Vibron and phonon hybridization in dielectric nanostructures

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Edited* by F. Fleming Crim, University of Wisconsin-Madison, Madison, WI, and approved February 23, 2011 (received for review January 5, 2011)

Plasmon hybridization theory has been an invaluable tool in advancing our understanding of the optical properties of metallic nanostructures. Through the prism of molecular orbital theory, it allows one to interpret complex structures as “plasmonic molecules” and easily predict and engineer their electromagnetic response. However, this formalism is limited to conducting particles. Here, we present a hybridization scheme for the external and internal vibrations of dielectric nanostructures that provides a straightforward understanding of the infrared signatures of these particles through analogy to existing hybridization models of both molecular orbitals and plasmons extending the range of applications far beyond metallic nanostructures. This method not only provides a qualitative understanding, but also allows for the quantitative prediction of vibrational spectra of complex nanoobjects from well-known spectra of their primitive building blocks. The examples of nanoshells illustrate how spectral features can be understood in terms of symmetry, number of nodal planes, and scale parameters.

infrared optical properties | vibrational spectroscopy | aerosols | nanoparticles

Aerosols and nanoparticles are ubiquitous in our world and indeed throughout the solar system. Their role in atmospheric processes, as industrial pollutants, in interstellar chemistry, and as drug delivery systems has become an increasingly important issue in recent years. Understanding how these particles absorb and scatter electromagnetic radiation is essential for a broad range of sensing applications (1) and for the study of global warming, which strongly depends on how solar radiation interacts with aerosols (2). However, these optical properties are complicated by their dependence on particle size and shape. The most well-known example of this phenomenon involves the electromagnetic surface modes of particles with subwavelength dimensions. These surface modes typically show a strong dependence on particle morphology (3, 4). As a result, this behavior has been studied extensively for both dielectric and conducting particles.

In conducting particles, surface modes are associated with collective electron oscillations called plasmons. These surface plasmons commonly lead to strong absorption and scattering at visible and near-infrared frequencies of light. Controlling particle morphology in order to engineer the location and width of these peaks for a broad range of applications is an active area of research. In this field, plasmon hybridization theory (PHT) has allowed for an intuitive understanding of the optical properties of coupled metallic nanostructures (5–7). This understanding has largely been possible because PHT is conceptually similar to molecular orbital theory and experience with the latter allows one to easily grasp the main results of PHT through analogy.

For dielectric nanomaterials, the motion of internal vibrations (vibrational excitons or *vibrons*) and external vibrations (phonons) can also lead to surface modes. These vibrations occur at much lower frequencies than those of surface plasmons and are typically located in the infrared region of the electromagnetic spectrum. Similar to surface plasmons, these oscillations can display a dependence on particle morphology. However, their shape-dependent peaks must fall between the longitudinal optical

(ω_{LO}) and transverse optical (ω_{TO}) modes of the excited vibrational transition (4). There currently exists no simple model that can be used to explain and predict the behavior of surface modes of more complex dielectric nanostructures from the well-known behavior of simple nanoobjects (primitive components). For dielectric structures, such a method could enhance our understanding of the origin of band shapes, just as PHT has for metallic nanostructures, but with a much broader range of applications. Naturally this model would be a valuable intuitive aid when designing nanomaterials with a specified infrared response (8–10), and it would also be of great utility in any field where particles are characterized through their vibrational spectra, such as the remote sensing of atmospheric aerosols (11–13) or the study of cosmic dust (14–17).

In this work, we develop a hybridization scheme that is valid for internal and external vibrations of dielectric nanostructures. We demonstrate for the example of dielectric shells of different shapes that the inner and outer surface-charge densities are admixtures of the surface-charge densities of the primitive components that form such a shell—a cavity and a core (Fig. 1). This example illustrates the general applicability of the hybridization scheme and demonstrates how vibrational spectra of complex dielectric nanostructures can be predicted from spectra of primitive building blocks.

Results and Discussion

PHT was originally developed by considering simple particle morphologies. However, in that work, conduction electrons, which are responsible for the plasmon mode, were treated as an incompressible fluid. Such a model is physically unrealistic for a dielectric material. Therefore, an alternative approach is needed. Here, we take the electrostatic eigenvalue method which has been extensively applied to plasmon resonances (18–23). Using this approach, we demonstrate (*SI Text*) that the charge density on the inner and outer surface of a shell can always be constructed from linear combinations of the surface-charge densities of its two primitive components (a core and a cavity). For a spherical shell (Fig. 1A) with an inner radius of a and an outer radius of b , the surface-charge density can be expressed using spherical harmonics and the surface resonances (eigenmodes) are

$$\omega_{\pm}^2 = \frac{\omega_{LO}^2}{2} \left(1 \pm \frac{1}{2l+1} \sqrt{1 + 4l(l+1) \left(\frac{a}{b}\right)^{2l+1}} \right) + \frac{\omega_{TO}^2}{2} \left(1 \mp \frac{1}{2l+1} \sqrt{1 + 4l(l+1) \left(\frac{a}{b}\right)^{2l+1}} \right) \quad [1]$$

Author contributions: T.C.P. and R.S. designed research; T.C.P. performed research; and T.C.P. and R.S. wrote the paper.

