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Vertical Excitation Energies and Ionization Potentials of H_2S. A Size-Consistent Self-Consistent Singles and Doubles Configuration Interaction $(SC)^2$-MR-SDCI Calculation

José Pitarch-Ruiz and José Sánchez-Marín*

Departament de Química Física, Institut de Ciència Molecular, Facultat de Ciències Químiques, Dr. Moliner, 50, E-46100 Burjassot, València, Spain

Inmaculada Martín and Ana María Velasco

Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid, Spain

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The size-consistent self-consistent singles and doubles configuration interaction method using both multireference (MR) and complete active space (CAS) as SDCI generator spaces has been used to calculate both vertical excitation energies and vertical ionization potentials for the H_2S molecule. A basis set of ANO functions, [4s3p2d1f] for S and [2s1p] for H, has been augmented with an adapted set of 4s4p4d2f Rydberg functions that have been built explicitly for this study. Several open questions concerning the vertical spectrum of the H_2S are discussed. Rydberg states of f character have been calculated for the first time. Transitions to the outer-valence $^2B_1(2b_1^{-1})$, $^2B_2(2b_2^{-1})$, and $^2A_1(5a_1^{-1})$ states and the inner-valence $^2A_1(4a_1^{-1})$ state of the H_2S^+ cation have also been dealt with. The occurrence of a peak at an energy below the excitation of the $^2A_1(4a_1^{-1})$ state and of various peaks associated to the $(4a_1^{-1})$ hole state in the photoelectron spectrum are discussed.

1. Introduction

The Rydberg spectrum of the hydrogen sulfide molecule has been the subject of many experimental investigations.[1−10] A large manifold of Rydberg states has been detected and analyzed. The origin of these Rydberg series has been attributed to a single excitation from the outermost filled orbital ($2b_1$) in the ground-state configuration. Since almost all of the bands correspond to transitions from this nonbonding $2b_1$ orbital, it may be reasonable to consider that the vertical excitation energies (VEE) to Rydberg states are a good approximation to the measured 0−0 vibronic energies (see ref 11 and also ref 10 and references therein for a detailed discussion). The theoretical calculations on the vertical spectrum of H_2S presently available in the literature, to our knowledge, have focused on the s, p, and d Rydberg series.[7,12,13] In the present work we have included the 4f and 5f states. The f Rydberg states have not been studied before, despite being located within the same energy ranges as those of many s, p, and d states. Some data concerning their location can be found in the work of Mayhew et al.[8] (even though the 3+1 MPI spectra measured by these authors are inconclusive on this aspect) and in the work by Ashfold et al.[10]

A problem that concerns the present calculations is the large number of existing states. For example, states belonging to the B_1 symmetry surpass the number of 20 states in only the 6−10 eV energy range. Another difficulty arises from the mixing of virtual orbitals with Rydberg-excited states. For some of the latter, it is very difficult to assign an orbital quantum number to the Rydberg electron and refer to them as s, p, and d orbitals. However, one dominant contribution is generally found at geometries vertically accessible from the ground electronic state (VEE) and there is not much risk in establishing a classification as “s-like” or “d-like” Rydberg orbitals.[8,10,14]

Other questions regarding the Rydberg spectra of the H_2S are still open. Some are related to the unambiguous assignment of observed Rydberg transitions. For instance, neither the first peak observed for the $(^1B_1)2b_1 \rightarrow 6a_1(ns)$ Rydberg series is clearly assigned nor is the degree of valence character of the $6^1A_1(4s)$ Rydberg state, through mixing with the $^1A_2$ state, established. Both states are probably located in the same region (see ref 6 and references therein). Other open questions are, for example, the lack of a general consensus about the assignment of the $^1B_1(ns)$ Rydberg series[12] and the importance of the mixing between the s and d states (which is in agreement with the conclusions of Ashfold et al.[10]). Our greatest difficulties have involved the assignment of the $^1B_1(5s)$ and $^1B_1(3d)$ states. The presence, in the lower part of the spectrum, of a state originated by an excitation from the $5a_1$ MO instead of the $2b_1$ MO has also been discussed by several authors.[7,11,13] Calculations on the outer-valence states and some excited states of A_1 symmetry have also been performed for the H_2S^+ cation, as they give rise to transitions reflected in the photoelectron spectrum of hydrogen sulfide. Several experimental measurements of the photoelectron spectrum of the H_2S molecule have been reported since the first detailed observations of its inner valence region by Cook and co-workers[15−17] through EMS techniques. Other works include He II UPS studies[18,19] and PES measurements using a synchrotron source by Adam et al.[20,21] These works have revealed a fairly good number of peaks located at excitation energies other than those of the well characterized outer-valence states: $^2B_1(2b_1^{-1})$, $^2B_2(2b_2^{-1})$, and $^2A_1(5a_1^{-1})$. The assignment and nature of these high-energy peaks has been a matter of discussion.[21−23] For instance, Adam et al.[21] confirmed the existence of a band at 19.4−19.6 eV that had been the subject of controversy, as it had been earlier assigned to N_2 impurities.[24] Nevertheless, it was finally accepted as belonging to the H_2S spectrum.[15,17,25] On the other hand, the studies of Adam et al.[21] and French et al.[23] led to the conclusion that the peaks appearing in the range 19−26 eV may be described as the poles of many-body processes arising from the $^2A_1(4a_1^{-1})$ hole state. Hence, we have focused our efforts on the 19−26 eV energy range that concerns the states of H_2S^+ with $^2A_1$ symmetry in order to get

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some additional information on the band at 19.4−19.6 eV, as well as on the other peaks.

