

# Theoretical treatment of predissociation in the $A^2\Sigma^+$ , $B^2\Pi$ , and $C^2\Sigma^+$ states of HeH

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Theoretical calculations have been carried out on the predissociation of the  $A^2\Sigma^+$  state of HeH by radial coupling to the ground state,  $X^2\Sigma^+$ , of the  $B^2\Pi$  state by rotational coupling to  $X^2\Sigma^+$ , and of the  $C^2\Sigma^+$  state by radial coupling to  $A^2\Sigma^+$  and by rotational coupling to the  $B^2\Pi$  state. The results are in good agreement with experimental data regarding the predissociation of the  $A^2\Sigma^+$  and  $C^2\Sigma^+$  states, while they also predict significant predissociation of the positive rotational levels of the  $B^2\Pi$  state.

## I. INTRODUCTION

The observation and analysis of emission spectra of HeH is a relatively recent development.<sup>1-5</sup> Both discrete and continuous spectra have been reported, involving the first four Rydberg states of HeH, and very recently<sup>6</sup> from higher Rydberg states. The ground state of HeH is repulsive, while the excited states have Rydberg character and are bound with minima near the equilibrium bond length of the cation, HeH<sup>+</sup>,<sup>7,8</sup> cf. Fig. 1. At short internuclear distances the ground state also takes on Rydberg character, allowing for significant radial coupling and predissociation of the excited  $^2\Sigma^+$  states: The first excited state of HeH,  $A^2\Sigma^+$ , is heavily predissociated, with a lifetime in the order of picoseconds.<sup>9</sup> Thus it is justified to assume that the  $A^2\Sigma^+$  state does not decay radiatively.<sup>10,11</sup> Similarly, the  $C^2\Sigma^+$  state of HeH shows predissociation at low rotational levels, which is attributed to interaction with the ground state.<sup>2,12</sup> For this state, predissociation is also possible due to interactions with the continua of the lower-lying bound states,  $A^2\Sigma^+$  and  $B^2\Pi$ . Indeed, Ketterle *et al.* in a recent publication<sup>13</sup> report breaking off of several bands in the  $C^2\Sigma^+ \rightarrow A^2\Sigma^+$  spectra, at energies of about 8000 cm<sup>-1</sup> above the minimum of the  $C^2\Sigma^+$  state.

Rotational-electronic coupling of the ground state and the first excited  $^2\Pi$  state,  $B^2\Pi$ , may lead to predissociation of the positive rotational levels ( $B^2\Pi^+$ ) of the  $B^2\Pi$  state, while the negative rotational levels ( $B^2\Pi^-$ ) of this state may only decay by photoemission. It has been generally assumed that the  $B^2\Pi$  state does not predissociate,<sup>10,11</sup> although it is difficult to distinguish experimentally predissociation from levels  $v$  of the  $A^2\Sigma^+$  state and levels  $v-1$  of the  $B^2\Pi$  state. Indeed, SCF calculations predict that predissociation should be at least as significant as radiative dissociation of the  $B^2\Pi^+$  state of <sup>4</sup>HeH and <sup>3</sup>HeD,<sup>14</sup> in contrast to the usual assumptions.<sup>10,11</sup>

Previous theoretical work on the predissociation of the  $A^2\Sigma^+$  state has dealt mainly with the variation of the rates

with different vibrational levels.<sup>9</sup> The latest experimental report on this system<sup>13</sup> provides average widths for groups of rotational levels of the first two vibrational levels of the  $A^2\Sigma^+$  state for the various isotopic combinations of HeH. It is thus instructive to generate the corresponding theoretical information for comparison, since it is possible to calculate

