Effects of an external electric field on $^1P^o$ resonances of H^-

John J. Wendoloski and William P. Reinhardt
Department of Chemistry, University of Colorado, Boulder, Colorado 80309
and Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, Colorado 80309
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Positions, widths, and oscillator strengths for the $2s$-$2p$ "shape" resonance and the lowest Feshbach resonance in the $^1P^o$ spectrum of H^- have been computed via the method of complex coordinates. The dc Stark broadening of the shape resonance has been determined giving a quantitative estimate of the effects of plasma microfields on the resonance and explaining the negative observational results of Ott *et al.* [Phys. Rev. A **12**, 2009 (1975)].

I. INTRODUCTION

Resonant structure in the H^- photodetachment spectrum has received considerable attention over the past several years.[1-11] Of particular interest has been the "$2s$-$2p$" shape resonance lying just *above* the threshold for detachment to the hydrogenic $n=2$ levels. This shape resonance has been previously discussed theoretically by Macek,[1] Macek and Burke,[2] Hyman *et al.*,[3] Wulfman,[4] Herrick and Sinanoğlu,[5] Lin,[6] and Broad and Reinhardt.[7] Based on early estimates [three-state close coupling (1967)[1] and (1972)[3]] of the resonant oscillator strength, Ott *et al.*[8] (1975) attempted to observe the shape resonance in uv emission from a local-thermodynamic-equilibrium (LTE) hydrogen arc plasma with negative results. Attempts at astronomical observation are discussed by Snow.[9] More recently, Broad and Reinhardt[7] (1976) recalculated the oscillator strength using highly correlated initial- and final-state wave functions and obtained an estimate smaller than the three-state close coupling result by a factor of ~2. This new estimate is consistent with the recent direct observation of the resonance by Bryant *et al.*[10] (1977) and new plasma experiments by Behringer and Thoma[11] (1977).

It is the purpose of this paper to apply the complex-coordinate technique to the problem of calculation of the dc Stark broadening of the H^- shape resonance. Additionally, new values of the field-free resonance energies, widths, and oscillator strengths for the shape resonance and lowest $^1P^o$ Feshbach resonance are obtained from the vectors arising in the complex-coordinate calculation, avoiding the necessity for the intuitive graphical estimate of Refs. 1 and 7.

A brief review of the necessary theory appears in Sec. II, results are presented in Sec. III, and a discussion appears in Sec. IV.

II. THEORETICAL BACKGROUND

A. Dilatation transformation and the Stark problem

The use of the theory of rotated complex coordinates (i.e., the transformation $r \to re^{i\theta}$, r being an interparticle distance) to investigate the spectrum of atomic systems is becoming increasingly common.[12] The basis of the technique is that under the dilatation transform $r \to re^{i\theta}$ the nonrelativistic atomic Hamiltonian H is transformed to $H(\theta)$, a non-self-adjoint operator some of whose complex eigenvalues are independent of θ and represent complex resonance energies, the real part giving the "position" E^{res} of the resonance, and the imaginary part the "width" $\frac{1}{2}\Gamma$. The theory of such coordinate transformations dates back to Reggie[13] and has been considerably generalized by Balslev and Combes[14] and Simon,[15] among others. The appropriateness of the dilatation transformation to the atomic problem relates both to the spherical symmetry and to the analyticity of the Coulomb potential. However, numerical experiments carried out in investigation of the H-atom dc Stark effect[16] have indicated that excellent results may be obtained even though the Stark operator

$$\sum_{i=1}^{N} Fz_i = \sum_{i=1}^{N} Fr_i \cos\alpha_i ,$$

(F being the field strength, and $z_i = r_i \cos\alpha_i$ the z coordinate of the "i" electron) lacks both the spherical symmetry and asymptotic boundedness properties necessary for the usual application of the theory of dilatation transformations, as is discussed more thoroughly in Ref. 16. Avron and Herbst,[17] and Cerjan and Reinhardt[17] have suggested that the "translation" transformation $z \to z + iq$ (q being a real distance) is more appropriate to the Stark problem, although the dilatation transformation used in the present paper has recently

been shown to also provide a correct analytic continuation of the resolvent.[18]