A brief summary of the method is presented in section 2. The MR- and CAS-SDCI spaces that can be generated with the CASDI computer code have both been extensively described elsewhere.[26] The computational details of the present calculations are given in section 3. In section 4, the results obtained for the vertical excitation energies (VEE) and vertical ionization potentials (VIP) are discussed and compared with other theoretical and experimental values.

2. Theoretical Aspects. $(SC)^2$ and CI

All the CI calculations performed in the present work have used as orthogonal basis a space of Slater determinants obtained from single and double excitations in a multideterminantal space that we refer to as the multireference space. Such a multireference space is denoted as CAS (for complete active space) if it is made of a $(n \times m)$ full-CI of n electrons in the m MO's that define the active space. The multireference space is denoted as MR if it is made of a selected subset of the CAS. Either the MR or the CAS spaces are used as principal (i.e., generator) spaces. The single and double excitations built thereof act as an intermediate space. The principal and intermediate spaces form the model space for the matrix dressing technique,[27] which is known as the size-consistent self-consistent or $(SC)^2$ dressing method.[28] This procedure corrects the truncated SDCI from improper scaling with the number of correlated electrons, thus avoiding the size-extensivity error. The dressing procedure also adds some contributions[28−30] to the energy that correspond to complete summations of series of the so-called exclusion principle violating (EPV) diagrams of the many body perturbation theory (MBPT). The foundations of the method as well as its detailed development have been the subject of a number of recent papers describing the applications of the method to both close and open shell systems and, thus, will not be repeated here.[28,30−33] Let us remember only that the procedure requires reaching iteratively a self-consistency condition between the elements of a diagonal dressing matrix Δ whose elements depend themselves on the coefficients of the eigenvector of a privileged state. This state acts as the dressing reference state. The dressing matrix Δ is added to the MR-SDCI or CAS-SDCI matrix at each iteration and only the reference-state eigenvector requires to be led to self-consistency. To get several roots, the Hamiltonian matrix with the appropriate space and spin symmetries is dressed, and the excited roots are obtained. Note that Δ is always built from the coefficients of a single converged reference state. The ground state is usually taken as the reference state, but other choices are possible.

As mentioned above, in the present calculations we have used the CASDI[34] code, including a recent option for large-scale MR-SDCI and $(SC)^2$-MR-SDCI calculations without the additional requirement that the MR space be a CAS.[26] This option has allowed us to report in the results section, particularly in Table 4, some calculations that compare dressed-MR to dressed-CAS results. The MR-SDCI option has the advantage that the dimension of the CI spaces generated in this way can be several orders of magnitude smaller that the corresponding CAS-SDCI spaces.

3. Computational Details

The following basis set of ANO functions[35] has been used: [4s3p2d1f] for the S atom and [2s1p] for the H atoms, and augmented with a series of 4s4p4d2f Rydberg functions allocated in the charge centroid of the $^2B_1(2b_1^{-1})$ cation state in order to get improved asymptotic conditions for the Rydberg series. The Rydberg functions were built by following the technique proposed by Fülscher et al. to generate a universal Gaussian basis set.[36] In Table 1 we display the coefficients and exponents obtained for the Rydberg functions basis set. The vertical excitation energies (VEE) have been obtained with the basis set described above that we will denote henceforth as B+R. For the calculations of the vertical ionization potentials (VIP) we have used the above ANO's basis set without the Rydberg functions. This will be denoted as basis B. Notwithstanding, some of the VIP calculations have been performed with the B+R basis set.

TABLE 1: Exponents and Coefficients for the Rydberg Functions of H_2S

exponents	coefficients			
	s Rydberg Functions			
0.005858	2.47049027	−8.29189071	6.97971060	−6.06106648
0.003346	−9.92026488	25.22495583	−27.03565591	27.34253247
0.002048	18.22873917	−48.62989712	51.78015332	−56.23043705
0.001324	−27.20069094	72.45235503	−73.84951294	76.03962544
0.000893	30.31165210	−80.21968028	83.30529034	−83.47819511
0.000624	−23.67060062	62.23915211	−65.10862273	68.35389093
0.000449	11.43989099	−29.90680219	31.50959059	−33.03513856
0.000332	−2.55183940	6.63839384	−7.03692269	7.42223935
	p Rydberg Functions			
0.009988	0.06214526	−3.86916234	2.39991029	−2.20544192
0.005689	−0.75353949	8.53980220	−6.42090805	6.65303564
0.003476	0.13614865	−14.65805601	9.20122838	−9.49400317
0.002242	−1.08640836	22.20181374	−14.26112020	13.23174549
0.001511	1.32424387	−24.92680133	18.24905620	−19.25378407
0.001055	−1.21118135	20.07164716	−14.23055755	16.32912191
0.000759	0.67286238	−10.13233691	7.42183847	−6.93470866
0.000560	−0.16979332	2.37460238	−1.76791382	2.07196216
	d Rydberg Functions			
0.014204	1.21581429	−1.61160414	1.41990936	−2.11877777
0.008077	−1.56909254	2.69333245	−2.88045963	5.60218444
0.004927	3.47747446	−4.55132738	4.20959640	−8.39814579
0.003175	−4.77562261	7.88224840	−7.74933655	12.68793715
0.002137	5.52967304	−8.51543074	9.26011541	−16.50694571
0.001491	−4.57676665	7.37439642	−6.92018283	13.32020133
0.001072	2.41087327	−3.94145736	4.32840192	−7.46839225
0.000790	−0.59553111	0.98929667	−1.00466211	3.19569029
	f Rydberg Functions			
0.018478	0.23537297	−0.52627897		
0.010493	0.01994585	0.44277880		
0.006395	0.75727550	−1.42882536		
0.004117	−0.34392389	1.81784821		
0.002770	0.83949826	−1.77605029		
0.001931	−0.60696780	2.25309904		
0.001387	0.35745907	−0.84488466		
0.001022	−0.09461188	0.34249241		

