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Ab initio study of the O_4H^+ novel species: spectroscopic fingerprints to aid its observation

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A detailed *ab initio* characterization of the structural, energetic and spectroscopic properties of the novel O_4H^+ species is presented. The equilibrium structures and relative energies for all multiplet states have been determined systematically analyzing static and dynamical correlation effects. The two and three body dissociation processes have been studied and indicate the presence of conical intersections in various states including the ground state. Comparison with available thermochemical data is very good supporting the applied methodology. The reaction, $H_3^+ + O_4 \rightarrow O_4H^+ + H_2$, was found to be exothermic $\Delta H = -19.4$ Kcalmol⁻¹ and therefore, it is proposed that the product in singlet state could be formed in the interstellar medium (ISM) via collision processes. To aid in its laboratory or radioastronomy detection in the interstellar medium we determined spectroscopic fingerprints. It is estimated for the most stable geometry of O_4H^+ dipole allowed electronic transitions in the visible region at 429 nm, 666 nm, an intense band at 1745cm⁻¹ in the infrared and signals at 40.6, 81.2 and 139.2 GHz in the microwave region at 10, 50 and 150K respectively, relevant for detection in the ISM.

1 Introduction

In a recent contribution,^{1,2} it was proposed that protonated molecular oxygen dimer, O_4H^+ , could be used as a tracer for detecting molecular oxygen and its dimer in the interstellar medium. Even though oxygen is the third most abundant element in the universe finding the different forms in which it could be present is an unresolved issue referred to as the oxygen problem³. In particular, molecular oxygen has been difficult to detect and only recently has it been definitely confirmed.^{4–6} Furthermore the usually fruitful procedure of searching for its protonated adduct HO_2^+ does not look promising on theoretical grounds given that its formation through reaction $H_3^+ + O_2 \rightarrow O_2H^+ + H_2$ is nearly thermoneutral.⁷

In addition to its astrophysical relevance, the system exhibits many interesting structural, spectroscopic and dynamical features which deserve to be studied in their own right. Among them we can mention the presence of different isomeric forms depending on the symmetrical or asymmetrical sharing of the proton between the two oxygen molecules analogous to the case of Eigen and Zundel species for protonated water dimer. Dissociation of the most stable structures into two or three fragments indicate a rich variety of processes such as non-adiabatic transitions as exemplified in the formation of molecular oxygen in its low-lying excited states a proof that conical intersections are common in this system. Charge

transfer processes are also of relevance and together with the excited state dynamics should lead to a rich photochemistry for this species.

A preliminary study on the O_4H^+ system based on full valence complete active space self-consistent field (CASSCF) calculations was reported recently^{1,2} in which generalities about minimized structures and fragmentation processes for the different spin states were discussed. Some methodological challenges were encountered in it. For example the use of a restricted active space where only the 2p atomic orbitals are included leads to artificial lowering of the complex symmetry. This behavior had been previously observed⁸ for the O_4^+ species. For example, in the case of the O_4H^+ system a C_{2h} structure for the singlet state obtained at the full valence active space level has its symmetry lowered to C_s when keeping the 2s orbitals closed, the converged structure having two OH bond lengths differing by 0.114Å. Although the problem can be solved by using a full active valence space it leads to calculations with millions of configurations which are computationally demanding when geometry optimization and harmonic frequency analysis are considered^{1,2}. The challenge is to include dynamical correlation with such large active spaces and is taken up in this work where we present an extension of the previous studies by including dynamical correlation effects through multireference configuration interaction with singles and doubles excitations (MRCI) and also present improved thermochemical and spectroscopic information to be compared with previous estimates and which should aid in the experimental characterization of this system.

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2 Methodology

The *ab initio* calculations of O_4H^+ were carried out at complete active space self-consistent field^{9,10} (CASSCF) and internally contracted multireference configuration interaction with single and double excitations^{11,12} (ic-MRCI) level of theory using augmented correlation consistent polarized valence triple zeta¹³ (aug-cc-pVTZ) basis set. In addition, restricted coupled cluster singles and doubles with perturbative triple correction¹⁴ (RCCSD(T)) calculations were performed using the same basis set and with the larger augmented correlation consistent polarized valence quadruple zeta¹³ (aug-cc-pVQZ) basis set only for the quintet state. All the calculations were done with MOLPRO2012.1 package.¹⁵

As has been discussed in previous works^{16,17} of the three possible multiplicities relevant for the interaction of two oxygen molecules only the highest which corresponds to quintet can be treated with single reference methods. In this case it is possible to obtain highly accurate results using the RCCSD(T) method. For the lower multiplicities multiconfigurational approaches are mandatory. In order to obtain the best possible thermochemical estimates for the lower multiplicities we follow a procedure which has been successfully applied in the case of the molecular oxygen dimer^{16–18}. In this approach we calculate reliable thermochemical properties for the singlet and triplet states using their energy splittings relative to the quintet state calculated at CASSCF or MRCI level and adding them to the RCCSD(T) result of quintet as summarized in the equations:

$$V^{s=0} = V_{\text{ccsd}(t)} + \Delta_{\text{cas/ci}}^{s-q} \quad (1)$$

$$V^{s=1} = V_{\text{ccsd}(t)} + \Delta_{\text{cas/ci}}^{t-q} \quad (2)$$

where

$$\Delta_{\text{cas/ci}}^{s,t-q} = V_{\text{cas/ci}}^{s=0,1} - V_{\text{cas/ci}}^{s=2} \quad (3)$$

are the singlet-quintet and triplet-quintet splittings respectively. $V_{\text{cas/ci}}^{s=n}$ ($n = 0, 1, 2$) are the multiplet state energies obtained by different multiconfigurational methods in our case CASSCF and MRCI. In this work, we will refer to this approach as the hybrid method.

As explained in the Introduction the use of a full valence approach in all the CASSCF calculations guarantees avoiding artificial symmetry breaking. However, these are computationally intensive calculations. For example, a C_{2h} , C_s and C_1 single point calculation produces roughly 2,4,9 million configuration state functions (CSFs) which require approximately 2, 5, 10 hours of computation time using 8 cores of an AMD Opteron node with 64 bits processors and clockspeed of 2.3GHz. Additionally when going to the MRCI level the use of a full active space becomes prohibitive. The tests of active

space were performed and found that the two lowest orbitals belonging to the 2s space can be safely defined as closed without compromising the accuracy of the results. This reduced active space was retained in the orbital optimization step of all MRCI calculations. Two different types of MRCI calculations were performed. The two orbitals that were closed in the optimization step are frozen in both types of MRCI calculations. In the first case we define a small or reduced active space comprised of the partially occupied Π_g orbitals of O_2 and the 1s orbital of hydrogen. The remaining orbitals had natural occupation numbers close to two and were defined as closed so that they will be correlated in single and double excitations in the final MRCI expansion. In this case it is possible to perform geometry optimizations followed by frequency analysis and test the effects of dynamical correlation albeit at a limited level. Still a typical optimization took 10 days running in 8 processors.

