MRSDCI Vertical Excitation Energies and MQDO Intensities for Electronic Transitions to Rydberg States in H_2S

A. M. Velasco and I. Martín*

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

J. Pitarch-Ruiz and J. Sánchez-Marín

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

Received: February 9, 2004; In Final Form: June 11, 2004

Vertical excitation energies and the ionization potential for H_2S have been calculated through the multireference singles and doubles configuration interaction method. We have used these values to calculate oscillator strengths of H_2S. The molecular quantum defect orbital method has been employed to determine analytical wave functions and transition intensities involving Rydberg states. The results have been analyzed on the grounds of the data available in the literature.

I. Introduction

Hydrogen sulfide, as a reduced sulfur compound, plays an important role in the global cycling of sulfur and has been discovered not only in the Earth's atmosphere but also in the interestellar medium.[1,2] It is mainly released into the Earth's atmosphere by volcanic and biogenic emissions, especially in the areas of oceans,[3,4] tropical rain forests,[5] wetland plant communities,[6] and during oil and natural gas recovery operations.[7] It has also been detected in the atmospheres of Jupiter[8] and Io as well as on the surface of the satellite,[9] in the outgassing of comets,[10,11] and even in star-forming regions.[12] In addition, H_2S is known to be one of the major pollutants of the Earth's atmosphere, and is involved in corrosive processes in metals.[13] Moreover, an atmosphere of H_2S is used[14] in the synthesis of a semiconductor, tungsten sulfide (WS_2), whose molecular structure is identical to that of fullerene (C_{60}).

Photoprocesses of H_2S have also been the subject of a number of experimental and theoretical studies. In addition to a fundamental interest in the electronic structure and excited states of hydrogen sulfide, electronic transition probability data are required to model equilibrium conditions in the stratosphere and troposphere, as well as to analyze observed data from planetary atmospheres and the interestellar space.[15,16] Therefore, quantitative studies of the interaction of hydrogen sulfide with visible, UV, VUV, and soft X-ray radiation are of importance in many areas of science and technology including astrophysics, the study of planetary atmospheres (aeronomy), dosimetry, and fusion.[17]

It is the purpose of the present study to supply new spectroscopic data on H_2S concerning Rydberg transition intensities. The procedures followed in the present work have recently been used satisfactorily to calculate vertical excitation energies (VEEs) and ionization potentials (IPs), in addition to absorption oscillator strengths and Einstein emission coefficients for the Rydberg states of ArH.[18] In this work, VEEs and IPs at the multireference singles and doubles configuration interaction (MR-SDCI) level, have been determined for H_2S at the equilibrium geometry ($R_{S-H} = 2.52$ au, $\vartheta_{H-S-H} = 92.2°$). In an unmixed molecular Rydberg state, the excited electron occupies a quasiatomic orbital of much greater dimensions than those of the singly charged molecular core. Consequently, Rydberg orbitals are usually not very important in determining the geometry of the excited states. Instead, it is the core vacancy what determines the geometry in a Rydberg excitation.

We have recently reported the vertical spectrum of H_2S[19] and pointed out several open questions concerning this spectrum. In the present work, both VEEs and IPs have been calculated using MR and complete active space (CAS) as generators of the complete SDCI spaces. For the first time, Rydberg states of *f* character have been dealt with.[19] We have mainly focused our efforts on the analysis of the Rydberg states of H_2S, determined with the aforementioned multireference SDCI procedure.

For transition-intensity calculations, the molecular-adapted version of the molecular quantum defect orbital (MQDO) method,[20,21] which has proven to yield correct intensities for Rydberg transitions in a variety of molecular species,[18,20−24] has been employed. We have considered those transitions that obey the Laporte, $\Delta l = \pm 1$, selection rule, in addition to symmetry constrains, as these are experimentally observed to be the strongest ones, with the exception of those involving states that show signs of important mixing with others. We have compared our calculated oscillator strengths with some experimental and theoretical values available in the literature.

II. Calculation of Transition Intensities

The QDO formalism adapted to deal with molecular Rydberg transitions has been described in detail elsewhere.[20,21] A very brief summary, thus, follows. The MQDO radial wave functions are the analytical solutions of a one-electron Schrödinger equation that contains a model potential of the form

$$V(r)_a = \frac{(c - \delta_a)(2l + c - \delta_a + 1)}{2r^2} - \frac{1}{r} \qquad (1)$$

---

* To whom correspondence may be addressed. Tel: +34-983-423272. Fax: +34-983-423013. E-mail: imartin@qf.uva.es.

10.1021/jp049415n CCC: $27.50

where *a* represents the set of quantum numbers and symmetry labels that define a given molecular state. Solutions of this equation are related to Kummer functions. The parameter δ_a is the quantum defect, which varies with the angular momentum of the electron and with the symmetry of the state (i.e., differs from one Rydberg series to another), and *c* is an integer within a narrow range of values that ensures the normalization of the orbitals and their correct nodal pattern. The number of radial nodes is equal to $n - l - c - 1$. The angular part of the molecular Rydberg orbitals is a symmetry-adapted linear combination of spherical harmonics so that the Rydberg molecular orbitals (MOs) form bases for the different irreducible representations of the molecular symmetry group.

