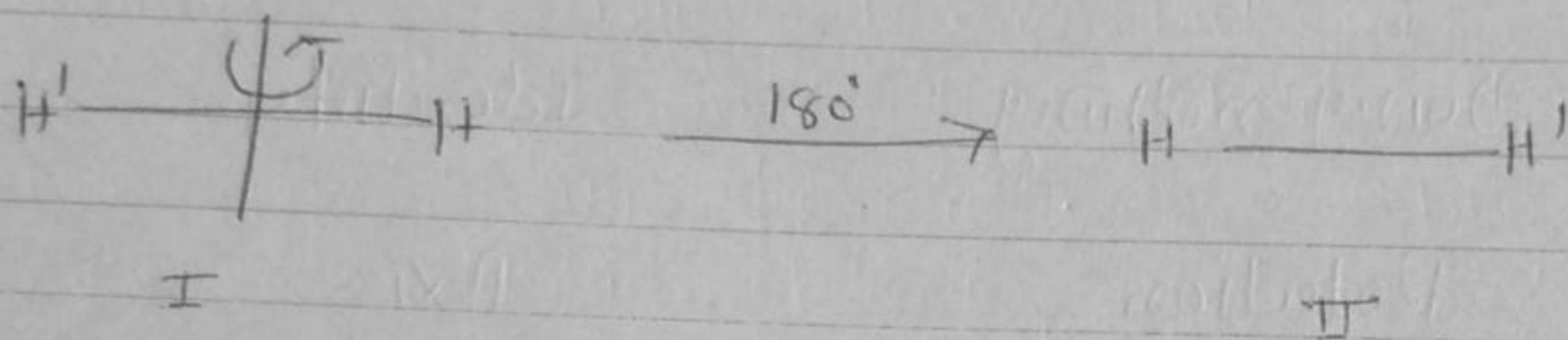


Unit III
Ther. Chem.

Group theory is concerned with operations in determining Symmetry.

Symmetry \Rightarrow Symmetry means that a certain part of an object looks exactly like another part. The Sun, the planets, the human beings, animals and plants are all symmetrical. An object is said to be symmetrical if it can take up more than one equivalent (indistinguishable) orientation. For example, let us consider hydrogen molecule in orientation I (H^1 and H^2 are same). It can be rotated by 180° to the orientation II. ~~(H^1 and H^2 are same)~~ II can be distinguished from I i.e., they are equivalent orientations.



Symmetry of an object or molecules is best described by mentioning certain operations like rotation, reflection etc. which brings the object in equivalent ~~orientation~~ position. The resulting geometric configuration is indistinguishable from the original one. Symm. arises when a molecule possess identical atom in certain part of it. For example, the H-atoms in H_2O are equivalent and cause symm. in H_2O .

Symmetry operation and Symmetry element \Rightarrow

Symmetry operation \Rightarrow Symm. operation is the process carried out on the molecule which brings it from the original orientation to another equivalent orientation.

Geometrical operation such as reflection, rotation, inversion etc. which produce a configuration not different from the original configuration is called symmetry operation. The two configurations may or may not be exactly identical but they look alike on all respects.

Symmetry element :- The various symm. operations are done with respect to a geometrical entity such as straight (rotation), plane (reflection), point (inversion) etc. are called symm. element.

Symm. operation	Symm. element	Symbol
(1) Doing nothing	Identity	E
(2) Rotation	Axis	C _n
(3) Reflection	Plane	σ
(4) Inversion	Centre of symm.	i
(5) Improper rotation	Rotation about an axis followed by reflection with a plane \perp to the rotation axis.	S _n

These operations do not change in the energy of the molecule. Also in these operations the centre of the molecule is not altered. If at least one point remain fixed in the operation, the operation is known as point group operation.

are possible

(1) Identity (E)

