probably higher than should be obtained with their basis set (Johnston, 1966, p. 74). Harris et al. (1965) calculated 0.061 eV using the Mulliken approximation. The first reliable calculation was that of Shavitt et al. (1968), who obtained 0.060 eV in their double-zeta-plus-polarization basis. Liu and Siegbahn (private communication) have carried out some calculations for nonlinear geometries but they are not published. Their value for the harmonic bending zero-point energy is 0.057 eV. Except for a few calculations related to the equilateral triangle geomerty (see next paragraph), extensive treatments of the nonlinear geometries have been published only by Conroy and Bruner (1967) and Shavitt et al. (1968). Conroy and Bruner studied only isosceles triangle configurations with bond angles 120°, 90°, and 60°. Shavitt et al. studied systems with 150° and 120° bond angles. For each constant value of the bond angle, Shavitt et al. determined the minimum-energy paths in the (R_1, R_2) coordinate system and the associated energy profile and barrier. They obtained saddle-point geometries with nearest-neighbor distances of $1.78a_0$ and $1.81a_0$, respectively, and barrier heights of 0.55 and 0.79 eV. The scaling suggested by Shavitt (1968) would lower these values to 0.50 and 0.74 eV, respectively. For comparison, Conroy and Bruner obtained about 0.65 eV for the saddle-point height for a 120° bond angle. The changes of saddle-point heights with bond angle are in good agreement.

Siegbahn and Liu (private communication) made calculations for the following bond angles: 180°, 165°, 150°, 135°, 120°, 90°, and 60°. They used a basis of nine *s*, three *p*, and one *d* Gaussian-type functions (GTF) on each center. The nine *s* functions were contracted to linear-combination basis functions. This four *s*, three *p*, and one *d* hydrogen basis corresponds to 42 functions of a' symmetry and 18 of a'' symmetry. Using an approximate natural orbital transformation, this basis set was truncated to 30 a' functions and 13 a'' functions. A CCI calculation in this truncated basis involves 14,060 configurations and such a calculation was performed to give the final H_3 energy at each geometry. The GTF calculation yields $E_b = 0.429$ eV, compared to Liu's STO result of 0.424 eV. But the GTF collinear surface is parallel to the STO surface within 0.001 eV for $R_1 < R_2 < 4.0a_0$. For bond angles 150° and 120° the minimum-energy path of the new surface approaches the equilibrium separation of H_2 more rapidly than does the path of Shavitt et al. and this difference is exaggerated compared to the difference at 180°. It appears that the nonlinear portion of the surface of Shavitt et al. is not as accurate as the linear portion. Another indication of this is that their bending force constant is too large by about 15%.

There have been a few calculations on equilateral triangle H_3 (Hirschfelder, 1938; Conroy and Bruner, 1967; Porter et al., 1968; Blustin and Linnett, 1974). Hirschfelder's early calculations were at the minimum-basis set CCI level with unoptimized orbital exponents. He showed that the ground state becomes doubly degenerate and discussed this in terms of the Jahn-Teller effect. He and Coulson (1935) calculated that the energy was higher than the energy for three separated H atoms. Conroy and Bruner (1967), however, found a minimum energy for a distance of about $2.0a_0$ for equilateral H_3 and that the energy there was about 1.8 to 2.0 eV higher than linear geometries with the same nearest-neighbor distances or 2.0 to 2.3 eV higher than the linear saddle point. Porter et al. (1968) obtained qualitatively similar results and obtained $1.965a_0$, 2.2 eV, and 2.4 eV for these same quantities using CCI with the same size basis set as Shavitt et al. (1968) used for other geometries. (For nonsymmetric nonlinear geometries this involves 680 configurations.) Their major interest was the Jahn-Teller effect at this geometry and their work is discussed further in connection with excited states.

In relating the saddle-point properties of a potential-energy surface to experiments on reactive collisions, one must be careful to differentiate between classical barrier height E_b and transition-state theory activation energy at 0°K (which are properties of the surface) and phenomenological threshold energy E_{thr} and Arrhenius activation energy E_a (which are dynamical properties). The relationships of these quantities are discussed elsewhere (Menzinger and Wolfgang, 1969; LeRoy, 1969; Truhlar and Wyatt, 1976). An example of how these distinct concepts have been confused in the literature is given by the following quotation (Bacskay and Linnett 1972): "Experimental estimates of the activation energy, defined as the difference between H_3 and H_2+H, range between 7 and 10 kcal/mole. The kinetic experiments of LeRoy et al. (1968) point to an activation energy of 9.2 kcal/mole whereas the more direct measurements of Kuppermann and White (1966) yield a value 7.6 ± 0.5 kcal/mole." This passage confuses E_b, E_a, and E_{thr}.

Now we return to the semiempirical valence-bond calculations. After the early work no new methods were developed until 1955 when Sato (1955, 1955a, 1955b) introduced a modified version of London's formula containing a new parameter k and a very approximate form of the H_2 triplet curve. He then obtained the Coulomb and exchange integrals by equating the Heitler-London expressions (including overlap) for the ground and triplet states of H_2 to these potential curves. For this purpose the constant k was treated as if it were the square of the orbital overlap integral although the real orbital overlap integral is not a constant but depends on internuclear distance. His modified London formula cannot be derived from valence-bond theory by letting k be the square of the overlap integral, and semiempirical values obtained for k are much smaller than the values of the square of the orbital overlap integral for the distances important along the reaction path. The parameter k must absorb all these inconsistencies plus the inconsistencies that remain from the LEP method (such as equating the Heitler-London expression to the accurate ground-state energy rather than the Heitler-London computed one). However, Sato's method, commonly abbreviated LEPS, had the advantage of leading to a symmetric saddle point for all values of k examined. Sato studied the barrier height as a function of k and suggested $k = 0.18$, which yields an E_b of 0.22 eV, as the "best" value. The Sato procedure was critically analyzed by Weston (1959; see also Weston, 1967). He found that $k = 0.1475$ led to a vibrationally adiabatic barrier height of 0.35 eV, which he deduced from experiments as the energy of activation. (The vibrationally adiabatic barrier height is the transition-state-theory activation energy at 0°K when the reaction coordinate is treated classically and the other degrees of freedom are treated quantum mechanically and it is given in the harmonic approximation by

$$E_0^{\mathrm{VAZC}} = E_b + \tfrac{1}{2}h\nu_s + h\nu_b - \tfrac{1}{2}\hbar\omega_e$$

where the last term is the harmonic approximation to the zero-point energy of H_2.) Weston emphasized the empirical nature of the scheme. The saddle-point properties of the Sato and Weston surfaces for H_3 are given in Table III where they are compared with Liu's accurate values and other semiempirical surfaces to be discussed below.

TABLE III

Properties of Several Semiempirical and Analytic Surfaces with Linear Symmetric Saddle Points

Surface	$R^\ddagger$ (a_0)	E_b (eV)	$\frac{1}{2}h\nu_s$ (eV)	$\frac{1}{2}h\nu_b$ (eV)	$\frac{1}{2}h\nu_a$ (eV)
Sato ($k = 0.18$)	1.73	0.219	0.133	0.054	$0.100i$
Sato ($k = 0.1475$)	1.76	0.358	0.131	0.054	$0.118i$
Sato ($k = 0.144$)	1.75	0.380	0.132	0.055	$0.128i$
Cashion–Herschbach	1.82	0.468	0.133	0.051	$0.152i$
Porter–Karplus (No. 1)	1.70	0.373	0.136	0.059	$0.143i$
Porter–Karplus (No. 2)	1.70	0.398	0.135	0.061	$0.137i$
Porter–Karplus (No. 3)	1.70	0.413	0.135	0.062	$0.130i$
Pedersen–Porter (No. 6)	1.79	0.450	0.133	0.072	$0.138i$
Salomon (No. 4)	1.70	0.373	0.128	0.063	$0.045i$
Salomon (No. 6)	1.71	0.407	0.129	0.062	$0.053i$
Truhlar–Kuppermann	1.765	0.424	0.125	—	$0.091i$
Jones–Rosenfeld	1.74	0.425	0.130	0.070	$0.092i$
Malcome–Lawes	1.85	0.391	0.136	0.056	$0.095i$
Yates–Lester	1.74	0.425	0.128	0.067	$0.104i$
Accurate	1.76	0.425 or 0.420	0.127	0.056	$0.094i$

With the new constant (k) set equal to zero, the Sato method may be reinterpreted as an LEP calculation except with variable ρ (Weston, 1959). It was realized by the early workers that the assumption of constant ρ was not strictly valid. This was reemphasized by Hirschfelder (1941; see also Hirschfelder et al., 1954; Weston, 1959; Yasumori, 1959; Eyring and Eyring, 1963; and Cashion and Herschbach, 1964). The Coulomb fraction, as computed in the Heitler-London-Sugiura treatment of H_2, is near 0.14 at large distance but drops sharply as the distance is decreased. Eyring and Polanyi (1931) performed a calculation using this variable ρ; they obtained a symmetrical basin 0.52 eV above the energy of $H+H_2$. However, Wall et al. (1958) calculated a variable-ρ surface that did not have a basin. It is often stated that the assumption of constant ρ is directly responsible for the existence of a spurious basin in the semiempirical surfaces; unfortunately, the real situation is more complicated. We have already mentioned that constant ρ may or may not lead to a basin depending upon its value and that the first variable-ρ treatments gave a basin. Eyring and Eyring (1963; see also Eyring, 1962) used a distance-dependent ρ equal to an adjustable constant times the Sugiura values. The constant was chosen to be 1.4 to obtain a symmetric basin 0.33 eV above the energy of $H+H_2$ and twin saddle points of height 0.41 eV located about $0.6a_0$ from the basin. This gives a very wide barrier to reaction; thus the energy is still 0.26 eV above $H+H_2$ at a distance $1.7a_0$ from the linear symmetric configuration (compare Table II). Eyring and Eyring claimed that previous transition-state theory calculations (e.g., Weston, 1959) had shown that the Sato barrier is too thin and predicts too much tunneling and that their new surface was in better accord with experiment than any that had been obtained so far. Now we know the true surface has a symmetric saddle point; we will return to the question of the width of the barrier.

A different way of using experimental or theoretical energy curves for H_2 to predict the surface for H_3 is diatomics-in-molecules theory, introduced by Ellison (1963). In this method, matrix elements of the Hamiltonian in a basis of valence-bond configurations are approximated by diatomic potential curves and atomic energies. Using a two-configuration basis and what they considered to be the most accurate available potential energies for ground-state and triplet H_2, Ellison et al. (1963) calculated a barrier of about 0.56 eV [later corrected to 0.57 eV (Ellison, 1964)]. Surprisingly, within their scheme, neglect of overlap changes the calculated energies by less than 4×10^{-5} eV. About the same time Cashion and Herschbach (1964) proposed a modification of the LEP method in which the Coulomb and exchange integrals were evaluated by equating the Heitler-London energy expressions for the ground and triplet states of H_2, neglecting orbital overlap, to what they believed were the most accurate available potential curves for H_2. They pointed out the sensitivity of their results to the value of the then poorly known triplet curve energy at the end-atom-to-end-atom distance of the H_3 saddle point. They obtained a barrier of 0.42 eV [later corrected to 0.47 eV (Cashion and Herschbach, 1964a)]. It was pointed out by Ellison (1964) that at least for the case of linear symmetric configurations the treatments are identical. Actually they are completely identical (Pickup, 1973). Then the difference in results is just the result of the different input potential curves.

Also at about this time, Porter and Karplus (1964) reexamined the whole semiempirical valence-bond scheme and attempted to remove not only the constant-ρ approximation (also removed by Cashion and Herschbach as discussed above) but also the other three most criticized aspects of the method: (i) neglect of overlap integrals, (ii) calculation of single-exchange integrals in H_3 as if they were the same as in H_2 at a given interatomic distance, (iii) neglect of multiple-exchange integrals. The orbital overlap integrals were calculated using a distance-dependent orbital exponent. Rather than use the most accurate available H_2 data they used reasonably accurate but simple fits to the H_2 potential curves. They obtained a barrier of 0.37 eV in their first calculation (No. 1). With a different choice of parameters (No. 2, explained below) they obtained 0.40 eV. If the latter calculation is repeated using the corrected potential curves of Cashion and Herschbach (1964, 1964a), the calculated barrier is lowered to 0.20 eV. If this calculation and the calculation of Cashion and Herschbach are repeated using the now accurately known potential curves (Kolos and Wolniewicz, 1965), the calculated barriers become 0.31 and 0.57 eV, respectively (unpublished calculations).

It is important to distinguish two different types of semiempiricism. One is to use H_2 potentials and valence theory to predict the properties of H_3. This was attempted using the London equation but the extreme assumptions involved prevented this approach from being very fruitful. Thus the parameters of the LEP and Sato methods were adjusted to give what was thought to be the correct barrier height for H_3 with the hope that other features of the surface would then be reasonable. The investigations discussed in the previous two paragraphs raised the hope that such empiricism might not be necessary if one used more accurate potential curves or in addition removed the three other most criticized assumptions of the LEP method. These hopes were vitiated by the extreme sensitivity of the calculated surfaces to the H_2 data and, in the Porter-Karplus method, to the two semiempirical parameters (δ and ϵ) they introduced into the three-center terms needed to remove approximations (ii) and (iii). This indicates that the three-center terms are very important, and that the method is still sensitive to its assumptions even when reasonable efforts are made to remove the most criticized ones. Thus later workers should have abandoned the first type of semiempiricism, that is, they should not have tried to use semiempirical valence-bond theory or diatomics in molecules to "predict" the surface without using kinetic data or accurately known surface features to calibrate the method. This predictive approach has been called the ab initio semiempirical approach. It was abandoned immediately by Porter and Karplus. Thus while the values of δ and ε on their surface No. 1 were obtained by considerations of computed theoretical integral values, they also presented three additional surfaces (Nos. 2 to 4) in which δ and ε were used to alter the form of the semiempirical surface. These surfaces provide an example of what we mean by the second type of semiempiricism. In particular, the values for surface No. 2, which has been used very often for dynamical studies, were obtained by adjusting the vibrationally adiabatic barrier height so it agreed approximately with the Arrhenius activation energy [which Weston (1959) had extracted from the experimental data] while maximizing the nearest-neighbor distance because the semiempirical value was less than the ab initio one of Boys and Shavitt (see Tables I and III). But their surface No. 3 agrees better with Liu's.

