

HEAT CAPACITY RATIO FOR GASES (γ)

OBJECTIVE: Measure the speed of sound in various gases, and determine the heat capacity ratio, γ , for nitrogen, carbon dioxide, helium and argon by both the adiabatic expansion (Clement and Desormes) and speed of sound methods.

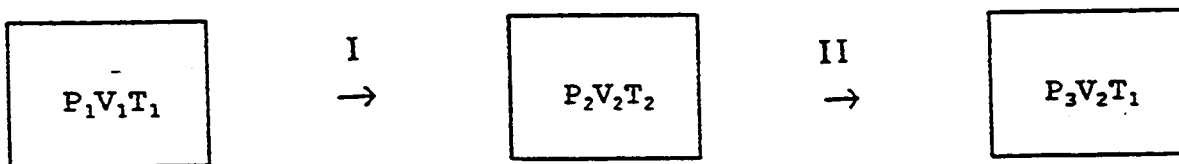
1. INTRODUCTION:

By definition C_v (or C_p) denotes the amount of heat energy which must be absorbed by one mole of a gas at constant volume (or pressure) to raise the temperature of the gas by one degree. The absorbed heat energy causes the molecules to move faster (increase in translational energy), to rotate faster (increase in rotational energy) and to vibrate faster (increase in vibrational energy). Thus the knowledge of heat capacities plays a role in understanding the complexity of gaseous molecules. Unfortunately the easiest method for determining the individual heat capacities of gases is beyond the capability of an undergraduate laboratory. The heat capacity ratio, $\gamma = C_p/C_v$, is just as useful in understanding the structure of gaseous molecules and is more accessible experimentally.

2. CLEMENT AND DISORMES METHOD FOR γ

2.1 Theory:

Consider the following two stage process carried out on a gas:



Stage I is a reversible adiabatic expansion of the gas from V_1 to V_2 with cooling from T_1 to T_2 since the gas is doing work of expansion and no compensating heat transfer is allowed.

Thus:
$$dU = dq + dw$$

$dq = 0$ for an adiabatic transformation, $dw = -PdV$ for a reversible expansion

$$\therefore dU = -PdV \quad (1)$$

The total differential of U is given by

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (2)$$

If we assume the gas is ideal

$$\left(\frac{dU}{dV}\right)_T = 0$$

and

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT = n\bar{C}_v dT \quad (3)$$

$$\therefore n\bar{C}_v dT = -PdV \quad (4)$$

and again for an ideal gas $PV = nRT$ so

$$n\bar{C}_v \frac{dT}{T} = -nR \frac{dV}{V} \quad (5)$$

integrating we find

$$n\bar{C}_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1} \quad (6)$$

or since

$$\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1}$$

for an ideal gas

$$\bar{C}_V \ln \frac{P_2}{P_1} = -(\bar{C}_V + R) \ln \frac{V_2}{V_1} = -\bar{C}_p \ln \frac{V_2}{V_1} \quad (7)$$

since, for an ideal gas $\bar{C}_V + R = \bar{C}_p$ (8)

therefore

$$\frac{\bar{C}_p}{\bar{C}_V} = \gamma = \frac{\ln (P_1/P_2)}{\ln (V_2/V_1)} \quad (9)$$

Stage II involves heat transfer to the gas at constant volume sufficient to restore the temperature to T_1 . Thus, assuming ideal gas behaviour,

$$\frac{P_3}{P_2} = \frac{T_1}{T_2} = \frac{P_1 V_1}{P_2 V_2} \quad (10)$$

$$1 \quad \frac{V_2}{V_1} = \frac{P_1}{P_3} \quad (11)$$

Thus

$$2 \quad \gamma = \frac{\ln(P_1/P_2)}{\ln(P_1/P_3)} \quad (12)$$

2.2 Experimental Method:

In this experiment we take a quantity of gas in a large bottle (carboy) at

pressure P_1 (greater than atmospheric) and temperature T_1 and remove the stopper for an instant to allow the gas to expand adiabatically to pressure P_2 , (atmospheric), cooling to T_2 (See Fig. 1).