The quantum defect, δ_a, corresponding to a given state, is related to the energy eigenvalue through the following equation

$$E_a = T - \frac{1}{2(n_a - \delta_a)^2} \qquad (2)$$

where *T* is the ionization energy. Both *T* and E_a are expressed here in Hartrees.

The absorption oscillator strength for an electronic excitation between two bound states *a* and *b* may be expressed as

$$f(a \rightarrow b) = \frac{2}{3} N(E_b - E_a) Q\{a \rightarrow b\} |R_{ab}|^2 \qquad (3)$$

N is the number of equivalent electrons in the MO where the transition originates, and $Q\{a \rightarrow b\}$, referred to as the angular factor, results from the integration of the angular parts of the MOs involved in the transition. R_{ab} is the radial transition moment. The detailed MQDO algebraic expressions for the radial transition moment are given in ref 21.

We find it relevant to mention here that all the radial transition integrals that involve quantum defect orbitals have closed-form analytical expressions. This makes the calculation of transition intensities free from numerical errors and convergence problems, which is, in our view, an important computational advantage.

III. Energies and Quantum Defects

The MR-SDCI energy calculations have been performed with the CASDI[25,26] code. This code includes a recent option that allows for large-scale MR-SDCI calculations without the additional requirement that the MR space be a CAS.[27] The MR-SDCI option removes, from the reference space of SDCI generators, the high-energy excitations occurring in the CAS, which play an irrelevant role in the description of the low-lying excited states. The dimension of the CI spaces generated in this way can be several orders of magnitude smaller than the corresponding CAS-SDCI spaces. Such a reduction is performed efficiently without a sensible loss of efficiency in the addressing and memory managing so that most algorithmic advantages inherent in the CAS description are retained.[27] Test calculations have shown that, as long as the MR set is not exceedingly small or badly adapted, the error relative to the corresponding CAS-SDCI values falls quickly with the dimension of the generated SDCI space, so that one easily gets stable (but asymptotically decaying) errors for the both ground state and the vertical excitation energies,[27] with only a small fraction of the computational effort.

The atomic natural orbitals (ANO)[28] basis sets [4s3p2d1f] for S and [2s1p] for H, respectively, have been 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 attain improved asymptotic conditions for the Rydberg series. More details on the basis set, in particular those concerning the augmented basis functions exponents and coefficients, can be found in ref 19. The MOs resulting from the RHF calculation have been adapted, separately for each C_{2v} symmetry representation, by means of equally weigthed state averaging. The first-order CAS self-consistent field (SCF) density matrixes of all the CASSCF states of each symmetry were combined, and the resulting pseudo natural orbitals have been used for the subsequent MR-SDCI calculations. The basis-set augmentation, the CASSCF calculations, and the state-averaging steps were performed by means of the MOLCAS 4 program.[29] In the CASSCF MOs generating step, four electrons were included in the active space in all symmetries. The active spaces in the CASSCF calculation step, given in the (a_1 b_1 b_2 a_2) order, were (2 13 0 0) for the A_1 symmetry, (22 2 1 0) for the B_1 symmetry, (2 1 2 6) for the B_2 symmetry, and (2 1 13 0) for the A_2 symmetry. The inactive space was (3 1 2 0), and the core $1a_1$ MO was frozen in all cases.

The MR space for the different MR-SDCI calculations has been selected by starting with the single-reference (SR)-SDCI calculation. The leading determinants in the wave functions have been then included, recursively, in the MR space. The final MR spaces included all the determinants having coefficients in the MR-SDCI wave function of the targeted states larger than 0.15. In this way, the MR spaces should be large enough to avoid significant errors in the excitation energies as compared to those of the corresponding CAS-SDCI calculation, i.e., a CAS-SDCI procedure that would include all the MOs involved in the MR excitations as active space. In most cases, a significant number of excited states can be calculated with a reference set (MR), in the same way as it has been described in ref 19.

The ground-state outer electronic configuration of H_2S may be written as follows, ...$(2b_2)^2(5a_1)^2(2b_1)^2X^1A_1$ in C_{2v} symmetry, where the highest-occupied molecular orbital, $2b_1$, is essentially a nonbonding $3p_x$ atomic orbital located on the sulfur atom, with its electron density being perpendicular to the molecular plane.[30] $5a_1$ is H−S bonding. Rydberg MOs in H_2S may be denoted as *n*s (a_1), *n*p (b_2, a_1, and b_1), and *n*d (a_1, a_1, b_1, a_2, b_2). It should be noted, however, that the s, p, and d description for Rydberg MOs is an oversimplification when valence−Rydberg or Rydberg−Rydberg mixing is present.

