

## REFERENCES

1. Klimisch, R.L., and Komarmy, J.M. In R.L. Klimisch and L.G. Larson (eds.), The catalytic Chemistry of Nitrogen Oxides, 305.
2. Iwamoto, M., and Hamada, H., Catal. Today, 10, pp. 57, 1991.
3. Li, Y., and Hall, K. H., J Catal., 129, pp. 202, 1991.
4. Iwamoto, M., Yahro, H., Tanda, K., Mine, Y., and Kagawa, S., Phys. Chem., 95, 37275, 1995.
5. Hightower, J.W., and Von Leirsberg, D.A. In R.L. Klimisch and L.G. Larson (eds.), The Catalytic Chemistry of Nitrogen Oxides, 63.
6. Nakatsuji, T., and Miyamoto, A., Catal. Today, 10, pp. 21-31, 1991.
7. Hamada, H., Kintaichi, Y., Sasaki, M., Ito, T., and Tabata, M., Appl. Catal., 64, pp. L1-L4, 1990.
8. Ukisu, Y., Sato, S., Muramatsu, G., and Yoshida, K., Catal. Lett., 16 pp. 11-16, 1992.
9. Iwamoto, M., Yahiro, H., Yoshiota, T., and Mizuno, N., Chem. Lett., 11 pp. 1967, 1990.
10. Inui, T., Kofo, S., Shibata, M., Yoshida, T., and Iwamoto, S., Stud. Surf. Sci. Catal. 69, pp. 355, 1991.
11. Cohn, G., Steek, D., and Andersen, H. 1961, U.S. Patent 2,975,025.
12. Bosch, H., and Janssen, F., Catal. Today, 2, pp. 369, 1988.
13. Kikuchi, E., Yogo, K., Tanaka, S., and Abe, M., Chem. Lett., pp. 1063, 1991.
14. Held, W., and Koenig, A., Richter, T., and Puppe, L., SAE paper, 900496, 1990.
15. Iwamoto, M., Proceedings of Meeting of Catalytic Technology for Removal of Nitrogen Oxides, January 25, 1990, Tokyo, Japan, Catal Soc of Japan, 17, 1990.
16. Iwamoto, M., Yahiro, H., Shundo, S., Yu-u, Y. and Mizuno, N., Shokubai, 33. pp. 430, 1990.
17. Yogo, K., Ihara, M., Terasaki, I., and Kikuchi, E., Appl. Catal.B, 2 , pp. L1-L5, 1993.

18. Bennett, C.J., Bennett, P.S., Golunski, S.E., Hayes, J.W., and Walker, A.P. Appl. Catal., 86, pp.L1-L6., 1992.
19. Petunchi, J.O., and Hall, W.K., Appl. Catal. B, 3, pp. 239-257, 1994.
20. Teraoka, Y., Pgawa, H., Furukawa, H., and Kagawa, S., Catal. Lett., 12, pp. 361-388, 1992.
21. Montreuil, C.N., and Ha, B.H., Appl. Catal. B, 5, pp. 7-21, 1994.
22. Hamada, H., Kintaichi, YY., Sasaki, M., and Ito, T., Chem. Lett., pp. 1069, 1990.
23. Iwamoto, M., Yahiro, H., and Tanda, K., Successful Design of Catalysis, pp. 219-226, Elsevier, Amsterdam, 1988.
24. Iwamoto, M., Sato S., Yu-u, H. Yahiro, H., and Mizuno, N., Appl. Catal., 70, pp. L1-L5, 1991.
25. Iwamoto, M., Mizuno, N., and Yahro, H., Sekiyu Gakkaishi, 34, pp. 375-390, 1991.
26. Iwamoto, M. and Mizuno, N., Proc. Instn. Mech. Engrs., 207, pp. 23-33, 1993.
27. Hamada, H., Kintaichi, K., Sasaki, M., Ito, T., and Tanabe, M., Appl. Catal., 70, pp. L15-L20, 1991.
28. Campa, M.C., Catal. Lett., 23, pp. 141-149, 1994.
29. Iwamoto, M., Kono, M., Chidanisa, T., and Murayama, SAE Paper, 920091, pp. 1-8, 1992.
30. Ansell, G.P., Diwell, A.F., Golunski, S.E., Hayes, J.W. Rafaram, R.R., Truex, T.J., and Walker, A.P., Appl. Catal. B, 2, pp. 81-100, 1993.
31. Halasz, I., Brenner, A., and Simon Ng, K.Y., Catal. Lett., 34, pp. 151-161, 1995.
32. Sasaki, ., Hamada, H., Kintaichi, Y., and Ito, T., Catal. Lett., 15, pp. 297-304, 1992.
33. D' itri, J.L., and Sachtler, W.M.H., Appl. Catal. B, 2, pp. L7-L15, 1993.
34. Bell, V.A., Feeley, J.S., Deeba, M., and Farrauto, R.J., Catal. Lett., 29, pp. 15-26, 1994.
35. Guyon, M., Lechanu, V., Gilot, P., Kessler, H. and Prado, G., Appl. Catal. B, pp. 183-196, 1996.

