PHYSICAL REVIEW B VOLUME 46, NUMBER 9 1 SEPTEMBER 1992-I

Far-infrared and Raman vibrational transitions of a solid sphere: Selection rules

Eugène Duval
Laboratoire de Physico-Chimie des Matériaux Luminescents, Université Lyon I-69622 Villeurbanne CEDEX, France
(Received 9 March 1992; revised manuscript received 15 June 1992)

The selection rules for far-infrared and Raman transitions of a solid sphere are derived from group theory. By far-infrared only the spheroidal dipolar modes are excited, by Raman scattering the spherical and spheroidal quadrupolar modes are observed.

Solids in the form of nanoparticles have particular physical properties originating from electron or vibration confinements, and surface effects. Far-infrared (FIR) spectroscopy, and especially low-frequency inelastic Raman scattering (LFR) are very interesting to study the geometry, the nature, and the structure of nanoparticles. With a size of a few nanometers the particles are, in general, spherical,[1] or sometimes ellipsoidal.[2] Using FIR and LFR we can observe the vibrational modes of a sphere or eventually of an ellipsoid.

For a correct interpretation of the FIR or LFR experiments it is necessary to be clear on the selection rules of transitions. We will determine the selection rules for the vibrations of a solid sphere. The symmetry group of the sphere is the group of the proper and improper rotations, that is isomorphic to O(3). The irreducible representations are noted $D_g^{(j)}$ and $D_u^{(j)}$ (see, for example, Heine[3]), $j=0,1,2,3,\ldots,g$ is for the even and u for odd by inversion. The dimension of a representation is $2j+1$. From the Wigner theorem,[4] to each vibration eigenfrequency corresponds a $D_g^{(j)}$ or $D_u^{(j)}$ representation, and the corresponding mode degeneracy is $2j+1$, the dimension of the irreducible representation. The $2j+1$ even or odd degenerate modes span an invariant subspace that transforms according to the irreducible representation $D_g^{(j)}$ or $D_u^{(j)}$, respectively.

The vibration modes of a spherical particle were, at first, studied by Lamb.[5] Two types of modes, spheroidal and torsional, are derived from the stress-free boundary condition of a spherical surface. A more recent theoretical work of Tamura, Higeta, and Ichinokawa[6] is an extension of the Lamb's theory. The displacements are deduced from the motion equation of an elastic sphere.[5-7] They are derived from Helmotz potentials—a scalar potential χ, and a vector potential $\mathbf{A}$—expressed in spherical coordinates:

$$\chi \propto j_l(hr)P_l^m(\cos\theta)\begin{Bmatrix}\cos m\phi\\ \sin m\phi\end{Bmatrix}\exp(-i\omega t) \tag{1}$$

and

$$\mathbf{A}=(r\Psi,0,0) \tag{2}$$

with

$$\Psi \propto j_l(kr)P_l^m(\cos\theta)\begin{Bmatrix}\cos m\phi\\ \sin m\phi\end{Bmatrix}\exp(-i\omega t)\ . \tag{3}$$

In these expressions j_l are the spherical Bessel functions, P_l^m the Legendre functions, $h=\omega/v_l$ and $k=\omega/v_t$, with v_l the longitudinal sound velocity and v_t the transversal one.

The torsional displacement $\mathbf{L}_t$ is given by the curl of the vector potential:

$$\mathbf{L}_t=\nabla\times\mathbf{A}\ . \tag{4}$$

Only the tangential components θ and ϕ exist.

The spheroidal displacement $\mathbf{L}_s$ is the combination of two displacements, $\mathbf{L}_{s1}$, which is the gradient of the scalar potential χ, and $\mathbf{L}_{s2}$, which is the curl of the curl of the vector potential:

$$\mathbf{L}_s=(\mathbf{L}_{s1}+\alpha\mathbf{L}_{s2})=\nabla\chi+\alpha(\nabla\times\nabla\times\mathbf{A})\ . \tag{5}$$

α is a coefficient determined by the stress-free boundary condition.

Each vector potential that transforms as the Y_l^m spherical harmonic corresponds to a torsional mode, from (4). In a similar manner, a couple comprised of a scalar potential and a vector potential both transform as Y_l^m corresponds to a spheroidal mode, from (5). Therefore the $2j+1$ degeneracy of the vibration model is equal to the $2l+1$ degeneracy of the potential and $j=l$. Furthermore from (4), the parity of a torsional mode is different from the parity of the corresponding potential. On the other hand, from (5), the parity of a spheroidal mode is identical to the one of the corresponding scalar and vector potentials. From the parity of the spherical harmonics, and the irreducible representations of the O(3) group, recalled before, it is directly deduced that the spheroidal modes transform according to the following irreducible representation of O(3).

$$D_g^{(0)},D_u^{(1)},D_g^{(2)},\ldots$$

and the torsional modes according to

$$D_g^{(1)},D_u^{(2)},D_g^{(3)},\ldots\ .$$

The radial displacement is zero for the torsional modes. The lowest-energy torsional $D_g^{(1)}$ modes consist in the rotation, in opposite direction, of two spherical layers as is shown in Fig. 1. For the lowest-energy odd torsional $D_u^{(2)}$ modes, they are the two different hemispheres, which rotate in opposite directions (Fig. 2). The torsional displacements induce shear strength. Conse-

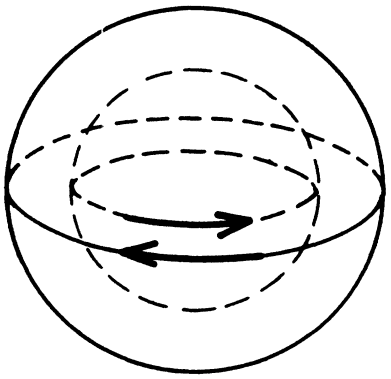

FIG. 1. Relative displacements in the lower-energy torsional $D_g^{(1)}$ modes.