B. Computational techniques

Numerical calculations using the method of rotated complex coordinates are very simply carried out using standard configuration-interaction (CI) techniques. The two-electron Stark Hamiltonian

$$H^{\text{Stark}} = H^{\text{atomic}}(\vec{r}_1, \vec{r}_2) + \sum_{j=1}^{2} F r_j \cos\alpha_j \tag{1}$$

gives rise to the CI matrix form

$$\underline{H}^{\text{Stark}} = \underline{H}^{\text{atomic}} + F\underline{V}^{\text{field}} \tag{2}$$

which, under the dilatation transformation converts to

$$\underline{H}(\theta)^{\text{Stark}} = e^{-2i\theta}\underline{T}^{\text{atomic}} + e^{-i\theta}\underline{V}^{\text{atomic}} + e^{i\theta}F\underline{V}^{\text{field}}, \tag{3}$$

where $\underline{T}^{\text{atomic}}$ and $\underline{V}^{\text{atomic}}$ are, respectively, the atomic kinetic and potential energy matricies. $\underline{H}(\theta)^{\text{Stark}}$ is thus a complex symmetric matrix, easily constructed from the real symmetric matricies $\underline{T}^{\text{atomic}}$, $\underline{V}^{\text{atomic}}$, and $\underline{V}^{\text{field}}$. As $\underline{H}^{\text{atomic}} = \underline{T}^{\text{atomic}} + \underline{V}^{\text{atomic}}$ is spherically symmetric it has a block structure labeled by the usual L-S manifolds of two-electron states ^1S, ^1P, ^1D, ... $\underline{V}^{\text{field}}$ has no diagonal block elements, and only couples the two-electron blocks of type ^1L to $^1(L \pm 1)$. The resulting block structure of $\underline{H}(\theta)^{\text{Stark}}$ is shown in Fig. 1.

The present computations were carried out by performing a full two-electron CI within a subspace defined by taking a finite number of orthogonal

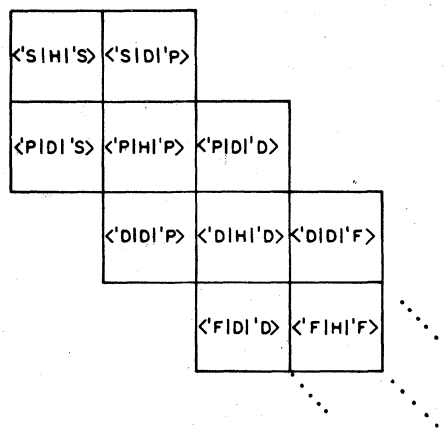

FIG. 1. Tridiagonal block structure of the two-electron Stark Hamiltonian. The LS-coupled two-electron blocks of ^1S, ^1P, ^1D, ··· symmetry of the atomic Hamiltonian H are coupled by the usual dipole coupling operator "D."

Laguerre functions of the form

$$\phi_{nl}(\lambda r) = \left(\frac{n!}{(2l+2+n)!}\right)^{1/2} (\lambda r)^{l+1} e^{-\lambda r/2} L_n^{2l+2}(\lambda r). \tag{4}$$

These radial functions were combined with $Y_{lm}(\theta, \phi)$'s and coupled to give atomic states of appropriate symmetry within the L-S coupling scheme. In general we will denote a basis by, for example,

$$^1P^o = i, j, k, \ldots (\lambda_s, \lambda_p, \lambda_d, \ldots) \tag{5}$$

with i, j, k denoting the number of $l = 0, 1, 2, 3, \ldots$ (s, p, d, f, ...) functions used in the CI, with the λ_l being the corresponding exponents defined in Eq. (4). (Note that the λ's are *twice* the corresponding Slater exponent.) When exponents of all symmetries are constrained to be identical only a single value of λ is reported ($\lambda = \lambda_s = \lambda_p = \lambda_d = \ldots$).

