Raman Spectra

Vibrational Raman Spectra

The selection rules for the vibrational Raman spectra are the same as those for pure vibrational spectra, i.e.,

$$\Delta v = \pm 1, \pm 2, \ldots.$$

For every vibrational mode, the vibrational energy expression is

$$\bar{\upsilon}_v = (v + \tfrac{1}{2})\,\tilde{\omega}_e\{1 - (v + \tfrac{1}{2})x_e\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(13)}$$

The difference in energy levels are

$v' = 1 \leftarrow v'' = 0$; $\Delta\bar{\upsilon}_{\text{fundamental}} = \tilde{\omega}_e(1 - 2x_e)$

$v' = 2 \leftarrow v'' = 0$; $\Delta\bar{\upsilon}_{\text{overtone}} = 2\tilde{\omega}_e(1 - 3x_e)$

$v' = 2 \leftarrow v'' = 1$; $\Delta\bar{\upsilon}_{\text{hot}} = \tilde{\omega}_e(1 - 4x_e)$

since the population in $v = 1$, $v = 2$, etc., level are very small, the overtones and hot lines are of very weak intensities as compared to the fundamental line. Restricting only to the fundamental transition, Raman lines will be observed at the following wavenumbers:

$$\bar{\upsilon}_{\text{fundamental}} = \bar{\upsilon}_0 \pm \tilde{\omega}_e(1 - 2x_e)$$

where the minus sign represent the Stokes' line and plus sign refers to anti-Stokes' line. Since the latter refers to the transitions $v' = 0 \leftarrow v'' = 1$, it is expected to be very weak ass very few molecules exist in the $v'' = 1$ state at normal temperature. On increasing temperature, the population of $v = 0$ state is decreased whereas that of $v = 1$ state is increased. It is, thus, expected that the intensity of Stokes' line will decrease where as that of anti-Stokes' line will increase on increasing the temperature of the sample.

As mentioned earlier, only those vibrational mode will be Raman active for which $\partial\alpha/\partial\zeta$ is nonzerpo. A molecule with little or no symmetry, all of its vibrational modes are usually Raman active. But a molecule with a considerible symmetry, it is not so. Moreover, the symmetry vibrations produce a large value of $\partial\alpha/\partial\zeta$ near the equilibrium position of vibration and hence produce intense Raman lines. For antisymmetric vibrations, $\partial\alpha/\partial\zeta$ is either zero or usually very small and hence they produce either no line or weak 9 and sometimes unobservable) Raman lines.
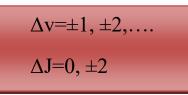
Rotational –Vibrational Raman Spectra

In general, the rotational fine structure associated with the vibrational Raman spectrum of a large molecule is ignored as it is beyond resolution. Only in case of diatomic gases molecules, the resolution is sufficient to be analyzed with the rigid –rotator model. Thus it may be written as

$$\bar{\nu}_{v,J} = BJ(J+1) + \{(v+½)\ \tilde{\omega}_e\{1-(v+½)x_e\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

The selection rules are

$$\Delta v = \pm 1, \pm 2, \ldots$$

$$\Delta J = 0, \pm 2$$

Restricting to the fundamental vibration transition, we have

$\Delta J = 0;$ $\qquad \Delta\bar{\nu}_Q = \tilde{\omega}_e(1-2x_e)$ $\qquad\qquad$ (for all J)

$\Delta J = +2;$ $\qquad \Delta\bar{\nu}_S = \tilde{\omega}_e(1-2x_e) + B(4J''+6); (J'' = 0, 1, 2, \ldots)$

$\Delta J = -2;$ $\qquad \Delta\bar{\nu}_O = \tilde{\omega}_e(1-2x_e) - B(4J''+6); (J' = 0, 1, 2, \ldots)$

Where the subscripts Q, S and O refer to the Q, S, and O branches, respectively.

If $\bar{\nu}_O$ is the wavenumber of the exciting radiation, Stokes' lines will be observed at the following wavenumbers.