Conventional analyses of the one-photon VUV absorption spectrum of H_2S have identified a number of well-defined Rydberg series converging to the first ionization potential. The former have been assigned in terms of electronic promotions from the $2b_1$ MO to different orbitals belonging to the $n\mathrm{sa}_1$, to the three different *n*p, and to the five different nd Rydberg series, respectively

$$2b_1 \rightarrow {}^1B_1(n\mathrm{sa}_1) \qquad n \geq 4$$

$$2b_1 \rightarrow {}^1A_2(n\mathrm{pb}_2),\ {}^1B_1(n\mathrm{pa}_1),\ {}^1A_1(n\mathrm{pb}_1) \qquad n \geq 3$$

$$2b_1 \rightarrow {}^1B_1(n\mathrm{da}_1\mathrm{I}),\ {}^1B_1(n\mathrm{da}_1\mathrm{II}),\ {}^1A_2(n\mathrm{db}_2),\ {}^1A_1(n\mathrm{db}_1),\ {}^1B_2(n\mathrm{da}_2) \qquad n \geq 3$$

Of these nine potential promotions, the two excitations to the Rydberg series of $n\mathrm{lb}_2$ symmetry, the $^1A_2(\mathrm{npb}_2)$ and $^1A_2(\mathrm{ndb}_2)$ series, for which the transition moment transforms as a_2 are C_{2v} symmetry forbidden. In addition, transitions of the type $2b_1 \rightarrow n\mathrm{p}$ are not allowed by the Laporte selection rule in the atomic limit. It has also been reported[31] that the upper state of the ($2b_1 \rightarrow 4\mathrm{sa}_1$) excitation contains some valence character.

TABLE 1: Vertical Excitation Energies (eV)

state	MR-SDCI[a]	exp[b]
1 $^{1}B_{1}(4sa_{1})$	6.567	6.33
2 $^{1}B_{1}(5sa_{1})$	8.760	8.837
11 $^{1}B_{1}(6sa_{1})$	9.585	9.656
17 $^{1}B_{1}(7sa_{1})$	9.8360	9.943
2 $^{1}B_{1}(4pa_{1})$	8.163	8.181
6 $^{1}B_{1}(5pa_{1})$	9.389	9.275
12$^{1}B_{1}(6pa_{1})$	9.693	9.764
20$^{1}B_{1}(7pa_{1})$	9.956	10.003
2 $^{1}A_{2}(4pb_{2})$	8.038	7.89
4 $^{1}A_{2}(5pb_{2})$	9.278	9.2
8 $^{1}A_{2}(6pb_{2})$	9.691	9.70
12 $^{1}A_{2}(7pb_{2})$	10.018	9.97
2 $^{1}A_{1}(4pb_{1})$	8.284	8.272
4 $^{1}A_{1}(5pb_{1})$	9.369	9.315
9 $^{1}A_{1}(6pb_{1})$	9.735	9.788
13 $^{1}A_{1}(7pb_{1})$	9.97	10.017
3 $^{1}B_{1}(3da_{1}I)$	8.569	8.661
7 $^{1}B_{1}(4da_{1}I)$	9.435	9.441
13 $^{1}B_{1}(5da_{1}I)$	9.732	9.839
18 $^{1}B_{1}(6da_{1}I)$	9.896	10.043
5 $^{1}B_{1}(3da_{1}II)$	8.967	8.914
10 $^{1}B_{1}(4da_{1}II)$	9.585	9.602
14 $^{1}B_{1}(5da_{1}II)$	9.781	9.919
19 $^{1}B_{1}(6da_{1}II)$	9.931	10.087
3 $^{1}A_{1}(3db_{1})$	8.854	8.81
7 $^{1}A_{1}(4db_{1})$	9.519	9.537
10 $^{1}A_{1}(5db_{1})$	9.821	9.88
14 $^{1}A_{1}(6db_{1})$	10.032	10.076
1 $^{1}B_{2}(3da_{2})$	8.796	8.79
2 $^{1}B_{2}(4da_{2})$	9.482	9.54
4 $^{1}B_{2}(5da_{2})$	9.798	9.88
6 $^{1}B_{2}(6da_{2})$	9.980	10.08

[a] This work. [b] References 31−34.

TABLE 2: Quantum Defects for Rydberg States of H_2S

state	MR-SDCI[a]	MR-SDCI[b]	exp[c]	exp[d]
$^{1}B_{1}(4sa_{1})$	2.13	2.13	2.19	2.18
$^{1}B_{1}(5sa_{1})$	2.17		2.10	
$^{1}B_{1}(6sa_{1})$	2.06		1.89	
$^{1}B_{1}(7sa_{1})$	2.33		1.87	
$^{1}B_{1}(4pa_{1})$	1.57	1.56	1.56	1.56
$^{1}B_{1}(5pa_{1})$	1.44		1.61	
$^{1}B_{1}(6pa_{1})$	1.79		1.58	
$^{1}B_{1}(7pa_{1})$	1.80		1.54	
$^{1}A_{2}(4pb_{2})$	1.63	1.63	1.70	1.70
$^{1}A_{2}(5pb_{2})$	1.61		1.71	
$^{1}A_{2}(6pb_{2})$	1.79		1.77	
$^{1}A_{2}(7pb_{2})$	1.80		1.73	
$^{1}A_{1}(4pb_{1})$	1.50	1.50	1.51	1.51
$^{1}A_{1}(5pb_{1})$	1.47		1.55	
$^{1}A_{1}(6pb_{1})$	1.67		1.50	
$^{1}A_{1}(7pb_{1})$	1.73		1.46	
$^{1}B_{1}(3da_{1}I)$	0.32	0.32	0.25	0.27
$^{1}B_{1}(4da_{1}I)$	0.36		0.35	
$^{1}B_{1}(5da_{1}I)$	0.68		0.32	
$^{1}B_{1}(6da_{1}I)$	1.09		0.29	
$^{1}B_{1}(3da_{1}II)$	−0.02	0.03	0.03	0.03
$^{1}B_{1}(4da_{1}II)$	0.06		0.02	
$^{1}B_{1}(5da_{1}II)$	0.52		−0.02	
$^{1}B_{1}(6da_{1}II)$	0.93		−0.04	
$^{1}A_{1}(3db_{1})$	0.09	0.12	0.13	0.13
$^{1}A_{1}(4db_{1})$	0.20		0.16	
$^{1}A_{1}(5db_{1})$	0.39		0.16	
$^{1}A_{1}(6db_{1})$	0.36		0.05	
1 $^{1}B_{2}(3da_{2})$	0.14	0.18	0.15	0.15
2 $^{1}B_{2}(4da_{2})$	0.27		0.15	
4 $^{1}B_{2}(5da_{2})$	0.47		0.16	
6 $^{1}B_{2}(6da_{2})$	0.68		0.016	

