

# Ab initio studies on complexes of ozone with diatomic molecules

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## Research Article

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# Abstract

Møller-Plesset MP2 and coupled cluster CCSD(T) calculations using the aug-cc-pVQZ basis set were performed on structures, energies and harmonic vibrational frequencies of the complexes  $O_3$ -HF,  $O_3$ -HCl,  $O_3$ -OH,  $O_3$ -H<sub>2</sub>,  $O_3$ -N<sub>2</sub>,  $O_3$ -CO,  $O_3$ -O<sub>2</sub>,  $O_3$ -F<sub>2</sub>,  $O_3$ -Cl<sub>2</sub> and  $O_3$ -FCl. Most complexes have C<sub>s</sub> symmetry, with the symmetry plane being the plane of ozone (for the hydrogen bonded  $O_3$ -HF to  $O_3$ -OH complexes) or the plane perpendicular to ozone (for most others). Dissociation energies  $D_e$  range from 718 cm<sup>-1</sup> to 1137 cm<sup>-1</sup> for the hydrogen bonded complexes  $O_3$ -HCl to  $O_3$ -HF, and from 200 cm<sup>-1</sup> to 477 cm<sup>-1</sup> for non-hydrogen bonded complexes from  $O_3$ -H<sub>2</sub> to  $O_3$ -Cl<sub>2</sub>. Due to complex formation harmonic vibrational frequencies of the diatomic molecules are red shifted in the hydrogen bonded complexes, from 39 cm<sup>-1</sup> for  $O_3$ -OH to 156 cm<sup>-1</sup> for  $O_3$ -HF. Corresponding infrared intensities increase by a factor of about five.

## Introduction

The importance of ozone for our climate has been well documented [1–4]. Although occurring at very low concentration in the atmosphere, ozone absorbs most of the harmful UV radiation from the sun. Much work has been done to reverse ozone depletion [5, 6].

It was recognized early that complexes of ozone with other gases in the atmosphere may play a role in ongoing chemical reactions [7]. Complexes of ozone with argon [8] (1979) and ethylene [9] (1989) were studied by microwave spectroscopy. Early theoretical work has been done on ozone-water [10] and ozone-acetylene complexes [11] (1991).

In this work, high level quantum mechanical methods are employed to study the structures and energetics of complexes of ozone with the diatomic molecules H<sub>2</sub>, N<sub>2</sub>, CO, O<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub>, HF, HCl, FCl, and with the hydroxyl radical OH.

High-level theoretical work is available on very few complexes of ozone with diatomic molecules. In a recent publication by Kalugina et al. [12] coupled cluster five-dimensional potential energy surfaces were constructed for the  $O_3$ -N<sub>2</sub> complex. A dissociation energy of 348.88 cm<sup>-1</sup> was obtained for the global minimum, and six additional stable structures could be identified.

## Methods

Due to the ground state of ozone having multiconfigurational character [13–15], low-level computational methods cannot be used. Alcamí et al. [16] found that that ozone and complexes with ozone are not described well by RHF methods and by other methods lacking proper correlation. However, QCI, CASSCF, and in particular CCSD(T) methods, as used here, appear to work well.

Both Møller-Plesset MP2 [17] and coupled cluster singles, doubles and perturbative triples CCSD(T) methods [18, 19], with the augmented correlation consistent aug-cc-pVQZ (AVQZ) basis sets, will be used.

In MP2 calculations all geometrical parameters are to be optimized. With the CCSD(T) method the geometry of the monomers will be held fixed at their optimized monomer values. Corrections for the basis set superposition error (BSSE) using the method of Boys and Bernardi [20] are applied to all dissociation energies. In several cases extrapolations to the complete basis set (CBS) limit are to be performed. They are based on the exponential method proposed by Halkier et al. [21], using CCSD(T)/AVXZ energies with X = D, T, Q. Harmonic vibrational frequencies are obtained by the MP2/AVQZ and CCSD(T)/AVDZ methods. All calculations are performed using the Gaussian 16 [22] and MOLPRO [23, 24] computer programs.

Table 1 Optimized geometries and harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) of ozone.

MP2/AVQZ and CCSD(T)/AVQZ results

Method	R(O-O) (Å)	Angle (degree)	Freq. v1 $A_1$	Freq. v2 $A_1$	Freq. v3 $B_2$
MP2	1.2780	116.81	1168	747	2211
CCSD(T)	1.2686	117.18	1169	727	1077
Expt.	1.2717 <sup>a</sup>	116.47 <sup>a</sup>	1135 <sup>b</sup>	716 <sup>b</sup>	1089 <sup>b</sup>
a. Tanaka et al. [25]					
b. Barbe et al. [26]					

Tests of geometries and harmonic vibrational frequencies of ozone have been done with both MP2 and CCSD(T) methods, in order to check on the suitability of these methods for the forthcoming calculations on ozone complexes. The results, shown in Table 1, indicate that the geometry of ozone is well described by both methods. Whereas the v1 and v2 frequencies of ozone calculated by the MP2 method are in good agreement with experimental values, the v3 frequency is in substantial error. The CCSD(T) frequencies, however, are close.

