

From Plasmon Spectra of Metallic to Vibron Spectra of Dielectric Nanoparticles

THOMAS C. PRESTON AND RUTH SIGNORELL*

Department of Chemistry, University of British Columbia, Vancouver, BC, V6T 1Z1, Canada

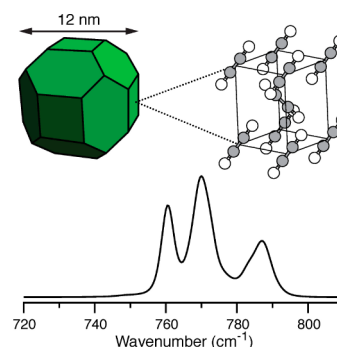
RECEIVED ON JANUARY 9, 2012

CONSPECTUS

Light interacts surprisingly differently with small particles than with bulk or gas phase materials. This can cause rare phenomena such as the occurrence of a “blue moon”. Spectroscopic particle phenomena of similar physical origin have also spawned countless applications ranging from remote sensing to medicine. Despite the broad interest in particle spectra, their interpretation still poses many challenges. In this Account, we discuss the challenges associated with the analysis of infrared, or vibron, extinction spectra of small dielectric particles.

The comparison with the more widely studied plasmon spectra of metallic nanoparticles reveals many common features. The shape, size, and architecture of particles influence the band profiles in vibron and plasmon spectra in similar ways. However, the molecular structure of dielectric particles produces infrared spectral features that are more diverse and detailed or even unique to vibron spectra. More complexity means higher information content, but that also makes the spectra more difficult to interpret. Conventional models such as classical electromagnetic theory with a continuum description of the wavelength-dependent optical constants are often no longer applicable to these spectra. In cases where accurate optical constants are not available and for ultrafine particles, where the molecular structure and quantum effects become essential, researchers must resort to molecular models for light–particle interaction that do not require the prior knowledge of optical constants. In this Account, we illustrate how vibrational exciton approaches combined with molecular dynamics simulations and solid-state density functional calculations provide a viable solution to these challenges.

Molecular models reveal two important characteristics of vibron spectra of small molecularly structured particles. The band profiles in vibron spectra are largely determined by transition dipole coupling between the molecules in a particle. Below a specific particle size limit, conventional models fail. Molecular models explain many other phenomena in particle spectra, such as size, shape, and mixing effects, providing the foundation for a better understanding of the interaction of solar radiation with aerosols and clouds and for the design of dielectric nanomaterials.



Introduction

Visual phenomena arising from the interaction of light with small particles have fascinated mankind for centuries and were exploited even before there was any understanding of their source or cause. The origin of the striking color of gold nanoparticles dispersed in water, for example, had been a mystery since the 19th century. Michael Faraday already studied this phenomenon,¹ but it was only in the early 1900s that Gustav Mie provided one of the first comprehensive theoretical explanations.² Countless applications of nanostructured metallic systems in nanotechnology, biophotonics, medicine, and sensing have since followed

and led to the emergence of a research field of its own: plasmonics (see refs 3–6 and references therein). Intriguing phenomena caused by the scattering and absorption of light by small particles are by no means restricted to metallic nanoparticles. They are the reason why milk is opaque and white, explain the uncommon occurrence of a “blue moon”, and even let us understand the influence of aerosols and clouds on the radiative balance of planets and moons.^{7–10} Global warming on Earth, for instance, sensitively depends on how solar radiation in the infrared interacts with aerosols and clouds.¹⁰ The spectroscopy of such systems is as essential to climate modeling as to remote sensing.

Atmospheric aerosol particles and cloud droplets consist of a particularly wide range of different chemical species, which makes the description of the light–particle interaction more complicated than that for metallic systems. The fact that spectroscopic properties of aerosols and clouds are often required over various spectral regions and at different temperatures, for example, in remote sensing, adds even more complexity.

This Account focuses on the analysis of infrared (IR) extinction spectra, or “vibron spectra”, of small dielectric particles, such as aerosol particles built from molecules or dielectric nanoparticles and nanostructures relevant to the design of nanomaterials or to the study of interstellar dust. Appropriate modeling approaches are a prerequisite for the analysis of particle vibron spectra.^{11–14} We discuss various issues that arise in this context and review the latest advances toward a comprehensive analysis of particle vibron spectra. Better known than vibron spectra of dielectrics are extinction spectra of metallic nanoparticles, or “plasmon spectra”, which typically exhibit strong resonances in the ultraviolet (UV), visible (VIS), and near-infrared (NIR) regions of the electromagnetic spectrum. Therefore we begin our review with a discussion of similarities and differences in plasmon spectra and vibron spectra of nanoparticles, with an emphasis on typical finite-size effects in extinction spectra.

