On the relative intensities of the U.V. transitions in HOCl and HOCl . H₂O

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HOCl provides a possible sink for stratospheric chlorine and can reduce the rate of ozone depletion by chlorinated species [1]. The effectiveness of HOCl as a sink has been the subject of much controversy due to the uncertainty of its U.V. spectrum [1, 2]. Recent experiments have identified two U.V. absorptions for HOCl of approximately equal intensity and centred at 240 nm and 320 nm [1]. However, theoretical studies and other experimental results indicate that the 320 nm absorption is significantly less intense than the one at 240 nm, an important *qualitative* difference [2]. A knowledge of the intensity of the 320 nm absorption is critical in obtaining a reliable photodissociation rate for HOCl since it is caused by absorption of solar U.V. flux which is significant only for wavelengths greater than 300 nm.

Niki *et al.* have examined the method used in [1] for producing HOCl ($Cl_2O + H_2O \rightleftharpoons 2HOCl$) and noted that HOCl produced in this fashion is probably hydrated to some degree [3]. This has led to speculation that the presence of hydrated HOCl in the experimental system is responsible for the apparent qualitative discrepancy between theory and experiment.

In this work we present the results of a set of calculations which compare the U.V. electronic transition dipole moments for HOCl and the HOCl . H₂O complex. Because the disagreement in intensities between theory and experiment is *qualitative* in nature the level of calculation presented here is meant only to assess the *qualitative* aspects of this problem. Quantitative precision will require further study with much larger basis sets and larger CI expansions.

Configuration interaction (CI) calculations were performed on the ground state ($1A'$) and two low lying electronic states ($2A'$ and $1A''$) of HOCl at its experimental geometry [2] using a double zeta (DZ) basis; for O and H Dunning's [4] $4S$, $2P$ and $2S$ contractions were used while for Cl Dunning's [5] $6S$, $4P$ contraction was employed. All states are singlet states. In order to provide a level of correlation similar to that for the HOCl . H₂O system (discussed later) only configurations with single and double excitations from the highest seven occupied orbitals of the Hartree–Fock (HF) $1A'$ reference wavefunction into its lowest eight virtual orbitals were included in the HOCl CI wavefunctions. This resulted in 883 spin adapted functions (SAFs) for the A' states and 770 SAFs for the A'' state. Electronic transition dipole moments were calculated for the U.V. transitions ($1A' \rightarrow 2A'$: 240 nm; $1A' \rightarrow 1A''$: 320 nm) and are listed in in row 1 of table 1. Our results agree with previous theoretical work [2] (row 2, table 1) which indicate the $1A' \rightarrow 2A'$ transition to be much more intense than the

$1A' \rightarrow 1A''$. The ratio of the transition probabilities (240 nm to 320 nm) is 25. The excitation energies for these transitions are given in table 2 and are seen to be in reasonable qualitative agreement with previous work.

Table 1. Electronic transition dipole moments (in atomic units) for HOCl and HOCl . H_2O.
Electronic transition moments/ea_0

	$1A' \rightarrow 2A'$			$1A' \rightarrow 1A''$			Transition probability
	x	y	z	x	y	z	ratio
HOCl	0·0611	0	0·152	0	0·327	0	25
	0·074	0	0·174	0	0·026	0	53†
HOCl . H_2O ($\theta = 0°$)	0·0854	0	0·197	0	0·0320	0	46
HOCl . H_2O ($\theta = 90°$)	0·0696	0	0·176	0	0·0346	0	30

† The DZ 100 μE_h result from [2] transformed to our coordinate system.