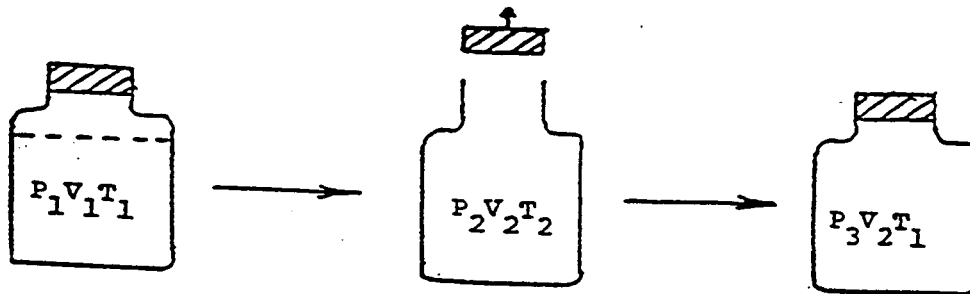


Figure 1 Clement and Désormes Method for Measuring γ

The stopper is immediately replaced and the gas is allowed to warm up to the original temperature, T_1 at constant volume V_2 and the final pressure P_3 is measured. From the measured values of P_1 , P_2 and P_3 , the heat capacity ratio, γ , can be calculated.

Note that the quantity of gas under consideration is not the total initially in the bottle but only the portion V_1 below an imaginary boundary which subsequent to stage I completely fills the bottle. The remainder is lost from the bottle and not accounted for.

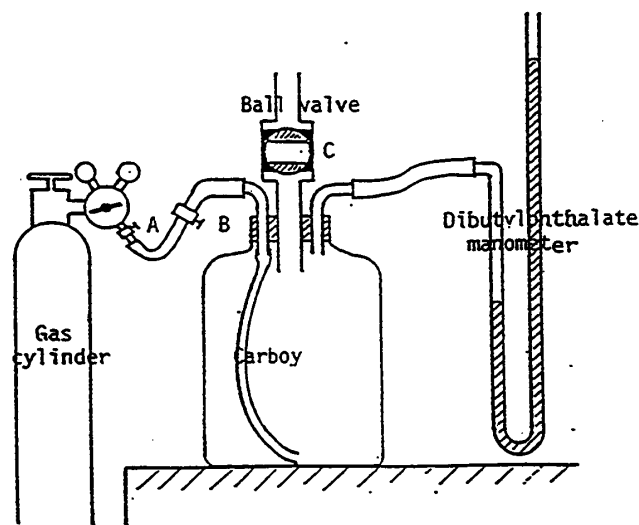


Figure 2. Clement & Désormes Apparatus

2.3 Procedure:

Assemble the apparatus as shown in Fig. 2. Note that the working fluid in the open-end manometer is dibutyl phthalate. All manometer readings must be converted to equivalent readings in cm Hg and then added to the barometric pressure.

- 1) Open clamp B and the ball valve C. Set the gas regulator to between 5 and 10 psig gas pressure.
- 2) Slowly open the needle valve A and sweep out the carboy with the gas for 15 minutes. Reduce the gas flow by partially closing A.
- 3) Close the ball valve C and pressurise the carboy to near the maximum pressure allowed by the manometer, taking care not to blow the manometric fluid out of the glass tube.
- 4) Finally close B. Initially the pressure usually falls. This is due to cooling of the gas which has warmed as a result of work done on it in the pressurising process (bicycle pump effect). It may also fall due to a leak in the system. Allow the gas to come to thermal equilibrium with the surroundings as indicated by constancy of pressure.
- 5) Record the levels of dibutylphthalate in the manometer.
- 6) Expand the gas adiabatically by quickly opening and closing the ball valve C. Allow the gas to warm up to room temperature and record the manometer readings.
- 7) Repeat the entire procedure two more times with the same gas, but omit the flushing unless air has got into the carboy. Record the ambient barometric pressure and temperature. **Note:** Do not open windows during the experiment. The temperature of the surroundings must be kept as constant as possible. (Why?)

2.4 Calculations:

Calculate γ for each run and determine the average value of γ . Calculate γ for each gas from the Equipartition of Energy Principle and the number of degrees of freedom. Identify the various degrees of freedom of each gas studied. Calculate the order of magnitude of the temperature drop of gas at the moment of expansion (assume an ideal gas).

