

## 1 Definitions

Phonon eigenvectors at  $\mathbf{q} = 0$  (or normal modes in finite systems) are denoted by  $U_s^\alpha(\nu)$  for atom  $s$  and Cartesian component  $\alpha$ . They are orthonormalized as follows:

$$\sum_{st,\alpha\beta} U_s^\alpha(\mu) M_s \delta_{st} \delta_{\alpha\beta} U_t^\beta(\nu) = \delta_{\mu\nu} \quad (1)$$

where  $M_s$  is the mass of atom  $s$ .

One introduces the normal mode coordinate  $q_\nu$  by defining the actual atomic displacements  $u_s^\alpha$  as

$$u_s^\alpha = \sum_\nu q_\nu U_s^\alpha(\nu). \quad (2)$$

Derivatives wrt  $q_\nu$  are then given by

$$\frac{\partial A}{\partial q_\nu} = \sum_{s,\alpha} \frac{\partial A}{\partial R_s^\alpha} U_s^\alpha(\nu) \quad (3)$$

where  $\mathbf{R}_s$  is the position of the  $s$ -th atom and the quantity  $A$  is a function of atomic positions:  $A \equiv A(\mathbf{R}_1, \dots, \mathbf{R}_n)$ .

## 2 IR cross section

The IR cross section,  $I_\nu^{IR}$ , for normal mode  $\nu$  in a gas is given by

$$I_\nu^{IR} = \frac{\mathcal{N}\pi}{3c} \left| \frac{\partial \mathbf{d}}{\partial q_\nu} \right|^2 \quad (4)$$

where  $\mathcal{N}$  is the particle density,  $c$  is the speed of light,  $\mathbf{d}$  is the electric dipole of the system. In a condensed-matter system,  $\mathcal{N} = 1/\Omega$ , where  $\Omega$  is the volume of the unit cell, and  $\mathbf{d}$  is the electric dipole per unit cell. The quantity  $f^{IR} = |\partial \mathbf{d} / \partial q_\nu|^2$  is usually referred to as the ‘‘absolute IR activity’’. In terms of effective charges  $Z^*$ :

$$f^{IR} = e^2 \sum_\alpha \left| \sum_{s\beta} Z_s^{*\alpha\beta} U_s^\beta \right|^2. \quad (5)$$

## 3 Raman cross section

The nonresonant Raman cross section is written in terms of the Raman tensor  $r_{\alpha\beta}(\nu)$ :

$$r_{\alpha\beta}(\nu) = \frac{\partial \chi_{\alpha\beta}}{\partial q_\nu} = \sum_{s\gamma} \frac{\partial \chi_{\alpha\beta}}{\partial R_s^\gamma} U_s^\gamma(\nu), \quad (6)$$

where  $\chi_{\alpha\beta}$  is the electronic polarizability of the system:  $\chi_{\alpha\beta} = (\epsilon_{\alpha\beta}^\infty - 1)\Omega/4\pi$  in terms of the electronic dielectric tensor  $\epsilon^\infty$ . The derivative of  $\chi$  is a third-order derivative of the energy  $E$ :

$$P_{\alpha\beta,s\gamma}^{Ram} = \frac{\partial^3 E}{\partial E_\alpha \partial E_\beta \partial R_s^\gamma} = \frac{\partial \chi_{\alpha\beta}}{\partial R_s^\gamma}, \quad (7)$$

where  $\mathbf{E}$  is the electric field. For a typical experimental setup: incident and outgoing signal along orthogonal directions, plane-polarized incident beam, what is measured (the Raman activity  $I^{Ram}$ ) is given by

$$I^{Ram} = 45a^2 + 7c^2, \quad (8)$$

where

$$a = \frac{1}{3}(r_{11} + r_{22} + r_{33}), c^2 = \frac{1}{2} [(r_{11} - r_{22})^2 + (r_{11} - r_{33})^2 + (r_{22} - r_{33})^2 + 6(r_{12}^2 + r_{13}^2 + r_{23}^2)] \quad (9)$$

and it is understood that all quantities refer to mode  $\nu$ . For degenerate modes one has to sum over different modes. The depolarization ratio  $\rho$  – the ratio between the intensity perpendicular and parallel to the incident polarization – varies from 0 to 3/4, vanishes for totally symmetric modes, and is given by

$$\rho = \frac{3c^2}{45a^2 + 4c^2}. \quad (10)$$

## 4 Clausius-Mossotti formula

For molecular systems,  $\chi$  should be replaced by the molecular polarizability  $\tilde{\alpha}$ . This can be estimated from a supercell calculation using a Clausius-Mossotti approach. For an isotropic system:

$$\tilde{\alpha} = \frac{3\Omega}{4\pi} \left( \frac{\epsilon - 1}{\epsilon + 2} \right) = \frac{3\chi}{\epsilon + 2} \quad (11)$$

and

$$\frac{\partial \tilde{\alpha}}{\partial R_s^\gamma} = \frac{3\Omega}{4\pi} \frac{\partial \epsilon}{\partial R_s^\gamma} \frac{3}{(\epsilon + 2)^2} = \frac{\partial \chi}{\partial R_s^\gamma} \left( \frac{3}{\epsilon + 2} \right)^2 \quad (12)$$

For weakly anisotropic system, one may replace the factor  $\epsilon + 2$  with  $\text{Tr}\epsilon/3 + 2$ .

## 5 Units

Absolute IR activities are typically given in units of  $(\text{Debye}/\text{\AA})^2 \text{amu}^{-1}$  (1 Debye/ $\text{\AA}$  =  $10^{-10}$  esu; 1 amu =  $1.660538 \times 10^{-27}$  Kg). Other frequently encountered unit are km/mol and  $\text{cm}^{-2} \text{atm}^{-1}$ : 1  $(\text{Debye}/\text{\AA})^2 \text{amu}^{-1} = 42.255 \text{ km/mol} = 171.65 \text{ cm}^{-2} \text{atm}^{-1}$  at 0 C and 1 atm. Third-order derivatives  $P^{Ram}$  are typically given in units of  $\text{\AA}^2$ , Raman activities  $I^{Ram}$  in units of  $\text{\AA}^4 \text{amu}^{-1}$ .

In the code, everything is in atomic Rydberg units (aRu):  $e^2 = 2, m = 1/2, \hbar = 1$ . Conversion factors :  $e^2 = 2 \text{ aRu} = 4.80324^2 \times 10^{-20} \text{ esu}^2 = 4.80324^2 (\text{Debye}/\text{\AA})^2$

1 aRu mass unit = 2 electron mass =  $1.821876376 \times 10^{-30} \text{ Kg} = 0.00109716 \text{ amu}$ ;

1 aRu length unit = 1 bohr radius =  $0.529177 \text{ \AA}$ . Note that  $Z^*$  is adimensional.

The conversion factors are:

- 1 aRu = 10514.0155  $(\text{Debye}/\text{\AA})^2 \text{amu}^{-1}$  for  $f^{IR}$ ;
- 1 aRu = 0.2800283  $\text{\AA}^2$  for  $P^{Ram}$ ;
- 1 aRu = 71.47166  $\text{\AA}^4 \text{amu}^{-1}$  for  $I^{Ram}$ .

## 6 Bibliography

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P. Umari, X. Gonze, and A. Pasquarello, Phys. Rev. **B** 69, 235102 (2004).