36. Radtke, F., Koeppel, R.A., and Bridger, A., J.Chem.Soc. Chem. Commun, 427 (1995)
37. Hayes, N.W., Grunert, W., Hutchings, G.J., Joyner, E.X. and Shpiro, S., J. Chem Soc. Chem. Comum. pp 531, 1994.
38. Kim, D.H., Hwang, I.C., and Woo, S.i., Progress in Zeolite and Microporous Materials, Studies in Surface Science and Catalysis, 105, pp. 1557-1563, 1997.
39. Curtin, T., Grange, P., Delmon, B., Catal. Today, 35, pp. 121-127, 1997.
40. Inui, T., Iwamoto, S., Kojo, S., and yoshida, T., Catal. Lett., 13 pp. 87-94, 1992.
41. Cho, B.K., J. Catal., 155, pp. 184-195, 1995.
42. Hamada, H., Kintaichi, y., Sasaki, M., Ito, T., and Tabata, M., Appl. Catal., 75, pp L1-L3, 1991.
43. Torikai, Y., Yahiro, H., Mizuno N., Iwamoto, M., Catal. Lett., 9, pp 91-96, 1991.
44. Montreuil, C.N., and Shelef, M., Appl. Catal. B, 1, pp L1- L3, 1992.
45. Flanigen, E.M. Zeolites and molecular sieves: an historical perspective. In H.V. Bekkum (ed.), Stud. Sur. Sci. Catal., 58: Introduction to Zeolite Science and Practice, pp. 13-34. Netherlands, Elsevier, 1991.
46. Szostak, R. Molecular Sieves: Principles of Synthesis and Identification, New York, Van Nostrand Reinhold, 1989.
47. Khouw, C.B., and Davis, M.E., J. Am. Chem. Soc., 115, pp.207-221, 1993.
48. Tanabe, K., Misona, M., Ona, Y., and Hattori, H. Acid and base centers: structure and acid-base property. In B. Delman and J.T. Yates (eds.), Stud. Sur. Sci. Catal., 51: New Solid Acids and Bases, pp. 142-161, Tokyo, Elsevier, 1989.
49. Know, C.B., and Davis, M.E. Shape-Selectivity Catalysts with Zeolites and Molecular Sieve. In M.E. Davis and S.L. Suib (eds.), ACS Symposium Series 517: Selectivity in Catalysis, pp. 206-211, Washington, 1993.
50. Meier, W.M., and Olson, D.H., Atlas of Zeolite structure Types, Boston : Butterworths, 1987.
51. Gates, B.C., Catalytic Chemistry, Singapore, John Wiley & Sons, 1992.

52. Kokotailo G.T. Zeolite crystallography. In F.R. Ribeiro et al. (eds.), Zeolites: Science and Technology, pp. 83-108, Netherlands, Martinus Nijhoff Publishers, 1984.
53. Barthomeuf, D. Acidic catalysis with zeolites. In F.R. Ribeiro et al. (eds.), Zeolites: Science and Technology, pp. 317-346, Netherlands, Martinus Nijhoff Publishers, 1984.
54. Ashton, A.G., Batmanian, S., Dwyer, F. Acidity in zeolites. In B. Imelik et al. (eds.), Catalysis by Acids and Bases, pp. 101-109. Amsterdam, Elsevier, 1985.
55. Sano, T., Fufisawa, K., and Higiwara, H. In B. Delmin and G.F. Fromant (eds.), Stud. Sur. Sci. Catal., 34: Catalyst Deactivation, pp. 613-624. Amsterdam, Elsevier, 1987.
56. Weisz, P.B., Frillete, B.J., Matman, R.W., and Mower, E.B., J. Catal. 1, pp. 307-312, 1962.
57. Cricsery, S.M., Zeolites, 4, pp. 202-213, 1984.
58. Anderson, M.W., and Klinowski, Nature, 339, pp. 200-203, 1989.
59. Satterfield, C.N., Heterogeneous Catalysis in Practice, New York, McGraw-Hill Book Co., 1980.
60. Derouane, E.G. New aspects of molecular shape selectivity. In B. Imelik et al. (eds.), Catalysis by Zeolites, pp. 5-27, Amsterdam, Elsevier, 1980.
61. Burch, R., and Millington, P.J., Appl. Catal B, 2, pp. 81-100, 1993.
62. Spoto, G., Bordiga, S., Scarono, D., and Zecchina, A., Catal. Lett., 13, pp. 39-43, 1992.
63. Narong Lim, Effect of promoters on coke formation on metal site of propane dehydrogenation catalyst, Thesis, Chulalongkorn University, 1996
64. Kunatippapong S., Determination of irreversible coke deposition of platinum active site of propane dehydrogenation catalyst. Dr. Eng. Dissertation, Chulalongkorn University, 1995.
65. McLellan, G.D., Howe, R.F., Parker, L.M., Bibby, D.H., J. Catal., 99, pp 486-491, 1986
66. Topsoe, N., Pedersen, K., and Derouane, B.G., J Catal., 70, pp. 41-52, 1981.

