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A restricted active space (RAS) SCF study of the lifetime of the $A^3\Pi$ state of OH^+

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Summary. Restricted Active Space (RAS) SCF calculations have been performed of the potential curves for the $X^3\Sigma^-$ and $A^3\Pi$ states of the OH^+ ion and on the lifetime of the $v = 0$–2 vibrational levels of the A state. The convergence of the transition moment integral as a function of the size of the active orbital space was used to select the active orbitals. The calculated value of the $v = 0$ lifetime is 2.4 μs. An estimate of the errors remaining in the calculation leads to a final theoretical value of 2.7 ± 0.1 μs. Computed bond distances and bond energies are 1.031 (1.029) Å and 5.05 (5.01) eV, respectively, for the X state, and 1.137 (1.135) Å and 1.57 eV, respectively, for the A state (experimental values within parenthesis).

Key words: Hydroxyl ion $A^3\Pi$ state – Restricted active space (RAS) SCF – Active orbitals – Bond distances

1. Introduction

It has been shown in a series of papers that the Complete Active Space (CAS) SCF method [1–3] is capable of yielding very accurate results for spectroscopic properties of small systems containing only a few valence electrons. CASSCF calculations were performed on low-lying excited states of BH [4], AlH [5], and SiH^+ [6]. The active space was chosen to include all natural orbitals with an occupation number larger than a given threshold of about 0.001. Such a choice results in a very compact wave function comprising less than a thousand configuration state functions (CSFs), for a system with only four active electrons. The results obtained for dipole moments, lifetimes, etc., show that the one-electron density, and transition density, matrices are accurately reproduced with this type of wave function. One important feature here is the separate optimization of the orbitals for each electronic state.

Calculations of this type can, however, not be extended to systems with many valence electrons. The number of CSFs then becomes a too steep function of the

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number of active orbitals. We show, however, in this paper that the same high accuracy can be achieved by the recently developed Restricted Active Space (RAS) SCF method [7–8]. The idea is to allow a general distribution of the electrons only among the valence orbitals. This part of the active space is then of the CAS type. The extra-valence orbitals used to improve the wave function will be occupied by at most two electrons. Cluster corrections can be included by increasing the maximum occupation number to four. A wave function of this type will still be very compact, since the number of extra-valence orbitals with an occupation number larger than 0.001 is limited. We illustrate in this contribution how such an approach can be used to compute spectroscopic properties for a six-valence electron system, OH^+, with special emphasis on the radiative lifetime of the $A^3\Pi$ state.

Molecular lifetimes have important applications in many fields of current research. In particular, ion-molecule systems are of considerable interest in astrophysics. The $A^3\Pi - X^3\Sigma^-$ system in OH^+ has been identified in several water-containing comets [9].

Measurements of optical lifetimes in molecular ions represents a particular difficult task due to the many different effects which have to be taken into account. In spite of such difficulties, the lifetime for the $A^3\Pi$ $(v = 0)$ state of the ionized hydroxyl radical has clearly been established to be about 2.5 μs [10–11]. A theoretical estimate of the lifetime has not been explicitly published, to our knowledge, even though it can rather easily be extracted from the data given by Saxon and Liu [12] in their extensive study of a number of excited states for OH^+. Actually their work serves as an excellent calibration point for the present study, since it is based on a second-order (SO) CI wave function and utilizes an extended Slater-type basis set. The most detailed experimental information is obtained from the work of Merer et al. [13] on the ultraviolet emission spectra of OH^+ and OD^+. This study together with the theoretical work of Saxon and Liu will be used here for comparison with the present results. They also include a number of references to earlier work on this system, which will not be further quoted here.

The paper is organized as follows. In the next section, the details of the calculations together with the discussion of the basis sets and some atomic calibration calculations are presented. The calculations performed for the choice of the active space are discussed in Sect. 3. Section 4 is concerned with the results. It includes a spectroscopic analysis, lifetimes, and comparison with previous theoretical and experimental data. Finally, in Sect. 5, a discussion and summary of the investigation is made.

