

High-level *ab initio* studies of the electronic excited states of the hydroxyl radical and water–hydroxyl complex

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The lowest-energy electronic transitions in the hydroxyl radical and the hydrogen bound complex $\text{H}_2\text{O}\cdot\text{HO}$ have been studied using *ab initio* methods. We have used the complete active-space self-consistent field and multireference configuration interaction (MRCI) methods to calculate vertical excitation energies and oscillator strengths. At the MRCI level the lowest-lying ${}^2\Sigma^+ \leftarrow {}^2\Pi$ electronic transition is redshifted by about 2500 cm^{-1} upon formation of the $\text{H}_2\text{O}\cdot\text{HO}$ complex. We propose that this transition could be used to identify the complex in the gas phase, which in turn could be used to examine the role of $\text{H}_2\text{O}\cdot\text{HO}$ in atmospheric reactions. © 2004 American Institute of Physics. [DOI: 10.1063/1.1687335]

I. INTRODUCTION

The hydroxyl radical (OH) is the primary oxidant in our troposphere. Many anthropogenic pollutants are removed via reaction with OH, including virtually all hydrocarbons and most sulfur and nitrogen containing compounds.¹ As a result, an accurate measurement of the OH concentration is required for a quantitative understanding of atmospheric chemistry. However, it is difficult to accurately measure the concentration of OH due to its highly reactive nature. Its lifetime is of the order of a second and its peak concentration of about 10^6 molecules cm^{-3} is very low.¹ The atmospheric concentration of OH is commonly determined from measurements of the ${}^2\Sigma^+ \leftarrow {}^2\Pi$ allowed electronic transition which occurs around 308 nm (Refs. 2 and 3).

The large electric dipole moment (1.668 D) of OH (Ref. 4) suggests that it will form strong hydrogen bonds and the hydrogen bound $\text{H}_2\text{O}\cdot\text{HO}$ complex is a species likely to be present in our atmosphere. Its binding energy is similar to that of the water dimer, which has recently been detected in our atmosphere.⁵

Previous studies have shown that both transition energies and intensities of monomeric units are altered upon complexation.^{6–9} Thus the electronic absorption spectrum of OH is likely to change upon formation of the $\text{H}_2\text{O}\cdot\text{HO}$ complex. As a result, measurements of the OH concentration using techniques based on detection of the ${}^2\Sigma^+ \leftarrow {}^2\Pi$ electronic transition may neglect hydroxyl radicals complexed as $\text{H}_2\text{O}\cdot\text{HO}$.

The self-reaction of HO_2 exhibits a rate dependence on water vapor concentration, suggesting a mechanism involving the $\text{H}_2\text{O}\cdot\text{HO}_2$ complex.¹ In a similar manner, the $\text{H}_2\text{O}\cdot\text{HO}$ complex may be important for OH reactions.¹⁰ Spectroscopic identification of the $\text{H}_2\text{O}\cdot\text{HO}$ complex in the gas phase is essential to determine the role that $\text{H}_2\text{O}\cdot\text{HO}$ plays in tropospheric reactions.

The potential energy curves of several excited states of OH, as well as the transition moments connecting the ground

state to these excited states, have been previously calculated.¹¹ Previous *ab initio* studies of $\text{H}_2\text{O}\cdot\text{HO}$ have predominantly focused on the calculation of geometries and harmonic vibrational frequencies in the ground and first electronic excited states.^{12,13} The vibrational spectrum of $\text{H}_2\text{O}\cdot\text{HO}$ trapped in an argon matrix has been recorded,^{14–16} but $\text{H}_2\text{O}\cdot\text{HO}$ has not been identified in the gas phase.

In this paper we calculate vertical excitation energies and oscillator strengths for the electronic transitions in OH and $\text{H}_2\text{O}\cdot\text{HO}$. The calculated vertical excitation energies and oscillator strengths for OH are compared to experimental values and to those calculated for the complex.

II. COMPUTATIONAL METHODS

We express the calculated transition intensities in terms of the oscillator strength f , which for a transition from the ground state to an electronic excited state is written

$$f_{eg} = 4.70165 \times 10^{-7} [\text{cm D}^{-2}] \bar{\nu}_{eg} |\vec{\mu}_{eg}|^2, \quad (1)$$

where $\bar{\nu}_{eg}$ is the transition wavenumber in cm^{-1} and $\vec{\mu}_{eg}$ is the transition dipole moment in debye.