67. Hwang, I.C. Kim, D.H., Woo, S.I., Catal. Letters, 42, pp. 177-184, 1996.
68. Lukyanov, D.B., Sill, G., d'Itri, J.L., and Hall, W.K., J.Catal., 153, pp. 265-274, 1995.
69. Yakoyama, C., Misuno, M., J. Catal., 150, pp 9-17, 1994.
70. Yogo, K., Umeno, M., Watanabe, H., and Kikuchi, E., Catal. Lett., 19 pp. 131-135, 1993.
71. Shelef, M., Monreuil, C.N., and Jen, H.W., Catal. Lett., 26, 277-284.
72. Ayler, A.W., Larsen, S.C., Reimer, J.A., Bell, A.T., J. Catal., 157, pp.592-602, 1995.
73. Burch, R., and Scire, S., Appl. Catal. B., 3, pp. 295-318, 1994.
74. Matushak, V.A., Krylov, O.V., Catal. Today, 25, pp 1-88, 1995.
75. Infrared Spectroscopy Committee of the Chicago Society for Coating Technology, An infrared spectroscopy atlas for the coating industry. Pennsylvania:(n, p.), 1980.
76. Skoog, D.A, and Leary, J.J., Principle of istrument analysis(4th ed.), Philadelphia: Suanders College Publishing, 1992.
77. Smith, A.L., Applied infrared spectroscopy, Newyork: John Wiley&Sons, 1979.
78. Pinchareonthaworn J., Effect of Hydrocarbon on the Performance of Cu/Na-MFI catalyst for NO Removal, Thesis, Chulalongkorn University, 1995.
79. Biswas, J., Bickle, G.M., Gray, P.G., Do, d.d., Barbier, J., Catal. Rev. Science and engineering, 30 (2), pp. 171-183, 1988.
80. Tanabe, Kozo, Misono, Ono, Yoshio, and Hideshi, Hattori, New Solid Acids and Bases, Studies in Surface and Catalysis, Vol. 51 pp. 340-341, Elsevier, Amsterdam, 1989.

## APPENDIX

**APPENDIX A**  
**SAMPLE OF CALCULATIONS**

**A-1 Calculation of Si/Al Atomic Ratio for ZSM-5**

The calculation is based on weight of Sodium Silicate ( $\text{Na}_2\text{O}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ ) in B1 and B2 solutions. (Topic 4.1.1)

$$\text{M.W. of Si} = 28.0855$$

$$\text{M.W. of SiO}_2 = 60.0843$$

$$\text{Weight percent of SiO}_2 \text{ in Sodium Silicate} = 28.5$$

$$\text{M.W. of Al} = 26.9815$$

$$\text{M.W. of AlCl}_3 = 133.3405$$

$$\text{Weight percent purity of AlCl}_3 = 97$$

For example, to prepare ZSM-5 at Si/Al atomic ratio of 50.

