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# Theoretical potential curves for excited states of ArH and the rate of collisional quenching of metastable Ar by H<sup>a</sup>)

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Energy curves for the ground state and the first seven excited states of ArH have been calculated using the multiconfiguration valence bond (MCVB) method. Important features of the excited curves include two distinct avoided crossings between the lowest Ar\*H and the highest ArH\* potential energy curves. Using these curves we have made a theoretical analysis of quenching of metastable Ar by collision with H at room temperature. Application of the Massey criterion indicates that the separation of the potential curves in the region of the crossing and the acceleration produced by the fall of the reactant channel potential curve from its asymptotic level combine to produce a relatively high probability for curve switching. A more quantitative estimate of the curve switching probability is given with the Landau-Zener formula and leads to a theoretical value of the quenching rate approximately ten times the experimental. In light of the many approximations involved this qualitative agreement is satisfactory and provides a rationale to explain the anomalously high rate constant for the quenching reaction. Structural features of the interacting potential curves are discussed in terms of the diabatic states involved.

## I. INTRODUCTION

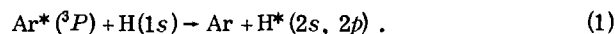
The theoretical understanding of energy transfer reactions involving metastable states of rare-gas atoms are of great scientific interest, as well as being important in the practical design of rare-gas-halide lasers. The collisional quenching of metastable Ar atoms by H atoms is a simple example of energy transfer and is an excellent prototypical system for theoretical study. In addition, during the past few years experimental results on the Ar-H system have been accumulating, and the interpretation of these results will be greatly aided by having reliable theoretical energy curves. In this article we report on an *ab initio* calculation of the seven lowest lying energy curves for Ar-H. We use these results to give an estimate of the second-order rate constant for quenching of metastable Ar by H-atom collision. We also include a discussion of the conclusions possible concerning the diabatic states involved.

Johns<sup>1</sup> reported the first gas phase emission spectrum of neutral argon hydride near 7060 Å. The spectrum was identified as being due to an ArH transition between two excited electronic states of <sup>2</sup>Σ<sup>+</sup> and <sup>2</sup>Π symmetry. Similar spectra are not observed for helium or neon hydrides.

Bondybey *et al.*,<sup>2</sup> in their study of the matrix isolation of H<sub>2</sub>Br in argon, observed a sharp infrared absorption at 644 cm<sup>-1</sup>. At the time the absorption was attributed to a reactive impurity and therefore ignored in their discussion of H<sub>2</sub>Br. However, Bondybey and Pimentel<sup>3</sup> demonstrated in later experiments that the 644 cm<sup>-1</sup> absorption is present in the absence of the halogen, that is, with only the argon matrix and deuterium. They concluded that the absorption is due to isolated H atoms trapped in O<sub>h</sub> interstitial sites in solid

argon. Their interpretation was later supported by *ab initio* calculations for H atoms trapped in a neon lattice.<sup>4</sup>

Even more recently, Setser and co-workers<sup>5</sup> have measured the room temperature rate constant for quenching of Ar(<sup>3</sup>P) by ground state H atoms.



Ar(<sup>3</sup>P) atoms have 11.54 eV of available energy, and since only 10.2 eV of this energy is needed to excite the H (2s and 2p) level, reaction (1) has a large energy defect of 1.3 eV. The measured rate constant,  $2.4 \times 10^{-10}$  cm<sup>3</sup>/sec is surprisingly large for a process with a single exit channel and an energy defect of this magnitude. They discuss the H atom excitation in terms of a double curve crossing mechanism. We shall return to this question later and compare their description of the process to our calculations.

Numerous theoretical calculations have been made of the ground state of argon hydride.<sup>6</sup> However, theoretical studies for low-lying excited states have been sparse. Recently, Matcha and Milleur<sup>7</sup> have reported the results of linear combination of atomic orbitals-self-consistent field-molecular orbitals (LCAO-SCF-MO) calculations for ground state ArH and the excited states of ArH\*(*n*=2). Also, Olson and Liu<sup>8</sup> have made SCF-configuration interaction (CI) calculations for ground state ArH and the excited states of ArH\*(*n*=2). However, there have been no reported theoretical calculations including the excited states of Ar\*(*n*=4) H.

In our studies we have directed our attention to the *ab initio* calculation of the potential curves needed to analyze the excitation transfer between excited <sup>3</sup>Ar and H. The multiconfiguration valence bond (MCVB) method has been used to obtain adiabatic potential curves for the ground state and first seven excited states. These provide the necessary energy parameters for an estimation of the rate constant for reaction (1) by the familiar Landau-Zener formula.<sup>9</sup> Comparisons with previous calculations will be made where possible.

<sup>a</sup>Based in part upon the thesis submitted by R. L. Vance to the Graduate Faculty in the University of Nebraska in partial fulfillment of the requirements for the Ph.D. degree.