The experimentally determined geometry of the neutral system has been adopted for both the VEE and VIP calculations: R_{S-H}= 2.520 au, θ_{H-S-H}= 92.2°. All calculations have been performed in the C_{2v} symmetry of the molecule, and the number of active orbitals for each irreducible representation are reported in the order (a_1 b_1 b_2 a_2). The MOLCAS 4 program system[37] has been used to yield the Rydberg functions collected in Table 1, and also in the CASSCF step required for obtaining the adapted MO's sets. All the calculations have been performed in a IBM-sp2 4xPower3 (350 MHz) node under AIX 4.3 operative system, running the codes in a single processor under scalar conditions.

3.1. VEE. For each of the C_{2v} irreducible representations dealt with in the present calculations, the MO's have been adapted at the CASSCF level through the diagonalization of the appropriately averaged first density matrixes. All the excited states of interest were included, with the same weight, in the averaging process. In these CAS' we have included the $2b_1$ MO as well as the virtual Rydberg orbitals involved in the description of the excited states. The CAS adopted for the B_2 symmetry was (2 1 2 6), and six states were averaged. In the CAS for the A_2 symmetry, (2 1 13 0), thirteen states were averaged, and in that for the B_1 symmetry, (22 2 1 0), twenty states were averaged. Finally, in the A_1 symmetry, thirteen states were averaged, with the CAS being (2 13 0 0) for the Rydberg states originating from the excitations of the $2b_1$ valence electron. The same CAS was adopted for the Rydberg state originating from the $5a_1 \rightarrow 4s$ excitation occurring in the same spectral region.

In the $(SC)^2$-CAS-SDCI step of the calculations the use of a large CAS space is highly demanding because the SDCI space increases sharply with the dimension of the CAS. Hence, MR-SDCI spaces, with a selected principal space have been used. When different MR spaces were employed, we will denote them as MR1, MR2, and MR3 spaces, and so on. In each case, the MR space has been selected in such a way that it can deal with a group of states. For example, in the A_2 symmetry we have considered two groups of states. One is that of the f states with this symmetry, and the other, that of the remaining states. The most difficult case was that of B_1 symmetry, due to the large number of states. To circumvent this problem, we selected up to six different MR spaces.

3.2. VIP. State-averaged adapted CASSCF MO's have been used for the VIP calculations, too. In this case, a CAS (3 2 2 1) with 7 electrons for all symmetries of the H_2S^+ cation (instead of the 8 electrons for the neutral system, H_2S) has been used. The CAS is equivalent to ($4a_1$ $5a_1$ $2b_2$ $2b_1$ $6a_1$ $3b_2$ $3b_1$ $1a_2$). For the VIP of the outer-valence states, in the CAS-SDCI calculations, the CAS' employed, have been ($5a_1$ $2b_2$ $2b_1$ $6a_1$ $3b_2$) for both the $^2B_2$ and $^2B_1$ states and ($4a_1$ $5a_1$ $2b_1$ $6a_1$ $3b_2$) for the $^2A_1$ states. In the calculations of some inner-valence states a larger CAS (5 3 3 1) has been used to adapt the MO's MR-SDCI spaces. The most relevant determinants occurring in the $(SC)^2$-MR-SDCI eigenvectors are reported in Table 4.

4. Results and Discussion

Our calculated vertical excitation energies (VEE) for more than 50 Rydberg states of the H_2S molecule are displayed in Table 2. For comparative purposes, the data supplied from coupled-channel static exchange (CC-SE) calculations by Diercksen and Langhoff (D&L),[7] the random phase approximation (RPA) calculations by Galasso[12] and the MRD-CI calculations by Petsalakis and Theodorakopoulos[13] have also been included. We have omitted the RPA calculations by Cacelli et al.[11] for simplicity, but they will be explicitly mentioned in the text whenever it matters, as regards the discussion of the results. We have also included the experimental values found in the literature.

The results of all the above theoretical procedures appear to be of good quality, on average. Unfortunately, Diercksen and Langhoff[7] did not include the A_2 states in their calculations. Letting the A_2 and f states apart, the mean absolute error (MAE) of the $(SC)^2$-MR-SDCI results with respect to the experimental data reported by D&L[7] is about 0.09 eV. The MAE derived by us for the other theoretical calculations is the following: 0.04 eV for the CC-SE procedure,[7] 0.12 eV for the RPA method,[12] and 0.26 eV for the MRD-CI method.[13] When the A_2 states are included, the above MAE's do not change significantly, with the exception of that of the RPA results[12] which varies to 0.16 eV. The MC−RPA and SC-RPA calculations of Cacelli et al.[11] also exhibit excellent MAE values. Putting aside the 3 $^1A_2$(3d) state, the maximum deviation of the present $(SC)^2$-MR-SDCI calculations is 0.21 eV and corresponds to the 7 $^1A_2$(4d) state. This deviation can be compared with the ones found in the RPA calculations:[12] 0.39 and 0.36 eV for the 7 $^1A_2$(4d) and the 3 $^1B_1$(3d) states, respectively; and with those of the MRD-CI procedure:[13] 0.44 and 0.46 eV for the 4 $^1B_1$(5s) and 11 $^1B_1$(6s) states, respectively. An inspection of Table 2 reveals certain disagreements among the experimental values from different sources, which makes the assessment of the theoretical results difficult for some of the states. Moreover, in many cases, the complexity of the spectral bands might call for an explicit account of vibronic coupling. Nevertheless, as already discussed, in the case of H_2S we can consider the VEE's to Rydberg states as a good approximation to the measured 0−0 vibronic energies.