The equilibrium geometry of HOCl . H_2O was determined at the Hartree–Fock level using a STO–4G minimal basis set [6]. The equilibrium geometry of the complex can be described by locating the water molecule in the xy plane. The x-axis bisects the HOH angle, the hydrogens are located along the negative x-axis and the oxygen is at the coordinate origin. The OH of HOCl is along the positive x-axis with its hydrogen between the oxygens of H_2O and HOCl. Cl projects off the positive x-axis in the positive z direction and the HOCl is wholly contained in the xz plane. The H_2O rotational angle (θ) is a rotation about the y coordinate axis and is positive when clockwise. The complex has C_s symmetry with the plane of symmetry being the xz axis. For these calculations the H_2O and HOCl molecules were fixed at their experimental geometries ; for H_2O the bond angle was taken to be 104·52° and R_{OH} to be 1·811 a_0. The STO–4G optimal geometry found for the HOCl . H_2O system is $R_{OO} = 4·8\ a_0$ and $\theta = -30°$. With the minimal basis set the stabilization energy of the complex relative to separated HOCl and H_2O was found to be -54 kJ mol^{-1}. The geometry was further optimized using the DZ basis with the result : $R_{OO} = 5·2\ a_0$; $\theta = 0°$; E_s (the stabilization energy) $= -46$ kJ mol^{-1}.

As is well known, the STO–4G and DZ basis sets tend to overestimate E_s thus leading to the somewhat large value of -46 kJ mol^{-1}. Double zeta plus polarization (DZP) [7] calculations were also performed at the DZ optimum geometry ; the DZP consisted of the DZ basis augmented by D functions on the Cl (exponent $= 0·837\ a_0^{-2}$) and oxygen (exponent $= 0·8\ a_0^{-2}$), and P functions on the H (exponent $= 1·1\ a_0^{-2}$). E_s was reduced to -28 kJ mol^{-1}, a value consistent with known hydrogen bond information.

CI calculations were done at the DZ optimal geometry using the DZ basis for the singlet states $1A'$ (ground state), $2A'$ and $1A''$. All single and double excitations from the 10 highest occupied molecular orbitals of the $1A'$ HF wavefunction into its 12 lowest cannonical virtual orbitals were included in the

CI wavefunctions. The final wavefunctions for $HOCl \cdot H_2O$ consisted of 3793 SAFs for the A' states and 3588 SAFs for the A'' state. The transition dipole moments obtained for the complex at this geometry are given in row 3 of table 1. The presence of H_2O causes an increase in the $1A' \rightarrow 2A'$ transition moment but has little effect on the $1A' \rightarrow 1A''$ transition. The overall result is an increase in the transition probability ratio, from 25 to 46, thus increasing the qualitative difference between experiment and theory. Also, an examination of table 2 shows a slight shift to higher energy (relative to HOCl) in the excitation energies for these transitions in $HOCl \cdot H_2O$.

Table 2. Excitation energies (in E_h) for the HOCl and $HOCl \cdot H_2O$ electronic transitions. CI energies are $E(1A' ; HOCl) = -534 \cdot 9341 \ E_h$ and $E(1A', HOCl \cdot H_2O) = -610 \cdot 9782 \ E_h$.

	$1A' \rightarrow 2A'$	$1A' \rightarrow 1A''$
HOCl	0·270	0·223
	0·219	0·182†
	0·211	0·167 [7]
$HOCl \cdot H_2O$	0·301	0·252

† The 100 μE_h DZ result from [2].

To assess how sensitive the computed transition moments are to variations in the complex geometry another series of calculations was done after rotating the H_2O molecule by $\theta = 90°$ from the equilibrium geometry. E_s (at the DZ level) for this structure is $-19 \ kJ \ mol^{-1}$. The electronic transition moments and the ratio of the two transition probabilities for the distorted complex are given in row 4 of table 1. The ratio of the transition probabilities is similar to that found for the equilibrium geometry indicating the ratio is not very sensitive to changes in complex geometry.

The results presented in table 1 show that the qualitative difference between the theoretical and experimental transitions probabilities for HOCl cannot be ascribed to the $HOCl \cdot H_2O$ complex. Addition of H_2O slightly enhances the $1A' \rightarrow 2A'$ transition and has little effect on the $1A' \rightarrow 1A''$.

Finally, the FTIR results of Niki *et al.* do not uniquely specify that $HOCl \cdot H_2O$ is responsible for the additional hydrogen bonding peaks they observe. Other hydrogen bonded species could exist in the experimental system. For example, hydration of Cl_2O could introduce a change in its U.V. spectrum (say, an enhancement) which could be responsible for the 320 nm peak. This is a possibility because the HOCl spectrum is obtained, in part, as the difference between the U.V. spectrum of the reacting system and Cl_2O. This and other possible reasons for the discrepancy between theory and experiment are being explored in our laboratory.

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