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Research Article

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Intermolecular potential of singlet O_4H^+ ion II

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Abstract

The displacement of proton cutting through the OO bridge seen in the established geometry of singlet O_4H^+ ion, (a proton-bound dimer of molecular O_2), is focussed by constructing the relevant ab initio potential energy curves computed at the state of the art multi reference configuration interaction level of accuracy with the augmented correlation consistent triple zeta basis set. The curves are presented for two possible conformers (cis and trans) with distinctly varying profile as a function of back and forth the motion of proton across the bridge along with the detailed account of their modelling. The model can be used to compute absorption and emission spectrum associated with the cis-trans interconversion subject to the Franck Condon principle. The reported spectrum has the potential to serve as a finger print for easy recognition when an experimental electronic spectrum is going to be available. At the moment, no such spectrum exists.

Keywords: potential energy surfaces, adiabatic, analytical fitting model, hermitian matrix, conical intersection, triple degeneracy, seam locus, matrix analytical diagonalisation

Introduction

This is the second part of our recently reported work[1] bearing the same title. It differs from earlier report[1] in the sense that the modelling details provided therein were not sufficient to meet the correct electronic correlation at the long range and also a discussion on cis conformer was not included. The present work is written to address these issues and hence, has the details of cis conformer including its complete analytical form describing proper electronic correlation at the asymptote. Using the cis and trans models, a finite number of vibrational levels for first three (0,1,2) rotational

states calculated followed by an electronic spectrum of vibronic transitions associated with cis-trans interconversion is presented. The computed spectra will be useful to someone who has measured such a spectra in a laboratory set up.

As written in the earlier work[1], the O_4H^+ ion, a protonated form of molecular O_2 dimer, was first detected[2] 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 the clusters of H_2 and O_2 when liquid helium nano droplets are introduced into the mixture. An infrared photodissociation spectrum of this ion has been documented[3] without resolving its multiple spin states. Consequently, assignment of the observed peaks to a specific modes of motion for a specific spin state proved to be a challenging task. Therefore, it is considered a spin average spectrum in true sense since the studies done by us few years back[4, 5] (computational) established beyond doubt the existence of multiple spin states with sizeable energy gap (spectroscopically resolvable). This trend follows exactly the same pattern as that of its parent molecule, unprotonated O_4 which was subjected to beam experiments[6, 7] at low collision energy to study the nature of inter molecular interaction and conclusively proving weak bonding of the complex in the singlet state.

Going by the literature survey in chronological order we were the first one to take up this molecular ion and performed a systematic study[4, 5] with the goal of identifying the molecular geometry in its ground electronic state, X^1A_g . Our search led us to a lowest energy configuration corresponding to a trans isomer with C_{2h} point group, strictly a non polar arrangement. The repeated efforts to look for another structure lower in energy than this went in vain and this made us to declare this geometry as the global minimum. The cis geometry (approximately 0.001 hartrees higher in energy) corresponding to the trans one was well characterised as a local minimum. Please see the optimised structures in any of our old works for clarity. Given that this molecule is relatively new, both theoretical and experimental investigations remain scarce but are anticipated to increase in future.

In contrast, the parent molecule, 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 was well characterised as a weak van der Waals complex, exhibiting a binding energy of 17 meV[4, 5] in the singlet state. In comparison, the protonated form demonstrates a significantly stronger binding energy of approximately 0.15 eV, indicating a robust bound molecular geometry 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[6–9], with theoretical work reinforcing these findings[10–15]. The investigation however did not stop at the level of dimer but was extended to cover the trimer[16, 17] and tetramer analogs[18, 19] of O_2 .

Considering these insights, we are revisiting the O_4H^+ ion, a protonated dimer, following the initial works[1, 4, 5]. It appears that previous studies focused primarily on the ab initio aspects followed by their modelling to some extent and till 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 providing a complete model form valid every where including the long range and calculating

