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Polarizabilities of the First Excited ($a^1\Delta_g$) and Ground ($X^3\Sigma_g^-$) States of Molecular Oxygen

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Ab initio computational methods have been employed to determine the frequency-dependent polarizabilities of both the first excited ($a^1\Delta_g$) and ground ($X^3\Sigma_g^-$) states of molecular oxygen. Polarizabilities are reported for oxygen in the gas phase as well as under both equilibrium and nonequilibrium conditions in four solvents. The data consistently show that, for any set of comparable solvation conditions, the polarizability of O_2($a^1\Delta_g$) is *smaller* than that of $O_2(X^3\Sigma_g^-)$. This phenomenon differs from that observed with most other molecules, where the polarizability of the excited state is typically much larger than that of the ground state. The results reflect unique changes in the orbital occupancy associated with electronic excitation in the oxygen molecule. The consequences of this finding are important, particularly with respect to the interpretation of the solvent effect on radiative transitions in oxygen.

I. Introduction

The effect of solvent on radiative transitions in molecular oxygen remains a subject of great interest.[1−13] Of special concern are the $O_2(a^1\Delta_g)-O_2(X^3\Sigma_g^-)$ and $O_2(b^1\Sigma_g^+)-O_2(a^1\Delta_g)$ transitions, which are forbidden in the isolated molecule but which become significantly more probable as a result of solvent perturbations. The $O_2(a^1\Delta_g)-O_2(X^3\Sigma_g^-)$ transition, in particular, has received a great deal of attention because it is now the method of choice by which to monitor $O_2(a^1\Delta_g)$, the reactive intermediate that has historically been called "singlet oxygen".

Efforts to interpret observed solvent effects on the probabilities and energies of these transitions are mounting. In particular, models have been constructed in which the polarizabilities, α, of oxygen are important parameters.[5,6,8−10] Unfortunately, values of α are only available for $O_2(X^3\Sigma_g^-)$ in the gas phase; the polarizabilities for $O_2(X^3\Sigma_g^-)$ in solution as well as $O_2(a^1\Delta_g)$ in both the gas and solution phases are not known.

Unlike most other molecules, production of the lowest excited electronic state in oxygen does not involve population of a more diffuse, higher energy orbital. Rather, the $O_2(X^3\Sigma_g^-)$ and O_2($a^1\Delta_g$) states differ only in the occupation of two degenerate π antibonding orbitals.[14] Thus, it is reasonable to expect that changes in α upon electronic excitation in oxygen will be significantly different than the corresponding changes in a molecule with a closed-shell singlet ground state and an open-shell excited state.

On the basis of these points, we set out to calculate frequency-dependent polarizabilities of $O_2(a^1\Delta_g)$ and $O_2(X^3\Sigma_g^-)$ in the gas phase as well as under both equilibrium and nonequilibrium solvation conditions. The results of this study are reported herein.

II. Method and Computational Details

The use of correlated methods based on a single determinant reference wave function is not advisable when one considers the electronic structure of open-shell systems such as in molecular oxygen. Instead, we used a multiconfigurational approach: the multiconfiguration self consistent field (MCSCF) method. For our work, the 1s and 2s electrons were considered inactive, and the complete active space was given by correlating eight electrons in eight orbitals. In order to describe the polarizability properly, it is necessary to use a basis set containing a sufficient number of diffuse functions. In this work, aug-cc-pVQZ was employed, which contains 160 basis functions.

The accuracy of our gas-phase $O_2(X^3\Sigma_g^-)$ polarizability can be assessed by comparison to the results of earlier calculations[15,16] and experimental data.[17] Unfortunately, there are no literature values available for the excited-state polarizability. Thus, in order to check the reliability of our results, we performed a basis set investigation. We observed that the smaller basis sets, aug-cc-pVDZ and aug-cc-pVTZ, did not contain enough diffuse functions to describe the occupation of the real orbitals correctly. However, the double augmented d-aug-cc-pVTZ basis set contains some extra polarization functions and a total of 124 basis functions. Values for the polarizabilities obtained with the basis sets d-aug-cc-pVTZ and aug-cc-pVQZ were very close, thus supporting the validity of our results.