III. RESULTS

In this section we present the results of numerical calculations to determine the positions and widths of the poles of the resolvent $\langle (z - \mathrm{H})^{-1} \rangle$ giving rise to the lowest member of the Feshbach series of resonances which occur *below* the hydrogenic $n = 2$ threshold, and for the $2s2p$ "shape" resonance occurring just above the $n = 2$ threshold. In Sec. III A we consider the field-free case [i.e., $F = 0$ in Eqs. (1) and (3)] to determine the positions and oscillator strengths of the two resonances, and in Sec. III B we consider the added effect of a dc electric field on the shape resonance.

A. $^1P^o$ resonances in H^-

Convergence to the complex eigenvalues of $H(\theta)^{\text{atomic}}$ must be carried out with great care. While in the limit of an infinite basis the resonance eigenvalues will be independent both of basis and of "θ" provided that θ is large enough to expose the resonance, in a truncated basis set neither of these results obtains. In practice the method of choice is to choose a basis set and to carry out calculations for a range of θ values, looking for a stationary point in these θ-trajectories, as discussed by Doolen[19] and illustrated for the Stark case in Ref. 16. Typical examples of this procedure are shown in Fig. 2, where the location of the $^1P^o$ shape resonance is investigated for the 9, 9, 7 ($\lambda = 0.5$) basis set, the sharp kink in the θ trajectories indicating stationary points of the calculation. Convergence seems reasonable for the shape resonance giving an energy (pole position) of $E^{\text{res}} = 0.124\,351$ a.u. and $\frac{1}{2}\Gamma$ and 2.60×10^{-4} a.u., which corresponds to 17.6 meV above the $n = 2$ threshold and a full width at half maximum

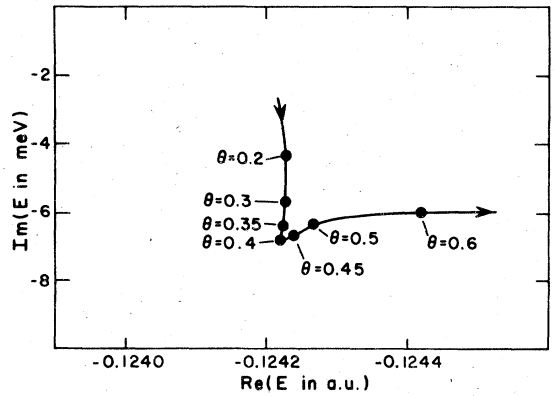

FIG. 2. θ trajectory for the field-free $2s$-$2p$ "shape" resonance in H^- with the 9, 9, 7 ($\lambda = 0.5$) basis described in the text, taking the "kink" in the trajectory as indicating the resonance position as $(E^{res} - \frac{1}{2}i\Gamma) = -0.124\,351 - i2.60\times10^{-4}$ a.u.

TABLE I. Convergence of the oscillator strength f for the $2s$-$2p$ shape resonance in H^-.

Resonance	^1P basis [a]	θ	f
Shape	10,10,8(0.4386)	0.3	0.011
		0.4	0.013
		0.425	0.014
		0.44 [b]	0.015
		0.5	0.040
	10,10,8(0.5)	0.425 [b]	0.016
	9,9,7(0.5)	0.4 [b]	0.015
Feshbach	10,10,8(0.4590)	0.2	0.0011
		0.27 [b]	0.0013
		0.4	0.0016

[a] All f's were calculated using $^1S = 10,10,7(2.0)$ H^- ground state which gave $E = -0.5274$ a.u.
[b] Kink points.