Gustav Mie's solution to the interaction of an electromagnetic plane wave with a spherical particle is the basis for much of our current understanding of how light is absorbed and scattered by small particles.² Mie exploited classical electrodynamics and linear optics to treat the light–particle interaction. More specifically, he solved Maxwell's equations analytically for an incident electromagnetic plane wave and spherical boundary conditions describing the interface between a particle and its surroundings. Since this fundamental contribution an impressive body of work has been devoted to the development of approximations and numerical techniques for the calculation of spectra of particles of arbitrary shape and architecture.^{8,15–17} Among the most popular is the discrete dipole approximation (DDA),¹⁸ which is also used in the present contribution.¹⁹ All of these approaches are essentially based on the same theoretical framework as Mie's solution, that is, classical electromagnetic theory with a continuum description of the wavelength-dependent optical constants (refractive indices) of a particle and its surroundings. Throughout this Account, these approaches are described as “conventional models”. They are usually considered satisfactory for the description of plasmon spectra.

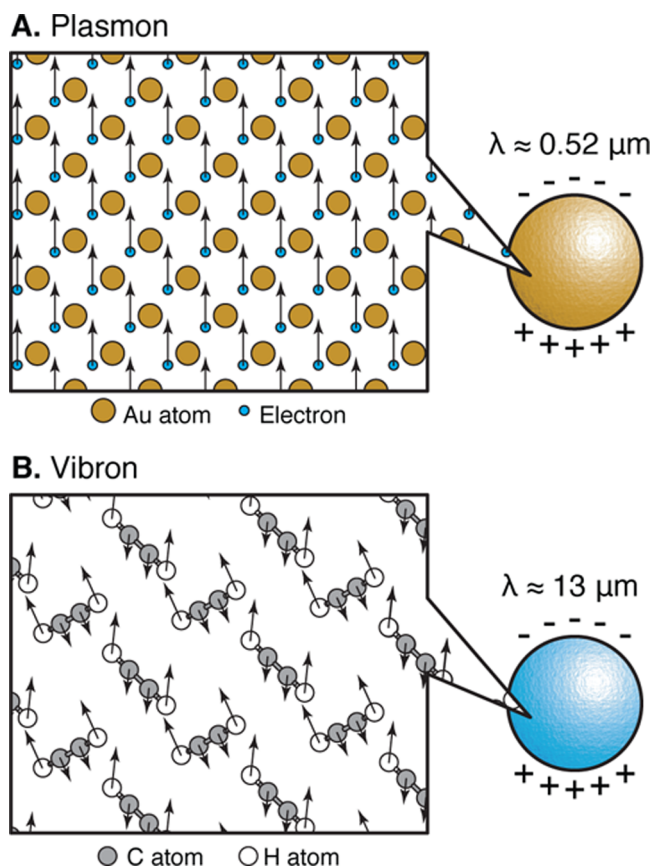


FIGURE 1. Sketches of the microscopic origin of (A) plasmons in metallic nanoparticles using gold as an example and (B) vibrons in dielectric nanoparticles using crystalline acetylene as an example. The positive and negative signs indicate surface polarization charges on the spherical particles.

It turns out, however, that they are insufficient for understanding spectral features arising from vibrons. Alternative approaches are required, and we review some of the possibilities.

In many cases, a qualitative understanding of the most prominent features in particle spectra would be highly desirable. The interaction of light with particles, however, is extremely complicated, so this is an elusive goal in general. We conclude with a description of a hybridization scheme that provides such a qualitative understanding in specific cases. It allows us to predict spectra of more complex nanostructures from the well-known spectra of their simple building blocks.

