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Excitation Energies and Molecular Quantum Defect Orbital Transition Intensities for Rydberg States of ArH

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The size-consistent self-consistent complete active space singles and doubles configuration interaction ((SC)^2-CAS-SDCI) procedure has been applied to the calculation of vertical excitation energies, as well as the ionization energy, of the Rydberg radical ArH. Absorption oscillator strengths and Einstein emission coefficients for a number of electronic transitions have been obtained with the molecular adapted quantum defect orbital (MQDO) method. The adequacy of the two theoretical procedures employed in the present work is discussed.

I. Introduction

Rydberg states form an important class of excited electronic states in atomic and molecular systems. At present, there is a renewed interest in high energy states that is stimulated by general problems of atmospheric and space research. A particularly interesting class of molecules in this context is that of "Rydberg molecules",[1] for which the ground electronic state is unstable but all the excited states have Rydberg character. They possess long lifetimes as compared to rotational or vibrational periods, and their corresponding core cation is quite stable. A number of diatomic and polyatomic Rydberg molecules have recently been observed in atmospherically and astrophysically important regions.[2] They also are of more general chemical interest as some of them have been detected as short-lived intermediates in several chemical reactions.[3]

The experimentally observed Rydberg series of the rare gas hydrides have progressively emerged in recent years. Numerous observations and analyses of Rydberg−Rydberg emission bands of the isotopic radicals ArH and ArD in the visible and infrared spectral regions have been reported by Dabrowski and coworkers.[4−7] Like the remaining rare gas hydrides, ArH is an excimer. Its emission spectrum was first recorded by Johns in 1970,[8] who reported a fluorescence observed at 7670 Å (13040 cm^{-1}) which he assigned to a $^2\Pi \rightarrow {}^2\Sigma^+$ band. Lipson[9] reported several discrete features of the ArH and ArD spectra, such as an nd $^2\Pi \rightarrow$ A $^2\Sigma^+$ Rydberg series whose first member was the band observed by Johns at 13 040 cm^{-1}. Möller et al.[10] recorded bound-free fluorescence and deduced the binding energies of several Rydberg states. These authors assigned their observed features to transitions from the B $^2\Pi$ state to the dissociative ground state, X $^2\Sigma^+$, by comparing their measurements to theoretical values obtained by Theodorakopoulos and co-workers through configuration interaction (CI) calculations.[11] Significant progress was achieved when Dabrowski et al.[12] analyzed for the first time the rotational structure of a band near 6120 cm^{-1}. This band, which had been observed by Johns but had resisted analysis, was now assigned[12] to a 4p → 5s transition and found to consist almost entirely of Q-branches. The lower state appeared to be the same as that of the first member of the Johns-Lipson nd $^2\Pi \rightarrow$ 5s Rydberg series, with $n = 3$ (4). Two other strong bands, measured near 6900 and 10 200 cm^{-1}, were assigned to the 3d $^2\Pi \rightarrow$ 4p and the 3d $^2\Sigma^+ \rightarrow$ 4p transitions, respectively.[12] The assignment of these spectra was also supported by CI calculations by Petsalakis and Theodorakopoulos.[13,14] Wunderlich et al.[15] remarked that the nd $^2\Pi$ as well as the 4f levels of ArH were more highly populated than its low-lying $^2\Sigma^+$ levels, which were thought of decaying mainly by predissociation. Dabrowski et al.,[4] in an analysis of the observed emission spectrum from np states of ArD, confirmed that the Rydberg states of ArD and ArH have very similar potential energy curves to those of their corresponding cations, ArD$^+$ and ArH$^+$. The rotational analysis of the np ($^2\Pi$, $^2\Sigma^+$) → n's $^2\Sigma^+$ (n, $n' = 5, 6$) bands of ArD helped to further characterize the np Rydberg series of the two isomers.[4] The most recently recorded spectra of ArD and ArH are, to our knowledge, those by Dabrowski and co-workers,[6,7] who have analyzed 0−0 vibrational bands of electronic transitions from nd and ns Rydberg states to the 4p Rydberg complex of ArH and ArD, pointing out, at the same time, the sharpness and lack of predissociation observed in the 4p levels of ArH[6] and the emission from the 4f complexes of the two isotopic molecules.[7] The latest theoretical work published on ArH is, to our knowledge, the multichannel quantum defect theory (MQDT) analysis of the 4f, $v = 0$ manifolds of levels of ArH, ArD, and KrD[16] observed by Dabrowski et al.[7] and by Dabrowski and Sadowskii.[17] Jungen and Roche claim that their calculations reproduce the experimental level fine structure, including nonadiabatic rotational l-uncoupling and electronic l-mixing perturbations.[16]