Another technical problem encountered was symmetry breaking in the frequency analysis when doing energy evaluations without symmetry. This problem can be overcome by transforming the symmetrized orbitals of the optimal (symmetrical) geometry to the basis without symmetry, confirming that the energy calculated without symmetry coincides with the case where symmetry is imposed. This transformation ensures that numerically there is no contamination of spurious orbital in the list of optimized orbitals and there are no anomalous values for any of the normal modes.

In order to obtain reliable energetics a second active space was considered for single point energy calculations. In this case we keep the same active space defined during the orbital optimization, i.e. its almost a full valence active space except the two lowest orbitals were kept frozen (their natural occupations are larger than 1.995). For the C_{2h} singlet the total number of contracted configurations is roughly 290 million and required 34 hours in 8 processors. For less symmetrical cases such as the quintet state a single point calculation took close to three weeks. These calculations are used to estimate multiplet splittings via Eq. 3 and combined with RCCSD(T) values for the quintet in accordance with Eq. 1 provide our most accurate predictions. They were also used to estimate the dipole allowed electronic transitions. The Davidson correction¹⁹ was applied for these cases. All thermochemical quantities have been corrected for zero-point energy (ZPE) (within the harmonic approximation) unless otherwise stated.

3 Results and Discussion

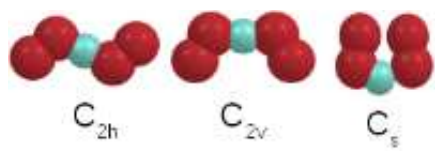
3.1 CASSCF properties

The generalities concerning the equilibrium geometries of ground multiplet states have been discussed in a previous communication^{1,2} so here we only briefly summarize those

Table 1 Molecular properties of equilibrium structures of singlet, triplet and quintet states obtained with various methodologies

theory/basis	Electronic states	r(O-O)	r(O-H)	$\angle(\text{O-H-O})$	$\angle(\text{O-O-H})$	$\mu(\text{D})$	A,B,C (GHz)	ZPE (cm^{-1})
CASSCF/AVTZ	X^1A_g (trans)	1.22	1.22	180.0	115.0	0.00	2.8, 46.7, 2.9	3606
	X^1A_1 (cis)	1.22	1.22	176.2	114.7	0.01	3.0, 26.1, 3.4	3650
	X^1A'	1.23	1.15	140.0	104.7	1.13	5.0, 6.6, 20.5	3944
		1.21	1.32		101.8			
	a^3B_u (trans)	1.22	1.22	180.0	115.0	0.00	2.8, 46.5, 2.9	3512
	a^3B_2 (cis)	1.22	1.22	175.0	115.2	0.04	3.0, 26.6, 3.4	3517
	b^5A	1.22	1.41	176.7	120.4	1.90	2.5, 2.6, 44.0	3652
		1.24	1.10		112.5			
RCCSD(T)/AVTZ	b^5A	1.22	1.22	175.7	117.7		2.9, 41.2, 2.8	3489
RCCSD(T)/AVQZ	b^5A	1.21	1.22	175.8	118.1		2.9, 41.8, 2.8	3401

findings. Three stable structures exist for the ground singlet state with C_{2h} (trans), C_{2v} (cis) and C_s point groups and they are shown in Figure 1. The triplet states also appear in cis

**Fig. 1** Equilibrium structures for various isomers of singlet O_4H^+

and trans structures and the quintet has no symmetry at this level of theory. The structural data is shown in Table 1. The molecular states are labelled according to Herzberg's molecular notation. As discussed in the previous section except for the quintet multiplicity all states are strongly multiconfigurational. The symmetric structures are reminiscent of the zundel species for protonated water dimer whereas the C_s structure is more akin to the eigen species. However notice that both O_2 moieties have short bond lengths to hydrogen indicating a much stronger interaction than would be expected for a van der Waals complex of O_2H^+ and O_2 units. The symmetric species present in both singlet and triplet states show no variation in O—O, O—H distances and only a small change in O—H—O angle when considering the cis to trans interconversion. As discussed in the previous study^{1,2} the interconversion between equivalent C_s minima proceeds through a small electronic barrier which disappears when ZPE is included thus making the vibrationally averaged structure of C_{2v} symmetry, an important point for future experimental studies. For the quintet state notice that the highly accurate RCCSD(T) method predicts a more symmetrical C_2 structure indicating the need of including higher levels of correlation to properly describe this state. This is in line with previous theoretical work⁸ on the O_4^+ system as reviewed in the previous section. Given the multiconfigurational character of the system it is natural to look at the

T_1^{20} and D_1^{21} diagnostic values, which in our case are 0.03 and 0.11, respectively. These values are larger than the recommended limits for high accuracy however further analysis is required to reach a conclusion. First we note that there are many examples of systems whose diagnostic values exceed the established limits and for which an accurate description is still achieved, for example the radical CN whose diagnostic values²¹ are similar to those of O_4H^+ . Furthermore from the multiconfigurational calculations we can estimate that the main configuration contributes 88% of the total wavefunction giving us confidence on the RCCSD(T) approach.

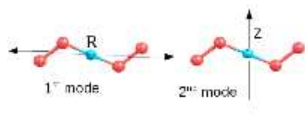
In Table 2 we summarize the relative energies of all calculated species. It is worth noting the large ZPE effects which change the relative order of the ground singlet state. The multiplet levels maintain the same stability ordering as in the unprotonated species but the splittings are much larger due to the stronger chemical interactions in the lower multiplicities. Intersystem crossing effects could be of major importance in the photochemistry of O_4H^+ given the relatively small splittings and difference in preferred geometrical structures. In the bottom portion we present the relative energies of the singlet excited states for the trans and cis structures which appear at roughly 1.5 and 2.6 eV respectively. These should be close to the vertical excitation energies given the small differences in equilibrium geometries between ground and excited states. According to dipole selection rules, for the trans isomer transitions to A_u and B_u are allowed while the analogous transitions for the cis isomer are to B_1 and B_2 states.