Plasmon versus Vibron Spectra

Surface modes in small particles can originate from different types of collective motions. Among them are plasmons in metallic systems and vibrons (also named vibrational excitons) in dielectric particles. Plasmons describe collective oscillations of conduction electrons (Figure 1A), while vibrons

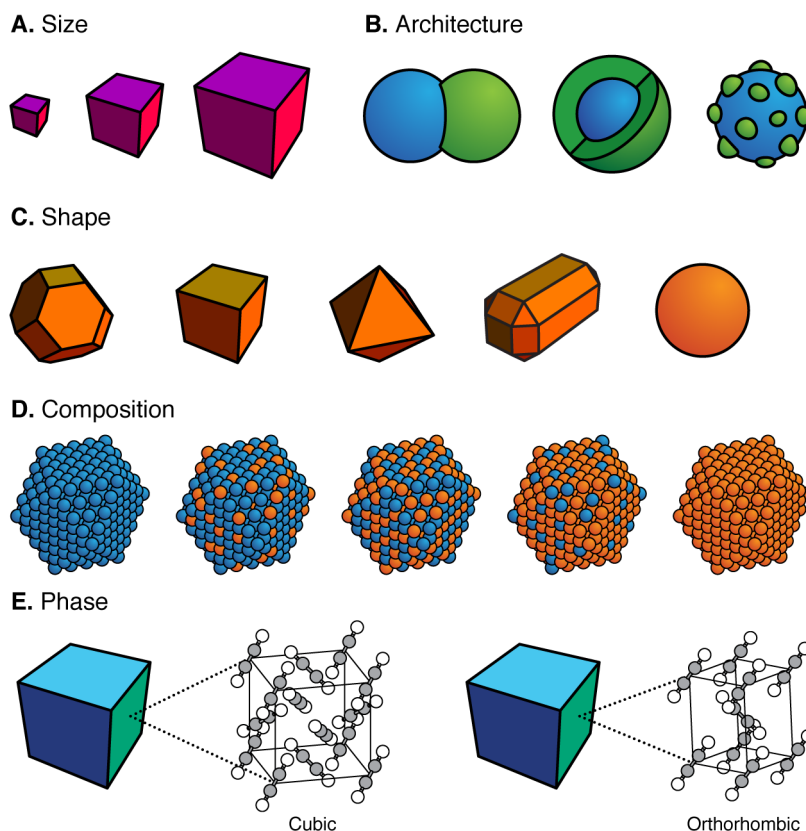


FIGURE 2. Illustration of particle properties that influence band profiles in vibron and plasmon extinction spectra. The different particle properties are shown as simple sketches. The crystal structures in panel E are for the cubic (left) and the orthorhombic (right) crystal phase of acetylene.

represent collective vibrations of molecules (Figure 1B). Vibrons are thus typical for systems built from molecules and arise from the intermolecular coupling of the internal molecular vibrations.²⁰ Both types of surface modes can be excited by an external electromagnetic field. The frequencies at which this happens, however, are very different. Vibron spectra typically show strong resonances in the mid-IR region, while plasmon resonances are usually excited by VIS/UV/NIR light.

Vibrons and plasmons have much in common. Although their microscopic origins are very different, their macroscopic effects (i.e., the surface polarization charge for small particles sketched in Figure 1) are similar. It does not come as a surprise that they also exhibit common spectroscopic properties, at least qualitatively. Vibron and plasmon spectra show diverse absorption and scattering features that are governed by the properties of the particles (Figure 2), of which the particle size is the most striking. It mainly determines the amount of light that is absorbed and elastically scattered by the particle. As a rule of thumb, the larger the particle, the higher the contribution from elastic scattering. With increasing scattering contribution, extinction bands in

vibron and plasmon spectra become broader and show more structure (several peaks and shoulders) as a result of the excitation of higher order normal modes of the nanoresonators.^{8,15–17} Many examples for extinction spectra with varying scattering contributions exist in the literature (see, for example, refs 11–13, 21, and 22). Conventional models, such as Mie's solution or DDA, are suitable here for modeling spectra, provided that the particle's optical constants are well-known (see subsequent section). Characteristic scattering features in spectra together with modeling allow for the determination of particle size distributions. This method is often exploited for aerosol particles that are too delicate for other more invasive sizing techniques. For vibron spectra in the mid-IR, scattering typically becomes "negligible" for particles smaller than about 100 nm,^{11–14} while for plasmon spectra in the VIS, this happens for particle sizes below about 20 nm. If the dimension of the particle is much smaller than the wavelength of the light, extinction bands no longer change their profile with decreasing particle size. Their appearance becomes size independent and the light–particle interaction can be treated within the so-called electrostatic approximation,⁸ which is an approximation