2. Details of the calculation

2.1. The basis set

Generally, contracted basis sets of the ANO type [14] have been used throughout the present work. They have been derived from a density matrix averaged over the atomic ground state, positive and negative ions, and the atom in a polarizing electric field. A detailed description of the averaging procedure, as well as the explicit primitive sets used can be found elsewhere [15]. These basis sets have been specifically designed to account for as much electron correlation as is possible within a given size. They are therefore especially suited for the type of calculations performed in the present work. These basis sets have only recently been published [15] and one motivation for this study has been to test the usefulness of them in accurate calculations. For this purpose the calculations have been performed using two different contracted sets, one which is close to saturation and one smaller set. The behaviour of the smaller set gives an indication of the usefulness of these basis sets in calculations on larger molecules.

The primitive sets are $14s9p4d3f$ and $8s4p3d$ for oxygen and hydrogen, respectively. The two different contracted sets which have been employed are $[O/4s,3p,2d/H/3s,2p]$, hereafter named BS1 and a larger set, BS2, where the contraction is $[O/5s,4p,3d,2f/H/3s,2p,1d]$. The s-component of d-type functions and the p-components of the f-type functions were deleted in all applications. The basis set size for OH^+ is 32 for BS1 and 60 for BS2. It is worth mentioning that the calculations with the two different basis sets takes about the same time, since the integral time only represents a minor-part of the total computer time and the time for the RASSCF calculations is almost independent of the basis set size in calculations of the type performed here, which are dominated by the CI step. All calculations have been performed on an IBM 3090-170VF computer using the MOLCAS-1 quantum chemistry software [16].

2.2. *Atomic calculations*

The $X^3\Sigma^-$ ground state and the $A^3\Pi$ state of OH^+ should both dissociate to the $O(^3P) + H^+$ limit, which spectroscopically lies 0.019 eV below $O^+(^4S) + H(^2S)$. It may be worth noting that in a non-relativistic calculation, using the infinite mass approximation for the nuclei, this order is reversed with the second limit 0.016 eV below the first [17]. As has been already pointed out in the previous theoretical studies [12, 18], the calculation of the correct asymptotic energies is an extremely difficult problem, since it essentially means that the basis set and correlation error in the ionization potential (IP) of the oxygen atom must be fully accounted for (the hydrogen IP is of course reproduced almost exactly with no difficulty).

In order to estimate what errors can be expected with the present basis sets, we have calculated the oxygen IP using a single (open-shell restricted Hartree–Fock) reference configuration and employing methods which include corrections for the size-consistency error. Table 1 shows the results obtained for the oxygen IP with singles and doubles CI (SDCI), also including the Davidson correction

Table 1. Calculated ionization potentials for the oxygen atom. Total energies are given in atomic units (au)

Method	$O^+(^4S)$	$O(^3P)$	*IP* (eV)
BS1 basis set			
SDCI	−74.474838	−74.953557	13.03 (13.10)[a]
CPF	−74.476519	−74.957386	13.09
BS2 basis set			
SDCI	−74.493206	−74.982414	13.31 (13.41)[a]
CPF	−74.495215	−74.987096	13.39
Experimental[b]			13.59

[a] SDCI results including the Davidson correction for cluster effects

[b] With relativistic correction subtracted (see Ref. [17]). The spectroscopic value from Ref. [25]

[19] (SDCIQ), and with the Coupled Pair Functional (CPF) method [20]. The oxygen 1*s* orbital was kept frozen in all these calculations. Additional RASSCF calculations were also carried out and show the same trends. These results will be presented later. Both the SDCIQ and the CPF calculations give an IP which is about 0.2 eV smaller than the experimental value, an error which reflects the limitations of the basis set used in the present study. Larger errors are found with the RASSCF wave function used to compute the potential curve. It is clear that to accurately reproduce the order of the asymptotes of the low-lying potential curves for OH^+, it is necessary to use a nearly saturated one-electron basis set and to include the effect of higher excitations. The present results give one more illustration to the fact that atomic relative energies are often very difficult to compute and require very accurate wave functions.