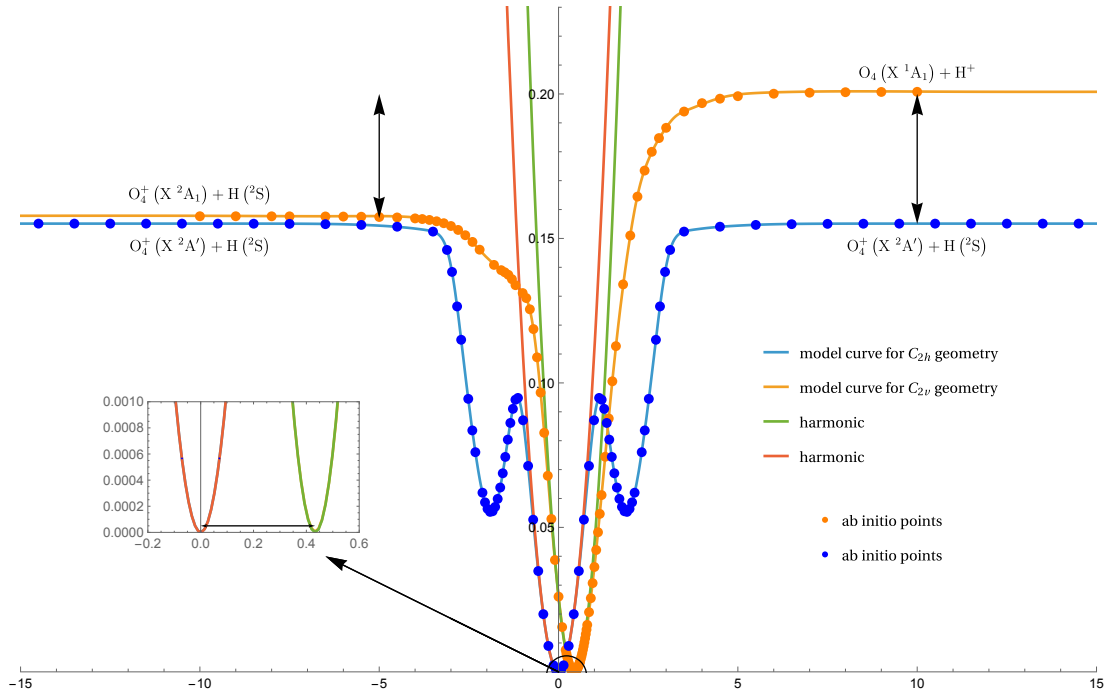


Fig. 1 The model curves of O_4H^+ ion under cis and trans conformations as a function of displacement (in Å) of proton back and forth in the molecular plane (see the previous article) The state of the art ab initio points are embedded in the model curves. The vertical axis refers to energy in Hartrees. Inside the small plot, a harmonic approximation to the model curves is given, valid near the equilibrium in C_{2h} and C_{2v} .

a vibronic spectrum for the cis-trans interconversion with the help of analytical models. The old literature concerned with this molecule did not cover modelling properly leaving a space for further improvements and spectroscopic aspect in full and therefore, needs serious reconsideration and also details regarding the ab initio theory was discussed briefly in the previous papers and hence no need to repeat them here as they remain unchanged.

Modelling cis-trans interconversion

In the ground electronic state of zero spin, three stationary points were confirmed to exist after extensive search and all of them were found planar and non linear with two existing as cis-trans (ct) pair and the third one being left alone. The optimised structures belonging to the pair were shown in the previous paper[1] and it shows a middle hydrogen atom flanked by oxygen atoms on either side known as OO bridge. It is this atom that is vibrating back and forth to produce the curves shown in Figure 1 while keeping other four oxygen atoms fixed and in fact, this is one of nine modes of motion permitted for the molecule. Interestingly, no linear as well as van der Waals stationary points were found in the ground electronic spin state. The ct pair is strongly

bound covalent molecule with a binding energy of 5.44 eV with slight polarity and for zero polarity this is just 4 eV.

Now, one can see the profile of the curves as a function of distance. The two dissociated fragments undergo electron exchanges between the two curves leading to high energy gap between them estimated as 1.36 eV which is underestimated in comparison to 1.9 eV, a value estimated with experimental values. The likely source of discrepancy is in the ab initio calculation of O_4 and O_4^+ fragments separately with strong electron correlation methods such as MRCI with a uniform active space throughout to compute the potential of fragments. However, the correlation does not fully account for the contributions of dispersion forces to the accurate potential of weakly bound molecules even though it helps to predict correct splitting pattern as expected, hence cannot be done away without it. This type of issue arises when dealing with dispersion interaction which dominates any weakly bound dimer.

The trans curve is the mutually reflecting one another across the midpoint at zero while it is not so for cis curve. In other words, permutational symmetry exists in trans and no such a reflection symmetry in the cis case. This will have profound influence on the model chosen to fit the curve to be discussed next and it is expected the mathematical model to possess the property of permutation. The minimum in the two curves do not merge together at the same location as Figure 1 seems displaying but at slightly different locations, trans curve at zero and cis at about $0.45\text{\AA}$, clearly visible in the inset plot. The harmonic approximation is good near the equilibrium for both the curves but fails once moving away from it. Therefore, a good model is mandatory for accurate prediction of points accounting anharmonicity all along the curve. The model is split into interaction as well as long range part and summing them up to form a full model expression.

The model given in Eq 1 is the analytical expression for the C_{2h} curve shown in Figure 1 a symmetrical blue line with points embedded over it. It is clear that the basis expansion is further expanded in a polynomial series as decided by the root mean square deviation of the fit. The general form of the basis expansion is chosen as the product of $\tanh \times \text{sech}$ multiplied with fitting coefficients and the expansion denoted as y is finite and limited to five terms in this model. y is again expanded in terms of a polynomial in y with the degree of polynomial fixed at 13. The polynomial takes care of the equilibrium region by minimising the root mean square deviation close to it and long range region is taken care by pure $\tanh$ function seen as an additive term in the model to correctly predict the electronic states of dissociated products. There are two similar looking $\tanh$ functions to account for asymptotes on either side of the curve. The parameters, (h_1, c_0) inside the $\tanh$ are known after fitting the data and the factor 0.15513 is used here from the ab initio data and this factor can also be obtained via fitting if one desires so but here, in this expression, this is inserted into it directly taken from the data. This factor is known as the dissociation energy of back and forth motion of proton in the C_{2h} geometry. r_1 is the running variable. In the basis expansion r_1 is computed as squared distance to maintain permutational symmetry on either side of mid-point meaning that potential at a point must be equal to its point of reflection across the inversion center $(x, y, x) \rightarrow (-x, -y, -z)$. All the

parameters of the model are given in the supplementary information (SI) and any one can reproduce the curve using the parameter given in SI

The model given in Eq 2 is the analytical expression for the C_{2v} curve shown in Figure 1, an asymmetrical orange line with points embedded over it. On both sides of dissociation, electrons are swapped among the fragments albeit with unequal exchange of energy from one fragment (say, O_4 , H^+) to another (say, O_4^+ , H) leading to asymmetrical energy correlation profile and this contrast is clearly visible in both curve in Figure 1. There is no permutational symmetry as there is no inversion centre in C_{2v} point group. The minima is now shifted by $0.45\text{\AA}$ from zero along the positive axis. This is obvious in the basis expansion where the running variable r_1 is accordingly shifted by r_0 , a numerical equilibrium value to be known from fitting the curve. Because of shifting of minimum, the expression for basis expansion, y looks shifted and squaring is not done just as in C_{2h} where $r_0 = 0$. This will not influence the fit as there is no symmetry constraints in this case unlike the previous case and hence, this expansion is retained. The model given in Eq 2 gives a fit with a accuracy of 37 cm^{-1} where else the model given in Eq 1 give a fit to the respective data with a accuracy of just 6.7 cm^{-1} . The model in Eq 2 deserves special mentioning since it takes care of two different asymptote's with two limiting values at infinity and term1 ($1 - \tanh(X_1)$) and term2 ($1 + \tanh(X_2)$), each of them is multiplied with two different values, picked up from ab initio data (could be subjected to optimisation to find one but not followed in this report and values should be similar to one given in the model even if obtained via explicit optimisation). The sum of term1 and term2 fits the long range part simultaneously, with X_1, X_2 differing in sign and parameters and the net sum is added to interactive term concentrating the region near the equilibrium and far to give the total potential. All the parameters given in Eq 1 and Eq 2 are given in SI and using them, it is possible to reproduce the curves with the same root mean square deviation as they are reported in the manuscript.