[a] Derived from the MR-SDCI energy values. [b] Derived from a least-squares fitting of MR-SDCI energies. [c] Derived from the experimental energy values**,** refs 31−34. [d] Derived from a least-squares fitting of the experimental energies, refs 31−34.

The energy data chosen for the present calculations of transition intensities have been the MR-SDCI vertical excitation energies computed in the present work, as well as the experimental values that were consistent with each other of those found in the literature.[31−34] As previously remarked,[19] there is certain disagreement among some of the experimental excitation energies. This fact made our assignment of the MR-SDCI values difficult for some of the states. Only the 1 $^{1}B_{1}(4sa_{1})$ state has been calculated with an error greater than 0.15 eV relative to the experimental value, which for this state has been taken from ref 33. However, a wide band ranging from 4.89 to 6.52 eV has been assigned to this state in a more recent reference (ref 32). Hence, the assignation of a vertical experimental value for this state is not clear. If this state is excluded, the absolute average error of the calculated excitation energies is about 0.07 eV. The presently calculated vertical excitation energies, together with experimental values, are collected in Table 1.

The value of 10.46 eV, adopted for the ionization energy (IP) from the outermost orbital. The ionization can be described as the $(2b_1)^{-1}$ process and has been recently reported from high-resolution measurements.[35,36]

In Table 2, we display the quantum defects for the molecular Rydberg states**.** These values have been calculated by means of eq 2 using both the experimental and the MR-SDCI vertical excitation energies reported in Table 1. The quantum defect values individually obtained for each state are collected in columns one and three. In columns two and four, we display the quantum defects extracted from the MR-SDCI and the experimental energies, respectively, after both were subject to a least-squares fitting procedure. The initial purpose of performing these fittings was to smooth the energy values. A single value for the quantum defect, which was assumed to be constant along a given Rydberg series, was adopted as the fitting parameter for each $nl\gamma$ series. The sum of the squared differences between the estimated and the reference energies was then minimized. The reproducibility of the results was verified for each fitting, starting from different guess values, especially in those cases where some single-state quantum defect occurred to be noticeably different from those resulting from the fitting. We find it worth comparing the quantum defects obtained from the least-squares fitting of the MR-SDCI energies, for each of the $nl\gamma$ Rydberg series under consideration to those derived from the fitting of the experimental data. The two sets of quantum defects conform rather well with each other. Nonetheless, we find it more important to point out that the whole set of residues from the fitting procedure (i.e., the differences between the fitted energy values and the least-squares estimates) show an absolute mean value of 0.001 au for both the MR-SDCI and the experimental energy fittings, while the sample standard deviations equals 0.002 and 0.001 au, respectively. All this leads us to the conclusion that, in situations where no experimental energies are available, quantum defects deduced from fitted MR-SDCI energies could be safely used.

The virtual $6a_1(\gamma^*)$ and $3b_2(\sigma^*)$ valence orbitals are antibonding conjugate partners of the bonding $5a_1(\gamma)$ and $2b_2(\sigma)$ orbitals, respectively. These antibonding orbitals are expected to contribute significantly to excitation or ionization intensities in accordance with their locations in the discrete or continuum spectral regions.[37] Accordingly, there is no evidence of an orbital that is separate from the nsa_1 Rydberg series that warrants a $6a_1(\gamma^*)$ designation. The angular antibonding (γ^*) nature of the $6a_1(\gamma^*)$ contribution is clarified through a detailed examination of the spatial characteristics of the resonance transition in the