Motivated by the general interest in excimer molecules, largely because of their applications in UV lasers of high power, and, more specifically, in the rare gas hydrides,[18] we have undertaken the theoretical study of some relevant spectral features of ArH. Our main purpose is to supply data that may

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TABLE 1: Rydberg States of ArH in eV

state[a]	$(SC)^2$-CAS-SDCI[a]	state[b]	MRD-CI[b]	state[c]	exptl[c]
A $^2\Sigma^+$ (5s)	3.502	A $^2\Sigma^+$ (2s)	3.34	$^2\Sigma^+$ (5s)	3.413
B $^2\Pi$ (4p)	4.310	B $^2\Pi$ (2p)	3.92	$^2\Pi$ (4p)	4.166
C $^2\Sigma^+$ (4p)	4.329	C $^2\Sigma^+$ (2p)	4.01	$^2\Sigma^+$ (4p)	4.169
E $^2\Pi$ (3d)	5.154	E $^2\Pi$ (Ar ^{1,3}P)	4.87	$^2\Pi$ (3d)	5.027
D $^2\Sigma^+$ (6s)	5.131	D $^2\Sigma^+$ (Ar ^{1,3}P)	4.90	$^2\Sigma^+$ (6s)	5.122
1 $^2\Delta$ (3d)	5.259	1 $^2\Delta$ (3d)	5.08	$^2\Delta$ (3d)	5.225
5 $^2\Sigma^+$ (3d)	5.410	5 $^2\Sigma^+$ (Ar ^{1,3}P)	5.17	$^2\Sigma^+$ (3d)	5.438[d]
3 $^2\Pi$ (5p)	5.591	3 $^2\Pi$ (Ar ^{1,3}P)	5.27	$^2\Pi$ (5p)	5.567[d]
6 $^2\Sigma^+$ (5p)	5.611	6 $^2\Sigma^+$ (3s)	5.35	$^2\Sigma^+$ (5p)	5.592[d]
4 $^2\Pi$ (4d)	5.852	4 $^2\Pi$ (3p)	5.63	$^2\Pi$ (4d)	5.834
9 $^2\Sigma^+$ (7s)	5.866	7 $^2\Sigma^+$ (3p)	5.66		
2 $^2\Delta$ (4d)	5.902	2 $^2\Delta$ (4d)	5.71		
8 $^2\Sigma^+$ (4f)	5.903	8 $^2\Sigma^+$ (3d)	5.68	$^2\Sigma^+$ (4f)	5.964
5 $^2\Pi$ (4f)	5.900	5 $^2\Pi$ (3d)	5.70	$^2\Pi$ (4f)	5.966
3 $^2\Delta$ (4f)	5.894	3 $^2\Delta$ (4f)	5.72	$^2\Delta$ (4f)	5.973
1 $^2\Phi$ (4f)	5.904	1 $^2\Phi$ (4f)	5.73	$^2\Phi$ (4f)	5.983
7 $^2\Sigma^+$ (4d)	6.011	9 $^2\Sigma^+$ (4s)	5.70	$^2\Sigma^+$ (4d)	6.039
6 $^2\Pi$ (6p)	6.075	6 $^2\Pi$(4p)	5.79	$^2\Pi$ (6p)	6.098[d]
10 $^2\Sigma^+$ (6p)	6.078	10 $^2\Sigma^+$ (4p)	5.78	$^2\Sigma^+$ (6p)	6.107[d]
MAE	0.06		0.24		

[a] Present work. [b] Theodorakopoulos and Petsalakis.[14] [c] Dabrowski et al.[7] [d] States not observed in ArH. These values correspond to Rydberg states of ArD reported by Dabrowski et al.[7]

TABLE 2: Values of Nonzero Angular Factors $Q\{A \rightarrow B\}$ for $C_{\infty v}$ Symmetry and for $l = 0, 1, 2$

$Q\{\Pi(p) \rightarrow \Sigma^+(s)\} = Q\{\Sigma^+(s) \leftrightarrow \Sigma^+(p)\} = 1/3$

$Q\{\Sigma^+(s) \rightarrow \Pi(p)\} = 2/3$

$Q\{\Sigma^+(p) \rightarrow \Pi(d)\} = Q\{\Pi(p) \leftrightarrow \Delta(d)\} = 2/5$

$Q\{\Sigma^+(p) \leftrightarrow \Sigma^+(d)\} = 4/15$

$Q\{\Pi(p) \leftrightarrow \Pi(d)\} = Q\{\Pi(d) \rightarrow \Sigma^+(p)\} = 1/5$

$Q\{\Pi(p) \rightarrow \Sigma^+(d)\} = 1/15$

$Q\{\Sigma^+(d) \rightarrow \Pi(p)\} = 2/15$

help in future experimental measurements and assignments concerning electronic transitions in this radical.

