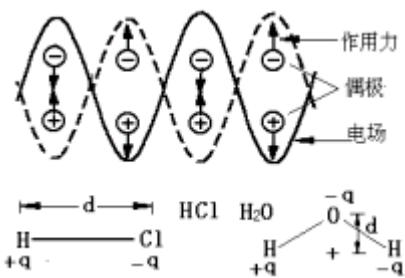


## § 8.1.2 Theoretical Backgrounds



### 1. Generation of IR

- (1). The radiation should match the energy needed for vibration transition.
- (2). Coupling exists between the radiation and the compounds.

Symmetric molecules: No change in dipole moment, no resonance after radiation, therefore, IR inactive

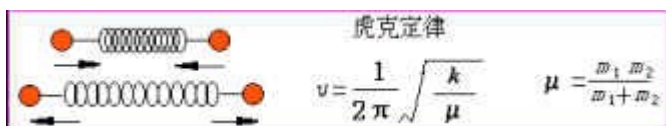
Such as : N<sub>2</sub>, O<sub>2</sub>, C<sub>12</sub>, etc.

Asymmetric molecules: change in dipole moment, IR active.

The interaction of dipole in the electro field:

### 2. Equation of vibration for molecules

- (1). Simple harmonic vibration and frequencies of diatoms



The vibration of chemical bond is like 2 little balls connected by a spring.

The vibration energy level in molecule can be write as :

$$E_v = (V + 1/2) h\nu$$

$\nu$  is the vibrational frequency of chemical bond,

$V$  is the vibration quantum number.

The energy difference between 2 adjacent levels is:

$$\Delta E = h\nu = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = 1370 \sqrt{\frac{k}{\mu}}$$

k : constant of chemical bond, which is determined by the bonding energy and bonding length.

$\mu$ : reduced mass,  $\mu = m_1 m_2 / (m_1 + m_2)$  .

The energy needed for transition between energy levels depend on k and  $\mu$  , which is in brief determined by the structure of molecule.

Table 9-2 Stretching force constants (mdy/Å)			
Bond type	—C≡C — >	—C=C — >	—C—C —
Force constant	15 ~17	9.5 ~9.9	4.5 ~5.6
Peak position	4.5mm	6.0 mm	7.0 mm

键	分子	k	键	分子	k
H-F	HF	9.7	H-C	CH <sub>2</sub> -CH <sub>2</sub>	5.1
H-Cl	HCl	4.8	H-C	CH=CH	5.9
H-Br	HBr	4.1	C-Cl	CH <sub>3</sub> Cl	3.4
H-I	HI	3.2	C-C		4.5~5.6
H-O	H <sub>2</sub> O	7.8	C=C		9.5~9.9
H-S	H <sub>2</sub> S	4.3	C≡C		15~17
H-N	NH <sub>3</sub>	6.5	C=O		12~13
H-C	CH <sub>3</sub> X	4.7~5.0	C=O		16~18

When the strength of bonding increases (the force constant increases), the reduced mass decreases, and the vibrational frequency will increase, so the absorption peak will appear at higher wave number levels.

Example:

For table 9-2, the force constant of C=C bonding is  $k = 9.5 \sim 9.9$ . Let  $k = 9.6$ , please calculate the C=C vibrational frequency in n-octane. (The

experimental frequency is 1652cm<sup>-1</sup>)

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = 1307 \sqrt{\frac{k}{\mu}} = 1307 \sqrt{\frac{9.6}{12/2}} = 1650 \text{cm}^{-1}$$

Key points: Application and theory of IR, the vibration equation and calculation, the vibration mode of each functional groups, factors that affect the peak

positions.

Questions: There are 4 vibration modes for CO<sub>2</sub> molecule, but why there are only 2 peaks on its IR spectroscopy?