A more pragmatic approach has been used in the present work. In order to calculate the lifetime of the $A\,^3\Pi$ state we need to compute the potential curves for the lowest $^3\Sigma^-$ and $^3\Pi$ states of OH^+. Experimentally both these states have the same asymptote. With the present basis set an accurate calculation would allow the Σ state to dissociate to $O^+ + H$, due to the error in the computed IP for the oxygen atom. This does not, however, happen in the RASSCF calculations discussed below, since the choice of input orbitals gives convergence to the other dissociation limit. Therefore the two states will again dissociate to the same limit, and the problem of the error for the IP of oxygen does not enter into the calculation.

2.3. *Computational methods*

The wave functions used in the present work have been obtained using the RASSCF method [7, 8], which is an extension of the CASSCF approach [1–3]. CASSCF is a special variant of the multiconfigurational SCF method, where the orbital space is divided into three subspaces: the inactive, active, and secondary orbitals. The inactive orbitals are doubly occupied in all CSFs, but are variationally optimized. The remaining (active) electrons occupy the active orbitals and the wave function is an expansion that includes all CSFs, which can be formed by distributing the active electrons among the active orbitals in all possible ways consistent with a given total spin and space symmetry. The secondary orbitals are not occupied.

In the RASSCF extension of this approach the orbitals are divided instead into five subspaces: the inactive orbitals, the RAS1 space, the RAS2 space, the RAS3 space, and the secondary space. The inactive and the secondary spaces have the same properties as for CAS wave functions. The RAS1 space consists of orbitals in which a certain maximum number of holes may be created (if n_1 is the number of RAS1 orbitals, the total occupation can vary between $2n_1$ and $2n_1 - x$, where x is a small number). The RAS2 space has the same properties as the active space in CAS type wave functions, i.e., all possible occupations and spin couplings are allowed. Finally, the RAS3 space is allowed to be occupied with up to a given (small) number of electrons. All CSFs which fulfil these restrictions are included into the RAS wave function. The RAS CSF space has the property of being closed under de-excitation.

Using the RAS concept a variety of wave functions can be generated. It combines the advantages of the CAS wave functions, mainly thought to account for static correlation effects, with advanced CI wave functions, which includes the major part of the dynamic correlation. As will be illustrated in this contribution, the effect of dynamic correlation can for many properties be concentrated into a limited set of molecular orbitals, provided that they are optimized. Thus the RAS concept allows a compact description (in terms of the number of configurations) of correlated wave functions. The optimization of all parameters in the wave function is also of crucial importance for the calculation of energy derivatives with respect to nuclear displacements. However, since the RAS wave function is not complete in the active orbital space, the orbital optimization becomes more complicated, which may in some cases lead to convergence problems. Such problems have, however, not been encountered in the present study.

Special attention has been devoted to the choice of the number of active orbitals for OH^+, in order to ensure the stability of the results for the computed transition moments. A detailed discussion of the approach is given in Sect. 3. Calculations of the transition moments have been performed using a special method developed for the calculation of transition densities between large RASSCF wave functions based on separately optimized orbitals [21, 22]. The program included in the MOLCAS package is called RASSI (RAS State Interaction) and is capable of computing efficiently the first and second order transition density matrices for a series of RAS wave functions. If needed this program also solves the corresponding secular problem. The resulting wave functions will then be both orthogonal and non-interacting. This procedure is, of course, not needed here, since the two states under consideration are of different symmetry.

The procedure followed to compute the vibrational-rotational energy levels and spectroscopic constants involves three steps. First, the computed points on the potential curve are approximated by a spline function. Secondly, the solutions to the radial Schrödinger equation are obtained through numerical integration. Finally, spectroscopic constants are obtained by a least square fit to the computed energy levels. Care has been taken to use the same levels as has been used in the fit of the experimental data. If this is not done the comparison with experimentally derived parameters becomes rather meaningless.

