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# Ab initio structures and quartic force fields of phosphine oxide and phosphine sulphide

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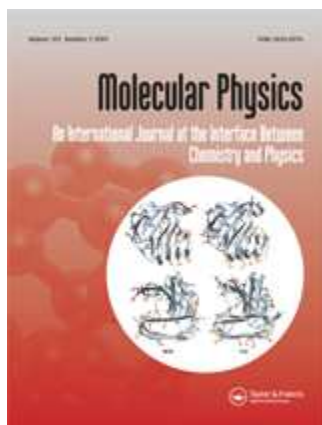
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### Ab initio structures and quartic force fields of phosphine oxide and phosphine sulphide

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**Abstract**

Phosphine oxide,  $\text{OPH}_3$ , and phosphine sulphide,  $\text{SPH}_3$  have been studied ab initio using various combinations of theoretical methods (MP2, CCSD, CCSD(T)) and basis sets (cc-pV(X+d)Z, cc-pCVXZ, X=T,Q). For both molecules, high-level ab-initio full-quartic force fields have been calculated, and these have been used to predict the most important spectroscopic constants for several isotopologues. For  $\text{OPH}_3$ , the semi-experimental equilibrium geometry and harmonic frequencies have been determined, by combining the theoretically calculated anharmonic corrections to the experimentally determined ground-state rotational constants and vibrational fundamentals. It is proved that, after applying anharmonic corrections, the unusually large disagreement between the experimental geometry and any high-level theoretical approach disappears.

**Keywords:** ab initio computations, spectroscopic parameters, anharmonic force field, anharmonic corrections, semi-experimental equilibrium structure,

## 1 Introduction

Phosphine oxide,  $\text{OPH}_3$  and phosphine sulphide,  $\text{SPH}_3$ , together with their tautomers  $\text{HOPH}_2$ ,  $\text{HSPH}_2$  and halogen derivatives have been extensively studied in several theoretical papers [1-17]. These studies were mainly focused on the molecular structure and the nature of the P-X (X=O,S) bond [1, 2, 4, 10, 13, 15], on the tautomerization energetics and reaction paths [1, 9, 14, 15, 17] and on vibrational spectra [1,3,5-8]

Comparatively, much less experimental work has been done. To date, only the Argon matrix infrared spectrum of  $\text{OPH}_3$  has been observed [18], while the identification of  $\text{SPH}_3$  from a similar experiment [19] has failed. In the gas phase, only the microwave spectrum of  $\text{OPH}_3$  has been detected [20], leading to the determination of its  $r_0$  molecular structure.

Our attention to the title molecules was drawn by the striking discrepancy between the experimental geometry of  $\text{OPH}_3$ , as deduced from its rotational spectrum [20] and any of the previous ab initio calculations, even those carried out at the Coupled Cluster level of theory [15]. Indeed Coupled Cluster methods [21], in particular those including perturbative treatment of triple excitations [CCSD(T)] [22], are nowadays acknowledged to be the most effective compromise between accuracy and computational effort, for the calculation of structures and force fields of closed-shell medium-sized molecules in their ground state [23, 24]. Differences between experimental and calculated geometries are usually within 0.1-0.3 pm for bond lengths and less than 0.5 degrees for bond angles [25]. Even if comparisons are made between calculated  $r_e$  and experimental  $r_0$  geometries, for non-flexible molecules the differences often remain within the above ranges.

It appears then noteworthy a difference of 3.7 pm and 2.6 degrees between the calculated [15] and the experimental [20] PH bond length and OPH bond angle of  $\text{OPH}_3$ , respectively. Similar unrealistic deviations have been reported also for the  $\text{OPH}_2$  radical [26, 27]. As pointed out in Ref.[15], the differences may be primarily attributed to the vibrational effects on the experimental geometry. These anharmonic corrections have never been considered in any of the previous theoretical studies, but they appear to be mandatory to make a direct comparison with experiment. Anharmonic effects must also be taken into account to quantitatively reproduce the observed vibrational frequencies [18], inasmuch the latest ab initio calculations published [7], dating back to our knowledge almost twenty years ago, show deviations as large as  $170\text{ cm}^{-1}$  from the experiment.

In this paper we will then calculate for the first time the full quartic force field for  $\text{OPH}_3$ , using state-of-the-art ab initio quantum chemical methods, in order to achieve a complete agreement with all the experimentally known data. The study has been extended, at the same level of theory, also to  $\text{SPH}_3$ , with the aim of providing information useful for the spectroscopic identification of this molecule.

## 2 Computational methodologies

All the ab-initio calculations have been performed with the ACES II suite of quantum chemistry programs, Mainz-Austin-Budapest version [28]. The ground state equilibrium geometry and harmonic frequencies have been calculated by means of different combinations of theoretical methods and basis sets. The methods we used are the second order Møller-Plesset perturbation theory (MP2)[29], the Coupled Cluster with Single and Double excitations (CCSD) [30] and the Coupled Cluster with Single and Double excitations with triples treated perturbatively [CCSD(T)][22]. The bases, of triple and quadruple  $\zeta$  quality, were chosen among the family of Dunning's correlation consistent sets. In particular we used the cc-pV(T+d)Z, cc-pV(Q+d)Z [31] bases, with only valence electrons correlated, and the cc-pCVTZ, cc-pCVQZ [32] bases, with all electrons correlated.

These combinations of methods and bases were chosen since they are most commonly used in similar studies [23]. For each combination, the harmonic frequencies and the dipole moment have been calculated at the corresponding equilibrium geometry.