$$\begin{aligned}
 y &= \underbrace{\sum_i^{i=5} a_i \left[\tanh(\beta_i r_1^2) \right] \left[\text{sech}(\mu_i r_1^2) \right]}_{\text{basis expansion}} \\
 V &= \underbrace{\left[\sum_i^{i=13} A_i y^i \right]}_{\text{interactive term}} + \underbrace{\left[\frac{1}{2} \times 0.15513 \left(1 - \tanh \left[h_1 (r_1 + c_0) \right] \right) + \frac{1}{2} \times 0.15513 \left(1 + \tanh \left[h_1 (r_1 - c_0) \right] \right) \right]}_{\text{an additive term accounting for correct electronic correlation on either sides of the curve}} \\
 &\quad \underbrace{\hspace{15em}}_{\text{long range term}}
 \end{aligned}
 \quad \left. \vphantom{\sum_i^{i=5}} \right\} \begin{array}{l} \text{preserving} \\ \text{permutational} \\ \text{symmetry} \end{array}
 \tag{1}$$

$$\begin{aligned}
y &= \underbrace{\sum_i^{i=5} a_i \left[\tanh(\beta_i(r_1 - r_0)) \right] \left[\operatorname{sech}(\mu_i(r_1 - r_0)) \right]}_{\text{basis expansion}} \\
V &= \underbrace{\left[\sum_i^{i=20} A_i y^i \right]}_{\text{interactive term}} + \underbrace{\left[\frac{1}{2} \times 0.1578 \underbrace{\left(1 - \tanh \left[h_1(r_1 + c_0) \right] \right)}_{\text{term1}} + \frac{1}{2} \times 0.2008 \underbrace{\left(1 + \tanh \left[h_2(r_1 - d_0) \right] \right)}_{\text{term2}} \right]}_{\text{long range term}} \quad \left. \vphantom{\sum_i^{i=20}} \right\} \begin{array}{l} \text{no} \\ \text{permutational} \\ \text{symmetry} \end{array}
\end{aligned} \tag{2}$$

Computing vibrational levels

With the models available, it becomes easy to compute vibrational Eigen values numerically for the back and forth motion (one of the normal modes) of proton in the molecular plane. The Hamiltonian to compute the Eigen values is given in Eq 3 which is non relativistic Schrödinger equation with effective potential energy function involving the orbital motion and the model potential energy function $V(y)$. Solving this equation is relatively simple except the model potential as defined in Eq 1 and 2 and can be done with any programming software. In this work, MATHEMATICA is being used to do the job and the results reported were obtained using it. The computed results are meant for L assuming 0, 1, 2 only and μ is the reduced mass as usual and the proton mass in atomic units were used for it since the vibrational motion refers to the oscillatory motion of proton alone in the specific mode. However, this is not entirely true but mass of proton could be used as a good approximation to start with as the relative vibration of other four oxygen atoms are negligibly small and can be ignored. This can be verified numerically by looking at the magnitudes of resulting Eigen vector containing normal coordinates of four oxygen atoms as well as that of proton. The normal mode displacement of proton is found to be higher than other four oxygen atoms and hence they do not contribute sizeably to the estimation of μ . E_{vib} refer to the resulting Eigen value after solving the Eq. 3 normally reported in the units of cm^{-1} in the form of Tables and Figures. The effective potential energy function is indicated inside the parenthesis in Eq. 3 as the sum of fitted model potential and the centrifugal potential.

In Fig 2, E_{vib} in cm^{-1} as a function of quantum states are plotted for different L values 0, 1, 2 for both the conformers. A maximum of 23 non degenerate levels were computed for the cis conformer and beyond 23, the results were not converged as well as ill conditioned and this made us to stop at 23 (please have a look at the supplementary

information (SI) for the values in the form of a Table as it is new and not published in the previous work[1] and also look at Fig 3 where the computed levels are shown for clarity on a measured scale for $L = 0$. Fig 2 also convey the same information but in the form of curve.) A maximum of 39 levels were computed for the trans conformer for $L = 0$, few of them doubly degenerate mostly near lower levels (see Fig 2) but assigned different quantum numbers. When $L = 1, 2$, the computed levels are paired up to form a doubly degenerate set of levels and for the cis conformer, numerically exact degeneracies are not seen for all three L values, 0, 1, 2.