The binding energy for dissociation into O_2H^+ and O_2 fragments have been determined in gas phase ion-equilibria measurements^{22,23}. Analysis is based on van't Hoff plots where the range of temperatures covered is roughly 400–500 K and the value reported for $T=300\text{K}$ is 20.6 Kcalmol^{-1} . It was found that thermal corrections are non-negligible and our estimate at 300K is reported. Using the combined RCCSD(T)/CASSCF approach we obtain a value of 18.7 Kcalmol^{-1} at 0K. Applying thermal corrections yields 19.2 Kcalmol^{-1} . Therefore, it

Table 2 Relative energies (meV) of various electronic states without/with ZPE correction

Electronic states	w/o ZPE	with ZPE
X^1A'	0	36.35
X^1A_g	5.57	0
X^1A_1	13.11	13.25
a^3B_u	63.76	46.57
a^3B_2	76.91	60.35
b^5A	181.69	181.84
A^1A_2	1444	1453
A^1B_g	1449	1462
B^1A_u	1510	1534
B^1B_1	1521	1544
C^1B_2	2643	2654
C^1B_u	2644	2657

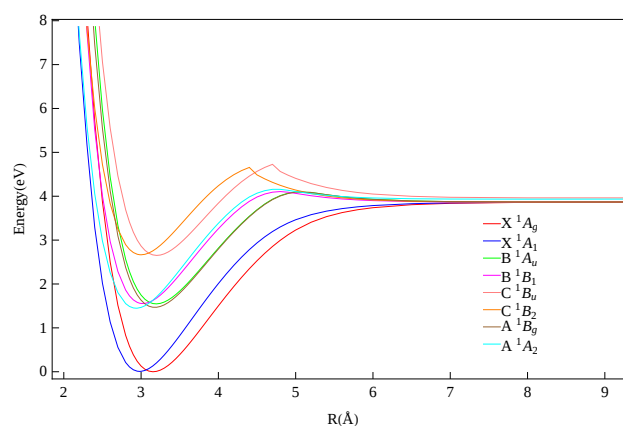
is concluded that the small remaining difference must be due mainly to lack of dynamical correlation on the CASSCF estimate of the singlet-quintet splitting and this will be confirmed in the MRCI section of results. However the difference is small enough that it could be explained within the experimental uncertainty.

**Fig. 2** The definition of molecular parameters used to generate potential energy curves(PECs)

In order to understand the collision dynamics and spectroscopy of O_4H^+ in greater detail, one needs the knowledge of its full dimensional adiabatic potential energy surfaces (PES). As a first step towards achieving this goal, we have generated one dimensional adiabatic potential energy curves (PECs) for two different modes of dissociation as explained below. The processes that give rise to two or three fragments using the coordinates defined in Figure 2 were considered. In the first mode, the active variable is the distance between the center of mass (cm) of two O_2 monomers, denoted as R in this work. In the second mode of dissociation, the active variable used is the vertical displacement of H^+ defined in cartesian coordinates moving up and down along the Z axis, as indicated in Figure 2. The other geometrical parameters are kept fixed at their equilibrium values so the excited state information coincides with a Franck-Condon(FC) picture. The PECs corresponding to ground spin electronic states in both modes were discussed in earlier work.^{1,2}

In Figure 3 we present PECs for the lowest singlet states of cis and trans conformations as a function of R . In the in-

teraction region, there occur three sets of states which can be grouped together on the basis of their absolute energies. For example, the lowest among them consists of X^1A_g and X^1A_1 states which represent two different minima in the same ground state PES and differ by few meV in energy. Similarly, the excited states are grouped by energy. One can no-

**Fig. 3** Franck-Condon PECs for various singlet states of cis and trans isomers.

tice that the minimum in each curve related by a FC transition has a very similar value of R , suggestive of 0-0 vibronic transition as the most probable one. In this mode, the curves lead to three body dissociation, O_2 , H and O_2^+ and all of them converge to the same asymptote characteristic of a charge-transfer (CT) channel considering as initial state $O_2(X^3\Sigma_g^-)+H^++O_2(X^3\Sigma_g^-)$. The electronic states of the three fragments were identified as $O_2(a^1\Delta_g)+H(^2S)+O_2^+(X^2\Pi_g)$. The lowest CT channel with $O_2(X^3\Sigma_g^-)$ in the ground electronic state and the lowest inelastic (IE) channel with both O_2 molecules in the ground state, $O_2(X^3\Sigma_g^-)+H^++O_2(X^3\Sigma_g^-)$, must lead to repulsive interactions in the FC region and we have not studied them in this work. There is a hump like structure in the excited state curves which is a consequence of avoided or curve crossing with the higher lying excited states of same symmetry. To analyze this point in more detail we performed state-average calculations for the cis isomer low-lying electronic states in all possible symmetries. The associated PECs and their avoided crossings are shown in Figure 4.

Except for the ground state, all other states are involved in Landau-Zener type coupling with their respective excited states in the region between $3.5\text{\AA}$ and $5\text{\AA}$. The three-body collision process at sufficiently high collision energies will explore the avoided-crossing regions which can lead to various electronic energy and charge transfer processes. For example for the B_2 state, the calculated energy gap at the avoided crossing point, $R=4.4\text{\AA}$, is 50 meV and the same gap for B_1 and A_2 is 271 meV at $R=4.6\text{\AA}$. In a diabatic picture the inter-

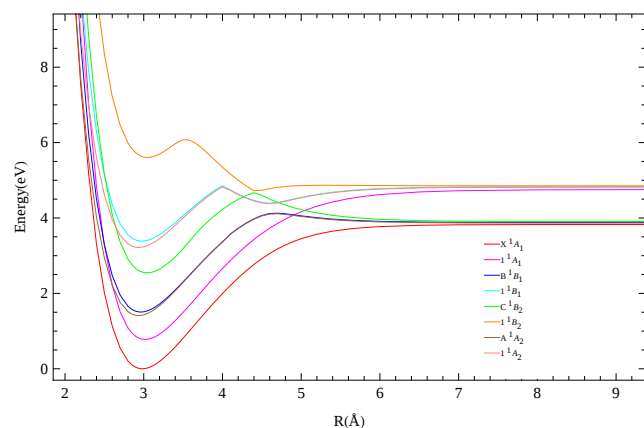


Fig. 4 State average PECs of ground and first excited states in singlet cis isomer for all spatial symmetries