The authors declare no conflict of interest.

*This Direct Submission article had a prearranged editor.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1100170108/-DCSupplemental.

Fig. 1. (A) Dielectric shell and the primitive components used to construct it: (B) a cavity and (C) a core. The permittivities of the core, shell, and the surrounding medium are ϵ_1 , ϵ_2 , and ϵ_3 , respectively.

when the band under consideration is well separated from all other optical modes, the high-frequency dielectric constant is set to one ($\epsilon_\infty = 1$), and the permittivity of the core and medium are also set to one ($\epsilon_1 = \epsilon_3 = 1$). This example is similar to what was initially presented for metallic shells (6) and the interpretation through analogy to molecular orbital theory can be applied here. The high-energy level (ω_{l+}) can be thought of as being antibonding and the low-energy level (ω_{l-}) as bonding. The antibonding mode involves an antisymmetric coupling between the charge on the inner and outer surface of the shell, whereas the coupling between the surfaces in the bonding mode is symmetric. Eq. 1 illustrates that a simple scale parameter a/b determines how the spectrum changes as a function of inner and outer radius.

Fig. 2 shows the energy levels for the dipolar eigenmodes ($l = 1$ in Eq. 1) and the corresponding absorption spectra for the ν_3 band of two spherical CO_2 shells with different thicknesses. As a dielectric substance, we have chosen crystalline CO_2 (see *SI Text* for details of the dielectric function used). This material is an excellent model system because its cubic crystal structure gives it a simple isotropic dielectric tensor. Furthermore, we have measured infrared spectra of various types of icy CO_2 aerosol particles, allowing for a direct comparison with experimental data (24, 25). Aerosol measurements also offer the advantage that substrate effects do not influence the measured spectra, keeping the example simple. Finally, the understanding of infra-

red signatures of CO_2 aerosols of various morphologies is crucial for the interpretation of current and future aerosol data from the Mars atmosphere, where CO_2 is one of the important cloud components (13). The current understanding of the morphology of these cloud condensates is that CO_2 forms a shell around H_2O -coated dust particles.

A simple explanation why the antibonding mode is higher in energy than the bonding mode is provided in Fig. 2. Analogous to molecular orbital theory, the energy increases with an increasing number of nodal planes (higher kinetic energy). The antibonding mode has three nodal planes (+−; −+; +−) whereas the bonding mode has only one (+−). Furthermore, the calculated absorption spectra for spherical CO_2 shells on the right-hand side of Fig. 2 show that an external electromagnetic field couples much more strongly to the bonding mode than to the antibonding mode, which is a consequence of the larger overall dipole moment of the bonding mode. A comparison of Fig. 2A to Fig. 2B shows that, as the shell thickness is increased, the splitting between the bonding and antibonding modes decreases. The source of this change is a decrease in coupling between the charges on the inner and outer surfaces of the shell with increasing shell thickness. Within the hybridization model, this result can be interpreted as the two primitive modes mixing less with each other as shell thickness increases. In the limit of an infinitely thick shell, the eigenmodes will be equal to those of the primitive structures. In contrast to metallic shells, the absorption peaks of dielectric shells are restricted to the LO–TO region. In this region, the dielectric material behaves like a conductor insofar as the real part of its dielectric function is negative. The consequence of this restriction is that, in the limit of an infinitely thin shell, the bonding mode approaches ω_{TO} while the antibonding mode approaches ω_{LO} . This behavior differs from the metallic case where in this limit the bonding mode approaches a frequency of zero and the antibonding mode approaches the plasma frequency of the metal. Therefore, plasmon modes of metallic nanostructures can be tuned over a much larger range of energies than vibrational modes of dielectric materials. The mode structures are of course also shape dependent. The restriction to the LO–TO region means that vibrational transitions with large LO–TO splittings exhibit pronounced shape dependence but those with very small or negligible splittings have little shape dependence.