The CCSD(T)/cc-pCVQZ geometry was chosen as reference geometry for the calculation of the full quartic force field. The harmonic part of the force field was obtained analytically at the same level of the geometry optimization, while the complete set of cubic and quartic force constants, in Cartesian coordinates, were obtained from the finite differences of the analytical Hessians evaluated at a lower level of theory (MP2/cc-pCVTZ). Such a hybrid approach relies on the smaller effects of basis set and electron correlation with increasing the order of the force fields [33]. The Cartesian geometries used in the finite differences procedure have been generated starting from the CCSD(T)/cc-pCVQZ equilibrium geometry, by increasing and decreasing the Cartesian coordinates with a step-size of 0.006 bohr, without taking into account symmetry relationships. 30 singly displaced and 210 doubly displaced structures are needed for a five atom molecule. The numerical stability of the procedure against the step size was checked by comparing the values of the  $F_{ijkl}$  and  $F_{klij}$  quartic force field elements in Cartesian coordinates. The maximum absolute differences was 0.03 aJÅ<sup>-n</sup>rad<sup>-m</sup> ( $m + n = 4$ ).

The transformation of force constants from cartesian to normal coordinates and the computation of the spectroscopic constants [34, 35] have been performed with the SPECTRO program[36], while the transformation from cartesian to internal coordinates was performed with the INTDER program [33, 37, 38]. In the transformation of the Cartesian force constants to internal coordinates, the small gradient term resulting from the choice of a non-stationary reference geometry was neglected, since the CCSD(T)/cc-pCVQZ and MP2/cc-pCVTZ geometries are almost coincident, differing at most 0.6 pm for the bond lengths and 0.3 degree for the angles.

### 3 Discussion

#### 3.1 Comparison of the *ab initio* methods

In Table 1 and 2 we compare the geometries, the dipole moments and the harmonic frequencies of  $\text{OPH}_3$  and  $\text{SPH}_3$ . The comparison is made, for  $\text{OPH}_3$ , against semi-experimental equilibrium structures and harmonic frequencies, obtained from experimental  $B_0$  [20] and anharmonic frequencies  $\nu$  [18] after applying the theoretically calculated anharmonic corrections (see below).

We can see that in general the calculated  $r_e(\text{PO})$  overestimate the semi-empirical PO bond length, with larger deviations when only valence electrons are correlated. The smallest deviation (+0.04 pm) is found at the CCSD(T)/cc-pCVQZ level, indicating that an high level of correlation treatment, including core correlation, is needed to accurately describe the PO bond.

On the other hand, the calculated  $r_e(\text{PH})$  are much less sensitive to the combination of method and basis, with both positive and negative deviations with respect to the semi-experimental value. The largest deviation is observed for the MP2/cc-pCVQZ approach, but it is less than 1 pm. Also OPH angle show little dependence on the method/basis combination, and they always overestimate the corresponding semi-empirical value by less than 0.5 degrees.

From the comparisons described above, it emerges that the best agreement with the semi-experimental equilibrium geometry is obtained at the CCSD(T)/cc-pCVQZ level. This "a posteriori" check validates its use as reference geometry for the calculation of the full quartic anharmonic force field and consequently of the anharmonic corrections which in turn are used to obtain the semi-experimental geometry itself, as described in the next section.

For what harmonic frequencies are concerned, the performance of the various approaches is ranked by calculating the root mean square deviation (RMSD) from the semi-experimental harmonic frequencies. These have been estimated by applying anharmonic corrections (see next section) to the observed fundamental frequencies obtained from rare-gas trapping experiments [18], as no gas-phase data was available at the time of writing. The largest RMSD ( $33.5 \text{ cm}^{-1}$ ) is obtained for MP2/cc-pCVQZ and the smallest ( $10.7 \text{ cm}^{-1}$ ) for CCSD(T)/cc-pCVQZ. The relatively high RMSD, even for the best theoretical treatment, probably reflects some frequency shifts of the fundamentals due to the solid state environment. It is then unlikely that higher levels of theory could markedly improve the RMSD with respect to these experimental data. The accuracy of the semi-experimental harmonic frequencies presented here is then affected by the unavoidable shifts due to the trapping matrix, which can be safely assumed to be about 1% of the frequency values [39]

For  $\text{SPH}_3$  the comparison is made against the values obtained from the CCSD(T)/cc-pCVQZ calculation, since experimental data are not currently available and this latter method has proved

to perform very well for  $\text{OPH}_3$ . Most methods tend to overestimate the SP bond length, with differences ranging from -2.54 pm (QCISD/6-311++G(d,p)[16, 17] to +0.99 pm (MP2/cc-pCVQZ). As for  $\text{OPH}_3$ , the PH bond length and SPH bond angles are comparatively more stable, with a largest deviation of +0.47 pm (MP2/cc-pCVTZ) and 0.21 degrees (CCSD(T)/cc-pV(T+d)Z), respectively.

For what frequencies are concerned, the QCISD/6-311++G(d,p) [16, 17] is particularly unsatisfactory, with a RMSD of  $36.0 \text{ cm}^{-1}$  and a largest deviation of  $+61.6 \text{ cm}^{-1}$  for  $\omega_2$ . In general, all MP2 approaches provide a poor description of the harmonic frequencies, with values always overestimated with respect to the CCSD(T)/cc-pCVQZ values and RMSD ranging from  $24.3 \text{ cm}^{-1}$  (MP2/cc-pV(T+d)Z) to  $30.6 \text{ cm}^{-1}$  (MP2/cc-pCVQZ) and a maximum deviation of  $+47.3 \text{ cm}^{-1}$  for  $\omega_4$  (MP2/cc-pCVQZ).

### 3.2 Anharmonic force fields

The quadratic, cubic and quartic force fields transformation from cartesian to symmetry coordinates was done by means of the INTDER program[33, 37, 38]. The definition of the symmetry coordinates is reported in Table 3. These are the same as in Ref.[5], but are reported also here for completeness. The definition of the internal coordinates is also shown in Figure 1.

The harmonic, cubic and quartic force field of  $\text{OPH}_3$  and  $\text{SPH}_3$  in symmetry coordinates are reported in Tables 4-6. These have been used to calculate fundamental frequencies, anharmonicity constants, rotational and rotation-vibration constants for most common isotopologues, in order to assist future identification and analysis of gas-phase spectra. These values are reported in Table 7, together with the latest computed and experimental values.