Some of the open questions regarding the spectrum of H_2S are related to the existence of different experimental values. First, the location of the peaks corresponding to excitations to the 1 $^1A_2$(Vp-Rd) and 1 $^1B_1$(4s) states is not clear yet. Second, the existing discrepancies on the location of the peak arising from the excitation to the 1 $^1B_1$(4s) state also have some consequences on other states and symmetries. The excitations to higher $^1B_1$(*n*s) states ($n = 5-7$) show, to more or less extent, differences in the reported experimental values. Third, the relative position of the *n*d states is another matter of concern, with most of the difficulties involving the $^1A_2$(3d) state, for which all the available theoretical results predict a VEE that surpasses by 0.4−0.5 eV the reported experimental value. Fourth, the strong mixture between $^1B_1$(3d) and $^1B_1$(5s) makes the assignment of these states difficult. In all the problematic cases, we have performed the assignment by a thorough inspection of the dominant excitations to each state, as discussed below.

The $(SC)^2$-MR-SDCI vertical excitation energies (VEE) reported in Table 2 include the values corresponding to the 4f and 5f states, unlike the other theoretical methods, and consequently, no comparison between our results and other theoretical values has been possible. We have also performed calculations with the B+R basis set described above, without the f functions. The differences in the VEE values so obtained with respect to the same calculations including the f functions are lower than 0.05 eV on average for the s, p, and d Rydberg states, with the largest discrepancy found to be about 0.1 eV. This shows that the f states, despite lying in the same energies region, interact only slightly with the states of smaller angular moment.

The states in Table 2 are reported in order of increasing $(SC)^2$-MR-SDCI energies, and the state labeling includes the 4f and 5f states. The symmetry labels assigned to each state are in accord with those of the MRD-CI calculations by Petsalakis et al.[13] One cannot but notice a tendency in the $(SC)^2$ calculations to slightly underestimate the VEE's in the higher region of the spectrum, when a comparison is made with the experimental and the CC-SE values.

Table 2 clearly shows the grouping of the different Rydberg series: 4s, 4p, 3d, 5s, ... The present VEE for the $^1B_1$(4s) state, of about 6.5 eV, is 0.2 eV higher than that of Masuko et al.[4] However, more recent works report a wide band in this region,[8] located between 4.5 and 6.52 eV (a detailed compilation of the experimental values is given by Diercksen and Langhoff[7]). Abuain et al.[6] pointed out the existence of a maximum in the spectrum at 6.4 eV, which they assigned to a transition to a $^1B_1$ state. The same authors attributed some valence character to this band, associated with the forbidden transition to the $^1A_2$ state. The lowest $^1A_2$ state lies at 6.33 eV over the molecular ground state and, indeed, exhibits a substantial valence character. It could be of help finding the energy location of the triplet $^3A_2$

TABLE 2: Vertical Excitation Energies (eV) of H_2S (B+R Basis Set)