## II. POTENTIAL CURVES

All calculations have been done with the multiconfigurational valence bond method.<sup>10</sup> We neglect magnetic effects in the Hamiltonian and use the Born–Oppenheimer approximation to obtain the adiabatic energy curves. The wave functions for a desired electronic state are expanded in terms of an  $N$ -particle basis of nonorthogonal tableau symmetry functions (TSF), each TSF being a linear combination of atomic orbital (AO) products.<sup>10</sup>

The AO's used consisted of a  $1s$ ,  $2s$ ,  $2p$  set on hydrogen and a  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ ,  $4s$ ,  $4p$  set on argon. The hydrogen orbitals are those given by Whitten<sup>11</sup> and the  $1s$ – $3p$  Ar orbitals are the SCF orbitals in terms of the  $[6s, 3p]$  set of Gaussian functions given by Petke *et al.*<sup>12</sup> The above  $[6s, 3p]$  set was augmented with a three term  $4s$  Gaussian-type orbital (GTO) and a set of three term  $4p$  GTO's given by Sramek and Gallup.<sup>13</sup> The  $4s$  and  $4p$  orbital parameters are given in Table I.

The argon  $4s$  and  $4p$  atomic orbitals were obtained by first performing a SCF calculation for the Ar atom. The basis set consisted of the  $[7s, 4p]$  set described above. From this calculation, the six lowest-energy SCF  $s$ -type orbitals (three closed and three virtual) and the four lowest-energy SCF  $p$ -type orbitals (two closed and two virtual) were used as the basis set for a limited CI calculation. The Ar:  $(1s)^2 (2s)^2 (2p)^6 (3s)^2$  SCF orbitals were frozen in all configurations. The CI wave function was expanded in terms of the ground state SCF configuration and all configurations resulting from a single excitation from the  $p_y$  orbital into one of the SCF virtual orbitals. Thus, there was a total of ten configurations.

The CI ground state wavefunction, because of Brillouin's theorem, consisted only of the SCF ground state configuration. The first excited state CI wave function consisted only of configurations resulting from a single excitation of a  $p_y$  electron into one of the SCF virtual  $s$ -type orbitals,

$$\Psi_{\text{CI}}^{(1)} = \sum_{i=1}^3 c_i^{(1)} (p_x)^2 (p_x)^2 (p_y)^1 (v_{s_i})^1, \quad (2)$$

where  $v_{s_i}$  represents one of the SCF  $s$ -type virtual orbitals. The argon  $4s$  atomic orbital is then taken as

$$c_1^{(1)} v_{s_1} + c_2^{(1)} v_{s_2} + c_3^{(1)} v_{s_3}. \quad (3)$$

TABLE I. Argon  $4s$  and  $4p$  orbital parameters.

Orbital	Coefficient	Scale factor
$4p^2$	0.226 178	0.032 694 9
	0.861 282	0.069 244 0
	-0.178 258	0.564 149
$4s$	0.125 882	0.021 965 6
	1.125 882	0.044 486 1
	-0.334 922	0.226 787

<sup>a</sup> $4p$  functions have lobe separations defined by the relationship  $\alpha_i \delta_i^2 = 0.01$ , where  $\alpha_i$  is the scale factor and  $\delta_i$  is the lobe separation.

TABLE II. Comparison of the MCVB asymptotic Ar\* ( $4s$ ) H energy difference and the experimental difference.

MCVB		Experimental <sup>a</sup>	
State	Energy (eV)	State	Energy (eV)
<sup>3</sup> Ar* ( $4s$ ) H, <sup>2</sup> $\Sigma^+$	11.618	Ar ( $4s_1, {}^3p_2$ )	11.548
<sup>3</sup> Ar* ( $4s$ ) H, <sup>2</sup> $\Pi$	11.622	Ar ( $4s, {}^3p_1$ )	11.623
<sup>1</sup> Ar* ( $4s$ ) H, <sup>2</sup> $\Sigma^+$	11.870	Ar ( $4s, {}^3p_0$ )	11.723
<sup>1</sup> Ar* ( $4s$ ) H, <sup>2</sup> $\Pi$	11.874	Ar ( $4s_1, {}^1p_1$ )	11.828

<sup>a</sup>Multiplet averages, Ref. 20.

The Ar\* ( $4s$ ) excited state is now representable by a single TSF

$$\Theta NPN[3p_x(1) 3p_y(2) 3p_x(3) 3p_x(4) 3p_y(5) 4s(6)], \quad (4)$$

where  $\Theta NPN$  is the Young operator appropriate for the desired multiplicity and  $4s = c_1^{(1)} v_{s_1} + c_2^{(1)} v_{s_2} + c_3^{(1)} v_{s_3}$ . The argon  $4p$  orbital was constructed in a manner completely analogous to the one just described.

In spite of the neglect of spin–orbit effects the above procedure produces good approximations to the energy spacings of the atomic  $4s$  and  $4p$  excited states of argon. A comparison between our asymptotic *ab initio* Ar\* ( $4s$ )H energy differences and experiment is given in Table II. As may be seen, the calculated differences are all within 0.1 eV of the experimental differences, and we have found it unnecessary to adjust the level of our calculated curves to match experiment.

For the molecular calculations, the Ar:  $(1s)^2 (2s)^2 \times (2p)^6 (3s)^2$  atomic orbitals have been frozen in all TSF's. Keeping the  $3s$  orbital doubly occupied is expected to have no serious effects except at close distances where significant amounts of Ar  $3s$ – $3p$  hybridization may occur.

The valence bond wave function for states of <sup>2</sup> $\Sigma^+$  symmetry include: (1) the TSF's

$$\Theta NPN[3p_x(1) 3p_x(2) 3p_y(3) H1s(4) 3p_x(5) \times 3p_x(6) 3p_y(7)]$$

and

TABLE III. Dominant molecular states of <sup>2</sup> $\Sigma^+$  symmetry.