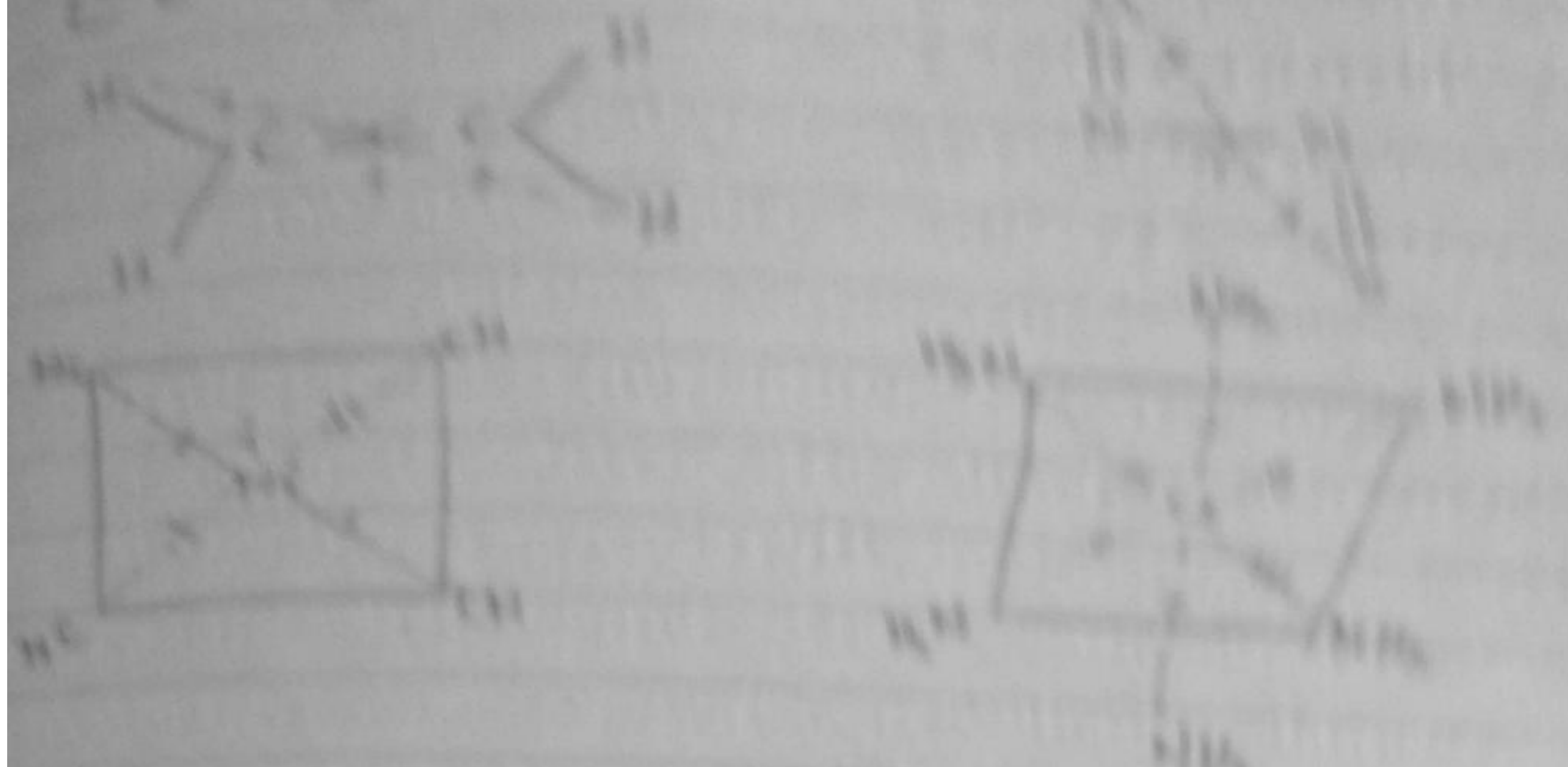
This is an operation which brings back the molecule to the original orientation. This is to the operation of not doing anything on the operation. The molecule remains unchanged and identical to the original in all respects. It is a mathematical necessity.

There are several different types of ~~operations~~ operations which bring back the molecule to its original orientation. They are not considered separately but are put together as identity. For example, in an axis of four fold symmetry, C_4 , C_2 and C_4^3 are considered as rotation operations. But C_4^2 i.e. rotation by 180° is not considered as rotation operation because it is an identity operation. Only a plane of symmetry only one reflection operation is considered. If the reflection is repeated, the original orientation is obtained and hence the second reflection is an identity operation.