## Results For Structures And Dissociation Energies

BSSE corrected MP2/AVQZ and CCSD(T)/AVQZ dissociation energies for complexes of ozone studied in this work are given in Table 2.

Table 2 BSSE corrected MP2/AVQZ and CCSD(T)/AVQZ dissociation energies  $D_e$  ( $\text{cm}^{-1}$ ) for complexes with ozone

System	Symm.	D <sub>e</sub> -MP2	D <sub>e</sub> -CCSD(T)
O <sub>3</sub> -HF	Cs-A cis	1140.1	1137.1 <sup>a</sup>
O <sub>3</sub> -HF	Cs-A trans	1090.8	1079.7
O <sub>3</sub> -HCl	Cs-A cis	793.3	718.3
O <sub>3</sub> -HCl	Cs-A trans	743.5	646.6
O <sub>3</sub> -OH	Cs-A cis	743.8	753.4
O <sub>3</sub> -OH	Cs-A trans	598.1	575.3
O <sub>3</sub> -H <sub>2</sub>	Cs-B inpl	255.6	194.9
O <sub>3</sub> -H <sub>2</sub>	Cs-B ppd	278.2	199.7
O <sub>3</sub> -N <sub>2</sub>	Cs-B inpl	523.5	335.4 <sup>b</sup>
O <sub>3</sub> -N <sub>2</sub>	Cs-B ppd	458.0	214.2
O <sub>3</sub> -O <sub>2</sub>	Cs-B inpl	344.2	248.8
O <sub>3</sub> -O <sub>2</sub>	Cs-B ppd	352.2	229.8
O <sub>3</sub> -CO	Cs-B inpl	602.1	433.5
O <sub>3</sub> -CO	C <sub>1</sub> ppd	373.3	235.5
O <sub>3</sub> -F <sub>2</sub>	Cs-B inpl	296.0	259.7
O <sub>3</sub> -F <sub>2</sub>	C <sub>1</sub> ppd	329.0	249.8
O <sub>3</sub> -Cl <sub>2</sub>	Cs-B inpl	728.2	476.7
O <sub>3</sub> -Cl <sub>2</sub>	C <sub>1</sub> ppd	687.6	409.3
O <sub>3</sub> -FCl	Cs-B inpl	520.7	441.7

a. CBS value is 1142.5 cm<sup>-1</sup>

b. CBS value is 328.1 cm<sup>-1</sup>

In most cases, the stable structures have C<sub>s</sub> symmetry. There are two different planes of symmetry. One is the plane of O<sub>3</sub>, to be named Cs-A, the other the plane perpendicular to the O<sub>3</sub> plane, named Cs-B.

The stable structures (no imaginary vibrational frequencies) of hydrogen bonded complexes, like  $O_3$ -HF, have all atoms lying in the Cs-A plane, with the diatomic molecule in cis or trans orientation relative to  $O_3$  (Table 2).

Stable structures of non-hydrogen bonded complexes, like  $O_3$ - $N_2$ , have the diatomic molecule,  $N_2$  in this case, placed in the Cs-B plane (inplane) or perpendicular to the Cs-B plane (ppd) (Table 2). Structures of non-hydrogen bonded complexes located in the Cs-A plane, in both cis and trans orientations, have much lower dissociation energies, and are not always stable as judged by calculated frequencies (results not included in Table 2, but mentioned in text).

## Hydrogen bonded $O_3$ -HF, $O_3$ -HCl and $O_3$ -OH complexes

IR spectra by Andrews et al. [27] showed that the terminal oxygens of ozone in the  $O_3$ -HF complex are not equivalent, implying that HF is attached to one of the terminal oxygens. For  $O_3$ -HF,  $O_3$ -HCl and  $O_3$ -OH planar structures in the Cs-A plane, the plane of  $O_3$ , were investigated. There is a cis form with the diatomic molecule located inside  $O_3$  (Fig. 1a for  $O_3$ -HF), and a trans form with H located outside  $O_3$  (Fig. 1b for  $O_3$ -HF).

A very large  $D_e$  of  $1137\text{ cm}^{-1}$  was found for cis  $O_3$ -HF, and a slightly smaller one,  $1080\text{ cm}^{-1}$ , for trans  $O_3$ -HF (CCSD(T) values). The CBS dissociation energy for the Cs-A cis structure of  $O_3$ -HF is  $1142\text{ cm}^{-1}$ , very close to the BSSE adjusted value. The dissociation energy for  $O_3$ -HCl is calculated to be  $718\text{ cm}^{-1}$  for the cis, and  $647\text{ cm}^{-1}$  for the trans structure. Dissociation energies obtained for  $O_3$ -OH, with  $753\text{ cm}^{-1}$  for cis and  $575\text{ cm}^{-1}$  for trans, are similar to the  $O_3$ -HCl values. Frequency calculations showed that both cis and trans structures of these three complexes are stable.

Using QCISD(T)/6-311++G(d,p)//QCISD/6-311+G(d) methods Tachikawa et al. [28] obtained for  $O_3$ -HF a dissociation energy of  $1190\text{ cm}^{-1}$  for the cis structure, close to the present result, and  $1260\text{ cm}^{-1}$  for the trans structure, exceeding the present value.