Molecular states	Tableau symmetry functions
I. ArH	$\Theta NPN[3p_x 3p_x 3p_y H1s 3p_x 3p_x 3p_y]^a$
II. ArH* ( $2s$ )	$\Theta NPN[3p_x 3p_x 3p_y H2s 3p_x 3p_x 3p_y]$
III. ArH* ( $2p_0$ )	$\Theta NPN[3p_x 3p_x 3p_y H2p_x 3p_x 3p_x 3p_y]$
IV. Ar* ( <sup>2</sup> $P_0$ ) H <sup>-</sup>	$\Theta NPN[H1s 3p_x 3p_y 3p_x H1s 3p_x 3p_y]$ $\Theta NPN[3p_x 3p_y H2s 3p_x 3p_x 3p_y H1s]$
V. Ar* ( $4s^2S$ ) H <sup>+</sup>	$\Theta NPN[3p_x 3p_y 3p_x 4s 3p_x 3p_y 3p_x]$
VI. Ar* ( <sup>3</sup> $P_0$ ) H	$\Theta NPN[3p_x 3p_y 4p_x 3p_x 3p_x 3p_y H1s]$
VII. Ar* ( <sup>1</sup> $P_0$ ) H	$\Theta NPN[3p_x 3p_y 4p_x 3p_x 3p_x 3p_y H1s]$ $\Theta NPN[3p_x 3p_y 4p_x H1s 3p_x 3p_y 3p_x]$

<sup>a</sup>The particle labels are 1, 2, ..., 7 in the same order as the orbital labels and are implied.

TABLE IV. Dominant molecular states of  ${}^2\Pi$  symmetry.

Molecular states	Tableau symmetry functions
I. ArH* ( $2p_\sigma$ )	$\Theta NPN[3p_x 3p_y 3p_z H2p_x 3p_x 3p_y 3p_x]^{a}$
II. Ar* ( ${}^2P_\sigma$ ) H	$\Theta NPN[3p_x 3p_y H1s 3p_x 3p_x 3p_y H1s]$
III. Ar* ( ${}^2P_\sigma$ ) H $^{-3}$ (1s, 2s)	$\Theta NPN[3p_x 3p_y H2s H1s 3p_x 3p_x 3p_x]$
IV. Ar* ( ${}^2P_\sigma$ ) H $^{-3}$ (1s, $2p_\sigma$ )	$\Theta NPN[3p_x 3p_x 3p_x H1s 3p_x 3p_x H2p_x]$ $\Theta NPN[3p_y 3p_x 3p_x H2p_x 3p_x 3p_x H1s]$
V. Ar* ( ${}^2P_\sigma$ ) H $^{-1}$ (1s, $2p_\sigma$ )	$\Theta NPN[3p_x 3p_x 3p_x H1s 3p_x 3p_x H2p_x]$ $\Theta NPN[3p_y 3p_x 3p_x H2p_x 3p_x 3p_x H1s]$
VI. Ar* (4s, ${}^3P_\sigma$ ) H	$\Theta NPN[3p_x 3p_y 4s 3p_x 3p_x 3p_y H1s]$
VII. Ar* (4s, ${}^1P_\sigma$ ) H	$\Theta NPN[3p_x 3p_y 4s H1s 3p_x 3p_x 3p_x]$ $\Theta NPN[3p_x 3p_y 4s 3p_x 3p_x 3p_x]$

<sup>a</sup>See footnote Table III.

$$\Theta NPN[H1s(1) 3p_x(2) 3p_y(3) 3p_x(4) H1s(5) \\ \times 3p_x(6) 3p_y(7)]$$

and (2) all TSF's resulting from single and double excitations into the H2s, H2p $_\sigma$ , Ar4s, Ar4p $_\sigma$ , and Ar4p $_\sigma$  atomic orbitals from the above two TSF's. Also, the charge on the hydrogen atomic state cannot be less than -1. The above procedure gives a total of 114 TSF's and produces the necessary functions for the description of all the  ${}^2\Sigma^+$  states under consideration. In Table III we have listed the seven dominant molecular configurations and the nine TSF's necessary for their representation in the MCVB wave function. If we were discussing a system like HCl, these principal configurations could be described in terms of covalent and ionic contributions to the bond. The extra electron in ArH clouds the distinctions between such terms, but each of these configurations contribute significantly both to covalent and

ionic type bonding between the two atoms in the excited states considered. Our excitation scheme also produces TSF's which contribute to the description of the molecular and asymptotic atomic states. Similar single and double excitation schemes have been used successfully with other systems to discuss both long-range forces<sup>14</sup> and chemical bonding in hydrogen fluoride.<sup>15</sup>