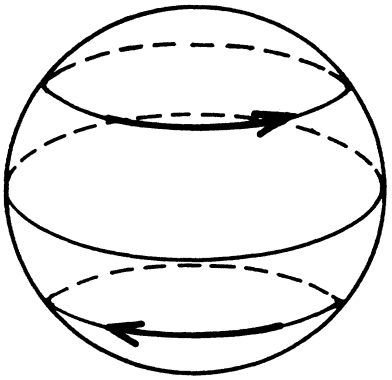

FIG. 2. Relative displacements of the two hemispheres in a torsional $D_u^{(2)}$ mode.

quently torsional vibrations exist only in solid spheres and do not occur, for example, in atomic nuclei and stars.

We are interested here, to solid spherical particles with a radius R smaller than the electromagnetic wavelength λ, so that the phase of the incident wave has negligible variation on the sphere. The vibration modes can be observed by one photon absorption (or emission), or by Raman scattering. The absorption (or emission) is electric dipolar. The electric dipole moment components $\sum_i e_i x_i$, $\sum_i e_i y_i$, and $\sum_i e_i z_i$ transform according to the irreducible representation $D_u^{(1)}$. Considering the representations corresponding to the vibration modes, the electric-dipolar transition will create (or annihilate) one phonon of the dipolar spheroidal modes $D_u^{(1)}$ only.

In Raman scattering the transition operator is the polarizability tensor α_{ij}, which is symmetric ($\alpha_{ij}=\alpha_{ji}$). Consequently the polarizability tensor components transform according to the irreducible representations resulting from the symmetrical product:[3]

$$[D_u^{(1)}\times D_u^{(1)}]_{\text{sym}}=D_g^{(0)}+D_g^{(2)} .$$

Therefore, the only observable Raman transitions are the transitions creating (Stokes) and annihilating (anti-Stokes) one phonon of the spherical mode $D_g^{(0)}$ or one phonon of the quadrupolar modes $D_g^{(2)}$. The torsional modes are not observed by Raman scattering.

This result contradicts the assertion of Fujii *et al.*[8] that Raman transitions exist for the $D_g^{(1)},D_g^{(3)},D_g^{(5)},\ldots$, modes. The parity is not a sufficient selection rule. On the other hand, it confirms that the observed Raman transitions are for the spherical $D_g^{(0)}$ and quadrupolar $D_g^{(2)}$ modes.[1,2]

Notice that, for the Raman transition that excites a spherical mode $D_g^{(0)}$, the polarizations of incident and scattered lights are parallel. On the other hand these polarizations can be parallel or perpendicular for the quadrupolar $D_g^{(2)}$ transitions. This fact allows us to assign the observed transitions easily.

Many observations of Raman scattering from nanoparticles, in different systems, have been carried out: insulating nanocrystals in glasses,[9] silica particles in silica aerogels,[10] metallic nanocrystals in alkali-halide crystals[2] or in glasses,[8] or semiconductor nanocrystals in glass.[11] The experimental results are in agreement with these selection rules based on group theory.

When the particles are ellipsoidal, as observed for silver particles in alkali halides,[2] the degeneracy of the quadrupolar modes $D_g^{(2)}$ is lifted, and one observes three different Raman transitions for the modes $m=\pm 2$, $m=\pm 1$, $m=0$, respectively. Obviously the splittings increase with the eccentricity.[2] It would be possible to observe the torsional modes $D_u^{(2)}$ by Raman scattering if the shape of the particle was slightly asymmetric due to the presence of an odd deformation.

The selection rules for far-infrared and Raman transitions from a solid sphere were not strictly stated before. They are very simple and must be known especially by experimentalists using low-frequency Raman scattering. This technique is powerful for the study of matter in the form of nanoparticles. Due to the special electric, magnetic and (nonlinear) optical properties of the solid nanoparticles, much research is now devoted to this domain of material science.

The author is very grateful to Professor M. Kibler and Professor R. Lacroix for criticisms and suggestions. Physicochimie des Matériaux Luminescents is a laboratory associated with the Centre National de la Recherche Scientifique (URA 442).

[1]E. Duval, A. Boukenter, and B. Champagnon, Phys. Rev. Lett. **56**, 2052 (1986).

[2]G. Mariotto, M. Montagna, G. Viliani, E. Duval, S. Lefrant, E. Rzepka, and C. Mai, Europhys. Lett. **6**, 239 (1988).

[3]V. Heine, in *Group Theory in Quantum Mechanics* (Pergamon, New York, 1960).

[4]E. P. Wigner, Z. Phys. **43**, 624 (1927).

[5]H. Lamb, Proc. London Math. Soc. **13**, 187 (1882).

[6]A. Tamura, K. Higeta, and T. Ichinokawa, J. Phys. C **15**, 4975 (1982).

[7]A. C. Eringen and E. S. Suhubi, in *Elastodynamics* (Academic, New York, 1975), Vol. II.

[8]M. Fujii, T. Nagareda, S. Hayashi, and K. Yamamoto, Phys. Rev. B **44**, 6243 (1991).

[9]B. Champagnon, A. Boukenter, E. Duval, C. Mai, G. Vigier, and E. Rodek, J. Non-Cryst. Solids **94**, 216 (1987).

[10]A. Boukenter, B. Champagnon, E. Duval, J. L. Rousset, J. Dumas, and J. Serughetti, J. Phys. C **21**, L1097 (1988).

[11]B. Champagnon, B. Andrianasolo, and E. Duval, J. Chem. Phys. **94**, 5237 (1991).