Bulanin et al. [29] performed IR spectroscopic studies on the  $O_3$ -HCl molecular complex in liquid argon, and also reported calculated dissociation energies. Using the QCISD/6-311++G(2d,2p) method they obtained for the cis structure a calculated  $D_e$  of  $6.3\text{ kJ/mol}$  or  $526\text{ cm}^{-1}$ , compared to  $718\text{ cm}^{-1}$  from the present calculations.

Mansergas and Anglada [30] studied theoretically the reaction between  $O_3$  and OH, obtaining with the CCSD(T)/AVTZ//QCISD/6-311+G(2df,2p) method a dissociation energy of  $2.57\text{ kcal/mol}$  or  $899\text{ cm}^{-1}$  for the cis  $O_3$ -OH complex, a value much higher than found in this work.

## $O_3$ - $H_2$ , $O_3$ - $N_2$ and $O_3$ - $O_2$ complexes

Geometry optimizations were started using the MP2 method at a lower level of basis set, with no symmetry constraints. All parameters including bond distances and angles of the monomers were optimized. Several different starting geometries were chosen.

For each of the three complexes optimizations resulted in two stable structures having Cs-B symmetry, where Cs-B is the plane perpendicular to the plane of ozone. The structures labelled "inpl" have both diatomic atoms lying in this plane, whereas the structures labelled "ppd" have the (homonuclear) diatomic molecule placed perpendicular to this plane (see Figs. 2a and 2b for O<sub>3</sub>-N<sub>2</sub> inpl and ppd, respectively).

For both structures of O<sub>3</sub>-H<sub>2</sub> CCSD(T) values for the dissociation energies D<sub>e</sub> are close to 200 cm<sup>-1</sup> (CCSD(T) values). No literature values were found on O<sub>3</sub>-H<sub>2</sub> complexes.

The D<sub>e</sub> value of 335 cm<sup>-1</sup> obtained for inplane O<sub>3</sub>-N<sub>2</sub> is close to the value obtained by Kalugina et al. (349 cm<sup>-1</sup>) [12]. The CBS dissociation energy for the inplane structure of O<sub>3</sub>-N<sub>2</sub> is 328 cm<sup>-1</sup>. For perpendicular O<sub>3</sub>-N<sub>2</sub> D<sub>e</sub> is much lower (214 cm<sup>-1</sup>). Inplane and perpendicular triplet O<sub>3</sub>-O<sub>2</sub> complexes have D<sub>e</sub>'s from 230 to 250 cm<sup>-1</sup>.

Structures with all atoms lying in the Cs-A plane, the plane of ozone, were investigated by MP2 methods. For O<sub>3</sub>-N<sub>2</sub> the BSSE adjusted MP2/AVQZ D<sub>e</sub> is 189 cm<sup>-1</sup> for the cis structure and 217 cm<sup>-1</sup> for the trans structure. For O<sub>3</sub>-O<sub>2</sub> the values of D<sub>e</sub> are 178 cm<sup>-1</sup> for cis and 165 cm<sup>-1</sup> for trans (MP2/AVQZ values). Cs-A planar minima for O<sub>3</sub>-H<sub>2</sub> could not be obtained.

Gadzhiev et al. [31] performed CCSD and CCSD(T) calculations on covalently bound molecules and van der Waals complexes of O<sub>n</sub> for n ≤ 6. For the triplet O<sub>3</sub>-O<sub>2</sub> cis and trans Cs-A complexes only planar structures were considered. Using the CCSD/cc-pVTZ method dissociation energies of 0.7 and 1.1 kJ/mol (59 and 92 cm<sup>-1</sup>) were reported for the cis and trans structures, respectively, values smaller than found here.

## O<sub>3</sub>-CO complex

As for the previous complexes, the inplane structure of O<sub>3</sub>-CO in Cs-B symmetry is found to be stable. It has a higher dissociation energy, 433 cm<sup>-1</sup>, than O<sub>3</sub>-N<sub>2</sub> and O<sub>3</sub>-O<sub>2</sub>.

Due to CO not being a homonuclear diatomic molecule, its ppd structure cannot have C<sub>s</sub> symmetry. In the optimized C<sub>1</sub> structure, O<sub>3</sub>-CO is close to a ppd configuration (Fig. 3). It has a lower dissociation energy of 235 cm<sup>-1</sup>.

The Cs-A planar structures of the O<sub>3</sub>-CO complex have MP2/AVQZ dissociation energies of 177 cm<sup>-1</sup> for the cis and 159 cm<sup>-1</sup> for the trans arrangement, compared with much higher values for the Cs-B complexes.

Raducu et al. [32] performed FTIR spectroscopy on the O<sub>3</sub>-CO complex in an argon matrix. They observed a vibration at 2140.44 cm<sup>-1</sup>, 2 cm<sup>-1</sup> above the CO frequency, concluding that O<sub>3</sub>-CO is a weakly bound complex. No literature on structures and energies of the O<sub>3</sub>-CO complex was found.