The MCVB wave function for states of  ${}^2\Pi$  symmetry include: (1) the eight TSF's

$$\Theta NPN[3p_y(1) 3p_x(2) 3p_x(3) H1s(4) 3p_y(5) 3p_x(6) H2p_x(7)], \\ \Theta NPN[3p_y(1) 3p_x(2) 3p_x(3) H2p_x(4) 3p_y(5) 3p_x(6) H1s(7)], \\ \Theta NPN[3p_x(1) 3p_x(2) 3p_y(3) H2p_x(4) 3p_x(5) 3p_x(6) H2p_y(7)], \\ \Theta NPN[3p_x(1) 3p_x(2) 3p_y(3) H2p_y(4) 3p_x(5) 3p_x(6) H2p_x(7)], \\ \Theta NPN[3p_x(1) 3p_y(2) H1s(3) 3p_x(4) 3p_x(5) 3p_y(6) H1s(7)], \\ \Theta NPN[3p_x(1) 3p_y(2) H2p_y(3) 3p_x(4) 3p_x(5) 3p_y(6) H2p_y(7)], \\ \Theta NPN[3p_x(1) 3p_y(2) H2p_x(3) 3p_x(4) 3p_x(5) 3p_y(6) H2p_x(7)],$$

and

$$\Theta NPN[3p_x(1) 3p_y(2) 3p_x(3) H2p_x(4) 3p_x(5) 3p_y(6) 3p_x(7)],$$

and (2) all TSF's resulting from single and double excitations into the H2p $_\sigma$ , H2s, Ar4s, Ar4p $_\sigma$ , and Ar4p $_\sigma$  atomic orbitals from the above set of TSF's. Again the wave function is restricted by requiring the hydrogen atomic states in each TSF to have a charge no less than -1. This gives a total of 165 TSF's. The seven dominant molecular configurations and their associated TSF's are given in Table IV. The computed energies for the ArH states are presented in Table V and depicted graphically in Fig. 1. The discussion of configuration selection above for the  $\Sigma$  states applies to these  $\Pi$  states as well.

TABLE V. Interaction potential energies for the eight lowest states of ArH (units are hartrees, 1 h = 27.2107 eV).

R (a $_0$ )	X ${}^2\Sigma^+$	A ${}^2\Sigma^+$	B ${}^2\Pi$	C ${}^2\Sigma^+$	D ${}^2\Pi$	E ${}^2\Sigma^+$	F ${}^2\Pi$	G ${}^2\Sigma^+$
1.50	-526.47139	-526.38925	-526.39770	-526.34709	-526.21303	-526.31787	-525.78632	-525.92616
1.75	-526.79269	-526.70901	-526.71464	-526.67380	-526.54246	-526.63513	-526.17749	-526.34288
2.00	-526.96373	-526.87486	-526.87305	-526.84583	-526.71123	-526.78596	-526.42104	-526.57963
2.25	-527.06625	-526.96058	-526.94842	-526.92784	-526.79481	-526.85073	-526.58083	-526.70634
2.50	-527.13659	-526.99816	-526.97997	-526.96146	-526.83240	-526.87090	-526.68915	-526.76898
2.60	...	-527.00466	-526.98541	-526.96720	...	...	...	...
2.70	...	-527.00796	-526.98811	-526.97007	...	...	...	...
2.75	-527.18630	-527.00865	-526.98865	-526.97066	-526.84503	-526.86862	-526.76414	-526.79733
2.80	...	-527.00883	-526.98876	-526.97079	...	...	...	...
2.90	...	-527.00787	-526.98786	-526.96988	...	...	...	...
3.00	-527.22116	-527.00559	-526.98581	-526.96779	-526.84472	-526.85725	-526.81650	-526.80881
3.25	-527.24542	-526.99631	-526.97769	-526.95937	-526.85299	-526.85039	-526.83770	-526.82621
3.50	-527.26226	-526.98478	-526.96765	-526.94897	-526.87776	-526.86777	-526.82815	-526.82859
3.75	-527.27395	-526.97315	-526.95762	-526.93863	-526.89419	-526.88544	-526.82104	-526.82682
4.00	-527.28202	-526.96254	-526.94851	-526.92949	-526.90460	-526.89661	-526.83183	-526.82766
4.50	-527.29142	-526.94597	-526.93461	-526.91821	-526.91365	-526.90310	-526.84537	-526.83362
5.00	-527.29583	-526.93485	-526.92635	-526.91519	-526.91373	-526.89871	-526.85229	-526.84189
6.00	-527.29882	-526.92254	-526.92032	-526.90953	-526.90389	-526.89979	-526.85898	-526.85741
7.00	-527.29939	-526.91971	-526.91934	-526.90631	-526.89194	-526.89755	-526.86241	-526.86314
8.00	-527.29943	-526.91927	-526.91927	-526.91186	-526.88251	-526.88787	-526.86406	-526.86542
9.00	-527.29936	-526.91917	-526.91929	-526.91535	-526.87685	-526.88068	-526.86442	-526.86600
10.00	-527.29927	-526.91914	-526.91930	-526.91725	-526.87420	-526.87650	-526.86413	-526.86556
20.00	-527.29905	-526.91931	-526.91930	-526.91895	-526.87195	-526.87208	-526.86269	-526.86281