Table 3 Assignment of electronic states to fragments from the 1st mode of dissociation of O_4H^+

O_4H^+ states	fragments
X^1A_1, A^1A_2	$O_2(a^1\Delta_g) + H(^2S) + O_2^+(X^2\Pi_g)$
C^1B_2, B^1B_1	$O_2(b^1\Sigma_g^+) + H(^2S) + O_2^+(X^2\Pi_g)$
$1^1A_1, 1^1A_2$	$O_2(b^1\Sigma_g^+) + H(^2S) + O_2^+(X^2\Pi_g)$
$1^1B_2, 1^1B_1$	$O_2(b^1\Sigma_g^+) + H(^2S) + O_2^+(X^2\Pi_g)$

action between the B_1 states is much stronger than for the B_2 and A_2 states. An interesting feature to note is the accidental near degeneracy that exists between ground and excited states of B_1 and A_2 symmetries over all regions of R . Lastly, this two state study shows two different asymptotic limits for all electronic states studied. The assignment to electronic states of the products is given in Table 3. In addition to being CT channels, notice the presence of the low-lying a and b states of molecular oxygen defining the asymptotes. The 2nd mode of dissociation (see Figure 2) is a two body fragmentation process. The fragments can be O_4/O_4^+ and H^+/H . This can be modelled as elementary two body collision process. Here too, we have performed state averaged calculations for the dissociative PECs in the case of the singlet cis isomer for X^1A_1 . The result of this calculation is shown in Figure 5. The x-axis denotes the vertical displacement of H^+/H up and down along the z -axis in the plane of the molecule. The minimum in the curve is at the equilibrium position of H^+/H which is slightly displaced towards the positive direction from zero of z -axis. This mode distinguishes itself from the 1st mode from the fact that it presents two asymptotic regions in the same surface a clear signature that a conical intersection characterizes these states. The positive region relates to $O_4 + H^+$ defined as entrance channel and the negative region relate to the CT channel. The CT channel is exothermic relative to the

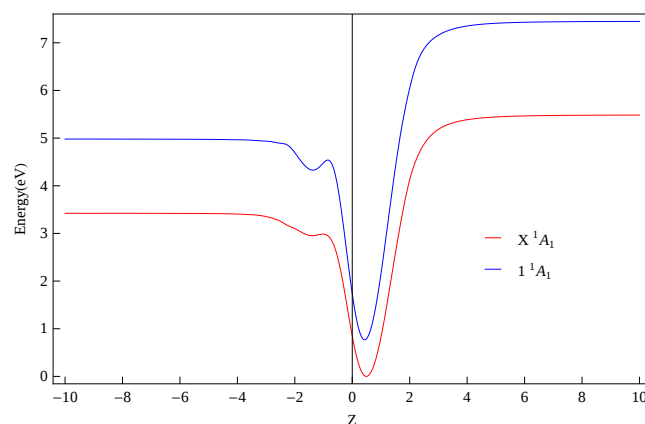


Fig. 5 State average PECs of ground and first excited states in singlet cis isomer for A_1 spatial symmetry

entrance channel by 2 eV in the ground state while for the excited state the calculated exothermicity is 2.5 eV. The excited state IE channel is endothermic by 2 eV relative to the same in the ground state while that of CT channel is endothermic by 1.5 eV. The small dip in both curves suggest the presence of a secondary minimum. They are not van der waals complexes because the intermolecular distance does not correspond to the long range region (well below $2\text{\AA}$). In fact, a test calculation reveals that optimization starting at this geometry finally ends in a minimum but we have not characterized them further. The assignment of electronic states to fragmented products is given in Table 4 (first two entries). Interestingly, another conical intersection characterizes the first excited state correlation on either side of vertical displacement connecting the neutral as well as the ionic O_2 dimer in their first excited states. Another obvious feature is that there exists no Landau-Zener type coupling in the PECs of two body dissociation unlike the three body case (1st mode).

In two body dissociation, the layout of PECs of different symmetries of singlet cis conformer can be known from the Figure 6. As expected different symmetries may cross each other and the fact that the asymptotic potentials do not coincide in the long range even if correlating to the same products is due to the difference in equilibrium geometrical parameters for different symmetries. B_1 and A_2 curves run closely parallel to each other particularly in the interaction region, a similar feature encountered in the 1st mode of dissociation. The correlation pattern for various symmetries are summarized in Table 4. Except for the ground state all other states of various symmetries in C_{2v} cis isomer correlate to their respective CT channel in both asymptotic regions. From the previous study,^{1,2} we recall that for the C_{2h} trans isomer the ground state correlates to the same products in both directions, ie, no conical intersection is present in that case. Other conical inter-

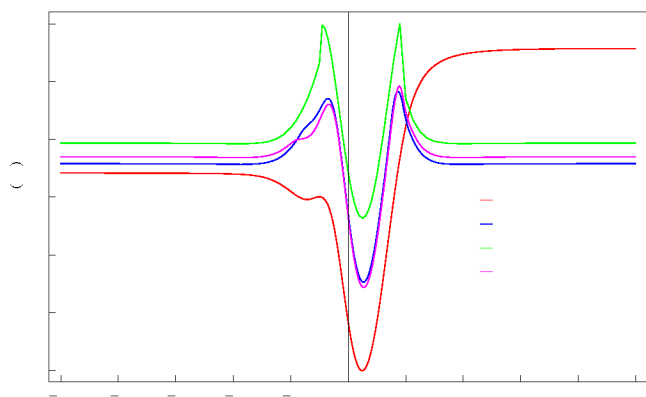


Fig. 6 Ground state PECs of different symmetries of singlet C_{2v} isomer in the 2nd mode

Table 4 Assignment of various electronic states to fragments from the 2nd mode of dissociation of O_4H^+ in all four symmetries. The fragments on the left correspond to negative values of Z and those on the right to positive

fragments	O_4H^+ states	fragments
$O_4^+(X^2A_1) + H(^2S)$	X^1A_1	$O_4(X^1A_1) + H^+$
$O_4^+(1^2A_1) + H(^2S)$	1^1A_1	$O_4(1^1A_1) + H^+$
$O_4^+(B^2B_1) + H$	B^1B_1	$O_4^+(B^2B_1) + H$
$O_4^+(C^2B_2) + H$	C^1B_2	$O_4^+(C^2B_2) + H$
$O_4^+(A^2A_2) + H$	A^1A_2	$O_4^+(A^2A_2) + H$

section occurs between the (X^1A_1) and (C^2B_2) states for positive vertical displacements which will allow CT processes.