A remark is in order regarding the notation employed by different authors when referring to the Rydberg states of ArH. Most of the authors who have studied experimentally the spectrum of this radical, e.g., Dabrowski et al.,[4−7,12,17] Lipson,[9] and others, have correlated the Rydberg states of ArH to those of its "united atom limit": potassium. They have, consequently, employed the *n* and *l* values that characterize the atomic orbitals of potassium, in addition to the appropriate molecular symmetry, to denote the levels of ArH. The pair of *n* and *l* quantum numbers assigned by other authors, such as Theodorakopoulos and Petsalakis,[14] who have reported theoretical multireference with double excitations configuration interaction (MRD-CI) transition intensities, correspond to the "separated atom limit", i.e., to levels of either atoms into which the excimer dissociates, hydrogen and an argon core. We have adopted for the Rydberg states of ArH the "united atom" notation, as is apparent in the labeling of the present results, collected in the tables.

A correlation between the two above different notation schemes for the Rydberg states of ArH has been presently established on the basis of the molecular symmetry and the energy of the different states of our interest, whenever possible (see Table 1). In this form, we have compared our calculated Einstein emission coefficients with the ones supplied in ref 14, and our absorption oscillator strengths with f-values obtained by us from the MRD-CI transition energies and Einstein coefficients.[14] In Tables 3 to 7 we have included the data reported by Theodorakopulos and Petsalakis[14] in our own notation.

Two procedures have been followed in the present work. First, the excitation energies of a number of states of ArH have been determined at the equilibrium distance of the lowest bound state by means of complete-active-space with single and double excitations configuration interaction (CAS-SDCI) calculations corrected to size-extensivity by means of the open-shell size-consistent self-consistent matrix-dressing method known as $(SC)^2$.[19−22] This method leads to both wave functions and energies that are corrected to the effects of nonlinked perturbation theory diagrams that occur through excitations of the outer space. Note that in a CAS-SDCI calculation, the outer space is made of all the triple and quadruple excitations that would generate holes in the MOs belonging to the complete active space and also in the so-called inactive MOs. These orbitals are referred to as inactive because they have not been selected for the CAS. However, they are occupied in the leading determinant of the ground-state wave function and their electrons are involved in the single and double excitation processes. The $(SC)^2$-CAS-SDCI method has been applied along with a basis set composed by atomic natural orbitals (ANOs)[23] as described below. The accuracy of the present calculations has been established by comparison with the MRD-CI binding energies by Theodorakopoulos and Petsalakis,[14] and with those experimentally determined (or deduced by us from the reported symmetry and effective quantum numbers) by Dabrowski et al.[7]

Second, intensities for vertical transitions involving Rydberg states which did not seem to be affected by problems such as nonadiabatic effects and *l*-uncoupling, have been calculated with the molecular-adapted quantum defect orbital (MQDO) formalism, which has proved to yield data, in recent applications to other Rydberg radicals,[18,24−28] of comparable quality to those supplied by rather more complex and costly procedures. It has long been established[29] for Rydberg states in molecules with a closed-shell core, as is the case in ArH, that the rotational and vibrational motions of the core can be safely considered as independent from the Rydberg electron's motions. As *n* increases, and the inner loops of the Rydberg MO become less and less important relative to the outer loops, the Rydberg electron withdraws more and more from influencing the rotational and vibrational motions of the nuclei. In the present calculations, we have considered electronic transitions originating and ending in the vibrational ground state of both the upper and lower Rydberg states. We have calculated transitions that obey the Laporte, $\Delta l = \pm 1$, selection rule, in addition to symmetry constraints, as these are the ones experimentally observed to be the strongest, with the exception of the ones involving states that show signs of important mixing with others.