The Porter-Karplus method was later reexamined by Pedersen and Porter (1967). They modified the formalism to use H_2^+ potential curves and the Mulliken approximation for removing approximations (ii) and (iii). They also used different approximations to the orbital exponents. Their best surface is given in Table III. Jones and Rosenfeld (1973) and Kung and Anderson (1974) recalibrated the Porter-Karplus method. The former authors used accurate cubic spline fits to the accurate H_2 potential curves and adjusted δ and ε so that the saddle-point properties are as close as possible to the scaled values recommended by Shavitt (1968). Thus they are also close to those for the accurate surface (see Table III). The surface of Kung and Anderson also uses fairly accurate H_2 curves but the parameters were not readjusted and the surface is less accurate.

Salomon (1969) reexamined the question of the width of the barrier. He modified the Cashion-Herschbach procedure to include orbital overlap integrals. These integrals were calculated using a distance-dependent orbital exponent with one adjustable parameter that was varied to obtain a symmetric saddle point and a wide barrier. The two surfaces he judged most accurate on the basis of transition-state theory calculations including tunneling are given in Table III. It is now seen, by comparison of $\frac{1}{2}h\nu_a$ to the last row, that there was some truth in the claim of Eyring and Eyring (1963) and Salomon that all previous semiempirical surfaces had a barrier that was too thin. But Salomon's surfaces overcompensated and produced a barrier that was too thick.

Steiner et al. (1973) have recently extended the diatomics-in-molecules calculation to include ionic configurations. The method was found to be stable with respect to addition of ionic terms only if overlap was neglected; without this assumption they found instabilities due to near linear dependences of the three-electron basis functions. But for H_3 the effect of ionic terms was small and did not remove the sensitivity of the barrier to the triplet curve. More recently Tully and Truesdale (1976) presented a more stable and consistent way to include overlap in the diatomics-in-molecules method.

A simple type of semiempirical scheme decomposes the binding energy of H_3 into a sum of two bonding functions for nearest neighbors and a triplet repulsion term between end atoms. Lipponcott and Liefer (1958) applied this to H_3 and found a barrier of 0.29 eV with attractive basins on either side. Johnston and Parr (1963; see also Johnston 1960, 1966) developed a scheme of this type, called the bond-energy bond-order scheme, which can be used to calculate the minimum-energy path, the energy profile along it, and saddle-point properties but, without new assumptions, not the whole surface. In this method the formation of a new bond "pays for" the breaking of the old bond in such a way that the sum of the bond orders (n_1+n_2) is unity. Pauling's relation between bond length and bond order yields the reaction path, and the relation $E_{\text{bond}}(n)=E_{\text{bond}}(1)n^p$ plus a triplet potential curve yields the energy profile. With no adjustable parameters the original results for the H_3 saddle point were very good (Johnston and Parr, 1963: $E_b=0.43$ eV and $R_1=1.74a_0$) and the minimum-energy path is also good (Truhlar, 1972). Zavitsas (1972) developed an alternative form of this theory for calculating barriers; he obtained $E_b=0.51$ eV. All three calculations involved very approximate triplet curves: an exponential in the first and 0.5 and 0.9 times Sato's triplet in the latter two. If more up-to-date values were used for the H_2 triplet curve or if more up-to-date experimental results are used in the Johnston-Parr calculation to calibrate p, the results are not as good. These methods are just as sensitive to the triplet curve as is the diatomics-in-molecules scheme.

The semiempirical valence-bond model has been used so extensively for H_3 that semiempirical molecular orbital models have been somewhat neglected. An early application of the crude form of Hückel theory to H_3 was not successful since H_3 was predicted to be bound with respect to $H+H_2$ by 0.83 times the bond energy of H_2 (Van Vleck and Sherman, 1935; Pearson, 1948). However, Bradley (1966) applied molecular orbital theory more successfully. He neglected overlap integrals, employed Pariser-Parr-Pople-type approximations (zero differential overlap and inclusion of nearest-neighbor interactions only), and evaluated the non-neglected integrals in terms of H_2 and H_2^+ potential curves. He obtained a linear symmetric barrier with $R_1=1.84a_0$ and a vibrationally adiabatic barrier height of 0.56 eV. Gimarc (1970) and Malcome-Lawes (1975) have applied extended Hückel theory to H_3. The latter adjusted one parameter so that the transition-state theory rate coefficient with no tunneling correction agrees with the result of Schulz and LeRoy (1965) at 423°K, but his barrier is too low (see Table III).

The semiempirical surfaces are usually easily programmed so it is easy to examine properties other than saddle-point height. Porter and Karplus (1964; see also Karplus, 1970) presented contour maps of one of their H_3 surfaces and profiles of the energy along the minimum-energy path for several bond angles. Several other collinear contour maps have been published. Apparently, the only accurately calculated minimum-energy paths that have been published for semiempirical surfaces are those determined in the (R_1, R_2) plane by Silver (1972) for four such surfaces and by Jones and Rosenfeld and Malcome-Lawes for their respective surfaces. Earlier minimum-energy paths for three semiempirical surfaces reported by Shavitt et al. (1968; see also Karplus, 1970) showed kinks. These were apparently due simply to errors in their determinations. A few other energy profiles have also been published (Bradley, 1966; Shavitt et al., 1968; Karplus, 1970; Malcome-Lawes, 1975). Malcome-Lawes's energy profile agrees remarkably well with that for surface No. 2 of Porter and Karplus.

Four analytical surfaces have not yet been mentioned. Russell and Light (1971) fitted the unscaled Shavitt et al. surface in natural collision coordinates and Anderson (1973) fitted it to a form suggested by work on bound triatomics. Anderson's fit had a spurious well 0.09 eV deep, but is worth consideration for fitting if augmented by other terms. Yates and Lester (1974) made an empirical modification of the formula used by Porter and Karplus and adjusted the parameters to fit Liu's collinear surface. They showed that the energy profiles for bent geometries agreed well with the scaled results of Shavitt et al. But Schatz (1975) has obtained a better fit using noncollinear points obtained by private communication from Liu.

Many properties of the surfaces are brought out more clearly when they are replotted in scaled and skewed coordinates that diagonalize the kinetic energy with the same reduced mass in each direction (Glasstone et al., 1941; Shavitt, 1968), in three-dimensional persepctive (Parr and Truhlar, 1971; Truhlar and Kuppermann, 1972), in natural collision coordinates (Jackson and Wyatt, 1973), or using a mapping in which all arrangement channels are represented even-handedly (Kuppermann, 1975; Ling and Kuppermann, 1975; Kuppermann et al., 1976).

There have been a few calculations on the very repulsive part of the potential-energy surface in the region where the atoms are very close. This part of the surface is important for the interpretation of high-energy atom-molecule scattering experiments. The first calculations involved approximations to the three-center integrals. Margeneau (1944) considered a single valence-bond configuration with special approximations designed for small distances. For an isosceles triangle with two sides $1.13a_0$ and one side $0.89a_0$ he calculated an interaction energy of 26 eV. He also considered closer separations for which the calculated interaction energy was even higher. Bauer (1951) obtained a simple spherically symmetric model potential by an approximate first-order perturbation-theory calculation. His potential is repulsive for $R[\mathrm{H}-\mathrm{H}_2(r_e)]$ less than $1.3a_0$ but for larger distances contains an attractive well about 1 eV deep, where $R[\mathrm{H}-\mathrm{H}_2(r_e)]$ is the distance from an H to the center of mass of an H_2 at its equilibrium distance. This well is much too deep and much too close. Aroeste and Jameson (1959) showed that the second valence-bond configuration neglected by Margenau is important. They performed four-configuration valence-bond calculations for perpendicular geometries that gave lower energies than Margeneau's by about a factor of 3 for $0.5a_0 < R[\mathrm{H}-\mathrm{H}_2(r_e)] < 0.9a_0$. Trivedi (1970) evaluated the three-center integrals accurately. He used the two-configuration covalent valence-bond method with a minimum basis set and separately optimized exponents. He evaluated the energy only for isosceles triangles and found an interaction energy even lower than Aroeste and Jameson's. His results are fitted by

$$V = 19.248\ \mathrm{eV} \exp\{-1.804a_0^{-1}R[\mathrm{H}-\mathrm{H}_2(r_e)]\}$$

for $0.5a_0 < R[\mathrm{H}-\mathrm{H}_2(r_e)] < 1.75a_0$. There are no reliable experiments to which these three sets of calculations may be compared. Vanderslice and Mason (1960) considered distances a little larger. They used a method that is very much like the LEP method with $\rho = 0$, but they obtained the exchange integral by approximating the H_2 triplet curve as an exponential for $1.63a_0 < R[\mathrm{H}-\mathrm{H}_2(r_e)] < 4.01a_0$. They obtained $V = 61.5$ eV $\exp\{-1.562a_0^{-1}R[\mathrm{H}-\mathrm{H}_2(r_e)]\}$ for the spherical average of the interaction potential. Recently, two more accurate calculations have been performed. Patch (1973) performed CCI minimum basis set and floating orbital calculations for linear, scalene, and isosceles geometries for $R[\mathrm{H}-\mathrm{H}_2(r_e)]$ in the range 1.0 to $4.0a_0$. Norbeck and Certain (1975; see also Norbeck, Certain, and Tang, 1975) calculated the interaction potential for $2.5a_0 < R[\mathrm{H}-\mathrm{H}_2(r_e)] < 5.0a_0$ for collinear and perpendicular approach. They used a valence-bond formalism with an extended basis set and 100 symmetry-adapted configurations at each geometry. For the collinear geometry at $R[\mathrm{H}-\mathrm{H}_2(r_e)] = 3.0a_0$, they obtained an interaction energy of 0.461 eV whereas the more accurate calculation of Shavitt et al. (1968) yielded 0.402 eV. At larger distances their calculations appear to be more accurate; thus for $R[H-H_2(r_e)]=4.0a_0$, their interaction energy is 0.128 eV compared to 0.113 eV obtained by Shavitt et al. (1968).

There has been no attempt to calculate the electronically nonadiabatic corrections (i.e., the Born-Oppenheimer breakdown terms) for the H_3 potential-energy surface, but these corrections are expected to be small at low energy. For example, they are small for the bound states of H_2 (Orlikowski and Wolniewicz, 1974).

B. Ground Electronic State: Long Range

At large $H-H_2$ separations, the attractive induced dipole-induced dipole dispersion interaction in the ground electronic state has the form

$$E_6(R,\chi)=-\frac{C_6}{R^6}\left[1+\Gamma P_2(\cos\chi)\right]$$

where R is the distance between the atom and the molecule center of mass and χ is the angle between R and the molecular axis ($\chi=0$, π denote collinear configurations). In most studies, the H_2 internuclear separation is regarded as frozen at $1.4a_0$ [see, however, Langhoff et al. (1971) where vibrational averaging is considered]. The anisotropy coefficient Γ determines the energy difference between the linear ($\chi=0$) and perpendicular ($\chi=\pi/2$) configurations:

$$E_6\left(R,\frac{\pi}{2}\right)-E_6(R,0)=\frac{3}{2}\frac{C_6\Gamma}{R^6}$$

which shows that the collinear geometry is preferred if Γ is positive. Also note that the angular average $\langle E_6(R,\chi)\rangle$ equals $-C_6R^{-6}$. Calculations of C_6 and Γ are summarized in Table IV. Margenau (1944) used experimental oscillator strengths and associated transition energies to provide the first estimate of C_6 for the $H-H_2$ interaction. He also provided virtually the only calculation of the long-range induced dipole-induced quadrupole ($-C_8/R^8$) dispersion interaction [the theory is developed in Margenau (1938)]. Mason and Hirschfelder (1957) provided the first information about the anisotropy coefficient. They estimated Γ from $\alpha_\parallel$ and $\alpha_\perp$, the components of the static electric-dipole polarizability of H_2 along and perpendicular to the bond axis, respectively, by the following approximate formula: $\Gamma=(\alpha_\parallel-\alpha_\perp)/(\alpha_\parallel+2\alpha_\perp)$ [Hirschfelder, Curtiss, and Bird (1964), pp. 969–970, 1089]. The available calculations are compared in Table IV; they all indicate that Γ is positive.