The existence and identification of O_4H^+ through radioastronomy in interstellar medium (ISM) is an interesting proposal but so far no experimental work was devoted in that direction. It is believed that this theoretical paper can serve as source material for experimental groups who wish to take up such a challenging undertaking in the future. In this sense it is important to point out that considerable effort has been already invested in detecting molecular oxygen in the ISM.⁴⁻⁶ Usually, some highly intense rotational transition characteristic of a given species is recorded and compared with laboratory spectrum at low temperature, a condition prevailing at ISM and this is said to confirm the existence of those species in ISM. Therefore, we provide some fingerprint values which will serve as guide for the experimentalist to look for this molecule in ISM via rovibrational radioastronomy. In Table 1, rotational constants of stable C_{2h} isomer are given and it can be classified as asymmetric rotor. As two of the constants are very close to each other, it is justified to approximate asymmetric rotor as symmetric prolate rotor. The closed form expression for the energy level of symmetric prolate ro-

tor (within rigid rotor approximation) is given as

$$E(J, K) = BJ(J+1) + (A-B)K^2 \quad (4)$$

$$J = 0, 1, 2, \dots; K = 0, \pm 1, \pm 2, \dots \pm J$$

where A and B are rotational constants and J, K are rotational quantum numbers and $E(J, K)$ are expressed in GHz. The selection rules governing the quantum numbers J and K are

$$\left. \begin{array}{lll} \Delta J = 0, \pm 1 & \Delta K = 0 & K \neq 0 \\ \Delta J = \pm 1 & \Delta K = 0 & K = 0 \end{array} \right\} \quad (5)$$

For O_4H^+ $B=2.83$ GHz (average value), $A=46.67$ GHz. To report energy of absorption of most intense rotational peak subject to the selection rule given above, we need to find the most probable transition from J to $J+1$ level for $K=0$ case. To do it, we use the following formula based on Boltzmann distribution

$$\frac{N_J}{N_0} = (2J+1) e^{-\frac{BJ(J+1)}{k_b T}} \quad J = 0, 1, 2, \dots; K = 0 \quad (6)$$

$$\frac{N_J}{N_0} = 2(2J+1) e^{-\frac{BJ(J+1) + (A-B)K^2}{k_b T}} \quad J = 1, 2, \dots; K = \pm J \quad (7)$$

where $\frac{N_J}{N_0}$ is the number of molecules in the J^{th} level relative to the number in $J=0$, k_b is the Boltzmann constant expressed as 20.84 GHz K^{-1} and T is temperature in absolute scale. In Fig-

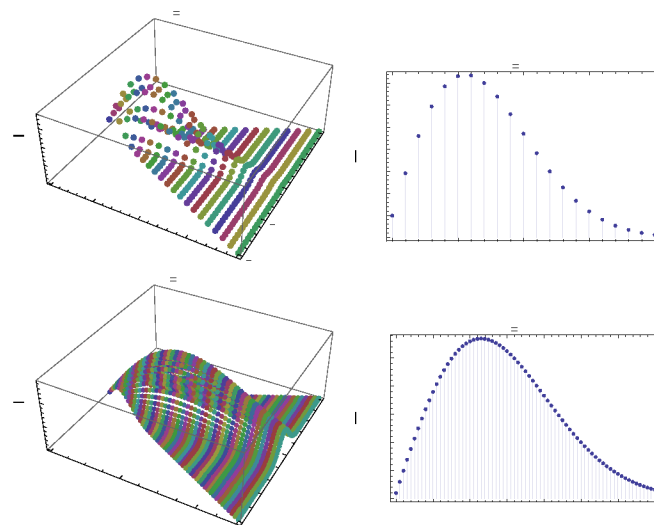


Fig. 7 Rotational population of O_4H^+ at two temperatures within rigid rotor approximation

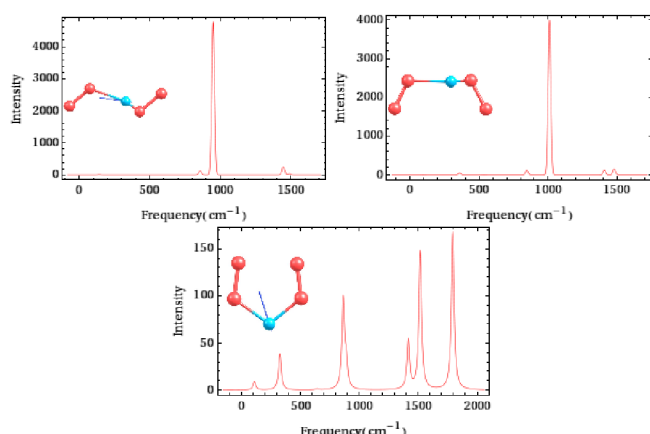
ure 7 relative populations as a function of J and K (left) and J alone (right) are plotted at 10K and 150K to look for J_{max} as obviously K_{max} is zero for prolate rotor as can be seen from the 3D plots irrespective of thermal conditions. The identified J_{max} are 6, 13 and 23 at 10K, 50K and 150K respectively. The

Table 5 CASSCF harmonic frequencies for singlet O_4H^+ isomers

C_{2h}	C_{2v}	C_s
42(A_u)	68(A_2)	107(A')
143(B_u)	94(A_1)	322(A')
265(A_g)	359(B_2)	348(A'')
587(A_g)	537(A_1)	639(A')
858(A_u)	847(B_1)	861(A'')
949 (B_u)	1010 (B_2)	887(A')
1447(B_u)	1409(A_1)	1414(A')
1474(A_g)	1480(B_2)	1516(A')
1489(B_u)	1498(A_1)	1793 (A')

energy of absorption at 10K corresponding to the most intense transition $J = 6 \rightarrow J = 7$ for $K=0$ is obtained as 39.6GHz and those at 50K and 150K corresponding to $J = 13 \rightarrow J = 14$, $J = 23 \rightarrow J = 24$ for $K=0$ are found out to be 79.2GHz and 136GHz. The range of temperatures covered are all relevant for ISM processes and in particular they are in the range mentioned in recent observations with the Herschel telescope^{4,5}. Although these estimates are only approximate they should give a first idea of where to look for.