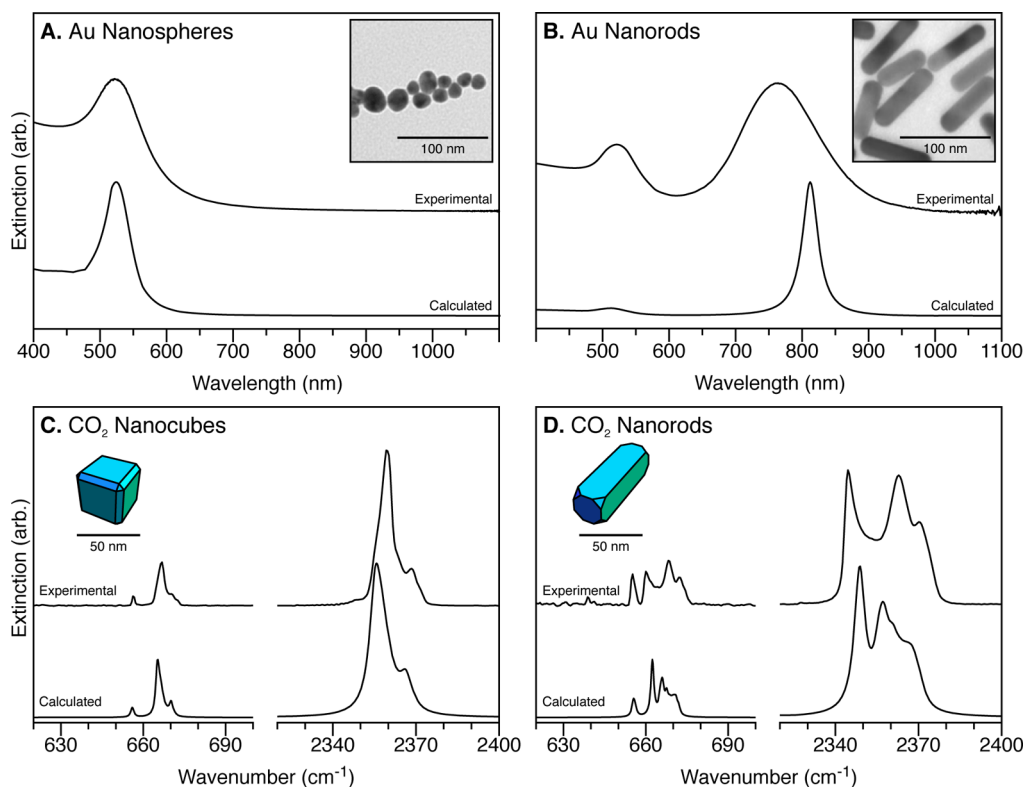


FIGURE 3. Shape effects in extinction spectra. Transmission electron microscope (TEM) images (insets) and experimental and calculated spectra of (A) Au nanospheres and (B) Au nanorods. Particle sketches, experimental, and calculated spectra of (C) CO₂ nanocubes and (D) CO₂ nanorods in the region of the bending and antisymmetric stretching vibrations.^{11,13,30,41} All simulated spectra were calculated with DDA (conventional model).¹⁹ The approximate sizes of the experimentally probed particles can be seen from the length scales shown in the figure.

within the above-mentioned conventional models. However, this is only true down to a characteristic particle size that depends among others on the chemical makeup of the particle (refs 11–14, 23, and 24 and references therein). Below this characteristic size, the molecular structure and quantum effects become important. As a consequence, unique extinction spectra are observed for each size (see subsequent section).

The particle shape and architecture also lead to characteristic spectral signatures.^{11–14,25–48} As is the case for size effects, they are qualitatively similar for plasmons and vibrons. Figure 3 compares shape-dependent plasmon spectra of gold particles (A and B) with shape-dependent vibron spectra of carbon dioxide aerosol ice particles (C and D). IR signatures of the latter are of interest for the interpretation of aerosol data from the Mars atmosphere, where CO₂ is one of the important cloud components.⁴⁹ The common trends observed in Figure 3 can be summarized as follows: Particle shapes with near unit axis ratios (Au nanospheres and CO₂ nanocubes) show narrower, only slightly structured bands with a pronounced maximum. For elongated particles (Au and CO₂ nanorods), the band widths increase, the bands become more

structured, and new bands appear. Particles can also have different architectures that influence the spectra. An example is given in the last section of this Account for a core–shell particle. The shell gives rise to a characteristic doublet structure both in vibron^{13,33,34,41} and in plasmon spectra.⁴⁴