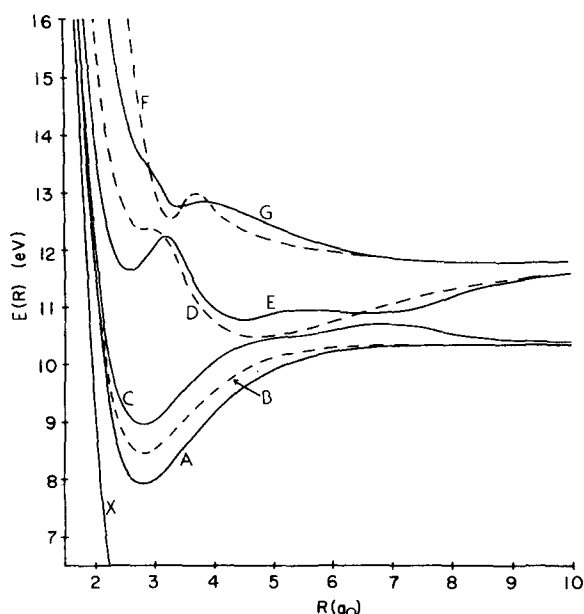


FIG. 1. Potential curves for the first seven excited states of ArH. The zero of energy is taken as the infinitely separated atoms in their ground states. The X, A, C, E, and G states are all  $^2\Sigma$ . (solid curves). The B, D, and F states are all  $^2\Pi$ . (Dashed curves.)

The first three excited states of ArH are usually thought of approximately as  $\text{ArH}^+$  with an electron in a Rydberg state, and the potential curves for these states should have shapes similar to that of the  $\text{ArH}^+(X^1\Sigma^+)$  potential. The interatomic potential for this system has been well characterized by Klingbeil.<sup>16</sup> Using elastic differential cross section data, he determined the binding energy to be 4.17 eV and the equilibrium separation to be 2.42 bohrs. Therefore, one would expect the states  $A^2\Sigma^+$ ,  $B^2\Pi$ , and  $C^2\Sigma^+$  to have equilibrium bond lengths of approximately 2.42 bohrs. This expectation is in agreement with the experimental work of Johns,<sup>1</sup> who reports an equilibrium separation for  $\text{ArH}(A^2\Sigma^+)$  of 2.45 bohrs. In Table VI we have given the binding energy and equilibrium separation for the first three excited states of ArH. For comparison the results from the work of Olson and Liu<sup>8</sup> and Matcha and Milleur<sup>7</sup>

TABLE VI. Binding energy and equilibrium separation for  $A^2\Sigma^+$ ,  $B^2\Pi$ , and  $C^2\Sigma^+$  symmetry states.

State	Quantity	SCF <sup>a</sup>	MCVB <sup>b</sup>	SCF-CF <sup>c</sup>
$A^2\Sigma^+$	$R_e$ (bohr)	2.63	2.80	2.40
	$D_e$ (eV)	2.250	2.436	3.856
$B^2\Pi$	$R_e$	2.58	2.79	2.43
	$D_e$	1.892	1.890	3.041
$C^2\Sigma^+$	$R_e$	2.60	2.79	2.39
	$D_e$	1.597	1.411	3.067

<sup>a</sup>Matcha and Milleur, Ref. 7.

<sup>b</sup>This work.

<sup>c</sup>Olson and Liu, Ref. 8.

have also been given. The absence of adequate polarization functions on H and the closed 3s subshell on Ar causes the MCVB to underestimate the dissociation energy and overestimate the equilibrium separation. We have tested the effect of opening the 3s shell by making a single calculation near the equilibrium separation. A 245 configuration calculation with open 3s subshell has a dissociation energy 0.15 eV greater than the closed calculation. We have not tested the effect of increasing the basis on H.

Toennies and co-workers<sup>17</sup> have obtained an accurate potential for the ground state ( $X^2\Sigma^+$ ) of ArH in the region (4.3 bohrs  $\lesssim R \lesssim$  9.1 bohrs). Measurements of the integral elastic cross sections for scattered hydrogen atoms have been analyzed and the experimental data fitted to a two parameter Lennard-Jones (6, 12) potential and a three parameter Slater-Buckingham  $\exp(\alpha, 6)$  potential. Results from our *ab initio* MCVB calculation are compared with the Lennard-Jones (6, 12) potential in Fig. 2.

### III. RATE OF QUENCHING OF $\text{Ar } ^3P$ BY H ATOMS

An examination of Fig. 1 shows that there is a somewhat isolated avoided crossing between the C and E curves at approximately 7 bohrs and another one between B and D at approximately 5 bohrs. If, during a collision, the diatomic system passes through these R values at an appropriate rate, then there is a high probability that the system will cross from one curve to another.

The Massey criterion<sup>18</sup> may be used to test this idea. The critical region between C and E has a  $\Delta E \sim 0.13$  eV,  $l \sim 1$  a.u., and  $v = 1.2 \times 10^6$  cm/sec. This relatively high velocity is due, of course, to the acceleration

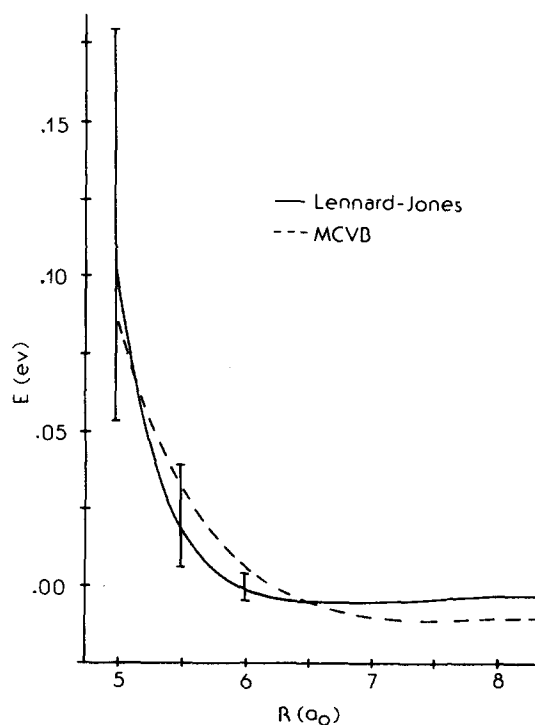


FIG. 2. Comparison of the *ab initio* ground state potential of ArH with the Lennard-Jones (6, 12) potential given by Toennies *et al.* (Ref. 16).