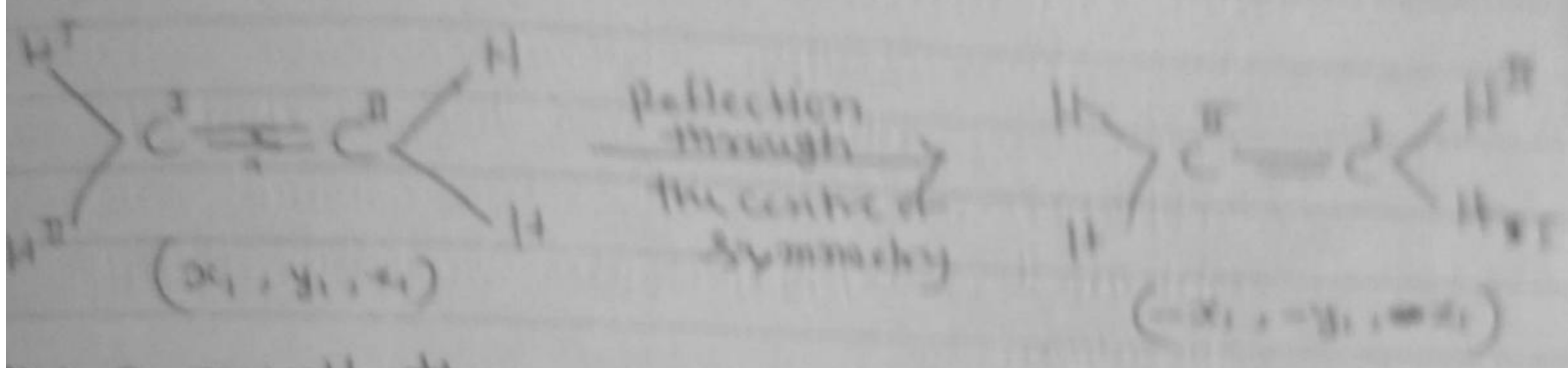
The identity operation, in effect, means doing nothing on the molecule and hence does not seem to be of much importance. But its importance lies on considering the molecules as a group and to apply the group theory to molecules.

(2) Centre of Symmetry or inversion centre (i)

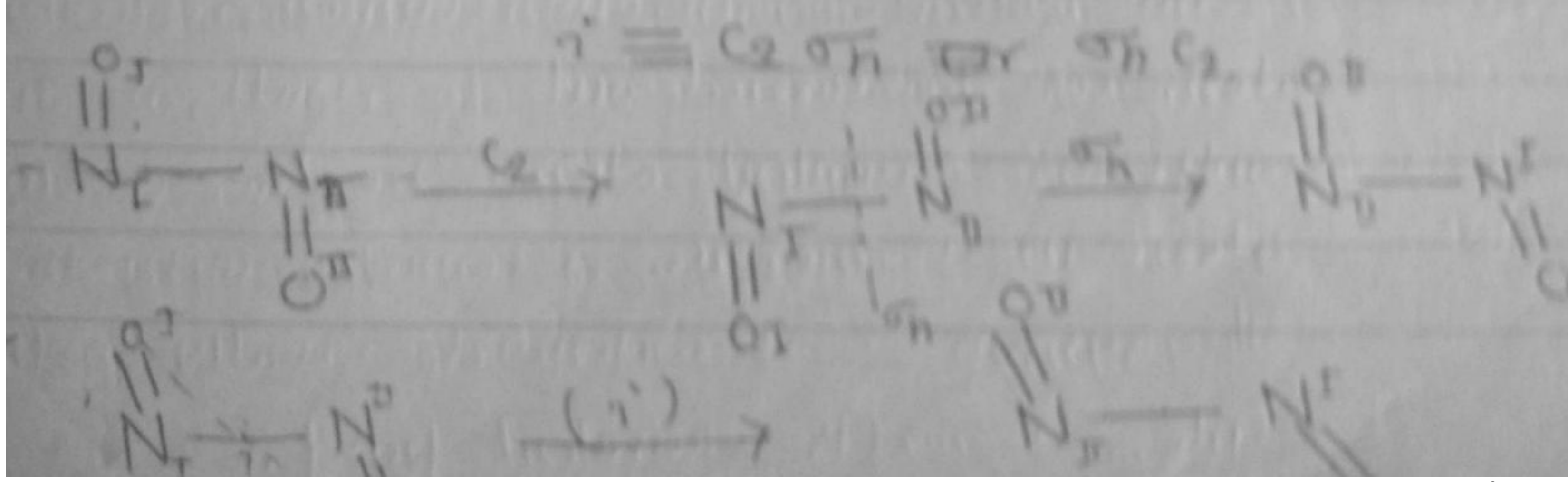
This is an imaginary point in the centre of the molecule, through which reflection of each atom can be carried out to result in its coincidence with an equivalent atom. In other words if any atom in a molecule is connected with the centre of symmetry and extended equally on the other side, it meets equivalent point.