Using Sodium Silicate 69 g with 45 g of water as B1 solution.

$$\begin{aligned} \text{mole of Si used} &= \frac{\text{wt. (\%)} * (\text{M.W. of Si}) * (1 \text{ mole})}{100 * (\text{M.W. of SiO}_2) * (\text{M.W. of Si})} && \text{(A-1.1)} \\ &= 69 * (28.5/100) * (1/60.0843) \\ &= 0.3273 \end{aligned}$$

$$\text{Si/Al atomic ratio} = 50$$

$$\begin{aligned} \text{mole of AlCl}_3 \text{ required} &= 0.3273/50 = 6.5458 * 10^{-3} \text{ mole} \\ \text{amount of AlCl}_3 &= 6.5458 * 10^{-3} * 133.34 (100/97) \\ &= 0.8998 \text{ g} \end{aligned}$$

which used in A1 and A2 solutions

### A-2 Calculation the amount of metal ion-exchanged ZSM-5

For example: Determine the amount of Cu into catalyst = 0.2 wt.%

the catalyst use = x g

$$\begin{aligned} \text{so that} \quad \text{Cu}/(\text{x}+\text{Cu}) &= 0.2/100 \\ 100*\text{Cu} &= 0.2*(\text{x}+\text{Cu}) \\ (100-0.2)*\text{Cu} &= 0.2*\text{x} \end{aligned}$$

$$\text{thus} \quad \text{Cu} = 0.2*\text{x}/(100-0.2) \text{ g}$$

use  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (M.W. 241.60, 26.30%Cu, purity 99.5%)

$$\text{weight of } \text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} = \{0.2*\text{x}/(100-0.2)\} * [(100/26.30)*(100/99.5)]$$

### A-3 Calculation gas velocity

The catalyst used = 0.50 g

packed catalyst into quartz reactor (diameter = 0.6 cm)

determine the average height of catalyst bed = x cm

So that, volume of catalyst bed =  $p * (0.3)^2 * x$  ml-catalyst  
used GHSV (Gas Hourly Space Velocity) = 4,000  $\text{h}^{-1}$

$$\text{GHSV} = \frac{\text{Volumetric flow rate}}{\text{Volume of Catalyst}} = 4,000 \text{ h}^{-1}$$

$$\begin{aligned} \text{Volumetric flow rate} &= 4,000 * \text{Volume of catalyst} \\ &= 4,000 * p (0.3)^2 * x \text{ ml/h} \\ &= 4,000 * p (0.3)^2 * x / 60 \text{ ml/ min} \end{aligned}$$

$$\text{at STP : Volumetric flow rate} = \frac{\text{Volume flow rate} * (273.15+\text{rt})}{273.15}$$

where : rt = room temperature, °C



#### A-4 Calculation of NO and C<sub>3</sub>H<sub>6</sub> conversion

The effluent gas was analyzed by gas chromatography, the NO reduction activity was evaluated in terms of the conversion of NO into N<sub>2</sub>.

$$\text{NO Conversion (\%)} = (2[\text{N}_2]_{\text{out}} / [\text{NO}]_{\text{in}}) * 100$$

The C<sub>3</sub>H<sub>8</sub> oxidation activity was evaluated in terms of the conversion of C<sub>3</sub>H<sub>6</sub> into CO and CO<sub>2</sub>.

$$\text{C}_3\text{H}_6 \text{ Conversion (\%)} = \frac{([\text{C}_3\text{H}_6]_{\text{in}} - [\text{C}_3\text{H}_6]_{\text{out}}) * 100}{[\text{C}_3\text{H}_6]_{\text{in}}}$$

#### A-5 Calculation of metal active site on catalyst

The weight of catalyst used	=	w	g.
Area of N <sub>2</sub> O peak after adsorption	=	A	unit.
Average area of 100 μl. standard N <sub>2</sub> O peak	=	B	unit.
Amounts of N <sub>2</sub> O adsorbed on catalyst	=	B-A	unit.
Volume of N <sub>2</sub> O adsorbed on catalyst	=	[(B-A)/B]*50	μl.
Volume of gas 1 mole at 30 °C	=	24.86*10 <sup>6</sup>	μl.
Mole of N <sub>2</sub> O adsorbed on catalyst (mole)	=	[(B-A)/B]*[50/24.86*10 <sup>6</sup> ]	

$$1 \text{ mole is } 6.02 * 10^{23} \text{ molecule}$$

Then, Molecule of CO adsorbed on catalyst

$$= 2.01 * 10^{-6} * [(B-A)/A] * 6.02 * 10^{23} \text{ molecules}$$

1 molecule of N<sub>2</sub>O react with 2 molecules of Cu as the equation



$$\text{Metal active site} = 1.21 * 10^{18} * [(B-A)/B]/w \text{ molecules of Cu / g. catalyst.}$$