Apart from rotational spectroscopy, vibrational spectroscopy could also be used to identify the presence of this molecule either in the laboratory or in ISM. In Figure 8, we

**Fig. 8** Calculated IR spectra of singlet O_4H^+ for C_{2h} , C_{2v} and C_s isomers. The most intense modes are shown.

have shown the calculated IR spectra for C_{2h} , C_{2v} and C_s isomers and one can clearly distinguish C_{2h} , C_{2v} structures from that of C_s . The corresponding spectral values are also given in the tabulated form in Table 5 where the number in bold is the frequency of the peak with maximum intensity. The C_{2h} molecule as a whole is non-polar while C_{2v} has slight dipole moment and C_s has appreciable dipole moment (see Table 1). In all the spectra, the most intense peak is associ-

ated with O-H stretching and the mode is shown as an inset. The exact frequencies are 949cm^{-1} , 1010cm^{-1} , 1793cm^{-1} which could be used as fingerprint values to identify and distinguish between the singlet O_4H^+ isomers in laboratory and ISM. Even though most stable trans structure is nonpolar, distinct strong peak arises due to induced dipole moment character for this mode. Similar is the case with cis isomer. For C_s case, one can see many intense peaks suggesting that many normal modes contribute to the change in dipole moment and anomalously high value of OH stretching frequency can be interpreted as due to the fact that this more asymmetric structure is closer to strongly bound fragments of O_2H^+ and O_2 so that the frequency approaches that of free O_2H^+ which is around 3000cm^{-1} .

3.2 MRCI results

The MRCI results are the extension of CASSCF results reported earlier in an effort to include dynamical correlation effects.^{1,2} The optimal structures and their molecular properties computed at this level are summarized in Table 6. The CI results agree well with CASSCF results in terms of geometrical shapes of multiplets and their ordering on relative energy scale (see Table 7). However, there are quantitative differences with respect to molecular and thermochemical properties. The bond length of O_2 is considerably shorter this time, most likely due to the reduced active space considered in this calculation. The singlet equilibrium structures exist in three forms: cis, trans and C_s structures with the same energy ordering found in the previous section once ZPE is included. Notice quantitative differences specifically in the stability of the C_s structure. It is interesting to analyze the case of the quintet state where accurate RCCSD(T) results are available. Compared with CASSCF the MRCI treatment corrects the geometrical parameters in the direction of a better agreement with RCCSD(T). This is clearly seen in the more symmetrical prediction for O-H distances and closer values for rotational constants. A more refined estimate of the binding energy of the trans C_{2h} molecule including higher level correlation is presented now. The Davidson's correction were not taken into account when reporting the energetics because its influence on single-quintet splitting was not substantial when the size of active space is enlarged. In fact, in a full valence CI calculation, invoking Davidson's correction do not alter the splitting, thus suggesting that reporting the energetics based on CI with single and double excitation will be reliable and trustworthy. Using the small active space at the level of hybrid CI/RCCSD(T) we obtain a value of 18.2Kcalmol^{-1} at 0K and thermal corrections at 300K yields 18.6Kcalmol^{-1} . At this level we found that the contribution of the s-q splitting to the bond breaking enthalpy increases by a fixed amount, 0.5Kcalmol^{-1} in the interval 300-500K compared to the 0K value. This fact can be

Table 6 Molecular properties of equilibrium structures of singlet, triplet and quintet states at MRCI level of theory

Electronic states	r(O-O)	r(O-H)	$\angle(\text{O-H-O})$	$\angle(\text{O-O-H})$	$\mu(\text{D})$	A,B,C (GHz)	ZPE(cm^{-1})
X^1A_g (trans)	1.18	1.21	180.0	116.9	0.00	2.8, 51.6, 3.0	3835
X^1A_1 (cis)	1.18	1.21	173.4	117.3	0.04	3.0, 30.0, 3.3	3863
X^1A'	1.20	1.06	135.8	108.1	1.26	5.0, 6.7, 22.0	4625
	1.17	1.48		100.1			
a^3B_u (trans)	1.18	1.21	180.0	117.1	0.00	2.8, 51.8, 3.0	3746
a^3B_2 (cis)	1.18	1.21	172.3	117.9	0.08	3.0, 30.9, 3.3	3737
b^5A	1.18	1.32	175.8	121.1	1.20	2.8, 2.9, 44.3	3799
	1.19	1.13		116.3			

Table 7 Relative energies (meV) of various multiplets without/with ZPE correction

Electronic states	w/o ZPE	with ZPE
X^1A_g	0	0
X^1A_1	16.58	19.99
X^1A'	85.13	183.06
a^3B_u	52.80	41.67
a^3B_2	73.03	60.86
b^5A	152.50	148.00

Table 8 MRCI harmonic frequencies for singlet O_4H^+ isomers

C_{2h}	C_{2v}	C_s
42(A_u)	53(A_2)	106(A')
123(B_u)	93(A_1)	337(A'')
264(A_g)	352(B_2)	356(A')
595(A_g)	530(A_1)	627(A')
861(A_u)	845(B_1)	775(A'')
870(B_u)	914(B_2)	1326(A')
1467(B_u)	1440 (A_1)	1574(A')
1745 (B_u)	1743(B_2)	1791(A')
1747(A_g)	1757(A_1)	2358 (A')

put to use in further refining above obtained enthalpy. A large scale MRCI calculation of the s-q splitting using the full valence active space were carried out. For practical purposes we use the ZPE corrections from the smaller active space MRCI calculations. The s-q splitting increases by 0.5 kcal/mol compared with CASSCF result. Our final estimate of the binding energy is 20 Kcalmol⁻¹ which brings it in closer agreement to the experimental value of 20.6 Kcalmol⁻¹.^{22,23}

In Table 7 we see that all the multiplet states are close to each other as expected and in particular, the C_s structure is highly distinguished by its ZPE corrected energy and is therefore isolated from the other two equilibrium geometries in the ground state PES in contrast to CASSCF result where all singlet states were close in energy. MRCI prediction of vertical excitation energies of X^1A_g state with the large active space to dipole allowed transition states of B^1A_u and C^1B_u were calculated and the calculated vertical energies are 1790 meV and 2851 meV for 1A_u and 1B_u from X^1A_g state to be compared with the CASSCF values of 1510 meV and 2644 meV reported in Table 2. The magnitude of vertical energies indicate that 1A_u and 1B_u states are amenable for visible spectral detection.