The equilibrium geometries for the ground states of OH and $\text{H}_2\text{O}\cdot\text{HO}$ were obtained at the quadratic configuration interaction including singles and doubles (QCISD) levels of theory with the 6-311++G(2d,2p) basis set. The QCISD/6-311++G(2d,2p) method has previously been shown to give reliable geometries for the water dimer.¹⁷ The geometry optimizations were performed with GAUSSIAN 98 (Ref. 18) using the “tight” convergence criterion. The geometries were confirmed as minima by harmonic frequency calculations.

Previous studies of the electronic excited states in a number of complexes have used the multireference configuration interaction including singles and doubles (MRCI) method^{6–9} and we have used a similar multiconfigurational approach in this work. We also provide results inclusive of the Davidson correction (MRCI+Q) which approximately accounts for the effect of quadruple excitations. We have calculated vertical excitation energies and oscillator strengths

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FIG. 1. The QCISD/6-311++G(2d,2p)-optimized structure of H₂O·HO.

using the complete active-space self-consistent field (CASSCF) and MRCI levels of theory.^{19,20} The MRCI calculations are based on the corresponding state-averaged CASSCF molecular orbitals.^{20,21} In all CASSCF calculations, a full valence active space was used and the $1s$ orbital of all oxygens was doubly occupied in all configurations and frozen at the Hartree–Fock level—i.e., not optimized.

We have used basis sets ranging in size from aug-cc-pVDZ to aug-cc-pV6Z (Refs. 22–27) for the calculation of vertical excitation energies and oscillator strengths. All CASSCF and MRCI calculations were performed using the MOLPRO 2002 program.²⁸

The hydroxyl radical has a doubly degenerate ${}^2\Pi$ ground state and belongs to the $C_{\infty v}$ point group. The MOLPRO suite of programs uses Abelian point groups only²⁸ and the largest Abelian point group for OH is C_{2v} . Within the C_{2v} point group the ${}^2\Pi$ ground state corresponds to states of 2B_1 and 2B_2 symmetry. We calculate only the transition from the ground state to the ${}^2\Sigma^+$ first excited state, which lies in the 2A_1 irreducible representation of the C_{2v} point group. The full valence active space consists of 7 electrons in 5 molecular orbitals or CASSCF(7,5). The sizes of the CAS matrices are 14 configuration-state functions (CSFs) for the A_1 state, and 10 CSFs for each of the B_1 and B_2 states.

H₂O·HO has C_s symmetry in its ground state. We have calculated the vertical excitation energies from the ground state to the first ${}^2A'$ and ${}^2A''$ electronic excited states. The full valence active space is CASSCF(15,11), and the sizes of the CAS matrices are 14 624 CSFs for the A' states and 14 416 CSFs for the A'' states.

Due to the relatively large active space used for H₂O·HO, we have limited the number of reference configurations used in the MRCI calculations. The reference used in generating the MRCI wave function was chosen to be those CSFs with the largest CI coefficients in the CASSCF expansion.

III. RESULTS AND DISCUSSION

When OH forms a complex with water the two degenerate components of the ${}^2\Pi$ electronic state split into ${}^2A'$ and ${}^2A''$ states. The ${}^2A'$ state has the singly occupied molecular orbital in the symmetry plane, while the ${}^2A''$ state has this orbital perpendicular to the symmetry plane. Previous *ab initio* calculations have found the ${}^2A'$ state to be more stable, although the energy difference is small.^{12–14} The QCISD/6-311++G(2d,2p) optimized geometry of H₂O·HO in the ${}^2A'$ ground state is shown in Fig. 1. The calculated structure is in good agreement with previous *ab initio* studies.^{12,13} The experimental structure of H₂O·HO has not yet been determined; however, the observed fundamental vibrational frequencies of H₂O·HO in an argon matrix are in good agreement with *ab initio*-calculated frequencies of the structure shown in Fig. 1.^{14,15} The QCISD/6-311++G(2d,2p)calculated binding energy of the complex is 5.69 kcal/mol.