In Fig 2 the presence of double degeneracy (numerically exact) is revealed by a pair of dots forming a step like feature for $L = 1, 2$ in the trans conformer and for $L = 0$ degeneracy formed by a pair of dots occurs at lower levels (levels less than 20 and higher than 5) and all other levels are non degenerate as well as linear as are seen clearly in the C_{2h} case (see the legends in Fig 2). In the case of cis conformer with C_{2v} geometry, the Fig 2 reveals the non degeneracy and smoothness of levels for $L = 0$ (see the curve with embedded points labelled with legend $L = 0 (C_{2v})$) but the spacing ($v \rightarrow v + 1$) between them gradually decrease as v increase and finally converge to dissociation energy. This can be seen clearly in Fig 3 for $L = 0$ case. For $L = 1, 2$, it is possible to see degeneracy occasionally but they are not strictly degenerate in the numerical sense but quasi degenerate. This can be seen in the plot given in Fig 3 for the levels of cis conformer. In Fig 3, the computed vibrational levels for the cis isomer with C_{2v} point group are shown for three angular momentum values, 0, 1, 2 and the zero point energy at the $v = 0$ level is seen shifted to higher energy as L changes. This trend happens for all v and any one can see it via dashed line pointing to higher energy levels as L changes. The two non degenerate level at $v = 5$ and $v = 6$ for $L = 0$ moves to degeneracy when $L = 1$ and again become non degenerate when $L = 2$ and this shows influence of orbital momentum on the vibrational energy levels. Similar case happens with non degenerate $v = 8$ and $v = 9$ levels, becoming degenerate at $L = 1$ and non degenerate at $L = 2$. The convergence of levels at 35000 cm^{-1} (a mode specific value) is a common result whatever be the L value and however irregular be the spacings among them. It applies to the levels of both C_{2h} and C_{2v} calculations. The C_{2v} result are shown in Fig 3 while that of C_{2h} is given in the supplementary information (SI) in the form of Tables. It gives credence to the calculation done on the system.

By looking at Fig 1 it is possible to conclusively decide that the wider potential wall of trans conformer can accommodate more levels than the narrow wall of cis conformer. This alters the associated derivatives of higher order found in Taylor expansion of both conformers. This is the reason why different number of levels were obtained as the topography of the two curves drastically differs in all the region.

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi(y)}{dy^2} + \underbrace{\left(\underbrace{V(y)}_{\text{model}} + \frac{\hbar^2 L(L+1)}{2\mu y} \right)}_{\text{effective potential energy}} \psi(y) = E_{vib} \psi(y) \quad (3)$$

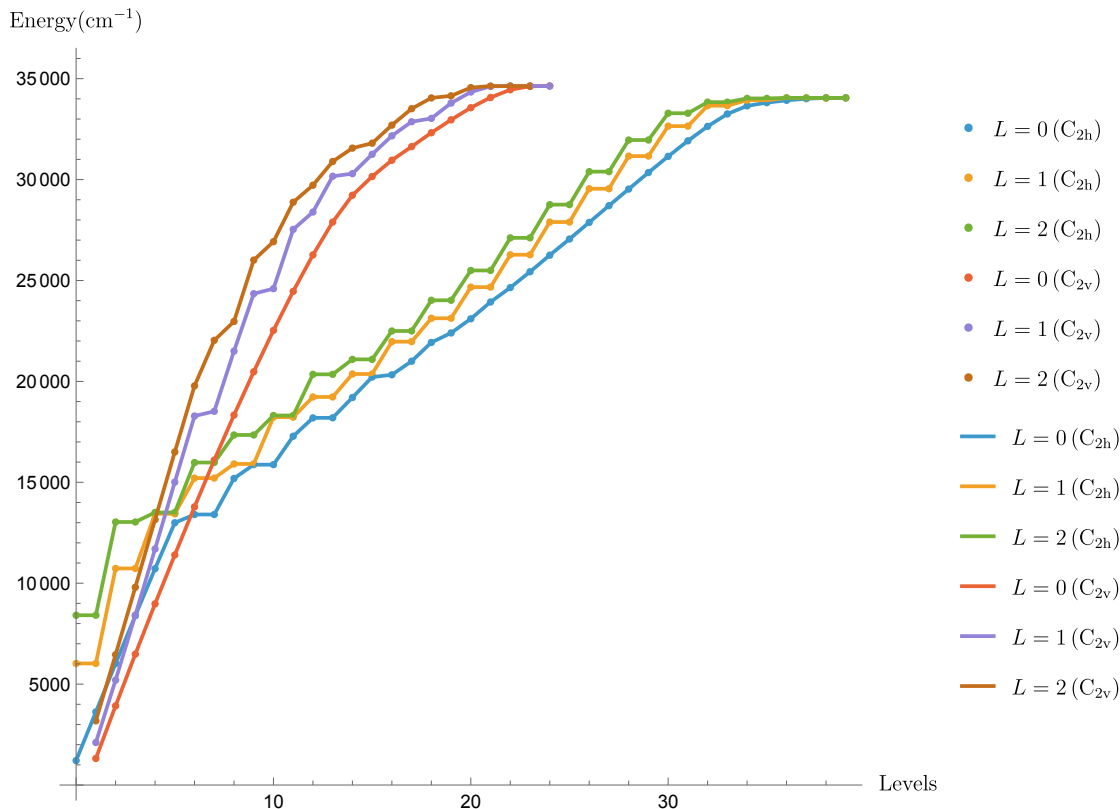


Fig. 2 The effect on vibrational levels in the presence $L = 1, 2$ and absence $L = 0$ of orbital angular momentum for the cis and trans conformers. It has a huge effect on the levels with regard to their degeneracy. See next figure too for more clarity.

Cis-trans interconversion spectrum

The previously discussed level calculation form the basis to compute the electronic spectrum based on vibronic transitions from lowest state to the highest one and the assumption of fixed nuclear geometry is well maintained in calculating the spectrum. As of now, direct experimental proof of the interconversion spectrum is not yet available. The computed spectrum will serve the purpose of easy identification to any one who are likely to do a spectral analysis in the days to come.

