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RESEARCH ARTICLE



Intermolecular potential of singlet O_4H^+ ion

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ABSTRACT

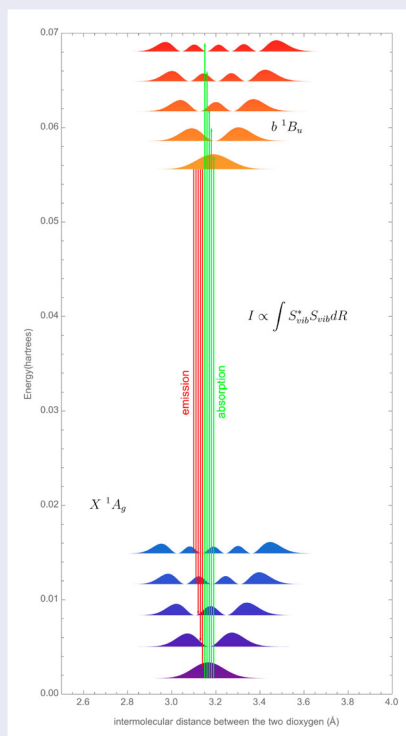
The singlet O_4H^+ ion, a proton-bound dimer of molecular O_2 , is investigated through theoretical rovibrational spectroscopy using an ab-initio potential energy surface calculated at the multi-reference configuration interaction level of accuracy with an aug-cc-pVTZ basis set. The protonated ion is thermodynamically stable and likely to form under laboratory conditions, providing an indirect method to measure the amount of weakly bound dimer O_4 , which is otherwise challenging to detect directly in the interstellar medium. This concept was originally proposed by us a few years ago and has since been validated through experiments. In this study, the ground state electronic configuration of the singlet O_4H^+ ion is assigned with two equally probable configurations of electrons in the molecular orbitals, with our proposed arrangement considered accurate. To further explore vibrational spectroscopy, two out of a total of nine normal modes of O_4H^+ are focused on to study their vibrational spectroscopy to compare with the experimental results. During the level calculation, a double degeneracy is observed among the levels due to the unique topography of the surface. A Franck–Condon analysis for one of the modes results in the electronic spectrum for the electronic transition $X^1A_g \rightarrow b^1B_u$, with the two states being nearly superimposed in terms of equilibrium position. It is likely that the actual experimental electronic spectrum for this transition, which has not yet been obtained by spectroscopists, will closely resemble the results shown in the conclusion of this study.

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Introduction

The O_4H^+ ion, a protonated dimer of molecular O_2 , was first detected [1] in a study combining mass spectral analysis and scattering techniques. This discovery highlighted it as the main product resulting from the gas phase reaction between clusters of H_2 and O_2 when liquid helium nanodroplets were present. An infrared photodissociation spectrum of this ion has been documented [2], although it did not resolve its multiple spin states. Consequently, linking the observed peaks to specific modes of motion within a designated spin isomer proves to be challenging. We previously conducted a computational study [3,4] on this molecule with the goal of identifying the molecular geometry in its ground spin electronic state, X^1A_g . Our findings indicated that the lowest energy configuration corresponds to a trans isomer within the C_{2h} point group. Given that this molecule is relatively new, both theoretical and experimental investigations remain scarce but are anticipated to increase in the future.

In contrast, the parent molecule, known as a dimer of molecular O_2 or O_4 , has been thoroughly explored from both theoretical and experimental perspectives. The primary distinction between the dimer and its protonated variant lies in their binding energies. The dimer is characterised as a weak van der Waals complex, exhibiting a binding energy of 17 meV. In comparison, the protonated form demonstrates a significantly stronger binding energy of approximately 0.15 eV, indicating a robust molecular structure formed upon the addition of a proton. The van der Waals characteristics of the dimer have been confirmed through molecular beam experiments and spectral studies [5–8], with the theoretical support reinforcing these findings [9–14]. The investigation, however, did not stop at the level of dimer and was extended to explore the trimer [15,16] and tetramer [17] of O_2 .

Considering these insights, we are revisiting the O_4H^+ ion, a protonated dimer, following the initial works [3,4]. It appears that previous studies focused primarily on the ab-initio aspects, and to date, this remains the sole work on the topic without any significant advancements. Thus we feel compelled to investigate this area further, specifically concentrating on the infrared spectroscopy of O_4H^+ . The old literature concerned with this molecule did not touch upon the level calculation providing the dissociation energy of a specific vibrational mode and the associated vibronic spectrum. These features constitute new insights into the current work compared to the existing literature where this is absent.

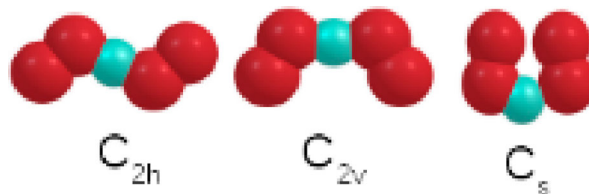


Figure 1. Stationary structures found in the ground potential energy surface of singlet spin state.

Orbital analysis

Electronic structure calculations [3,4] on O_4H^+ ion revealed that it is a planar molecule of net spin equal to zero resulting from vectorial addition of spin momentum of two triplet molecular O_2 and the identified point group is C_{2h} with two dioxygen units being aligned trans to each other. This geometry was characterised as global minimum with the assigned electronic state of ^1A_g indicating that it is a fully symmetric spin paired system. The other possibility, a cis isomer with $^1A_1$ state of C_{2v} group, is lying about 20 meV higher than trans isomer. The third isomer, a loosely bound planar geometry of $^1A'$ state, is lying 36 meV above the trans isomer. All of them shown in Figure 1 lie in the ground state potential energy surface of singlet spin state.

For this 32 electron system, there are nine normal modes, each one corresponding to different types of stretching and bending motions, some of them with the wave numbers as few as 100 cm^{-1} fit enough to be classified as soft modes. Among them, a potential energy cut along a mode displacing the middle proton up and down in the plane of the molecule and a similar cut along a mode stretching the two molecular oxygen in opposing direction keeping middle proton fixed are focussed in this study. While both the modes represent intermolecular potential energy curves essentially, their significance differ drastically, one being a dissociation curve leading to the formation of three fragments (two molecular O_2 and a hydrogen atom) and the other being a dissociation curve leading to the formation of two fragments (an atomic hydrogen and a positively charged dimer of molecular O_2) at long range. The insight one gains from the normal mode displacement is the unique pathway leading to different types of chemical reactions upon molecular fragmentation. All nine modes cover full set of chemical reactions. The definition of coordinates used in computing the curves is explained in Figure 2 with the directional arrow marks indicating the direction of motion of molecular fragments.