The calculations were performed with the DALTON program package.[18] We performed the calculations with the correct spin multiplicity but without spatial symmetry restrictions, thereby imposing as few constraints as possible. We used response theory to calculate the excitation energies and frequency-dependent polarizabilities in vacuum[19] and in solvent.[20,21] The

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TABLE 1: Gas-Phase Static Polarizabilities of the Oxygen Ground State (au)[a]

polarizability	this work	literature	
$\bar{\alpha}$	9.95	9.68[b]	10.22[c]
		9.76[d]	10.66[e]
$\Delta\alpha$	7.13	7.09[b]	7.16[c]
		7.22[d]	

[a] 1 au = 1.4818 × 10^{-25} cm^3. [b] CAS calculation.[16] [c] RAS calculation.[16] [d] CI calculation.[15] [e] Refractivity measurement.[17]

components of the frequency-dependent dipole polarizability tensor were obtained directly from the linear response functions, and the excitation energies were achieved from the corresponding poles.

In the solution-phase computations, the solvent was regarded as a dielectric continuum in a self-consistent reaction field model. The solute (O_2) was embedded in a cavity and surrounded by a dielectric medium characterized by optical ($\epsilon_{op} = n^2$) and static (ϵ_{st}) dielectric constants. The total polarization is the sum of two contributions:[20−32]

$$P(r) = P_{op}(r) + P_{in}(r) \tag{1}$$

The optical polarization, P_{op}, represents the response from the electronic degrees of freedom of the solvent, and P_{op} is assumed always to be in equilibrium with the charge distribution of the solute because of its very short relaxation time. The inertial polarization, P_{in}, represents the response from the nuclear degrees of freedom of the solvent molecules (vibrational, rotational, and translational degrees of freedom). This part of the polarization remains fixed during an electronic transition, and it is thus not always in equilibrium with the molecular charge distribution of the solute. We then have two situations: (1) a situation where the solvent is not in equilibrium with the molecular charge distribution of the solute, and the solvent−solute interactions depend on ϵ_{op} as well as ϵ_{st}, and (2) an equilibrium situation in the limit of a static perturbation where the dielectric medium is represented only by the static dielectric constant, ϵ_{st}. The variable solvent parameters are the cavity radius of the solute (O_2) and the two dielectric constants of the solvent. The cavity, assumed to be spherical, has a radius r_c that is calculated from:

$$r_c = 0.5r_{O_2} + r_{vdw} \tag{2}$$

where r_{O_2} is the oxygen bond length[33] and r_{vdw} is the van der Waals distance for oxygen, which is 1.40 Å.[34] We find that the polarizabilities are relatively insensitive to minor changes in the cavity radius; an increase of the cavity radius by 5% led to a decrease in the average polarizability of less than 3%. The cavity radius employed for the ground state was 3.797 au. The bond length of the first excited state is only slightly larger than that of $O_2(X^3\Sigma_g^-)$ and yields $r_c = 3.878$ au. To cover a broad range of static and optical dielectric constants, the following solvents were chosen: benzene, C_6H_6 ($\epsilon_{st} = 2.284$, $\epsilon_{op} = 2.253$); diethyl ether, $C_2H_5OC_2H_5$ ($\epsilon_{st} = 4.20$, $\epsilon_{op} = 1.844$); benzonitrile, C_6H_5CN ($\epsilon_{st} = 25.7$, $\epsilon_{op} = 2.3348$); and acetonitrile, CH_3CN ($\epsilon_{st} = 37.5$, $\epsilon_{op} = 1.8058$).

III. Results and Discussion

A. Gas Phase. In Table 1, we compare the static polarizability for the ground state obtained in our work to values from the literature, including an experimental estimation of the polarizability. We employ the average value calculated from $\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$. We also tabulate the difference between the parallel and the perpendicular components of the polarizability, $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$. In both cases, our results agree with existing information. Although the absolute value of our polarizability appears to be good, we are nevertheless principally interested only in relative polarizability changes between the ground and excited states.

TABLE 2: Gas-Phase Average Polarizabilities for the Ground and the First Excited States of Oxygen (au)[a]

frequency[b]	ground state	excited state
0.0000	9.95	9.41
0.0345	9.99	9.44
0.0556	10.05	9.48
0.0932	10.24	9.60

[a] 1 au = 1.4818 × 10^{-25} cm^3. [b] 1 au = 4.1342 × 10^{16} s^{-1}.