TABLE 3: Absorption Oscillator Strengths for the $X^1A_1(3pb_1)-{}^1A_1(ndb_1)$ ($n = 3-6$) Electronic Transitions in H_2S

transition	f MQDO[a]	f MQDO[b]	f MQDO[c]	f MQDO[d]	exp[e]	SC[f]	CI[f]	MCRPA[g] f_L	f_V
$X^1A_1(3pb_1)-{}^1A_1(3db_1)$	0.0569	0.0625	0.0610	0.0631	0.0606	0.0457	0.0706	0.051	0.044
$X^1A_1(3pb_1)-{}^1A_1(4db_1)$	0.0293	0.0276	0.0258	0.0264	0.0296	0.0175	0.0247	0.020	0.017
$X^1A_1(3pb_1)-{}^1A_1(5db_1)$	0.0170	0.0136	0.0129	0.0132		0.0082	0.0147	0.009	0.007
$X^1A_1(3pb_1)-{}^1A_1(6db_1)$	0.0091	0.0068	0.0073	0.0075		0.0051	0.0097		

[a] MQDO calculations with presently obtained MR−SDCI energies. [b] MQDO calculations with experimental energies. [c] MQDO calculations with fitted MR-SDCI energies. [d] MQDO calculations with fitted experimental energies. [e] Lee et al.[43] [f] Diercksen and Langhoff[42] (single-channel, SC, and configuration-mixing, CI). [g] Cacelli et al.[44] (MCRPA, length and velocity oscillator strengths).

TABLE 4: Absorption Oscillator Strengths for the $X^1A_1(3pb_1)-{}^1B_1(nda_1I)$ ($n = 3-6$) Electronic Transitions in H_2S.

transition	f MQDO[a]	f MQDO[b]	f MQDO[c]	f MQDO[d]	exp[e]	SC[f]	CI[f]
$X^1A_1(3pb_1)-{}^1B_1(3da_1I)$	0.0319	0.0275	0.0318	0.0284	0.0362	0.0416	0.0397
$X^1A_1(3pb_1)-{}^1B_1(4da_1I)$	0.0121	0.0119	0.0115	0.0107	0.0139	0.0201	0.0166
$X^1A_1(3pb_1)-{}^1B_1(5da_1I)$	0.0060	0.0054	0.0054	0.0051	0.0053	0.0101	0.0078
$X^1A_1(3pb_1)-{}^1B_1(6da_1I)$	0.0014	0.0029	0.0029	0.0028		0.0063	0.0045

[a] MQDO calculations with presently obtained MR-SDCI energies. [b] MQDO calculations with experimental energies. [c] MQDO calculations with fitted MR-SDCI energies. [d] MQDO calculations with fitted experimental energies. [e] Lee et al.[43] [f] Diercksen and Langhoff[42] (single-channel, SC, and configuration-mixing, CI).

TABLE 5: Absorption Oscillator Strengths for the $X^1A_1(3pb_1)-{}^1B_1(nda_1II)$ ($n = 3-6$) Electronic Transitions in H_2S

transition	f MQDO[a]	f MQDO[b]	f MQDO[c]	f MQDO[d]	exp[e]	SC[f]	CI[f]
$X^1A_1(3pb_1)-{}^1B_1(3da_1II)$	0.0434	0.0495	0.0491	0.0489	0.0564	0.0504	0.0432
$X^1A_1(3pb_1)-{}^1B_1(4da_1II)$	0.0232	0.0216	0.0221	0.0220	0.0323	0.0254	0.0198
$X^1A_1(3pb_1)-{}^1B_1(5da_1II)$	0.0182	0.0107	0.0114	0.0114		0.0133	0.0098
$X^1A_1(3pb_1)-{}^1B_1(6da_1II)$	0.0067	0.0060	0.0066	0.0066		0.0067	0.0048

[a] MQDO calculations with presently obtained MR-SDCI energies. [b] MQDO calculations with experimental energies. [c] MQDO calculations with fitted MR-SDCI energies. [d] MQDO calculations with fitted experimental energies. [e] Lee et al.[43] [f] Diercksen and Langhoff[42] (single-channel, SC, and configuration-mixing, CI).

$2b_1 \rightarrow nsa_1$ series, which suggests the designation $2b_1 \rightarrow 4sa_1/6a_1(\gamma^*)$. The ($2b_1 \rightarrow 4sa_1$) band shape suggests[31] the presence of some valence character in the excited state, and this has been confirmed by theoretical computations.[38,39] Theory[38,40] and experiment[41] also indicate that a (largely dissociative) mixed Rydberg ($3db_2$)/valence($3b_2$*) state of $^1A_2$ symmetry lies at an energy of comparable magnitude to that of a $^1B_1$ state. This appears to be consistent with the observation of homogeneous predissociation in the first members of the $^1A_2$ Rydberg series.[34] As regards the $2b_1 \rightarrow nda_2$ Rydberg series, although configuration mixing with other excitations leaves the calculated energy positions unchanged, evidence of significant perturbations has been found. This effect is attributed to mixing with both $5a_1 \rightarrow 3b_2(\sigma^*)$ and $2b_2 \rightarrow 6a_1$ (γ^*) intravalence transitions of $^1A_1 - {}^1B_2$ symmetry.[41]

