

Acid sites, basic sites and the ammonia molecule

Broadly speaking, there are two definitions for basic-acidic substances. Brønsted (or Brønsted-Lowry) definition: an acid is a proton (H^+ ion) donor, and so a base is a proton acceptor; the Lewis definition: an acid is an electron acceptor, and a base is an electron donor. On the surface of metal oxides, acidic sites favour the adsorption of basic reactants and enhance the desorption of acidic products, thereby protecting their further oxidation. The surface of an oxide therefore represents an array of acidic and basic centres of the so-called Brønsted and Lewis type. Brønsted acids are formed by covalently bonded OH groups, Brønsted bases by O^{2-} and OH^- ions. Lewis acids are formed by surface cations and Lewis bases by O^{2-} ions.

From the point of view of catalytic oxidation, the presence on the surface of the oxides of redox centres is of great importance, which may accept or donate electrons. These redox centres are frequently connected with the presence of lattice defects in the surface or in the near-to-surface of the oxides. In fact, many reactants participating in the reactions of catalytic oxidation are characterised by pronounced acidic or basic properties and therefore may interact with acid-base centres present at the surface of a metal oxide. This may affect the process of oxidation in two ways*:

- as the result of an acid-base reaction between the reactant and the metal oxide, an active species may be generated which then more easily undergoes the redox process, the acid-base reaction being one of the elementary steps of the oxidation
- due to acid-base interaction with the metal oxide strong chemisorption of reactants may take place, and their residence time at the metal oxide surface may be changed, the conditions of their interaction with oxygen are thus strongly modified.

While carbon dioxide is generally used to test the basic properties of a metal oxide, ammonia, which is a strong base, has been used on metal oxides as a probe molecule to test the acidic properties of the surface. Besides, this molecule has a considerable affinity for the proton, due to which the presence of weak Lewis and Brønsted acid centres on the surface can be detected.

Ammonia has symmetric top structure, with one central *N*-atom above a tripod of three *H*-atoms (Fig. 1). The *A*-axis corresponds to the figure axis of a symmetric top, and thus is

* *A. Bielanski, J. Haber, Oxygen in catalysis, Marcel Dekker Inc., New York (1991).*

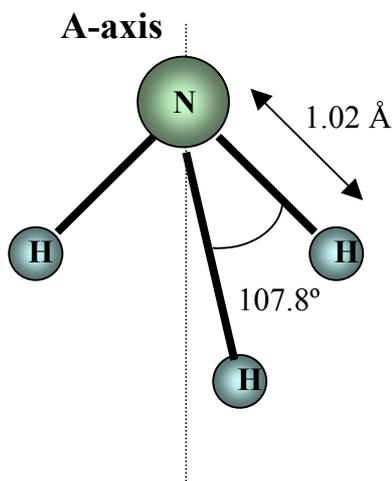


Fig. 1: NH_3 's structure and symmetry axis.

also the main axis of symmetry. Table 1* lists the rotational constants for NH_3 along with some other properties of the molecule. This figure also shows the molecule's structure as well as its main symmetry axis, which coincides with the figure axis, along which lies the dipole moment. Three rotations of 120° about this axis each produce an indistinguishable change in the molecule. Thus, the main axis is 3-fold symmetric. In addition, NH_3 has three planes of symmetry through the molecule at mutual angles of 120° , giving ammonia c_{3v} molecular symmetry.

Property	Value
Mass	$m = 17$
Bond length	$r_0(\text{NH}) = 1.02 \text{ [\AA]}$
Bond angle	107.8°
Rotational constants	$A_0 = 6.196 \text{ [cm}^{-1}\text{]}$ $B_0 = 9.944 \text{ [cm}^{-1}\text{]}$ $C_0 = 9.944 \text{ [cm}^{-1}\text{]}$
Symmetry number	$\sigma = 3$
Dipole moment	$\mu = 1.471$