(FWHM) of 14.1 meV, in good agreement with Broad and Reinhardt's photoabsorption values of 18 and 15 meV,[7] respectively, and with the e-H scattering results of Macek and Burke.[2] As the position and width are very close to those determined from the photoabsorption work of Ref. 7, we compare the calculated photoabsorption line shape [resulting from a 10, 10, 6 ($\lambda = 0.5$) J-matrix calculation] with the recent experimental results of Bryant *et al.*[10] in Fig. 3. Agreement is seen to be excellent. The graphically estimated oscillator strength of the shape resonance was determined to be 0.024, compared to Macek's estimate of 0.044. Direct calculation of the oscillator strength using the eigenvectors corresponding to points on the θ trajectories gives a value of 0.015 as is documented in Table I. This lower value indicates the ambiguity in separating resonant from nonresonant contributions in the graphical analyses of Refs. 2 and 7.

With the limitations of modest CI calculations the Feshbach resonance is less well converged. Typical θ trajectories are shown in Fig. 4 for 10, 10, 8 (0.4590) calculations for a variety of values of λ. Although the position is well converged, the width is not well converged as a function of λ. The width was determined by taking the θ-trajectory "kink" points and determining whether these kinks had a stationary point when plotted as

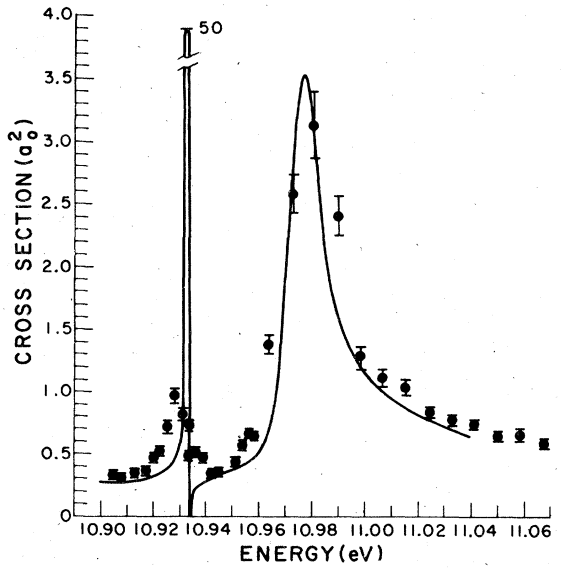

FIG. 3. Comparison of the experimental data of Bryant *et al.* (Ref. 10) and the theory of Broad and Reinhardt (solid curve) (Ref. 7) for photodetachment of H^- near the opening of the $n = 2$ final-state threshold.

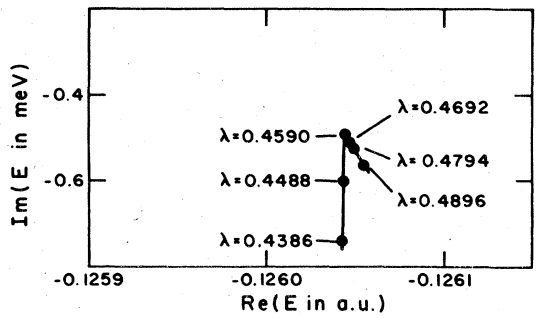

FIG. 4. Convergence of the lowest field-free $^1P^o$ Feshbach resonance in H^-. The trajectory shown in this case results from a plot of the kink points of individual θ trajectories as a function of λ, the basis set of scale parameter, for a 10, 10, 6 (λ) basis. If we identify the *second-order* kink in the above plot with resonance position, we find $E^{res} - \frac{1}{2}i\Gamma = -0.126\,048 - i1.9\times10^{-5}$ a.u.