## O<sub>3</sub>-F<sub>2</sub> and O<sub>3</sub>-Cl<sub>2</sub> complexes

For both systems, geometries for inpl (F<sub>2</sub> or Cl<sub>2</sub> in Cs-B plane) and ppd (F<sub>2</sub> or Cl<sub>2</sub> perpendicular to Cs-B plane) structures were optimized. The inplane structures were found to be stable, with dissociation energies of 260 cm<sup>-1</sup> for O<sub>3</sub>-F<sub>2</sub> and 477 cm<sup>-1</sup> for O<sub>3</sub>-Cl<sub>2</sub>. However, for both complexes the ppd structures in C<sub>s</sub> symmetry are not stable. Lowering their symmetry to C<sub>1</sub> gave in both cases stable structures, with dissociation energies of 250 cm<sup>-1</sup> for ppd-O<sub>3</sub>-F<sub>2</sub> and 409 cm<sup>-1</sup> for ppd-O<sub>3</sub>-Cl<sub>2</sub>, both slightly lower than the corresponding inplane values. The geometry of these C<sub>1</sub> structures deviates slightly from C<sub>s</sub> symmetry (see Fig. 4 for O<sub>3</sub>-F<sub>2</sub>).

As in previous cases, structures restricted to lie in the O<sub>3</sub> plane, Cs-A, have lower dissociation energies. The BSSE adjusted MP2/AVQZ values for O<sub>3</sub>-F<sub>2</sub> are 261 cm<sup>-1</sup> for cis and 286 cm<sup>-1</sup> for trans, compared with 296 and 300 cm<sup>-1</sup> for the Cs-B structures. For O<sub>3</sub>-Cl<sub>2</sub> the Cs-A dissociation energies are 637 cm<sup>-1</sup> for the cis and 629 cm<sup>-1</sup> for the trans structures, similar to 728 and 688 cm<sup>-1</sup> values for the Cs-B structures. The differences between Cs-A and Cs-B dissociation energies for both O<sub>3</sub>-F<sub>2</sub> and O<sub>3</sub>-Cl<sub>2</sub> are much smaller than for the previously described complexes.

Schrivier-Mazzuoli et al. [33] performed FTIR studies on mixtures of O<sub>3</sub> with Cl<sub>2</sub> and Br<sub>2</sub>. There is, however, no mention of observed O<sub>3</sub>-Cl<sub>2</sub> or O<sub>3</sub>-Br<sub>2</sub> complexes. Literature on structures and energies of O<sub>3</sub>-F<sub>2</sub> or O<sub>3</sub>-Cl<sub>2</sub> complexes could not be found.

## O<sub>3</sub>-FCl complex

The inplane structure with FCl lying in the Cs-B plane has a dissociation energy of 442 cm<sup>-1</sup>, and is found to be stable (Fig. 5). Optimization of a C<sub>1</sub> structure starting with FCl perpendicular to this plane led to the inplane structure. Structures with FCl lying in the Cs-A plane have much lower dissociation energies. For the cis structure a MP2/AVQZ value of 109 cm<sup>-1</sup>, and for the trans structure a value of 273 cm<sup>-1</sup> was obtained, compared to 521 cm<sup>-1</sup> for the Cs-B structure. No literature was found on complexes of ozone with chlorine monofluoride.

## Results For Geometries

### O<sub>3</sub>-HF, O<sub>3</sub>-HCl, O<sub>3</sub>-OH complexes

Table 3 Geometries of cis and trans O<sub>3</sub>-HF, O<sub>3</sub>-HCl, O<sub>3</sub>-HO (O<sub>3</sub>-HB) complexes in Cs-A (O<sub>3</sub>) plane. Distances in Å, angles in degree<sup>a</sup>

System	Symm.	O1-X2	X1-O1-H	O1-H-B	Shortest dist.
O <sub>3</sub> -HF	Cs cis	2.730	162.90	161.59	O2-H 1.968
O <sub>3</sub> -HCl	Cs cis	2.924	168.19	164.59	O2-H 2.253
O <sub>3</sub> -OH	Cs cis	3.317	171.50	160.65	O2-H 2.259
O <sub>3</sub> -HF	Cs trans	2.580	76.15	144.95	O2-H 1.913
O <sub>3</sub> -HCl	Cs trans	2.754	71.33	140.02	O2-H 2.170
O <sub>3</sub> -OH	Cs trans	3.172	75.50	135.68	O2-H 2.119
a. X1 is a point on the C <sub>2</sub> symmetry axis of O <sub>3</sub> above the central oxygen.					
X2 is the midpoint of the HB diatomic molecule. O1 is the central oxygen of O <sub>3</sub> .					

In Table 3 geometrical parameters are listed for the hydrogen bonded O<sub>3</sub>-HF, O<sub>3</sub>-HCl and O<sub>3</sub>-HO (O<sub>3</sub>-HB) complexes. As expected, the shortest distances between a terminal oxygen of ozone and hydrogen is lowest for O<sub>3</sub>-HF, increasing for O<sub>3</sub>-HCl and more so for O<sub>3</sub>-OH. The distances from the central oxygen O1 to the midpoint of the diatomic HB (O1-X2) are about 0.6 to 0.8 Å longer. The X1-O1-H angles are large for the cis structures, but small for the trans structures due to their different arrangement. The O1-H-B angles are 160° to 170° for the cis, and about 140° for the trans structures.