II. $(SC)^2$-CAS-SDCI Excitation Energies of ArH

The vertical spectrum of the open-shell ArH molecule has been calculated at the distance of 2.500 Bohr, which corresponds to the equilibrium distance of the first clearly bound excited-state A $^2\Sigma^{+\ 5s}$. This distance has also been adopted by other authors.[14,30] The basis set has been 5s4p3d1f for Ar and 3s2p1d for H. The atomic natural orbital basis set obtained by Widmark et al.[23] has been employed. This set was augmented by a group of diffuse 3s3p2d1f Rydberg functions centered in the charge centroid of the ionization limit, represented by the ground state of ArH^+. In this way, we expect to have treated adequately the excitations to Rydberg states up to $n = 7$ for s states and to $n = 4$ for f states. These ANO-like Rydberg basis functions have been built following the procedure developed by Roos et al. to generate a universal Gaussian basis set, which has been successfully employed in many vertical excitation energy calculations.[31]

State-averaged CAS-SCF MOs have been used for each symmetry. The calculations have been performed within the C_{2v}

TABLE 3: Emission Transition Probabilities (in s^{-1}) and Absorption Oscillator Strengths and for the $^2\Pi$ (*n*p) → $^2\Sigma^+$ (5s) and $^2\Sigma^+$ (*n*p) → $2\Sigma^+$ (5s) ($n = 4-6$) Electronic Transitions in ArH[a]

transition	ΔE/cm^{-1}	A (MQDO)[b]	A (MQDO)[c]	A (T&P)[d]	f (MQDO)[b]	f (MQDO)[b]	f (T&P)[d]
$^2\Pi$ (4p) → $^2\Sigma^+$ (5s)	6517	7.75(6)	5.44(6)	3.3(6)	0.5469	0.4422	0.4522
$^2\Pi$ (5p) → $^2\Sigma^+$ (5s)	16849	8.7(5)	4.72(6)	3.3(5)	0.00923	0.0465	0.0041
$^2\Pi$ (6p) → $^2\Sigma^+$ (5s)	20753	2.48(4)	2.87(6)	3.4(3)	0.000173	0.0183	0.00003
$^2\Sigma^+$ (4p) → $^2\Sigma^+$ (5s)	6672	8.35(6)	5.49(6)	2.2(6)	0.2815	0.2218	0.1129
$^2\Sigma^+$ (5p) → $^2\Sigma^+$ (5s)	17010	0.38(6)	3.81(6)	2.6(6)	0.0020	0.0185	0.0148
$^2\Sigma^+$ (6p) → $^2\Sigma^+$ (5s)	20777	6.91(3)	2.38(6)	4.7(5)	0.000024	0.0076	0.0018

[a] In this and the remaining tables A (B) indicates A.10^B. [b] MQDO calculations with presently obtained $(SC)^2$-CAS-SDCI energies. [c] MQDO calculations with energies from Dabrowski et al.[7] See footnotes to Table 1. [d] Theodorakopoulos and Petsalakis.[14]

TABLE 4: Emission Transition Probabilities (in s^{-1}) and Absorption Oscillator Strengths and for the $^2\Sigma^+$ (*n*s) → $^2\Pi$ (4p) and $^2\Sigma^+$ (*n*s) → $^2\Sigma^+$ (4p) − ($n = 6, 7$) Electronic Transitions in ArH

transition	ΔE/cm^{-1}	A (MQDO)[a]	A (MQDO)[b]	A (T&P)[c]	f (MQDO)[a]	f (MQDO)[b]	f (T&P)[c]
$^2\Sigma^+$ (6s) → $^2\Pi$ (4p)	6622	6.85(6)	9.42(6)	2.2(6)	0.1171	0.1188	0.0264
$^2\Sigma^+$ (7s) → $^2\Pi$ (4p)	12550	2.33(6)		2.0(6)	0.0111		0.0076
$^2\Sigma^+$ (6s) → $^2\Sigma^+$ (4p)	6469	3.32(6)	4.70(6)	1.8(7)	0.1190	0.1190	0.5273
$^2\Sigma^+$ (7s) → $^2\Sigma^+$ (4p)	12397	1.14(6)		1.6(6)	0.0111		0.0135

[a] MQDO calculations with presently obtained $(SC)^2$-CAS-SDCI energies. [b] MQDO calculations with energies from Dabrowski et al.[7] See footnotes to Table 1. [c] Theodorakopoulos and Petsalakis.[14]