				other calculations		
states[a]	formal character	exp[f]	$(SC)^2$- MR-SDCI	RPA[g]	MRD-CI[h]	CC-SE[i]
1 $^1A_2$	Vp-Rd	4.6−7.5, 7.4	$6.329^{c(1)}$	6.54	6.80	
1 $^1B_1$	4s	6.33, 4.59−6.52	$6.472^{d(1)}$	6.57	6.16	6.44
2 $^1A_2$	4p	7.85, 7.89	$7.980^{c(1)}$	8.08	7.70	
2 $^1B_1$	4p	8.27, 8.18−8.32, 8.18	$8.090^{d(1)}$	8.16	7.80	8.16
2 $^1A_1$	4p	8.03, 8.19, 8.27	$8.236^{e(1)}$	8.32	7.97	8.26
3 $^1B_1$	3d	8.66	$8.485^{d(1)}$	9.02	8.65	8.48
4 $^1B_1$	5s	8.13, 8.84	$8.698^{d(1)}$	8.75	8.40	8.80
1 $^1B_2$	3d	8.79−8.81	8.766	9.03	8.69	8.91
3 $^1A_1$	3d	8.81	$8.809^{e(1)}$	9.05	8.70	8.92
5 $^1B_1$	3d	8.91	$8.913^{d(1)}$	9.05	8.69	8.98
3 $^1A_2$	3d	8.46, 8.55, 8.20	$9.000^{c(1)}$	9.19	8.85	
4 $^1A_2$	5p	9.17, 9.2, 9.11	$9.239^{c(1)}$	9.32	8.98	
6 $^1B_1$	5p	9.27, 9.31, 9.32	$9.301^{d(2)}$	9.35	9.00	9.34
4 $^1A_1$	5p	9.27, 9.31, 9.34	$9.329^{e(2)}$	9.39	9.04	9.29
7 $^1B_1$	4d	9.44	$9.355^{d(2)}$	9.66	9.32	9.42
2 $^1B_2$	4d	9.54	9.451	9.67	9.30	9.59
5 $^1A_2$	4f		$9.460^{c(2)}$			
8 $^1B_1$	4f		$9.463^{d(3)}$			
9 $^1B_1$	4f		$9.468^{d(3)}$			
10 $^1B_1$	4d	9.60	$9.476^{d(2)}$	9.68	9.33	9.64
6 $^1A_2$	4f		$9.477^{c(2)}$			
5 $^1A_1$	4f	9.61	$9.478^{e(3)}$			
6 $^1A_1$	4f		$9.482^{e(3)}$			
3 $^1B_2$	4f		9.487			
7 $^1A_1$	4d	9.54−9.55	$9.488^{e(3)}$	9.68	9.30	9.58
8 $^1A_1$	4s[b]	9.2−9.5	$9.510^{e(2)}$		9.28	9.45
11 $^1B_1$	6s	9.27, 9.66	$9.550^{d(4)}$	9.55	9.20	9.54
7 $^1A_2$	4d	9.36	$9.571^{c(1)}$	9.75	9.42	
12 $^1B_1$	6p	9.76, 9.79	$9.603^{d(4)}$	9.82	9.47	9.80
8 $^1A_2$	6p	9.70	$9.653^{c(1)}$	9.81	9.48	
9 $^1A_1$	6p	9.76, 9.79	$9.704^{e(1)}$	9.80	9.46	9.81
13 $^1B_1$	5d	9.84	$9.716^{d(3)}$	9.97	9.56	9.83
9 $^1A_2$	5d	9.83	$9.741^{c(2)}$	10.00	9.57	
14 $^1B_1$	5d	9.92	$9.746^{d(4)}$	9.98	9.63	9.95
4 $^1B_2$	5d	9.88	9.767	9.98	9.60	9.91
10 $^1A_2$	5f		$9.784^{c(2)}$			
15 $^1B_1$	5f		$9.787^{d(3)}$			
10 $^1A_1$	5d	9.88−9.89	$9.789^{e(1)}$	9.98	9.64	9.91
11 $^1A_1$	5f	9.92	$9.791^{e(3)}$			
11 $^1A_2$	5f		$9.793^{c(2)}$			
12 $^1A_1$	5f		$9.803^{e(3)}$			
16 $^1B_1$	5f		$9.806^{d(3)}$			
5 $^1B_2$	5f		9.809			
17 $^1B_1$	7s	9.77, 9.94	$9.810^{d(4)}$	9.91	9.74	9.89
18 $^1B_1$	6d	10.04	$9.851^{d(4)}$		9.63	10.04
6 $^1B_2$	6d	10.08	9.935		9.85	10.08
19 $^1B_1$	6d	10.09	$9.962^{d(6)}$		9.84	10.12
13 $^1A_1$	7p	10.00	$9.970^{e(3)}$		9.77	10.03
12 $^1A_2$	7p	9.97	$9.988^{c(1)}$		9.80	
20 $^1B_1$	7p	10.02	$9.990^{d(5)}$		9.78	10.03
14 $^1A_1$	6d	10.08	$10.009^{e(3)}$		9.84	10.09

[a] Dominated by $2b_1 \rightarrow$ Ryd monoexcitations. [b] Exceptionally, this state originates from a $5a_1 \rightarrow$ Ryd(s) monoexcitation. [c] Calculated with different MR spaces. Symmetry A_2: (1) ≡ MR1, (2) ≡ MR2. [d] Calculated with different MR spaces. Symmetry B_1: (1) ≡ MR1, (2) ≡ MR2, (3) ≡ MR3, (4) ≡ MR4, (5) ≡ MR5, (6) ≡ MR6. [e] Calculated with different MR spaces. Symmetry A_1: (1) ≡ MR1, (2) ≡ MR2, (3) ≡ MR3. [f] See text for comments on the experimental values. [g] RPA calculations. Galasso, ref 12. [h] MRD-CI calculations. Petsalakis et al., ref 13. [i] CC-SE: coupled-channel static-exchange calculations, ref 7.

and $^3B_1$ states. The present $(SC)^2$-MR-SDCI procedure predicts for these states excitation energies of 5.90 and 6.09 eV, respectively. Our calculations agree with the occurrence of two states, $^1A_2$ and $^1B_1$, between 6.3 and 6.5 eV. The RPA values reported by Galasso[12] for these states are approximately 6.5 eV, whereas the RPA calculations by Cacelli et al.[11] locate these states between excitation energies of 6.5 and 6.6 eV. D&L[7] did not include A_2 states in their calculations, but they found the first $^1A_1 \rightarrow {}^1B_1(4s)$ transition to take place at 6.44 eV, which is in good agreement with our $(SC)^2$ results.