The centre of symmetry is the symmetry element and the process of reflection through it leading to an inverted orientation is the symmetry operation.



Thus, as a result of this operation the molecule gets completely inverted to an equivalent orientation. Hence, the operation is termed inversion (i) and the centre of symmetry is also called inversion centre. Only one inversion operation is possible. Second reflection gives back the original orientation. A two fold rotation reflection operation is equivalent to an inversion operation, i.e.,



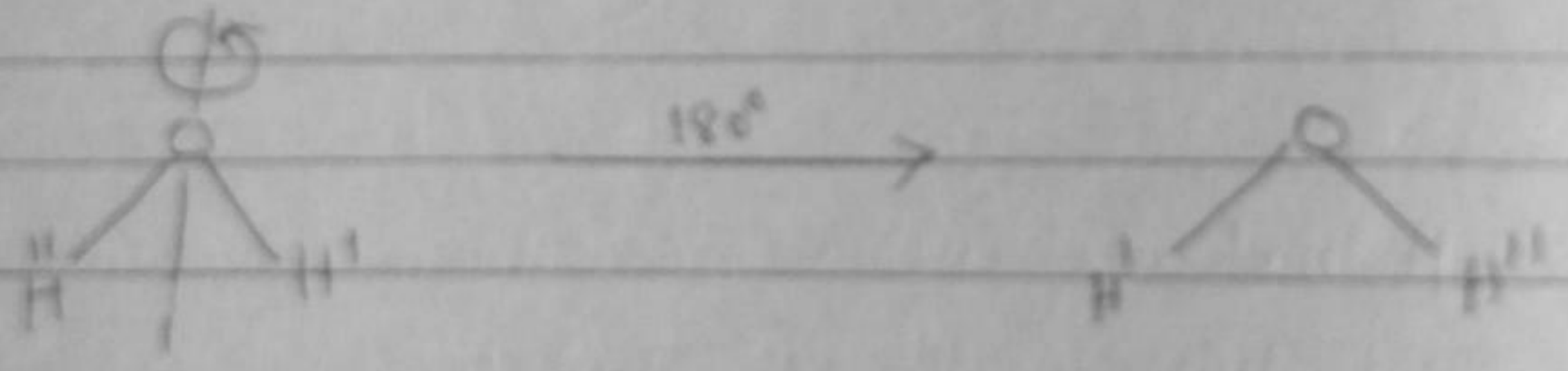
(3) Axis of Symmetry or Rotation
 This is an imaginary axis passing through the molecule, over which rotation can be carried out to take the molecule from one orientation to another equivalent orientation. This is represented by C_n . Where n is the order of axis, i.e. the number of times of equivalent orientations occur on rotation through 360° .

(Rotation means making a circular motion about an axis passing through the C.G. of the molecule. If an equivalent config. is obtained by rotating an object through an angle θ , and if successive rotation by an angle θ the object returns to original.)

$$n = \frac{360}{\theta}$$

Example: \rightarrow

H_2O In H_2O molecule the axis passing through oxygen atom and in between two H-atoms has order 2 i.e. $n=2$ or is axis of two fold symm. The molecule has to be rotated by 180° to get equivalent orientation.



order of ammonia (NH_3) \rightarrow The axis passing through N-atom and the center of the triangle containing three H-atoms is the three fold axis i.e. ($n=3$). The molecule has to be rotated by 120° to get equivalent orientations.