IV. Results and Discussion

The great prominence of Rydberg series in H_2S is a clear evidence of the atomic-like nature of the $(2b_1)^{-1}$ core vacancy. As in the case of atoms, the three nd, $^1A_1(ndb_1)$, $^1B_1(nda_1I)$, $^1B_1(nda_1II)$, with $n \geq 3$, Rydberg series in H_2S are the most intense of all that arise from the excitation of the outermost valence electron. It is now generally accepted that nd Rydberg promotions are responsible for the Rydberg series that dominate the VUV absorption spectra of H_2S as the first ionization threshold is approached.[42] This is one of the reasons why we have studied the excitations from the outermost MO in the ground state to the unperturbed Rydberg $^1A_1(ndb_1)$, $^1B_1(nda_1I)$, and $^1B_1(nda_1II)$ Rydberg series in the present work. Provided that the MO that gives rise to the existence of Rydberg states in this molecule is a nonbonding orbital, the adopted vertical transition picture appears to lead to transition intensities that are a good approach to the experimental values. The results are collected in Tables 3−5. We have also calculated oscillator strengths for excitations involving np Rydberg states of $^1B_1$, $^1A_1$, and $^1A_2$ symmetries to the $^1B_1(nsa_1)$ Rydberg series, given their great relevance in astrophysics and astrochemistry.[1,2] The corresponding oscillator strengths are displayed in Table 6. Higher transitions of the presently studied symmetries have not been included in the table because they turn out to be rather weak for H_2S. Diercksen and Langhoff attribute this feature to the higher nsa_1 states being more sensitive to mixing effects than the lower Rydberg states of $^1B_1(nsa_1)$ symmetry.[42] Finally, transitions between the $^1B_1(4sa_1)$ and the np Rydberg states of symmetries $^1B_1$, $^1A_1$, and $^1A_2$, respectively, are displayed in Table 7. Neither measurements nor theoretical calculations seem to have been reported up to date for the transitions object of the last two tables.

TABLE 6: Absorption Oscillator Strengths for $4p-{}^1B_1(nsa_1)$ Transitions in H_2S

transition	f MQDO[a]	f MQDO[b]	f MQDO[c]	f MQDO[d]
$^1B_1(4pa_1)-{}^1B_1(5sa_1)$	0.3093	0.3135	0.3825	0.3729
$^1A_2(4pb_2)-{}^1B_1(5sa_1)$	0.3098	0.2745	0.3737	0.3608
$^1A_1(4pb_1)-{}^1B_1(5sa_1)$	0.2932	0.3128	0.3727	0.3554
$^1B_1(4pa_1)-{}^1B_1(6sa_1)$	0.0202	0.0297	0.0105	0.0058
$^1A_2(4pb_2)-{}^1B_1(6sa_1)$	0.0253	0.0271	0.0195	0.0262
$^1A_1(4pb_1)-{}^1B_1(6sa_1)$	0.0140	0.0282	0.0043	0.0015

[a] MQDO calculations with presently obtained MR-SDCI energies. [b] MQDO calculations with experimental energies. [c] MQDO calculations with fitted MR-SDCI energies. [d] MQDO calculations with fitted experimental energies.

In Tables 3−7, the f values presently calculated with the MQDO procedure, using four different sets of quantum defects, have been collected. The latter comprise the ones directly resulting from the present MR-SDCI calculations, those extracted from the experimental energies by Lee et al.[43] with a synchroton radiation measurement (their uncertainty is reported

TABLE 7: Absorption Oscillator Strengths for $^1B_1(4sa_1)-np$ Transitions in H_2S

transition	*f* MQDO[a]	*f* MQDO[b]	*f* MQDO[c]	*f* MQDO[d]
$^1B_1(4sa_1)-{}^1B_1(4pa_1)$	0.3071	0.2850	0.2826	0.2591
$^1B_1(4sa_1)-{}^1B_1(5pa_1)$	0.0314	0.0214	0.0211	0.0234
$^1B_1(4sa_1)-{}^1B_1(6pa_1)$	0.0002	0.0074	0.0063	0.0073
$^1B_1(4sa_1)-{}^1B_1(7pa_1)$	0.0000	0.0039	0.0028	0.0033
$^1B_1(4sa_1)-{}^1A_2(4pb_2)$	0.3101	0.3009	0.2885	0.2737
$^1B_1(4sa_1)-{}^1A_2(5pb_2)$	0.0168	0.0115	0.0146	0.0120
$^1B_1(4sa_1)-{}^1A_2(6pb_2)$	0.0001	0.0014	0.0040	0.0032
$^1B_1(4sa_1)-{}^1A_2(7pb_2)$	0.0045	0.0010	0.0017	0.0014
$^1B_1(4sa_1)-{}^1A_1(4pb_1)$	0.2941	0.2659	0.2701	0.2445
$^1B_1(4sa_1)-{}^1A_1(5pb_1)$	0.0293	0.0264	0.0257	0.0265
$^1B_1(4sa_1)-{}^1A_1(6pb_1)$	0.0026	0.0098	0.0081	0.0087
$^1B_1(4sa_1)-{}^1A_1(7pb_1)$	0.0004	0.0051	0.0037	0.0040

[a] MQDO calculations with presently obtained MR-SDCI energies. [b] MQDO calculations with experimental energies. [c] MQDO calculations with fitted MR-SDCI energies. [d] MQDO calculations with fitted experimental energies.

