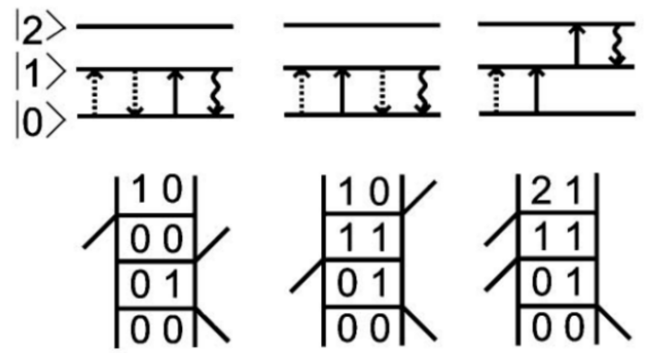
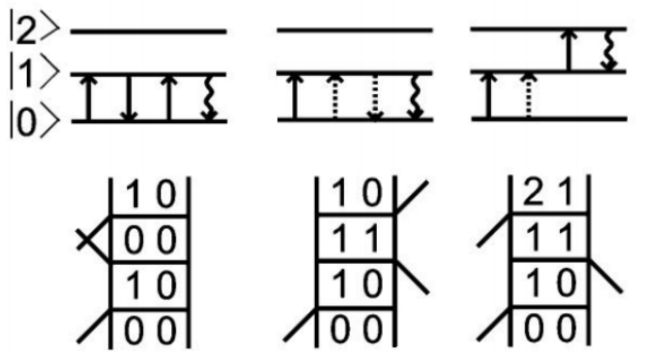
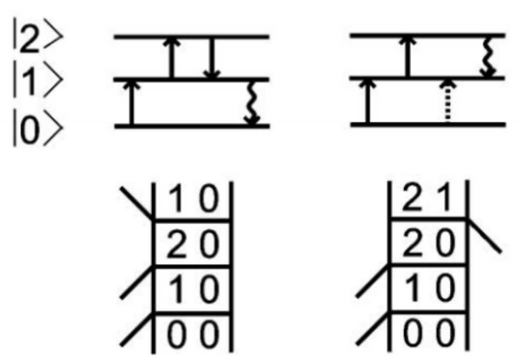
# 2.8: Appendix- Third-order diagrams for a vibration

The third-order nonlinear response functions for infrared vibrational spectroscopy are often applied to a weakly anharmonic vibration. For high frequency vibrations in which only the $\nu = 0$ state is initially populated, when the incident fields are resonant with the fundamental vibrational transition, we generally consider diagrams involving the system eigenstates $\nu = 0, 1$ and 2, and which include v=0-1 and v=1-2 resonances. Then, there are three distinct signal contributions:

| Signal | $k_{sig}$ | Diagrams and Transition Dipole Scaling | R/NR |
|---|---|---|---|
| $S_{\mathrm{I}}$ | $-k_1+k_2+k_3$ |  $\lvert\mu_{10}\rvert^4$ $\lvert\mu_{10}\rvert^4$ $\lvert\mu_{10}\rvert^2\lvert\mu_{21}\rvert^2$ | rephasing |
| $S_{\mathrm{II}}$ | $+k_1-k_2+k_3$ |  $\lvert\mu_{10}\rvert^4$ $\lvert\mu_{10}\rvert^4$ $\lvert\mu_{10}\rvert^2\lvert\mu_{21}\rvert^2$ | non-rephasing |
| $S_{\mathrm{III}}$ | $+k_1+k_2-k_3$ |  $\lvert\mu_{10}\rvert^2\lvert\mu_{21}\rvert^2$ $\lvert\mu_{10}\rvert^2\lvert\mu_{21}\rvert^2$ | non-rephasing |

Note that for the $S_I$ and $S_{II}$ signals there are two types of contributions: two diagrams in which all interactions are with the v=0-1 transition (fundamental) and one diagram in which there are two interactions with v=0-1 and two with v=1-2 (the overtone). These two types of contributions have opposite signs, which can be seen by counting the number of *bra* side interactions, and have emission frequencies of $\omega_{10}$ or $\omega_{21}$. Therefore, for harmonic oscillators, which have $\omega_{10}=\omega_{21}$ and $\sqrt{2}\mu_{10}=\mu_{21}$, we can see that the signal contributions should destructively interfere and vanish. This is a manifestation of the finding that harmonic systems display no nonlinear response. Some deviation from harmonic behavior is required to observe a signal, such as vibrational anharmonicity $\omega_{10} \neq \omega_{21}$, electrical anharmonicity (\sqrt{2}\mu_{10}\ne\mu_{21}\), or level-dependent damping $\Gamma_{10} \neq \Gamma_{21}$ or \(\Gamma_{00}\ne\Gamma_{11}.

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