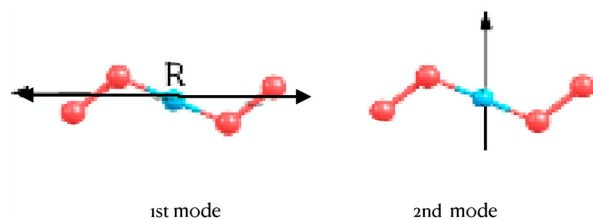


Figure 2. The definition of coordinates used in computing the curves in this study. The curves are computed at the internally contracted multi-reference configuration interaction (ic-MRCI) level of accuracy employing expandable aug-cc-pVTZ basis set.

The potential energy curves for the chosen modes are initiated at the optimised geometry for a given spin electronic state. The optimised molecular orbitals (MOs) obtained for the trans isomer are given in Figure 3 and are grouped into a' and a'' irreducible representation in reduced point group symmetry C_s . Both the isomers, cis and trans, interconvertible by torsional rotation share the same set of orbital energies. The molecular orbitals shown are the frontier molecular orbital (FMO) and more specifically, highest occupied molecular orbital (HOMO) having the tendency to take part in chemical reaction. HOMO is one, $3a''$ but FMO is two, $3a''$ and $13a'$, one in each representation. The lowest unoccupied molecular orbital (LUMO) is $4a''$ and LUMO+1 is $14a'$ which is slightly higher in energy. The HOMO–LUMO gap is estimated as 0.03 eV and the HOMO–LUMO+1 gap is found to be 0.06 eV, equivalent to a light of 20 millimetre wavelength in the microwave region. This light has sufficient energy to bring about an excitation from HOMO either to LUMO or to LUMO+1. Looking at the shape and phase of the orbitals shown in Figure 3, it is easy to conclude that they are formed from the linear combination of π and π^* MO of one O_2 with π and π^* MO of another O_2 and vice versa. Therefore, there must be eight such resulting linear combination, four bonding and four antibonding characteristics. What is shown in Figure 3 are the four MOs ($13a'$, $3a''$, $4a''$, $14a'$) with antibonding character and the corresponding four bonding MOs are deeply buried in the energy scale shown and hence not visible. The highest σ antibonding orbitals of a' symmetry are also shown in the bottom right corner (unscaled) and the $17a'$ orbital has considerable s orbital character centred on middle H atom. All of the three orbitals (15,16,17) are fully vacant and numerically, the occupational strength is 0.037, 0.037, 0.014 which means that all of them are empty. The excitation from HOMO to these orbitals requires very high energy (more 1 eV) and hence not probable.

The arrangement of electrons in $13a'$ and $3a''$ orbitals seen in Figure 3 is incomplete. The full arrangement is

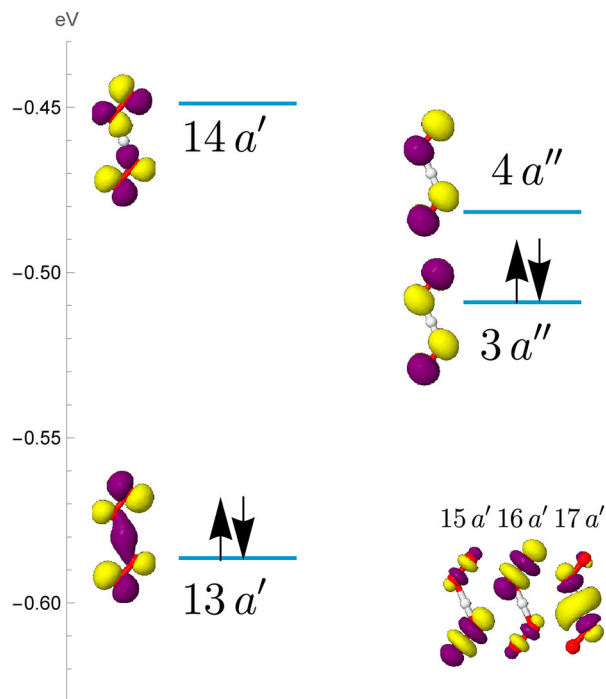


Figure 3. Frontier molecular orbitals (FMO) computed with the expandable aug-cc-pVTZ basis set at the internally contracted multireference configuration interaction level of accuracy at the reduced point group, C_s , splitting the full set of orbitals into a' and a'' symmetries. The highest energy MOs numbered 15,16,17 are shown unscaled.

given in the first row of Table 1 with the weightage factor of 0.54 highest one among all (each pair red circled). The first eight orbitals are chemically inactive and do not take part in molecular interaction. Out of eight orbitals, first four are of purely atomic character and the next four are the tightly bound MOs formed from the lowest lying sigma orbitals of each O_2 units. Hence the arrangement of electrons starting from ninth MO is considered as the ground state electronic configuration of the singlet trans isomer of O_4H^+ ion. However, the second arrangement competes equally well to be a good candidate for electronic configuration taking into account weightage factor which is almost close to the first one. This aspect suggests that this configuration is also equally probable, now with the electron pair shifted to the $4a''$ orbital. Both first- and second row electronic configurations are valid for the singlet ground state. The shifting of pair between $4a''$ and $3a''$ orbitals is favourable because of too close the energy gap between them. The other arrangements seen below the first and second rows contribute less to the overall description of the geometry as evident from the weightage factor. Since many configurations are possible with appreciable weight factor for the singlet electronic

Table 1. The arrangement of paired electrons in the orbitals of a' and a'' symmetries at the reduced point group, C_s , is shown for the singlet isomer as predicted by ic-MRCI/ aug-cc-pVTZ level of accuracy. For accurate description, singlet spin state is obviously multiconfigurational in nature justifying the choice of methodology in computing the ab-initio points.

$9a'$	$10a'$	$11a'$	$12a'$	$13a'$	$14a'$	$15a'$	$16a'$	$17a'$	$1a''$	$2a''$	$3a''$	$4a''$	weight
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$					$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		0.54
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$					$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	0.48
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$				$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		0.34
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$				$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	0.33
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$				$\uparrow\downarrow$	$\uparrow\downarrow$	$\downarrow$	$\downarrow$	0.23
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\downarrow$	$\downarrow$				$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	0.23
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\downarrow$				$\uparrow\downarrow$	$\uparrow\downarrow$	$\downarrow$	$\uparrow$	0.13
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\downarrow$	$\uparrow$				$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\downarrow$	0.13
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\downarrow$	$\uparrow$				$\uparrow\downarrow$	$\uparrow\downarrow$	$\downarrow$	$\uparrow$	0.10
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\downarrow$				$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\downarrow$	0.10

state, it is termed as having multiconfigurational character warranting us to go for multireference ab-initio calculation for the best results.