It has been reported⁷ that O_2H^+ is elusive to detection in the ISM because its formation reaction $\text{H}_3^+ + \text{O}_2 \rightarrow \text{O}_2\text{H}^+ + \text{H}_2$ is nearly thermoneutral. In previous work^{1,2} it was noted that due to the much larger proton affinity(PA) of O_4 compared with that of O_2 the protonated molecular oxygen dimer O_4H^+ could serve as a tracer for oxygen. The formation reaction in

this case, $\text{H}_3^+ + \text{O}_4 \rightarrow \text{O}_4\text{H}^+ + \text{H}_2$ is clearly exothermic(-18 kcal/mol at RCCSD(T)/CASSCF level^{1,2}) and hence provides the hope that it could be detected in ISM. Our combined estimate for the exothermicity with reduce active space is -18.5 Kcalmol⁻¹ and the singlet-quintet splitting for O_2 dimer used in this calculation was taken from Carmona-Novillo et al.²⁴. Estimating with single point large CI calculation performed on the relevant equilibrium structure, we obtain a value of -19.4 Kcalmol⁻¹ which is our best estimate.

Now is the time to proceed to compare the MRCI IR spectra with that computed at CASSCF level in the previous section. Again it is possible to distinguish between different structures in the singlet state because of the presence of characteristic peaks for each structure as shown in Figure 9 where the molecular model shows the normal mode of maximum intensity. For comparative purpose the CI frequencies are listed in Table 8 with most intense frequency in bold. The 9 modes of vibration is represented by irreducible representation for the three isomers as follows : $3A_g + 2A_u + 4B_u, 4A_1 + 3B_2 + A_2 + B_1, 7A' + 2A''$. Regarding the frequency positions there are quantitative differences specially for the highest frequency modes and this can again be understood on the basis of the smaller active space involved in the MRCI calculations which lead to shorter O-O and O-H bond lengths and thus associated higher frequencies. The relative intensities also vary significantly such

that the most intense peaks differ between both methods perhaps not surprisingly. In the case of the C_{2h} structure there are two nearly-degenerate vibrations of symmetric and asymmetric O-O stretching, with the latter one being IR active. The asymmetric stretching of each O_2 monomer also has significant vibrational contribution from the movement of H^+ and 1745cm^{-1} is the predicted frequency for this mode with maximum intensity. Another peak at 122cm^{-1} with less intensity relates to asymmetric bending mode of H^+ in the presence of O_2 dimer. These modes alone produce induced dipole moment in an otherwise non polar molecule and hence are IR active. The totally symmetric IR inactive mode at 595cm^{-1} lies along the reaction coordinate of three body dissociation. The most intense peak for the C_{2v} structure is symmetrical O-H-O bending along vertical direction occurring at 1440cm^{-1} with sizeable dipole change and next peak at 1743cm^{-1} correspond to asymmetric stretching of O_2 monomers. The spectra of C_s geometry contains many peaks of moderate intensity unlike other two isomers. The most intense peak at 2058cm^{-1} relates to O-H stretching of O_2H^+ fragment within O_4H^+ complex and the other peaks of sufficient intensity occur at 1574cm^{-1} , 1790cm^{-1} corresponding to symmetric and asymmetric stretches of O_2 monomers. A peak at 356cm^{-1} relates to the vibrational dissociation mode between bound O_2H^+ and O_2 units.

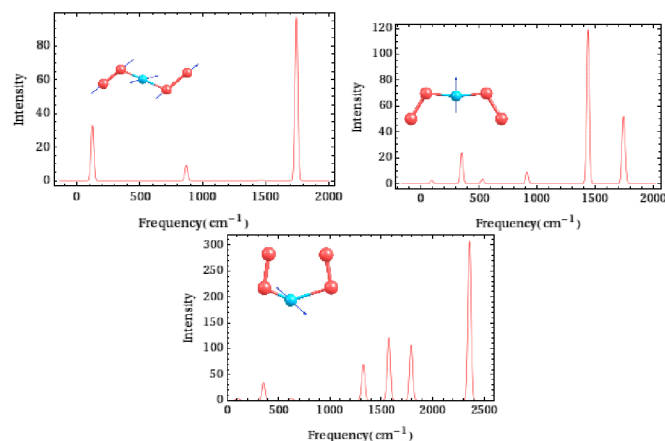


Fig. 9 Calculated IR spectra of singlet O_4H^+ for C_{2h} , C_{2v} and C_s isomers

The ground state PECs were computed at MRCI level of theory for the two modes of dissociation shown in Figure 2. In the first mode, the computed PECs are presented in Figure 10. Though it is a three body dissociation mode for symmetrical structures, for asymmetrical structures this mode produces two dissociated fragments at the asymptotic region. The equilibrium intermolecular distance (R) in the quintet state is larger by $1.36\text{\AA}$ than the C_s singlet and this is due first to the different conformations in particular the twisted nonpla-

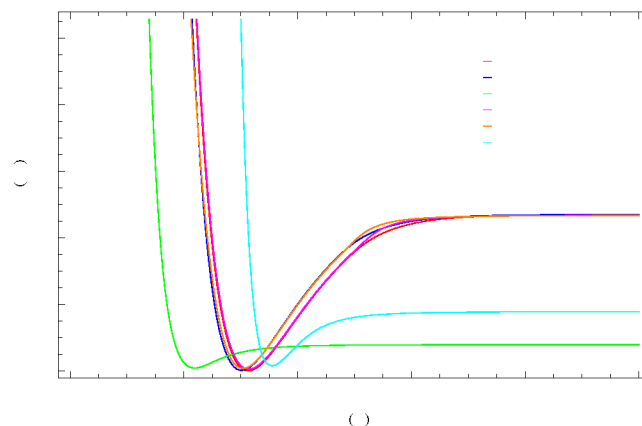


Fig. 10 Ground state PECs for all multiplets as a function of R in 1st mode of dissociation

Table 9 Assignment of electronic states to fragments from the 1st mode of dissociation of O_4H^+