In Table 2, we list the frequency-dependent polarizabilities for $O_2(X^3\Sigma_g^-)$ and $O_2(a^1\Delta_g)$. For each state, the polarizability increases with an increase in the frequency, as expected.[35] More importantly, for each frequency, we find that the excited-state polarizabilities are consistently *smaller* than the corresponding values for the ground state. For most molecules, excited-state polarizabilities are larger than those for the ground state. For instance, for butadiene the polarizability of the first excited state is about twice as large as the ground-state polarizability.[36] This remarkable difference between oxygen and other molecules can be explained in terms of the unique changes in orbital occupancy associated with electronic excitation in oxygen. Specifically, the $O_2(X^3\Sigma_g^-)$ and $O_2(a^1\Delta_g)$ states differ only in the occupation of the degenerate π_g level; in the ground state, there is one electron in each of the $\pi_{g,x}$ and $\pi_{g,y}$ orbitals, whereas in $O_2(a^1\Delta_g)$ both electrons are in the same orbital (either $\pi_{g,x}$ or $\pi_{g,y}$). For other molecules, however, electronic excitation populates higher energy and more diffuse orbitals, thus yielding more polarizable excited states.

Although the relationship between polarizabilities and Raman cross sections can be complicated,[37] it is interesting to note the recent report that the gas-phase Raman cross section of $O_2(a^1\Delta_g)$ is likewise smaller than that of $O_2(X^3\Sigma_g^-)$.[38]

B. Solution Phase. The results of our calculations for solvated oxygen are shown in Table 3 and they are in accord with those obtained for oxygen in the gas phase. Specifically, for any set of comparable solvation conditions, the polarizability of $O_2(a^1\Delta_g)$ is consistently smaller than that of $O_2(X^3\Sigma_g^-)$. The data also indicate that the difference between the $O_2(a^1\Delta_g)$ and $O_2(X^3\Sigma_g^-)$ polarizabilities is larger in solution than that in the gas phase and that this difference is most pronounced in the equilibrium solvation situation. Furthermore, we observe that the magnitude of these differences depends on the solvent dielectric constants.

We also find that, in solution, the absolute values of the polarizabilities are uniformally larger than those obtained for the gas phase and that these values likewise depend on the solvent dielectric constants. These effects are consistent with previously published results on other molecules[20,21] and are expected from the sum-over-states expression for the polarizability,[19] knowing that the energy differences between ground and excited states decrease with an increase in ϵ_{st}. When oxygen is in equilibrium with the solvent, the polarizability increases with an increase in ϵ_{st}; the largest value of α obtained is in acetonitrile, where $\epsilon_{st} = 37.5$. For the nonequilibrated solvation condition, however, the polarizabilities depend on both ϵ_{st} and ϵ_{op}, and the largest value of α is obtained in benzonitrile, which has a large optical dielectric constant. In all cases, the nonequilibrium polarizabilities are smaller than those obtained for the corresponding equilibrium situation.

In order to find an explanation for the relative values of the observed polarizabilities, we consider both the equilibrium, $E_{\text{sol}}^{\text{eq}}$, and nonequilibrium, $E_{\text{sol}}^{\text{neq}}$, solvation energies for a spectroscopic transition from an initial to final state[20,21]

$$E_{\text{sol}}^{\text{eq}} = \sum_{l,m} g_l(\epsilon_{\text{st}}) \langle T_{lm}(\rho_{\text{i}}) \rangle^2 \tag{3}$$

$$\begin{aligned} E_{\text{sol}}^{\text{neq}} &= \sum_{l,m} g_l(\epsilon_{\text{op}}) \langle T_{lm}(\rho_{\text{f}}) \rangle^2 + \sum_{l,m} g_l(\epsilon_{\text{st}}, \epsilon_{\text{op}}) \langle T_{lm}(\rho_{\text{i}}) \rangle \times \\ &\qquad [2\langle T_{lm}(\rho_{\text{f}}) \rangle - \langle T_{lm}(\rho_{\text{i}}) \rangle] \\ &= \sum_{l,m} g_l(\epsilon_{\text{st}}) \langle T_{lm}(\rho_{\text{f}}) \rangle^2 - \sum_{l,m} g_l(\epsilon_{\text{st}}, \epsilon_{\text{op}}) \times \\ &\qquad [\langle T_{lm}(\rho_{\text{i}}) \rangle - \langle T_{lm}(\rho_{\text{f}}) \rangle]^2 \end{aligned} \tag{4}$$

where ρ_{i} and ρ_{f} are the molecular charge distributions of the initial and final states of the solute, respectively, and $\langle T_{lm}(\rho) \rangle$ are the charge moments. The reaction field factors, g_l, are given by[20]

$$g_l(\epsilon) = -\frac{r_{\text{c}}^{-(2l+1)}(l+1)(\epsilon - 1)}{2[l + \epsilon(l+1)]} \tag{5}$$

$$g_l(\epsilon_{\text{st}},\epsilon_{\text{op}}) = g_l(\epsilon_{\text{st}}) - g_l(\epsilon_{\text{op}}) \tag{6}$$