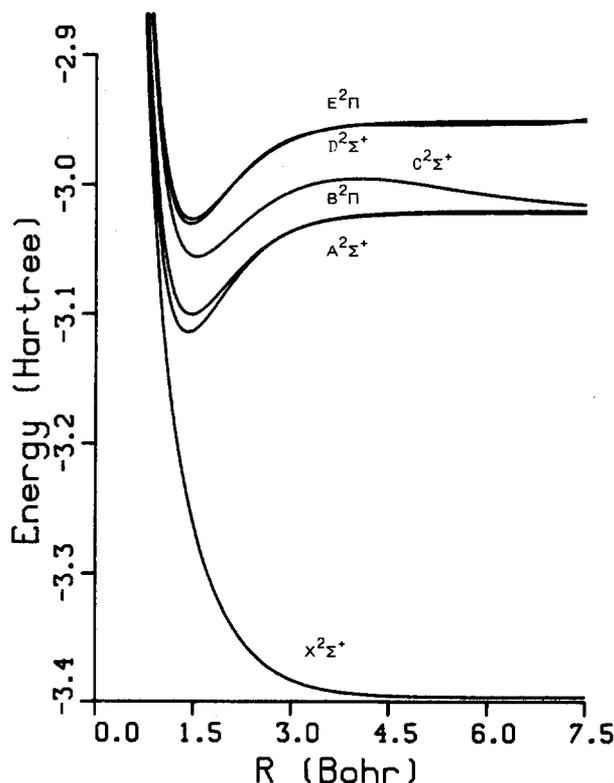


FIG. 1. Potential energy curves of HeH as calculated in Ref. 8. The Rydberg states correlate with ground state He and excited states of the H atom:  $A^2\Sigma^+$  with H( $2s^2S$ ),  $B^2\Pi$  and  $C^2\Sigma^+$  with H( $2p^2P$ ) and the higher Rydberg states with  $n=3$  excited states of the H atom.

widths for the individual rotational levels. An SCF study of this problem has reproduced the observed trends, but the calculated lifetimes are shorter than the experimental by a factor of 2–10,<sup>14</sup> whereas it is possible to obtain far better agreement by employing more accurate theoretical methods.<sup>9</sup> Similarly, it is of interest to calculate the predissociation of  $B^2\Pi$  with CI calculations and also to determine the process which is likely to cause the breakoff in the observed  $C^2\Sigma^+ \rightarrow A^2\Sigma^+$  system.

In the present work, theoretical calculations are presented on the rates of predissociation of the  $A^2\Sigma^+$  state at different rotational levels, on the rotational predissociation of the  $B^2\Pi^+$  state and on the predissociation of the  $C^2\Sigma^+$  state by radial coupling to the vibrational continuum of the  $A^2\Sigma^+$  state and by rotational coupling to the continuum of the  $B^2\Pi$  state.

### METHOD OF CALCULATION

The line widths are calculated with the aid of the golden rule formula,

$$\Gamma = 2\pi |\langle \varphi_v | \text{Op}(R) | \chi_i \rangle|^2, \quad (1)$$

where  $\varphi_v$  and  $\chi_i$  stand for the bound and the continuum wave function, respectively, at energy  $\epsilon_v$ . The operator  $\text{Op}(R)$  in the case of radial coupling is given by

$$\text{Op}(R) = -\frac{\hbar}{2\mu} \left[ B(R) + 2A(R) \frac{\partial}{\partial R} \right], \quad (2)$$

where  $A(R)$  and  $B(R)$  are analytic fits to the calculated electronic radial coupling matrix elements,  $\langle \Psi_i^{\text{el}} | \partial / \partial R | \Psi_j^{\text{el}} \rangle$  and  $\langle \Psi_i^{\text{el}} | \partial^2 / \partial R^2 | \Psi_j^{\text{el}} \rangle$ , respectively.

For rotational-electronic coupling the operator is given by

$$\text{Op}(R) = -\frac{\hbar}{2\mu} \sqrt{(N' \pm \Lambda')(N' + 1 \mp \Lambda')} \langle \Psi_i^{\text{el}} | L_{\pm} | \Psi_j^{\text{el}} \rangle, \quad (3)$$

where the quantum numbers  $N'$ ,  $\Lambda'$  refer to the bound level.

A quantity related to the width is the rate of predissociation, which is obtained using

$$K_{\text{pre}} = \frac{1}{\tau} = \frac{\Gamma}{\hbar}, \quad (4)$$

where  $\tau$  is the associated predissociation lifetime in seconds.