## O<sub>3</sub>-H<sub>2</sub>, O<sub>3</sub>-N<sub>2</sub>, O<sub>3</sub>-O<sub>2</sub>, O<sub>3</sub>-CO, O<sub>3</sub>-F<sub>2</sub>, O<sub>3</sub>-Cl<sub>2</sub> and O<sub>3</sub>-FCl complexes

In Tables 4 and 5 geometrical parameters are given for complexes relating to the Cs-B plane, with the inplane structures in Table 4, and the perpendicular structures in Table 5. In both cases the shortest distances between ozone and the diatomic molecule are listed.

Table 4  
Geometries of O<sub>3</sub>-H<sub>2</sub>, O<sub>3</sub>-N<sub>2</sub>, O<sub>3</sub>-O<sub>2</sub>, O<sub>3</sub>-CO, O<sub>3</sub>-F<sub>2</sub>, O<sub>3</sub>-Cl<sub>2</sub> and O<sub>3</sub>-FCl (O<sub>3</sub>-AB) complexes in Cs-B inplane (inpl) configurations. Distances in Å, angles in degree<sup>a</sup>

System	Symm.	O1-A	X1-O1-A	O1-A-B	Shortest dist.
O <sub>3</sub> -H <sub>2</sub>	Cs inpl	2.965	126.97	103.77	O2-H 2.836
O <sub>3</sub> -N <sub>2</sub>	Cs inpl	3.106	116.53	158.11	O2-N 3.070
O <sub>3</sub> -O <sub>2</sub>	Cs inpl	3.072	115.13	113.42	O2-O 3.054
O <sub>3</sub> -CO	Cs inpl	3.187	122.16	148.63	O2-C 3.086
O <sub>3</sub> -F <sub>2</sub>	Cs inpl	3.073	84.19	77.21	O1-F 3.073
O <sub>3</sub> -Cl <sub>2</sub>	Cs inpl	3.403	80.37	73.86	O2-Cl 3.397
O <sub>3</sub> -FCl	Cs inpl	2.948	109.00	106.96	O1-F 2.948
a. The Cs-B plane of reference lies perpendicular to the O <sub>3</sub> plane.					
X1 is a point on the C <sub>2v</sub> symmetry axis of O <sub>3</sub> above its central oxygen.					
O1 is the central oxygen of O <sub>3</sub> .					

For the inplane structures the O1-A distances and the X1-O-A, O1-A-B angles are shown. As before, X1 lies on the C<sub>2</sub> symmetry axis of O<sub>3</sub> above the central oxygen. The distances are close to 3 Å, except for the distance in O<sub>3</sub>-Cl<sub>2</sub>, which is about 3.4 Å. The X1-O1-A angles of the inplane complexes are about 120° for the H<sub>2</sub> to CO complexes, changing to around 80° for F<sub>2</sub> and Cl<sub>2</sub>, indicating that the latter complexes are much more bent, less stretched out. The O1-A-B angles of the inplane complexes are largest for O<sub>3</sub>-N<sub>2</sub> and O<sub>3</sub>-CO (about 150° to 160°) and smallest for the O<sub>3</sub>-F<sub>2</sub> and O<sub>3</sub>-Cl<sub>2</sub> complexes (about 70-80°), again indicating their more bent structures.

For the perpendicular complexes, the O1-X2 distances, with X2 being the midpoint of the AB diatomic molecule, are slightly longer than for the inplane structures. The X1-O1-X2 angles are quite uniformly 110° to 120°.

Table 5 Geometries of O<sub>3</sub>-H<sub>2</sub>, O<sub>3</sub>-N<sub>2</sub>, O<sub>3</sub>-O<sub>2</sub>, O<sub>3</sub>-CO, O<sub>3</sub>-F<sub>2</sub> and O<sub>3</sub>-Cl<sub>2</sub> (O<sub>3</sub>-AB) complexes in perpendicular (ppd) configurations. Distances in Å, angles in degree<sup>a</sup>

System	Symm.	O1-X2	X1-O1-X2	Shortest dist.
O <sub>3</sub> -H <sub>2</sub>	Cs ppd	3.027	115.55	O <sub>2</sub> -H 2.894
O <sub>3</sub> -N <sub>2</sub>	Cs ppd	3.236	112.32	O1-N 3.283
O <sub>3</sub> -O <sub>2</sub>	Cs ppd	3.325	115.01	O <sub>2</sub> -O 3.141
O <sub>3</sub> -CO	C <sub>1</sub> ppd	3.313	117.84	O <sub>3</sub> -C 3.083
O <sub>3</sub> -F <sub>2</sub>	C <sub>1</sub> ppd	3.222	109.22	O <sub>3</sub> -F 2.910
O <sub>3</sub> -Cl <sub>2</sub>	C <sub>1</sub> ppd	3.726	115.16	O <sub>3</sub> -Cl 3.247

a. The Cs-B plane of reference lies perpendicular to the O<sub>3</sub> plane. X1 is a point on the C<sub>2v</sub> symmetry axis of O<sub>3</sub> above its central oxygen. X2 is the midpoint of the AB diatomic molecule. O1 is the central oxygen of O<sub>3</sub>.