The total energy of the system is the sum of the energy of the system in vacuum, E_{vac}, and the solvation energy, E_{sol}. Thus, for the terms in the multipole expansion which correspond to the molecular dipole ($l = 1$) and quadrupole ($l = 2$) moments, respectively, one obtains the following expressions for the total energy (it is assumed that higher order terms do not contribute significantly)

$$E^{\text{eq}} = E_{\text{vac}} + g_1(\epsilon_{\text{st}}) \sum_m \langle T_{1m}(\rho_{\text{i}}) \rangle^2 + g_2(\epsilon_{\text{st}}) \sum_m \langle T_{2m}(\rho_{\text{i}}) \rangle^2 \tag{7}$$

$$\begin{aligned} E^{\text{neq}} &= E_{\text{vac}} + g_1(\epsilon_{\text{st}}) \sum_m \langle T_{1m}(\rho_{\text{f}}) \rangle^2 + g_2(\epsilon_{\text{st}}) \sum_m \langle T_{2m}(\rho_{\text{f}}) \rangle^2 - \\ &\qquad g_1(\epsilon_{\text{st}},\epsilon_{\text{op}}) \sum_m [\langle T_{1m}(\rho_{\text{i}}) \rangle - \langle T_{1m}(\rho_{\text{f}}) \rangle]^2 - \\ &\qquad\qquad g_2(\epsilon_{\text{st}},\epsilon_{\text{op}}) \sum_m [\langle T_{2m}(\rho_{\text{i}}) \rangle - \langle T_{2m}(\rho_{\text{f}}) \rangle]^2 \\ &= E_{\text{sol,f}}^{\text{eq}} - g_1(\epsilon_{\text{st}},\epsilon_{\text{op}}) \sum_m [\langle T_{1m}(\rho_{\text{i}}) \rangle - \langle T_{1m}(\rho_{\text{f}}) \rangle]^2 - \\ &\qquad g_2(\epsilon_{\text{st}},\epsilon_{\text{op}}) \sum_m [\langle T_{2m}(\rho_{\text{i}}) \rangle - \langle T_{2m}(\rho_{\text{f}}) \rangle]^2 \end{aligned} \tag{8}$$

where the equilibrium solvation energy of the final state, $E_{\text{sol,f}}^{\text{eq}}$, is

$$E_{\text{sol,f}}^{\text{eq}} = E_{\text{vac}} + g_1(\epsilon_{\text{st}}) \sum_m \langle T_{1m}(\rho_{\text{i}}) \rangle^2 + g_2(\epsilon_{\text{st}}) \sum_m \langle T_{2m}(\rho_{\text{f}}) \rangle^2 \tag{9}$$

Since O_2 has no permanent dipole moment, the lowest nonvanishing contribution to the solvation energy in the multipole expansion is for $l = 2$, which corresponds to the molecular quadrupole moment. However, even though the $l = 1$ term does not contribute to the energy, it is a dominant term for a property like the polarizability.[39] In the limit of a static field, the components of the polarizability, α_{jk}, as well as the molecular dipole moment, μ_j, can be defined by taking the derivative of the total energies of the solvated system with respect to a perturbing field, F[35]

$$\alpha_{jk}^{\text{sol}} = \left(\frac{\partial \mu_j^{\text{sol}}}{\partial F_k} \right)_{F_k = 0} = \left(\frac{\partial^2 E^{\text{sol}}}{\partial F_j\, \partial F_k} \right)_{F_j, F_k = 0} \tag{10}$$

where the label sol refers to either equilibrium or nonequilibrium solvation.

TABLE 3: Frequency-Dependent Average Polarizabilities, $\bar{\alpha}$, of the Ground and the First Excited States of Oxygen (au)[a]

	ground state				excited state			
freq[b]	C_6H_6	ether	C_6H_5CN	CH_3CN	C_6H_6	ether	C_6H_5CN	CH_3CN
Equilibrium Solvation								
0.0000	11.02	11.63	12.46	12.52	10.29	10.75	11.41	11.49
0.0345	11.07	11.68	12.53	12.59	10.32	10.78	11.45	11.53
0.0556	11.15	11.77	12.63	12.69	10.37	10.84	11.51	11.60
0.0932	11.39	12.04	12.95	13.02	10.52	11.00	11.70	11.79
Nonequilibrium Solvation								
0.0000	11.01	10.77	11.06	10.75	10.28	10.08	10.35	10.11
0.0345	11.05	10.82	11.10	10.79	10.31	10.11	10.39	10.14
0.0556	11.13	10.89	11.18	10.87	10.36	10.16	10.44	10.19
0.0932	11.37	11.16	11.42	11.09	10.51	10.30	10.59	10.33

[a] 1 au = 1.4818×10^{-25} cm^3. [b] 1 au = 4.1342×10^{16} s^{-1}.