Ab-initio methods

The ab-initio calculations of O_4H^+ were carried out in a complete active space self-consistent field [18,19] (CASSCF) and internally contracted multireference configuration interaction with the single and double excitation [20,21] (ic-MRCI) levels of theory using the augmented correlation consistent polarised valence triple zeta [22] (aug-cc-pVTZ) basis set. In addition, restricted coupled cluster singles and doubles with perturbative triple correction [23] (RCCSD(T)) calculations were performed using the same basis set and the larger augmented correlation consistent polarised valence quadruple zeta [22] (aug-cc-pVQZ) basis set only for the quintet state. However, whatever reported in this work is solely based on the CASSCF/ic-MRCI methodology using aug-cc-pVTZ basis set. A total of 21 molecular orbitals (MOs) with a break up of $17a' + 4a''$ symmetries were considered for this 32 electron system and this is the size of electronic space over which electrons are permitted to move around. Among the 21 orbitals, first four of them in the energy ladder are atomic like MOs and kept frozen. Next four are the MOs formed from the linear combination of 2s atomic orbitals of each oxygen atom. The excitation to higher MOs is allowed. The first eight orbitals have a' symmetry formed from σ MOs of individual O_2 units. Starting from the ninth orbitals, real active space begins contributing significantly to the intermolecular bonding forces. All of them are listed in Table 1 giving an active space of 16 electrons in 13 MOs. The distribution of electrons with this active space for the singlet ground state is shown in Table 1. While the chosen active space remains

the same, the distribution will differ among the three possible electronic spin states, the one shown here is for the singlet with those for triplet and quintet states being similar but with no spin paired arrangements. The calculation done with the active space of $16e^-/13$ produced sensible results in which the experimental [24] molecular distance of O_2 is retained in the optimised geometry of O_4H^+ within the spectroscopic accuracy. The parent dimer (unprotonated form) is a weak complex while the protonated form is a strongly bound chemical molecule. The ab-initio results were found to be size consistent at the CASSCF level leaving us not seeking for counterpoise correction because of these two factors. The correction term is essential when dealing with weak complexes such as oxygen dimer without protonation but here this is not the case. All the calculations were done using the molpro [25,26]

Two fragments dissociation curve

The two fragments are obtained when H/H^+ is displaced in the molecular plane along the direction as shown by the arrow mark in Figure 2. The electronic structure calculation performed on the individual fragments reveals their electronic state which are $H(^2S)$ and $O_4^+(X^2A')$ on either side of fragmentation pattern as the curve preserves symmetric operation of permutation during the displacement. The curve is shown in Figure 4 wherein three minimums are visible, the one at zero indicates the global minimum of trans geometry and others at ± 1.8 angstrom indicates a local minimum across zero. The points are fitted to an analytical form possessing the property of permutation which is nothing but reproducing one half if other half of raw data ranging from 0 to 10 angstrom is fitted. In Figure 4, the model curve obeying this property is shown along with 39 computed

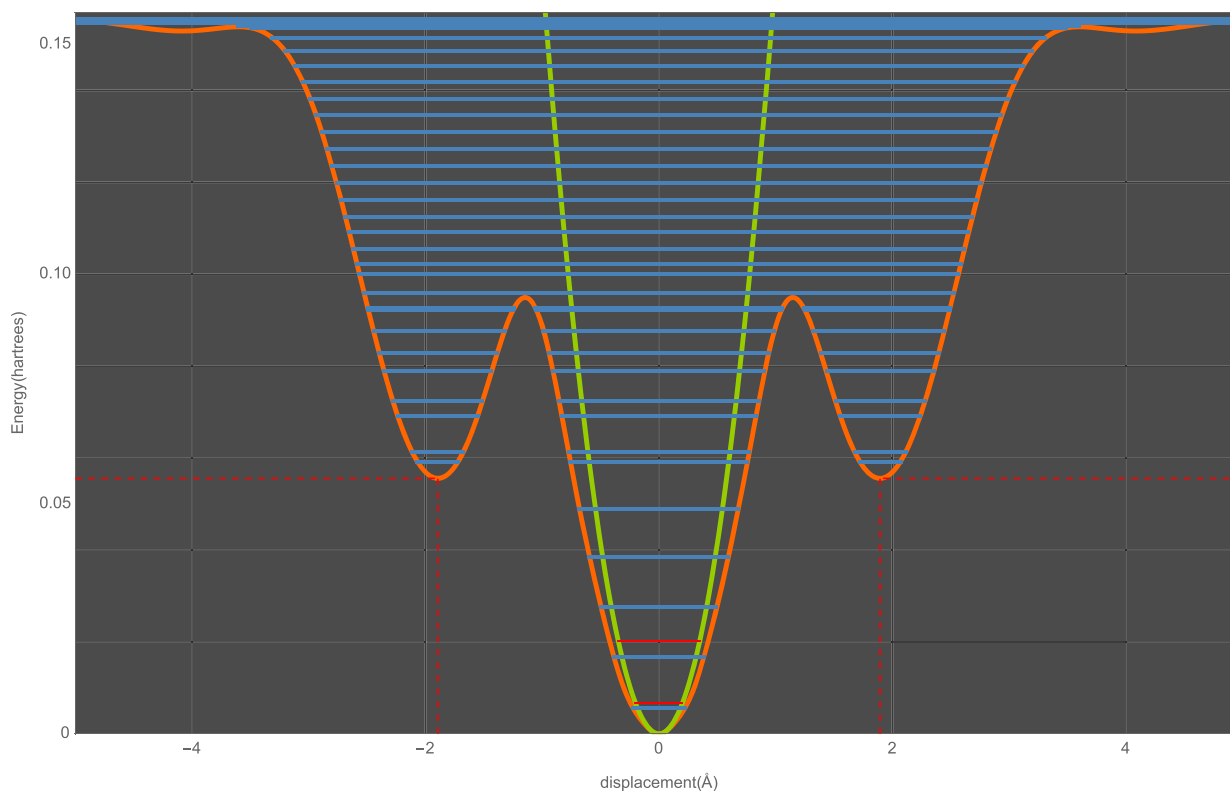


Figure 4. This curve is produced by the second normal mode indicated in Figure 2. It remains invariant to permutational symmetry. The harmonic approximation (green line) to the actual curve is compared and found valid near zero. Maximum number of levels accommodated is 39.

vibrational levels for $J = 0$ case. 39 is the maximum permissible number of levels that can be computed. Because of the property of permutation the model curve possesses, all the levels are found to be either doubly degenerate or singly degenerate and gets mixed up alternatively along the energy ladder.