In the present work the calculation of the vibrational functions, both bound and continuum, is carried out employing expansions in a basis of square integrable functions. The density of states is introduced using either the Stieltjes derivative formula,

$$\tilde{F}(E) = \frac{(f_k + f_{k+1})}{2(\epsilon_{k+1} - \epsilon_k)} \quad \text{with} \quad \epsilon_{k+1} > E > \epsilon_k \quad (5)$$

or the interpolation formula

$$\tilde{F}(E) = \frac{2f_k}{\epsilon_{k+1} - \epsilon_{k-1}} \quad \text{for} \quad E = \epsilon_k. \quad (6)$$

In the Eqs. (5) and (6),  $f_k$  stands for the value of a property calculated using the unit-normalized functions  $\varphi_k$  instead of the corresponding continuum function  $\chi_k$ .  $\tilde{F}(E)$  then refers

to the energy normalized quantity corresponding to  $f_k$ . This procedure has been described elsewhere.<sup>9</sup> As in the previous calculations<sup>9</sup> the basis set employed is a set of trigonometric functions

$$\left\{ \frac{1}{\sqrt{R_L}}, \left( \frac{2}{R_L} \right)^{1/2} \cos \frac{2\pi n R}{R_L}, \left( \frac{2}{R_L} \right)^{1/2}, \sin \frac{2\pi n R}{R_L}, \right. \\ \left. \text{with } n = 1, 2, \dots, M \right\}, \quad (7)$$

where  $R_L$  is the upper integration limit. For the present calculations  $R_L = 6.0$  bohr and  $M = 45$ . The above basis has been employed for the matrix representation of the Hamiltonian operator,

$$H = -\frac{1}{2\mu} \nabla_R^2 + V(R) + \frac{N(N+1) - \Lambda^2}{2\mu R^2}, \quad (8)$$

where  $\mu$  is the reduced mass,  $V(R)$  is the potential provided by the solution of the electronic Schrödinger equation and  $N$  stands for the rotational quantum number. Diagonalization of the Hamiltonian matrix yields the eigenfunctions  $\varphi_v$  or  $\varphi_k$  depending on whether  $V(R)$  is bound or repulsive.

The electronic radial coupling matrix elements have been calculated previously.<sup>8,15</sup> The rotational coupling matrix elements have been generated in the present work, using electronic wave functions calculated as in the previous work. For these calculations the MRD-CI programs<sup>16,17</sup> were employed. The calculated rotational matrix elements are displayed in Fig. 2. They have been computed between each of

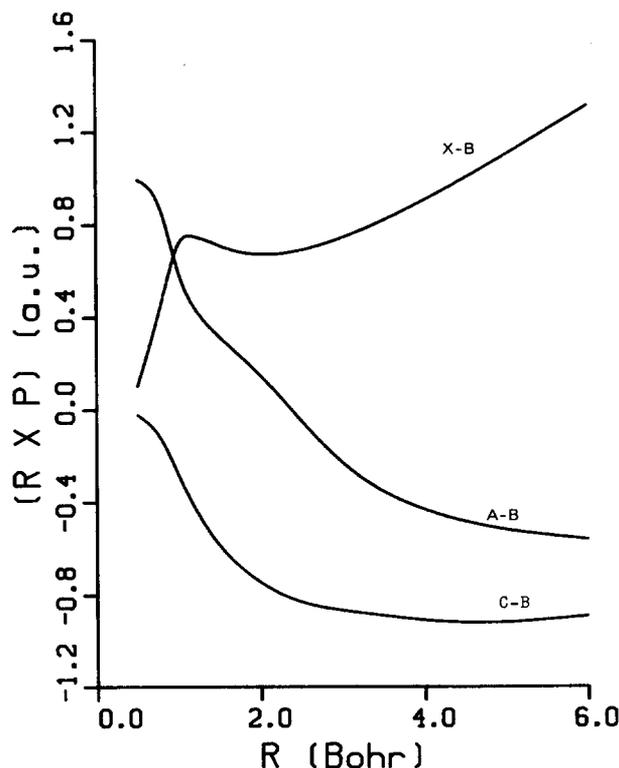


FIG. 2. Rotational-electronic coupling matrix elements for the  $C^2\Sigma^+ - B^2\Pi$ ,  $A^2\Sigma^+ - B^2\Pi$  and  $B^2\Pi - X^2\Sigma^+$  pairs of states.