to be 10% of their given value),[43] as well as the quantum defects derived from the least-squares fitting of the theoretical and experimental excitation energies, respectively, as mentioned above. It is generally observed, with the exception of the transitions originating in the 4p Rydberg states belonging to three different symmetries $^1B_1$, $^1A_1$, and $^1A_2$ and ending in the $^1B_1(6sa_1)$ Rydberg state (see Table 6), that a better accord is achieved between the two sets of MQDO oscillator strengths calculated through the fitted theoretical and experimental energies than between the sets obtained with the individual-state quantum defects. We understand this feature on the grounds that fitting the energies of a given Rydberg series is tantamount to smoothing the errors inherent in both the experimental and theoretical energies. In the present case, such a smoothing is achievable with absolute mean values and sample standard deviations of the order of 1−2 milliHartree, so that it can be considered as a reliable approach to assign a unique quantum defect to each $nl\gamma$ Rydberg series.

The comparative *f* values, also included in Tables 3−5, are the experimental measurements determined by Lee et al.[43] and the theoretical values reported by Diercksen and Langhoff[42] and by Cacelli et al.[44] The former authors[42] performed two sets of calculations, one following the vertical-electronic single-channel static exchange approach and the other with the single-excitation coupled-channel configuration-mixing procedure. Cacelli et al.[44] employed extended basis sets of integrable functions and the Stieltjes imaging procedure in a random-phase approximation (MCSEA) method to yield oscillator strengths in the length (f_L) and velocity (f_V) gauges.[44] Cacelli et al. consider[44] their MCSEA calculations to be directly comparable with the ones by Diercksen and Langhoff,[42] except for the different basis sets employed.

An inspection of Tables 3−5 reveals that the present results conform rather well with the comparative experimental and theoretical data. A general good accord between the two sets of MQDO *f* values, the ones calculated with the present MR-SDCI excitation energies and those obtained with the experimental energies of Lee et al.,[43] is apparent, in particular for the stronger transitions. Some irregularities in the trends of the *f* values as the excitation energy increases can be noticed in those Rydberg series that seem to be subject to configuration mixing.[42,43]

We may summarize our analysis by remarking that both energy and transition intensity indicators in the present calculations show consistency with the values obtained from experimental data. Even though the present excitation energies do not represent a significant improvement over those of CI methods that take into account the coupling with the electron exit channels, they contribute to assess the accuracy and effectiveness of the chosen approach, that is, a MR-SDCI calculation with a chosen basis set of ANOs complemented with a consistently builtsingle set of Rydberg ANOs centered in the molecule, and the use of the MQDO technique to supply transition probability data.

Acknowledgment. This work has been supported by the D. G. I. of the Spanish Ministry for Science and Technology within Project Nos. BQU2001-2935-C01 and -C02 as well as by the DGEUI (Generalitat Valenciana, Projects INF00-15 and INF01-051). A.M.V. wishes to acknowledge her research grant from the former institution. A.M.V. and I.M. are also indebted to the J.C.L. for awarding them the research grant VA119/2002.

References and Notes

(1) Watson, W. D. *Rev. Mod. Phys.* **1976**, *48*, 513.

(2) Dalgarno, A.; Black, J. H. *Rep. Prog. Phys.* **1976**, *39*, 573.

(3) Toon, O. B.; Kasting, J. F.; Turco, R. P.; Liu, M. S. *J. Geophys. Res. D: Atmos.* **1987**, *92*, 943.

(4) Pos, H. W.; Milne, P. J.; Riemer, D. D.; Zika, R. D. *J. Geophys. Res. D: Atmos.* **1997**, *102*, 12831.

(5) Bingemer, H. G.; Andreae, M. O.; Andreae, T. W.; Artaxo, P.; Helas, G.; Jacob, D. J.; Mihalopoulos, N.; Nguyen, B. C. *J. Geophys. Res. D: Atmos.* **1992**, *97*, 6207.

(6) Cooper, W. J.; Cooper, D. J.; Saltzman, E. S.; De Mello, W. Z.; Savoie, D. L.; Zika, R. G.; Prospero, J. M. *Atmos. Environ.* **1987**, *21*, 1491.

(7) Tarver, G. A.; Dasgupta, P. K. *Atmos. Eviron.* **1995**, *29*, 1291.

(8) Hiemann, H. B.; Atreya, S. K.; Carignan, G. R.; Donahue, T. M.; Haberman, J. A.; Harpold, D. N.; Hunten, D. M.; Wayne, T. *Science* **1996**, *272*, 846.

(9) Nash, D. B.; Howell, R. R. *Science* **1989**, *244*, 454.

(10) Biver, N.; Bockelee-Morvan, D.; Colom, P.; Crovisier, J.; John, J. K.; Dent, W. R. F.; Despois, D.; Gerard, E.; Lellouch, E.; Rauer, H.; Moreno, R.; Paubert, G. *Science* **1997**, *275*, 1915.

(11) Bockelee-Morvan, D.; Colom, P.; Crovisier, J.; Despois, D.; Pubert, G. *Nature* **1991**, *350*, 318.

(12) Minh, Y. C.; Ziurys, L. M.; Irvine, W. M.; McGonagle, D. *Astrophys. J.* **1991**, *366*, 182.