The application of the vibration-rotation second order perturbation theory equations [34, 35] needed in this step, has been accomplished by means of the SPECTRO [36] code. Fermi resonances have been taken into account following Ref.[35], by removing the divergent terms from the expression of the anharmonicity constants and explicitly diagonalizing the  $2 \times 2$  matrix involving the resonant states. The effect of Coriolis resonances has been accounted by properly modifying the analytical expression of the vibration-rotation constants [34].

The listed spectroscopic constants have been finally used to calculate the anharmonic contribution to fundamental frequencies and to rotational constants, in order to estimate semi-experimental harmonic frequencies and equilibrium rotational constants. The semi-experimental harmonic frequencies  $\omega_i^{se}$  have been obtained from the experimental fundamentals  $\nu_i^e$  using the following equations, obtained from the vibrational term value expression for symmetric tops (see e.g. [34]):

$$\omega_i^{se} = \nu_i^e - 2x_{ii} - \frac{1}{2} \sum_{s \neq i} x_{si} - \sum_t x_{ti} \quad \text{non - degenerate modes} \quad (1)$$



$$\omega_i^{se} = \nu_i^e - 3x_{ii} - g_{ii} - \frac{1}{2} \sum_s x_{si} - \sum_{t \neq i} x_{ti} \quad \text{degenerate modes} \quad (2)$$

where  $s$  denotes a non-degenerate and  $t$  a degenerate mode. The semi-experimental harmonic frequencies for  $\text{OPH}_3$  are reported in Table 1.

Semi experimental equilibrium rotational constants  $B_e^{se}$  for  $\text{OPH}_3$  are obtained from the experimental  $B_0^e$  [20] by applying the following expression for all available isotopologues

$$B_e^{se} = B_0^e + \sum_i \frac{d_i}{2} \alpha_i^B \quad (3)$$

where  $d_i$  is 1 for non-degenerate and 2 for degenerate modes. The vibrational corrections to the ground state rotational constants turned out to be 107.586, 83.738 and 97.157 MHz, for the  $^{16}\text{OPH}_3$ ,  $^{16}\text{OPD}_3$  and  $^{18}\text{OPH}_3$  isotopologues, respectively. By applying these corrections to the experimental  $B_0^e$  values [20], one obtains the semi-experimental  $B_e^{se}$ : 17534.2077, 14683.5899 and 16355.8216 MHz. Finally, by fitting the symmetric top geometrical parameters to these values, by means of the STRFIT program [40], we obtained the best estimate of the experimental  $r_e$  structure of  $\text{OPH}_3$ :  $r_e(\text{PO}) = 1.4703 \text{ \AA}$ ,  $r_e(\text{PH}) = 1.4043 \text{ \AA}$  and  $\angle \text{HPO} = 116.72^\circ$ , which is also reported in Table 1. As pointed out in the previous subsection, the CCSD(T)/cc-pCVQZ geometry is almost coincident with the semi-experimental one, hence settling this molecule for the apparent disagreement between theory and experiment.

## 4 Conclusions

Phosphine oxide and phosphine sulphide have been studied ab-initio using different combinations of theoretical methods and basis sets. Among the various possibilities, we have chosen those most widely adopted for spectroscopic studies [23], that is MP2 (bases cc-pV(T+d)Z, cc-pV(Q+d)Z, cc-pCVTZ, cc-pCVQZ), CCSD (bases cc-pV(T+d)Z, cc-pV(Q+d)Z), and CCSD(T) (bases cc-pV(T+d)Z, cc-pV(Q+d)Z, cc-pCVTZ, cc-pCVQZ). For phosphine oxide, an almost perfect agreement with respect to the semi-experimental results is obtained only by taking into account core correlation. The same agreement is guessed also for phosphine sulphide, which unfortunately is completely lacking of experimental data.

For both molecules, high-level ab-initio full-quartic force fields have been also calculated. These have been used to both predict the most important spectroscopic constants for several isotopologues and to estimate, for  $\text{OPH}_3$ , the anharmonic corrections needed to obtain the semi-experimental equilibrium geometry and harmonic frequencies. The large disagreement between the experimental geometry and any high-level theoretical approach, as pointed out by some authors [15, 20], is then completely eliminated. Work is in progress to solve an analogous problem observed for the  $\text{OPH}_2$

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## Figure captions

### Figure 1.

Internal coordinates used for the definition of the symmetry coordinates of  $\text{OPH}_3$  and  $\text{SPH}_3$

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Table 1: Computed equilibrium geometries, dipole moments and harmonic vibrational frequencies of  $\text{OPH}_3$ . Bond lengths in Angstrom, bond angles in degrees, dipole moments in Debye and vibrational frequencies in  $\text{cm}^{-1}$

Method	$r_e(\text{PO})$	$r_e(\text{PH})$	$\angle\text{OPH}$	$\mu_e$	$\omega_1$	$\omega_2$	$\omega_3$	$\omega_4$	$\omega_5$	$\omega_6$	RMSD
MP2/6-311G** <sup>a</sup>	1.4855	1.4061	117.68	3.473	2531	1327	1203	2505	1181	893	47.1
MP2/cc-pV(T+d)Z <sup>b</sup>	1.4785	1.4039	117.18	3.502	2503.6	1299.2	1182.5	2488.1	1165.6	867.3	27.2
MP2/cc-pV(Q+d)Z <sup>b</sup>	1.4781	1.4027	116.86	3.628	2510.6	1283.8	1174.0	2498.0	1161.3	863.5	27.9
MP2/cc-pCVTZ <sup>c</sup>	1.4767	1.4014	117.16	3.516	2513.0	1300.3	1182.9	2499.6	1167.2	867.3	33.2
MP2/cc-pCVQZ <sup>c</sup>	1.4733	1.3989	116.87	3.627	2516.9	1288.6	1177.3	2505.5	1164.2	866.7	33.5
CCSD/cc-pV(T+d)Z <sup>b</sup>	1.4707	1.4058	117.04	3.611	2480.6	1307.5	1189.0	2463.1	1160.6	872.3	23.2
CCSD/cc-pV(Q+d)Z <sup>b</sup>	1.4688	1.4046	116.75	3.726	2490.2	1298.1	1181.4	2475.1	1155.9	870.8	20.0
CCSD(T)/cc-pV(T+d)Z <sup>b</sup>	1.4767	1.4085	117.17	3.512	2455.2	1289.4	1171.9	2438.4	1147.7	858.5	20.9
CCSD(T)/cc-pV(Q+d)Z <sup>b</sup>	1.4754	1.4074	116.86	3.638	2464.6	1277.1	1163.5	2450.6	1142.5	856.0	11.1
CCSD(T)/cc-pCVTZ <sup>c</sup>	1.4749	1.4064	117.15	3.523	2463.9	1292.0	1173.3	2448.7	1149.8	859.3	16.9
CCSD(T)/cc-pCVQZ <sup>c</sup>	1.4707	1.4040	116.88	3.633	2469.8	1283.4	1168.1	2456.6	1145.9	860.0	10.7
Experimental <sup>d,e</sup>	1.4703	1.4043	116.72		2472.4	1261.1	1164.9	2475.1	1140.6	864.3	—