O_4H^+ state	dissociated fragments
X^1A'	$O_2H^+(X^3A'')+O_2(X^3\Sigma_g^-)$
X^1A_1, X^1A_g	$O_2(a^1\Delta_g)+H(^2S)+O_2^+(X^2\Pi_g)$
a^3B_2, a^3B_u	$O_2(a^1\Delta_g)+H(^2S)+O_2^+(X^2\Pi_g)$
b^5A	$O_2H^+(X^3A'')+O_2(X^3\Sigma_g^-)$

narity of the quintet state but more importantly it also reflects a stronger binding in the singlet state. This is further seen in the well depths 0.7 eV and 1.6 eV for the quintet and singlet respectively. As stated before the difference in energy at the asymptotes reflects the different geometries of the fragments which are fixed at the respective equilibrium values in the complex. The three body dissociation is significantly more exothermic since it involves breaking one more bond which can be anticipated to be of chemical strength: the O_2H bond. The exothermicities for all multiplets of the C_{2h} and C_{2v} structures are roughly 4.5 eV . The cis and trans singlet and triplet PECs are close-lying for all values of R their average separation being about 50 meV which leaves open the possibility of intersystem crossing effects in the photochemical and collision dynamics of the system. The asymptotic correlation of electronic states is given in Table 9. As stated in the previous section in the three-body breakup O_2 is formed in the first electronic excited state which implies a conical intersection with the state correlating with O_2 in the ground state most likely in the long range region due to a repulsive interaction in the latter state.

The MRCI results for the 2nd mode of dissociation for all multiplets are shown in Figure 11 and its correlation analysis are given in Table 10. As can be seen from Figure 11 there are two asymptotic regions for this dissociation pathway. The C_{2h}

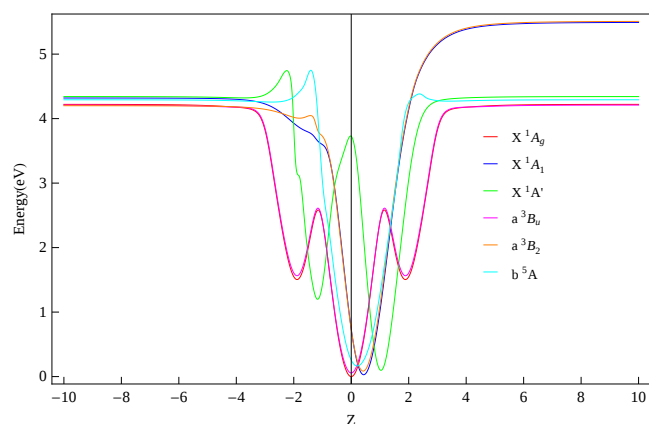


Fig. 11 Ground state PECs in the 2nd mode of dissociation for singlet, triplet and quintet states

Table 10 Assignments of different electronic states of dissociated products to a given electronic state of O_4H^+ in second mode. The fragments on the left correspond to negative values of Z and those on the right to positive

fragments	state	fragments
$O_4^+(X^2A') + H(^2S)$	X^1A'	$O_4^+(X^2A') + H(^2S)$
$O_4^+(X^2A_1) + H(^2S)$	X^1A_1	$O_4(X^1A_1) + H^+$
$O_4^+(X^2A') + H(^2S)$	X^1A_g	$O_4^+(X^2A') + H(^2S)$
$O_4^+(X^2A_1) + H(^2S)$	a^3B_2	$O_4(a^3B_2) + H^+$
$O_4^+(X^2B_u) + H(^2S)$	a^3B_u	$O_4^+(X^2B_u) + H(^2S)$
$O_4^+(X^4A) + H(^2S)$	b^5A	$O_4^+(X^4A) + H(^2S)$

curve has a dip around $2.5\text{\AA}$ which is most likely due to the formation of distorted O_2H^+ when H^+ is moved vertically up and down with respect to O-H-O vector but we notice that the corresponding curve at CASSCF level presented in previous work^{1,2} did not show it. The C_s curve shows an asymmetrical double-minimum structure as can be expected from its structure. This also appeared at CASSCF level. Finally for the C_{2v} structure we again see that both singlet and triplet states correlate to different asymptotic limits which are summarized in Table 10. An important property for this work is the proton affinity (PA) of O_2 dimer which in the end determines the exothermicity of the protonation reaction with H_3^+ . According to the hybrid estimate based on RCCSD(T)/CI/aug-cc-pVTZ with reduced active space the value is 5.12 eV, much higher than the experimental value²⁵ of 4.38 eV for the PA of O_2 and the theoretical value of 4.36 eV estimated at RCCSD(T)/aug-cc-pVTZ level. By enlarging the active space size of calculation, we obtain 5.16 eV.

The calculation of rotational transitions obtained at MRCI level of theory is similar as described above and we summarize the main results. Here, $B=2.9\text{GHz}$ (average value) and

$A=51.55\text{GHz}$. Therefore, applying Eq 6, Eq 7 and Eq 5 yields $J_{max} = 6, 13, 23$ at 10K, 50K and 150K respectively. The most probable transitions are for $J = 6 \rightarrow J = 7$ 40.6GHz, for $J = 13 \rightarrow J = 14$ 81.2GHz and for $J = 23 \rightarrow J = 24$ 139.2GHz. The fundamental weak transition $J = 0 \rightarrow J = 1$ at 5.8GHz may also be of interest to astronomers. This shows that when predicting rotational spectrum CASSCF and MRCI levels of theory provide very similar results for the approximated prolate symmetric rotor. Thus, the matching of results lends more reliability to the calculation performed in this work which should be of help for the astrophysical search in the ISM.

4 Summary and Conclusions

A detailed theoretical characterization of the O_4H^+ novel species were carried out and it could be used as a tracer for molecular oxygen in the ISM and which presents bonding, spectroscopic and dynamical features which make it interesting in its own right. It was shown that by a judicious combination of single and multireference methods it is possible to accurately predict various thermochemical properties as compared with the limited available experimental data. The feasibility of forming O_4H^+ from the exothermic reaction $H_3^+ + O_4 \rightarrow O_4H^+ + H_2$ has been confirmed by extending the previous study to include higher levels of electron correlation.

The study of two and three body dissociation processes indicate a rich variety of possibilities for dynamical processes such as conical intersections, production of molecular oxygen in low-lying excited states and charge transfer processes, all of which are of relevance to characterize the photochemistry and collision dynamics of this species.

In order to facilitate its identification in laboratory and radioastronomy search we have characterized electronic, vibrational and rotational transitions. The former fall in the range of visible and near infrared making them amenable for laboratory studies, the vibrational spectra shows intense bands associated with hydrogen motion which distinguish between the three isomeric forms. Finally we present rotational transitions at relevant temperatures for radioastronomy detection and hope this will motivate further studies.

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