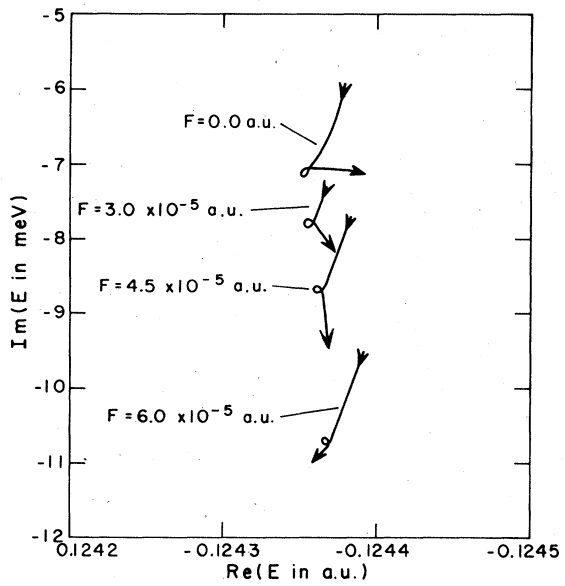

FIG. 5. Stark field dependence of the position and width of the shape resonance for fields of $F = (0, 3, 4.5, \text{ and } 6) \times 10^{-5}$ a.u. (1 a.u. $= 5.1 \times 10^9$ V/cm). The Stark broadening parameters of Table III were obtained from the kink positions of the θ trajectories shown in the figure. Im $E = -\frac{1}{2}\Gamma$ where Γ = FWHM for a Breit-Wigner line shape.

a function of λ. This second-order variational technique yielded $E^{\text{res}} = -0.126\,048$ a.u. and $\frac{1}{2}\Gamma = 1.9 \times 10^{-5}$ a.u., (FWHM = 1.05 meV) for the lowest $^1P^o$ Feshbach resonance. The resonance position is in good agreement with previous values.[18] The FWHM is ~20 times that determined by Lipsky[21]; however, the final-state wave function used by Lipsky was quite crude, lacking the capability of representing both correlation and polarization. Additionally, Lipsky's resonant wave function was converged within the framework of the *incomplete* set of bound hydrogenic functions, whereas the Laguerre-type functions of Eq. (4) form a complete discrete set.

The oscillator strength of the Feshbach resonance was estimated to be ~0.03 (see Table I) giving an approximate ratio of $f_{\text{Fesh}}/f_{\text{shape}} \sim 1/11.5$ which compares reasonably well with the estimate of 1/14 from the data of Gram *et al.*[22]

B. dc Stark effect

As shown in Fig. 1, the field couples the ^1P shape resonance with the neighboring ^1S and ^1D manifolds; the ^1D is in turn coupled to ^1F, ^1G, etc. For the hydrogen atom in a dc Stark field it was found[16] that a very large number of angular momenta were needed to be included to obtain convergence of the Stark widths at low fields. However, for the H atom the zero-order atomic states are all effectively closed channels, and thus the Stark ionization is determined by tunneling as in the conventional picture. However, for H^- even at the rather low electric fields in the plasma experiments of Ott *et al.* (10^5 V/cm), we expected that the dominant broadening would arise from coupling of the $^1P^o$ resonances to the neighboring $1sks$, $2sks$, $1skd$, $2skd$, $2pkp$, $^1S^e$, $^1D^e$ continua, and that both "back coupling" of these manifolds of states to the $^1P^o$ states and inclusion of ^1F, ^1G, and higher L states would be negligible. This turned out to be the case. The reasoning was simply that the $^1S^e$ and $^1D^e$ manifolds of states are "open" channels and thus Stark ionization (and hence width of the resonance) is dominated by direct coupling to neighboring open channels, rather than by tunneling.[23] Typical θ trajectories are shown as a function of field strength F for the shape resonance (Fig. 5) in the limit of the $^1P^o$ resonant state coupled only to the neighboring $^1S^e$, $^1D^e$ manifolds. Table II documents the fact that inclusion of higher partial waves does not affect the Stark broadening of the shape resonance. The results of the field dependence of the resonance

TABLE II. Effect of indirectly coupled L states on the shape resonance.[a] As discussed in the text the direct coupling of the ^1P resonance (lying above the $n=2$ hydrogenic threshold) to the neighboring open ^1S, ^1D continua $1sks$, $2sks$, $2pkp(^1S)$, $1skd$, $2skd$, $2pkp(^1D)$ dominates the Stark broadening.