## Changes In Harmonic Vibrational Frequencies And Ir Intensities

It is well known that the HF vibrational frequency is red shifted in HF complexes. For example, Kolenbrander and Lisy [34] observed a red shift of 43 cm<sup>-1</sup> for the HF frequency in HF-N<sub>2</sub>. IR spectra for O<sub>3</sub>-HF in solid argon were reported by Andrews et al. [27]. They found for isolated HF a frequency of 3919 cm<sup>-1</sup>. Compared to 3803 cm<sup>-1</sup> in the O<sub>3</sub>-HF complex, this corresponds to a red shift of 116 cm<sup>-1</sup>. The MP2 results for the HF frequency obtained in this work are 3999 cm<sup>-1</sup> for O<sub>3</sub>-HF cis, and 3982 cm<sup>-1</sup> for O<sub>3</sub>-HF trans. With a calculated frequency of 4138 cm<sup>-1</sup> for the HF monomer, the red shifts are 139 cm<sup>-1</sup> for cis and 156 cm<sup>-1</sup> for trans O<sub>3</sub>-HF. (CCSD(T)/AVDZ values are 133 cm<sup>-1</sup> for cis and 164 cm<sup>-1</sup> for trans.) In both complexes, the calculated HF distance increased by about 0.006 Å. The ozone frequencies for O<sub>3</sub>-HF change by much smaller amounts. In the order ν<sub>1</sub>, ν<sub>2</sub>, ν<sub>3</sub> (see Table 1) they change by 0, +14, +6 cm<sup>-1</sup> for the cis structure, and by -4, +14, -11 cm<sup>-1</sup> for the trans structure.

The calculated intensity of the HF vibration in O<sub>3</sub>-HF increases from 122 km/mol in the HF monomer to 466 km/mol in the cis complex, and to 519 km/mol in the trans complex (MP2 values). Intensity changes for the ozone vibrational modes are quite small.

Results obtained by Tachikawa et al. [28] for harmonic frequencies and IR intensities of O<sub>3</sub>-HF differ widely from the present results due differences in method and basis set (QCISD/6-31G\* used).

Smaller red shifts are expected for the O<sub>3</sub>-HCl complex. Here the MP2 frequencies are 2974 cm<sup>-1</sup> for HCl in O<sub>3</sub>-HCl cis and 2962 cm<sup>-1</sup> for HCl in O<sub>3</sub>-HCl trans. With a calculated vibrational frequency of 3041 cm<sup>-1</sup>

<sup>1</sup> for isolated HCl, the red shifts are 67 cm<sup>-1</sup> for cis and 79 cm<sup>-1</sup> for trans. The IR intensities of the HCl vibrations increase from 54 km/mol in HCl to 262 km/mol for the cis and 282 km/mol for the trans complex.

Bulanin et al. [29] performed IR spectroscopic studies of the O<sub>3</sub>-HCl molecular complex in liquid argon. The complex showed a new feature at 2840 cm<sup>-1</sup>, ascribed to the HCl stretching frequency in the complex. With a frequency of 2921 cm<sup>-1</sup> for HCl, the red shift amounts to 81 cm<sup>-1</sup>, very close to the calculated value for the trans structure.

The calculated OH frequencies for the O<sub>3</sub>-OH complex are 3767 cm<sup>-1</sup> for the cis and 3778 cm<sup>-1</sup> for the trans complex, with IR intensities of 129 km/mol for cis and 113 km/mol for trans. Compared to the OH monomer values of 3817 cm<sup>-1</sup> and 21 km/mol, the red shifts are 50 cm<sup>-1</sup> for the cis and 39 cm<sup>-1</sup> for the trans complex, with intensity increases by a factor of about five.

For the other complexes included in this paper, the shifts in frequency and IR intensity are small. For O<sub>3</sub>-FCl, a red shift of only 2 cm<sup>-1</sup>, and a very small change in intensity were found for the FCl vibration. For the O<sub>3</sub>-CO complex there is a blue shift of 6 cm<sup>-1</sup> for the CO vibration, with an intensity increase from 36.5 km/mol to 42.8 km/mol. A blue shift of 2 cm<sup>-1</sup> has been found experimentally [32]. For complexes of O<sub>3</sub> with homonuclear diatomic molecules, changes in frequency are small (about - 2 cm<sup>-1</sup> for N<sub>2</sub> in O<sub>3</sub>-N<sub>2</sub>), and changes in intensity negligible (from 0 to 0.045 km/mol for N<sub>2</sub> in O<sub>3</sub>-N<sub>2</sub>).

## Discussion

The diatomic molecules forming complexes with ozone included in this work can be divided into three categories, (a) the hydrides HCl, HF and OH, forming hydrogen bonds with ozone; (b) the singly bonded molecules H<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub> and FCl; (c) the doubly or triply bonded molecules N<sub>2</sub>, O<sub>2</sub> and CO. One expects the hydrogen bonded complexes to be most stable, followed by complexes of ozone with the singly bonded molecules and least by complexes with doubly and triply bonded diatomics.