the  ${}^2\Sigma^+$  states ( $X^2\Sigma^+$ ,  $A^2\Sigma^+$ , and  $C^2\Sigma^+$ ) and the  $\Pi_x$  component of the  $B^2\Pi$  state, and they must be multiplied by a factor of  $\sqrt{2}$  to obtain the actual matrix element needed in Eq. (3).

## RESULTS AND DISCUSSION

### Predissociation of $A^2\Sigma^+$ by $X^2\Sigma^+$

This particular process has been treated elsewhere<sup>9</sup> for the  $N = 0$  level of the  $\nu = 0-5$  vibrational levels, and it was found that the predissociation widths increase with vibrational level. Ketterle *et al.*<sup>13</sup> have observed a decrease in the widths with increasing rotational level, and reported average widths for the levels  $N < 5$  and  $N > 5$ . The widths calculated in the present work are listed in Tables I and II, for the  $\nu = 0$  and the  $\nu = 1$  levels, respectively, along with the available experimental data. As shown in Table I, there is a gradual decrease in the widths of the rotational levels, without a definite break between the two groups of levels,  $N < 5$  and  $N > 5$ . The theoretical values fall within the error bars of the experimental results. Thus the agreement between theory and experiment is excellent. For  $\nu = 1$ , cf. Table II, widths of only the  $N > 5$  levels of  ${}^3\text{HeD}$  and  ${}^4\text{HeD}$  have been measured. The theoretical values again show a gradual decrease with  $N$  while on the basis of the theoretical values, the experimental values correspond to  $N > 8$  in  ${}^3\text{HeD}$  and  $N = 0-14$  in  ${}^4\text{HeD}$ .

### Predissociation of $B^2\Pi$ by $X^2\Sigma^+$

As noted in the introduction, it is generally assumed that there is no predissociation of  $B^2\Pi$ . The radiative lifetime  $\tau_0$  is calculated as 17.9 ns,<sup>9</sup> while the experimental radiative lifetime is  $18 \pm 1$  ns.<sup>3</sup> The calculated predissociation lifetimes of the present work are listed in Table III, for different  $\nu$ ,  $N$  levels of the  $B^2\Pi$  state of  ${}^3\text{HeH}$ ,  ${}^4\text{HeH}$ ,  ${}^3\text{HeD}$ , and  ${}^4\text{HeD}$ . The present results show that predissociation should

TABLE I. Theoretical linewidths ( $\text{cm}^{-1}$ ) for different rotational levels ( $N$ ) of the  $\nu = 0$  level of the  $A^2\Sigma^+$  state.

$N$	${}^3\text{HeH}$	${}^4\text{HeH}$	${}^3\text{HeD}$	${}^4\text{HeD}$
0	5.10	4.27	1.31	0.83
1	5.03	4.21	1.30	0.82
2	4.89	4.11	1.28	0.81
3	4.69	3.95	1.25	0.79
4	4.09	3.75	1.21	0.77
5	3.81	3.52	0.98	0.75
6	3.50	2.94	0.94	0.72
7	3.16	2.68	0.89	0.68
8	2.81	2.40	0.83	0.53
9	2.24	2.12	0.68	0.50
10	1.92	1.67	0.60	0.46
11	1.62	1.42	0.55	0.43
12	1.21	1.19	0.50	0.33
13	0.98	0.88	0.45	0.30
14	0.77	0.70	0.33	0.27
15	0.53	0.55	0.29	0.24
Exp. (Ref. 13, average values)				
$N < 5$	$3.9 \pm 1$	$3.1 \pm 1$	$1.2 \pm 0.4$	$1.1 \pm 0.4$
$N > 5$	$2.1 \pm 0.4$	$1.2 \pm 0.4$	$0.0 \pm 0.4$	$0.5 \pm 0.4$

TABLE II. Theoretical lifetimes ( $\text{cm}^{-1}$ ) for different rotational levels ( $N$ ) of the  $\nu = 1$  level of the  $A^2\Sigma^+$  state.