<sup>a</sup> From Ref.[7]. To facilitate the comparison with the present data, the empirical scaling factor of 0.943 has been removed. A recent high level structure calculation [CCSD(T)/cc-pVQZ] is reported also in ref [15]

<sup>b</sup> Only valence electrons correlated

<sup>c</sup> All electrons correlated

<sup>d</sup> Semi-experimental  $r_e$  structure obtained from the experimental  $B_0$  of Ref.[20], corrected by the anharmonic contribution (see text).

<sup>e</sup> Semi-experimental harmonic frequencies obtained from the fundamentals of Ref.[18], corrected by the anharmonic contribution (see text)

Table 2: Computed equilibrium geometries, dipole moments and harmonic vibrational frequencies of  $\text{SPH}_3$ . Bond lengths in angstrom, bond angles in degrees, dipole moments in debye and vibrational frequencies in  $\text{cm}^{-1}$

Method	$r_e(\text{PS})$	$r_e(\text{PH})$	$\angle\text{SPH}$	$\mu_e$	$\omega_1$	$\omega_2$	$\omega_3$	$\omega_4$	$\omega_5$	$\omega_6$	RMSD
QCISD/6-311++G(d,p) <sup>a</sup>	1.9507	1.4053	117.55	—	2503	1205	641	2482	1129	742	36.0
MP2/cc-pV(T+d)Z <sup>b</sup>	1.9258	1.4025	117.79	3.569	2501.1	1165.0	749.1	2488.6	1153.0	703.6	24.3
MP2/cc-pV(Q+d)Z <sup>b</sup>	1.9225	1.4017	117.58	3.583	2507.6	1157.0	748.9	2496.3	1148.3	706.4	26.5
MP2/cc-pCVTZ <sup>c</sup>	1.9220	1.4002	117.81	3.567	2509.9	1165.5	703.6	2499.3	1154.6	748.3	29.1
MP2/cc-pCVQZ <sup>c</sup>	1.9154	1.3981	117.63	3.565	2513.2	1159.7	708.8	2502.8	1151.4	750.7	30.6
CCSD/cc-pV(T+d)Z <sup>b</sup>	1.9336	1.4042	117.67	3.702	2479.6	1159.1	740.5	2464.8	1147.9	680.4	11.1
CCSD/cc-pV(Q+d)Z <sup>b</sup>	1.9286	1.4032	117.44	3.737	2489.7	1151.8	743.4	2476.2	1143.7	686.2	13.8
CCSD(T)/cc-pV(T+d)Z <sup>b</sup>	1.9363	1.4070	117.83	3.582	2453.7	1148.8	731.2	2438.6	1134.8	677.8	10.1
CCSD(T)/cc-pV(Q+d)Z <sup>b</sup>	1.9317	1.4061	117.59	3.628	2463.3	1139.6	732.8	2449.9	1129.5	682.7	4.1
CCSD(T)/cc-pCVTZ <sup>c</sup>	1.9330	1.4048	117.83	3.584	2462.4	1150.2	678.5	2448.9	1136.9	731.4	6.0
CCSD(T)/cc-pCVQZ <sup>c</sup>	1.9253	1.4028	117.62	3.615	2468.2	1143.4	686.0	2455.5	1133.0	735.6	—

<sup>a</sup> Ref.[16, 17], EPAPS document No. E-JCPSA6-127-302742

<sup>b</sup> Only valence electrons correlated

<sup>c</sup> All electrons correlated



Table 3: Definition of symmetry coordinates for OPH<sub>3</sub> and SPH<sub>3</sub> according to ref.[5]

Coordinate	Definition <sup>a</sup>
$S_1$	$(\Delta r_1 + \Delta r_2 + \Delta r_3)/\sqrt{3}$
$S_2$	$(K\Delta\alpha_1 + K\Delta\alpha_2 + K\Delta\alpha_3 - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)/\sqrt{3 + K^2}$
$S_3$	$\Delta R$
$S_{4a}$	$(2\Delta r_1 - \Delta r_2 - \Delta r_3)/\sqrt{6}$
$S_{4b}$	$(\Delta r_2 - \Delta r_3)/\sqrt{2}$
$S_{5a}$	$(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)/\sqrt{6}$
$S_{5b}$	$(\Delta\alpha_2 - \Delta\alpha_3)/\sqrt{2}$
$S_{6a}$	$(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)/\sqrt{6}$
$S_{6b}$	$(\Delta\beta_2 - \Delta\beta_3)/\sqrt{2}$

<sup>a</sup>  $r = r_{PH}$ ,  $R = r_{PX}$ ,  $\alpha = \angle(\text{HPH})$  (101.16 for OPH<sub>3</sub>, 100.23 for SPH<sub>3</sub>),  $\beta = \angle(\text{HPX})$  (116.88 for OPH<sub>3</sub>, 117.62 for SPH<sub>3</sub>)

<sup>b</sup>  $K = -3 \sin \beta \cos \beta / \sin \alpha$

Table 4: Calculated CCSD(T)/cc-pCVQZ harmonic force fields of OPH<sub>3</sub> and SPH<sub>3</sub> in symmetry coordinates, as defined in Table 3. Units are in aJÅ<sup>-n</sup>rad<sup>-m</sup> where  $n$  is the number of stretches and  $m$  the number of bendings in the definition of the force constants. For the harmonic force field  $m + n = 2$ . Only force constants independent and non-zero by symmetry are reported. Previous theoretical values reported in ref.[5] are shown in parentheses.