TABLE VII. *Ab initio* parameters for the Landau-Zener model.

Parameter	$E^2\Sigma^+, C^2\Sigma^+$	$D^2\Pi, B^2\Pi$
$V_{12}(R)$ (eV)	0.065	0.159
$\Delta V$ (eV/bohr)	0.501	0.513
$\Delta E$ (eV)	0.768	1.154

produced by the fall of the  $E$  potential curve from its asymptotic level to the value near 7 bohrs. Combining these quantities we see that  $\Delta E/\hbar v \sim 0.8$  which is neither very large nor very small. Although the Massey criterion is crude, it suggests that circumstances have cooperated in this system to give a reasonably high probability for curve switching under the conditions of the quenching experiments.

A more quantitative estimate of the rate constant is obtainable by use of Landau-Zener formula.<sup>9</sup> The probability for an electronic nonadiabatic transition between two molecular states is given as

$$P = 2e^{-w}(1 - e^{-w}), \quad (5)$$

where  $w$  is given as

$$w = \frac{2\pi V_{12}}{\hbar |\Delta V'|} |v|.$$

The cross section for the process is given as

$$\sigma(v) = 2\pi \int_0^{b'} bP db, \quad (6)$$

where

$$b' = \left( R_c^2 + \frac{2\Delta E}{v^2} R_c \right)^{1/2}$$

and  $\Delta E$  is the change in the reactant channel potential curve from its asymptotic value to its value at  $R_c$ , the internuclear separation at which the crossing takes place. The rate constant for the adiabatic transition can now be calculated by the introduction of the Boltzmann velocity distribution and integration over the entire velocity range.

We assume that the transfer of excitation from  $\text{Ar}^*(n=4)$  to  $\text{H}(n=2)$  proceeds via two different avoided crossings. One avoided crossing involves an interaction between the states  $E^2\Sigma^+$  and  $C^2\Sigma^+$  at  $R=6.61$  bohrs, while the second avoided crossing involves the states  $D^2\Pi$  and  $B^2\Pi$  at  $R=5.26$  bohrs. The rate constant for the proposed mechanism is given as

$$K = \frac{1}{2} k_{II} + \frac{1}{2} k_{E}. \quad (7)$$

Parameters for the Landau-Zener model are given in Table VII and we calculate a rate constant of  $25.2 \times 10^{10}$   $\text{cm}^3/\text{sec}$ .

#### IV. DISCUSSION

The description of experimental processes for excited states in terms of diabatic curves and their crossings can give a very useful picture of the physical effects operating. However, such curves are difficult to obtain

from variational calculations, which, in practical cases, must give approximations to adiabatic states. Nevertheless, the MCVB wave functions are linear combinations of basis functions which correspond to well-defined asymptotic states, and an examination of the coefficients in the wave function can give insight concerning diabatic states.

When Ar and H are near the equilibrium position for  $R$  in the  $A$  state, the overlap between MCVB basis functions can be large, and several coefficients of wave function configurations can also be large due to near cancellations. At larger separations, the overlaps are considerably smaller. The significance of the coefficients in the MCVB wave function depends upon the purity of the corresponding basis functions. This can be tested by considering the inverse of the overlap matrix  $S^{-1}$ .<sup>19</sup> For the basis functions and corresponding coefficients we consider in the following analysis, the purity is never less than 0.3 [ $=1/(S_{ii}^{-1})^{1/2}$ ] at any interatomic distances greater than 5 a.u. This means that there are no cancellations possible beyond this level, and a given coefficient in the MCVB wavefunction is describing the amount of superposition of a unique attribute of its basis function. At longer distances the situation is even more favorable for this type of interpretation, of course, and we do not attempt to carry this analysis to small distances. When we examine the  $A$ ,  $C$ , and  $E$  states specifically we find that in one or more of these the principal components of the wave function are the seven configurations listed in Table III.

In Figs. 3-5, we give the coefficients as a function of  $R$  for these configurations (where important) for each of the molecular states  $A$ ,  $C$ , and  $E$ , and we refer to these for discussion.

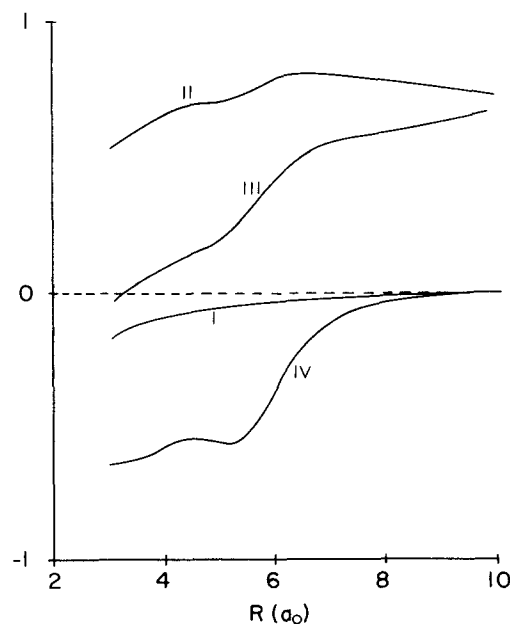


FIG. 3. Selected coefficients of the  $A^2\Sigma^+$  molecular wave function as a function of  $R$ . Roman numerals indicate coefficients of similarly numbered molecular states in Table III.