A. Hydroxyl radical

Our calculated vertical excitation energy for the ${}^2\Sigma^+ \leftarrow {}^2\Pi$ transition in OH is given in Table I. It can be seen that the vertical excitation energy calculated with the CASSCF method is well converged at the aug-cc-pVTZ basis set size, with only a 5-cm⁻¹ lowering of energy on increasing the basis set to aug-cc-pV6Z. The MRCI-calculated vertical excitation energy is about 3000 cm⁻¹ lower than the CASSCF vertical excitation energy and is more dependent on basis set size. Our MRCI+Q calculated vertical excitation energies are around 500 cm⁻¹ lower than the MRCI calculated values. There is a continual lowering of the MRCI and MRCI+Q vertical excitation energy as the basis set size is increased from aug-cc-pVDZ to aug-cc-pV6Z. The experimental electronic energy (T_e) of the ${}^2\Sigma^+$ state in OH is 32 684 cm⁻¹ (Ref. 4). The vertical excitation energy is expected to be somewhat larger than the T_e value due to a change in bond length between the ground and electronic excited states. Our MRCI+Q/aug-cc-pVQZ vertical excitation energy is 33 147 cm⁻¹, in reasonable agreement with the experimental T_e value.

In Table II we give the calculated oscillator strength of the ${}^2\Sigma^+ \leftarrow {}^2\Pi$ electronic transition in OH. The calculated transition dipole moment has been multiplied by the corresponding vertical excitation energy from Table I according to

TABLE I. Calculated vertical excitation energy ($\bar{\nu}_{eg}$ in cm⁻¹) and wavelength (λ_{eg} in nm) of the ${}^2\Sigma^+ \leftarrow {}^2\Pi$ transition of the hydroxyl radical.

	aug-cc-pVDZ		aug-cc-pVTZ		aug-cc-pVQZ		aug-cc-pV5Z		aug-cc-pV6Z	
	$\bar{\nu}_{eg}$	λ_{eg}	$\bar{\nu}_{eg}$	λ_{eg}	$\bar{\nu}_{eg}$	λ_{eg}	$\bar{\nu}_{eg}$	λ_{eg}	$\bar{\nu}_{eg}$	λ_{eg}
CASSCF	36984	270.4	36672	272.7	36671	272.7	36668	272.7	36667	272.7
MRCI ^a	33941	294.6	33708	296.7	33610	297.5	33574	297.8	33556	298.0
MRCI ^b	33937	294.7	33700	296.7	33602	297.6	33566	297.9	33547	298.1
MRCI ^c	33937	294.7	33700	296.7	33602	297.6	33566	297.9	33547	298.1
MRCI+Q ^d	33497	298.5	33254	300.7	33147	301.7	33111	302.0	33093	302.2

^a0.01 reference threshold.

^b0.001 reference threshold.

^cFull-CAS reference threshold.

^dMRCI+Q results for 0.001 and full-CAS reference thresholds are identical to five significant figures.

TABLE II. Calculated oscillator strength ($\times 10^3$) of the ${}^2\Sigma^+ \leftarrow {}^2\Pi$ transition of the hydroxyl radical.

	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pV6Z
CASSCF	3.47	3.43	3.43	3.44	3.44
MRCI ^a	1.79	1.74	1.74	1.74	1.74
MRCI ^b	1.79	1.73	1.73	1.73	1.73
MRCI ^c	1.79	1.73	1.73	1.73	1.73
MRCI+Q ^d	1.76	1.70	1.71	1.71	1.71

^a0.01 reference threshold.^b0.001 reference threshold.^cFull-CAS reference threshold.^dMRCI+Q results for 0.001 and full-CAS reference thresholds are identical to three significant figures.

Eq. (1) to give the oscillator strength. The oscillator strength appears to be well converged at the aug-cc-pVTZ basis set size with all methods. The oscillator strength calculated with the CASSCF method is a factor of 2 larger than that obtained at the MRCI and MRCI+Q levels. An experimental oscillator strength of 1.31×10^{-3} for the ${}^2\Sigma^+ \leftarrow {}^2\Pi$ transition is obtained by summation of all the observed lines in the HITRAN database.²⁹ The MRCI/aug-cc-pVQZ and MRCI+Q/aug-cc-pVQZ calculated oscillator strength for the hydroxyl radical is approximately 30% larger than this experimental value and we expect that our calculated oscillator strengths are accurate to within a factor of 2.

van Dishoeck and Dalgarno have previously studied the electronic excited states in OH using a configuration interaction method.¹¹ They used a large Slater-type basis set to calculate a vertical excitation energy of 4.05 eV ($32\,700\text{ cm}^{-1}$) and an oscillator strength of 1.0×10^{-3} (Ref. 11). These values are in reasonable agreement with our MRCI/aug-cc-pVQZ-calculated values.

