Interstellar Molecules

• Importance of radiation from molecules:
  • Emission from molecules T=10 - 100 K is a vital probe of star formation in cold molecular gas.
  • Cooling determines the mass of the first structures that can collapse and form at high redshift.
  • In low metallicity gas, molecular hydrogen can be the main coolant at higher temperatures T ~ 10000-1000 K.

• Molecular spectra are more complicated than atomic. e.g., diatomic molecule:
  - Electronic transitions as in atoms.
  - Vibrational transitions.
  - Rotational transitions of the molecule as a whole.

• Different characteristic energies, so can be treated more or less independently.
Energy scales for molecular transitions

- **Electronic** transitions in a molecule occur between energy levels that have comparable energies to those in atoms.
  - → Visible or UV photons.
- Energy level structure is very different, because the potential is not at all spherically symmetric.
- Nuclei have masses $M >> m_e$, yet see similar potential to the electrons. **Vibrational** motions involve energies that are smaller than electronic ones by a factor of $(m_e/M)^{1/2}$.
  - → Near or mid-infrared photons, ~0.1-0.01 eV
- **Rotations** involve energies a factor of $(m_e/M)$ times smaller than electronic transitions.
  - → Millimetre-wave region of the spectrum, ~0.001 eV
- At low enough energies we can see spectra that only involve rotation.
- Energies large enough to change the vibrational state usually change the rotation too.
- Electronic transitions will be split into many lines due to rotational *and* vibrational fine structure.
Pure rotation spectra for diatomic molecules

- Consider molecule as a rigid rotor, with a rotation axis perpendicular to the internuclear line.
- Moment of inertia \( I = \mu r_0^2 \), where
  - \( r_0 \) is the equilibrium internuclear distance, and
  - \( \mu \) is the reduced mass,
    \[
    \mu = \frac{M_1 M_2}{M_1 + M_2}
    \]
- Quantizing the angular momentum gives an expression for the energy eigenvalues,
  \[
  E_K = \frac{\hbar^2}{2I} K(K + 1)
  \]
- where the angular momentum quantum number \( K \) of the molecule is an integer.
Rotational stretching

- Real molecules stretch slightly as they spin faster (i.e., $r_0$ increases due to centrifugal forces). For fixed angular momentum, the kinetic energy of rotation is reduced $\rightarrow$ high rotational levels are closer together than for a rigid rotor.

- Expanding the potential in a Taylor series,

$$V(r) = V_0 + \frac{1}{2} k_0 (r - r_0)^2 + \ldots$$

- We get

$$E_K = V_0 + \frac{\hbar^2}{2I} K(K + 1) \left[ 1 - \frac{2\hbar^2 K(K + 1)}{k_0 \mu r_0^4} \right]$$

- where $k_0$ is a kind of spring constant for the molecule.
Allowed transitions between two rotational energy levels must obey selection rules analogous to those for electronic transitions in atoms. For dipole radiation,

- Molecule must have a permanent dipole moment:
  \[ d = Z_1 r_1 + Z_2 r_2 + d_e \neq 0 \]

- where nuclear charges are \( Z_1 \) and \( Z_2 \), the displacements from the centre of mass are \( r_1 \) and \( r_2 \), and \( d_e \) is the electronic contribution.
  - Homonuclear diatomic molecules (\( \text{H}_2, \text{O}_2 \) etc) cannot show pure rotation spectra in the dipole approximation.

- \( K \) must change by unity,
- \( \Delta K = -1 \) (emission)
- \( \Delta K = +1 \) (absorption)

because of angular momentum conservation. Emission frequencies for rotational transitions are almost equidistant in frequency.
Rotation-vibration spectra

- Energies required to excite vibrational modes are much greater than for rotation.
- Hence we do not get a pure vibration spectrum. Instead, both vibration and rotation states change together giving a rotation-vibration (“ro-vibrational”) spectrum.
- To the same level of approximation as before, vibrational energy levels are,
  \[ E = \hbar \omega_K (\nu + 1/2) \]
  where \( \nu \) is the harmonic oscillator quantum number, \( \nu = 0, 1, 2 \) etc and,
  \[ \omega_K \approx \mu^{-1/2} \left[ k_0 + \frac{3\hbar^2 K(K + 1)}{\mu r_0^4} \right] \]
Ro-vibrational selection rules

A more realistic treatment shows that the energy levels for vibration (like rotation) get closer together at large $\nu$.