TABLE IV

Calculations of Coefficients in the Long-Range $H+H_2$ Interaction Potential Given Approximately by $-C_6R^{-6}[1+\Gamma P_2(\cos\theta)]-C_8R^{-8}$

Reference	C_6 (a.u.)[a]	Γ	C_8 (a.u.)[a]	Method, comments
Margenau (1944)	8.40	—	148	From semiempirical H_2 oscillator strengths
Mason and Hirschfelder (1957)	8.40	0.117	—	C_6 from Margenau; Γ from static polarizabilities for H_2
Dalgarno (1963)	9.20	—	—	From H_2 oscillator strengths forced to satisfy sum rules
Karplus and Kolker (1964)	9.91	0.154	—	From dynamic polarizabilities from uncoupled Hartree-Fock calculations
Dalgarno and Williams (1965)	9.24	—	—	From H_2 oscillator strengths that satisfy seven sum rules
Langhoff and Karplus (1970)	8.57	—	—	From bounds on C_6 established with Padé approximants
Victor and Dalgarno (1970)	8.92	0.104	—	From semiempirical dynamic polarizabilities of H_2
Langhoff, Gordon, and Karplus (1971)	8.57	0.099	—	From bounds on C_6 established with Gaussian quadratures or Padé approximants
	8.95	0.111	—	Same but corrected for H_2 vibration

[a] The atomic unit of energy is the hartree (1 hartree $=27.2116$ eV $=4.35981\times10^{-18}$ J); the atomic unit of length is the bohr (1 bohr $=1a_0=0.529177\times10^{-10}$ m).

In the studies of Dalgarno (1963) and Dalgarno and Williams (1965), oscillator strengths from the ground state of H_2 were modified and extended so that sum rules were satisfied exactly. In the latter case, the oscillator strengths were required to satisfy seven sum rules. [See Langhoff et al. (1971) for other applications of sum rules.]

A different formulation of the dispersion interaction problem was provided by Casimir and Polder (1948). They showed that C_6 can be expressed as an integral over imaginary frequency of the product of the dynamic (frequency-dependent) polarizabilities of the interacting species. The first application to the $H-H_2$ interaction was provided by Karplus and Kolker (1964), who evaluated both C_6 and Γ. The Casimir-Polder formulation has also been applied to the $H-H_2$ interaction by Langhoff and Karplus (1970), Victor and Dalgarno (1970), and Langhoff et al. (1971). Langhoff and Karplus (1970) and Langhoff et al. (1971) have shown how to use bounds on the dynamic polarizabilities in the Casimir-Polder formulas to establish upper and lower bounds on the dispersion coefficients. The values of C_6 and Γ listed in Table IV are not in complete agreement, but the most recent calculations indicate a value of C_6 about 9 a.u. with Γ close to 0.1. There has been no recent work on the higher-order (R^{-8} etc.) interactions.

The shallow van der Waals well in the ground-state potential surface $V(r,R,\chi)$ is an important feature in the determination of cross sections for elastic and rotationally inelastic scattering (Sections III and IV.A) and in the transport properties of partly dissociated H_2 (Section IV.D). Margenau (1944) and Mason and Hirschfelder (1957) attempted to calculate the surface in the vicinity of the well by adding the first-order exchange forces (calculated by approximate valence-bond theory) to the second-order dispersion forces. They obtained well depths of 2 to 3 meV at $R=6$ to $7a_0$. They obtained the result, still believed correct, that the well is deeper for a perpendicular geometry than for a collinear one. Conroy and Bruner (1965, 1967), Michels and Harris (1968), Shavitt et al. (1968), and Blustin and Linnett (1974) all briefly commented on the appearance of shallow wells at large R in their ab initio H_3 potential surfaces, but the basis sets employed were too small to accurately characterize the surface topology near the well minimum. However, the order of magnitude of the well depth can be estimated as 0.001 eV from the calculations of Shavitt et al. (1968). In contrast, the semiempirical Porter-Karplus (1964) surfaces and most other semiempirical surfaces are repulsive at large R. The characteristics of several semiempirical and ab initio surfaces have recently been compared by Norbeck, Certain, and Tang (1975; see also Norbeck and Certain, 1975) over the range $2a_0 < R < 5a_0$ (see Section IV.A). In this region the rotational anisotropy coefficient $V_2(R)$ in the expansion $V(R,\chi)=V_0(R)+V_2(R)P_2(\cos\chi)+\cdots$ (where $r=1.4a_0$) changes rapidly. (Note that for $V_2>0$, the perpendicular approach of H to H_2 is favored). V_2 from Porter-Karplus surface No. 2 is negative at all R and becomes increasingly negative as R decreases, but V_2 from a new ab initio surface calculated by Norbeck et al. (1975) is positive near $R=5a_0$, increases to a maximum near $3.5a_0$, and becomes negative for $R<3.1a_0$.

Because of the difficulty of characterizing the van der Waals well and the long-range potential through ab initio calculations, a number of hybrid potentials have been proposed that smoothly join one set of potential expansion coefficients $\{V_0(R), V_2(R)\}$ at short range to another set at long range. For example, Dalgarno, Henry, and Roberts (1966) joined the Mason-Hirschfelder (1957) potential onto an $E_6(R,\chi)$ long-range attractive tail. Chu and Dalgarno (1975) joined the Porter-Karplus values of $V_0(R)$ and $V_2(R)$ onto the same long-range tail that Dalgarno et al. (1966) employed. (Rotationally inelastic-scattering calculations on both joined potentials are discussed in Section IV.A.) Takayanagi (1957; see also

Takayanagi and Nishimura, 1960) and Tang (1969) also constructed joined potentials. Tang's merges into Porter-Karplus surface No. 2 at small R. This potential was later used in the calculation of transport coefficients (see Section IV.D). In addition, Shui and Appleton (1971) constructed a spherically averaged potential $V_0(R)$ for use in trajectory studies of $\mathrm{H}+\mathrm{H}+\mathrm{H}_2 \rightleftarrows 2\mathrm{H}_2$ recombination. The characteristics of a number of spherically averaged potentials near the well minimum are compared in Table V.

In order to fit the velocity dependence of the total scattering cross section of H on H_2, Stwalley et al. (1969) used several spherically symmetric potentials for which the reduced velocity parameter $v_0 = 2\varepsilon R_{\mathrm{min}}/\hbar$, where ε is the well depth and R_{min} is the position of the minimum, was in the range 1.4 to 2.7 km/sec. The reduced velocity parameters for other proposed $V_0(R)$ potentials are listed in Table V. The potentials used by Stwalley et al. included those of Browning and Fox (1964) and Tang and Karplus (1968). To discuss their measurements of the $\mathrm{D}+\mathrm{H}_2$ total scattering cross section, Gengenbach et al. (1975) introduced a joined potential involving Born exponential repulsion at small R, cubic splines at intermediate R, and $-C_6/R^6 - C_8/R^8$ attraction at long range. Gengenbach et al. also used a number of older semiempirical $\mathrm{H}-\mathrm{H}_2$ spherically averaged potentials to predict $\mathrm{D}+\mathrm{H}_2$ total scattering cross sections. The Lennard-Jones potential of Clifton (1961), the exp-6 potential of Weissman and Mason (1962), the Dalgarno-Henry-Roberts (1966) potential, and the Tang (1969) potential all gave about the same disagreement (in a least-squares sense) with the experimental data. The Khouw et al. (1969) 12-6 potential with parameters fitted from diffusion data predicted cross sections in worse agreement with the scattering data than the previous four potentials. This clearly illustrated that bulk-transport measurements can be fitted by a variety of effective spherical potentials, some of which are not really very accurate.

C. Excited Electronic States

Van Volkenburgh et al. (1973) recently pointed out that, "Since H_3 is the simplest polyatomic molecule but one, several of its electronically excited states should be reasonably well known theoretically. This is by no means the case... ." Ab initio and semiempirical studies of H_3 excited states are summarized in Table VI, which shows that they have been limited to the lower surfaces at or near selected geometries (D_{3h}, C_{2v}, or $D_{\infty h}$) over small ranges of internuclear distances. In the first study of H_3 excited electronic states, Hirschfelder (1938) calculated a correlation diagram that illustrates how the energies of the $\tilde{X}\,{}^2\Sigma_u^+$, ${}^2\Sigma_g^+$, and ${}^4\Sigma_u^+$ states of symmetric linear H_3 change as the system is bent (with the constraint that $R_{ab} = R_{bc}$ for atoms

TABLE V

Van der Waals Well Characteristics in the $H-H_2$ Spherically Averaged Potential[a]

Reference	ε (meV)	R_0 (a_0)	R_{min} (a_0)	v_0 (km/sec)	C_6 (a.u.)	Form of potential,[b] comments
Clifton (1961)	2.78	5.20	5.84	2.61	8.04	12-6; fit to Margenau (1944) calculations
Wise (1961)	3.12	5.39	6.05	3.03	11.24	12-6; fit to Margenau (1944) calculations
Weissman and Mason (1962)	1.44	5.80	6.60	3.02	8.40	exp-6; fit to Margenau (1944) calculations
Browning and Fox (1964)	2.85	5.18	5.81	2.66	8.09	12-6; fit to Margenau's (1944) calculations; used to analyze viscosity data
Dalgarno, Henry, and Roberts (1966)	1.29	6.07	6.84	1.43	9.26	exp-6; fit to Mason-Hirschfelder (1957) potential at small R
Tang and Karplus (1968)	1.29	6.07	6.84	1.43	9.26	Fit to Porter-Karplus (1964) potential at small R and Dalgarno-Henry-Roberts (1966) potential at large R
Tang (1969)	0.46	6.31	7.41	0.55	9.26	
Sancier and Wise (1969)	1.44	6.48	7.37	1.71	16.36	exp-6; parameters adjusted to fit diffusion data
Khouw, Morgan, and Schiff (1969)	7.32	4.39	4.73	5.56	7.70	12-6; parameters adjusted to fit diffusion data
Shui and Appleton (1971)	3.27	5.54	6.43	3.38	—	Morse; used in trajectory studies of $H+H+H_2$ recombination
Cheng and Blackshear (1972)	2.79	4.84	5.43	2.43	5.27	12-6; parameters chosen to fit viscosity data
Gengenbach, Hahn, and Toennies (1975)	2.34	5.94	6.71	2.52	8.80	exp. repulsion/spline/$(-C_6R^{-6}-C_8R^{-8})$; parameters chosen to fit $D+H_2$ total scattering cross section

[a] ε is the well depth and R_{min} (or R_m) is the position of the minimum. At $R=R_0$, $V_0=0$. The reduced radial velocity is $v_0=2(\varepsilon R_{min})/\hbar$.

[b] exp-6 potential: $V_0(R)=\frac{\varepsilon}{1-(6/\alpha)}\left\{\left(\frac{6}{\alpha}\right)e^{\alpha(1-R/R_{min})}-\left(\frac{R_{min}}{R}\right)^6\right\}$; 12-6 potential: $V_0(R)=\varepsilon\left\{\left(\frac{R_{min}}{R}\right)^{12}-2\left(\frac{R_{min}}{R}\right)^6\right\}$.

TABLE VI

Studies of H_3 Excited Electronic States

Reference	Method[a]/basis,[b] if any	Surfaces/geometries studied
Hirschfelder (1938)	VB/ETF: 1*s*	D_{3h} for $2a_0 < R < 3a_0$: ^2E, $^4A_2$, $^2A_2$, $^2A_1$ $D_{\infty h} \rightarrow D_{3h} \rightarrow C_{2v}$ correlation diagram: $^2\Sigma_u^+$, $^2\Sigma_g^+ \rightarrow {}^2E$; $^4\Sigma_u^+ \rightarrow {}^4A_2$
Jameson and Aroeste (1960)	VB/ETF: 1*s* on each center of molecule; 2*s*, 2*p* on atom	C_{2v} only: $^2A_1$, $^2B_2 \rightarrow H_2(X\,^1\Sigma_g^+) + H(n=2)$
Ellison, Huff, and Patel (1963)	DIM/1*s*	Table of energies for two lowest $^2\Sigma$ states, linear configurations only
Matsen (1964)	Spin-free quantum chemistry/discussion only	$D_{\infty h} \rightarrow D_{3h} \rightarrow C_{2v}$ correlation: $^2\Sigma_u^+ \rightarrow {}^2E \rightarrow {}^2A_1$; $^2\Sigma_g^+ \rightarrow {}^2E \rightarrow {}^2B_2$
Smirnov (1964)	VB/qualitative discussion only	Discussion of process $H_3(^2E;\, D_{3h}) \rightarrow \begin{cases} H + H_2(^1\Sigma_g^+) \\ H + H_2(^3\Sigma_g^+) \rightarrow H + H + H \end{cases}$
Porter, Stevens, and Karplus (1968)	Semiempirical VB[c] and ab initio/ETF: two *s*, one *pσ*, one *pπ*	$D_{3h}(^2E)$ surfaces near intersection in normal-mode space $D_{\infty h} \rightarrow D_{3h} \rightarrow C_{2v}$ correlation for two lowest surfaces
Frenkel (1970)	MO and CI/GTF: four *s*, two *pσ*, two *pπ* on each center of molecule; four *s* on atom	D_{3h} for $1a_0 < R < 3a_0$: $X\,^2E$, $^2A_1$, ^2E Symmetric $D_{\infty h}$ for $2a_0 < R < 6a_0$: $^2\Sigma_u^+$, $^2\Sigma_g^+$, $^2\Sigma_g^+$, $^2\Pi_u^+$ $D_{\infty h} \rightarrow D_{3h} \rightarrow C_{2v}$ correlation for: $^2\Sigma_u^+$, $^2\Sigma_g^+ \rightarrow {}^2E \rightarrow {}^2A_1$, $^2B_2$ and $H_2(^1\Sigma_g^+) + H(2p)\,^2\Pi_u \rightarrow {}^2A_1$
Tully (unpublished), quoted in Van Volkenburgh *et al.* (1973)	DIM/not given	Attractive long-range interaction for $H(n=2) + H_2(X\,^1\Sigma_g^+)$; $H_2(b\,^3\Sigma_g^+) + H$; $H_2^+(B\,^2\Sigma_u^+) + H$

[a] Abbreviations: VB, valence bond; DIM, diatomics-in-molecules; MO, molecular orbital; CI, configuration-interaction.