In Fig 4, the potential energy curves involved in the cis-trans interconversion is presented with a portion of computed absorption and emission spectrum in certain wave length range shown. A detailed spectrum is given in Fig 5 covering all the peaks. In the curves in Fig 4 are shown anharmonic probability densities at different levels and the blackish vertical lines (solid and dashed) stand for electronic transitions. The lowest is the C_{2h} trans curve and the above is C_{2v} cis curve. The layout of vibrational levels is complicated by the existence of degeneracies among themselves in the C_{2h}

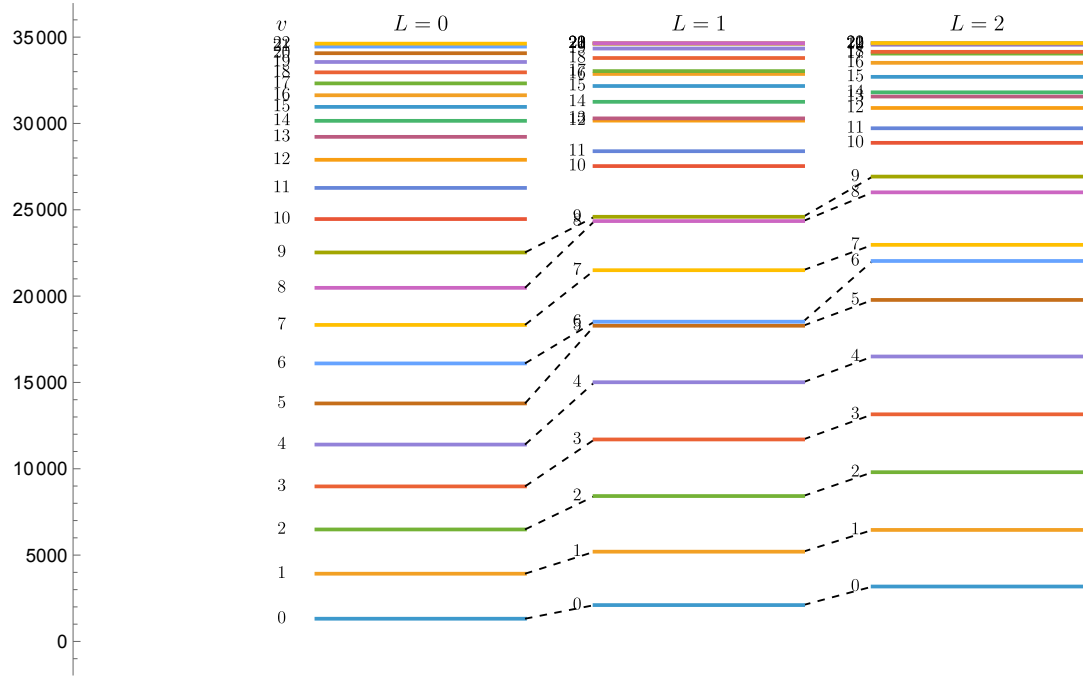


Fig. 3 The computed vibrational levels for the cis isomer are shown for three angular momentum values, $L = 0, 1, 2$.

case[1] and in the other case, no such complication arises even though the convergence of levels are not numerically uniform until the dissociation limit (see Fig 3 for $L = 0$). An interesting note worthy point is the number of levels contained in each potential energy profile. The total number of acceptable levels differ drastically in both the point groups on account of the degeneracy issue and is found to be more (exactly 39) when some of the Eigen functions (not all) are nearly quasi degenerate. The labels are given for the counting purpose distinctly level by level inclusive of the degenerate pair assigned distinct labels. The total number of computable levels in the absence of such degeneracies is exactly 23 for the non degenerate C_{2v} arrangement. Beyond this number, converged bound levels were found to be impossible. This is about fifty percent reduction when compared with the degenerate C_{2h} arrangement. This made us to think that a pair of levels at degeneracy correlate to a well defined single level at non degenerate configuration when the cis-trans conversion takes place. This could be one reason for the reduction in the total number of bound levels. Another valid reason lies in the shape of potential energy curves shown in Fig 1. The densities of levels contained inside the wider potential (the distance between right and left turning point is considerably more relative to the same aspect near equilibrium region based on C_{2h} curve) wall is higher suggesting that they are closely spaced even though degeneracy does not play any role in increasing or decreasing the number of overall levels since wider wall is energetically well separated from the degeneracy in the particular case