Selection rules are similar to for rotation,

- $d \neq 0$ (dipole moment)
- $d$ must change during a change in vibrational state
- $\Delta \nu = \pm 1$ (harmonic oscillator q.n.)
- $\Delta K = \pm 1,0$ (rotational q.n.) – R, P, Q branch
The resulting spectra are somewhat similar to atomic spectra - a given vibrational transition is split by the fine structure arising from rotations, eg. the spectrum of a young star shows absorption lines from the \( \nu = 0 \) to \( \nu = 1 \) transition of \( \text{CO} \), where the individual lines correspond to different rotational states. Note that you can see both strong absorption from \( ^{12}\text{CO} \), and much weaker absorption from the rarer isotope \( ^{13}\text{CO} \) (figure from Mitchell et al. 1989).
Gas Cooling

- 300,000 to 10,000 K: collisional excitation of the electronic states of atomic hydrogen
- 10,000 to 100 K: collisional excitation of vibrational and rotational states of molecular hydrogen
- Less than 100 K: coolant molecules, e.g., CO
Molecules as tracers of density and temperature

• **Hydrogen molecules** are the main constituent of dark clouds in the galactic plane. However:

• Hydrogen is a symmetric molecule. Selection rules mean that both the vibration and rotation spectrum are weak and hard to observe.

• At $T \sim 2000$ K, collisions can excite vibrational modes of $\text{H}_2$, which decay radiatively. In primordial gas (no metals, dust) cooling via $\text{H}_2$ is the dominant mechanism at temperatures of a few thousand degrees.

• In star forming regions where the temperature is only 10 - 100 K, $\text{H}_2$ is excited only into low-lying rotational states. The lifetime of these states via radiative decay is extremely long.

• $\text{H}_2$ is generally inferred from observations of other molecules, rather than directly detected.
CO: carbon monoxide

- Carbon and oxygen are produced in large quantities in stellar nucleosynthesis → CO most abundant molecule after H\(_2\) and possibly H\(_2\)O.
- Robust - not easily destroyed or locked up onto grains.
- Most common tracer of molecular gas.
- Most common isotope is \(^{12}\text{C}^{16}\text{O}\). The rotational transition \(K=1\) to \(K=0\) of this molecule is generally optically thick and thermal, so measurements of the line intensity yield good estimates of the kinetic temperature of molecular clouds with \(T \sim 10\) K.
- Rarer isotopes include \(^{13}\text{C}^{16}\text{O}\), \(^{12}\text{C}^{17}\text{O}\), \(^{12}\text{C}^{18}\text{O}\). Lines from these isotopes are optically thin up to much higher column densities → tracer of density in higher density regions of molecular clouds.
CS

- $K=1 \text{ to } K=0$ transition is observed from collisionally excited CS only at higher densities than for CO. Useful probe of the transition region between the envelopes and cores of molecular clouds.
- Higher transitions such as $K=5 \text{ to } K=4$ (emitting at 1.2 mm) are excited only at very high densities of $n_{H_2} \sim 10^{13} \text{ m}^{-3}$. Observations signal recent or impending star formation.

NH$_3$

- More complex molecules such as ammonia ($NH_3$) are also observed - good probe of temperature.

Dust

- Dust forms through rapid nucleation process during mass-loss of cool stars (soot-like grains in carbon-rich envelopes). There is continuum emission from dust. Dust opacity:

$$K(\nu) \propto \nu^\beta$$

with $\beta \sim 1-2$.
- Observations provide estimates of the mass and temperature of the dust. Converting this to an estimate of the gas mass is usually uncertain.
Further reading

- Williams, D A 2000, A&G 41, 3.8
- Williams, D A 2003, A&G 44, 6.14