3. SPEED OF SOUND METHOD FOR γ (KUNDT'S TUBE)

3.1 Theory:

Only a brief outline of the theory underlying the measurement of the speed of sound is given here. [For a more detailed discussion of the subject matter the student is referred to more specialized texts (1) dealing with sound.] Sound-waves require elastic media for their propagation, for a train of sound-waves consists essentially of a sequence of elastic displacements of elements of the medium. These displacements take place in the direction of propagation so that sound-waves are longitudinal in nature. The longitudinal waves are produced by a disturbance applied to the elastic medium causing compressions and rarefactions. Fig. 3 shows elements of an elastic medium at "rest". A stimulus when applied to the medium at rest, causes the elements to vibrate about their mean positions and, because they do not vibrate in phase, this causes pressure (hence density) differences in the medium resulting in compressions and rarefactions along the wavefront, as denoted by the letters C and R in Fig.3. These compressions and rarefactions are taking place with such rapidity that the process for all intents and purposes is adiabatic; there is no time for heat exchange between the vibrating elements and their surroundings, i.e. $q = 0$. The adiabatic compressions and expansions of ideal gases are governed by

$$PV^\gamma = \text{constant} \quad (13)$$

(c.f. $PV = \text{constant}$ for an isothermal expansion of an ideal gas)

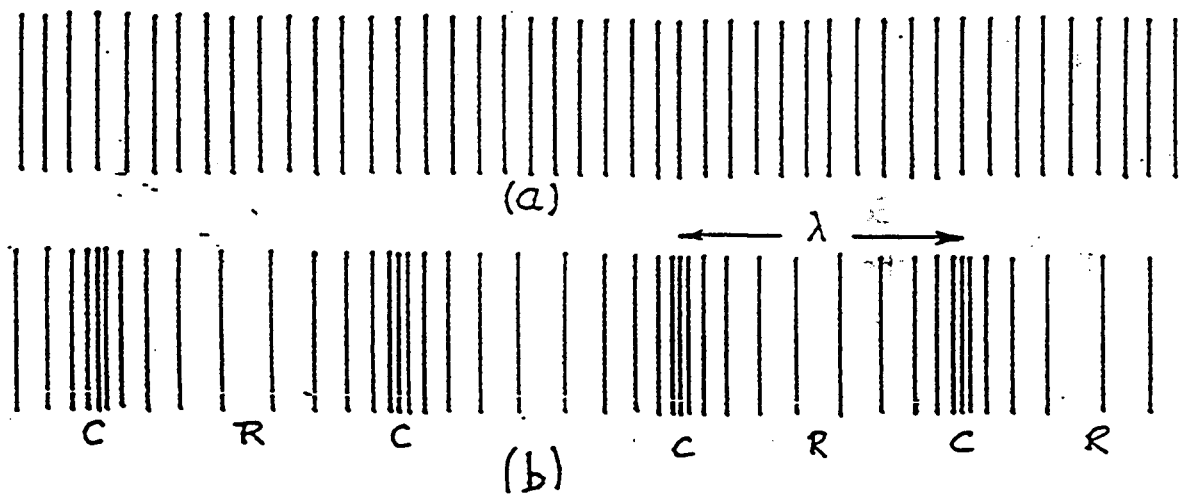


Fig. 3 (a) elements of elastic medium at "rest". (b) a disturbance passing through the medium causes compressions (C) and rarefactions (R).

The speed of sound in any medium depends on the elasticity of the medium and its density.

It can be shown (1) that the speed of sound, c , in any medium is given by the equation

$$c = \sqrt{K / \rho} \quad (14)$$

where K is the bulk modulus of elasticity of the medium and D its density. For a gas undergoing adiabatic pressure changes the bulk modulus of elasticity is simply γP , where P is the (absolute) pressure of the gas. Thus

$$c = \sqrt{\gamma P / \rho} \quad (15)$$

If an assumption be made that the gas behaves ideally, then $PV = nRT$ also applies, which upon rearrangement gives

$$\frac{P}{\rho} = \frac{RT}{M} \quad (16)$$

where M is the molar mass of the gas.