The hydrogen bonded complexes O<sub>3</sub>-HF, O<sub>3</sub>-HCl and O<sub>3</sub>-OH have stable cis and trans structures lying in the Cs-A plane, the plane of O<sub>3</sub>, with the cis structures being more stable than the trans structures. The hydrogen of HF, HCl and OH is close to one of the terminal oxygens of O<sub>3</sub> which is slightly negative.

All other complexes, not hydrogen bonded, have stable structures with the diatomic molecule lying in the Cs-B plane (Cs-B inpl), the plane perpendicular to the O<sub>3</sub> plane. The complexes O<sub>3</sub>-H<sub>2</sub>, O<sub>3</sub>-N<sub>2</sub> and O<sub>3</sub>-O<sub>2</sub> also have stable C<sub>s</sub> structures with the diatomic molecule lying perpendicular to the Cs-B plane (Cs-B ppd). For O<sub>3</sub>-F<sub>2</sub> and O<sub>3</sub>-Cl<sub>2</sub>, however, the structures with F<sub>2</sub> or Cl<sub>2</sub> lying perpendicular to the Cs-B plane are unstable, but close-lying C<sub>1</sub> structures are stable. Complexes with heteronuclear diatomic molecules, CO and FCl, have C<sub>1</sub> structures close to a Cs-B ppd arrangement. Structures lying in the Cs-A plane, the plane of O<sub>3</sub>, have much lower dissociation energies.

Not surprisingly, the highest dissociation energy of  $1137\text{ cm}^{-1}$  was found for the  $\text{O}_3\text{-HF}$  complex, which is followed by the other hydrogen bonded complexes  $\text{O}_3\text{-OH}$  with  $753\text{ cm}^{-1}$  and  $\text{O}_3\text{-HCl}$  with  $718\text{ cm}^{-1}$ .  $\text{O}_3\text{-Cl}_2$ ,  $\text{O}_3\text{-FCl}$ ,  $\text{O}_3\text{-CO}$  and  $\text{O}_3\text{-N}_2$  have intermediate dissociation energies from  $477$  to  $335\text{ cm}^{-1}$ , still rather large values. The remaining complexes,  $\text{O}_3\text{-F}_2$ ,  $\text{O}_3\text{-O}_2$  and  $\text{O}_3\text{-H}_2$ , have much lower values, from  $260$  to  $200\text{ cm}^{-1}$ .

Extrapolations to the complete basis set limit done for  $\text{O}_3\text{-HF}$  and  $\text{O}_3\text{-N}_2$  resulted in dissociation energies almost equal to the BSSE adjusted values (within  $7\text{ cm}^{-1}$ ). The fact that CBS corrections are very close to BSSE corrections indicates a very high level of calculation. Due to the closeness of these CBS dissociation energies with BSSE corrected values (see also other cases in the literature) CBS corrections were not found to be necessary for other complexes included in this work.

Significant frequency shifts have been calculated for the hydrogen bonded complexes of HF, HCl and OH with ozone. A large frequency shift for  $\text{O}_3\text{-HF}$  is confirmed by experimental studies. Such large frequency shifts are combined with increases in intensity by a factor of about five.

The most extreme case of a HF frequency red shift encountered so far applies to the  $\text{NH}_3\text{-HF}$  complex in the 0L structure, with a MP2 calculated red shift of  $792\text{ cm}^{-1}$  (from  $4138$  to  $3346\text{ cm}^{-1}$  for the HF frequency) [35]. The calculated IR intensity of this vibrational mode increases from  $122$  to  $1605\text{ km/mol}$ , a factor of about thirteen.

According to (low level) TD-DFT calculations performed on  $\text{O}_3\text{-HF}$ , the UV line of  $\text{O}_3$  at  $244.7\text{ nm}$ , with an oscillator strength  $f = 0.0875$ , changes very little in the complex (to  $245.1\text{ nm}$  with  $f = 0.0865$ , all TD-DFT values). One may assume that the absorption of solar UV radiation remains essentially unchanged in complexes with ozone.

## Conclusion

Structures, energies and vibrational spectra of ozone complexes have been calculated by high-level computational methods. Small diatomic molecules, most of atmospheric interest, have been chosen for the monomers. It is seen that ozone forms rather strong intermolecular bonds, especially with hydrogen bonded molecules like HF and HCl, but also with molecules like CO and  $\text{N}_2$ . Well known and well documented large vibrational frequency shifts for complexes of other molecules with HF, like for  $\text{HF-N}_2$ , are also found for  $\text{O}_3\text{-HF}$ .

For five of ten complexes dealt with in this work no theoretical results on structures, energies and vibrational spectra (but several experimental investigations) were available in the literature. For other four complexes with ozone literature results obtained at a lower level of theory could be improved.

Work is in progress on complexes of ozone with triatomic and larger molecules.

# Declarations

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**Availability of data and material** No additional data or material is available.

