the absorption spectrum-

the signature of molecular motions

Photons absorbed by a molecule induce transitions, separately or in combination, between its quantized rotational, vibrational, and electronic energy states. Rotational energy states involve motions of a molecule that produce a net angular momentum about its center of gravity. Vibrational energy states involve oscillations of the nuclei about the center of gravity. And electronic energy states involve motions of the bonding electrons. Therefore, encoded in a molecule's absorption spectrum is much information about its dynamics and structure. The basis for decoding this information is the fact that the energy of an absorbed photon equals the difference between two of the molecule's energy states.

One can approximate the energy difference ΔE between two adjacent rotational energy states of a gaseous molecule by assuming that the molecule is a rigid rotor, that is, by assuming that no molecular deformation accompanies the rotation. Then,

$$\Delta E = \left(\frac{h}{2\pi}\right)^2 \frac{J+1}{I} ,$$

where the rotational quantum number J *can* assume any nonnegative integral value and I is the molecule's moment of inertia about the axis of rotation. Note that ΔE is inversely proportional to Z and increases with increasing J. Numerical values of ΔE based on reasonable estimates of I correspond to the energies of photons in the microwave and far

infrared. Thus, the absorption spectrum of a molecule in this region provides information about its moment of inertia, that is, about bond lengths and bond angles.

Vibrational energy states are regarded as being the result of bending or stretching of individual bonds, skeletal motions of the molecule as a whole, or combinations and overtones of these motions, For a diatomic molecule the energy difference between two adjacent vibrational states in the harmonic oscillator approximation is given by

$$\Delta E = \frac{h}{2\pi} \left(\frac{k}{\mu}\right)^{1/2} .$$

Here μ is the reduced mass of the vibrating nuclei, and k *is* the proportionality constant between the restoring force and the displacement. (Note that the assumption of harmonic oscillation leads to a constant energy difference between vibrational levels, a prediction that is not borne out by experiment.) For reasonable estimates of k, numerical values of ΔE correspond to those of photons in the mid and near infrared. This portion of a molecule's absorption spectrum thus provides information about restoring forces, that is, about bond strengths.
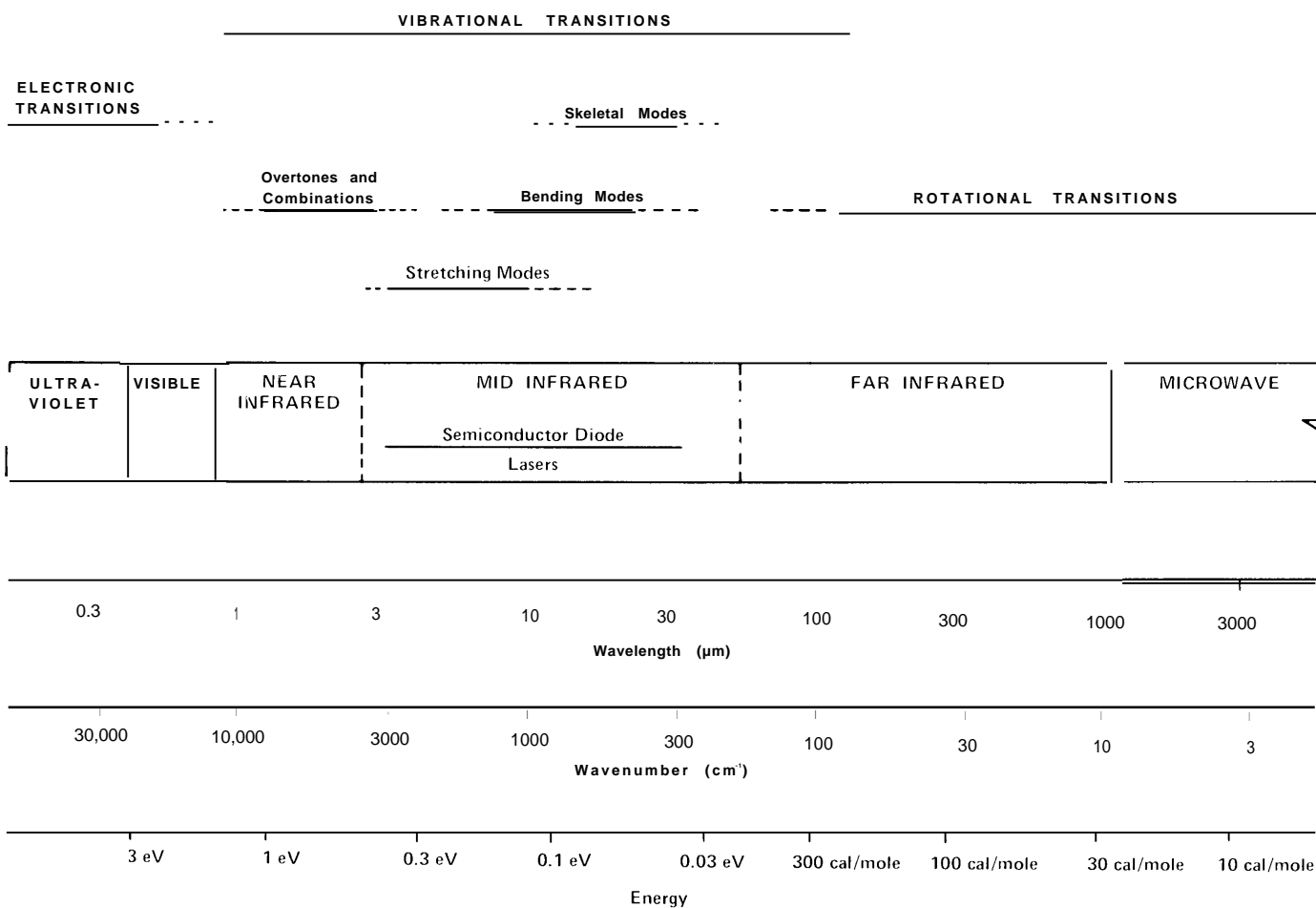
Since photons in the mid and near infrared have sufficient energy to induce rotational transitions along with vibrational transitions, rotational tine structure is associated with each vibrational absorption feature of a gaseous molecule. Therefore, the rotational-vibrational absorption spectrum also