## APPENDIX B

### Infrared Absorption Spectroscopy

#### 1. Electromagnetic Radiation

Infrared waves like X-rays, light and radio waves are classified as electromagnetic radiation since they consist of both alternating electric and magnetic fields. Each of these types of radiation has a different amount of energy. The classification of radiation according to its energy gives to electromagnetic spectrum. This is illustrated in figure B.1

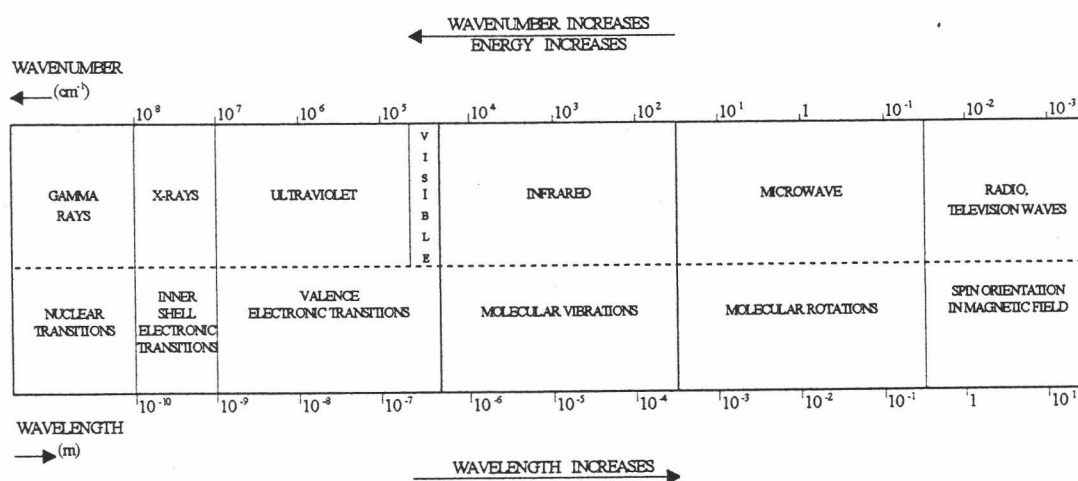


Figure B.1 Electromagnetic Spectrum [75]

The classical description of electromagnetic radiation can be described in terms of wavelength and frequency.

The wavelength,  $\lambda$ , of radiation is the distance between two successive maxima or minima of the wave motion .

The frequency,  $\nu$ , is defined as the number of cycles which pass a given point per unit of time, in unit of  $\text{sec}^{-1}$  or hertz (Hz);  $1 \text{ Hz} = 1 \text{ sec}^{-1}$  .

Wavelength and frequency are interrelated according to the following equation :

$$\lambda = \frac{C}{\nu} \quad (\text{eq. B.1})$$

where:  $\lambda$  = wavelength ( cm. )

$C$  = velocity of light (  $2.99793 \times 10^{10}$  cm./sec. in vacuum)

$\nu$  = frequency ( Hz )

An additional parameter is often used in vibrational spectroscopy:

The wavenumber,  $\bar{\nu}$ , which is defined as the reciprocal of the wavelength, and has dimension 1/length. The relation between wavelength, wavenumber, frequency, and velocity of light is given by following equation:

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{C} \quad (\text{eq. B.2})$$

The energy of the electromagnetic radiation is proportional to its frequency and its wavenumber, as follows :

$$E = h\nu = hc\bar{\nu} = \frac{hc}{\lambda} \quad (\text{eq. B.3})$$

where:  $E$  = energy of electromagnetic radiation ( J )

$h$  = Planck's constant (  $6.626 \times 10^{-34}$  J.sec )

The infrared region extends from 0.78 to 1000  $\mu\text{m}$  or wavenumbers from about 12800 to 10  $\text{cm}^{-1}$ . From the standpoint of both application and instrumentation, it is convenient to divide the infrared region into three sections as near-, mid-, and far- infrared radiation, shown in figure 3.2. The majority of analytical applications have been confined to a spectrum of the mid- infrared region extending from 4000 to 400  $\text{cm}^{-1}$  (2.5 to 25  $\mu\text{m}$  )

region	wavelength ( $\lambda$ ), $\mu\text{m}$	wavenumber( $\nu$ ), $\text{cm}^{-1}$	frequency ( $\nu$ ),Hz
near	0.78 to 2.5	12800 to 4000	$3.8 \times 10^{14}$ to $1.2 \times 10^{14}$
middle	2.5 to 50	4000 to 200	$1.2 \times 10^{14}$ to $6.0 \times 10^{12}$
far	50 to 1000	200 to 10	$6.0 \times 10^{12}$ to $3.0 \times 10^{11}$
most used	2.5 to 15	4000 to 670	$1.2 \times 10^{14}$ to $2.0 \times 10^{13}$