Mayhew et al.[8] have pointed out that for low *n* values, the proximity of the Rydberg electron to the nonspherical molecular core leads to a substantial splitting of the various components of each atomic-like “d states set”. This symmetry-breaking effect gives rise to the so-called C, D, and E series, according to Price.[1] Our results lead to three groups of 3d states, one corresponding to the first $^1B_1(3d)$ state, another to the $^1B_2(3d)$ and $^1A_1(3d)$ states, and the last group to the remaining $^1B_1(3d)$ state. Experimentally, the VEE’s for these three groups of Rydberg states are 8.66, 8.81, and 8.91 eV,[8] respectively, in accord with our $(SC)^2$-MR-SDCI predictions. However, one of the largest discrepancies between our calculations and the experimental values involves the $^1A_2(3d)$ state. We obtained a VEE of 9.00 eV, while some experimental measurements[4,6] locate this state at about 8.46−8.55 eV above the ground state. The RPA[12] and the MRD-CI[13] calculations predict for the $^1A_2$(3d) excitation energies of 9.19 and 8.85 eV, respectively, included in Table 2. Cacelli et al.[11] found, through SC-RPA calculations, a VEE for the $^1A_2$(3d) state of 9.17 eV. It is apparent that all the different calculations predict the $^1A_2$(3d) state to lie between 0.4 and 0.5 eV above the experimental value. To sort out the discrepancies, we performed additional calculations for this state with a CAS-SDCI space, where the CAS(2e,6o) space included the most relevant orbitals to the description of the $^1A_2$(3d) state. The resulting CI matrix involved 5 929 996 determinants and yielded a VEE of 9.09 eV. Additional calculations following several size-consistency-error-free approaches such as the (SC)^2, the MR-AQCC, and the standard low-order Davidson correction for the MR-CI procedure were also performed. The resulting VEE's were 9.01, 9.07, and 8.95 eV, respectively. These results do not fall yet satisfactorily close to the experimental assignment, but they reveal that the discrepancies between the theoretical and experimental values for the $^1A_2$(3d) state cannot be associated with an insufficient correction of the size-extensivity error.

The 3d states of $^1B_1$ symmetry appear to be strongly mixed with the $^1B_1$(5s) state. Different experimental VEE values have been reported for the $^1B_1$(5s) state, such as that of 8.13 eV by Ashfold et al.[8,10] and that of 8.84 eV by Masuko et al.[4] The present work predicts a VEE of 8.7 eV for this state, and the wave function reflects an important mixing between 3d and 5s Rydberg excitations. The comparison with the results by D&L[7] is excellent, as they locate the $^1B_1(3d_{z^2})$, $^1B_1$(5s), and $^1B_1(3d_{x^2-y^2})$ states at VEE's of 8.48, 8.80, and 8.98 eV, respectively. The large mixing to which these states are subjected has been earlier discussed by Cacelli et al.[11] These authors remarked that the mixing with the a_1 excited orbitals leads to difficulties when it comes to establishing a conventional s or d labeling of the $^1B_1$ states. In the present calculations, the weightings for the $1b_1 \rightarrow$ 5s and $1b_1 \rightarrow$ 3d excitations are actually similar to those found in the description of the $^1B_1$(5s) and the $^1B_1$(3d) wave functions. The assignment of these states has then been made by determining which of these excitations is slightly dominant in each state. Cacelli et al.[11] found the VEE's of three states with $^1B_1$ symmetry, through a MC-RPA procedure, to be 8.50, 8.74, and 8.97 eV, respectively. These values conform fairly well with the present (SC)^2 ones.

It can be noticed that as *n* increases, the splittings in the *n*d states becomes smaller. The VEE's of the four $^1B_1$, $^1B_2$, and $^1A_1$ 4d states are located experimentally between 9.44 and 9.60 eV. The three series C, D, and E occur at excitations of 9.44, 9.54, and 9.60 eV,[8] respectively. The (SC)^2-MR-SDCI values for these states fall within a narrow range of 0.1 eV, which is of the same order as that of the experimental values. The splittings in the five 5d states are still smaller. Experimentally, these five states have been located between VEE's of 9.84−9.92 eV, whereas our values are situated 0.1 eV below that range, showing the same trend mentioned above for the rest of the states with VEE's over 9.7 eV.

Sizable discrepancies between different experimental VEE's can also be noticed in Table 2 for the $^1B_1$(6s) and $^1B_1$(7s) states. While Ashfold et al.[10] and Mayhew et al.[8] report values of 9.27 and 9.77 eV, respectively, the ones measured by Masuko et al.[4] were 9.66 for $^1B_1$(6s) and 9.94 eV for $^1B_1$(7s). The present (SC)^2 theoretical values are 9.55 eV for the $^1B_1$(6s) state and 9.81 eV for the $^1B_1$(7s) state, in better agreement with those of ref 4 than the ones of ref 10, but still slightly too low in magnitude. The calculations of D&L lead to VEE's that conform well with the experimental values of Masuko et al.[4]

TABLE 3: Vertical Ionization Potentials (eV) of H_2S Compared with Experimental Values

state	CAS−SDCI CI	CAS−SDCI (SC)^2	exp[a]
$^2B_1(2b_1^{-1})$	10.20	10.29	10.50
$^2A_1(5a_1^{-1})$	13.27	13.32	13.45
$^2B_2(2b_2^{-1})$	15.50	15.57	15.50
$^2A_1(4a_1^{-1})$[b]	22.77	22.45	22.37
MAE	0.22	0.12	

[a] See refs 21 and 23. [b] See also comments in the text.