$\bar{\nu}_Q = \bar{\nu}_O - \Delta\bar{\nu}_Q$

$\bar{\nu}_S = \bar{\nu}_O - \Delta\bar{\nu}_S$

$\bar{\nu}_O = \bar{\nu}_O - \Delta\bar{\nu}_O$

Much weaker anti –Stokes' line will occur at same distance from $\bar{\nu}_O$ towards the high wavenumber side.

Rule of Mutual Exclusion

A general rule, known as the rule of mutual exclusion, for molecules having centre of symmetry has been established. This rule state that :

If a molecule has a centre of symmetry, then Raman active vibrational modes are infrared inactive, and vice versa

Thus by comparing Raman and infrared spectra of substance, it is possible to establish whether the molecule has a centre of symmetry or not and hence its structure can be established. If the two spectra do not include the common absorptions, it implies that the molecule has a centre of symmetry. On the other hand, if the two spectra include common lines, it implies that the molecule has no centre of symmetry.

The rule of mutual exclusion may be exemplified by taking the examples of CO_2 and SO_2 molecule. The structure of CO_2 is linear and thus it possesses the centre of symmetry. The SO_2 molecule is nonlinear and thus it does not possess the centre of symmetry. The CO_2 molecule has four vibrational modes, whereas the SO_2 molecule has three vibrational modes. These modes along with the associated change in dipole moment and polarizability are described in the following.

(1) Symmetrical Stretch: $\leftarrow O = C = O \rightarrow$

During this vibration, the dipole moment of this molecule remains zero throughout the vibration, i.e., the dipole moment does not alter periodically and hence this vibrational mode will be infrared inactive. Since during the vibration, volume of the molecule changes, it may be concluded that there occurs a change in the polarizability of the molecule and hence this vibrational mode will be Raman active . More precisely, the slope of the α versus ζ curve will be nonzero near the equilibrium position of the vibrational motion i.e., the small displacements near the equilibrium position produces a change in the polarizibility.

(2) Anti-symmetrical Stretch: $\quad O = C = O$

$$\rightarrow \quad \leftarrow \quad \rightarrow$$

Since during the vibration, one of the bond undergoes stretching whereas the other bond undergoes shortening of the bond length it is expected that there will occir a change in dipole moment of the molecule and hence this vibrational mode will be infrared active. Since the lengthening and shortening of bond occur by the same amount, it is expected that the polarizability (or volume) of the molecule does not change during the vibration. More precisely,

$d\alpha/d\zeta=0$ near the equilibrium position of the vibrational motion. Thus, this vibrational mode will be Raman inactive.

(2) Bending mode (doubly degenerate) :

$$\uparrow \qquad \uparrow$$
$$O = C = O$$
$$\downarrow$$

During the bending motion, the dipole moment of the molecule changes but not polarizability and hence this vibrational will be infrared active and Raman inactive.

Thus, it a vibrational mode of CO_2 is infrared active, it is necessarily Raman inactive, on the other hand if it is infrared inactive, then it is a Raman active. This is due to the fact he CO_2 molecule has a centre of symmetry.

Coming to the SO_2 molecule, it will be find that all the three vibrational modes are infrared and Raman active. The analysis of symmetry stretch is described below.

The sulphur dioxide molecule has a permanent dipole moment and its value changes periodically during the symmetrical stretch vibrational mode. Since the volume of the molecule changes during the vibration, it is expected that there will also occur a change in polarizability of the molecule. Hence, this vibrational mode will be infrared as well as Raman active.

Differences between Raman and vibrational spectra :

	Raman	IR
1	Due to the scattering of light by the vibrating molecules.	Result of absorption of light by vibrating molecules.
2	The vibration is Raman active if it causes a change in polarizability.	The vibration is IR active if the dipole moment changes during the vibration.
3	The molecule need not possess a permanent dipole moment.	The vibration should have a dipole moment change due to that vibration.

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