(13) Rolle, D.; Kalfa, H.; Buhler, H. E. *Werkstoffe Korosion* **1993**, *44*, 1.

(14) Tenne, R.; Margulis, L.; Genut, M.; Hodes, G. *Nature* **1992**, *360*, 444.

(15) Jaeschke, W.; Claude, H.; Hermann, J. *J. Geophys. Res*. **1980**, *85*, 5639.

(16) Sze, N.; Ko, M. K. W. *Atmos. Eviron.* **1980**, *14*, 1223.

(17) Gallagher, W.; Brion, C. E.; Samson, J. A. R.; Langhoff, P. W. *J. Phys. Chem. Ref. Data* **1988**, *17*, 9, and references therein.

(18) Martín, I.; Lavín, C.; Pérez-Delgado, Y.; Pitarch-Ruiz, J.; Sánchez-Marín, J. *J. Phys. Chem. A* **2001**, *105*, 9637

(19) Pitarch-Ruiz, J.; Sánchez-Marín, J.; Martín, I.; Velasco, A. M. *J. Phys. Chem. A* **2002**, *106*, 6508.

(20) Martín, I.; Lavín, C.; Velasco, A. M.; Martín, M. O.; Karwowski, J.; Diercksen, G. H. F. *Chem. Phys.* **1996**, *202*, 307.

(21) Martín, I.; Lavín, C.; Karwowski, J. *Chem. Phys. Lett.* **1996**, *255*, 89.

(22) Bustos, E.; Velasco, A. M.; Martín, I.; Lavín, C. *J. Phys. Chem. A* **2002**, *106*, 35.

(23) Martín, I.; Velasco, A. M.; Lavín, C. *Adv. Quantum Chem.* **2001**, *39*, 145.

(24) Velasco, A. M.; Bustos, E.; Martín, I.; Lavín, C. *J. Phys. Chem. A* **2002**, *106*, 6401.

(25) Maynau, D.; Ben-Amor, N.; Pitarch-Ruiz, J. CASDI program; University of Toulouse: France, 1999.

(26) Ben-Amor, N.; Maynau, D. *Chem. Phys. Lett.* **1998**, *286*, 211.

(27) Pitarch-Ruiz, J.; Sánchez-Marín, J.; Maynau, D. *J. Comput. Chem.* **2002**, *23*, 1157.

(28) Widmark, P. O.; Malmqvist, P. A.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291.

(29) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P. A.; Neogrody, P.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Widmark, P. O. MOLCAS 4; University of Lund: Sweden, 1997.

(30) Ashfold, M. N. R.; Bayley, J. M.; Dixon, R. N.; Prince, J. D. *Chem. Phys.* **1985**, *98*, 289.

(31) Abuain, T.; Walker, I. C.; Donce, D. F. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 811−816.

(32) Mayhew, C. A.; Connerade, J. P.; Baig, M. A.; Ashfold, M. N. R.; Bayley, J. M.; Dixon, R. N.; Prince, J. D. *J. Chem. Soc., Faraday Trans II* **1987**, *83*, 417.

(33) Masuko, H.; Marioka, Y.; Nakamura, M.; Ishigura, E.; Sasanuma, M. *Can. J. Phys.* **1979**, *57*, 745.

(34) Ashfold, M. N. R.; Hartree, W. S.; Salvato, A. V.; Tutcher, B.; Walker, A. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2027.

(35) Adam, M. Y.; Neves de Brito, A.; Keane, M. P.; Svensson, S.; Karlsson, L.; Kallen, E.; Correia, N. *J. Electon Spectrosc. Relat. Phenom.* **1991**, *56*, 241.

(36) Baltzer, P.; Karlsson, L.; Lundqvist, M.; Wannberg, B.; Holland, D. M. P.; MacDonald, M. A. *Chem. Phys.* **1995**, *195*, 403 and references therein.

(37) Langhoff, P. W. In *Resonances in electron−molecule scattering, van der Waals complexes, and reactive chemical dynamics*; Truhlar, D. G., Ed.; Americal Chemical Society: Washington, 1984; p 113.

(38) Shih, S.; Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys.* **1976**, *17*, 391.

(39) Hatano, Y. *Chem Phys. Lett.* **1978**, *56*, 314.

(40) Roberge, R.; Salahub, D. R. *J. Chem. Phys.* **1979**, *70*, 1177.

(41) Van Veen, G. N. A.; Mohamed, K. A.; Baller, T.; de Vries, A. E. *Chem. Phys.* **1983**, *74*, 261.

(42) Diercksen, G. H. F.; Langhoff, P. W. *Chem. Phys.* **1987**, *112*, 227.

(43) Lee, L. C.; Wang, X.; Suto, M. *J. Chem. Phys.* **1987**, *86*, 4353.

(44) Cacelli, I.; Carravetta, V.; Moccia, R. *Chem. Phys.* **1988**, *120*, 51.

(45) Martin, W. C.; Wiese, W. L. In *Atomic, Molecular, and Optical Physics Handbook*; Drake, G. W. F., Ed.; American Institute of Physics: Woodbury, NY, 1996.