[b] On each center (except as indicated otherwise); ETF, exponential-type functions; GTF, Gaussian-type functions.

[c] Method of Porter and Karplus (1964).

labeled *a-b-c*). In this correlation, the $\tilde{X}\,^2\Sigma_u^+$ and $^2\Sigma_g^+$ states of the linear $D_{\infty h}$ geometry form the degenerate ^2E level of the equilateral triangle D_{3h} geometry while the $^4\Sigma_u^+$ excited state correlates with the $^4A_2$ state in D_{3h}. The variation of the energy of these states (and excited $^2A_2$ and $^2A_1$ states as well) was also studied as a function of internuclear distance for D_{3h} geometries. Correlation diagrams for the $D_{\infty h}\rightarrow C_{2v}\rightarrow D_{3h}$ deformation have also been discussed by Smirnov (1964), Matsen (1964), Porter, Stevens, and Karplus (1968), Frenkel (1970), and Van Volkenburgh et al. (1973). Only the two lowest states, which originate as $\tilde{X}\,^2\Sigma_u^+$ and $^2\Sigma_g^+$ in $D_{\infty h}$, were considered by Matsen (1964) and Porter et al. (1968).

The topology of the intersection between the two lowest electronic surfaces at the D_{3h} geometry depends upon what coordinates are used. For example, if the *a-b-c* angle is fixed at 60° and the two surfaces are plotted as functions of R_{ab} and R_{bc}, then intersection occurs along the diagonal "ridge" where $R_{ab}=R_{bc}$ (see Porter and Karplus, 1964 and Porter et al., 1968). However, if energy contours are plotted in the (q_1, q_2) normal-mode space for the equilateral triangular geometry (where q_1 and q_2 correspond to asymmetric stretch and bending deformations), then the lower and upper surfaces join at the vertices of two cones (the vertex for the lower cone points "up" at the descending cone of the upper surface). Pictures of both surfaces near the intersection were shown by Porter et al. (1964), while Matsen (1964) displayed only the lower cone. [A perspective picture of the intersection in natural collision coordinates was displayed by Jackson and Wyatt (1973).] The ridge or conical intersection between the two lowest H_3 surfaces in the D_{3h} geometry gives rise to Jahn-Teller instability (all nonlinear nuclear configurations for an electronically degenerate state of a polyatomic molecule are unstable), which is relieved as the linear geometry is approached and the degeneracy is removed.

In addition to the two lowest surfaces that intersect as the ^2E state with D_{3h} geometry, Frenkel (1970) calculated a correlation diagram for several states ($^2B_2$, $^2A_1$ for C_{2v} geometries) that correlate with $H_2(X\,^1\Sigma_g^+)+H\,(n=2)$. It was found that several such states ($^2A_1$ and ^2E) possess deep minima near the D_{3h} geometry. Jameson and Aroeste (1960) also calculated a C_{2v} correlation diagram for states that dissociate to $H_2(X\,^1\Sigma_g^+)+H\,(n=2)$. In unpublished studies, J. C. Tully (quoted in Van Volkenburgh et al., 1973) found that excited states correlating with $H\,(n=2)+H_2(X\,^1\Sigma_g^+)$, $H+H_2(b\,^3\Sigma_g^+)$ or $H_2^+(B\,^2\Sigma_u^+)+H$ are attractive at long range. A number of features of the H_3 excited-state correlation diagram for doublet states have been discussed by Van Volkenburgh et al. (1973) (also see Section IV.C).

III. ELASTIC AND TOTAL SCATTERING CROSS SECTIONS

The final process competing with reaction, dissociation, and other inelastic scattering processes in $H+H_2$ collisions is elastic scattering. In fact, elastic scattering often dominates the integral total scattering cross section for $H+H_2$, where "integral" refers to the integration of the differential cross section over all scattering angles and "total" refers to a sum over all processes. Elastic scattering dominates when the large-impact-parameter small-angle scattering dominates the total scattering cross section and is itself mainly elastic scattering. Then measurements of the elastic scattering and the total scattering provide similar information and can be used to learn about the interaction potential. In addition, the differential elastic scattering cross section is needed to interpret other experiments such as the hot-atom experiments discussed elsewhere (Truhlar and Wyatt, 1976). For $H+H_2$ there have been four kinds of experiment on elastic or total scattering: (1) high-energy measurements of H-beam attenuation by H_2 gas, which yield the magnitude of the incomplete total scattering cross section $S(\theta_0, E_{rel})$ as a function of relative translational energy E_{rel} where "incomplete" means the integral over scattering angles θ excludes the region $\theta < \theta_0$; (2) low-energy measurements of H-beam attenuation by H_2 gas, which yield the relative magnitude of the integral total scattering cross section $S(E_{rel})$ as a function of E_{rel}; (3) a few low-energy measurements of the magnitude of $S(E_{rel})$ at selected E_{rel}; (4) low-energy measurements of the relative magnitude of the differential nonreactive scattering cross section $d\sigma_{nr}/d\theta\,(E_{rel})$ as a function of θ.

The first experiments were at high energy because it is easier to produce a beam of H atoms at very high energies. The beams involved in the high-energy experiments had laboratory energies of 196 to 7000 eV. Thus E_{rel} is 131 to 4667 eV. This is high enough (the de Broglie wavelength is of the order of $10^{-2}a_0$) and θ_0 should be large enough (0.1° to a few degrees in relative coordinates) for a classical description of the scattering and for the measurement to be sensitive to the repulsive region of the potential and not at all to the long-range van der Waals' attraction. But θ_0 is also small enough that the interaction energy during a collision that scatters at angle θ_0 is only a small fraction of E_{rel} and is of the order of magnitude of 1 eV.

The first high-energy experiments on $H+H_2$ were by Amdur and Pearlman (1940; Amdur, 1943, 1949) and were repeated by Amdur et al. (1950). More recently, high-energy experiments on $H+H_2$ were reported by Belyaev and Leonas (1967), whose results disagree with those of Amdur and co-workers. Using the same techniques, Belyaev and Leonas (1967) also reported results for other systems including $He+H_2$. A disadvantage of the small value of θ_0 used in these experiments is that the results are sensitive to the analysis of the data in terms of an effective angular aperture, which depends on beam size, length of the scattering chamber over which collisions occur, and detector aperture. Jordan and Amdur (1967) pointed out that the apparatuses used by Amdur and co-workers before the 1950s were primitive and that as effects such as beam-detector geometry and intensity distribution in the beam were better understood the apparatuses were improved and so was the accuracy of the experimental results. They also pointed out that it is necessary to measure the diameter of the intensity distribution of the beam because the results are very sensitive to the ratio of beam and detector radii when this is near unity. They corrected this error in their He-He experiments and resolved a longstanding discrepancy between theory and experiment for the He-He short-range interaction potential. It is interesting that a similar longstanding discrepance existed between theory and the experiments of Amdur and co-workers for the short-range interaction in $H+H_2$ but it was overshadowed in the published discussions by the He-He controversy, presumably at least in part because the theoretical calculations were easier for He-He. Many suggestions, such as breakdown of the Born-Oppenheimer adiabaticity approximation, were considered and rejected in an attempt to resolve this discrepancy. Amdur and co-workers continued to perform new experiments and, when comparison was possible, all their results from 1967 and after were in reasonably good agreement with the results that have been reported by Leonas and co-workers. This includes studies on $He-H_2$ (Amdur and Smith, 1968). The interaction potential deduced from these experiments agrees with that obtained by Belyaev and Leonas within 55%. Thus is is reasonable for $H+H_2$ to reject the early results of Amdur and co-workers and to accept as essentially correct the experimental results of Belyaev and Leonas.

For most cases (usually atom-atom scattering) studied by Belyaev and Leonas, a log-log plot of $S(\theta_0, E_{rel})$ versus E_{rel} was linear. But for $H+H_2$ this was not the case. They attributed this anomalous energy dependence to the pronounced nonsphericity in the interaction potential and possibly to electronic nonadiabaticity at E_{rel} of 2.4 keV. Thus they analyzed only the lowest energy part of their curve in terms of an effective spherical interaction potential. For $1.89a_0 < R[H\text{-}H_2(R_e)] < 2.34a_0$, they obtained for this potential

$$V = 12.8 \text{ eV } a_0^{4.15}/R^{4.15}$$

For $R = 2.0a_0$ this is 0.72 eV.

Wartell and Cross (1971) have concluded that if electronic excitation and dissociation do not occur, high-energy scattering measurements may be interpreted in terms of a spherically symmetric potential and this potential is the average of the true potential over orientations evaluated at the equilibrium internuclear separation of the target. Wartell and Cross also added the proviso that the anisotropy and vibrational dependence of the potential must not be too high. Since $H+H_2$ is reactive, their conclusion is not necessarily applicable to $H+H_2$. For $H+H_2$, elastic scattering may not dominate rotationally and vibrationally inelastic scattering at a few hundred eV at the angles involved in the Amdur-type measurements. Nevertheless, it is interesting to attempt to compare the derived potential to theoretical calculations of the spherically averaged potential. The calculation of Mason and Vanderslice (1958) yields 2.70 eV for the spherical average of the potential at $2.0a_0$. The large difference from experiment is not surprising in view of the crudeness of the theoretical method (see above). The spherical average of Porter-Karplus surface No. 2 at $2.0a_0$ is 1.13 eV (Tang and Karplus, 1968), in better agreement with the experiment. The spherical averages of the potentials of Yates and Lester (discussed above) and Gengenbach et al. (discussed below) are more repulsive than the spherical average of Porter and Karplus's surface No. 2 (see comparison in Choi and Tang, 1975a).

Because of the Heisenberg uncertainty principle, the elastic differential cross section is flat for θ less than a small angle that is inversely proportional to velocity. Thus at low energies θ_0 can be made small compared to this angle and the complete integral total scattering cross section can be measured. The first such measurement was made by Harrison (1962). He used a thermal H beam and a mass spectrometer detector. The mean relative velocity of these experiments corresponds to E_{rel} in the range 0.20 to 0.29 eV. In this range Harrison found $S(E_{\mathrm{rel}})$ constant within experimental error and equal to 196 a_0^2. Fluendy et al. (1967) used an H beam that was velocity selected in an inhomogeneous magnetic field and for detection they used a Pt bolometer. They measured only the relative cross section and found an $E_{\mathrm{rel}}^{-0.09}$ dependence over the energy range 0.04 to 0.39 eV. Since $S(E_{\mathrm{rel}})$ is essentially a measure of the range over which the interaction is strong enough that the classical deflection of the particle is greater than its quantal uncertainty, they and all subsequent workers have assumed that is is reasonable to interpret $S(E_{\mathrm{rel}})$ in terms of an effective spherical interaction potential $V(R)$. The dependence measured for $S(E_{\mathrm{rel}})$ is weaker than the $E_{\mathrm{rel}}^{-0.20}$ expected for scattering from an R^{-6} potential, which indicates that the van der Waals' attraction is so weak that even at the lowest energy the scattering is caused mainly by the shorterrange repulsive forces. In this way one obtains a bound $\varepsilon R_m \lesssim 0.024$ eV a_0 where ε is the well depth and R_m the H to H_2 distance at the minimum of the well. Using a modified apparatus, Stwalley et al. (1969) remeasured the dependence of $S(E_{rel})$ on E_{rel} in the range 0.19 to 1.0 eV. They concluded the previous measurements for $E_{rel}<0.08$ eV were unreliable. The data were not sufficient to determine a potential. But the two recent experiments described next, when combined, have been used to determine a $V(R)$ although its uniqueness and its precise meaning have not been established. Bauer et al. (1975) measured the E_{rel} dependence of $S(E_{rel})$ for the range 0.007 to 0.93 eV for $H+D_2$ and 0.007 to 0.63 eV for $H+H_2$. Their cross sections are in good agreement with those of Stwalley et al. (1969) in the region of overlap. By comparing to results calculated for various central potentials, they obtained εR_m equal to 0.016 eV a_0 from the $H+D_2$ data and 0.020 eV a_0 from the $H+H_2$ data. The difference is within the uncertainty of the determination. They compared this to a value of 0.016 eV a_0 obtained from semiempirical combining rules used for analyzing data on other systems. Gengenbach et al. (1975) measured the absolute value of $S(E_{rel})$ for $D+H_2$ at E_{rel} equals 0.31 eV and 0.48 eV with estimated accuracy of 1.5%. They obtained $142a_0^2$ at both energies. They used these results to normalize the data of Bauer et al. and used the normalized data to obtain a multiparameter $V(R)$. At $2.0a_0$, their potential is 2.18 eV but their experiment probably is not too sensitive to R values this small. Their potential has εR_m equal to 0.014 eV a_0 with $\varepsilon=0.0023$ eV and $R_m=5.93a_0$. They compare it to many of the available theoretical potentials for distances greater than about $2\frac{1}{2}a_0$. More recently, Toennies, Welz, and Wolf (unpublished, see Welz, 1976) have measured the integral cross section for $H+H_2$ down to E_{rel} equals about 0.001 eV. Analysis of this experiment yields $\varepsilon=0.0026$ eV and $R_m=6.56$ a_0.