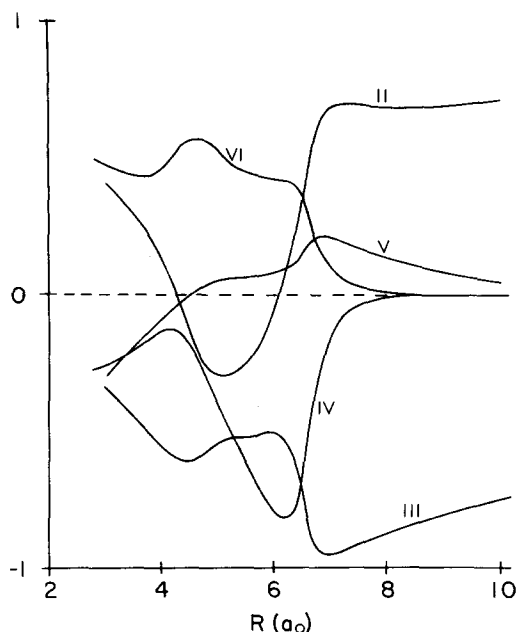


FIG. 4. Selected coefficients of the  $C^2\Sigma^+$  molecular wave function as a function of  $R$ . Roman numerals indicate coefficients of similarly numbered molecular states in Table III.

#### A. A state

This state, which our calculations indicate to be largely uninvolved in the excitation exchange, is quite simple at long distances and is essentially a linear combination of II and III of equal admixture. We must mention that the H-atom basis in this calculation was oriented so that  $(2s) + (2p_z)$  is polarized away from the Ar atom. The very large polarizability of H in the  $n=2$  state allows the electron to get away from the Ar effectively. The large dipole produced at the H end of the system also contributes to attraction at long distances by dipole-induced dipole interactions. The consequent polarization of Ar is not visible in any coefficients that can be seen at the scale in Fig. 3, of course. As  $R$  decreases, III is largely replaced by IV, the charge transfer state. This gives the A state at small distances the appearance of being a two-electron bond between Ar  $3p_z$  and H  $1s$  "underneath" a hydridelike  $1s'$  orbital. As can be seen, I is small at all distances.

#### B. C state

At large distances the C state is an admixture of II and III with the H( $n=2$ ) state polarized strongly toward the Ar. As the internuclear distance decreases, there is a fairly sharp rearrangement of the states in the region of the 7 bohr C-E avoided crossing, with the charge transfer state IV and excited Ar state VI becoming important. At closer distances IV disappears and the H( $n=2$ ) state changes to a polarization toward the Ar.

The presence of the V-type charge transfer state probably indicates a small coupling of state C to H Rydberg and continuum states and may in part be due to deficiencies in our basis.

#### C. E state

In referring to Fig. 5 it is seen that the E state is a complex mixture of II-VII asymptotic states. At long distances, we have predominantly VI with a significant amount of VII. As the critical region is approached, the IV charge transfer state grows significantly, while VI and VII fall. Again at  $\sim 7$  bohrs there is a relatively sharp switch to the states II and III with relative coefficients such that H( $n=2$ ) is strongly polarized toward Ar. Farther in, the VI and VII states return strongly as II and III reduce in importance.

A close examination of C and E show that the sequence of events suggested by Setser is qualitatively substantiated by these calculations for the  $^2\Sigma$  channels leading to exchange. In the present terms we have the system coming together in the E state, during which time the structure changes relatively slowly from Ar( $^3P$ )\*-H to Ar<sup>+</sup>-H<sup>-</sup>. At the critical region near 7 bohrs, the velocity and energy curve separation induce a transition to the C state with reasonable probability and in so doing the structure remains largely as Ar<sup>+</sup>-H<sup>-</sup>. As the two atoms continue towards one another, complicated changes we do not consider take place. However, as the two atoms eventually separate the systems which remain on the C curve through the 7 bohr region convert from an Ar<sup>+</sup>-H<sup>-</sup> structure to Ar-H\*( $n=2$ ) which is the output channel we are interested in. Of course, a significant fraction of the system could execute the E-C transition on the outward rather than the inward transit of the 7 bohrs region. The sequence of events and structures for these is qualitatively similar to those described above.