In the supplementary data, all the analytical forms used and the values of unknown coefficients and the numerical values of vibrational levels are given to reproduce the model curve anytime if anyone wants to. The harmonic model (green) gives a good description to the present model near the region close to 0 and therefore, the fundamental transition from the harmonic model is expected to agree well with that from the present model. The level calculation in principle is heavily influenced by the presence of inverse mass factor while solving the Schrödinger equation, higher the mass lower the separation of levels contained in the potential well. The mass used hence will be reported explicitly in this work. In Table 2, harmonic approximation predicts far higher fundamental frequency than morse which in turn predicts a value similar to the one obtained from the present model. The fundamental transition of pure proton stretching mode from the ab-initio frequency calculation carried out in C_s point group lies close to the value from the

Table 2. Prediction from three models and their comparison with ab-initio and experimental results [2].

	harmonic	morse	present	ab-initio	expt
ν_0	1473	1282	1250		
ν_1	4420	3772	3657		
ω	2947	2490	2404	2358	2463

present model. When calculating levels for a specific normal mode shown in Figure 2, it is assumed that the middle H^+ atom alone undergoes motion and four other oxygen atoms remain at rest. Thus the mass of proton is used in calculating levels based on this assumption which will be reflected in the resulting levels. In the C_{2h} ab-initio frequency calculation, the second mode is always contaminated with the motion of four oxygen atoms albeit with different amplitudes in addition to the highest amplitudes motion of H^+ , giving a different fundamental transition than expected. This is because of the fact that the motion of proton is not pure and getting mixed up with the motion of oxygen atoms as well. Hence, fundamental transition coming from level calculation using proton mass is compared with ab-initio frequency calculation performed on C_s point group where one of the normal mode among all nine purely involves the stretching motion of proton.

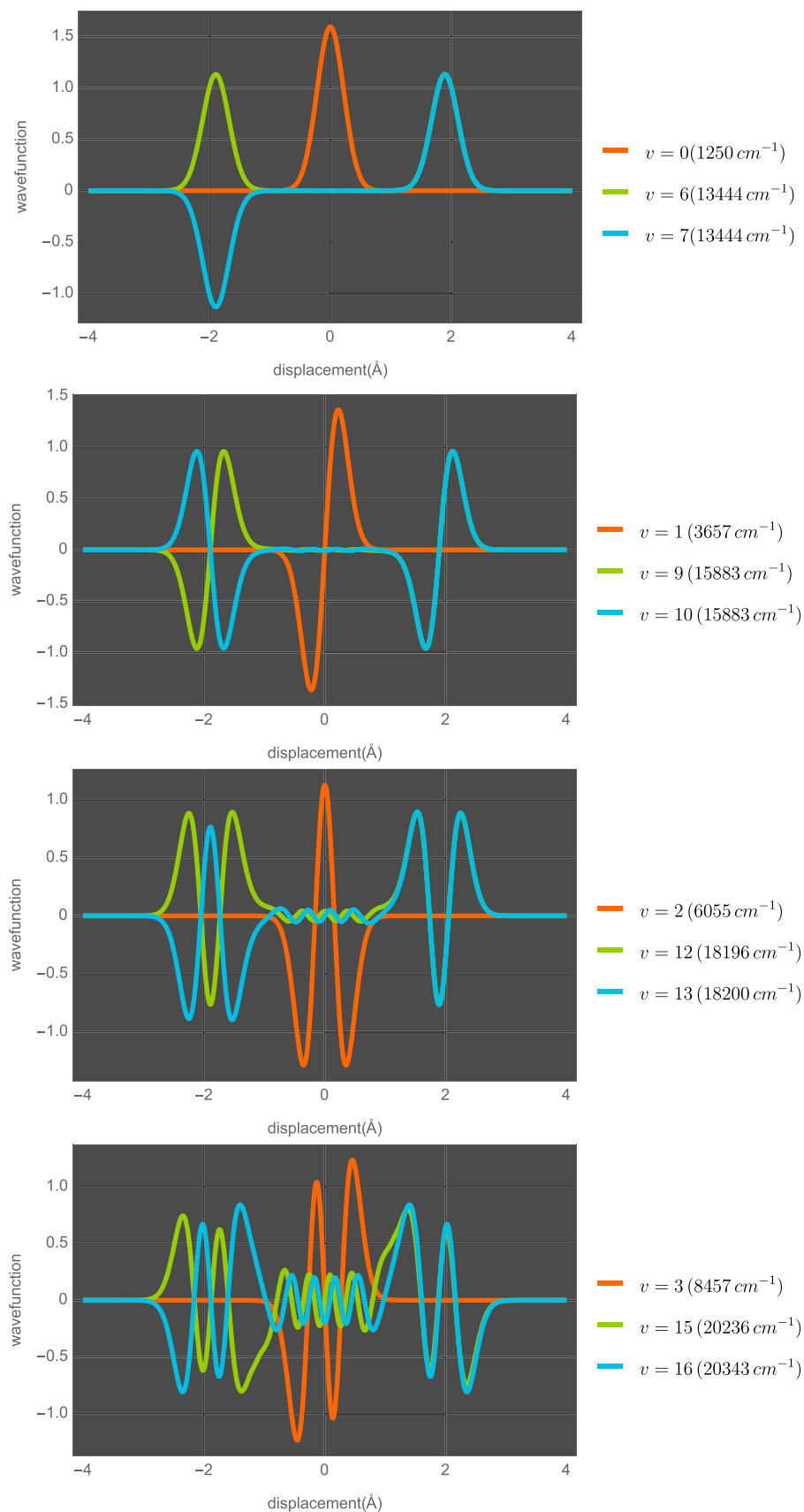


Figure 5. The pair of doubly degenerate wave functions is shown. The levels for which the degeneracy exists are labelled with appropriate quantum numbers. The levels with $v = 0, 1, 2, 3$ are nondegenerate and with $v = 6, 7$ are first pair of degeneracy.

In the recent spectroscopic studies [2] on this molecule, few infrared spectra have been published without resolving spin issues and the study does not specifically mention the spectral values for the singlet isomer in the ground state. On account of this, in Table 2,

a value that matches better with the one from the ab-initio calculation is chosen to be the stretching motion of proton. The spectral study says that even this value has got contamination from the displacement of other four oxygen atoms in addition to middle proton and is