The differential cross section for nonreactive scattering has been measured by Fite and Brackman (1964, 1965) and Geddes et al. (1972) using thermal beams. The second measurement makes the first one obsolete. The differential cross section is forward peaked and drops by a factor of about 20 from 10° to 45° then flattens out. These measurements were not in absolute units and were therefore normalized to the measurement of Harrison (1962) but they have now been renormalized by Gengenbach et al. (1975). The differential cross section has not yet been measured with velocity-selected beams.

There have not been many calculations of the elastic scattering. We consider first the thermal and low-energy range. Almost all published calculations (Tang and Karplus, 1968; Stwalley et al., 1969; Gengenbach et al., 1975) are based on spherically symmetric approximations to the potential. One interesting result is that Gengenbach et al. (1975) showed that their multiparameter potential, obtained from analyzing integral total cross sections, yields a differential cross section for nonreactive scattering in good agreement with the experiment of Geddes et al. (1972). McCann and Flannery (1975, 1975a; see also Flannery and McCann, 1975) and Schatz and Kuppermann (1976) have peformed distinguishable-atom elastic scattering calculations that do include the anisotropy of the potential. McCann and Flannery used both a "multichannel semiclassical orbital treatment" and a multistate eikonal treatment for their calculations. The anisotropy seems to lower the pure elastic differential cross section at large angles. Schatz and Kuppermann calculated the differential and integral elastic scattering cross sections at $E_{rel}=0.70$ eV using potential energy surface No. 2 of Porter and Karplus (1964). Their calculated integral total cross section ($221a_0^2$) is considerably larger than experiment because of the inaccuracy of the potential surface so the results cannot be compared quantitatively to experiment. But they tested the assumption of a spherically symmetric potential by comparing their results to a calculation involving the spherical average of the potential. They found that the integral total cross section was affected only 0.1% by the anisotropy and that for center-of-mass scattering angles θ less than 30° the elastic differential and total differential cross sections were both essentially identical to that computed with the spherical approximation. Schatz and Kuppermann also found that the effect of particle indistinquishability on the elastic differential cross section was small (less than 10% for $30° < \theta < 90°$).

Ioup and Russek (1973) performed some calculations for energies in the 1 to 10 keV range. They are discussed in Section IV.A.

IV. INELASTIC SCATTERING CROSS SECTIONS AND TRANSPORT PROPERTIES

A. Rotational Energy Transfer

There are no experimental measurements of cross sections for rotationally inelastic nonreactive scattering of $H+H_2$, but there are several quantum-mechanical calculations for this scattering process in the ground electronic state. These calculations are described in this section. An earlier discussion was given by Takayanagi (1973).

For rotational excitation it is convenient to represent the interaction potential as an expansion in Legendre polynomials as

$$V(r,R,\chi)=\sum_{\lambda=0,2,\ldots} v_\lambda(r,R)P_\lambda(\cos\chi)$$

where r is the H_2 internuclear separation, $\mathbf{R}$ is a vector (of magnitude R) from the molecular center of mass to the atom, and χ is the angle between the internuclear axis and $\mathbf{R}$. The coefficients $v_\lambda(r,R)$ can be calculated by expanding one of the potential functions $V(r,R,\chi)$ discussed in Section II or they may be approximated directly. The interaction potential is thus specified by the set $\{v_\lambda(r,R), \lambda=0,2,\ldots\}$, and several such sets have been used for dynamical calculations. Cross sections for rotational inelastic transitions ($j\to j\pm 2, j\pm 4\cdots$) have been shown in these studies to depend primarily upon the first rotational anisotropy term, $v_2(r,R)$, and upon the spherical term $v_0(r,R)$, which may serve to "shield" $v_2(r,R)$ at certain values of R. Norbeck et al. (1975) have recently compared the $v_2(r_e,R)$ anisotropy coefficients on several H_3 surfaces; they also presented results of a new ab initio calculation of $v_2(r_e,R)$. In most scattering calculations the rigid-rotor approximation has been used; that is, r was set equal to r_e (the H_2 equilibrium distance) in both the $v_0(r,R)$ and $v_2(r,R)$ coefficients so they become functions $v_\lambda(R)$ of R alone. An examination of the breakdown of this approximation has been presented recently by Wolken et al. (1972). Before proceeding to results for $H+H_2$, we note that Secrest (1973) has presented an extensive review of the theory of inelastic energy transfer.

The first approximate calculations of cross sections for $H+H_2$ rotational inelastic processes were presented by Takayanagi (1957). He used the distorted-wave formalism to study the $j=0\to j'=2$ process. An approximate fit [$v_0(R)$ approximated as a shallow Morse curve and $v_2(R)$ as an exponential repulsive term] to the early Margenau (1944) potential was used. In order to simplify the calculations, the modified-wave-number approximation was used; this involves replacing the transition probability for nonzero orbital angular momentum (l) at relative translational energy E_{rel} by the s wave ($l=0$) probability evaluated at a modified (lower) energy $\bar{E}_{\mathrm{rel}}=E_{\mathrm{rel}}-l(l+1)\hbar^2/2\mu R_0^2$, where R_0 is at (or near) the classical turning point in the relative motion. These calculations were then extended (within the modified-wave-number–distorted-wave framework) by Takayanagi and Nishimura (1960) to include transitions out of initial rotor states $j=2$, 4, and 6. Thermal rate coefficients for temperatures up to 5000°K were then calculated.

Choi and Tang (1975) recently presented extensive calculations of $H-H_2$ rotational inelastic processes on three different model potential surfaces for translational energies in the 0.05 to 0.25 eV range. They compared their results with a number of earlier calculations, both approximate and accurate, that employed these potentials. We first briefly discuss the different potentials with the notation of Choi and Tang; then we compare the scattering results.

(a) DHR potential. Dalgarno, Henry, and Roberts (1966) defined a model $H+H_2$ potential that smoothly joined the short-range (exponential repulsion) Mason-Hirschfelder (1957) potential to a long-range R^{-6} attractive tail; the long-range component of the $v_0(R)$ term was based upon Dalgarno and Williams' (1965) study, and the long-range part of $v_2(R)$ was computed from static electric polarizabilities (Hirschfelder et al., 1954). In contrast to the potentials considered below, $v_2(R)>0$ for all R in the DHR model; that is, the perpendicular approach of H to H_2 is favored over the collinear one for fixed r and R.

(b) PK potential. This is calculated from surface No. 2 of Porter and Karplus (1964). The resulting spherical potential $v_0(R)$ is considerably softer than the DHR spherical term. Also, the PK anisotropy term is negative at moderate to large R, meaning that the collinear approach of H to H_2 is preferred.

(c) TANG potential. Tang (1969) defined a potential [containing $v_0(R)$ and $v_2(R)$ terms] by smoothly joining the Porter-Karplus surface No. 2 at small R onto the DHR potential at large R. In this potential, $v_0(R)$ has a small van der Waals well at large R (unlike the spherical average of the PK surface). Also, $v_2(R)$ in the TANG potential contains a negative region at moderate R and a positive region for $R>3.6a_0$. In the negative $v_2(R)$ region, the collinear geometry is preferred. Shavitt (private communication) has emphasized that a potential which favors the perpendicular over collinear approach for fixed r and R might still favor the collinear approach over a bent approach at fixed R_1 and R_2. Thus a detailed comparison is necessary to determine how calculations at fixed R_1 and R_2 compare with the Legendre expansions discussed here. However, Norbeck et al. (1975) have shown that the sign change of the TANG potential is qualitatively consistent with the diatomics-in-molecules potential of Steiner et al. (1973), with a potential obtained by combining Liu's (1973) collinear calculation and the spherically symmetric component determined by fitting beam measurements (Gengenbach et al. 1975), and with their own ab initio valence-bond calculations for two different basis set sizes.

In addition to the potentials discussed above, other Legendre-expanded potentials have been proposed for $H+H_2$ at various times. Thus, for example, Tang and Karplus (1968) considered not only the Legendre expansion for the $H+H_2$ potential with the H_2 distance fixed but also the spherically symmetric effective potential obtained under the assumption that the molecule adiabatically follows the incoming atom. They also considered a modified version of this adiabatic potential that includes a long-range attractive term. Of course, such spherically symmetric potentials do not lead to rotational excitation. Micha (1969) has used a different adiabatic approximation to obtain an effective potential that is nonspherical and complex (i.e., it has a negative imaginary component). Micha's starting point was a Cashion-Herschbach-like potential; his final potential has apparently not been used for scattering calculations. The TANG potential is not the only attempt to match the Porter-Karplus surface No. 2 at short range to a long-range attractive potential. An alternative version of such a potential has been presented by Wolken et al. (1972). The hybrid potential of Wolken et al. just consists of joining the PK values of $v_0(R)$ and $v_2(R)$ at small R to the DHR values at the positions [$R=4.6a_0$ for $v_0(R)$ and $R=7.0a_0$ for $v_2(R)$] where these curves cross. Thus the major difference between the hybrid potential and the PK potential is in $v_0(R)$. Although the resulting potential has cusps at the connection points, they do not directly affect the scattering. The hybrid potential of Wolken et al. will be abbreviated the WMK hybrid potential. Another attempt to make an analytic Legendre-expanded surface that is accurate at both small and large R was made by Ioup and Russek (1973); see below.

We first consider scattering calculations using the DHR potential. Dalgarno et al. (1966) used this potential in distorted-wave Born approximation (DWBA) calculations for the $j=0\rightarrow j'=2$, $2\rightarrow 4$, and $1\rightarrow 3$ transitions in $H+H_2$ collisions, and in studies of the $0\rightarrow 2$ transition in $H+D_2$. Differential cross sections, integral cross sections, and rate coefficients (up to 5000°K) were computed. In a later study, Allison and Dalgarno (1967) studied the 0→2 rotational transition in the close-coupling (CC) formulation. For translational energies up to 0.30 eV, the DWBA results were slightly larger than the CC cross sections. In their recent close-coupling studies, Choi and Tang (1975) obtained good agreement with the Allison-Dalgarno results for this potential.

We now turn to several calculations of rotational inelastic cross sections that employed the TANG potential. Tang (1969) first reported a series of DWBA calculations, then Hayes et al. (1971) reported CC results; they also compared their results with those of Tang. Integral cross sections for the 0→2 process agreed well with Tang's DWBA results; differential cross sections also agreed well, with strong forward peaking predicted in both calculations. Choi and Tang (1975) also obtained CC results for this potential; excellent agreement was obtained with the earlier results of Hayes et al.

Calculations of rotational inelastic processes on the PK potential include the CC results of Wolken et al. (1972), Choi and Tang (1975), and Schatz and Kuppermann (1976). Unlike all the other workers, Wolken et al. (1972) and Schatz and Kuppermann did not make the rigid rotor assumption. Integral cross sections for all three calculations are in good agreement, although many oscillations reported by Wolken et al. in the 0→2 differential cross section (particularly for scattering angles $\theta \lesssim 90°$) were not reproduced in the other calculations. Schatz (private communication) has compared the unpublished phases of his and Kuppermann's scattering matrix elements to the published ones of Wolken et al. There is good agreement for the detailed channel-to-channel 0→2 probabilities as a function of total angular momentum J and for $l=J\pm2$ there is good agreement for the phases. But for $l=J$ the phases differ by π. Thus it seems likely that these oscillations are spurious and are due to phase errors in the scattering matrix elements of Wolken et al. For both the PK and DHR potentials, the low-energy (relative translational energy $E_{\text{rel}}\lesssim0.5$ eV) 0→2 differential cross section is generally backpeaked with very smooth behavior in the backward direction (for $\theta\gtrsim90°$); the TANG potential predicts forward peaking at similar energies. In the calculations of Choi and Tang and of Wolken et al. the effect of higher anisotropy coefficients $v_\lambda(R)$ ($\lambda>2$) was demonstrated to be very small, even for the 0→4 transition. In contrast to the other calculations mentioned so far, Schatz and Kuppermann (1976) included closed vibrational channels and allowed the anisotropy terms to have explicit r dependence (as well as R dependence) to produce vibrational coupling. However, it is interesting to note that the Wolken et al. calculations, which employed a single vibrational channel in their CC expansion, predicted 0→2 integral cross sections in good agreement with that of Schatz et al. Thus for low-energy integral cross sections for 0→2 rotational excitation on this surface, closed vibrational channels do not seem very significant (but this comment is not true for reactive scattering). Wolken et al. found that the rigid rotor approximation was unsatisfactory; it led to partial (fixed total angular momentum) integral cross sections as much as 25% less than the fully vibrationally averaged potential. The calculations by Schatz et al. allowed for simultaneous reactive and nonreactive $j\to j'$ excitation, so that antisymmetrized scattering amplitudes and cross sections were constructed to allow for interference between the direct and reactive amplitudes. The antisymmetrized 0→2 differential cross section has symmetry oscillations mostly confined to low angles, but the amplitude of the oscillations becomes larger as the relative translational energy increases from 0.5 to 0.7 eV. [Antisymmetrized cross sections had been computed previously by Saxon and Light (1972) and Shatz and Kuppermann (1976a) for coplanar $H+H_2$ scattering. In addition, antisymmetrization was explicitly included by Wolken and Karplus (1974) in their formulation of the H_3 reactive scattering problem. Their results for the 0→2 transition probability, when compared with purely nonreactive (Wolken et al., 1972), clearly show the effect of reaction at higher energies.]