**Code availability** No new code was used in this work.

**Conflict of interest** The author declares no competing interests.

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## Figures

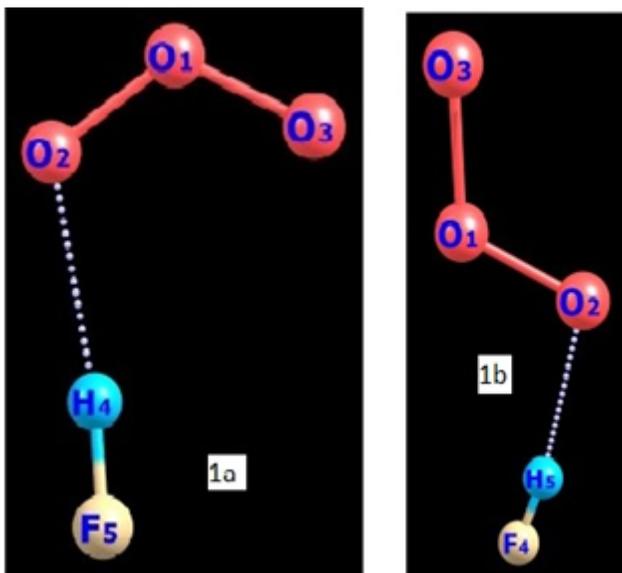


Figure 1

Structure of O3-HF cis (1a) and trans (1b) complex

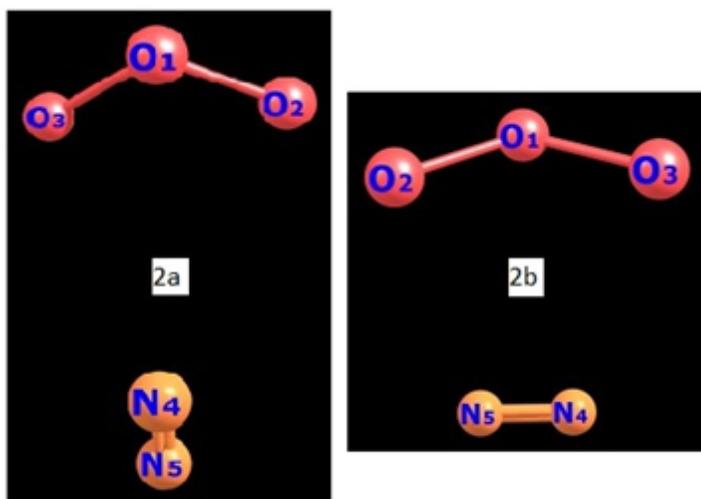


Figure 2

Structure of O3-N2 inplane (2a) and perpendicular (2b) complex

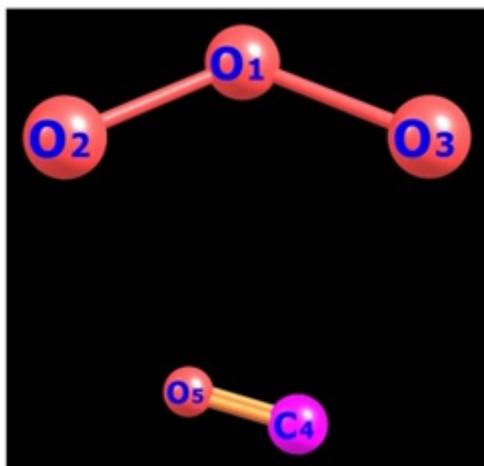


Figure 3

Structure of O3-CO complex close to perpendicular structure

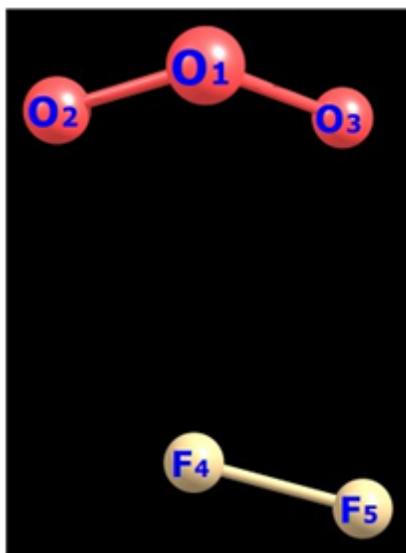


Figure 4

Structure of O3-F2 complex close to perpendicular structure

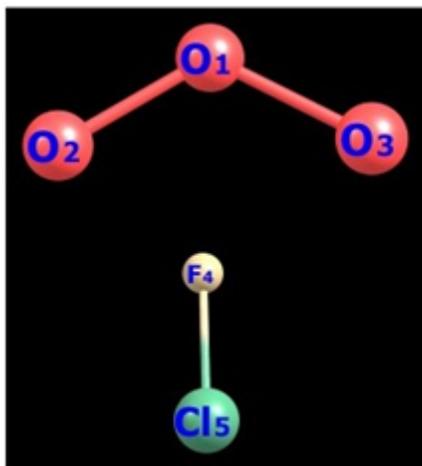


Figure 5

Cs-inplane structure of O<sub>3</sub>-FCl complex