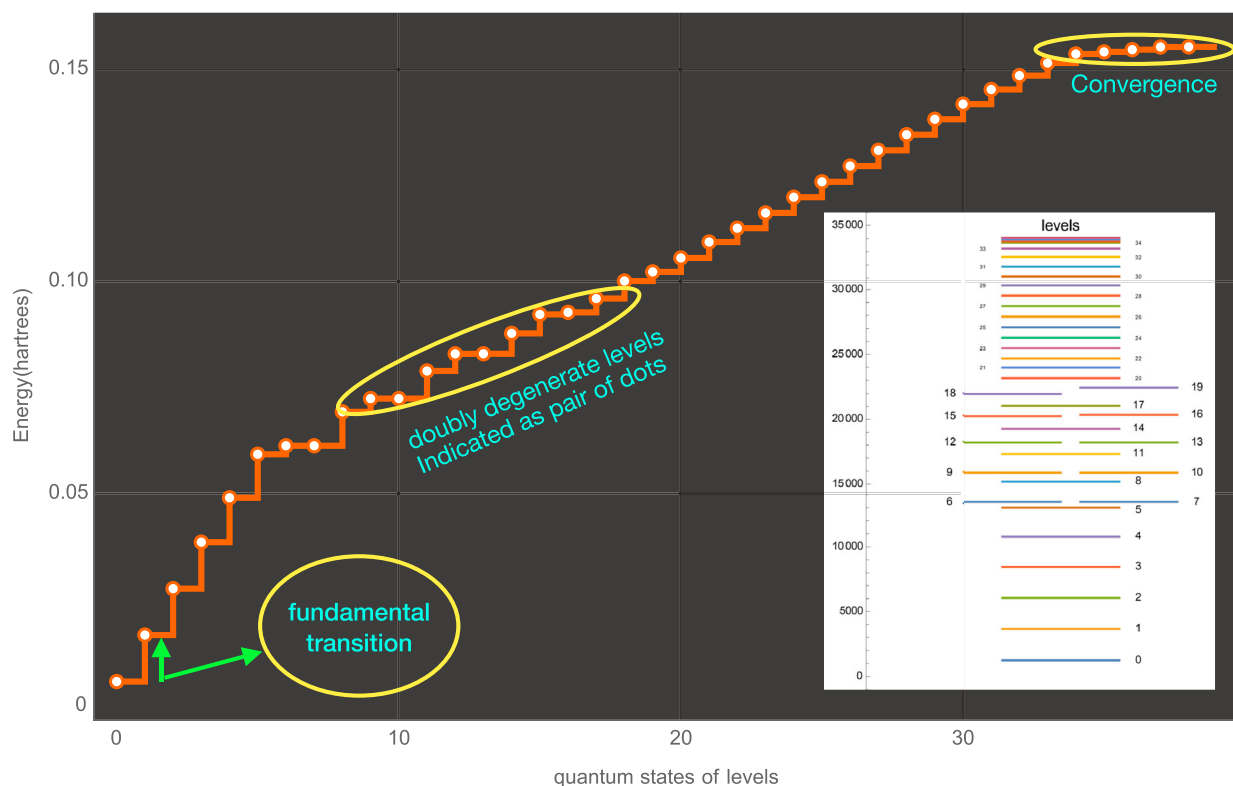


Figure 6. The dependence of vibrational levels with quantum states is shown. Look at the linearity at the middle part before the convergence limit.

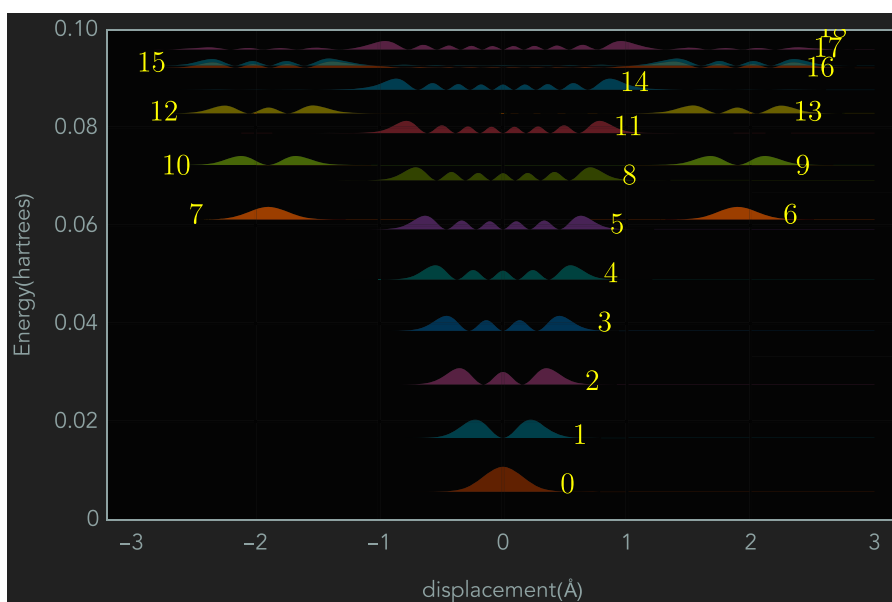


Figure 7. The anharmonic probability density is shown from $v = 0$ to $v = 17$. The nodal points are easy to count. It is clear that the levels at $v = 6$ and $v = 7$ are degenerate but with less amplitude compared to the one at $v = 0$. This is an example for a triple well-potential energy profile with the possibility of tunnelling across the deep well.

not due to pure motion of proton alone. It further raises doubts over the formation of protonated dimer as the characteristic symmetric stretching band of proton in the moiety of dimer is found missing. Further experimental studies are required to make spin selective results as clear as possible. Thus getting a spin pure spectra will help to solve all doubts concerning the assignment of peaks to various normal modes firmly.

The calculated vibrational levels are shown in Figure 5 to highlight certain points. Four plots are given one by one with each one presenting three levels of which two being a degenerate pair. Looking at the first plot, the normalised nuclear wave function for the level $\nu = 0$, lower most level, is given around global minimum with

the amplitude of the function being relatively high. The other two functions for the excited states $\nu = 6$ and $\nu = 7$ occur in degenerate pair with one half of the function being either symmetric or antisymmetric to other half and are centred around the local minimum found at both sides of global minimum. The Eigen value for each Eigen function is given in the plot legends. The other plots follow the same idea: degenerate pair centring local minimum and nondegenerate function centring global minimum for different vibrational quantum numbers. The Eigen values become slightly unequal in a pair when going down the plots. When this happens the amplitude of the pairwise Eigen functions starts rising in the middle part indicating that the levels are

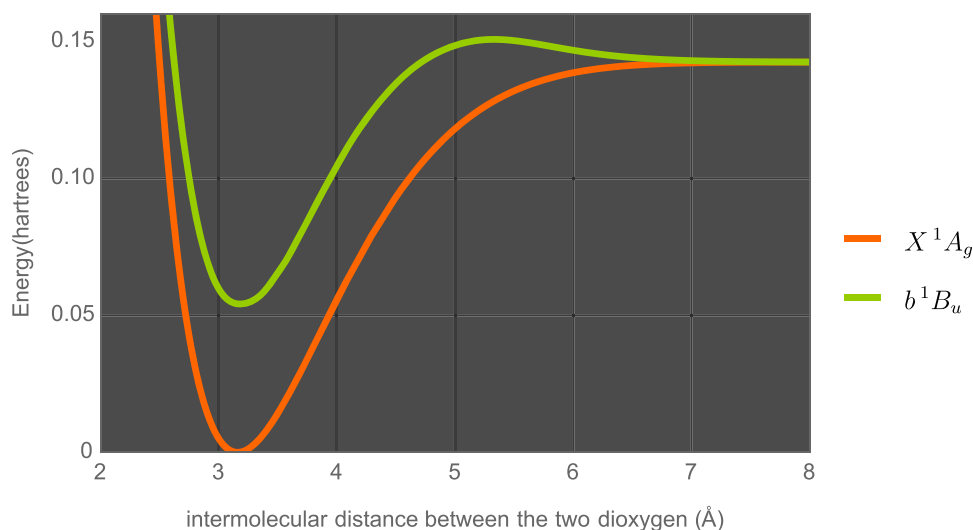


Figure 8. The potential energy curves for the first normal mode defined in Figure 2 are shown for the ground as well as excited states as a function of intermolecular distance.