Cross sections for 0→2 excitation differ greatly on these three potentials. Above threshold, the ordering is $\sigma_{02}(\text{DHR})\gg\sigma_{02}(\text{PK})>\sigma_{02}(\text{TANG})$. Choi and Tang (1975) have qualitatively discussed why [in terms of the range and hardness of $v_0(R)$ and the sign and shape of $v_2(R)$] the three potentials are expected to produce such different integral and differential cross sections. Wolken et al. (1972) found that their hybrid potential led to significantly more rotational excitation than the unperturbed PK potential at $E=0.1$ eV, although the results were similar at $E=0.25$ eV. This also shows that $v_0(R)$ is important for the magnitude of σ_{02}.

Choi and Tang (1975) also compared DWBA and CC calculations on these surfaces; the DWBA results were generally quite favorable at low energies, and they were obtained with about 1% of the computer time required for full CC calculations.

As the total energy increases, the number of rotational channels required in a quantum close-coupling study increases very rapidly. For this reason, channel-decoupling methods have recently been employed to decrease the number of coupled equations to be solved. Chu and Dalgarno (1975) employed the effective-potential method (Rabitz, 1972; Zarur and Rabitz, 1973), which eliminates dependence of the potential on m_j quantum numbers for a space-fixed z-axis. They used the WMK hybrid potential. After testing the effective close-coupling method at a total energy E of 1.0 eV, they computed elastic and inelastic cross sections for total energies up to 1.5 eV. McGuire and Kruger (1975) used a different decoupling method, the body-fixed centrifugal decoupling approximation, which is based on neglect of coupling between different components of total angular momentum along the z-axis of a coordinate system that rotates with the three-body system (Pack, 1974; McGuire and Kouri, 1974). They used a spherical potential that was estimated in recent scattering experiments (Gengenbach et al., 1975) along with the $v_2(R)$ term of the PK potential. This will be called the MK potential. The $0\to2$ inelastic cross sections are lower than the results of Chu and Dalgarno (who employed a different potential). The $0\to2$ differential cross section gradually shifted to the forward direction as E increased from 0.5 to 1.5 eV. At each energy, it was observed that as the amount of rotational energy transferred in the $j=0\to j'$ collision increased, the differential cross section was more back-peaked. An information-theory analysis of the McGuire and Kruger $0\to2$ cross section for $H+H_2$ and $D+H_2$ has been presented (Levine et al., 1976).

Most recently, Choi and Tang (1976) performed CC and DWBA calculations at $E=0.5$ eV for the WMK hybrid potential, for the MK potential, and for a potential (called potential I) that consists of the $v_0(R)$ of Gengenbach et al. (1975) and the $v_2(R)$ of Norbeck et al. (1975). For the WMK hybrid potential their CC results for the integral cross sections were in good agreement with effective close-coupling results of Chu and

Dalgarno for low j but there were very large errors at high j. DWBA results were slightly in error (by up to 26%) at low j but were more accurate for $\Delta j = 2$ transitions at high j. The effective close-coupling method did not predict the differential cross section very well but the DWBA did. The CC calculations for the MK potential were compared with the calculations of McGuire and Kruger (1975). The comparison showed that the body-fixed centrifugal decoupling approximation and the DWBA are much better than the effective close-coupling approximation for the $0 \to 2$ transition. However, the body-fixed centrifugal decoupling approximation also predicted the $0 \to 4$ and $0 \to 6$ integral within 24% but the DWBA is not useful for $\Delta j > 2$. Both approximations were fairly good for the differential cross section for $\theta > 10°$.

The integral cross sections obtained by Choi and Tang (1976) by converged CC calculations for potential I were over an order of magnitude smaller than those obtained for the other potentials for the $0 \to 2$ transition and were about 2-to-3 orders of magnitude smaller than those obtained with the other potentials for the $0 \to 4$ and $0 \to 6$ transitions. The differential cross sections for potential I, however, had very similar shape to those for the TANG potential. Hopefully, the question of which of these potentials, if any, is qualitatively correct will be answered when the calculations of Siegbahn and Liu become available.

The WMK hybrid potential was employed by McCann and Flannery (1975, 1975a; Flannery and McCann, 1975) in a "multistate semiclassical orbital treatment" (this is sometimes called the classical path method) of $H + H_2$ rotational inelasticity over the total energy range 0.5 to 1.5 eV. This time-dependent formulation treated translational motion classically, but allowed coupling between this motion and the quantum rotational states of H_2 through an "optical potential." Integral cross sections agreed well with the results of Chu and Dalgarno. The semiclassical differential cross sections averaged out quantum oscillations for $\theta > 90°$. McCann and Flannery (1975a) also considered the use of the Rabitz-Zarur effective potential formalism in conjunction with their multistate orbital treatment.

In an approximate study based upon the (high-energy) Born approximation, Ioup and Russek (1973) computed integral and differential cross sections for several nonreactive pure rotational and vibrational-rotational transitions for energies between 1 and 10 keV. They derived analytic formulas for differential and integral cross sections in terms of a parametrized potential. For $H + H_2$ calculations, they employed the ab initio surface of Shavitt et al. (1968) to adjust their parameters. In the Born-approximation calculations, the target molecule was treated as a harmonic oscillator, while relative atom-molecule motion was described by a plane wave; electronic nonadiabaticity, ionization, and molecular dissociation were neglected. The stress in this paper was on development of a fast approximate method that could eventually be used to extract potential surface information from experimental cross-section data in the keV range.

B. Vibrational Energy Transfer

Heidner and Kasper (1972) measured the rate coefficient at 299°K for

$$H+H_2(n_1=0)\rightarrow H_2(n_2=1)+H$$

where n_1 and n_2 are the initial and final vibrational quantum numbers. However, quasiclassical trajectory histogram calculations (Karplus and Wang, unpublished, quoted by Heidner and Kasper, 1972) indicate that the nonreactive contribution is negligible with respect to the reactive one. Thus this is not a measure of the rate coefficient for nonreactive vibrational energy transfer. In fact, there is no measurement available for this process and hardly any theory. The little theory that does exist is reviewed in this section.

Clark and Dickinson (1973) performed collinear calculations of vibrational excitation probabilities for the $H+H_2$ mass combination using an exponential repulsion interaction potential between the incoming H and the nearest H of H_2. Because the important rotation-vibration coupling is missing in such a calculation, it is difficult to assess its relevance to experiment. Quantum-mechanical (Truhlar and Kuppermann, 1972) and quasiclassical and semiclassical (Bowman and Kuppermann, 1973) calculations of collinear nonreactive vibrational excitation probabilities have also been carried out using the more accurate potential-energy surface of Truhlar and Kuppermann.

Smith and Wood (1973) reported both collinear and three-dimensional quasiclassical trajectory calculations in $H+H_2$ where H_2 is initially in its first or second excited vibrational state. They used a semiempirical potential-energy surface similar to the Weston (1959) surface. They used the histogram method to interpret these trajectories in terms of cross sections for energy transfer, but they included only those trajectories for which $R_1 < R_2$ or $R_3 < R_2$ at some point in the trajectory (where R_1 and R_3 are the interatomic distances that initially are infinite and R_2 is the other interatomic distance). This may be a serious approximation and it is not clear how much reliance can be placed on their results. It is also probable that even if their approximation were not made and a more accurate surface were used, the quasiclassical trajectory histogram method would not yield an accurate result for the vibrational excitation cross section for $H+H_2$ except at fairly high energies (at least a few eV).

Gengenbach et al. (1975) estimated a crude upper limit of 10^{-6} Å^2 for the cross section for vibrational exciation at a relative translational energy of about 0.5 eV. This was based on an analogy to available data for $He + H_2$ and $Li^+ + H_2$.

If one excludes from consideration the out-of-data calculation by Bauer (1952), no three-dimensional quantum-mechanical calculations have yet been reported for nonreactive vibrational excitation cross sections in $H + H_2$ collisions at energies below 1 keV. The calculations of Ioup and Russek (1973) at energies 1 to 10 keV are discussed in the previous subsection. Schatz and Kuppermann (1975a) reported calculations on the potential energy surface No. 2 of Porter and Karplus (1964) of the reactive vibrationally inelastic probability for zero total angular momentum at $E_{rel} < 0.83$ eV. They also calculated (Schatz, private communication) the corresponding nonreactive probability and found (in contrast to the quasiclassical result) that both reactive and nonreactive vibrationally inelastic probabilities and cross sections are comparable in magnitude for this surface.

Shui (1973) made a classical trajectory calculation on the same Porter-Karplus surface of the one-way equilibrium transition-rate kernel of internal energy changes for $H + H_2$ collisions at 3000°K.

C. Electronic Energy Transfer and Other Processes Involving Excited Electronic States

In this section, collisional processes involving electronically excited H atoms interacting with H_2 are reviewed. H atoms in the 2*s* state have an excitation energy of 10.2 eV and are metastable; in vacuum the population of this state decays by a two-photon process to H(1*s*) with an extremely long natural lifetime of about 1/8 sec. By contrast, H(2*p*) has a radiative lifetime of 2×10^{-9} sec and decays via a one-photon process to H(1*s*) with emission of Lyman-α (L_α) radiation. If H(2*s*) is in the presence of an electric field (either external or from gas in the apparatus), 2*s*-2*p* mixing occurs with subsequent emission of L_α radiation. This mixing occurs quite readily because the energy separation of these states is less than 1 cm^{-1}. The following processes involving collisions of metastable H(2*s*) with H_2 have been studied:

$$H(2s) + H_2 \xrightarrow{2s \to 2p} H(2p) + H_2 \to H(1s) + H_2 + L_\alpha$$

$$H(2s) + H_2 \xrightarrow{2s \to 1s} H(1s) + H_2$$

$$H(2s) + H_2 \xrightarrow{\substack{2s\ \text{associative-} \\ \text{ionization}}} H_3^+ + e^-$$

The H-atom interconversion rate coefficient $k_{2s\rightarrow 2p}$ in the presence of H_2 was first studied by Fite et al. (1959), who produced metastable H by electron impact on H and measured L_α emission as a function of the concentration of the added quenching H_2 gas. The measured rate coefficient was converted to a cross section $\sigma_{2s\rightarrow 2p}$, presumably by the common approximation of dividing by the mean relative speed. For a mean "atom speed" of 8×10^5 cm/sec, the interconversion cross section was first reported as 70 Å^2; however, an erratum later indicated that the cross section should be increased by 50%. The interpretation of this experiment is complicated by the need to konw the polarization of the L_α emission; the value originally assumed has now been corrected but revised quenching rate coefficients were not presented (Fite et al., 1968; Ott et al., 1970). A recent re-evaluation (Czuchlewski and Ryan, unpublished, quoted by Van Volkenburgh et al., 1973) yields $\sigma_{2s\rightarrow 2p}=120$ Å^2.

The associative ionization process was studied in a mass spectrometer by Chupka et al. (1968). This process is about 1 eV exothermic. ***Assuming*** that the excited H atoms they produced by photodissiciation were in the 2*s* state, they obtained an associative ionization cross section of about 1 Å^2, which decreased by a factor of about 1.8 as the kinetic energy of H(2*s*) was increased from 0.07 ± 0.10 eV to 0.18 ± 0.16 eV. If their excited H atoms were in the 2*p* state, then the above analysis does not apply. Associative ionization was also observed by Comes and Wenning (1969). The reverse of the associative ionization process is electron recombination with H_3^+; it is discussed in Section V.

The cross section $\sigma_{2s\rightarrow 2p}$ for $2s\rightarrow 2p$ interconversion and its ratio to the cross section $\sigma_{2s\rightarrow nr}$ for nonradiative destruction of the 2*s* state can also be measured by producing H(2*s*) by photodissociation in a bulb, determinimg the fraction of H atoms formed in the 2*s* state, and measuring the L_α flourescence intensity and its ratio to the photodissociation cross section. (Note: the nonradiative process is generally assumed to be the $2s\rightarrow 1s$ process.) Since photodissociation at a given wavelength produces excited atoms of known kinetic energy, these cross sections may be obtained as a function of relative kinetic energy. This technique was first applied by Comes and Wenning (1969, 1969a, 1970), who found $\sigma_{2s\rightarrow 2p}\cong 60$ to 70 Å^2 and $\sigma_{2s\rightarrow nr}\cong 50$ Å^2 at a mean relative speed of 3.5×10^5 cm/sec. At the same mean relative speed, deuterium substitution for H and H_2 increased $\sigma_{2s\rightarrow 2p}$ by a factor of 2. As the mean relative speed increased to 8×10^5 cm/sec, $\sigma_{2s\rightarrow 2p}/\sigma_{2s\rightarrow nr}$ was found to increase to 2 and the total destruction cross section $\sigma_{2s\rightarrow 2p}+\sigma_{2s\rightarrow nr}$ increased to over 150 Å^2. Mentall and Gentieu (1970) made similar measurements and they found that $\sigma_{2s\rightarrow 2p}/\sigma_{2s\rightarrow nr}$ increased from about $2\frac{1}{2}$ to 3 as the mean relative speed increased over the same interval.

Dose and Hett also used photodissociation to produce H(2*s*) and D(2*s*) of known velocity. They measured the sum of the elastic scattering cross section and the total cross section for destruction by measuring the exponential decrease of H(2*s*) intensity in a flight-timed beam as a function of molecular H_2 target gas thickness. For metastable H, their measured cross section over the speed interval 3.5×10^5 to 8×10^5 cm/sec decreased from about 120 Å^2 to 85 Å^2. As the mean relative speed further increased to 3×10^6 cm/sec, their cross section decreased to 55 to 60 Å^2. Very similar results were obtained for metastable D. Especially at high speeds, these results are obviously inconsistent with the bulb experiments discussed in the previous paragraph. Similar but unpublished beam experiments by Czuchlewski and Ryan are quoted by Van Volkenburgh et al. (1973).