It is desirable to use a full-CAS reference: however, this is not computationally feasible for the $\text{H}_2\text{O}\cdot\text{HO}$ complex if the aug-cc-pVQZ basis set is used. We have performed the MRCI calculations using three different reference thresholds. A reference threshold of 0.001 is sufficient to provide results converged to those obtained with a full-CAS reference threshold as shown in Tables I and II, and is the smallest reference threshold used in the calculations on $\text{H}_2\text{O}\cdot\text{HO}$. Inclusion of more states in the CASSCF calculations resulted in only small changes in both vertical excitation energy and oscillator strength, and therefore we have limited the number of states as described in Sec. II. This is perhaps not surprising as the next electronic state in OH is much higher in energy at $69\,774\text{ cm}^{-1}$ (Ref. 4).

We have estimated an “experimental” vertical excitation energy from the experimental bond lengths, Morse potential energy curve, and T_e of the ${}^2\Sigma^+$ excited state given in Huber and Herzberg.⁴ The calculated energy of the ${}^2\Sigma^+$ potential energy curve at the ${}^2\Pi$ ground-state equilibrium bond length added to the electronic energy of the excited state (T_e) leads to an estimated “experimental” vertical excitation energy of $32\,917\text{ cm}^{-1}$. This “experimental” value can be directly compared with our calculated vertical excitation energy. Our MRCI/aug-cc-pVQZ-calculated vertical excitation energy is around 700 cm^{-1} higher in energy than this approximated “experimental” vertical excitation energy. If we add the Davidson correction (+Q), our calculated vertical excitation energy improves to $33\,147\text{ cm}^{-1}$, and if we further increase the basis set to aug-cc-pV6Z, the calculated vertical excitation energy becomes $33\,093\text{ cm}^{-1}$, only 176 cm^{-1} (0.5%) higher than the experimental value.

We can also compare to the experimental T_e of the ${}^2\Sigma^+$ state directly by optimizing the geometry of OH in the ${}^2\Pi$ and ${}^2\Sigma^+$ electronic states. With the MRCI/aug-cc-pVQZ method we obtain a T_e of $33\,325\text{ cm}^{-1}$. This calculation overestimates the T_e by around 700 cm^{-1} , similar to the overestimate in vertical excitation energy. If we include the Davidson correction, the calculated T_e value becomes $32\,820\text{ cm}^{-1}$, which is within 136 cm^{-1} of the experimental value.

We have tested the effect of a larger than full valence active space. We extended the active space of OH by including another four unoccupied molecular orbitals—i.e., CASSCF(7,9). Based on these CASSCF orbitals, the MRCI+Q/aug-cc-pVQZ-calculated vertical excitation energy is $33\,107\text{ cm}^{-1}$ (302 nm) with an oscillator strength of 1.49×10^{-3} , in good agreement with experiment. This vertical excitation energy is within 0.6% of our estimated “experi-

TABLE III. Calculated vertical excitation energy ($\bar{\nu}_{eg}$ in cm^{-1}) and wavelength (λ_{eg} in nm) of the ${}^2A' \leftarrow {}^2A'$ electronic transition in $\text{H}_2\text{O}\cdot\text{HO}$.

	aug-cc-pVDZ		aug-cc-pVTZ		aug-cc-pVQZ	
	$\bar{\nu}_{eg}$	λ_{eg}	$\bar{\nu}_{eg}$	λ_{eg}	$\bar{\nu}_{eg}$	λ_{eg}
CASSCF	32527	307.4	32227	310.3	32216	310.4
MRCI ^a	31400	318.5	31208	320.4	31135	321.2
MRCI ^b	31374	318.7	31181	320.7	31107	321.5
MRCI+Q ^b	30965	323.0	30807	324.6	30736	325.3

^a0.01 reference threshold.^b0.001 reference threshold.

TABLE IV. Calculated oscillator strength ($\times 10^3$) of the ${}^2A' \leftarrow {}^2A'$ electronic transition in $H_2O \cdot HO$.

	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ
CASSCF	2.68	2.64	2.64
MRCI ^a	1.88	1.80	1.79
MRCI ^b	1.88	1.80	1.79
MRCI+Q ^b	1.86	1.78	1.77

^a0.01 reference threshold.^b0.001 reference threshold.

mental” vertical excitation energy and our calculated oscillator strength is within 14% of the experimental value. However, a calculation of this type is not possible for $H_2O \cdot HO$.