		OPH <sub>3</sub>	SPH <sub>3</sub>
$i$	$j$	$f_{ij}$	$f_{ij}$
1	1	3.556 (3.371)	3.552 (3.370)
1	2	0.047 (0.041)	0.085 (0.074)
1	3	0.168 (0.201)	0.140 (0.151)
2	2	0.633 (0.610)	0.562 (0.537)
2	3	-0.173 (-0.181)	-0.181 (-0.190)
3	3	9.879 (9.423)	4.569 (4.210)
4	4	3.452 (3.239)	3.448 (3.264)
4	5	-0.098 (-0.079)	-0.090 (-0.067)
4	6	0.010 (0.036)	-0.018 (0.003)
5	5	0.724 (0.653)	0.697 (0.611)
5	6	-0.208 (-0.205)	-0.152 (-0.130)
6	6	0.826 (0.777)	0.666 (0.587)

Table 5: Calculated MP2/cc-pCVTZ cubic anharmonic force fields of OPH<sub>3</sub> and SPH<sub>3</sub> in symmetry coordinates, as defined in Table 3. Units are in aJÅ<sup>-n</sup>rad<sup>-m</sup> where  $n$  is the number of stretches and  $m$  the number of bendings in the definition of the force constants. For the cubic force field  $m + n = 3$ . Only force constants which are independent and non-zero by symmetry are reported

	OPH <sub>3</sub>		SPH <sub>3</sub>		OPH <sub>3</sub>		SPH <sub>3</sub>	
<i>i j k</i>	<i>f<sub>ijk</sub></i>	<i>f<sub>ijk</sub></i>	<i>i j k</i>	<i>f<sub>ijk</sub></i>	<i>f<sub>ijk</sub></i>	<i>i j k</i>	<i>f<sub>ijk</sub></i>	<i>f<sub>ijk</sub></i>
1 1 1	-10.226	-10.270	3 4 4	0.011	0.169			
1 1 2	-0.111	-0.115	3 4 5	0.060	0.052			
1 1 3	-0.143	-0.005	3 4 6	-0.269	-0.140			
1 2 2	-0.168	-0.099	3 5 5	-0.156	-0.079			
1 2 3	0.162	0.094	3 5 6	0.182	0.163			
1 3 3	-0.327	-0.332	3 6 6	-0.798	-0.791			
2 2 2	0.361	0.254	4 4 4	-7.000	-7.095			
2 2 3	-0.368	-0.325	4 4 5	-0.191	-0.182			
2 3 3	0.304	0.425	4 4 6	0.044	0.021			
3 3 3	-62.034	-23.705	4 5 5	0.077	0.081			
1 4 4	-9.962	-10.088	4 5 6	0.023	0.025			
1 4 5	0.089	0.078	4 6 6	-0.102	-0.043			
1 4 6	0.004	0.011	5 5 5	0.009	0.016			
1 5 5	-0.302	-0.306	5 5 6	-0.286	-0.234			
1 5 6	0.053	0.023	5 6 6	0.416	0.337			
1 6 6	-0.193	-0.079	6 6 6	-0.779	-0.595			
2 4 4	0.050	0.056						
2 4 5	0.139	0.142						
2 4 6	0.027	-0.031						
2 5 5	-0.507	-0.479						
2 5 6	0.089	0.077						
2 6 6	0.090	0.063						

Table 6: Calculated MP2/cc-pCVTZ quartic anharmonic force fields of OPH<sub>3</sub> and SPH<sub>3</sub> in symmetry coordinates, as defined in Table 3. Units are in aJÅ<sup>-n</sup>rad<sup>-m</sup> where  $n$  is the number of stretches and  $m$  the number of bendings in the definition of the force constants. For the quartic force field  $m + n = 4$ . Only force constants independent and non-zero by symmetry are reported