Transition dipole matrix elements are obtained by numeric integration using the vibrational wave functions obtained in the numerical solution of the Schrödinger equation. The values, so obtained, were used to compute the radiative lifetimes, τ, for the A state vibrational bands, based on the following expression:

$$\tau_{iv'}^{-1} = 2.02608 \times 10^{-2} \sum_{f,v''} \nu^3_{iv',fv''} \langle iv' | \mu^{if}(R) | fv'' \rangle^2,$$

where ν is the excitation energy in cm^{-1}, $\mu^{if}(R)$ is the electronic part of the transition moment as a function of the internuclear distance R (in atomic units), and the lifetime so computed is obtained in μs.

3. Selection of the RAS active space

The RAS active orbital selection was performed by simultaneous calculations, at a given internuclear distance of 1.85 Å, for both states of interest, using as the main criterion the stability of the computed transition moment for the X–A system. The procedure followed implies a search for the saturation of the σ, π, and δ orbital subspaces. Actual calculations were carried out in C_{2v} symmetry, so special care has been taken to avoid broken symmetry solutions.

In all calculations the 1σ orbital, which correlates with the oxygen $1s$ atomic orbital, has been kept inactive. The RAS1 space has been kept empty. The RAS2 space consists of all valence orbitals in OH^+, that is, orbitals formed from hydrogen $1s$ and oxygen $2s$ and $2p$ AOs. This space thus contains three σ and one π orbital (3110 in C_{2v} symmetry, where the notation n_1, n_2, n_3, n_4 represents the number of active orbitals belonging to the C_{2v} symmetry species a_1, b_2, b_1, and a_2, respectively). The size of the RAS3 space will be varied systematically. The maximum number of electrons allowed in this subspace is two.

The results obtained by a systematic increase of the number of active orbitals in the RAS3 subspace are listed in Table 2. The criterion for saturation of the active subspace in a given symmetry was, that the transition moment value should change with less than 10^{-3} au. This limit was reached with 3 σ-type, 3 π-type orbitals, which corresponds to entries 3 and 7 in Table 2. A slightly larger convergence threshold was accepted for the orbitals of δ-type (entries 9 and 10 in Table 2) and only one pair of δ-type orbitals was included in the final selection. The final calculation was thus made with the RAS3 space 4331 (note that one δ-type orbital resides in symmetry a_1 when C_{2v} symmetry is used). One notices, however, that the most profound single orbital contribution to the transition dipole moment comes from the first orbital pair of δ-type. Actually the effect of the second δ-type orbital was larger than expected, considering the small occupation number (see below). The omission of this orbital in the RAS3 space is expected to lead to lifetimes, which are between 0.1 and 0.2 μs too small.

The convergence of the computed transition moment is parallelled by a corresponding convergence of the energy difference between the two states to about 0.02 eV. Moreover, a detailed analysis of the occupation numbers of the

Table 2. Selection of the RAS3 active space using the BS1 basis set at the interatomic distance $1.85\,a_0$. The RAS1 and RAS2 active spaces are kept at *0000* and *3110*, respectively (see text). Total energies and transition dipole moments are given in atomic units[a]

Step	RAS3	$X^3\Sigma^-$	$A^3\Pi$	Δ (eV)[b]	$\langle A^3\Pi_x \vert y \vert X^3\Sigma^-\rangle$
0	0000	−75.027037	−74.875191	4.13	0.19824
σ-selection					
1	1000	−75.042907	−74.882924	4.35	0.19924
2	2000	−75.054147	−74.889304	4.49	0.19244
3	3000*	−75.056571	−74.890268	4.53	0.19427
4	4000	−75.058243	−74.891107	4.55	0.19352
π-selection					
5	4110	−75.090402	−74.939736	4.10	0.18617
6	4220	−75.115216	−74.967169	4.03	0.16719
7	4330*	−75.118310	−74.969705	4.04	0.16558
8	4440	−75.119421	−74.970977	4.04	0.16558
δ-selection					
9	5441*	−75.147115	−75.002927	3.92	0.14271
10	6442	−75.147901	−75.004540	3.90	0.13734
Final, BS1	4331	−75.144178	−75.000291	3.92	0.14305
Final, BS2	4331	−75.149221	−75.008363	3.83	0.14600

