

atoms has  $N = 3n - 6$  normal modes if it is nonlinear, or  $N = 3n - 5$  if it is linear.

**Problem 9.4:** Chlorofluorocarbons (CFCs) are synthetic compounds that have strong absorption bands in the IR band. One of the simplest CFCs has the formula  $\text{CFCl}_3$ . Given that it is a nonlinear molecule, how many vibrational normal modes does it have?

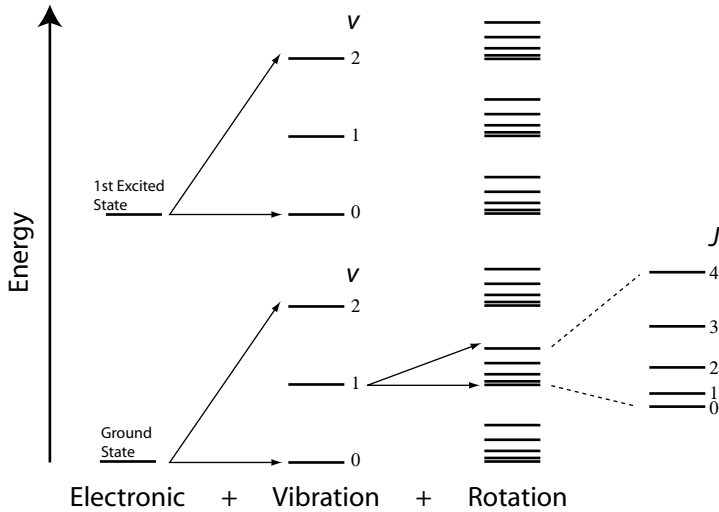
**Problem 9.5:** Assume that a molecule has  $N$  distinct vibrational quantum numbers  $v_i$ . How many possible simultaneous (nonzero) energy transitions of the form  $\Delta v_i = \{-1, 0, 1\}$  exist?

### 9.2.3 Electronic Transitions

Having discussed rotational and vibrational transitions, we now briefly consider a third transition type, which involves the energy levels of the electrons orbiting an atomic nucleus. Just as energy has to be added to a satellite in order to raise it to a higher orbit above the earth's surface, the energy associated with an electron increases with its mean distance from the nucleus. As before, the allowed energy levels of electronic orbits are quantized. Also, the more tightly bound an electron is to a nucleus, the larger the magnitude of the energy steps  $\Delta E$  between levels.

In general, a photon can be absorbed when its energy corresponds to the excitation of an electron to a more energetic state; a photon of an appropriate wavelength can be emitted when an excited electron drops back to a lower state.

For the purposes of this book, it is principally the outermost electrons that are of interest, since transitions between their ground state and the first excited state are associated with photon wavelengths in the near IR, visible and ultraviolet bands. Inner electrons, which are more strongly bound by attractive forces to the nucleus, tend to have energy transitions corresponding to very short wavelengths.



**Fig. 9.5:** Schematic depiction of the superposition of electronic, vibrational and rotational energy levels. The absorption spectrum of a molecule is determined by all nonforbidden transitions between pairs of levels in the righthand column.

At ordinary atmospheric temperatures, collisions between molecules are very rarely energetic enough to kick electrons into excited states. Those few that do briefly find themselves in an excited state, for whatever reason, usually give up their energy again in the course of subsequent collisions without emitting a photon. There are therefore extremely few electrons found *naturally* in excited states and even fewer opportunities for the spontaneous emission of photons due to electronic transitions back to the ground state. This fact is of course consistent with the sharp fall-off in thermal emission at the short wavelength end of the Planck function.

When electron orbits in atmospheric molecules *are* found in an excited state, it is usually because of the absorption of an incoming photon with the right energy, usually one of solar origin. As for rotational and vibrational transitions, we therefore expect to find discrete absorption lines associated with each allowed transition to higher electronic orbital states.

### 9.2.4 Combined Energy Transitions and Associated Spectra

As noted in the previous subsections, each atmospheric molecule has associated with it a number of discrete energy levels associated with electronic, vibrational, and rotational quantum states. Electronic energy states are the most widely separated and therefore correspond to photon absorption/emission at the shortest wavelengths; vibrational and rotational transitions, respectively, are associated with intermediate- and low-energy transitions.

The combination of all three modes of excitations leads to a set of discrete energy levels that are depicted schematically in Fig. 9.5. The total absorption line spectrum of the molecule is determined by all *allowed* transitions between pairs of energy levels (recall that not all transitions are allowed by quantum mechanics) and by whether the molecule exhibits a sufficiently strong electric or magnetic dipole moment (either permanent or otherwise) to be able to interact with the radiation field.

## 9.3 Line Shapes

The above introduction of absorption line spectra might have understandably left you with the impression that absorption by molecules can occur only at the precise wavelengths determined by the permitted energy transitions. If this were indeed the case, line absorption would be completely unimportant. Why? Recall that, for natural radiation, the energy (or flux) associated with exactly one wavelength is zero. In order to account for a finite percentage of the total radiation field, it is necessary to consider a finite interval of wavelength. That being the case, if absorption lines had zero width, then no matter how strong they were and no matter how many of them were scattered through the spectrum, their practical impact on atmospheric radiative transfer would be zilch. The observed *broadening* of absorption lines is therefore of tremendous practical importance for radiative transfer, as it permits a given atmospheric constituent to absorb radiation not only at the nominal wavelength associated with a transition but also at nearby wavelengths as well (Fig. 9.6). Where absorption lines are closely spaced, as they are in