To validate this model against experimental results, the infrared spectra of CO_2 nanoshells with a cubic shape (lower trace in Fig. 3A) and CO_2 cubes (lower trace in Fig. 3B) were measured as aerosols in a bath gas cooling cell ($T = 78$ K). CO_2 ice cubes were formed by injecting pure CO_2 into the cell, whereas CO_2 ice nanoshells with a cubic shape were prepared by condensing CO_2 onto cubic N_2O templates (24). Although the spherical shells discussed above are useful for illustrative purposes, their application is limited as real CO_2 aerosols are known to contain particles that are cubic in shape because of their crystalline structure (25). The same holds for the N_2O templates. We used equimolar amounts of N_2O and CO_2 to generate the nanoshells and assume that this ratio is the same for each particle in the ensemble. The ratio of shell thickness to core size can then be determined from the known molar volumes of crystalline N_2O and CO_2 .

Based on the known shapes of CO_2 particles and of the N_2O templates used to construct CO_2 shells, a cubic particle model is more suitable here. The discussion of the eigenmodes of this object is more complicated as multiple modes possess a net dipole moment and couple to an external field in the electrostatic limit. However, the strengths of all these dipole active modes are not equal. For a cube, Fuchs has shown that six of these modes are responsible for 96% of the absorption spectrum (26)—a result that is easily verified using the electrostatic eigenvalue method—and it is reasonable to expect a similar type of convergence with

Fig. 2. Energy level diagrams (Left) and corresponding absorbance spectra (Right) for the ν_3 band of spherical CO_2 nanoshells. The scale parameters b/a are (A) 1.2 and (B) 2.

Fig. 3. Calculated (upper traces) and experimental (lower traces) spectra for (A) cubic CO₂ shells and (B) CO₂ cubes in the region of the antisymmetric stretching vibration ν_3 and the bending vibration ν_2 of CO₂. For the calculations, the ratio of outer-side length to inner-side length (scale parameter) is 1.26, and the corners and edges of the cube have been rounded. The eigenmodes with the largest dipole moment are labeled in both the spectra. The energy level diagrams for the cubic shell are given in Fig. 4. For the two optical modes whose splitting can be resolved experimentally, calculated (experimental) splittings in wavenumbers are $|\nu_3 \text{ CUBE}\rangle - |\nu_3 -\rangle = 6.5(7.7)$, $|\nu_3 \text{ CUBE}\rangle - |\nu_3 +\rangle = -18.2(-19.2)$, $|\nu_2'' \text{ CUBE}\rangle - |\nu_2'' -\rangle = 2.8(3.9)$, and $|\nu_2' \text{ CUBE}\rangle - |\nu_2' +\rangle = -8.2(-9.5)$.

a cubic shell. The surface-charge density integrals of both a cube and cubic shell were evaluated numerically (20) and energy level diagrams for the ν_3 and ν_2 bands of cubic CO₂ shells are shown in Fig. 4 A and B, respectively. For all three sets of optical modes (ν_3 , ν_2' , and ν_2''), the splitting that results from the mixing of the surface modes of the primitive components is more complex because hybridization involves a larger number of modes with dipole moments. Despite these details, the general result is again straightforward, as highlighted in Fig. 4: Bonding and antibonding modes fall into low- and high-energy bands, respectively, with increasing energy for increasing numbers of nodal planes.

In Fig. 3A, the calculated spectrum for the cubic shell (upper trace) is compared to the experimental spectrum (lower trace). The ν_2 band of CO₂ consists of two modes. The small LO-TO splitting of the low-frequency ν_2' mode and its proximity to the higher frequency ν_2'' mode (Fig. 4B) means that its shape-dependent features cannot easily be resolved and thus simply appear as a single peak. More detail and a clear shape dependence is seen in the ν_2'' mode and the sole mode of the ν_3 band. For each mode, the strongest bonding (|−⟩) and antibonding (|+⟩) components are labeled. If only these components were used to calculate the spectrum, there would be little difference between the band shapes of the spectrum of a cubic shell and that of a spherical shell. It is the presence of the other dipole active modes that gives the characteristic asymmetric band shape toward higher wavenumbers for $|\nu_2'' -\rangle$ and $|\nu_3 -\rangle$ and toward lower wavenumbers

Fig. 4. Energy level diagrams for the (A) ν_3 and (B) ν_2 band of CO₂. The eigenmodes with the largest dipole moment are labeled in the diagrams. The illustrations depicting surface-charge distributions in A are associated with these modes. For clarity, only eigenmodes that contribute significantly to the absorption spectra in Fig. 3 are listed (in all cases, these modes account for at least 96% of the absorbance in the calculated spectra).

for $|\nu_2'' +\rangle$ and $|\nu_3 +\rangle$. Similar to the spherical shell, the peaks of the antibonding and bonding modes are essentially scaled reflections of each other. This result is true for any shell whose inner and outer surface are scaled versions of each other.