$N$	${}^3\text{HeH}$	${}^4\text{HeH}$	${}^3\text{HeD}$	${}^4\text{HeD}$
0	13.6	11.6	4.33	2.96
1	13.4	11.5	4.30	2.93
2	13.1	11.2	4.22	2.89
3	12.6	10.8	4.11	2.82
4	11.9	10.2	3.98	2.74
5	10.3	9.59	3.81	2.64
6	9.51	8.87	3.18	2.52
7	8.62	7.49	2.99	2.38
8	7.71	6.74	2.79	2.24
9	6.78	5.97	2.57	1.80
10	5.87	5.20	2.35	1.66
11	4.58	4.46	2.13	1.52
12	3.82	3.41	1.65	1.38
13	3.12	2.82	1.46	1.24
14	2.50	2.79	1.28	0.93
15	1.75	1.82	1.11	0.81
Exp. (Ref. 13, average values)				
$N < 5$	...	...	...	...
$N > 5$	...	...	$1.9 \pm 1$	$2.0 \pm 1$

be significant in  ${}^3\text{HeH}$  and  ${}^4\text{HeH}$ , even for the lowest  $\nu$ ,  $N$  levels. In  ${}^3\text{HeD}$  it is slower than radiative dissociation at the low  $N$  levels, but should be significant for the  $N = 5$  level, which seems to be the most populated level in the experimental studies of this problem.<sup>12</sup> Similarly, the  $N = 5$  level of  $\nu = 0$ ,  $B^2\Pi$  in  ${}^4\text{HeD}$ , has shorter predissociation lifetime than the radiative lifetime (cf. Table III). Thus the present results are in support of the previous SCF calculations on this problem,<sup>12</sup> and indicate that assumptions of absolutely no predissociation in the  $B^2\Pi$  state are probably not correct. The theoretical results show that  $B^2\Pi^+$  undergoes predissociation in addition to photoemission.

### Predissociation of $C^2\Sigma^+$ by $A^2\Sigma^+$ and $B^2\Pi$

The low rotational levels of the  $C^2\Sigma^+$  state of HeH undergo predissociation by radial coupling to the ground state. However, the observed predissociation at energies of

TABLE III. Predissociation lifetimes (ns) of the  $B^2\Pi$  state.<sup>a</sup>

$\nu, N$	${}^3\text{HeH}$	${}^4\text{HeH}$	${}^3\text{HeD}$	${}^4\text{HeD}$
0, 1	6.1	6.4	90.0	220.1
2	2.1	2.1	30.1	73.3
3	1.1	1.5	15.1	36.7
4	0.6	0.9	9.1	22.0
5	0.4	0.7	6.2	14.7
1, 1	1.7	2.4	29.5	46.1
2	0.6	0.8	9.9	15.4
3	0.3	0.4	5.0	11.5
4	0.2	0.3	3.0	6.9
5	0.1	0.2	2.0	4.6
2, 1	0.9	1.2	12.3	27.1
3, 1	0.7	0.9	7.4	15.5
4, 1	0.7	0.9	5.7	11.5

<sup>a</sup> See the text, Eq. (4).