TABLE 5: Emission Transition Probabilities (in s^{-1}) and Absorption Oscillator Strengths for the $^2\Pi$ (*n*d) → $^2\Pi$ (4p), $^2\Delta$ (*n*d) → $^2\Pi$ (4p) and $^2\Sigma^+$ (*n*d) → $^2\Pi$ (4p) ($n = 3, 4$) Electronic Transitions in ArH

transition	ΔE/cm^{-1}	A (MQDO)[a]	A (MQDO)[b]	A (T&P)[c]	f (MQDO)[a]	f (MQDO)[b]	f (T&P)[c]
$^2\Pi$ (3d) → $^2\Pi$ (4p)	6807	9.57(6)	8.34(6)	1.0(7)	0.3096	0.2593	0.2554
$^2\Pi$ (4d) → $^2\Pi$ (4p)	12437	0.18(5)	5.73(5)	2.4(5)	0.0002	0.0048	0.0019
$^2\Delta$ (3d) → $^2\Pi$ (4p)	7654	2.74(7)	3.18(7)	3.4(7)	0.7023	0.6537	0.5823
$^2\Delta$ (4d) → $^2\Pi$ (4p)	12840	1.42(6)		1.3(6)	0.0129		0.0094
$^2\Sigma^+$ (3d) → $^2\Pi$ (4p)	8872	1.39(7)	1.77(7)	2.4(7)	0.1323	0.1259	0.1770
$^2\Sigma^+$ (4d) → $^2\Pi$ (4p)	13719	3.94(6)	2.90(6)	4.2(4)	0.0157	0.0095	0.0002

[a] MQDO calculations with presently obtained $(SC)^2$-CAS-SDCI energies. [b] MQDO calculations with energies from Dabrowski et al.[7] See footnotes to Table 1. [c] Theodorakopoulos and Petsalakis.[14]

TABLE 6: Emission Transition Probabilities (in s^{-1}) and Absorption Oscillator Strengths and for the $^2\Pi$ (*n*d) → $^2\Sigma^+$ (4p) and $_2\Sigma^+$ (*n*d) → $^2\Sigma^+$ (4p) ($n = 3, 4$) Electronic Transitions in ArH

transition	ΔE/cm^{-1}	A (MQDO)[a]	A (MQDO)[b]	A (T&P)[c]	f (MQDO)[a]	f (MQDO)[b]	f (T&P)[c]
$^2\Pi$ (3d) → $^2\Sigma^+$ (4p)	6654	9.04(6)	8.29(6)	8.6(6)	0.6125	0.5179	0.5360
$^2\Pi$ (4d) → $^2\Sigma^+$ (4p)	12284	4.48(3)	5.82(5)	3.8(5)	0.00009	0.0097	0.0067
$^2\Sigma^+$ (3d) → $^2\Sigma^+$ (4p)	8719	2.68(7)	3.52(7)	4.3(6)	0.5291	0.5035	0.0736
$^2\Sigma^+$ (4d) → $^2\Sigma^+$ (4p)	13566	7.46(6)	5.76(6)	2.6(6)	0.0608	0.0379	0.0210

[a] MQDO calculations with presently obtained $(SC)^2$-CAS−SDCI energies. [b] MQDO calculations with energies from Dabrowski et al.[7] See footnotes to Table 1. [c] Theodorakopoulos and Petsalakis.[14]

TABLE 7: Emission Transition Probabilities (in s^{-1}) and Absorption Oscillator Strengths and for $^2\Sigma^+$ (*n*p) → $^2\Pi$ (3d), $^2\Pi$ (*n*p) → $^2\Pi$ (3d), $^2\Sigma^+$ (*n*p) → $^2\Sigma^+$ (3d), $^2\Pi$ (*n*p) → $^2\Sigma^+$ (3d), and $^2\Pi$ (*n*p) → $^2\Delta$ (3d) ($n = 5, 6$) Electronic Transitions in ArH

