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8 Exercise - Introduction to Group Theory

8.1 (Symmetries of normal modes of vibrations)

8.1.1 HOCl

While we got 3 atoms, we expect $3 \cdot 3 - 6 = 3$ vibrational degrees of freedom. First we want to get the reducible representation for cartesian coordinate transformation. Therefore we first have to get the point group which in this case is C_s. The character table is given with

C_s	E	σ_h
A'	1	1
A''	1	-1

From this we get the reducible representation

C_s	E	σ_h
Γ	9	1

Therefore we can reduce Γ to

$$\Gamma^{tot} = 5a' + 4a''$$

Now subtracting 3 translational and 3 rotational degrees of freedom we get:

$$\begin{aligned} \Gamma^{vib} &= \Gamma^{tot} - \Gamma^{trans} - \Gamma^{rot} \\ &= 5a' + 4a'' - (2a' + a'') - (a' + 2a'') \\ &= 2a' + a'' \end{aligned}$$

We got the same kind of modes like for H_2O which was treated in the lecture, therefore we can identify the modes:

1. symmetric stretching mode (1) with a', 2. symmetric bending mode (2) with a' and 3. asymmetric stretching mode (3) with a''.

Figure 1: symmetric stretching mode

Figure 2: symmetric bending mode

Figure 3: asymmetric stretching mode

8.1.2 PHHH

The number of vibrational degrees of freedom is $4 \cdot 3 - 6 = 6$. The point group of PH_3 is C_{3v}. Character table is given with

C_{3v}	E	$2C_3\,(z)$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

With the reducible representation for cartesian coordinate transformation of

C_{3v}	E	$2C_3\,(z)$	$3\sigma_v$
Γ	12	-4	4

This cannot be reduced, meaning I did something wrong.
Well, what we further would have liked to to is, reducing to vibrational modes

$$\begin{aligned}\Gamma^{vib} &= \Gamma^{tot} - \Gamma^{trans} - \Gamma^{rot} \\ &= \Gamma^{tot} - (a_1 + e) - (a_2 + e)\end{aligned}$$

but since Γ^{tot} cannot be reduced using the irreducible representations (at least it would not contain $a_1 + a_2 + 2e$) we abort here and just do some minor work on the other tasks.

8.1.3 CHHHH

There is a total number of $5 \cdot 3 - 6 = 9$ vibrational degrees of freedom. The point group of CH_4 is T_d.

8.1.4 CHCHCH+

We have $6 \cdot 3 - 6 = 12$ vibrational degrees of freedom.