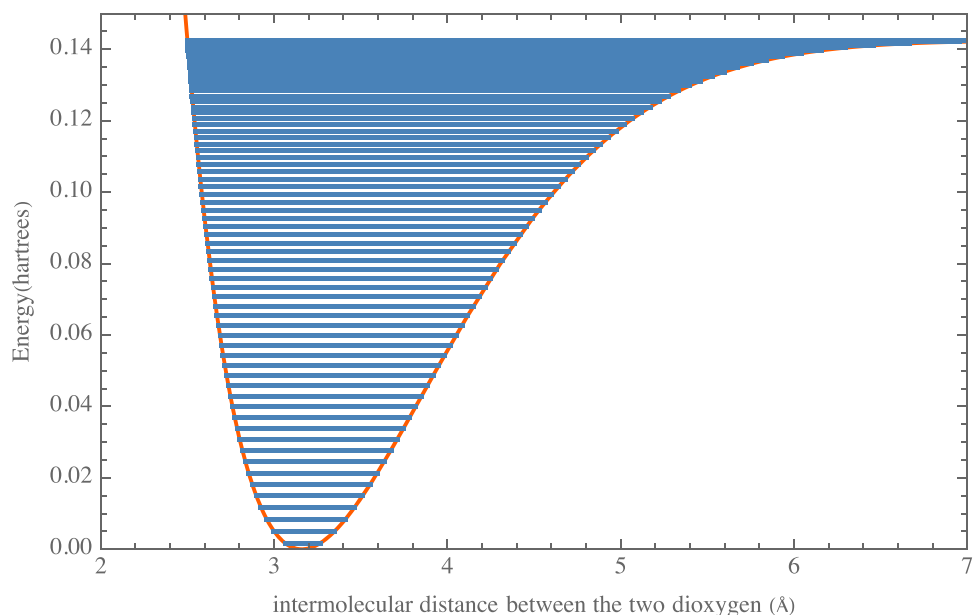


Figure 9. The potential energy curve in the ground state and its computed levels for the first mode are shown. The spectroscopic properties of the state are listed in Table 3.

Table 3. The spectroscopic properties of two electronic states calculated by fitting the level data with Dunham expansion.

Properties	X^1A_g	b^1B_u
T_e	0	11851
D_e	31255	19375
$Y_{1,0} = \omega_e$	742.8	635.8
$Y_{2,0} = -\omega_e x_e$	3.38	-9.3
$Y_{3,0} = \omega_e y_e$	-0.033	2.6
$Y_{4,0} = \omega_e z_e$	0.004	-0.55
$Y_{0,1} = B_e$	0.39	9.3
$Y_{1,1} = -\alpha_e$	0.035	-24.4
$Y_{2,1} = \gamma_e$	0.01	18.8
$Y_{0,2} = -D_e$	0.001	-1.97
$Y_{1,2} = -\beta_e$	0.005	-5.39
$Y_{0,3} = H_e$	-0.0001	0.16
$Y_{0,4} = L_e$	0.00001	-0.004

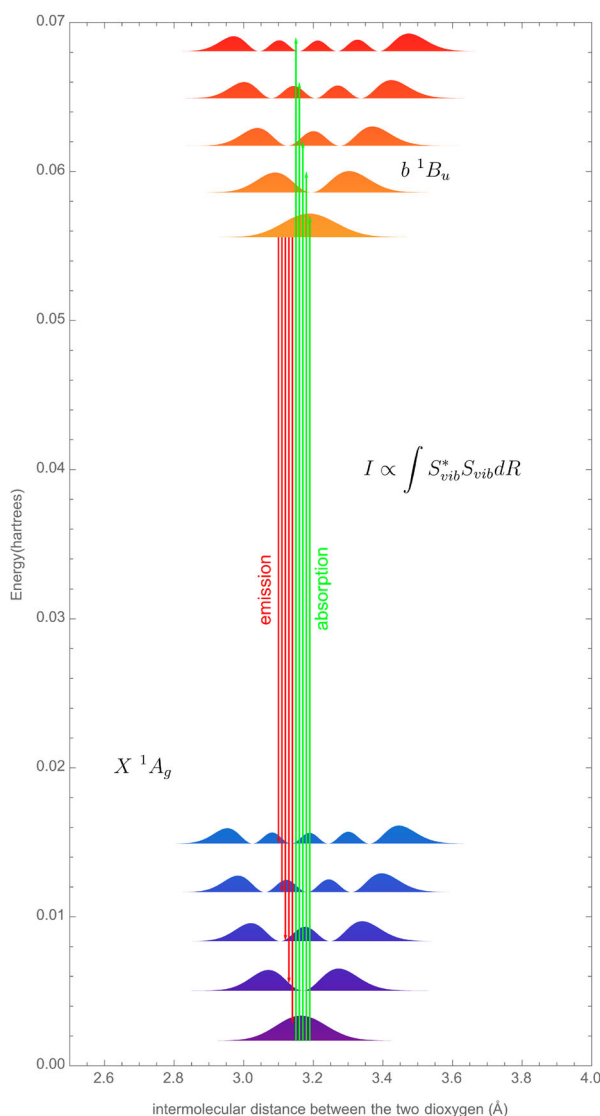


Figure 10. This diagram is illustrative of absorption and emission processes. Both the processes start from $v = 0$ to $v' = 0, 1, 2, 3, \dots$ and from $v' = 0$ to $v = 0, 1, 2, 3, \dots$

going to be nondegenerate subsequently and can be observed in the last two plots of Figure 5 and finally, merge with other higher lying levels at high quantum states.

In Figure 6, the variation of levels with quantum states is plotted in the form of steps. First thing to note is that the calculation converges and gives us an estimate of dissociation energy of fragmentation for the second mode shown in Figure 2. The step size tends to zero at the convergence limit shown inside an ellipse. The presence of degenerate levels is indicated by a pair of dots with zero step size (height) inside an ellipse and also marked in the form of scaled ladder (see the inset picture) of all levels where the closely spaced levels can be seen at the top of the scale. Finally, the fundamental transition is indicated by the length of first step marked by an upward arrow.