Table 1: Some properties of NH_3

Ammonia's four vibrations modes are illustrated in Figure 2, and listed in Table 2**. The two parallel modes, $\parallel 1$ and $\parallel 2$, are symmetric, while the two perpendicular modes, $\bullet 3$ and $\bullet 4$, are asymmetric and degenerate. Ammonia also has inversion doubling due to the motion of the N -atom through the H_3 -atomplane that produces two equilibrium positions for the N -atom: the normal pyramidal structure with N above the plane, and an inverted configuration. Because there are two equilibrium positions, the result of the inversion motion is that the dipole moment, which lies along the symmetry axis, also moves back and forth. Thus,

* S.V. Krhistenko et al., *Molecules and their spectroscopic properties*, Springer-Verlag 1998.

** G. Herzberg, *Molecular spectra and molecular structure II: infrared and Raman spectra of polyatomic molecules*. Krieger Publishing Company, 1991.

the value for the dipole moment that is typically quoted in the literature and is listed in Table 1, is the inversion-transition moment, not the permanent dipole moment. For a detailed identification of acid centres on metal oxides by ammonia vibrations, see references [7-11] of Chapter 5 and references therein.

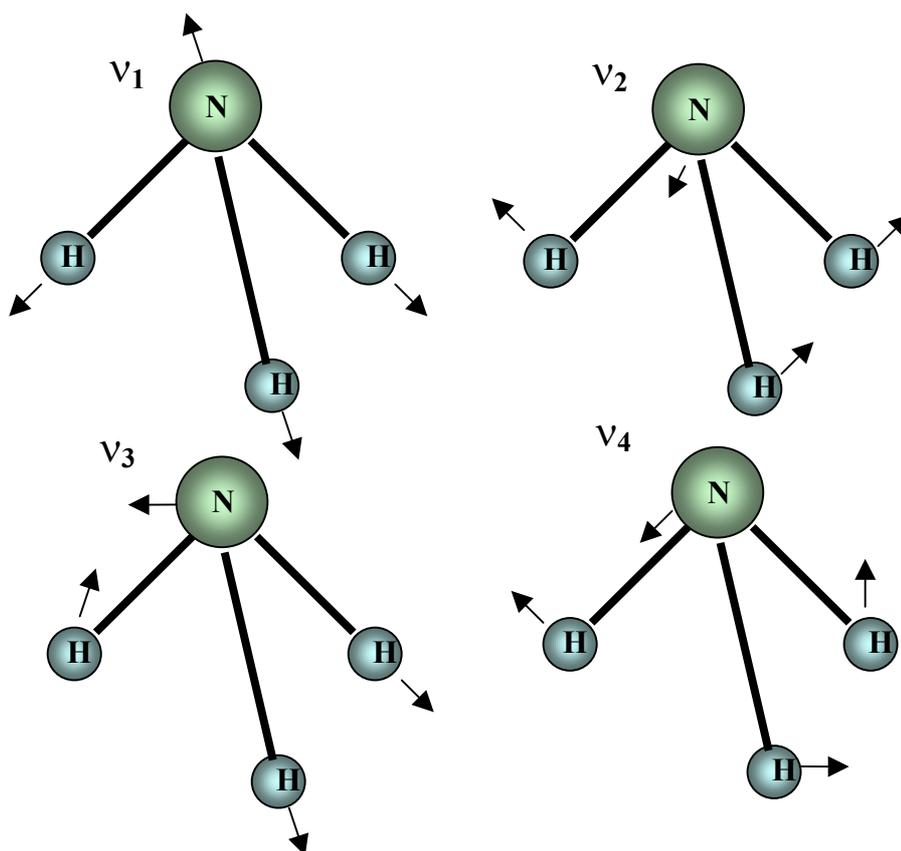


Fig. 2: NH₃'s vibrational modes

Vibration	Frequency [cm ⁻¹]	Type	Description
v ₁	3357		Symmetric Stretch
v ₂	950		Symmetric Bend
v ₂	3444	•	Asymmetric Stretch (Degenerate)
v ₂	1627	•	Asymmetric Bend (Degenerate)

Table 2: Fundamental vibrations, frequencies, types and description for NH₃