Table B.1 Infrared Spectral Regions [77]

## 2. Molecular Energy

In the general case a molecule can have the following types of motions [77]

- (1) translation of the whole molecule, which can be regarded as translation of the center of mass.
- (2) rotation of the molecule as a framework around its center of mass.
- (3) vibrations of the individual atoms within the framework, which occur in such a manner that the center of mass is not changing and the framework does not rotate.
- (4) motions of the electrons inside the molecule.
- (5) spins of the electrons and the nuclei of the atoms.

When a molecule absorbs electromagnetic radiation there is an increase in its total energy. According to the quantum theory, only a radiation of specific energy can be absorbed by a molecule, thereby raising its energy from the ground state to an excited state. This process is shown in figure 3.3 where  $E_1$  and  $E_2$  represent the energy of the molecule in the ground state and excited state, respectively, and  $E_p$  is the energy of the photon. The energy of transition,  $\Delta E$ , is equal to the energy of the interacting photon and, thus, equal to  $h\nu$ . This is stated mathematically according to equation 3.4.

$$\Delta E = E_2 - E_1 = E_p = h\nu \quad (\text{eq. 3.4})$$

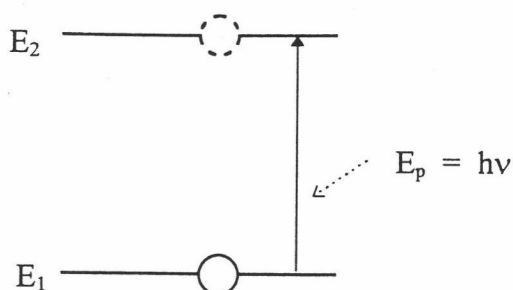


Figure B.2 Absorption of Electromagnetic Radiation [71]

The total energy of a molecule is comprised of electronic, vibrational, rotational and translational energies. That is

$$E_{\text{total}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elect.}}$$

The energy involved in the transition from the electronic ground state to the first excited electronic state of a molecule usually requires radiation of greater energy than that available in the infrared region of the electromagnetic spectrum. Therefore, electronic energies usually do not have to be considered in discussion the theory of infrared spectroscopy.

### 3. Degree of Freedom and Molecular Motions

The remaining of a molecule are due to vibrational, rotational, and translational motions associated with the molecule. These molecular motions are commonly referred as degrees of freedom. For every atom in molecule there are three degrees of freedom corresponding to motions along the three mutually perpendicular x,y, and z coordinates in space. For nonlinear molecule containing N atoms, there will be 3N degrees of freedom: three translational, three rotational, and the remainder, 3N-6, will be vibrational. These degrees of freedom are illustrated in Figure 3.4 .

For a linear molecule there are 3N-5 vibrational degrees of freedom since a linear molecule has only two degree of rotational freedom. No change occurs in a linear molecule because rotation about its bond axis. Of these vibrational degrees of freedom, N-1 modes will be due to stretching vibrations and 2N-4 modes will be due to deformations. For a nonlinear molecule, 2N-5 modes will be due to deformations.

Absorption of infrared radiation is thus confined largely to molecular species for which small energy differences exist between various vibrational and rotational states.