In Figure 7, the scaled anharmonic probability density of wave function is plotted as a function of displacement of proton after adding the corresponding eigen value to the scaled squared wave function. The scaling factor used to multiply with the function is 0.001. Here, it is clear that the levels or its equivalent probability density for $v = 6$ and $v = 7$ share the same energy, $13,444 \text{ cm}^{-1}$ on energy axis and the labelling index are interchangeable and indistinguishable based on densities. Above $v = 17$ and $v = 18$ levels, intensities of colours on either sides and in the middle part remain the same suggesting merger of levels with higher ones. There is zero node at $v = 6$ and $v = 7$ levels, a single node at $v = 9$ and $v = 10$ levels, two nodes at $v = 12$ and $v = 13$ levels, and three nodes at $v = 15$ and $v = 16$ levels, and the amplitudes keep decreasing when going up and merger happens. As stated above, $v = 7$ and $v = 6$ are degenerate to each other but not with level $v = 5$ though it looks so. The spacing is, however, small and is about 440 cm^{-1} and in the same way, it goes up for other degenerate pair but not drastically, something like 650 cm^{-1} , 900 cm^{-1} , 1200 cm^{-1} , etc. can be expected.

Three fragments dissociation curve

Three fragments results in the first mode of dissociation are illustrated in Figure 2 which shows pulling the two molecular O_2 units apart in the opposing direction producing three fragments at infinite separation in their respective electronic states, $\text{O}_2(a^1\Delta_g) + \text{H}(^2S) + \text{O}_2^+(X^2\Pi_g)$ and the neutral molecular oxygen is determined in the first excited state and the other two fragments in the ground state. This mode, similar to the other mode, preserves permutational symmetry during

the intermolecular stretching maintaining the C_{2h} symmetry throughout and is studied focussing lowest electronic states, X^1A_g and b^1B_u of singlet spin states. A_g is the ground state and B_u is the excited state. The curves as a function of intermolecular distance for the two electronic states correlate to same asymptotic products as mentioned above and are shown in Figure 8. The minimum of the two curves differs by $0.02 \text{ \AA}$, a short distance sufficient enough to assume that the excited state is just above the minimum of the ground state which exactly passes through the global minimum. This will profoundly influence the vibronic spectra.

In Figure 9, vibrational levels for this mode in the ground state are shown with maximum computable levels which is found to be at 67 and the closely spaced levels

are due to inversely related heavy mass of two molecular oxygen units. In the excited state curve, first 34 levels are computed with densely spaced levels. The convergence of levels is difficult to achieve in the excited state after 34 as the excited curve has hump like feature in the long range region. The two electronic states are well separated by $11,850 \text{ cm}^{-1}$ and the well depth of each state is determined to be $31,255, 19,375 \text{ cm}^{-1}$ for the ground as well as the excited state respectively. For both of them, rotation–vibration energies are estimated to be used in the Dunham expansion fit to obtain few spectroscopic properties. Those properties are listed in Table 3. All the values of fitting parameters obtained in the Dunham fit are given in the supplementary information.

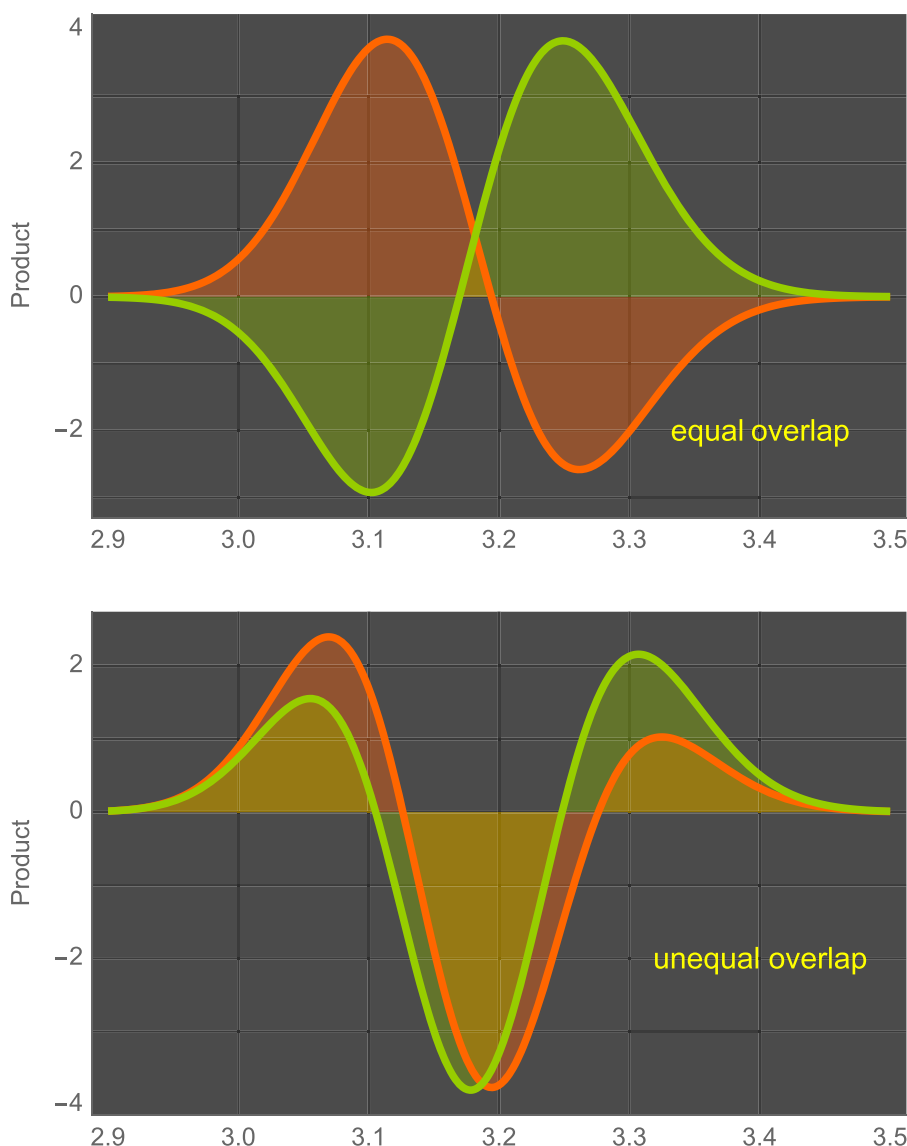


Figure 11. Intensity depends on the overlap of wave function. The first plot shows equal overlap for the transition $0 \rightarrow 1$ and for the transition $1 \leftarrow 0$. Equal overlap means area covered by the product of functions, S^*S , must be approximately equal and well obvious from the plot. Next plot is for the transition $0 \rightarrow 2$ and for the transition $2 \leftarrow 0$. The area (shaded region) under the product of functions look different and hence for this transition, intensities will be different.