OPH <sub>3</sub>			SPH <sub>3</sub>			OPH <sub>3</sub>			SPH <sub>3</sub>		
<i>i j k l</i>	<i>f<sub>ijkl</sub></i>	<i>f<sub>ijkl</sub></i>	<i>i j k l</i>	<i>f<sub>ijkl</sub></i>	<i>f<sub>ijkl</sub></i>	<i>i j k l</i>	<i>f<sub>ijkl</sub></i>	<i>f<sub>ijkl</sub></i>	<i>i j k l</i>	<i>f<sub>ijkl</sub></i>	<i>f<sub>ijkl</sub></i>
1 1 1 1	24.340	24.554	2 2 4 5	-0.104	-0.095	2 5 5 6	0.227	0.181			
1 1 1 2	-0.065	-0.161	2 2 4 6	0.021	-0.035	2 5 6 6	-0.317	-0.250			
1 1 1 3	-0.063	-0.114	2 2 5 5	0.112	0.052	2 6 6 6	0.316	0.328			
1 1 2 2	-0.163	-0.145	2 2 5 6	0.012	0.003	3 4 4 4	-0.247	-0.168			
1 1 2 3	-0.002	0.077	2 2 6 6	0.115	0.035	3 4 4 5	0.068	0.079			
1 1 3 3	0.349	0.232	2 3 4 4	-0.022	0.060	3 4 4 6	-0.060	-0.103			
1 2 2 2	-0.097	0.016	2 3 4 5	-0.025	-0.025	3 4 5 5	0.025	0.021			
1 2 2 3	0.248	0.097	2 3 4 6	-0.225	-0.021	3 4 5 6	-0.058	-0.067			
1 2 3 3	-0.329	-0.238	2 3 5 5	0.135	0.121	3 4 6 6	0.341	0.147			
1 3 3 3	1.546	0.789	2 3 5 6	-0.028	0.007	3 5 5 5	-0.088	-0.016			
2 2 2 2	1.108	0.670	2 3 6 6	-0.283	-0.253	3 5 5 6	0.266	0.280			
2 2 2 3	-0.465	-0.409	3 3 4 4	0.401	0.198	3 5 6 6	-0.309	-0.306			
2 2 3 3	0.201	0.316	3 3 4 5	-0.019	0.058	3 6 6 6	0.797	0.717			
2 3 3 3	-0.955	-0.292	3 3 4 6	0.707	0.545	4 4 4 4	36.972	37.200			
3 3 3 3	332.850	95.180	3 3 5 5	0.134	0.124	4 4 4 5	0.219	0.211			
1 1 4 4	24.429	24.587	3 3 5 6	-0.069	-0.024	4 4 4 6	-0.042	0.018			
1 1 4 5	0.061	0.069	3 3 6 6	0.247	0.484	4 4 5 5	-0.269	-0.301			
1 1 4 6	-0.067	-0.023	1 4 4 4	17.166	17.298	4 4 5 6	0.074	0.054			
1 1 5 5	0.018	-0.010	1 4 4 5	0.122	0.115	4 4 6 6	-0.258	-0.181			
1 1 5 6	0.032	0.030	1 4 4 6	0.021	0.042	4 5 5 5	-0.253	-0.229			
1 1 6 6	-0.127	-0.094	1 4 5 5	0.041	0.046	4 5 5 6	0.154	0.134			
1 2 4 4	-0.092	-0.155	1 4 5 6	-0.034	-0.007	4 5 6 6	-0.122	-0.057			
1 2 4 5	-0.043	-0.020	1 4 6 6	-0.045	-0.037	4 6 6 6	0.227	0.006			
1 2 4 6	0.082	0.027	1 5 5 5	-0.081	-0.095	5 5 5 5	1.376	1.241			
1 2 5 5	0.098	0.078	1 5 5 6	0.075	0.036	5 5 5 6	-0.789	-0.667			
1 2 5 6	-0.032	-0.042	1 5 6 6	-0.112	-0.071	5 5 6 6	0.804	0.638			
1 2 6 6	0.024	0.081	1 6 6 6	0.176	0.033	5 6 6 6	-1.324	-1.013			
1 3 4 4	-0.268	-0.178	2 4 4 4	-0.144	-0.196	6 6 6 6	2.224	1.686			
1 3 4 5	-0.012	0.004	2 4 4 5	0.235	0.227	4a 4a 5b 5b	-0.733	-0.750			
1 3 4 6	-0.008	-0.115	2 4 4 6	0.047	0.014	4a 4a 5b 6b	0.076	0.044			
1 3 5 5	-0.009	-0.054	2 4 5 5	0.082	0.092	4a 4a 6b 6b	-0.079	-0.055			
1 3 5 6	-0.091	-0.032	2 4 5 6	-0.021	-0.024	4a 5a 6b 6b	-0.048	-0.031			
1 3 6 6	0.544	0.237	2 4 6 6	-0.009	0.035	4a 6a 5b 6b	-0.037	-0.013			
2 2 4 4	-0.274	-0.234	2 5 5 5	-0.372	-0.431	5a 5a 6b 6b	0.553	0.440			

Table 7: Calculated spectroscopic parameters of  $^{16}\text{OPH}_3$ ,  $^{16}\text{OPD}_3$ ,  $^{18}\text{OPH}_3$ ,  $^{18}\text{OPD}_3$ ,  $^{32}\text{SPH}_3$ ,  $^{32}\text{SPD}_3$ ,  $^{34}\text{SPH}_3$  and  $^{34}\text{SPD}_3$ . All values are in  $\text{cm}^{-1}$ . Experimental values are shown in parentheses, while most recent theoretical values are reported in square brackets

	$^{16}\text{OPH}_3$	$^{16}\text{OPD}_3$	$^{18}\text{OPH}_3$	$^{18}\text{OPD}_3$	$^{32}\text{SPH}_3$	$^{32}\text{SPD}_3$	$^{34}\text{SPH}_3$	$^{34}\text{SPD}_3$
$\nu_1$	2356.4 <sup>a</sup> (2359.0) <sup>d</sup>	1722.3 <sup>b</sup> (1721.1) <sup>d</sup>	2340.4 <sup>a</sup> (2367.0) <sup>d</sup>	1720.2 <sup>b</sup> (1720.0) <sup>d</sup>	2366.2	1716.5 <sup>c</sup>	2366.1	1716.4 <sup>c</sup>
$\nu_2$	1262.6 (1240.2) <sup>d</sup>	1236.6 (1217.3) <sup>d</sup>	1235.5 (1213.7) <sup>d</sup>	1193.3 (1174.1) <sup>d</sup>	1118.0	832.9	1118.0	832.3
$\nu_3$	1146.7 (1143.5) <sup>d</sup>	848.0 (843.6) <sup>d</sup>	1127.2	844.5 (840.5) <sup>d</sup>	676.7	655.6	666.5	645.7
$\nu_4$	2353.1 (2371.5) <sup>d</sup>	1715.3	2357.9 (2371.6) <sup>d</sup>	1714.3	2348.5	1713.7	2348.5	1713.6
$\nu_5$	1117.1 (1114.3) <sup>d</sup>	808.8	1117.0 (1114.3) <sup>d</sup>	808.7	1102.2	794.8	1102.2	794.8
$\nu_6$	846.6 (853.0) <sup>d</sup>	653.8 (655.9) <sup>d</sup>	842.7 (849.4) <sup>d</sup>	648.9 (651.3) <sup>d</sup>	723.8	544.1	723.2	543.3
$\omega_1$	2469.8 [2531] <sup>e</sup>	1768.2	2469.8	1767.9	2468.3 [2506] <sup>f</sup>	1762.6	2468.3	1762.6
$\omega_2$	1283.4 [1327] <sup>e</sup>	1253.5	1257.4	1209.1	1143.4 [1205] <sup>f</sup>	846.6	1143.4	846.1
$\omega_3$	1168.1 [1203] <sup>e</sup>	860.8	1146.3	857.2	686.0 [642] <sup>f</sup>	663.9	675.5	653.7
$\omega_4$	2456.7 [2505] <sup>e</sup>	1770.1	2456.7	1770.0	2455.5 [2485] <sup>f</sup>	1768.8	2455.5	1768.8
$\omega_5$	1145.9 [1181] <sup>e</sup>	823.5	1145.9	823.4	1133.1 [1129] <sup>f</sup>	810.5	1133.1	810.5
$\omega_6$	860.0 [893] <sup>e</sup>	661.7	856.1	656.7	735.6 [741] <sup>f</sup>	550.8	735.0	550.0
$x_{11}$	-14.74 [-12.02] <sup>g</sup>	-7.41	-14.75	-7.42	-15.01	-7.64	-15.01	-7.64
$x_{12}$	-9.70 [-16.88] <sup>g</sup>	-1.21	-26.57	-1.31	-1.14	-6.86	-1.14	-6.92
$x_{13}$	-6.74 [-12.90] <sup>g</sup>	-7.59	-5.75	-7.48	0.76	-0.10	0.75	-0.07
$x_{14}$	-57.51 [-47.53] <sup>g</sup>	-28.95	-57.51	-29.00	-60.12	-30.63	-60.12	-30.63
$x_{15}$	-7.82 [-4.25] <sup>g</sup>	-3.59	-7.82	-3.59	-8.57	-4.25	-8.57	-4.25
$x_{16}$	-4.69 [-4.08] <sup>g</sup>	-2.65	-4.68	-2.62	-3.24	-1.63	-3.24	-1.63
$x_{22}$	-2.82 [-3.75] <sup>g</sup>	-5.87	2.16	-5.36	-4.60	-0.92	-4.60	-0.91
$x_{23}$	-6.15 [3.79] <sup>g</sup>	-1.87	-6.67	-1.91	-2.22	-2.36	-2.20	-2.27
$x_{24}$	0.38 [1.34] <sup>g</sup>	-0.73	-1.80	-1.66	-6.76	-2.52	-6.76	-2.58
$x_{25}$	-1.43 [0.00] <sup>g</sup>	-0.62	-1.79	-0.60	-4.44	-1.93	-4.44	-1.95