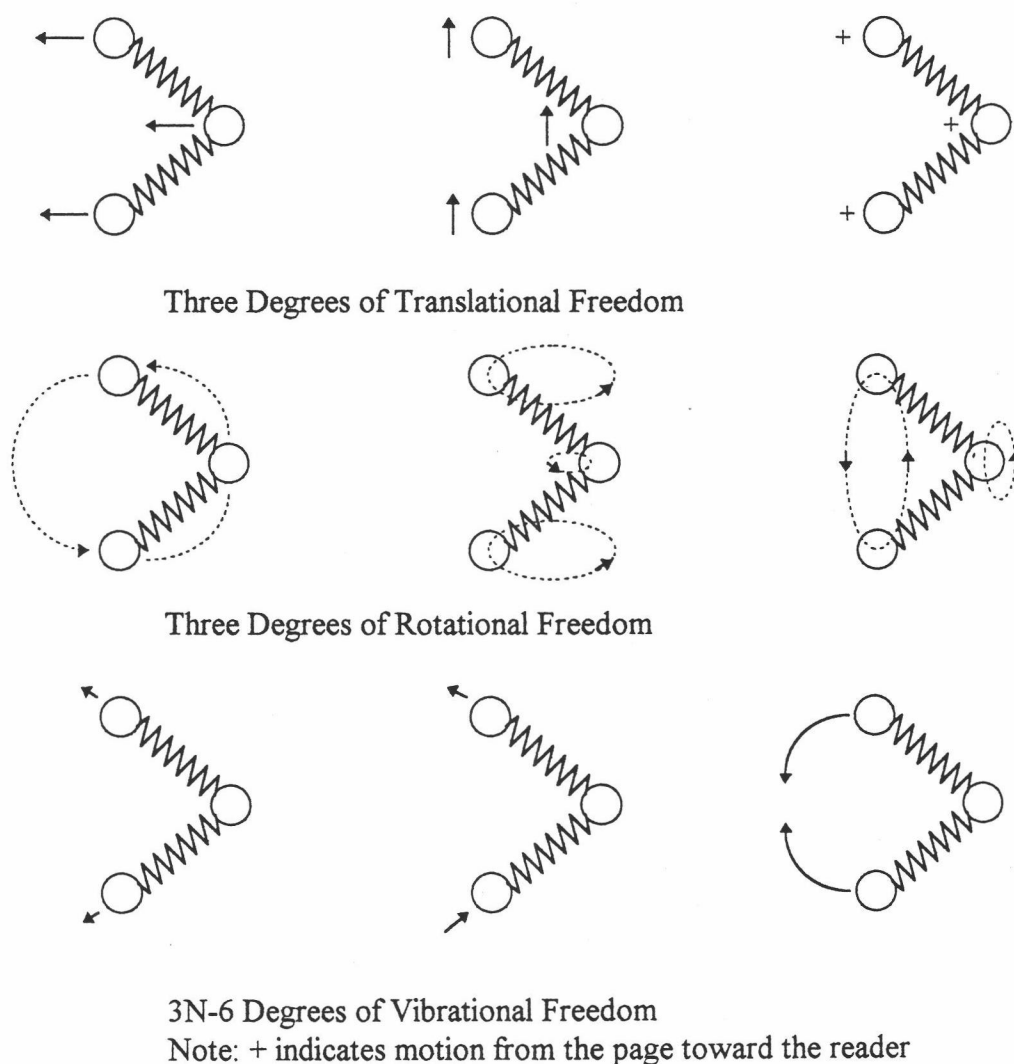


Figure B.13 Degrees of Freedom of a Molecule [75]

#### 4. Dipole Changes during Vibrations and Rotations

In order to absorb infrared radiation, a molecule must undergo a net change in dipole moment as a consequence of its vibrational or rotational motion. Only under these circumstances can the alternating electrical field of the radiation interact with the molecule and cause changes in the amplitude of one of its motions. For example, the

charge distribution around a molecule such as hydrogen chloride is not symmetric, because the chlorine has a higher electron density than the hydrogen. Thus, hydrogen chloride has a significant dipole moment and is said to be polar. The dipole moment is determined by the magnitude of the charge difference and the distance between the two centers of charge. As a hydrogen chloride molecule vibrates, a regular fluctuation in dipole moment occurs, and a field is established that can interact with the electrical field associated with radiation. If the frequency of the radiation exactly matches a natural vibrational frequency of the molecule, a net transfer of energy takes place that results in a change in the amplitude of the molecule vibration; absorption of the radiation is the consequence. Similarly, the rotation of asymmetric molecules around their centers of mass results in a periodic dipole fluctuation that can interact with radiation. No net change in dipole moment occurs during the vibration or rotation of homonuclear such as  $O_2$ ,  $N_2$ , or  $Cl_2$ ; consequently, such compounds cannot absorb in the infrared.

#### 5. Rotational Transitions

The energy required to cause a change in rotational level is minute and corresponds to radiation of  $100\text{ cm}^{-1}$  or smaller ( $> 100\mu\text{m}$ ). Because rotational levels are quantized, absorption by gases in this far-infrared region is characterized by discrete, well-defined lines. In liquid or solids, intramolecular collisions and interactions cause broadening of the line into a continuum.

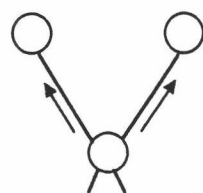
#### 6. Vibrational and Rotational Transitions

Vibrational energy levels are also quantized, and for most molecules the energy differences between quantum states correspond to the mid-infrared region. The infrared spectrum of a gas usually consists of a series of closely spaced lines, because there are several rotational energy states for each vibrational state. On the other hand, rotation is highly restricted in liquids and solids; in such samples, discrete vibrational/rotational lines disappear, leaving only broadened vibrational peaks.