The $5a_1 \rightarrow$ 4s excitation occurs among the lowest $^1A_1 \rightarrow {}^1A_1$ transitions. The $^1A_1$(4s) state is the only one reported in Table 2 that is dominated by an excitation from the $5a_1$ MO. It is located, according to our (SC)^2 calculations, at a VEE of 9.51 eV. Other reported values are the one equal to 9.45 eV by D&L,[7] and that of 9.28 eV supplied by the MRD-CI calculations.[13] Galasso[12] did not report any data on this excitation. The $^1A_1$ states reveal a mixing between excitations arising from the $5a_1$ and the $2b_1$ MO's. This mixing has been earlier pointed out by Cacelli et al.,[11] who attributed a value of 9.44 eV to the $^1A_1$($5a_1 \rightarrow$ 4s) excitation, with a MC-RPA calculation.

As regards the f states, the present results predict the 4f and 5f states to lie, respectively, at about 9.5 and 9.8 eV above the ground state. These values conform rather well with the measurements by Asfhold et al.,[10] 9.6 and 9.9 eV, respectively.

In the calculation of vertical ionization potentials (VIP) of the outer-valence states of H_2S, we have used the open-shell version of the matrix-dressing (SC)^2 procedure. Our results are collected in Table 3, together with the experimental values measured by Adam et al.[21] Other experimental data found in the literature[17−19,38] are slightly different from the ones in Table 3, but the discrepancies never are greater than the experimental error ranges, which are about 0.2 eV.

The weighting of the one-hole Koopmans' determinant in the CI wave functions for the lowest states of each symmetry ($^2B_1(2b_1^{-1})$, $^2B_2(2b_2^{-1})$, and $^2A_1(5a_1^{-1})$) are higher than 0.95. However, for the $^2A_1(4a_1^{-1})$ state, the $(4a_1^{-1})$ Koopmans' determinant weighting is only about 0.5−0.6, as a result of strong mixing with other processes, such as the ionization-excitation $2b_1^{-2}7a_1^1$. It is apparent that for this inner-valence state, the dressed CI calculation leads to an error of less than 0.1 eV. On average, the absolute error is reduced from 0.22 to 0.12 eV by the dressing procedure.

As is well-known, one of the most important issues in photoelectron spectra is the proper analysis of the inner-valence region. In the case of H_2S this analysis is particularly difficult. The studies by Adam et al.[21] and French et al.[23] led to the occurrence of at least four to eight peaks in the range 19−36 eV, all of which were claimed to be related to processes that involve the $4a_1$ orbital. In all our calculations we have found an A_1 excited state that belongs to the H_2S^+ cation and it is located immediately below 20 eV. The origin of this state is a mixing between the $2b_1^{-2}6a_1^1$ process and the $(4a_1^{-1})$ Koopmans' determinant. The excitation energy of the A_1 state has been found to be near 19.8 eV (19.78 eV with the B+R basis set and 19.82 with the B basis set in the (SC)^2-CAS-SDCI calculations). Wasada and Hirao[39] reported two states at 22.28 and 24.14 eV, respectively, after performing SAC-CI calculations with a DZP-augmented basis set. We have found, in the present calculations, two states of similar nature at 19.8 and 22.45 eV, respectively. Wasada and Hirao[39] appear to have

TABLE 4: Excited States of A_1 Symmetry of H_2S^+ [$(SC)^2$-ref-SDCI Calculations with the B Basis Set]

		ref		
label number	states[a]	CAS1[d]	CAS2[d]	MR
1	$5a_1^{-1}$	13.33	13.37	13.34
2[b]	$2b_1^{-2}6a_1^1$	19.82	19.93	19.91
3[b]	$4a_1^{-1}$, $2b_1^{-2}7a_1^1$	22.45	22.34	22.31
4	$5a_1^{-1}2b_2^{-1}3b_2^1$	22.93	22.99	22.97
5[b]	$2b_1^{-2}na_1^1$	23.35	23.32	23.15
6[b]	$2b_1^{-2}na_1^1$	23.83	24.06	23.64
7	$5a_1^{-1}2b_1^{-1}3b_1^1$	23.83	24.12	23.92
8[c]	$5a_1^{-1}2b_2^{-1}3b_2^1$, $5a_1^{-2}6a_1^1$	25.30	25.32	25.41
9[c]	$5a_1^{-1}2b_2^{-1}3b_2^1$, $5a_1^{-1}2b_1^{-1}3b_1^1$	25.64	25.80	25.66

[a] Dominant confirguration. [b] Important contribution to the $4a_1^{-1}$ Koopmans' determinant. [c] Less important contributions to the $4a_1^{-1}$ Koopmans determinant. [d] CAS1 is the same CAS as that in Table 3. See text for more details.

incorrectly assigned these two states to the EMS experimental peaks[23] at 22.37 and 24.07 eV, respectively, and did not report any state below 20 eV. However, more recently, Ehara et al.,[40] also using the SAC-CI method with a correlation-consistent polarized valence triple-ζ (cc-pVTZ) basis set augmented with three s-, p-, and d-type Rydberg functions,[40] found a state at 20.00 eV, which is similar in nature to our state displayed in the second row of Table 4. Ehara et al.[40] assigned the experimentally observed peak at about 19.6−19.9 eV to an excitation to this state. We present a more detailed study in Table 4, where we have collected CAS- and MR-SDCI calculations on states with A_1 symmetry up to 25.7 eV. We have focused our interest on this state at energies below 20 eV, and on the two experimental peaks at 22.37 and 24.07 eV, by a thorough analysis of the states falling in the range 19−26 eV.