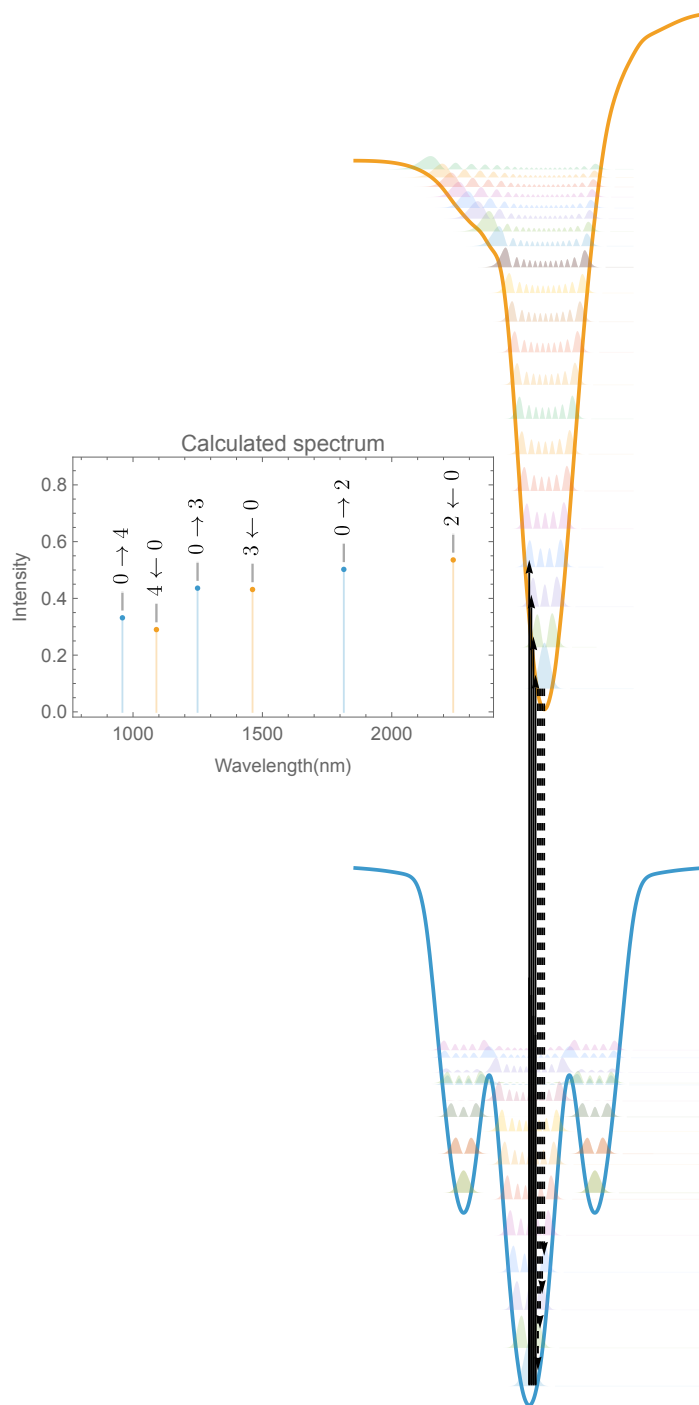


Fig. 4 Cis-trans interconversion electronic spectrum based on vibronic transitions of emission and absorption. The intensities are decided by overlap of vibrational Eigen functions. The emission and absorption lines are shown in the simulated spectrum for the corresponding vertical transitions depicted as black dashed and solid lines.

under focus. It is strongly believed both these reasons have the potential to exert influence in changing the number of bound vibrational levels during the cis-trans interconversion. Which one dominates over the other is a matter to be discussed in depth considering the shape and the nature of potential energy curves. In this example, lower energy regime favours the change in bound levels via degeneracy while higher energy regime favours the same via lowering the densities of levels across the rigid walls. Whatever stated here is valid only for this system and cannot be generalised to cover other systems not discussed in this manuscript. If so, care must be exercised thoroughly to study the involved potential energy curves of interconversion to arrive at a correct conclusion.

A model plot of calculated spectrum is shown as an example within a specific range of wavelength on the left side of Fig 4. It shows both absorption (light blue) and emission (light yellow) lines and as usual, emission lines occur at higher wave length than the corresponding absorption line for a given transition. The full calculated range is given in Fig 5 which has more broader range covering all the lines starting from the transition originating from the ground level to higher levels. The height (intensity) of the lines are overlap dependent of vibrational wave functions, higher the overlap higher the intensity. It shows lines of few transitions that fall within the specified range and the transition which fall outside the range are shown in a separate plot in Fig 5 As pointed out above, each absorption transition is followed by a corresponding emission but at higher wavelength. $0 \leftrightarrow 0$ is an exception as the energy of transition in both direction remain the same rendering both the peaks indistinguishable and appear as one single line. In other words, $0 \leftrightarrow 0$ is a peak referring to the transition from $v = 0$ level in the lowest curve to the same level in the higher lying curve and back at the same wavelength (frequency) and the same frequency for both direction and happens only for $0 \leftrightarrow 0$, lowest energy transition among all. There is huge gap between $0 \leftrightarrow 0$ and $0 \rightarrow 1$ or $0 \leftarrow 1$, next lowest energy transition. Unlike $0 \leftrightarrow 0$ case, the energy of transition differs a lot in both the direction, mostly $1 \leftarrow 0$ (emission) at a higher wavelength. Please have a look at the computed spectrum in Fig 5 to see if this is indeed so. This behaviour is obeyed every except $0 \leftrightarrow 0$ where two lines merge one over other at the same wavelength. The intensity of emission line decreases rapidly in comparison with the absorption lines because of existence of degeneracy in the lowest energy state reducing the overlap between the vibrational wave functions for few transitions. The emission line after $7 \leftarrow 0$ is almost zero while the corresponding line for the absorption for $0 \rightarrow 7$ survives and can well be seen in the spectrum. The spectrum is computed for the transition originating from $v = 0$ of both the curves and it looks like what is shown in Fig 5 and the maximum intensity is achieved for this case. For the transitions originating from other levels, say $v = 1$, of both the curve, the intensity will not be maximum and be less than the intensity already predicted in the Fig 5. This study is restricted starting from $v = 0$ level in both the directions.