While plasmon and vibron spectra have qualitative similarities, Figure 3 also reveals quantitative differences. On the one hand, vibron resonances cover a much narrower frequency range than plasmon resonances. On the other hand plasmon resonances can be tuned over a much broader range of energies by modifying the particle's properties, which is attractive for various applications.^{3–6} Features in vibron spectra, however, are less blurred with more detailed structures and the quantitative agreement between experiment and simulation that can be achieved here is often better than in the case of plasmon spectra. Moreover, vibron spectra are modulated by the particle's molecular structure, which makes them much more diverse than plasmon spectra. Pronounced effects that arise from mixing of different substances on a molecular level,^{28,30,31,33–35,39,40,50} from multifarious phase behavior,^{31,32,35,37,38,40,51–53} and from surface contributions in small particles^{31,32,37,52,54–59} are

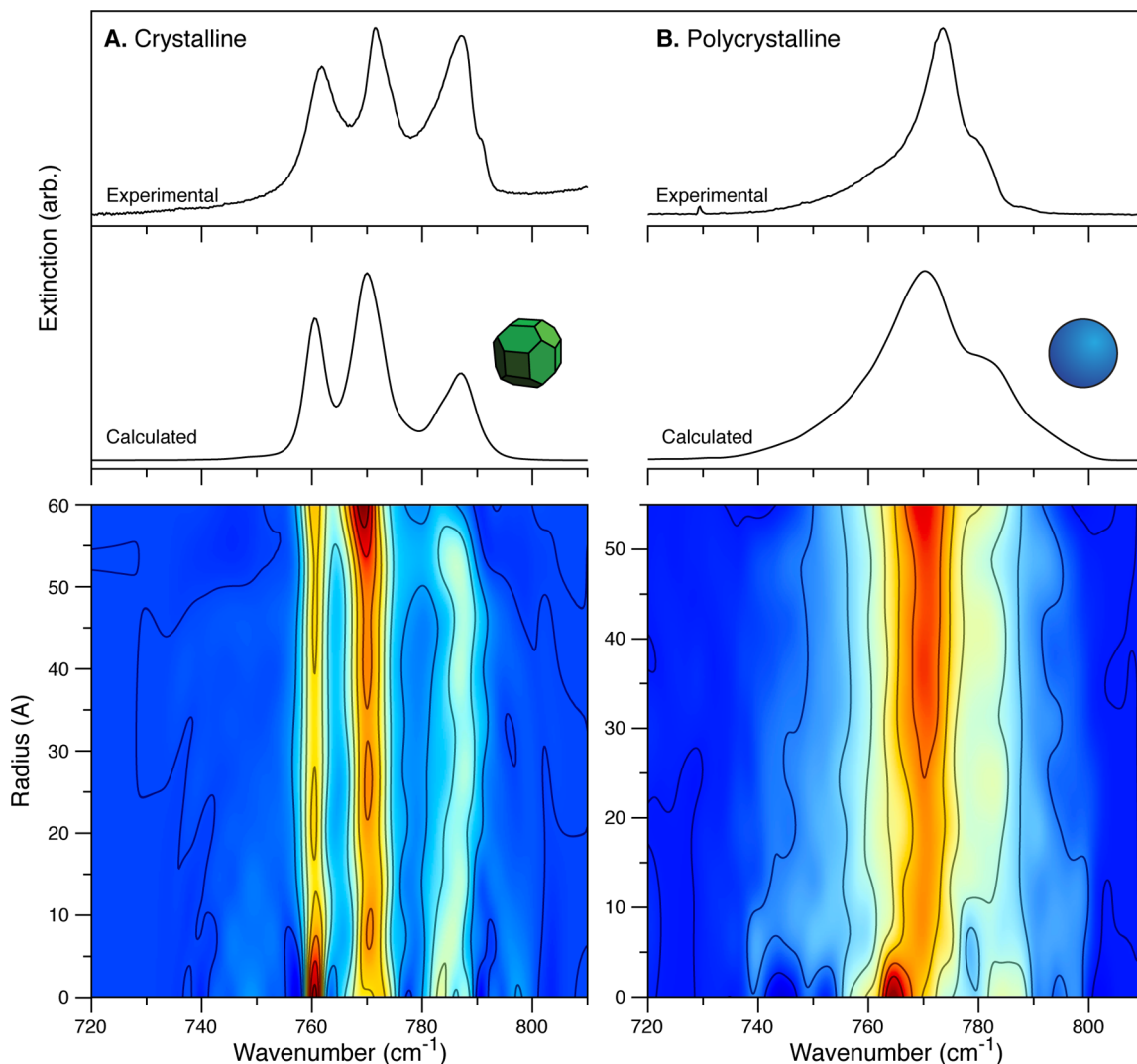


FIGURE 4. IR extinction spectra in the region of the bending vibration of icy C_2H_2 aerosol particles in different phases.³⁸ Experimental spectra (top), calculated spectra (middle), and contour plots of the excitation density (bottom) for (A) crystalline orthorhombic C_2H_2 aerosol particles and (B) polycrystalline C_2H_2 aerosol particles with orthorhombic polycrystallites. The diameters of the experimentally probed particles were between 10 and 50 nm (Note that the spectrum is size-independent in this size range). Particle spectra were calculated with the exciton model (molecular model).^{13,14,29} The excitation density increases from blue to white to red color.

more common or even unique to vibron spectra (Figure 2). As an example, Figure 4 shows the spectral differences that arise from different phases of icy acetylene aerosol particles. Similar to CO_2 particles, C_2H_2 plays a role in a number of planetary and lunar atmospheres such as Titan's. Even the relatively small change in the phase from a crystalline structure (Figure 4A) to a slightly disordered structure (Figure 4B) significantly affects the spectra. The calculated spectrum for the crystalline particle depicted in the middle trace of Figure 4A is for a polyhedron with a perfect orthorhombic crystal structure (see structure on the right-hand side of Figure 2E). The calculated spectrum for the particle with a slightly disordered structure in the middle trace of Figure 4B