θ	Energy $(E - \frac{1}{2}i\Gamma)$ ^1S, ^1P, ^1D basis[b]		^1S, ^1P, ^1D, ^1F, ^1G basis[c]	
0.3	−0.124 209	−0.000 033 1i	−0.124 209	−0.000 033 2i
0.4	−0.124 051	−0.000 036 4i	−0.124 052	−0.000 036 4i
0.5	−0.124 181	−0.000 026 6i	−0.124 181	−0.000 026 6i

[a] $F = 1.0 \times 10^{-4}$ a.u.
[b] $^1S = 5,5,3(0.5)$, $^1P = 9,9,7(0.5)$, $^1D = 5,5,3(0.5)$.
[c] $^1S = 5,5,3(0.5)$, $^1P = 9,9,7(0.5)$, $^1D = 5,5,3(0.5)$, $^1F = 5,0,0,5(0.5)$, $^1G = 5,0,0,0,5(0.5)$.

TABLE III. Effect of dc Stark field on the width (FWHM) of the shape resonance (1 a.u. = 5.1×10^9 V/cm).

Field (a.u.)	Width (meV) [a]
0.00	14.1
0.10(−5)	14.1
3.00(−5)	15.5
4.50(−5)	17.4
6.50(−5)	21.0
7.50(−5)	26.1

[a] Taken from the kink values.

positions are shown in Table III. Inspection of the coefficients in the configuration interaction representation of the wave function indicated that the oscillator strength for transition to the ground state was essentially independent of the field for the values considered here.[24]

Comparison with the plasma experiments of Ott *et al.*[8] was made by first simulating the molecular H_2 background on a sloping baseline. Then the theoretical curve of Broad (Fig. 3) was averaged over the appropriate Holtzmark distribution of fields[25] and folded into the molecular background using the relative intensities of Ott *et al.*[8] Finally, the 10% signal-to-noise ratio of Ott was included, giving the spectrum shown in Fig. 6, which is compared to the experimental observations of Ott *et al.* at 15 000 °K. The simulated experimental results are clearly consistent with the negative results of Ott *et al.* However, as is evident from the simulated spectrum, there is a slight remnant of the resonance at 1130 Å, suggesting that appropriate signal averaging might have revealed the resonance. More recently Behringer *et al.*[11] have repeated the Ott experiment at somewhat lower temperatures, employing extensive signal averaging and careful modeling of the molecular background radiation, and have observed the resonance as is shown in Fig. 7.

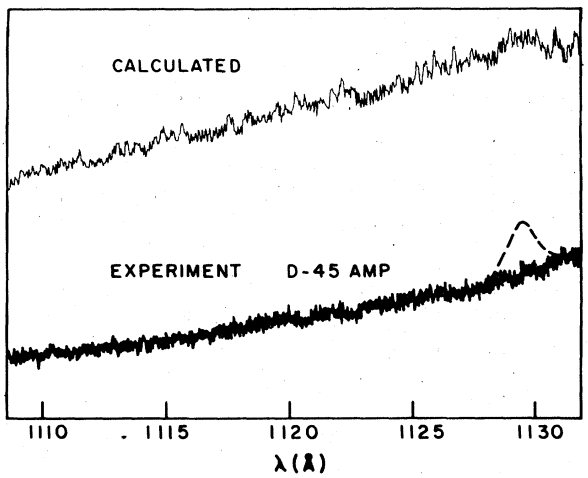

FIG. 6. Comparison with the Ott *et al.* experiment. The lower curve shows the experimental data of Ott *et al.* (Ref. 8); the dashed peak indicates the line shape expected by them based on an estimated oscillator strength of 0.044 and no microfield Stark broadening. Recalculation of the oscillator strength (Broad and Reinhardt, Ref. 7) reduces the expected peak resonance signal by a factor of roughly 2; the dc Stark broadening reduces this by an additional 30%. The calculated spectrum was obtained by taking the theoretical curve of Broad and Reinhardt (Ref. 7; see also Fig. 3) averaging over a Holtzmark distribution of microfields appropriate to an LTE plasma at 15 000 K, adding a simulated molecular background and finally convoluting the spectrum with a 10% random signal-to-noise ratio of a frequency appropriate to the Ott *et al.* experiment.