[a] A star (*) is added at the place of the final choice for each symmetry

[b] $\Delta = E(A^3\Pi) - E(X^3\Sigma^-)$

active orbitals shows that this convergence is achieved when the lowest occupation numbers fall below 0.001. The values obtained for the lowest occupation numbers were in the *4331* calculation: 0.0009 (σ), 0.0004 (π), and 0.0039 (δ) for the X state, and 0.0005 (σ), 0.0005 (π), and 0.0046 (δ) for the A state. The occupation number for the second orbital of δ-type in the *6442* calculation was 0.0001 (X) and 0.0003 (A), respectively. These results seem to be quite general. Similar findings have been reported by Larsson and Siegbahn [23] for CH^+ and by Blomberg and Liu [24] for CH^+ and CH. Based on the above considerations we have chosen the *4331* (3σ, 3π, 1δ) RAS3 space to build the potential curves for the X and A states of OH^+ and to compute the lifetimes of the vibrational levels of the A state.

The calculations discussed above were performed with the smaller basis set, BS1. It is not obvious that the results should be basis set independent, since the use of a larger basis set may introduce new types of correlation effects. However, when the *4331* calculations were repeated with the larger, BS2, basis set, the occupation numbers remained almost unchanged. The smallest values are for the X state: 0.0009 (σ), 0.0005 (π), and 0.0037 (δ), and for the A state: 0.0006 (σ), 0.0005 (π), and 0.0045 (δ). Also the computed transition moment was unaffected (cf. Table 2). It therefore seems quite clear that the calibration of the active space could safely be performed using the smaller basis set. This set is also rather extended, including two sets of polarization functions. Furthermore, both basis sets are selected from the same oxygen and hydrogen ANO basis sets, in which the atomic natural orbitals are ordered after falling occupation numbers. Therefore a major part of the correlation effects described by the MOs is intrinsic already in the choice of the atomic basis set. This is a very positive feature of the ANOs when used in connection with RASSCF calculations. Both basis sets were used in the final calculations, in order to verify the usefulness of the smaller BS1 set, and the results confirm this preliminary view: the additional radial and angular correlation effects introduced by the larger basis set have only a small influence on the computed properties.

4. Results and discussion

The calculated lifetimes of OH^+ ($A^3\Pi$) and molecular constants for the two spectroscopic states will be presented and discussed in this section. Comparison with available experimental data and earlier theoretical calculations will be made.

The corresponding potential curves for the $X^3\Sigma^-$ and $A^3\Pi$ states of OH^+ were built using the selected RASSCF (*0000*; *3110*; *4331*) wave function, where the information within parenthesis gives the number of active orbitals per symmetry species for each of the three active subspaces. The same 17 points were computed for each potential curve. A grid size of 0.05 au was used for points close to the minima of the two curves. Table 3 shows the total energies for two given points, 2.0 a_0 and 100.0 a_0. As already discussed above, the present RASSCF calculations for the two states lead to the same asymptotic limit, $O(^3P) + H^+$ in spite of the fact that calculations on the oxygen atom place the other limit, $O^+(^4S) + H(2S)$, well below. The small energy difference obtained at 100.0 a_0 is partly due to a symmetry breaking between the σ and π part of the oxygen $2p$ orbitals, which cannot be avoided in a molecular calculation, and partly to a small remaining interaction term. The behaviour of the RASSCF

Table 3. Total energies (in atomic units) at two interatomic distances, R, in the OH^+ system