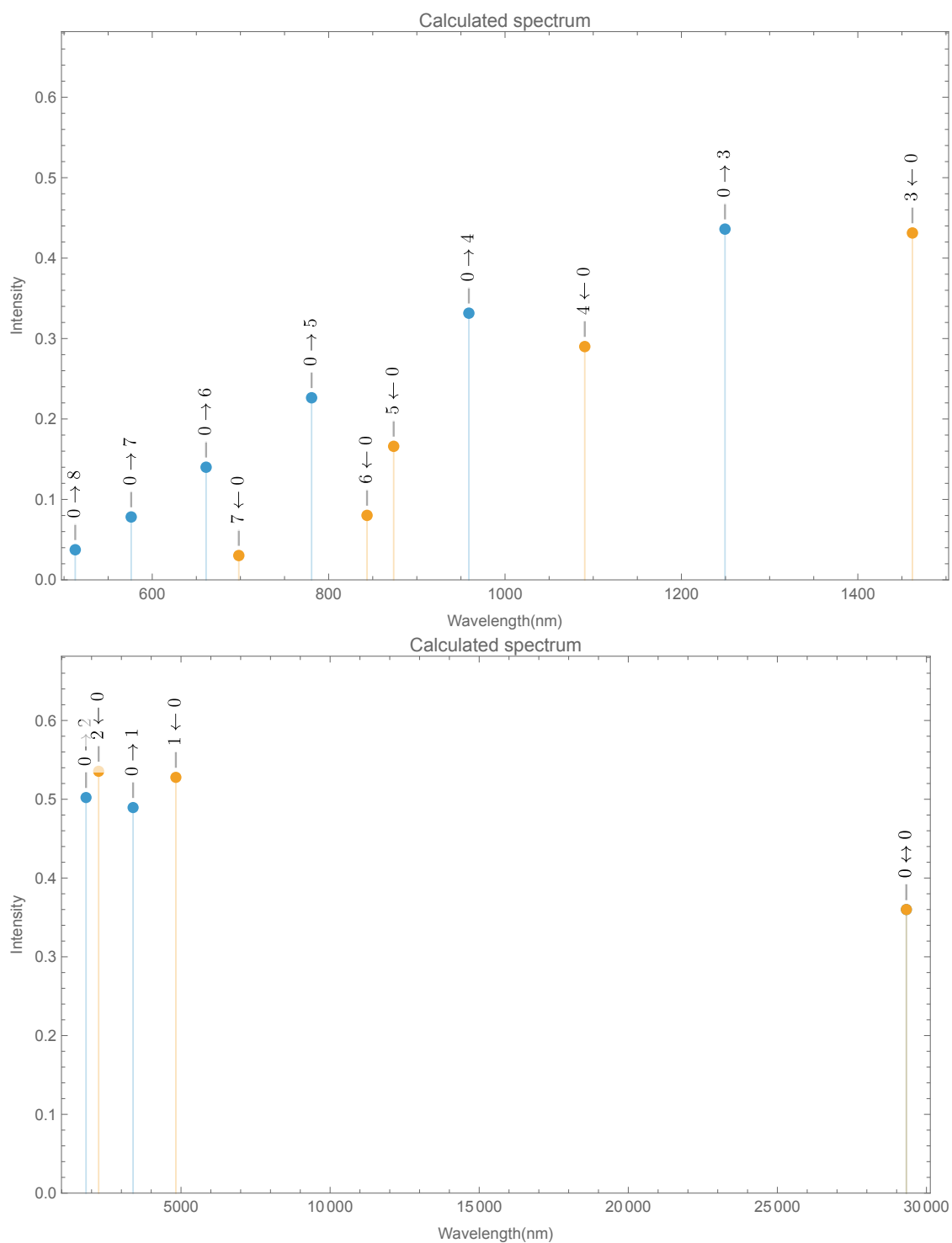


Fig. 5 Interconversion vibronic spectrum with $0 \leftrightarrow 0$ transition is left isolated and other lines are close together with a average spacing of roughly 300nm and the intensity is overlap dependent. This is a single spectrum split into two for clarity.

Conclusion

The two curves have been modelled with a correct analytical models which accounts the curves every where giving smallest possible fitting error well within the spectroscopic accuracy. The models have the same frame work but structurally different as they need to explain the curves with permutational symmetry and without such symmetry. The models have been subjected to computing the vibrational levels accurately with and without angular momentum contribution whose effect on the levels is well tested. Finally, the models have been used to compute and discuss the vibronic spectrum based on Franck Condon principles and most intense peak distribution is found to be away from the $v = 0$ level as both the curve are not directly one over other but slightly moved away from the centre.

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Disclosure statement

The author has no conflicts of interest to disclose in this work.

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.

References

- [1] Xavier, F.G.D.: Intermolecular potential of singlet O_4H^+ ion. *Molecular Physics* **0**(0), 2636747 (2026) <https://doi.org/10.1080/00268976.2026.2636747>
<https://doi.org/10.1080/00268976.2026.2636747>
- [2] Renzler, M., Ralser, S., Kranabetter, L., Barwa, E., Scheier, P., Ellis, A.M.: Observation of stable HO_4^+ and DO_4^+ ions from ion–molecule reactions in helium nanodroplets. *Phys. Chem. Chem. Phys.* **18**, 13169–13172 (2016) <https://doi.org/10.1039/C6CP01895E>
- [3] Franke, P.R., Duncan, M.A., Douberly, G.E.: Infrared photodissociation spectroscopy and anharmonic vibrational study of the HO_4^+ molecular ion. *The Journal of Chemical Physics* **152**(17), 174309 (2020) <https://doi.org/10.1063/5.0005975> https://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0005975/15574212/174309_1.online.pdf