In principle, one can also measure cross sections for collisions of H(2*p*). In fact, measurements of the quenching of L_α radiation might be interpreted this way. But in fact (as illustrated by the large interconversion cross sections discussed above), small perturbations may easily mix the 2*s* and2*p* states and L_α-quenching measurements have also been interpreted as referring to some mixture of $n=2$ states. The first such quenching measurements involving H_2 as collision partner were carried out by Wauchop et al. (1969). They measured quenching of L_α fluorescence in an optically thick discharge-flow system with added H_2. Their total rate coefficient for all processes that quench H(2*p*) was 2.4×10^{-12} cm^3/(molec·sec), from which they calculated a cross section of about 0.03 Å^2. This value is much lower than subsequent measurements, possibly because of the difficulty of the analysis involving radiation trapping in their optically thick system.

The collisional deactivation of L_α fluorescence was next studied by Braun et al. (1970) in an optically thin discharge-flow system. From their measured rate coefficient at 300°K they calculated the quenching cross section to be about 84 Å^2. Then Van Volkenburgh et al. (1973) studied the quenching of H($n=2$) and D($n=2$) by H_2 and D_2; they measured rate coefficients in the range 1.9 to 2.5×10^{-9} cm^3/(molec·sec) at 295°K for the four isotopically different processes. Dividing these by the average relative thermal speed they obtained the quenching cross sections 84 Å^2 for H($n=2$) by H_2 or D_2, 89 Å^2 for D($n=2$) by D_2, and 91 Å^2 for D($n=2$) by H_2. These quenching cross sections include all processes that deactivate H($n=2$) and D($n=2$) including associative ionization, reactive electronic energy exchange, nonreactive transfer of the excitation energy to electronic, vibrational, or rotational degrees of freedom or to relative translational energy, and dissociative deexcitation. Using dc ion-collection techniques, the cross section for associative ionization was measured as 1.11 Å^2

for the $H(n=2)+H_2$ case with value from 0.82 to 1.06 $Å^2$ for the three isotopically substituted cases. In addition, by observing simultaneous L_α fluorescence from $D(n=2)$ and $H(n=2)$, the cross section for near-resonant reactive electronic energy transfer in the reaction $H(n=2)+D_2 \rightarrow HD + D(n=2)$ was found to be 0.28 $Å^2$. Branching ratios in other channels were not measured. However, the diatomic electronic excitation channel has been observed by Chow and Smith (1970), who saw fluorescence of the Lyman bands ($B\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$) of H_2, which they interpreted as caused by the reaction

$$H(2p)+H_2(X\,^1\Sigma_g^+,v'') \rightarrow H(1s)+H_2(B\,^1\Sigma_u^+,v')$$

where v'' and v' are vibrational quantum numbers. Energetic considerations showed that $v'' \geqslant 2$ was required for this process to occur.

It is unfortunate that some experimenters measured rate coefficients but presented only derived cross sections and confused relative speed and atomic speed in presenting their results. This leads to some confusion concerning their experimental results.

Two semiclassical calculations have been made for the $2s \rightarrow 2p$ interconversion cross section involving H_2 collision partner. Gersten (1969) computed elements of the S matrix, $S_{2sjm \rightarrow 2pj'm'}$ (where jm and $j'm'$ are the initial and final H_2 angular momentum and magnetic quantum numbers) from approximate time-dependent perturbation theory. An instantaneous atomic dipole-molecular quadrupole interaction was assumed, with classical relative translational (straight-line trajectory) and quantum or classical molecular rotational motion assumed. The calculated probability of quenching diverged at small impact parameter and so it had to be cut off at unity. Using classical rotational motion, averaging over the impact parameter, and assuming a relative speed of 8×10^5 cm/sec, a cross section of 76 $Å^2$ was obtained. Further assuming a large moment of inertia so the molecule does not rotate during the collision yielded a simpler formula that predicts $\alpha_{2s \rightarrow 2p} = 87$ $Å^2$ at the same relative speed and a velocity dependence of $v^{-2/3}$. In a similar treatment, Slocumb et al. (1971) also assumed a dipole-quadrupole interaction. They used the Born approximation with semiclassical approximations to evaluate S-matrix elements and transition probabilities and a cutoff at small impact parameters. Their final cross-section formula is similar to the large-moment-of-inertia formula of Gersten, differing only in a numerical coefficient that is smaller by a factor of $3^{-1/3}$; thus they predicted $\alpha_{2s \rightarrow 2p} = 63$ $Å^2$ at the same relative speed. Dose and Hett (1971) used the treatment of Gersten, taking "correct" account of rotational motion, to calculate the cross section for $D(2s)+H_2 \rightarrow D(2p)+H_2$ over the relative-speed interval 3.5×10^5 to 8.0×10^6 cm/sec.

The calculated values agreed very well with their experiment over this whole range.

Frenkel (1970) discussed the interconversion, the quenching, and the associative ionization processes in terms of his calculated excited-state potential surfaces.

Less quantitative theoretical work has been done by others on the L_α quenching process. Comes and Wenning (1970) argued that their measured D/H isotope effect could be explained by the smaller rotational spacing of D_2 compared to H_2 if the D_2 and H_2 molecules are rotationally excited in collisions with the excited atoms. Braun et al. (1970) argued that the large quenching cross sections might be explained in terms of a virtual electron jump from H($n=2$), which has an ionization potential of only 3.4 eV, to H_2. Chow and Smith (1970) interpreted the electronic energy-transfer process they observed in terms of an avoided crossing of two potential surfaces and an H_2^- intermediate. They predicted that an isotopic experiment would reveal the process occurs with atom exchange. Slocumb et al. (1971) claimed the $2s \rightarrow 1s$ deexcitation cross section should be less than 1 Å^2, but this is contradicted by the experiments already discussed. Van Volkenburgh et al. (1973) discussed the quenching results in terms of electronic correlation diagrams linking asymptotic electronics states to equilateral triangle geometries of H_3 and H_3^+. They concluded that quenching occurs by the following mechanism:

$$H(n=2)+H_2(X\,{}^1\Sigma_g^+)\rightarrow H(1s)+H_2(b\,{}^3\Sigma_u^+)$$

where the $b\,{}^3\Sigma_u^+$ is strongly repulsive and hence dissociative and that there is little likelihood of

$$H(n=2)+H_2(X\,{}^1\Sigma_g^+)\rightarrow H(1s)+H_2(X\,{}^1\Sigma_g^+,\text{ vibrationally excited})$$

They also concluded that the lowest-energy $^2A''$ potential surface provides a likely route for reactive electronic energy exchange and they rationalized associative ionization in terms of vibronic coupling between a Rydberg state and the electronic continuum of the ion.

D. Transport Properties of Partly Dissociated H_2

The temperature dependence of viscosity and diffusion coefficients for H-H_2 mixtures has provided information about the effective spherically averaged (orientation-independent) interaction potential $V_0(R)$ between H and H_2. The first measurements on transport coefficients involving H-H_2 were Harteck's (1928) results on the viscosity of H-H_2 mixtures. The viscosity of the mixture η_{mix} was determined from the Poiseuille equation following measurement of the pressure drop for H-H_2 mixtures flowing through a capillary tube. The relative viscosity (η_{mix}/η_{H_2}) was reported at -80, 0, and 100°C, but the lowest-temperature results may have been affected by ice formation on the inner walls of the U-tube viscometer. Later, Browning and Fox (1964) measured viscosities of H-H_2 mixtures over the same temperature range. Their viscosity data are in good agreement with those of Harteck, except at the lowest temperature. In order to analyze the data, Browning and Fox partitioned the total viscosity into contributions from H-H interactions (η_1), H_2-H_2 interactions (η_2), and H-H_2 interactions (η_{12}). (The term η_{12} has no direct physical significance, but it can be imagined as the viscosity of a hypothetical pure substance whose mass is twice the reduced mass of an H-H_2 pair.) Values of the multicomponent viscosity coefficient η_{12} were extracted from the data by assuming a theoretical value for η_1. Information about $V_0(R)$ can be extracted from η_{12} by fitting the parameters in an assumed form of $V_0(R)$ [the Lennard-Jones (12-6) or modified Buckingham (exp-6) forms have usually been used] so that the theoretical η_{12} values agree well with the experimental values. Collision theory provides the result that $\eta_{12} \approx T^{1/2}/\Omega_{12}^{(2,2)*}$, where T is the temperature and $\Omega_{12}^{(2,2)*}$ is a (reduced) collision integral, which can be evaluated from the assumed form of $V_0(R)$ (Hirschfelder, Curtiss, and Bird, 1954, pp. 523 to 528). The experimental η_{12} values were fitted by Browning and Fox with a 12-6 potential but a three-parameter exp-6 potential could also be fitted to the data. Parameters in spherically averaged potentials deduced from transport data are listed in Table V.

Cheng and Blackshear (1972) have recently remeasured the viscosity of H-H_2 mixtures between -72 and 100°C. They extracted η_{12} from the data on η_{mix} and found that the temperature dependence was fitted by a 12-6 potential. The previously measured values of η_{mix} provided by Browning and Fox are somewhat lower the Cheng and Blackshear values; the discrepancy may be due to violation of the constant-flow-rate assumption (for the mixture versus pure H_2) used by Browning and Fox.

In addition to the viscosity measurements, several determinations of the multicomponent H-H_2 diffusion coefficient $D_{12}(T)$, where the temperature-dependence is explicitly indicated, have been reported. Wise (1961) measured the steady-state distribution of H atoms diffusing along a cylinder toward a catalytically active surface where recombination occurred. The steady-state distribution results from a compromise between diffusion away from the source and removal on the surface. [The diffusion equations for this experimental arrangement had been previously considered by Wise and Ablow (1958). In addition, Wise (1959) had used the steady-state method to measure the diffusion coefficient of H through Ar/H_2 mixtures.

See also Wise and Wood (1961).] These measurements provided *relative* diffusion coefficients $D_{12}(T_2)/D_{12}(T_1)$. From the collision-theory expression $D_{12}(T) \cong T^{1/2}/\Omega_{12}^{(1,1)*}$, where $\Omega_{12}^{(1,1)*}$ is another reduced collision integral [which can be computed from the deflection function for the H-H_2 spherically averaged potential (Hirschfelder, Curtiss, and Bird, 1954, pp. 523 to 528).] Wise fitted the temperature dependence of the experimental diffusion coefficient ratios with a 12-6 potential (see Table V). In a later study, Sancier and Wise (1969) measured the absolute value of $D_{12}(T)$ at one temperature, 298°K. Two types of measurements (of the relative atom concentration as a function of the distance from the source under steady-state conditions and of the relative atom concentration as a function of time just after the source, which produced steady-state conditions, was removed) were combined to produce $D_{12}(T)$. The previous relative diffusion coefficients of Wise (1961) were then converted to absolute values (over the range 298 to 719°K). Parameters in an exp-6 potential were then adjusted so that the collision-theory prediction for $D_{12}(T)$ agreed with the experimental temperature dependence.

A second direct determination of $D_{12}(T)$ was reported by Khouw et al. (1969). They studied the lower temperature range 202 to 364°K. They too measured the concentration of H atoms in a flowing H-H_2 mixture that was in contact with a catalytic sink. The H-atom concentration was determined by introducing small amounts of NO into the stream and measuring the HNO emission. A 12-6 potential, when used to compute the $\Omega_{12}^{(1,1)*}$ collision integrals, produced $D_{12}(T)$ values that reproduced the experimental temperature dependence. However, the authors were careful to point out that potentials involving other parameter sets also reproduced the experimental temperature dependence.

All of the $D_{12}(T)$ coefficients that have been directly measured or inferred from viscosity data are plotted in Fig. 1. Notice that the recent direct measurements of Khouw et al. (1969) are in good agreement with the results inferred by Cheng and Blackshear (1972) from viscosity data. An earlier discussion of the use of viscosity data to predict diffusion coefficients is given by Dalgarno and Henry (1964).

In analyzing the experimental studies discussed above, parameters in a model spherically symmetric potential wrere determined such that the temperature dependence of the experimental viscosity or diffusion coefficients, as calculated from the potential and the collision integrals, was reproduced. The properties of the various derived potentials are compared in Table V. From this table it is apparent that these potentials are not in close agreement, but as a group they do provide approximate limits on the effective spherically averaged H-H_2 interaction.

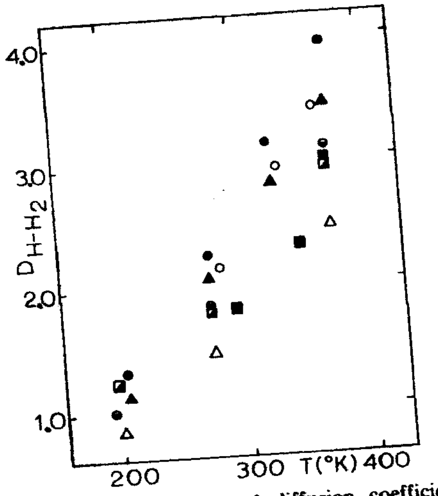

Fig. 1. Temperature dependence of mutual diffusion coefficient $D_{H\text{-}H_2}$ (or D_{12}) in cm²/sec at 1 atm from theory and experiment. △ Amdur (1936), from analysis of Harteck's (1928) viscosity data; ◪ Weissman and Mason (1962); computed from 12-6 potential fit to Margenau's (1944) calculations; ○ Browning and Fox (1964); computed from 12-6 potential fit to Margenau's (1944) calculations; ◒ Khouw, Morgan, and Schiff (1969), direct measurement; ■ Sancier and Wise (1969), direct measurement; ▲ Cheng and Blackshear (1972); computed from 12-6 potential inferred from viscosity data; ● Tang and Wei (1974); computed from Tang (1969) potential.