Method	$R = 2.0\,a_0$ $X^3\Sigma^-$	$A^3\Pi$	$R = 100\,a_0$ $X^3\Sigma^-$	$A^3\Pi$
BS1 basis set				
RASSCF	−75.145840	−75.008880	−74.951320	−74.950414
Average RASSCF[a]				
Root 1: $O^+(^4S) + H(^2S)$			−74.968274	
Root 2: $O(^3P) + H^+$			−74.945740	
BS2 basis set				
RASSCF	−75.150607	−75.017113	−74.958629	−74.956752
Saxon and Liu[b], Second-order CI	−75.15697	−75.02245		

[a] Average RASSCF (*0000*; *3110*; *4331*) calculation for the two lowest roots of $^3\Sigma^-$ symmetry, with equal weights

[b] Data from Ref. [12]

calculation at large interatomic distances is due to the choice of start orbitals, which leads to convergence to the desired dissociation limit. This is further illustrated in Table 3 by an average RASSCF calculation on the two lowest roots of $^3\Sigma^-$ symmetry. One active orbital is now forced to be located on the hydrogen atom and the order of the states is reversed.

The error in the IP of oxygen was also investigated in separate calculations on the free atom, using the RASSCF method, and following a procedure for the selection of the RAS3 space similar to the one described in Sect. 3. Calculations were performed in D_{2h} symmetry with the 2*s* and 2*p* orbitals in RAS2 and 3*s*, 3*p*, and 3*d* in RAS3. In order to investigate also the effect of higher excitations on the IP two sets of calculations were performed: one with a maximum of two electron in the RAS3 space and one where up to four electrons were allowed to occupy these orbitals. The results of these calculations are presented in Table 4. We notice that the RASSCF method with only a few orbitals in the RAS3 space is not able to reproduce the results obtained with the CPF method (cf. Table 1). The RASSCF IPs are about 0.14 eV smaller with the BS1 basis set, a difference that increases to 0.40 eV when the larger basis set is used. This error can be avoided by a proper choice of dissociation limit.

Table 4. Results from RASSCF calculations on $O(^3P)$ and $O^+(^4S)$. Total energies in atomic units

N.P.[a]	$O^+(^4S)$	$O(^3P)$	*IP* (eV)
BS1 basis set			
2	−74.472295	−74.946098	12.89
4	−74.473462	−74.949193	12.95
BS2 basis set			
2	−74.473129	−74.947416	12.91
4	−74.474282	−74.950554	12.96

[a] N.P. meaning maximum number of electrons allowed to occupy RAS3 orbitals

The results given in Table 3 are also compared to the SOCI results of Saxon and Liu [12]. Clearly, their energies are lower, but the difference is small, considering that they used an extended Slater-type basis set and more extended wave functions. The current compact RASSCF wave function (*2413* and *2412* CSFs for the $^3\Sigma^-$ and $^3\Pi$ states, respectively, in C_{2v}) is capable of recovering almost all of the energy given by Slater-type orbital based SOCI wave functions [12] (*23821* and *42122* CSFs for the $^3\Sigma^-$ and $^3\Pi$ states, respectively, in $C_{\infty v}$). A CASSCF calculation with the same active space would use *37220* and *37184* CSFs, respectively, in C_{2v}.

Table 5 shows the computed lifetimes using the two different basis sets and two types of RASSCF wave functions. A valence space only RASSCF (*0000*; *3110*; *0000*) calculation was performed with the small basis set in order to estimate the effect of the extra-valence correlation orbitals on the lifetime. The necessity to include these correlation effects in a calculation of transition moments is obvious from the results presented in Table 5. A much too large value is obtained if the active orbitals are restricted to the valence space, leading to a gross underestimate of the lifetime. It is clear already from the data presented in Table 2, that the major extra-valence contributions to the lifetime comes from angular correlation effects.

As expected, the results obtained with the two basis sets and RASSCF (*0000*; *3110*; *4331*) wave functions are very close. Only a small increase in the lifetime is obtained with the larger basis set. The energies and transition moments published by Saxon and Liu have also been fed into our program for solving the radial Schrödinger equation. The resulting lifetimes are included in Table 5. We notice the great similarity between these results and the results obtained with the present RASSCF wave functions. This similarity is slightly surprising, since we estimate that the present lifetimes are about 0.2 μs too small due to the neglect of the contribution from the second orbital pair of δ-type.