Substitution of (3.16) into (3.15), gives

$$c = \sqrt{\frac{\gamma RT}{M}} \quad (17)$$

or

$$\gamma = \frac{M c^2}{RT} \quad (18)$$

If the distance between corresponding points on the wave front (e.g. maximum compressions) is called the wave-length, λ , and the rate at which such compressions pass a given section is called the frequency, f , then the speed of sound is also given by

$$c = f\lambda \quad (19)$$

and

$$\gamma = \frac{M f^2 \lambda^2}{RT} \quad (20)$$

In this experiment, which is based on a modified Kundt's tube, a sound-wave of known frequency is sent down a long glass tube (2) and is made to reflect from a movable piston creating a standing wave with a series of maxima, called antinodes, A, and minimum points in between, called nodes, N, Fig. 4.

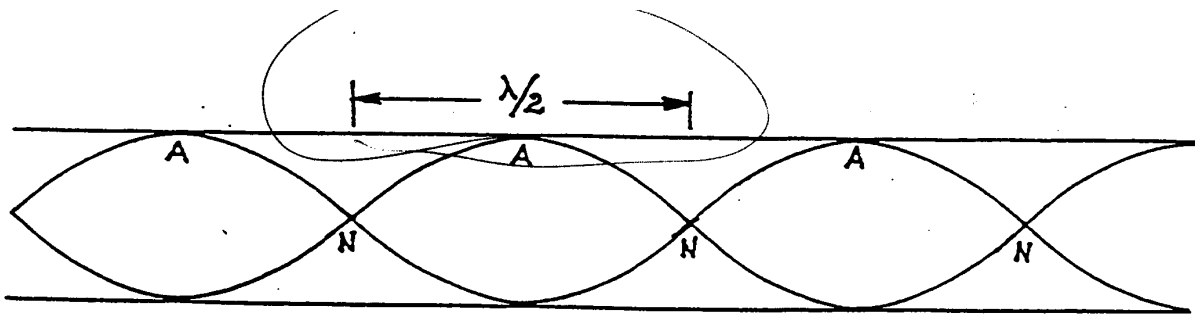


Fig. 4 A standing wave with nodes, N, and antinodes, A, created by reflection of a wave from the piston P.

The wave appears to be standing which is a result of interference between two waves of the same frequency travelling with the same speed in opposite directions. The distance between nearest nodes (or anti-nodes) is equal to $\lambda/2$. The successive nodes (or anti-nodes) are in opposite phase, i.e. they differ in phase by 180 degrees (a fact which we will take advantage of in this experiment), with maximum sound intensity occurring at the nodes and minimum at the anti-nodes.

3.2 Procedure:

The apparatus is shown in Fig. 5

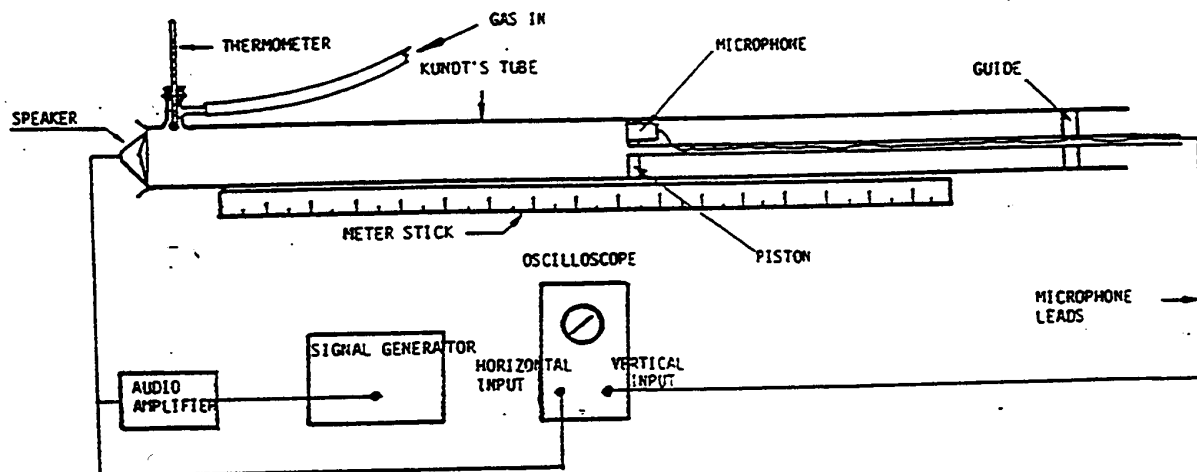


Fig. 5 Kundt's Tube

- 1) Move the piston furthest away from the speaker and let the gas sweep out air from the Kundt's tube. It may be necessary to support the piston rod to reduce leverage on the tube.
- 2) Reduce the flow of the gas to a slow stream, but sufficient to prevent air from diffusing in during the experiment. Be careful with CO_2 as it cools considerably upon expansion from the cylinder.
- 3) The microphone is powered by a small battery which you should obtain from, and return to, your T.A. Make sure that the polarities of the circuit, including the

microphone battery, are correct.