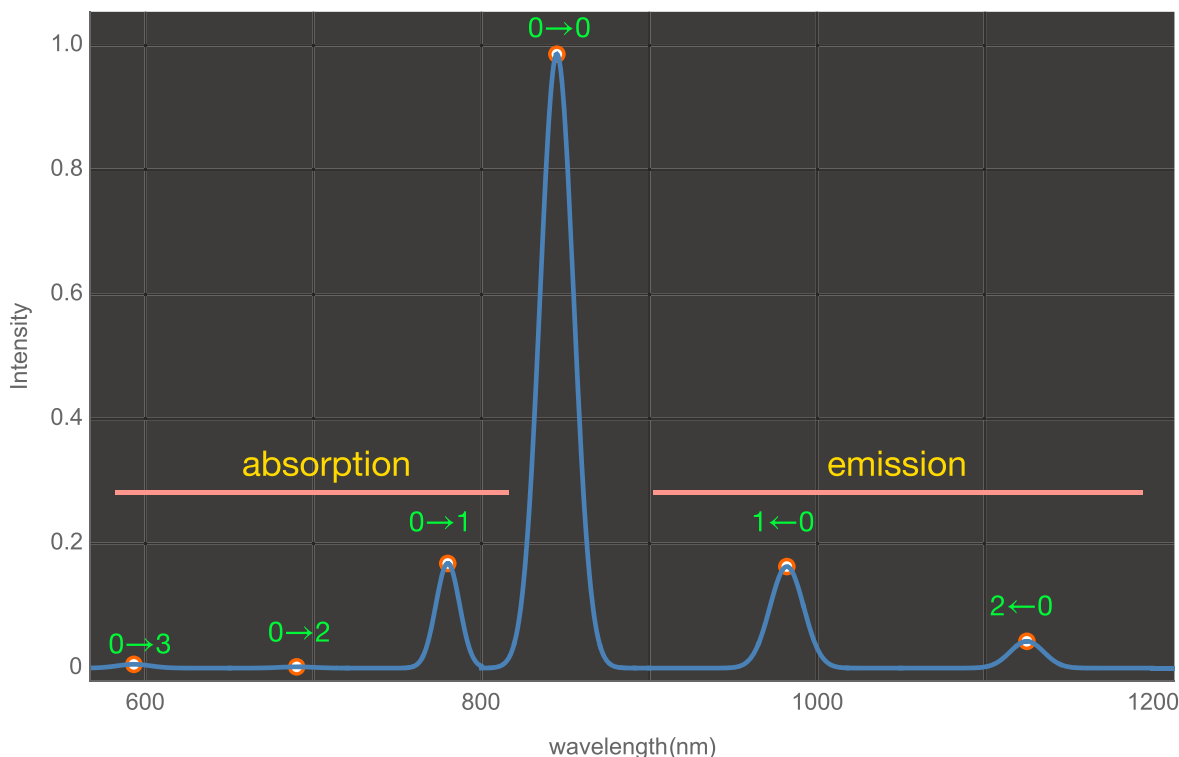


Figure 12. The computed spectrum for the transition, $X^1A_g \rightarrow b^1B_u$ and for the transition, $X^1A_g \leftarrow b^1B_u$ is shown and intensity profile is not the same in both absorption and emission regions. This is because of the unequal overlap between the involved states. The most intense peak is $0 \rightarrow 0$ as the overlap between the level $\nu = 0$ in the ground as well as the excited levels, close to unity.

Electronic excitation and de-excitation between the two states are illustrated in Figure 10. The vertical line indicates either absorption or emission from $\nu = 0$ level in the ground electronic state to all the levels in the excited electronic state in the case of absorption and from $\nu' = 0$ level in the excited electronic state to all the levels in the ground electronic state in the case of emission. The intensity of transition is computed using the integral given in Figure 10 in which S, S^* denotes vibrational wave function in the ground as well as the excited state surface and the intensity is a measure of overlap between them in different electronic states implying higher the overlap stronger the intensity. However, the vibrational overlap integral is computed without multiplying electronic transition integral and therefore should be viewed as an rough estimate of intensity of vibronic transition. Franck Condon factor is square of this integral. The minimum of the ground and that of the excited state falls approximately in the same region and hence the overlap tends to be maximum for $0 \rightarrow 0$ transition both in the absorption and emission. Even then, intensities may differ slightly between them on account of difference in overlapping area. Therefore, a strict mirror image pattern in the absorption–emission spectrum need not be expected. In Figure 11, the calculated vibronic spectrum is shown splitting it into absorption and emission

parts which differ visibly on either side of main peak. $2 \leftarrow 0$ intensity is not the same as $0 \rightarrow 2$ and this is explained using simple graphics in Figure 12. This shows two plots, top one for $0 \rightarrow 1$ and $1 \leftarrow 0$ transition with the shaded region giving the area under each curve. Upon the visual inspection, the area of shaded region remain equal in both the curves. So the intensity also remains equal for both absorption and emission as predicted by the calculated spectrum. In the bottom plot for the $0 \rightarrow 2$ and $2 \leftarrow 0$ transitions, the shaded area remains unequal for both curves upon inspection. This suggests that intensity differs for both transition types as seen in the given spectrum. In the y -axis, it refers to the product of two interpolating Eigen wave function.

Concluding remarks

The orbital analysis clearly demonstrates the correct arrangement of electrons in orbitals with almost equal probability based on the state-of-the-art ab-initio methods involving dynamic correlation among the valence electrons. Among the most dominant arrangements differing in the distribution of electrons in the occupying orbitals of a'' symmetry, the energy difference HOMO–LUMO gap is merely of the order of millimetre

wave length with the shifting of electron pair from $3a''$ orbital to $4a''$ orbital being rapid and spontaneous at the shine of light of microwave length. Thus the excitation of electrons from HOMO to LUMO requires only radiation of microwave length range. FMO is clearly identified from the orbital diagram as they are the ones which have the potential to take part in chemical reaction.

The two intermolecular modes relevant to bond rupture are studied via spectral methods. The degenerate Eigen functions in the vibrational levels are observed because of the unique shape of the curves. Important spectroscopic constants are extracted via the fitting of levels with Dunham expansion. Finally, absorption–emission spectrum is presented for a given electronic transition. The dissimilarity arises because of unequal overlap between the involved states or because of variation in the energy gap between the levels in the ground and excited state surfaces. This case is an example of strong $0 \rightarrow 0$ transition as the ground and excited states are just vertically above.

This is the second computational study on singlet O_4H^+ ion and the first molecular orbital analysis which helps us to extract a correct molecular electronic configuration. An experimental study was attempted on this ion to produce an infrared spectrum which provided some signatures for OH stretching band while such a stretching was found missing directly from the bound O_4H^+ ion chemically sandwiching between two molecular oxygen units.

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Data availability statement

The data generated in this work is given in the supplementary information for easy reproduction of the results discussed in the manuscript.

Disclosure statement

No potential conflict of interest was reported by the author.

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