transition	ΔE/cm^{-1}	A (MQDO)[a]	A (MQDO)[b]	A (T&P)[c]	f (MQDO)[a]	f (MQDO)[b]	f (T&P)[c]
$^2\Sigma^+$ (5p) → $^2\Pi$ (3d)	3686	1.07(6)	1.69(6)	1.6(6)	0.0591	0.0611	0.800
$^2\Sigma^+$ (6p) → $^2\Pi$ (3d)	7452	3.80(5)	5.97(5)	3.2(4)	0.0051	0.0059	0.0004
$^2\Pi$ (5p) → $^2\Pi$ (3d)	3525	5.23(5)	8.37(5)	2.8(5)	0.0631	0.0640	0.0403
$^2\Pi$ (6p) → $^2\Pi$ (3d)	7428	1.92(5)	2.94(5)	2.0(6)	0.0052	0.0059	0.0545
$^2\Sigma^+$ (5p) → $^2\Sigma^+$ (3d)	1621	1.61(5)	0.806(5)		0.0918	0.0784	
$^2\Sigma^+$ (6p) → $^2\Sigma^+$ (3d)	5388	9.80(4)	2.21(4)	1.8(4)	0.0051	0.0011	0.0011
$^2\Pi$ (5p) → $^2\Sigma^+$ (3d)	1460	3.14(4)	1.50(4)	3.1(5)	0.0442	0.0364	1.4289
$^{2\prime}$ (6p) → $^2\Sigma^+$(3d)	5364	2.33(4)	0.343(4)	3.9(4)	0.0024	0.0004	0.0047
$^2\Pi$ (5p) → $^2\Delta$ (3d)	2678	6.82(5)	8.08(5)	4.4(5)	0.1425	0.1511	0.2809
$^2\Pi$ (6p) → $^2\Delta$ (3d)	6582	3.07(5)	2.74(5)	1.2(5)	0.0106	0.0083	0.0055

[a] MQDO calculations with presently obtained $(SC)^2$-CAS−SDCI energies. [b] MQDO calculations with energies from Dabrowski et al.[7] See footnotes to Table 1. [c] Theodorakopoulos and Petsalakis.[14]

symmetry group, a subgroup of the actual molecular point group, $C_{\infty v}$. The active orbitals belonging to the different irreducible representations are reported in the order (a_1, b_1, b_2, a_2). For the A_1 (Σ^+ and Δ Rydberg states) and the B_1 (Π and Φ Rydberg states) irreducible representations, 13 states and 7 states have been averaged, respectively. The assignment of the Δ states has been assessed through independent calculations within the A_2 irreducible representation, with three states being averaged in this case. All the excitations of the unpaired electron in a set of (14, 7, 7, 3) active orbitals have been included in the CAS at the CASSCF level. At the CAS-SDCI level, the CAS has included the unpaired electron in addition to all the virtual orbitals that have been considered relevant for the states of different symmetry. A significant mixing among several configurations with the same symmetry occurs in the Σ^+ states. Notwithstanding, the X $^2\Sigma^+$ ground state (GS) is dominated by a unique determinant that corresponds to the unpaired electron in the highest occupied MO. We have thus considered this state as the dressing reference state for the dressing procedure applied to all other states and symmetries in the $(SC)^2$ method. The GS wave function shows nonnegligible contributions from excitations that involve Rydberg MOs anyway. Consequently, we have included these MOs in the various CAS spaces. In particular, within the A_1 symmetry, we have selected two CAS sets, (10, 0, 0, 0) for the Σ^+ states and (6, 0, 0, 0) for the Δ states. The CAS for the Δ states of the A_2 symmetry has been (5, 0, 0, 3). Within the B_1 symmetry, the CAS has been (5, 8, 0, 0) for the Π and Φ Rydberg states. All the single and double excitations that could be formed on those CAS spaces of determinants have been included in the CAS-SDCI procedure. The $(SC)^2$ matrix dressing method has then been applied to the CAS-SDCI diagonalization. All the CI and dressed-CI calculations have been performed with the program CASDI developed by D. Maynau and co-workers[20] and implemented by the authors on IBM R6000 SPII and SGI origin-2000 computers. The results so obtained are displayed in Table 1, together with the mean average error (MAE) of our excitation energies and those of ref 14, with respect to the experimental values.

The $(SC)^2$-CAS-SDCI vertical binding energy of the unpaired electron at the assumed geometry has been determined to be 6.711 eV with respect to the GS. The GS being dissociative, the IP is commonly reported by some authors[6,7] at 3.4 eV relative to the first excited state, A $^2\Sigma^+$ 5s. We find this state at 3.502 eV above the GS for this geometry, so that our IP relative to the A state is 3.209 eV, in good agreement with the experimental value.

III. Calculation of Transition Intensities with the MQDO Method

The molecular-adapted quantum defect orbital (MQDO) method, formulated for calculating absorption oscillator strengths and emission coefficients for transitions involving Rydberg states, has been described in detail.[24] We thus only summarize here its most fundamental aspects.