4) Switch on the wave generator and connect its leads to the audio amplifier and through it to the speakers and the horizontal input of the oscilloscope.

5) Switch on the oscilloscope and the power supply unit for the amplifier. Insert the microphone battery in its holder and connect the microphone leads to drive the vertical sweep of the oscilloscope.

6) Select an appropriate frequency (1000 Hz for CO₂, air and N₂. 2000 Hz for He) and adjust the intensity of the sound using the attenuator on the signal generator. Do not "overblast"! Details of adjustment of the oscilloscope will be provided by the T.A. as the instruments may not be of the same type. Ideally the components should be adjusted so that the two signals to the oscilloscope are about equal in magnitude and a circle is seen on the screen when the signals are 90° out of phase.

7) Slowly move the piston towards the speaker until a straight line pattern is observed on the screen. Record the position of the piston and note whether the phase shift is 0° or 180° (0° shift occurs when the line is inclined 45° to the right and the 180° phase shift occurs when the line is inclined 45° to the left).

8) Move the piston inward again until a next straight line pattern is obtained. Note the position of the piston and the phase shift.

9) Continue taking as many readings as the geometry of the tube allows. Record the temperature of the gas at the inlet. If necessary, repeat the entire procedure until satisfactory results are obtained.

10) Repeat with the other gases provided. If time permits do the measurements at a different frequency.

3.3 Calculations:

Average the spacings $\lambda/2$ and using the known frequency calculate γ for the gas from equation (4.20). Compare these experimental values with the theoretical values calculated from the Principle of Equipartition of Energy (3) and with the accepted literature values (4). Calculate the standard deviation σ for γ on the assumption that the main sources of error are due to uncertainty in λ and f . The uncertainty of the latter may be taken as 0.5% of the reading.

3.4 Discussion:

Discuss your results in terms of the Microscopic Interpretation of the Heat Capacities of Gases.

4. MICROSCOPIC INTERPRETATION OF THE HEAT CAPACITY OF GASES

4.1 Degrees of freedom:

The number of degrees of freedom of the molecule is the number of independent co-ordinates which must be specified in order to locate the molecule and its component atoms in space. Thus for a molecule containing N atoms, $3N$ co-ordinates will be required and the molecule has $3N$ degrees of freedom.

4.2 Classification of degrees of freedom:

Rather than consider each degree of freedom to be a position co-ordinate it is convenient to classify the degrees of freedom as follows:

- (a) **Translational degrees of freedom** represent the three co-ordinates required to specify the position of the centre of mass of the molecule. For a monatomic gas, of course $N = 1$ and the total number of degrees of freedom will be 3, all of which are translational.
- (b) **Rotational degrees of freedom** are possessed by polyatomic molecules since different orientations in space are possible. For linear molecules we must specify the orientation of the molecule with respect to rotation about two

mutually perpendicular axes passing through the centre of mass of the molecule perpendicular to the axis of the molecule.

Different orientations with respect to the molecular axis cannot be recognized and so a linear molecule has only two rotational degrees of freedom.

For non-linear molecules we must specify the orientation with respect to three mutually perpendicular axes and therefore a non-linear molecule possesses three rotational degrees of freedom.

- (c) **Vibrational degrees of freedom** make up the remaining $3N-5$ degrees of freedom for linear molecules and $3N-6$ degrees of freedom for non-linear molecules. These specify the displacement of the atoms from their equilibrium positions due to vibration.