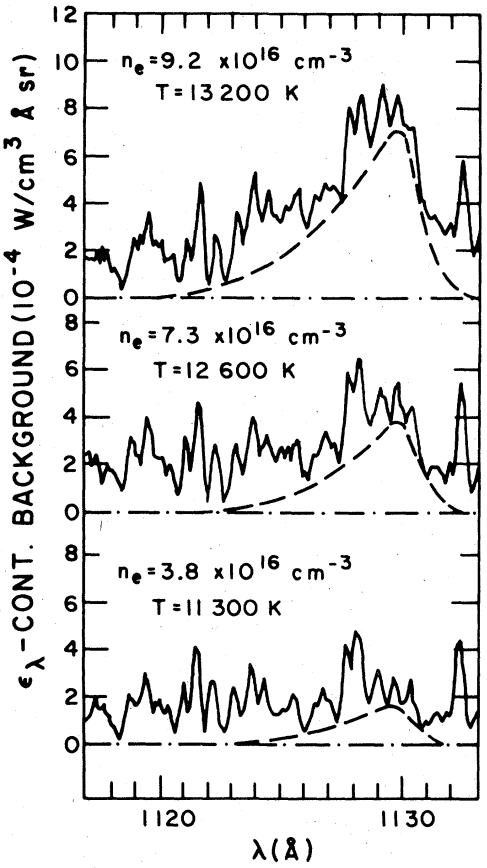

FIG. 7. Data from the plasma experiment of Behringer and Thoma (Ref. 11) obtained by extensive signal averaging of the uv emission from hydrogen at slightly lower temperatures than the Ott experiment. The remaining spectrum consists of molecular lines superimposed on the shape resonance indicated by the dashed line. This analysis of the plasma data gives an oscillator strength consistent with that of Ref. 7, but a Stark width about a factor of 2 larger than determined by the complex-coordinate method used here.

IV. DISCUSSION

We have employed the method of complex rotation to find the complex eigenvalues associated with the lowest $^1P^o$ Feshbach resonance and the $^1P^o$ shape resonance in H^-. By extending the calculations to include the effect of a dc Stark field the field dependence of the width of the shape resonance was determined. This field dependence was then used to estimate the line shape expected to appear in uv photoemission from an LTE hydrogen arc plasma thereby qualitatively explaining the negative results of Ott *et al.*,[8] and is also qualitatively consistent with the more recent experiments of Behringer *et al.*[11] However, although Behringer *et al.* observe roughly the oscillator strength (graphically estimated) found by Broad and Reinhardt,[7] their work suggests more substantial Stark broadening of the shape resonance than indicated either by the results of Table III or the recent measurements of Gram *et al.*[22]

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[23]Making contact with the hyperspherical coordinate "potential curves" of Lin (Ref. 6) we note that the zero field shape resonance appears to be caused by a (generalized) angular momentum barrier, and thus in the Lin picture the natural life time is determined by tunneling. However, in the presence of the dipole coupling due to the Stark field, the Lin curves will be mixed and modified by the presence of coupling to all other angular momentum states. The electric field will of course "lower" the $^1P^o$ angular momentum barrier, but additionally will make the potential curve complex, as direct autoionization into open channels (corresponding to the other of Lin's potential curves) can occur in the presence of the field. Our CI calculations seem to indicate that it is this direct process which dominates the Stark broadening of the resonance; however, it would be most interesting to perform a detailed hyperspherical analysis to verify this conclusion.
[24]A discussion of the various effects influencing radiative line shapes appears in J. Davis and V. L. Jacobs, Phys. Rev. A 12, 2017 (1975).
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