The MQDO wave functions are represented by orbitals that are the exact solutions of a one-electron Schrödinger equation,

$$\left[-\frac{1}{2}\Delta + V(r,\vartheta,\varphi)_{\mathrm{M}}\right]\psi(r,\vartheta,\varphi)_{nl\mu\nu} = E_{nl\nu}\,\psi((r,\vartheta,\varphi))_{nl\mu\nu} \quad (1)$$

where V_{M} is an effective potential of the molecular core. These solutions can be written as follows,

$$\psi((r,\vartheta,\varphi))_{nl\mu\nu} = \frac{1}{r}R(r)_{nl}\,\Xi(\vartheta,\varphi)_{l\mu\nu} \quad (2)$$

where n and l are, respectively, the principal and the orbital angular momentum quantum numbers; μ and ν label different wave functions corresponding to the same (n, l) pair. The radial part of the wave function is obtained from the equation

$$\left[-\frac{d^2}{2dr^2} + \frac{l(l+1)}{2r^2} + V(r)\right]R(r) = ER(r) \quad (3)$$

The effective central field potential is defined as

$$V(r) = \frac{(c-\delta)(2l+c-\delta+1)}{2r^2} - \frac{1}{r} \quad (4)$$

where the parameter δ is the quantum defect and c is an integer chosen to ensure the normalization of the orbitals and their correct nodal pattern − the number of radial nodes is equal to $n - l - c - 1$. The quantum defect, δ, for a given state, is related to the energy eigenvalue through the following equation, where T is the ionization energy.

$$E = T - \frac{1}{2(n-\delta)^2} \quad (5)$$

In the case of spherically symmetric systems, the pairs of indices μ and ν correspond to the magnetic quantum number $m = -l, -l + 1, ...l$, and the angular functions, $\Xi(\vartheta,\varphi)_{l\mu\nu}$ are equal to the spherical harmonics $Y(\vartheta,\varphi)_{lm}$. In the case of molecules, the angular part of the MQDO wave function is expressed as a symmetry-adapted combination of spherical harmonics. Index ν in this case identifies the irreducible representation of the appropriate symmetry group, and ν labels the basis functions of this representation. For ArH, the molecular point-group symmetry is $C_{\infty v}$. The combinations of the spherical harmonics which form bases for the irreducible representations may readily be constructed using standard techniques. One of the main advantages of this procedure is that it leads to closed-form analytical expressions for the transition integrals.

The absorption oscillator strength for a transition between two states a and b may be expressed as

$$f(a \rightarrow b) = \frac{2}{3}(E_{\mathrm{b}} - E_{\mathrm{a}})Q\{a \rightarrow b\}|R_{\mathrm{ab}}|^2 \quad (6)$$

where $Q\{a \rightarrow b\}$, referred to as the *angular factors*, result from the angular integration, and the radial transition moment integrals are defined, for the presently studied E1, or electric-dipole, transitions as

$$R_{\mathrm{ab}} = < R_{\mathrm{a}}(r)|r|R_{\mathrm{b}}(r) > \quad (7)$$

The values of $Q\{a \rightarrow b\}$ for the group $C_{\infty v}$ are collected in Table 2.

MQDO absorption oscillator strengths and Einstein emission coefficients have been calculated with the quantum defects for ArH extracted from the present $(SC)^2$-CAS-SDCI excitation and ionization energies, and with the quantum defects directly reported by Dabrowski and collaborators.[7]

IV. Results and Analysis

As mentioned at the end of section II, the excitation energies calculated in the present work are reported in Table 1. The included mean absolute error (MAE) summarizes the smaller dispersion of the $(SC)^2$-CAS-SDCI energy differences relative to the experimental values reported in ref 7, as compared to the previous multireference CI data from ref 14. The highest discrepancies, of about 0.15 eV, occur in the two 4p states, i.e., B $^2\Pi$ and C $^2\Sigma^+$. The E $^2\Pi$ 3d state shows an error of 0.13 eV and the other states show absolute errors lower than 0.1 eV. The highest states appear to be slightly underestimated with respect to the experimental values. The MRD-CI excitation energies from ref 14 show a general agreement with experiment. Their MAE is affected by an overall underestimation of all levels. This fact might be due to an unbalanced treatment of the GS relative to the excited-state manifold.