4.3 Normal modes of vibrations are associated with each vibrational degree of freedom and have characteristic vibrational frequencies. Thus for linear and non-linear triatomic molecules there are, respectively, four and three vibrational degrees of freedom and the normal modes associated with them are classified as:

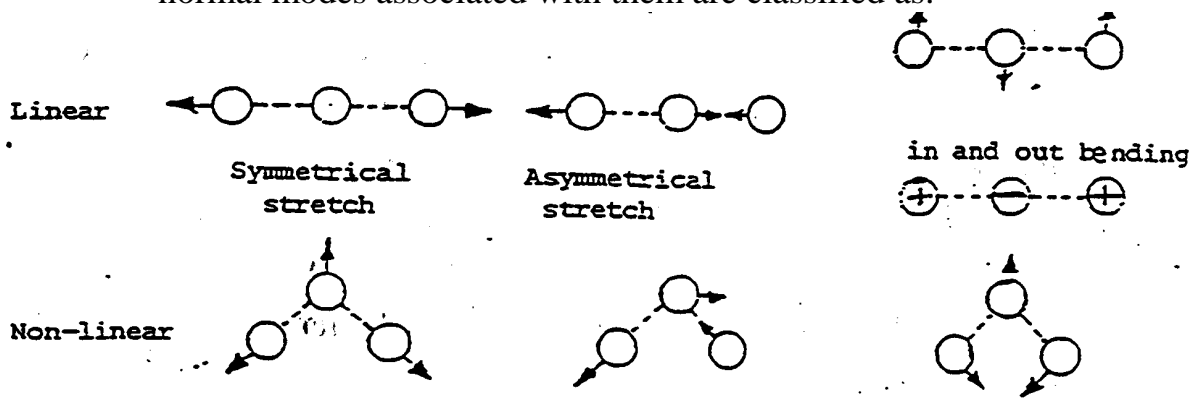


Fig. 6 Normal modes of vibration of a triatomic molecule.

Equipartition of Energy:

According to the kinetic theory of gases, the average kinetic energy per molecule for an ideal gas is given by

$$1/2 \bar{m} \bar{u}^2 = \frac{3}{2} kT \quad (21)$$

Since the energy of a monatomic gas is entirely kinetic energy of translation we can write for the energy per mole

$$\bar{U} = \frac{3}{2} RT \quad (22)$$

and thus for a monatomic gas

$$\bar{C}_V = \left(\frac{\delta U}{\delta T} \right)_V = \frac{3}{2} R \approx 12.4 J mol^{-1} \quad (23)$$

Why is this C_V and not C_P ?

Polyatomic molecules possess internal degrees of freedom and the internal motions will make a contribution to the energy of the gas, but to what extent? A monatomic gas has only 3 degrees of freedom (translation) and if we assume that they are independent of each other then they will each contribute $1/2 kT$.

The principle of equipartition of energy states that each square term (e.g. $1/2 m u_x^2$ for the kinetic energy in the x direction) in the expression for the total energy of the molecule contributes $1/2 kT$ to the total energy.

Rotational motions have rotational kinetic energy $1/2 I \omega^2$ for each axis of rotation, where I = moment of inertia about the axis and ω = angular velocity. Thus each rotational degree of freedom contributes $1/2 kT$ to the total energy.

Vibrational motions affect both the kinetic and potential energy, each of which can be expressed by a square term ($1/2 \mu u^2$ and $1/2 \kappa x^2$ where μ is the reduced mass and κ is the force constant) and thus each vibrational degree of freedom will contribute kT to the total energy.

$$\bar{U} (total) = \bar{U} (trans) + \bar{U} (rotation) + \bar{U} (vibration) \quad (24)$$

Thus according to the classical equipartition principle the molar energy of a diatomic molecule will be

$$\bar{U} = \frac{3}{2} RT + RT + RT = 3.5RT \quad (25)$$

and

$$C_V = 3.5 R = 29.1 J. mol^{-1} \quad (26)$$

The value observed is actually close to 21 J. mol⁻¹ for most diatomic gases. This is the value to be expected in the absence of the vibrational degree of freedom. This is a quantum mechanical effect. Thus, classically, one can gradually "turn on" vibrational or rotational motions but quantum mechanically these motions increase in jumps and it turns out that the energy required per jump for vibrational motions is greater than the average energy available per molecule at room temperature. Thus the vibrations are "inactive". The rotational energy quantum jump is much smaller and rotational motions are "active" at room temperature but at lower temperatures these can also become "inactive".

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