In Table 4, CAS1 denotes the same CAS space used in the calculations for which our results are shown in Table 3. CAS2 includes an additional virtual MO of a_1 symmetry, thus being ($4a_1$ $5a_1$ $2b_1$ $6a_1$ $7a_1$ $3b_2$). The use of the MR-SDCI space instead of the whole CAS-SDCI space reduces the dimension of the CI problem to about 400 000 determinants, which is more convenient for the multiroot searching process. A slightly larger CASSCF was also adopted for these calculations as mentioned in subsection 3.2. The results collected in Table 4 provide us with an additional test on the extent of the errors introduced by the use of the less demanding $(SC)^2$-MR-SDCI instead of the larger $(SC)^2$-CAS-SDCI calculations.

The first relevant feature in Table 4 is that only four among the nine states displayed in the table show a relevant contribution from the ($4a_1^{-1}$) process. Only for the state labeled as 3 is the ($4a_1^{-1}$) process the leading contribution. With the $(SC)^2$-MR-SDCI calculations we have found two of these states at excitation energies of 19.9 and 22.3 eV, respectively (in agreement with the EMS peaks), and two others at 23.1 and 23.6 eV. There are two more states (placed in the eighth and ninth rows of Table 4) at 25.4 and 25.7 eV, with a lesser contribution of the ($4a_1^{-1}$) process. All of the states in Table 4 could contribute to the intensity of satellite lines in the corresponding region of the photoelectron spectrum.

In Table 5 we have compiled the experimental values known to us in the 19−27 eV energy range. We find it of relevance to note the great variety of peaks reported in this region, although they seem to differ in the measurements by different authors. In particular, in one of the most recent works available, Adam et al.[21] report up to 10 peaks. If we take the measurements by French et al.[23] as a reference, the first two peaks can be related to our second and third states displayed in Table 4, as mentioned above. The fifth and sixth states, with a high contribution of the ($4a_1^{-1}$) process, are involved in the two peaks experimentally located at 23.05 and 23.57 eV, respectively (values in column 6 of Table 5 in ref 21), as well as with those calculated by Ehara et al.[40] at the respective energies of 23.20 and 23.62 eV, and with a high intensity. The rest of the peaks are of difficult assignment, given the intricate manifold of states of the H_2S^+ cation. However, it is important to note that our calculations and analysis agree well with the conclusions of French et al.[23] and Adam et al.[21] and with the recent SAC-CI calculations by Ehara et al.[40] as regards the existence of a large variety of peaks connected to the $4a_1$ orbital.

TABLE 5: 19−27 eV Region of Photoelectron Spectrum of H_2S (Energies in eV)

states no.[a]	He(II)[b]	(e,2e)[c]	(40.8 eV)[d]	X-ray 1254 eV[e]	50 eV[f]	EMS[g]
1	19.4	19.4		19.4	19.6	19.63
2	22.0	22.0	22.1		22.0	
3			22.7		22.54	22.37
4			23.0	23.0	23.05	
5	23.3	23.4	23.3		23.31	
6					23.57	
7					23.72	
					23.98	24.07
					24.5	
8		27.0			26.7	26.89

[a] As found in the work of Adam et al.[21] [b] Reference 18. [c] Reference 17. [d] Reference 19. [e] References 19 and 38. [f] Reference 21. [g] Reference 23.

5. Conclusions

Accurate calculation on a large manifold of excited states are of relevant importance for the study of the low lying series of Rydberg states. The availability of very accurate coupled-channel static-exchange CI calculations, as well as of a good number of experimental transition energies, makes H_2S an interesting test system in this context. Moreover, the origin of the electronic excitations that leads to the existence of the Rydberg states of H_2S is a nonbonding orbital from the ground electronic configuration of this molecule. As a consequence, the vertical transition picture leads to results of theoretical calculations that are a good approach to the experimental values.

The present results are, to our knowledge, the most complete series of theoretical vertical excitation energies calculated and include, for the first time, the 4f and 5f Rydberg series. A comparison with the experimental values shows that the mean absolute error for the present calculations is about 0.1 eV. Notwithstanding, further work is in progress to overcome the tendency of our procedure to slightly underestimate the excitation energies of the states lying in the higher region of the spectrum.

A general discrepancy between the experimental excitation value for the $^1A_2(3d)$ state and the different theoretical results has manifested itself, which cannot be associated either to a limitation in the basis set size or to a lack of size extensivity. Coupled channel calculations or accounting for vibronic coupling may be in order in this particular case, but the excitation to this state is optically forbidden and the experimental information is difficult to obtain.

The important mixing between the 3d and 5s ($^1B_1$) states has been discussed, and their assignment is accurately established on the basis of the leading transitions. Work is in progress in order to assess this assignment by means of the calculation of transition probabilities to the Rydberg series of the H_2S molecule.

The present VIP calculations confirm the existence of a $^2A_1$ state (found, for the first time to fall below 20 eV) that can be responsible for the small satellite peak occurring in the low-energy side of the main ($4a_1^{-1}$) photoionization peak. This peak was initially assigned to nitrogen impurities,[24] but later there was general consensus among the experimentalists on its belonging to the H_2S spectrum,[17,25] as discussed above. Nevertheless, theoretical calculations on this system feature are scarce and hardly discuss this aspect.

The present work illustrates the advantages of using a selected MR space of generators instead of a CAS space in the calculations of a large manifold of states, as it provides a convenient compromise between flexibility (a few different choices of the MR space have been required), practicability (final CI dimensions are distinctly reduced) and accuracy (as illustrated, e.g., in Table 4).

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