Other attempts have been made to extract potential parameters from the experimental transport data. The earliest was Amdur's (1936) reevaluation of Harteck's viscosity data. He assumed that H and H_2 are each "van der Waals gases" (hard elastic spheres with R^{-1} attraction), and then calculated D_{12} for the H-H_2 mixture. His results, shown in Fig. 1, are somewhat lower than the other D_{12} values. A second calculation of D_{12} from Harteck's data on η_{mix} was the study of Weissman and Mason (1962). They employed a theoretical calculation of η_1 from the best available H_2 potential curves, and also calculated the collision integral $\langle A^*_{12} \rangle$ (which is related to η_{12}) from 12-6 or exp-6 potentials fitted to Margenau's (1944) H_3 calculation. They then extracted D_{12} from Harteck's η_{mix} data. Their results, also shown in Fig. 1, are about 30% greater than Amdur's earlier estimates.

In a later theoretical study of the transport coefficients for H-H_2 mixtures, Clifton (1961) used a 12-6 potential to calculate high-temperature (1500 to 5000°K) values for η_{12} and D_{12} and for the coefficient of thermal conductivity (Clifton, 1962). The 12-6 potential used by Clifton was parameterized by fitting it to a weighted average of Margenau's (1944) early H_3 potential for parallel or perpendicular approach of H to H_2. Vanderslice et al. (1962) computed the transport properties (coefficients of viscosity, diffusion, thermal conductivity, and thermal diffusion) of dissociating H_2 as a function of the mole fraction in the mixture over the temperature range 1000 to 15,000°K. The H-H, H-H_2, and H_2-H_2 interactions were all considered, but ionization and electronic excitation were neglected. The spherically symmetric exponential repulsive potential of Vanderslice and Mason (1960) was used. At high temperatures, the collision integrals $\Omega_{12}^{(1,1)}$ and $\Omega_{12}^{(2,2)}$ for H-H_2 are smaller than the corresponding values for H-H, or H_2-H_2. The Vanderslice and Mason potential was also used by Estrup (1964) in a study of the cooling of hot T atoms in D_2.

Tang and Wei (1974) have recently computed D_{12} from what is probably a much more accurate spherically symmetric H-H_2 potential than was used in the previous studies. In earlier work, Tang (1969) smoothly joined the Porter-Karplus (1964) potential No. 2 to the Dalgarno-Henry-Roberts (1966) attractive long-range R^{-6} potential. (Rotationally-inelastic-scattering results obtained with this potential are discussed in Section IV.A.) Tang and Wei used a fit to this joined potential to evaluate the collision integrals that are required to compute η_{12} and D_{12} (see Fig. 1 for their D_{12} results). Their computed D_{12} values are somewhat higher than the experimental values of both Cheng and Blackshear (who extracted D_{12} from viscosity measurements) and of Khouw et al. (who directly determined D_{12}).

In an interesting study, Belov (1966) examined how the kinetic properties of dissociating H_2 are influenced by the $H+H_2$ exchange reaction at temperatures over 1000°K. At high temperature the differential reaction cross section for reactive scattering becomes forward peaked in scattering angle θ (see Truhlar and Wyatt, 1976). Belov therefore argued that the effective cross sections for diffusion and viscosity, which weight the differential cross section by $(1-\cos^l\theta)$ (where l is 1 and 2 for diffusion or viscosity, respectively) before integration over $\sin\theta\, d\theta$, are much smaller than the diffusion and viscosity cross sections due to nonreactive scattering computed, for example, by Vanderslice et al. (1962). The reactive process would make a much greater contribution for a given integral cross section if the differential reaction cross section were isotropic. It is important to reexamine this question with more accurate estimates of the reactive differential cross sections.

Now that the potential energy surface for H_3 can be accurately calculated by ab initio electronic structure calculations and accurate calculations of rotational-vibrational transition probabilities and elastic scattering in atom-diatomic systems are possible, it is finally possible to test the assumptions of spherically symmetric potentials and no inelasticity that have been used to calculate transport coefficients in H-H_2 mixtures. In an early approximate quantum-mechanical treatment, Dalgarno and Henry (1964) estimated that rotationally inelastic processes contributed 7.5% of the $H + D_2$ diffusion cross section and 5.4% of the viscosity cross section at a relative translational energy of 0.0625 eV. More accurate calculations could now be made by integrating the more accurate differential cross sections now available (see Sections III and IV.A). It is now possible to compute accurate elastic scattering and rotational excitation differential cross sections, to integrate them to obtain transport cross sections, and to make a thermal average to obtain viscosities and diffusion coefficients as functions of temperature. This has not been done.

E. Other Processes and Applications

Rotational excitation of H_2 by collisions with H followed by emission of radiation has been considered as a possible mechanism for cooling of interstellar clouds in regions of neutral hydrogen, but the most recent work indicates it is not the most important mechanism for such cooling (Hollenbach et al., 1976). Takayanagi and Nishimura (1960) and Dalgarno et al. (1966) calculated rate coefficients for rotational excitation in H-H_2 collisions from their approximate quantum-mechanical cross sections. Their cross sections agree within a factor of 2.2, but it now appears that the DHR interaction potential used by Dalgarno et al. (1966) leads to rotational excitation cross sections that are much too large (see the work of Choi and Tang, 1975, discussed in Section IV.A). Hydrogen molecules formed on grains in interstellar space may leave with excess kinetic energy greater than the thermal average of the surrounding gas. To understand the loss of kinetic energy it is also necessary to know the differential cross sections for nonreactive collisions, especially elastic scattering (Chu and Dalgarno, 1975).

The rate of interconversion of o-H_2 and p-H_2 is very important in interstellar space because of the different radiative rates for these species (Takayanagi and Nishimura, 1960; Field, 1966) and observations of the ratios of o-H_2 to p-H_2 are important because their interpretation provides a clue as to the physical conditions in interstellar space. The mechanisms for this interconversion have been discussed most recently by Dalgarno et al. (1973), who conclude that the $H + H_2$ reaction, involving thermal or hot atoms, is probably not too important for this interconversion in interstellar space.

The pressure-induced vibrational absorption coefficient of H_2 is needed for various radiant heat-transfer calculations. At high temperatures, such as encountered in gaseous-core nuclear rockets and late-type stars, there is appreciable dissociation of H_2, and $H+H_2$ collisions become almost as important as H_2+H_2 collisions. The only theoretical or experimental work on absorption due to $H+H_2$ collisions is the work of Patch (1973, 1974) in the region of the fundamental vibrational absorption. The collision-induced dipole moment was found by CCI calculations with a minimum-basis set for small H-to-H_2 separations of 1 to $4a_0$ and from the quadrupole-induced dipole in H at separations greater than $6a_0$. The ab initio calculations were performed with floating orbitals and with two sets of exponents for nuclear-centered orbitals. The latter choice with optimized exponents was judged best and yielded dipole moments in the range 0.0062 to 1.0 *D*. Unfortunately, the energies were not very accurate, so the induced absorption calculations were based on an interaction potential computed from the calculations of Mason and Hirschfelder (1957) for H-to-H_2 separations greater than $4.33a_0$ and from Porter-Karplus surface No. 2 for smaller separations. The $H+H_2$ collisions accounted for 32% of the absorption calculated, including both $H+H_2$ and H_2+H_2 collisions at 5500 cm^{-1}, 3750°K, and 1 atm pressure.

The simplest inelastic event in $H+H_2$ collisions is change of the hyperfine state of the H atom. This process has been measured (Gordon et al. 1975), but since it gives information about the reaction probability it should have been included in our review of reactive collisions.

V. RECOMBINATION OF H_3^+ WITH ELECTRONS

Several beam studies aimed at producing H_3 by recombination of H_3^+ with electrons have been carried out.

The electron-ion recombination rate $\alpha(T)$ for e-H_3^+ collisions was measured by Leu, Biondi, and Johnson (1973) by using a microwave afterglow technique to measure the time rate of decay of electron density in a plasma containing H_3^+. The recombination rate coefficient decreased from 2.9×10^{-7} $\text{cm}^3/(\text{molec}\cdot\text{sec})$ at 205°K to 2.0×10^{-7} $\text{cm}^3/(\text{molec}\cdot\text{sec})$ at 450°K and varied as $T^{-1/2}$ over this temperature range. In an incline-beam experiment, Peart and Dolder (1974) measured cross sections σ for dissociative recombination of electrons with H_3^+ with negligible vibrational energy over the relative translational energy (E_{rel}) range 0.38 to 4.0 eV. The cross section varied from 23.8 Å^2 at 0.38 eV to 2.7 Å^2 at 4.0 eV with an $E_{\text{rel}}^{-0.87}$ energy dependence. Peart and Dodler then converted the recombination rate coefficients of Leu et al. to cross sections with the usual approximate relation $\alpha(T)=\langle v\rangle_T\sigma$, where $\langle v\rangle_T$ is the mean speed of the thermal beam (at temperature T). The cross sections obtained in this way from the Leu et al. data at low relative translational energies ($E_{\text{rel}}\lesssim0.1$ eV) are about 200Å^2 and are in excellent agreement with cross sections extrapolated from the higher-energy beam measurements.

Caudano et al. (1975) used merged electron-ion beam techniques to measure the relative recombination cross sections for $0.05 \text{ eV} \leqslant E_{\text{rel}} \leqslant 4 \text{ eV}$ with better initial energy resolution than Peart and Dodler. Their results are consistent with Peart and Dodler's but show structure in the energy dependence that was attributed to "the resonant nature of the recombination process."

The first direct attempts to generate H_3 were the merging-beam experiments of Devienne (1967, 1968, 1968a) in which an H_3^+ beam was passed through H_2 to generate a neutral H_3 beam by charge exchange. The neutral beam was then merged with an He^+ beam to reform H_3^+, which was then detected. In a later double-chamber experiment, Devienne (1969) first passed an H_3^+ beam through D_2 in a charge-exchange chamber. The ions were deflected, and the neutral beam (presumed to be H_3) was passed into a collision chamber containing D_2. Mass-spectrometric analysis of ions formed in the collision chamber showed that H_3^+, H_2^+, and H^+ were all produced from ionization of the neutral beam that entered the second chamber. In a different set of experiments, Gray and Tomlinson (1969) passed an He/H_2 beam through an rf discharge. The resulting ion beam was directed through a charge-exchange region containing H_2 and D_2 and the ions were deflected from the beam. A fraction of the remaining neutral beam was reionized, but mass analysis did not show evidence for H_3 (or isotopic variants) with lifetimes the order of 10^{-8} sec (the transit time of the beam past electrostatic deflector plates that remove the ions). In more recent experiments, Barnett and Ray (1972) passed a beam of H_3^+ through H_2 to form H_3. The outer electron was stripped off in an intense electric field and the H_3^+ was detected. The H_3 "molecules" were thought to consist of a stable H_3^+ core and a highly excited Rydberg electron (principal quantum number $n \geqslant 11$). Additional experiments on the production and properties of excited H_3 would be very interesting.

VI. CONCLUDING REMARKS

The ground-state potential-energy surface of H_3 has now been calculated accurately for many geometries, especially in the vicinity of the barrier for reaction. The C_6 and Γ coefficients of the long-range H-H_2 interaction are also well known from theory (see Table IV), but the topology of the van der Waals well is not accurately known (see Table V). Recent scattering experiments (Gengenbach et al., 1975) should motivate more theoretical attention to this problem. The excited states are much more poorly understood, at least as far as quantitative results are concerned. The states correlating with $H(n=2)+H_2(X\,^1\Sigma_g^+)$ are particularly important in fluorescence-quenching experiments. The long-range interactions in excited states of H_3 may also be important for the interpretation of experiments. It is difficult to deduce an accurate interaction potential from experimental cross sections and rate coefficients for elastic scattering and the various energy-transfer processes. However, it is now possible to make realistic calculations for some of these processes and to use theory to understand the qualitative features of others. Nevertheless, the effect of the nonsphericity of the interaction potential on the elastic scattering and transport properties is not well studied, vibrational-rotational energy transfer in $H+H_2$ is poorly understood compared to the same processes in inert-gas collisions with homonuclear diatomics, electronic-energy transfer is poorly understood compared to analogous processes involving alkali atoms, the theory of associative ionization requires more work, and the transport data have not yet been interpreted using the most accurate available potentials. Experimental studies of rotational and vibrational energy transfer in $H+H_2$ collisions would be particularly valuable because reasonably accurate ab initio calculation of cross sections for simultaneous vibrational-rotational energy transfer in both reactive and nonreactive H-H_2 collisions should be possible in the near future. More detailed experimental studies of other energy-transfer processes and of associative ionization would also be valuable. In particular, the energy dependence of the branching ratios that determine the outcome in $H(n=2)+H_2$ collisions needs further study.

In some respects, $H+H_2$ provides an important test case for studying inelastic processes in chemically reactive systems because the relatively high (compared to other atom-molecule atom-transfer reactions) energy barrier to reaction in either direction in the ground electronic state means that under many low-energy conditions reaction is negligible. However, the relevant interactions are still more representative of a reactive system than, for example, an inert-gas collision with a molecule. For this reason we hope the $H+H_2$ inelastic collision processes will be the subject of continued study in the near future.

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