B. $H_2O \cdot HO$

The CASSCF-, MRCI-, and MRCI+Q-calculated vertical excitation energy and oscillator strength of the lowest energy ${}^2A' \leftarrow {}^2A'$ transition in $H_2O \cdot HO$ are listed in Tables III and IV. The energies and oscillator strengths converge with increasing basis set in a similar manner to that observed for OH. The change in MRCI-calculated vertical excitation energy with decreasing threshold is similar for both $H_2O \cdot HO$ and OH.

The main CSF of the ${}^2A'$ ground state in $H_2O \cdot HO$ is (core)⁴(3-5)*a*'²6*a*'²7*a*'²8*a*'²9*a*'¹10*a*'². The 9*a*' and 10*a*' molecular orbitals correspond to the *p*-like orbitals centered on the oxygen atom of OH. Here 8*a*' is a bonding σ orbital also centered on the oxygen atom in OH. The main CSFs of the ${}^2A''$ and ${}^2A'$ excited states in $H_2O \cdot HO$ have the 10*a*' and 8*a*' orbitals singly occupied, respectively and in both excited states the main CSF has the 9*a*' orbital doubly occupied.

The lowest-energy ${}^2A'' \leftarrow {}^2A'$ electronic transition in $H_2O \cdot HO$ is calculated to lie at 187 cm^{-1} with the MRCI+Q/aug-cc-pVQZ method and corresponds to the transition between the in- and out-of-plane *p*-like orbitals of the hydroxyl oxygen. This transition has a very low oscillator strength of 8.64×10^{-11} . The energy of this transition is similar to the 126- cm^{-1} spin-orbit splitting of the ${}^2\Pi$ ground state in OH.⁴ However, this transition is not the focus of this paper and spin-orbit coupling is not included in the present calculations.

The ${}^2A' \leftarrow {}^2A'$ transition corresponds to the ${}^2\Sigma^+ \leftarrow {}^2\Pi$ transition of the hydroxyl radical and we compare the MRCI+Q/aug-cc-pVQZ-calculated results for this electronic transition in OH and $H_2O \cdot HO$ in Table V. A substantial redshift of 2411 cm^{-1} and a minor oscillator strength increase

TABLE V. MRCI+Q/aug-cc-pVQZ-calculated vertical excitation energies ($\bar{\nu}_{eg}$ in cm^{-1}), wavelengths (λ_{eg} in nm), and oscillator strengths of the ${}^2\Sigma^+ \leftarrow {}^2\Pi$ transition of OH and $H_2O \cdot HO$.^a

	OH	$H_2O \cdot HO$
$\bar{\nu}_{eg}$	33147	30736
λ_{eg}	301.7	325.3
<i>f</i>	1.71×10^{-3}	1.77×10^{-3}

^aA 0.001 reference threshold is used.

are predicted upon formation of the complex. The transition in $H_2O \cdot HO$ is shifted well outside the rotational envelope of the OH transition.

This calculated redshift is significantly larger than the small blueshift of $\sim 150\text{--}250\text{ cm}^{-1}$ recently calculated for the low-lying ${}^1\Delta_g \leftarrow {}^3\Sigma_g^-$ and ${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transitions in O_2 upon formation of the $H_2O \cdot O_2$ complex.⁹ However, the $H_2O \cdot O_2$ complex is less strongly bound than $H_2O \cdot HO$ and small perturbations to the vertical excitation energies are to be expected.

Aloisio *et al.* have calculated the three lowest-lying electronic transitions in HO_2 and the $H_2O \cdot HO_2$ complex.⁸ They found a larger percentage change in vertical excitation energy upon complexation than we have found in OH. This is again perhaps not surprising considering the larger binding energy of $H_2O \cdot HO_2$ compared to $H_2O \cdot HO$.

IV. CONCLUSIONS

We have calculated the vertical excitation energies and oscillator strengths of the lowest-lying electronic transitions in OH and the $H_2O \cdot HO$ complex using multireference configuration interaction methods. Our MRCI+Q/aug-cc-pVQZ-calculated vertical excitation energy for the ${}^2\Sigma^+ \leftarrow {}^2\Pi$ transition of OH is within 230 cm^{-1} of our estimated experimental value. The orbitals involved in the electronic transition to the second excited state of $H_2O \cdot HO$ are very similar to those involved in the ${}^2\Sigma^+ \leftarrow {}^2\Pi$ transition of OH. The MRCI+Q/aug-cc-pVQZ-calculated vertical excitation energy of this transition is 2411 cm^{-1} lower in the complex than in OH. Such a substantial shift suggests that this transition may be used to identify $H_2O \cdot HO$ in the gas phase.

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