Table 8: Table 7 continued

	$^{16}\text{OPH}_3$	$^{16}\text{OPD}_3$	$^{18}\text{OPH}_3$	$^{18}\text{OPD}_3$	$^{32}\text{SPH}_3$	$^{32}\text{SPD}_3$	$^{34}\text{SPH}_3$	$^{34}\text{SPD}_3$
$x_{26}$	-6.26 [-6.78] <sup>g</sup>	-2.23	-5.98	-1.20	-3.39	-2.86	-3.39	-2.83
$x_{33}$	-1.76 [-2.45] <sup>g</sup>	-0.22	-1.97	-0.22	-3.07	-2.43	-2.98	-2.39
$x_{34}$	-6.97 [-5.67] <sup>g</sup>	-4.51	-4.99	-4.53	1.36	0.25	1.34	0.29
$x_{35}$	-2.04 [-0.76] <sup>g</sup>	-1.20	-1.56	-1.20	-0.27	-0.29	-0.27	-0.28
$x_{36}$	-2.42 [-2.30] <sup>g</sup>	-1.88	-2.38	-1.77	-3.47	-2.16	-3.41	-2.14
$x_{44}$	-21.35 [-17.62] <sup>g</sup>	-11.28	-21.35	-11.28	-22.66	-11.98	-22.66	-11.98
$x_{45}$	-10.80 [-7.52] <sup>g</sup>	-5.23	-10.84	-5.25	-11.54	-5.91	-11.54	-5.91
$x_{46}$	-3.46 [-2.59] <sup>g</sup>	-2.75	-3.49	-3.23	-2.67	-1.20	-2.68	-1.20
$x_{55}$	-4.08 [-4.12] <sup>g</sup>	-2.24	-4.07	-2.23	-3.90	-2.04	-3.90	-2.04
$x_{56}$	-3.31 [-2.70] <sup>g</sup>	-1.38	-3.35	-1.41	-4.23	-1.96	-4.24	-1.97
$x_{66}$	-0.41 [-0.12] <sup>g</sup>	-0.30	-0.42	-0.30	-0.51	-0.34	-0.51	-0.34
$g_{44}$	7.60 [6.45] <sup>g</sup>	4.16	7.60	4.16	7.95	4.35	7.95	4.35
$g_{45}$	-0.98 [-3.12] <sup>g</sup>	-0.96	-1.03	-0.95	-0.21	-0.36	-0.21	-0.36
$g_{46}$	0.59 [0.81] <sup>g</sup>	-0.41	0.53	-0.89	0.22	0.42	0.22	0.42
$g_{55}$	3.15 [2.49] <sup>g</sup>	1.39	3.15	1.40	3.20	1.56	3.20	1.56
$g_{56}$	-1.73 [-1.43] <sup>g</sup>	-0.62	-1.71	-0.62	-1.39	-0.76	-1.38	-0.75
$g_{66}$	1.30 [1.15] <sup>g</sup>	0.60	1.30	0.60	1.66	0.76	1.66	0.76