- [4] Xavier, F.G.D., Hernández-Lamonedá, R.: Ab initio study of the O_4H^+ novel species: spectroscopic fingerprints to aid its observation. *Phys. Chem. Chem. Phys.* **17**, 16023–16032 (2015) <https://doi.org/10.1039/C5CP01822F>
- [5] Xavier, G.D., Bernal-Uruchurtu, M.I., Hernández-Lamonedá, R.: Communication: Ab initio study of O_4H^+ : A tracer molecule in the interstellar medium? *The Journal of Chemical Physics* **141**(8), 081101 (2014) <https://doi.org/10.1063/1.4894068> https://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/1.4894068/15482360/081101.1_online.pdf
- [6] Aquilanti, V., Ascenzi, D., Bartolomei, M., Cappelletti, D., Cavalli, S., Castro Vitores, M., Pirani, F.: Molecular beam scattering of aligned oxygen molecules. the nature of the bond in the $\text{O}_2\text{--O}_2$ dimer. *Journal of the American Chemical Society* **121**(46), 10794–10802 (1999) <https://doi.org/10.1021/ja9917215> <https://doi.org/10.1021/ja9917215>
- [7] Aquilanti, V., Ascenzi, D., Bartolomei, M., Cappelletti, D., Cavalli, S., Castro Vitores, M., Pirani, F.: Quantum interference scattering of aligned molecules: Bonding in O_4 and role of spin coupling. *Phys. Rev. Lett.* **82**, 69–72 (1999) <https://doi.org/10.1103/PhysRevLett.82.69>
- [8] Campargue, A., Biennier, L., Kachanov, A., Jost, R., Bussery-Honvault, B., Veyret, V., Churassy, S., Bacis, R.: Rotationally resolved absorption spectrum of the O_2 dimer in the visible range. *Chemical Physics Letters* **288**(5), 734–742 (1998) [https://doi.org/10.1016/S0009-2614\(98\)00294-2](https://doi.org/10.1016/S0009-2614(98)00294-2)
- [9] Biennier, L., Romanini, D., Kachanov, A., Campargue, A., Bussery-Honvault, B., Bacis, R.: Structure and rovibrational analysis of the $[\text{O}_2(^1\delta_g)_{v=0}]_2 \leftarrow [\text{O}_2(^3\sigma_g^-)_{v=0}]_2$ transition of the O_2 dimer. *The Journal of Chemical Physics* **112**(14), 6309–6321 (2000) <https://doi.org/10.1063/1.481192> https://pubs.aip.org/aip/jcp/article-pdf/112/14/6309/19137792/6309.1_online.pdf
- [10] Hernández-Lamonedá, R., Bartolomei, M., Hernández, M.I., Campos-Martínez, J., Dayou, F.: Intermolecular potential of the $\text{O}_2\text{--O}_2$ dimer. an ab initio study and comparison with experiment. *The Journal of Physical Chemistry A* **109**(50), 11587–11595 (2005) <https://doi.org/10.1021/jp053728g> <https://doi.org/10.1021/jp053728g>. PMID: 16354051
- [11] Bartolomei, M., Carmona-Novillo, E., Hernández, M.I., Campos-Martínez, J., Hernández-Lamonedá, R.: Accurate ab initio intermolecular potential energy surface for the quintet state of the $\text{O}_2(^3\sigma_g^-)\text{--O}_2(^3\sigma_g^-)$ dimer. *The Journal of Chemical Physics* **128**(21), 214304 (2008) <https://doi.org/10.1063/1.2929852> https://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/1.2929852/15411502/214304.1_online.pdf
- [12] Pérez-Ríos, J., Bartolomei, M., Campos-Martínez, J., Hernández, M.I.,

- Hernández-Lamonedá, R.: Quantum-mechanical study of the collision dynamics of $\text{O}_2(^3\sigma_g^-) - \text{O}_2(^3\sigma_g^-)$ on a new ab initio potential energy surface. *The Journal of Physical Chemistry A* **113**(52), 14952–14960 (2009) <https://doi.org/10.1021/jp905045b> <https://doi.org/10.1021/jp905045b>. PMID: 20028175
- [13] Bartolomei, M., Carmona-Novillo, E., Hernández, M.I., Campos-Martínez, J., Hernández-Lamonedá, R.: Global ab initio potential energy surfaces for the $\text{O}_2(^3\sigma_g^-) + \text{O}_2(^3\sigma_g^-)$ interaction. *The Journal of Chemical Physics* **133**(12), 124311 (2010) <https://doi.org/10.1063/1.3479395> https://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/1.3479395/13342687/124311.1_online.pdf
- [14] Carmona-Novillo, E., Bartolomei, M., Hernández, M.I., Campos-Martínez, J., Hernández-Lamonedá, R.: Ab initio rovibrational structure of the lowest singlet state of $\text{O}_2 - \text{O}_2$. *The Journal of Chemical Physics* **137**(11), 114304 (2012) <https://doi.org/10.1063/1.4752741> https://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/1.4752741/13547758/114304.1_online.pdf
- [15] Valentín-Rodríguez, M.A., Bartolomei, M., Hernández, M.I., Campos-Martínez, J., Hernández-Lamonedá, R.: An unrestricted approach for the accurate calculation of the interaction potentials of open-shell monomers: The case of $\text{O}_2 - \text{O}_2$. *The Journal of Chemical Physics* **152**(18), 184304 (2020) <https://doi.org/10.1063/5.0005171> https://pubs.aip.org/aip/jcp/article-pdf/doi/10.1063/5.0005171/14105138/184304.1_online.pdf
- [16] Castro-Gómez, L.B., Campos-Martínez, J., Hernández, M.I., Hernández-Lamonedá, R.: Molecular oxygen trimer: Multiplet structures and stability. *ChemPhysChem* **24**(23), 202300387 (2023) <https://doi.org/10.1002/cphc.202300387> <https://chemistry-europe.onlinelibrary.wiley.com/doi/pdf/10.1002/cphc.202300387>
- [17] Hernández-Lamonedá, R., Pérez-Ríos, J., Carmona-Novillo, E., Bartolomei, M., Campos-Martínez, J., Hernández, M.I.: Properties of the molecular oxygen trimer from pairwise additive interactions. *Chemical Physics* **399**, 80–85 (2012) <https://doi.org/10.1016/j.chemphys.2011.06.033>. New trends in atomic and molecular clusters
- [18] Bartolomei, M., Carmona-Novillo, E., Hernández, M.I., Pérez-Ríos, J., Campos-Martínez, J., Hernández-Lamonedá, R.: Molecular oxygen tetramer $(\text{O}_2)_4$: Intermolecular interactions and implications for the ϵ solid phase. *Phys. Rev. B* **84**, 092105 (2011) <https://doi.org/10.1103/PhysRevB.84.092105>
- [19] A. Gamboa-Suárez, O.H.-C.L.B.C.-G. A. Alcaraz-Torres, Hernández-Lamonedá, R.: Molecular oxygen tetramer: multiplet structure and global minima. *Phys. Chem. Chem. Phys.* **28**, 9653–9658 (2026) <https://doi.org/10.1039/D5CP04648C>

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