As we have seen above a significant number of the encounters undergo the transition in a  $^2\Pi$  state. The states given in Table IV constitute the important components of B and D, and we give graphs of the coef-

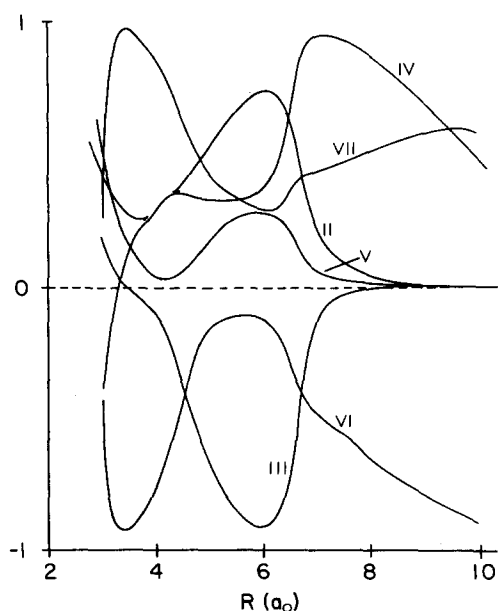


FIG. 5. Selected coefficients of the  $E^2\Sigma^+$  molecular wave function as a function of  $R$ . Roman numerals indicate coefficients of similarly numbered molecular states in Table III.

ficients in Figs. 6 and 7.

We first see that these curves are rather featureless compared to the  $^2\Sigma$  ones, even in the critical region near 5 bohrs.

#### D. B state

The B state is made up of only two states. At long distances I is the the only component, and by 5 bohrs III has become important. A covalent bond between Ar  $3p_\sigma$  and H  $1s$  has formed "underneath" the H  $2p_r$  orbitals. This involves a charge transfer state in which H<sup>-</sup> is predominately triplet  $1s, 2p_z$ . Such a state is certainly in the continuum for H<sup>-</sup> alone, but in our system the presence of the Ar<sup>+</sup> nearby provides stabilization and makes it an important term in the B state, even at 5 bohr.

#### E. D state

At long distances, D is predominately VI and VII. As  $R$  decreases the normal charge transfer state II and the III increase slowly. In the critical region there is an increase in I which then falls off again. However, no great changes occur in any of the coefficients.

When considering the excitation exchange via the  $^2\Pi$  channels we see that the charge transfer state plays a role somewhat different from that in the  $^2\Sigma$  channels. As the atoms approach one another in the D state, the charge transfer effect grows slowly, but when the transition occurs there is some considerable rearrangement and the  $\pi$ -like character of the system jumps from Ar to H almost exclusively, still retaining the ionic character, however. As the atoms separate in the B state, the Ar pulls the H  $1s$  back with it and leaves the H excited in the state which is the wanted exit channel for the reaction.

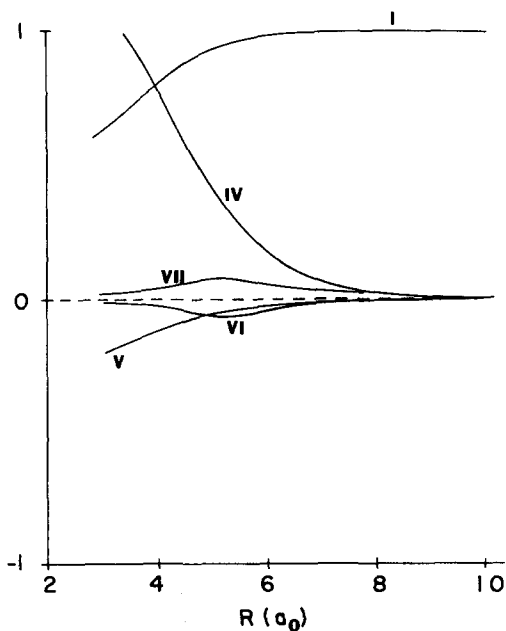


FIG. 6. Selected coefficients of the  $B^2\Pi$  molecular wave function as a function of  $R$ . Roman numerals indicate coefficients of similarly numbered molecular states in Table IV.

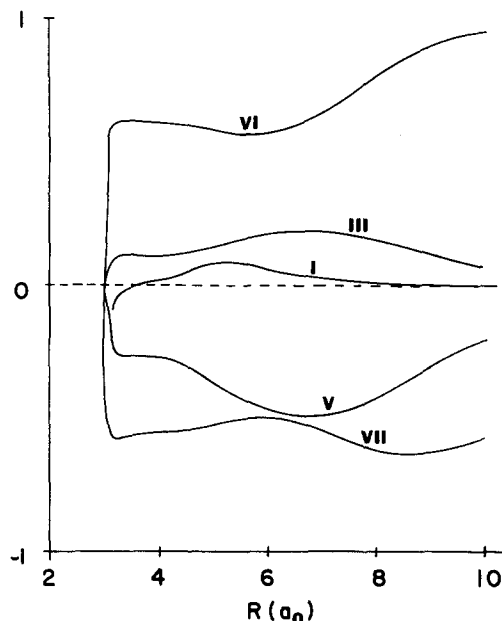


FIG. 7. Selected coefficients of the  $D^2\Pi$  molecular wave function as a function of  $R$ . Roman numerals indicate coefficients of similarly numbered molecular states in Table IV.

#### V. CONCLUSIONS

We feel that the foregoing discussion gives a reasonable and convincing description of the processes leading to the quenching of Ar( $^3P$ ) by H atoms. More complete CI calculations including additional configurations are not expected to modify the qualitative conclusions we have made from the present calculation.

Our calculated value of the rate constant is some ten times too large, but this reflects the special features of this system which cooperate to produce this large rate constant. In addition, all our qualitative estimates of curve switching rates have used two-state models. In a region with as many curves as this, there are other outgoing channels leading to other products and perhaps returning to the reactants, all of which we have ignored. All of these are expected to reduce the calculated rate constant.

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