Table 5. Calculated radiative lifetimes (τ) for the $^3\Pi$ state of OH^+, using different basis sets and electronic wave functions (see text)

Wave function	Vibrational quantum number	τ (μs)
BS1 basis set		
RASSCF (*0000*; *3110*; *0000*)	0	0.75
	1	0.84
	2	1.07
RASSCF (*0000*; *3110*; *4331*)	0	2.35
	1	2.48
	2	2.80
BS2 basis set		
RASSCF (*0000*; *3110*; *4331*)	0	2.41
	1	2.56
	2	2.93
Derived from data given by Saxon and Liu[a]	0	2.39
	1	2.56
	2	2.93
Experimental data	0	2.4 ± 0.3[10], 2.5 ± 0.3[11]

[a] Calculated using potential and transition moment curves published in Ref. [12]

Contributions from higher angular momentum orbitals, which have not been included, are expected to be smaller.

The molecular constants have been derived from the potential curves by solving the vibrational Schrödinger equation numerically for a number of rotational quantum numbers. The rotational constants were subsequently derived from the computed spacings between the rotational lines, while vibrational constants were obtained from the computed band origins, that is, $J = 0$ for the $^3\Sigma^-$ state and $J = 1$ for the $^3\Pi$ state.

The band system studied experimentally [13] comprised three vibrational levels ($v = 0$–2). The vibrational Schrödinger equation was solved for these levels and rotational quantum numbers in the range 0–10. The molecular constants presented in Tables 6 and 7 have been obtained from these vibrational-rotational eigenvalues.

Comparing these results with previous work and with experiment, one should remember that the derived spectroscopic constants depend crucially on the fitting procedure applied. Here ω_e and $\omega_e x_e$ have been fitted to the three computed band origins, yielding the values 3090 and 80.8 cm^{-1}, respectively (OH^+ with the BS2

Table 6. Molecular constants for the $X^3\Sigma^-$ and $A^3\Pi$ states of OH^+ (values within parenthesis correspond to OD^+)

	BS1	BS2	Saxon and Liu [12]	Exp. [13]
$X^3\Sigma^-$				
R_e (Å)	1.033	1.031	1.031	1.029 (1.028)
D_e (eV)	5.30	5.24	5.36	–
D_o (eV)	5.11	5.05 (5.10)	5.16	5.01[26]
ω_e (cm^{-1})	3085	3090 (2248)	3088	3113 (2272)
$\omega_e x_e$ (cm^{-1})	81.7	80.8 (42.3)	72.8	78.5 (44.2)
B_e (cm^{-1})	16.67	16.75 (8.88)	16.58	16.79 (8.91)
α_e (cm^{-1})	0.75	0.75 (0.29)	0.77	0.75 (0.29)
γ_e (cm^{-1})	0.0119	0.0101 (0.0022)	–	0.0110 (0.0030)
$\Delta G_{1/2}$ (cm^{-1})	2919	2926 (2162)	2943	2956 (2185)
$\Delta G_{3/2}$ (cm^{-1})	2760	2768 (2077)	2797	2799 (2100)
$\Delta G_{5/2}$ (cm^{-1})	–	– (1994)	–	– (2018)
$A^3\Pi$				
R_e (Å)	1.135	1.137	1.134	1.135 (1.135)
D_e (eV)	1.65	1.70	1.79	–
D_0 (eV)	1.52	1.57 (1.61)	1.65	–
ω_e (cm^{-1})	2170	2178 (1576)	2220	2134 (1558)
$\omega_e x_e$ (cm^{-1})	88.4	86.4 (43.5)	83.2	79.6 (44.4)
B_e (cm^{-1})	13.79	13.76 (7.29)	13.80	13.79 (7.31)
α_e (cm^{-1})	0.87	0.85 (0.33)	0.88	0.89 (0.34)
γ_e (cm^{-1})	0.0076	0.0092 (0.0030)	–	0.0173 (0.0037)
$\Delta G_{1/2}$ (cm^{-1})	1982	1994 (1483)	2053	1974 (1470)
$\Delta G_{3/2}$ (cm^{-1})	1822	1838 (1400)	1887	1815 (1385)
$\Delta G_{5/2}$ (cm^{-1})	–	– (1319)	–	– (1301)
T_e (cm^{-1})	29675	28914	28689	28438