The Rydberg states of ArH have been arranged in Table 1 in increasing order of excitation energy, as reported by Dabrowski et al.[7] As mentioned in the previous section, we have correlated our Rydberg states with the ones experimentally observed by Dabrowski and co-workers for ArH, or the ones corresponding to ArD, when the former were not available, as collected in

Table 14 of ref 7. Both sets of data are given in the "united-atom" notation. Also collected in Table 1 are the results of the MRD-CI calculations by Theodorakopoulos and Petsalakis[14] in the notation employed by these authors. A correlation has been established, when possible, with the other two sets of energies on the basis of the molecular symmetry of the Rydberg states. The MRD-CI states, which are labeled according to their dissociation limit (H in the ground state and Ar excited to a ^{1,3}P term), i.e., the states labeled as E $^2\Pi$, D $^2\Sigma^+$, 5 $^2\Sigma^+$, and 3 $^2\Pi$ by Theodorakopoulos and Petsalakis,[14] have been included in Table 1 and correlated with the $^2\Pi$ 3d, $^2\Sigma^+$ 6s, $^2\Sigma^+$ 3d, and $^2\Pi$ 5p states, respectively.

Most of the states have been found in our calculations to be affected, to greater or lesser degree, by contributions from excitations to different Rydberg MOs. As a rough indication of the multiconfigurational nature of the Σ^+ states, we may point out that all of them comprise at least four determinants with a weight equal to or greater than 10% in their wave functions. The most difficult states to assign have been D $^2\Sigma^+$ 6s and 6 $^2\Sigma^+$ 5p. For these, we have performed independent calculations using state-averaged MOs obtained with a larger CAS of 7 electrons in 14 orbitals (9, 2, 2, 1). In this case, the highest *n* Rydberg functions have been excluded from the basis set, as they are not directly involved in the D $^2\Sigma^+$ 6s and 6 $^2\Sigma^+$ 5p states. Seven states have been included in the averaging process. Then, (SC)^2-CAS-SDCI calculations have been performed using a 5e,8o complete active space. In this way, the wave functions of both states were easier to assign while their excitation energies did not change significantly.

In Tables 3 to 7 are displayed the (SC)^2-CAS-SDCI transition energies, in cm^{-1}, the Einstein emission coefficients (also known as transition probabilities), and the absorption oscillator strengths calculated with the MQDO procedure (described in section III) with the two sets of energies, those obtained in the present calculation and the experimental values of ref 7. Further details are given as table footnotes. The A-values from ref 14 involving Rydberg states that we could correlate with the ones presently calculated have also been included in the tables. In the tables, the absorption oscillator strengths which we have derived from the excitation energies and emission coefficients reported by Theodorakopoulos and Petsalakis,[14] all expressed in the "united atom" notation, have also been included.

A general good accord between the three sets of A-values, and between the corresponding groups of f-values collected in Tables 3 to 7, is apparent, in particular those corresponding to the stronger transitions. Even for the weaker transitions, the three sets of results conform with each other reasonably well. Overall, there is a better coincidence between the two groups of MQDO transition probabilities and of oscillator strengths between themselves (i.e., the ones obtained with the present (SC)^2-CAS-SDCI energies and with those deduced from the measurements of Dabrowski et al.[7]) than between either of these and the MRD-CI results.[14] In fact, the mean absolute difference between the two groups of MQDO f-values collected in Tables 3 to 7 is 0.02, whereas the same parameter amounts to about 0.15 if the MRD-CI oscillator strengths are compared with either of the former. It may be stressed that in most of the calculations and measurements on molecular Rydberg transitions currently available in the literature, the intensities from different sources seldom conform very well with each other, and more so for the weaker transitions.

The transition probabilities of the three strong bands reported in ref 12, in the neighborhood of 6120, 6900, and 10200 cm^{-1}, and assigned, respectively, to the 4p $^2\Sigma^+ \rightarrow$ 5s $^2\Pi$, 3d $^2\Pi \rightarrow$ 4p $^2\Pi$, and the 3d $^2\Sigma^+ \rightarrow$ 4p $^2\Pi$ transitions, are also found to be strong bands in the MQDO intensity calculations with the (SC)^2-CAS-SDCI energies.

We may summarize our analysis by remarking that both energy and transition probability indicators in the present calculations show consistency with the values obtained from the measurements of Dabrowski et al., as collected in ref 7. The excitation energies represent a significant improvement relative to previous work. We take this fact as an assessment of the accuracy of the (SC)^2-CAS-SDCI energies, and also, of the adequacy of the MQDO technique to supply transition probability data.

Overall, we are confident in the potential usefulness of the excitation energies and intensities supplied on ArH in the present work, as well as in the appropriateness of our theoretical procedures for dealing with spectroscopic features of molecular Rydberg states. Studies of Rydberg transitions in both the discrete and continuous spectrum of molecules of atmospheric and astrophysical importance are in progress.

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