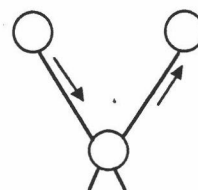
#### 7. Types of Molecular Vibrations

The relative positions of atoms in a molecule are not exactly fixed but instead fluctuate continuously as a consequence of a multitude of different types of

vibrations. Vibrational transitions or fundamental modes of vibration are classified as stretching modes and deformation modes. Stretching modes are described as a continuous change in the interatomic distance along the axis of the bond between two atoms and deformation modes as a change in the angle between two bonds and are of four types : scissoring , rocking , wagging and twisting. The fundamental modes of vibration are shown in figure B.4.

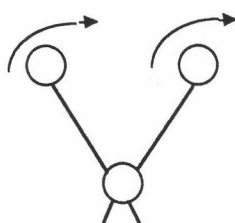


Symmetric

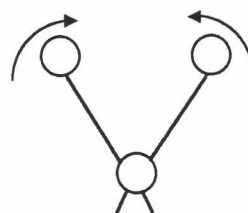


Asymmetric

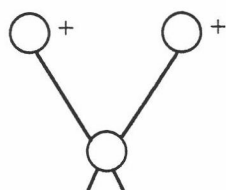
( a ) Stretching vibrations



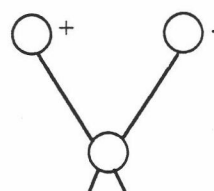
In - plane rocking



In - plane scissoring



Out - of - plane wagging



Out - of - plane twisting

( b ) Bending Vibrations

Note : + indicates motion from the page toward the reader  
 - indicates motion away from the reader

Figure B.4 Types of Molecular Vibrations [60]

All of the vibration types may be possible in a molecule containing more than two atoms. In addition, interaction or coupling of vibrations can occur if the



vibrations involve bonds to a single central atom. The result is a change in the characteristics of the vibrations involved.

## 8. Theoretical Considerations

As a heteronuclear molecule vibrates, the interatomic distance between atoms changes as does its dipole moment. The vibrating molecule produces an alternating dipolar electric field. The magnitude of this alternating dipolar electric field changes periodically with time at a frequency equal to the vibrational frequency. It is this dipolar electric field which interacts with the electrical component of the electromagnetic radiation giving rise to the absorption of energy. This absorption of electromagnetic radiation is what is observed when recording an infrared spectrum.

If a diatomic molecule is homonuclear, there is no change in dipole moment with the vibration and no alternating dipolar electric field is produced. Thus, the molecule does not interact with or absorb infrared radiation.

Whenever a change in dipole moment occurs, the fundamental vibration is said to be infrared active. When a vibrating molecule produces no change in its dipole moment because of symmetry, the fundamental vibration is said to be infrared inactive.

In molecules with a high degree of symmetry, many of the vibrations may occur between groups of atoms with the same reduced mass and the same force constant. These vibrations will have the same frequency and will be superimposed on the spectrum. When this occurs, the vibrations are said to be degenerate. In symmetrical molecules several modes of vibration may occur at identical frequencies, such as the three asymmetric C-H stretching vibrations in  $\text{CH}_3\text{Cl}$ . Also, many normal modes of vibration can have nearly identical frequencies, such as the  $\text{CH}_2$  vibrations in linear polyethylene. In cases like these, symmetry does not require the frequencies to coincide; however, due to chemical considerations, the absorption bands overlap. Thus a highly symmetrical molecule of many atoms, such as benzene, will give a simple infrared spectrum because many of its modes of vibration are degenerate. Also, the spectra of polymers can appear simpler than expected due to the accidental degeneracy of the chemically similar groups.

Vibrational motions, both stretching and deformation of any particular atom pair, occur even when other atoms or functional groups are involved in the

vibrational transitions. However, depending on the types of atoms involved and their environment in the molecule, each transition will have a specific energy. Each of these vibrational modes will give rise to the absorption of infrared radiation in a specific region of the infrared spectrum.

## VITA

Mr. Pongphrom Chalmvanapong was born in Bangkok on May 10, 1973. He graduated high school from Suankularb College in 1990 and received his Bachelor of Engineering Degree in major of Chemical Engineering, from the Faculty of Engineering, King Mongkut's Institute of Technology Thonburi in 1995.