The earlier discussion concerning the thickness of a spherical shell and its effect on the splitting between modes also applies to cubic shells. This behavior is highlighted in Fig. 5 where the spectra of spherical (upper traces) and cubic shells (lower traces) are compared to each other as a function of the scale parameter b/a (which defines the thickness of the shell relative to its core for both shapes). With increasing shell thickness, the bonding modes shift to higher energies, while the antibonding modes shift to lower energies, thus reducing the splitting between the two sets of modes. Simultaneously, the splitting of the antibonding modes relative to the bonding modes becomes smaller until, finally, they appear only as shoulders in the case of the thickest shells (Fig. 5D). Although these trends hold for both shapes, Fig. 5 also illustrates the small but characteristic difference between their spectra. Apart from a systematic shift of band positions, the cubic shells give rise to characteristic asymmetric band shapes, whereas the infrared bands of the spherical shells are almost perfectly symmetric. The asymmetry of the infrared bands is clearly visible in the experimental spectra of the cubic shells in Fig. 3A. It is noteworthy that the normalized spectra only depend on the scale parameter and on the particle shape, but not on the particle size as long as the latter falls into the range where the electrostatic approximation as used here applies. Larger particles have additional contributions from effects such as elastic scattering, and much smaller particles (usually well below 5 nm) require a different treatment because their spectra are dominated by the interplay of molecular structure and finite size (see ref. 25 for further details).

Fig. 5. Calculated absorbance spectra for spherical (upper traces) and cubic (lower traces) CO_2 shells with N_2O cores. The scale parameters b/a are (A) 1.2, (B) 1.6, (C) 2, and (D) 4. The scale parameter for the spherical shell is defined as ratio of outer and inner radius. For the cubic shell, this parameter indicates the ratio of outer-side length to inner-side length of the cubic shell.

Both PHT and the electrostatic eigenvalue method work within the long-wavelength (electrostatic) approximation, which assumes that particle dimensions are much less than the wavelength

of light impinging on them. This approximation is often very poor for metallic nanostructures and means that, despite the insight that PHT provides to our understanding of optical properties, it can often only predict spectral trends without being able to reproduce observed spectra in detail. In the midinfrared region where most fundamental internal vibrations occur, wavelengths range from 2.5 to 25 μm (4,000 to 400 cm^{-1}). Therefore, the quantitative reproduction of absorbance spectra of nanometer-sized dielectric particles should be superior to plasmon spectra of metallic nanoparticles calculated within this approximation. The overall correspondence between the observed and calculated spectra in Fig. 3 is indeed excellent. The predicted splitting that occurs between the modes of the cube and those of the cubic shell closely match the experimental observation, as does the asymmetric shape of the infrared bands (see the caption of Fig. 3). Due to the small dimensions of the particle relative to the wavelength of light, the electrostatic approximation is well satisfied. Therefore, not only does this hybridization model provide an intuitive understanding of the phonon and vibron spectra of complex dielectric nanostructures but it allows one to perform accurate numerical calculations.

We have demonstrated that a hybridization scheme similar to what has been previously established for molecular orbitals and plasmonic nanostructures can be constructed for internal and external vibrations of dielectric nanoparticles. For example, vibrational modes of dielectric shells of various shapes can be understood as being admixtures of the surface-charge densities of the primitive components, a cavity and a core, that form the shell. Not only does this hybridization scheme provide insight into the infrared spectral features of dielectric particles, but it can also be used to accurately reproduce and predict those spectra, which is not usually possible when electrostatic methods are applied to metallic nanostructures. Finally, the generality of this model means that it can find application in areas ranging from infrared spectroscopic explorations of CO_2 clouds on Mars to the design of SiC nanomaterials.

Methods

The method for the construction of the surface-charge density of a shell from the surface-charge densities of its primitive components is described in [SI Text](#). A derivation of Eq. 1 is provided. Furthermore, we also describe the procedure used to calculate the spectra shown in Figs. 2, 3, and 5, along with the eigenmodes that are listed in Figs. 2 and 4. Finally, the details of the CO_2 dielectric function used in the various calculations are given (optical modes, high-frequency dielectric constant, and damping).

ACKNOWLEDGMENTS. Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Canada Foundation for Innovation is gratefully acknowledged. This research has been enabled through the generous allocation of advanced computing resources by West-Grid and Compute/Calcul Canada. T.C.P. acknowledges an NSERC fellowship.

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