Table 9: Table 7 continued

	$^{16}\text{OPH}_3$	$^{16}\text{OPD}_3$	$^{18}\text{OPH}_3$	$^{18}\text{OPD}_3$	$^{32}\text{SPH}_3$	$^{32}\text{SPD}_3$	$^{34}\text{SPH}_3$	$^{34}\text{SPD}_3$
$A_0$	3.51115	1.76314	3.51101	1.76311	3.60893	1.80634	3.60893	1.80634
$B_0$	0.58078	0.48647	0.54186	0.45568	0.24682	0.21725	0.23971	0.21099
$\alpha_1^A \times 10^3$	(0.58128953) <sup>h</sup> 34.548 [29.071] <sup>g</sup>	(0.48699864) <sup>h</sup> 13.200	(0.54233067) <sup>h</sup> 34.546	13.192	33.453	12.790	33.453	12.790
$\alpha_1^B \times 10^3$	0.649 [0.469] <sup>g</sup>	3.846	0.576	2.952	0.075	0.243	0.070	0.231
$\alpha_2^A \times 10^3$	-3.128 [-2.472] <sup>g</sup>	0.178	-6.588	0.059	-15.998	-5.385	-15.998	-5.443
$\alpha_2^B \times 10^3$	2.778 <sup>i</sup> [0.122] <sup>g</sup>	2.553	2.018 <sup>i</sup>	2.313	0.288 <sup>m</sup>	0.307 <sup>m</sup>	0.279 <sup>m</sup>	0.289 <sup>m</sup>
$\alpha_3^A \times 10^3$	-10.948 [-10.795] <sup>g</sup>	-5.610	-7.530	-5.503	1.343	-0.089	1.323	-0.041
$\alpha_3^B \times 10^3$	1.188 <sup>i</sup> [-1.062] <sup>g</sup>	0.372 <sup>l</sup>	1.562 <sup>i</sup>	0.325 <sup>l</sup>	1.573	0.852	1.457	0.815
$\alpha_4^A \times 10^3$	21.099 [16.046] <sup>g</sup>	7.657	21.114	7.659	20.069	7.286	20.069	7.286
$\alpha_4^B \times 10^3$	0.665 [0.416] <sup>g</sup>	-0.801	0.583	-0.467	0.008	0.091	0.005	0.086
$\alpha_5^A \times 10^3$	14.862 [13.570] <sup>g</sup>	2.509	15.040	2.839	19.885	6.730	19.887	6.735
$\alpha_5^B \times 10^3$	-0.946 <sup>i</sup> [5.727] <sup>g</sup>	-1.175 <sup>l</sup>	-0.822 <sup>i</sup>	-1.003 <sup>l</sup>	-0.112 <sup>m</sup>	-0.188 <sup>m</sup>	-0.105 <sup>m</sup>	-0.176 <sup>m</sup>
$\alpha_6^A \times 10^3$	-2.331 [-5.673] <sup>g</sup>	1.689	-2.359	1.391	-9.462	-3.369	-9.432	-3.357
$\alpha_6^B \times 10^3$	1.562 [1.567] <sup>g</sup>	1.384	1.402	1.222	0.367	0.405	0.380	0.392

<sup>a</sup> Fermi resonances of the second type between  $\nu_1$  and  $\nu_2 + \nu_3$ , and between  $\nu_4$  and  $\nu_2 + \nu_5$ , taken into account.

<sup>b</sup> Fermi resonance of the first type between  $\nu_1$  and  $2\nu_3$  taken into account

<sup>c</sup> Fermi resonance of the first type between  $\nu_1$  and  $2\nu_2$  taken into account

<sup>d</sup> From Ref.[18]

<sup>e</sup> MP2/6-311\*\* calculation from ref.[7]. The scaling factor of 0.943 has been removed

<sup>f</sup> QCISD/6-311+G(d,p) calculation from Ref.[17]

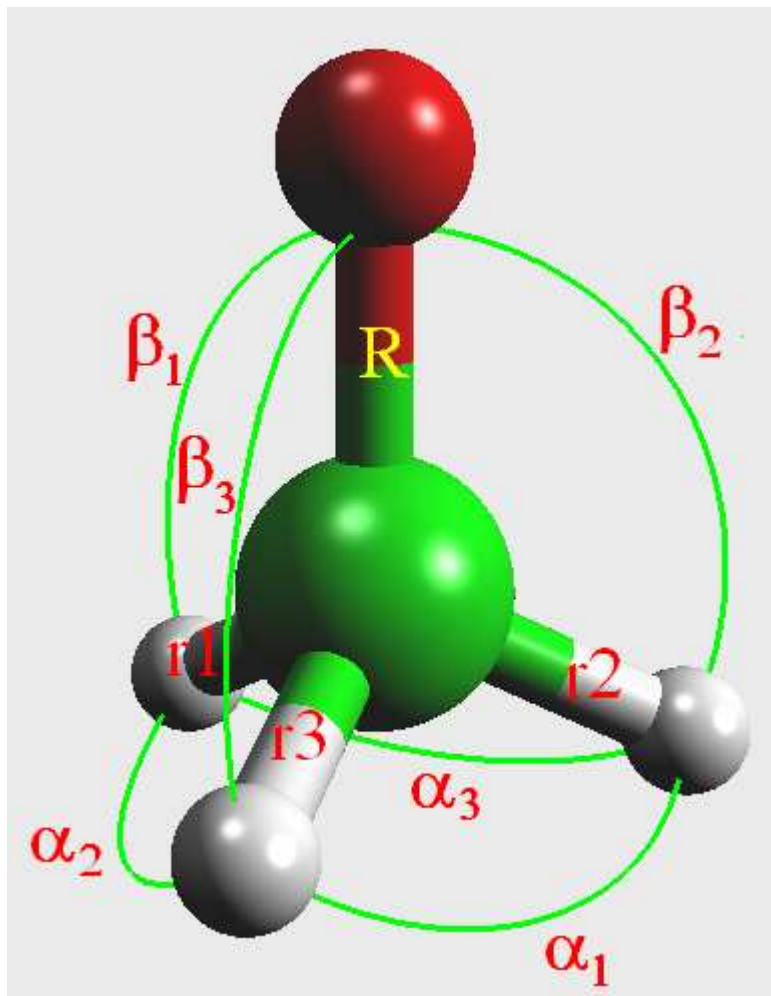
<sup>g</sup> From Ref.[6]

<sup>h</sup> From Ref.[20]

<sup>i</sup> Coriolis resonances between  $\nu_2$  and  $\nu_5$ , and between  $\nu_3$  and  $\nu_5$  taken into account

<sup>l</sup> Coriolis resonance between  $\nu_3$  and  $\nu_5$  taken into account

<sup>m</sup> Coriolis resonance between  $\nu_2$  and  $\nu_5$  taken into account



Internal coordinates used for the definition of the symmetry coordinates of  $\text{OPH}_3$  and  $\text{SPH}_3$   
102x131mm (96 x 96 DPI)

only