Calculations on $O_2(X^3\Sigma_g^-)$ in CH_3CN under solvent equilibrated conditions with $l_{\text{max}} = 0, 1, 2, 10$ indeed show that we get the largest contribution to the polarizability of the solvated molecule from $l = 1$, as can be seen from the following results: $l_{\text{max}} = 0$ (gas phase), $\bar{\alpha} = 9.95$ au; $l_{\text{max}} = 1$, $\bar{\alpha} = 12.43$ au; $l_{\text{max}} = 2$, $\bar{\alpha} = 12.44$ au; and $l_{\text{max}} = 10$, $\bar{\alpha} = 12.52$ au.

Although the dielectric continuum model is expected to be useful for assessing relative changes in the polarizabilities of solvated oxygen, it is not likely to be a proper model for absolute information. Specifically, discrepancies between the solvent shift calculated utilizing the dielectric continuum model and the experimental data indicate that O_2–solvent interactions are better described by the formation of a discrete collision complex.[9,11] It is thus reasonable to expect that the relative polarizability changes shown underestimate true changes.

A significant amount of experimental data has been collected to indicate that, in solution, the $O_2(a^1\Delta_g)-O_2(X^3\Sigma_g^-)$ emission spectrum is red-shifted relative to the gas-phase value and that the extent of this shift increases as the optical dielectric constant of the solvent increases.[9,10] Recently, the London formula has been employed to model these data.[6] In that work, (1) the gas-phase value was used for the polarizability of $O_2(X^3\Sigma_g^-)$ and (2) it was assumed that the $O_2(a^1\Delta_g)$ polarizability was almost twice as large as the $O_2(X^3\Sigma_g^-)$ polarizability. Because a parameter such as the calculated spectral shift depends significantly on the oxygen polarizabilities in a dispersion interaction, it is inappropriate to discuss the validity of such a model until more accurate polarizabilities have been employed.

In order to apply our data to $O_2(a^1\Delta_g)-O_2(X^3\Sigma_g^-)$ *emission*, we consider that the initial state, $O_2(a^1\Delta_g)$, is in equilibrium with the surrounding solvent, whereas the final state, $O_2(X^3\Sigma_g^-)$, is not. Investigation of Table 3 shows that, under these conditions, there is no trend in the relative magnitudes of the polarizabilities. For acetonitrile and benzonitrile, the excited state indeed has a larger polarizability than the ground state. The respective polarizabilities are similar for ether, whereas for benzene the ground state has the largest polarizability. Our data thus indicate that the effect of solvent on the $O_2(a^1\Delta_g)-O_2(X^3$

Σ_g^-) transition is more complex than is currently believed[6] and that variables other than simple dispersion forces must play a significant role in the oxygen−solvent interaction. If we consider the corresponding *absorption* spectrum $O_2(X^3\Sigma_g^-)$−$O_2(a^1\Delta_g)$, the $O_2(X^3\Sigma_g^-)$ state is now in equilibrium with the solvent, whereas $O_2(a^1\Delta_g)$ is not. In this case, the polarizabilities for the ground state are all larger than the corresponding values for the excited state. Thus, the effect of solvent on the absorption spectrum could provide an interesting contrast to the emission data and potentially lead to a better understanding of the interactions between oxygen and solvent molecules.

IV. Conclusions

The main purpose of the present work has been to obtain the polarizabilities for the first excited, ($a^1\Delta_g$), as well as the ground, ($X^3\Sigma^-{}_g$), states of molecular oxygen. We find that, for any set of comparable conditions, the polarizability of $O_2(a^1\Delta_g)$ is smaller than that of $O_2(X^3\Sigma_g^-)$. This phenomenon is a manifestation of the unique changes in orbital occupancy associated with electronic excitation in oxygen. The data indicate that current models for the effect of solvent on the $O_2(a^1\Delta_g)$−O_2-($X^3\Sigma_g^-$) emission spectrum need to be modified.

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