yields much of the information available from the pure rotational spectrum and is of particular interest to molecular spectroscopists. In addition, this spectrum is a powerful tooI for qualitative and quantitative analysis.

Photons in the ultraviolet with still higher energies induce transitions between electronic energy states. Thus, the ultraviolet absorption spectrum reveals information about the forces binding valence electrons in molecules, Both vibrational and rotational fine structures are superimposed on the electronic transitions, but this spectrum is more difficult to decode than the rotational-vibrational spectrum,

Shown here are the infrared and adjacent portions of the electromagnetic spectrum. The term infrared radiation refers to radiation with wavelengths between the red limit of the visible spectrum at 0.8 micrometer (μm) and the beginning of the microwave region at 1000 Wm. The infrared spectrum thus covers a factor of 1250 in wavelength; in contrast, the extreme limits of sensitivity of the human eye cover only a factor of 2.

Infrared radiation is usually characterized by its wavenumber, or reciprocal wavelength, rather than by its frequency or wavelength. Further, it is customary to use the reciprocal centimeter (cm-l) as the wavenumber unit. Somewhat confusingly, both wavenumber and frequency are designated by the symbol v. The two quantities are, of course, related by the speed of light, $v(\text{cm}^{-1}) = v\,(\text{hertz})/c$, so that $1 \text{ cm}^{-1} \simeq$ 30,000 megahertz. ∎

VIBRATIONAL TRANSITIONS

ELECTRONIC
TRANSITIONS   Skeletal Modes

                    Overtones and
                    Combinations   Bending Modes   ROTATIONAL TRANSITIONS

                Stretching Modes

ULTRA-VIOLET	VISIBLE	NEAR INFRARED	MID INFRARED	FAR INFRARED	MICROWAVE
			Semiconductor Diode Lasers		

0.3	1	3	10	30	100	300	1000	3000

Wavelength (μm)

30,000	10,000	3000	1000	300	100	30	10	3

Wavenumber (cm⁻¹)

3 eV	1 eV	0.3 eV	0.1 eV	0.03 eV	300 cal/mole	100 cal/mole	30 cal/mole	10 cal/mole

Energy

Depending on the energy of a photon, its absorption by a molecule can give rise to rotational, vibrational, or electronic transitions. The energy of a photon equals the product of its frequency and Planck's constant or, equivalently, the product of its wavenumber, Planck's constant, and the speed of light.

Various units are used for photon energies. Listed here are electron volts (eV), the customary unit in the ultraviolet, visible, and mid- and near-infrared regions, and calories per mole of photons (cal/mole), the customary unit in the far-infrared and microwave regions.