Table 7. B_v and D_v rotational constants for the $X^3\Sigma^-$ and $A^3\Pi$ states of OH^+ and OD^+

	B_v (cm^{-1})				D_v (10^{-4} cm^{-1})		
v	BS1	BS2	Ref. [18]	Exp. [13]	BS1	BS2	Exp. [13]
$OH^+(X^3\Sigma^-)$							
0	16.29	16.38	16.22	16.42	19.08	19.29	19.17
1	15.56	15.64	15.52	15.69	18.66	18.81	18.69
2	14.86	14.93	14.84	14.99	18.28	18.41	18.22
$OH^+(A^3\Pi)$							
0	13.35	13.34	13.24	13.35	22.25	21.92	22.50
1	12.50	12.50	12.50	12.50	21.65	21.26	21.83
2	11.67	11.69	11.63	11.68	21.99	21.54	21.89
$OD^+(X^3\Sigma^-)$							
0		8.73		8.77		5.46	5.45
1		8.45		8.48		5.35	5.33
2		8.17		8.21		5.25	5.22
3		7.89		7.93		5.13	5.04
$OD^+(A^3\Pi)$							
0		7.13		7.14		6.21	6.39
1		6.80		6.81		6.06	6.29
2		6.49		6.49		5.93	6.14
3		6.18		6.17		6.07	6.09

basis set). If instead ω_e, $\omega_e x_e$, and $\omega_e y_e$ are fitted to the same energies, the values 3097, 89.2, and 2.30 cm^{-1} are obtained.

As Table 6 shows, the calculated molecular constants and $\Delta G_{1/2}$ values for OH^+ and OD^+ are in reasonable agreement with experiment [13] and with the earlier results of Saxon and Liu [12]. It should perhaps be pointed out that the emphasis in the present work has been on the study of the convergence of the transition moment as a function of the number of orbitals included in the RAS3 space, rather than on a very accurate calculation of the potential curves for OH^+. In this perspective the deviation of the present results from the experimental values are quite acceptable: the error in the bond distance is 0.002 Å, in the bond energy 0.04 eV, and in the ΔG values about 30 cm^{-1}, for the X state, with similar errors for the A state. Rotational constants are reproduced very well, as can be seen in Table 7, where a comparison is also made to an earlier theoretical investigation by Hirst and Guest [18].

5. Conclusions

RASSCF wave functions have been used to compute the lifetime of the $A^3\Pi$ state of OH^+. The major issue has been to study the convergence of the transition moment and other properties as a function of the number of active orbitals. The valence orbitals are used to specify the RAS2 subspace and an increasing number of extra-valence orbitals are then included in the RAS3 subspace. It has been shown that accurate results can be obtained with a limited number of orbitals in the RAS3 space, leading to a very compact wave function comprising only a few thousand configurations.

The lifetime computed in the present work is 2.4 μs ($v = 0$). However, the contribution from a second RAS3 orbital of δ-type and higher angular momentum functions will increase this value to around 2.6 μs. The deviation of the computed values of the excitation energies from experiment is another source of error. The calculated T_e value is 475 cm^{-1} (0.06 eV) larger than the experimental value. This error is small, but the third power of the excitation energy appears in the expression for the lifetime. Introducing this correction increases the lifetime to 2.7 μs with an estimated uncertainty of about 0.1 μs. The value derived from the calculations is thus slightly larger than the two experimental values: 2.4 ± 0.3 [10] and 2.5 ± 0.3 [11] μs, respectively, but is within the error limits of the experiments.

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