TABLE IV. Theoretical rates<sup>a</sup> (s<sup>-1</sup>) of predissociation of the C<sup>2</sup>Σ<sup>+</sup> state.

v'	N'	<sup>3</sup> HeH		<sup>4</sup> HeH	
		C-A	C-B	C-A	C-B
v' = 0	14	9.63[8]	3.41[8]	-	-
	15	1.25[9]	2.80[8]	1.04[9]	2.06[8]
	16	3.49[9]	2.32[8]	1.22[9]	1.07[8]
	17	4.86[9]	1.79[8]	2.29[9]	1.52[8]
	18	5.43[9]	1.56[8]	3.91[9]	1.27[8]
	19	5.24[9]	1.13[8]	4.37[9]	9.71[7]
v' = 1		<sup>3</sup> HeD		<sup>4</sup> HeD	
		C-A	C-B	C-A	C-B
	14	6.52[9]	6.19[7]	-	-
	15	6.25[9]	7.31[7]	-	-
	16	3.49[9]	5.90[7]	5.76[9]	3.59[7]
	17	4.02[9]	5.90[7]	4.67[9]	3.27[7]
v' = 2		<sup>3</sup> HeD		<sup>4</sup> HeD	
		C-A	C-B	C-A	C-B
	11	9.37[9]	1.06[8]	-	-
	12	9.71[9]	1.04[8]	7.70[9]	4.67[7]
	13	7.78[9]	9.91[7]	8.75[9]	5.56[7]
	14	6.97[9]	1.12[8]	7.52[9]	5.05[7]
15	5.74[9]	1.25[8]	7.03[9]	6.11[7]	
16	5.14[9]	1.16[8]	6.36[9]	6.20[7]	
17	3.99[9]	1.17[8]	5.83[9]	6.79[7]	
18	2.88[9]	1.15[8]	5.09[9]	6.07[7]	
19	1.98[9]	1.06[8]	4.16[9]	6.03[7]	

<sup>a</sup> See the text, Eq. (4). Values in brackets denote powers of ten.

8000 cm<sup>-1</sup> above the equilibrium energy of the state may be due to different processes. As noted by Ketterle *et al.*,<sup>13</sup> the levels at the above energy are imbedded in the vibrational continua of the two lower states A<sup>2</sup>Σ<sup>+</sup> and B<sup>2</sup>Π (see Fig. 1) and radial C<sup>2</sup>Σ<sup>+</sup>-A<sup>2</sup>Σ<sup>+</sup> coupling, as well as rotational-electronic C<sup>2</sup>Σ<sup>+</sup>-B<sup>2</sup>Π coupling may lead to the observed predissociation. The results of the present calculations are given in Table IV, where the predissociation rates for the energy levels corresponding to the experimental observations have been compiled. As shown in Table IV, the present results confirm the existence of predissociation of the C<sup>2</sup>Σ<sup>+</sup> state by A<sup>2</sup>Σ<sup>+</sup> and B<sup>2</sup>Π at the energy levels considered. The contribution of the C<sup>2</sup>Σ<sup>+</sup>-A<sup>2</sup>Σ<sup>+</sup> interaction leads to higher predissociation rates than the C<sup>2</sup>Σ<sup>+</sup>-B<sup>2</sup>Π interaction by one to two orders of magnitude. Thus it might be expected that the present two-state treatment of this multi-state problem is adequate. A more accurate, multichannel

approach might alter the actual numbers somewhat, but is not expected to alter the overall picture obtained in the present work.

## CONCLUSION

Calculations have been presented on several predissociation processes in <sup>3</sup>HeH, <sup>4</sup>HeH, <sup>3</sup>HeD, and <sup>4</sup>HeD. The results on the predissociation of A<sup>2</sup>Σ<sup>+</sup> by X<sup>2</sup>Σ<sup>+</sup> are in excellent agreement with experiment. Predissociation of the positive rotational levels of the B<sup>2</sup>Π state is predicted to be significant, indicating that the observed bound-free emission assigned to the B<sup>2</sup>Π → X<sup>2</sup>Σ<sup>+</sup> must originate mostly from the negative rotational levels of the B<sup>2</sup>Π state.

The results on the predissociation of high rotational levels of the C<sup>2</sup>Σ<sup>+</sup> state show that the observed breakoffs in the C<sup>2</sup>Σ<sup>+</sup> → A<sup>2</sup>Σ<sup>+</sup> spectra are caused mainly by the interaction of C<sup>2</sup>Σ<sup>+</sup> with the vibrational continuum of A<sup>2</sup>Σ<sup>+</sup>.

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