is that of a sphere with a polycrystalline structure. The polycrystal is modeled by randomly oriented multiple crystalline inclusions each with an orthorhombic crystal structure. The broken symmetry in the polycrystalline case modifies the particle's vibrational mode structure. A molecular model, such as the exciton model used in Figure 4, not only affords a reasonable prediction of the experimental spectra. It also provides information about the mode structure inside the particle. The lower panels in Figure 4 are contour plots of what has been called excitation density (see refs 13, 14, and 38 for details). This is the probability that light of a certain wavenumber excites molecules at a given location inside the particle; here the location is specified by the radial

distance from the center of the particle. The excitation density of the crystalline particle shows three modes extending uniformly over the entire particle. Since this mode structure is a result of the regular crystalline structure, it is no longer visible in the excitation density of the polycrystalline particles where the individual polycrystallites prevent the formation of distinct delocalized modes.

Vibron Spectra: Beyond Conventional Models

The biggest challenge in the field is the analysis of vibron spectra outside the range where conventional models are valid. There are essentially two different situations when this happens, which are briefly discussed here. First, conventional models are not applicable whenever the optical constants (complex refractive index, complex dielectric function) are not available (e.g., Figure 4),^{13,30,33,34,36,38,40} because these are the fundamental quantities needed as input for any of the conventional models (Mie, DDA, electrostatic approximation, etc.^{2,8,15–17}). Likewise, the conventional models are of little use for the spectral analysis if frequency-dependent optical constants are not sufficiently accurate,^{13,60} which is often the case in the mid-IR. Second, conventional models completely fail below a certain particle size, typically around 10 nm (“ultrafine particles”) for vibron spectra of molecular systems as mentioned above.^{11–14,32,37,54,56–59} The influence of molecular structure and quantum effects, which become important in this size range, cannot be described by conventional models. Situations where optical data are missing as well as ultrafine particles require molecular approaches to simulate the spectra.^{11–14,25,29,37,38,40,54–58,60} A large part of our work has been devoted to the development of molecular models for the analysis of particle spectra in the IR and in particular to their validation by comparison with various experimental results. In our approach, we employ vibrational exciton calculations^{11–14,29,34,60} in combination with molecular dynamics simulations^{14,37,38,58} and solid-state density functional (DFT) calculations.^{40,61}

The lack or inaccuracy of frequency-dependent optical constants is a particular issue for molecular systems, because they can consist of a wide variety of different compounds, exhibit a multifarious phase behavior (several crystalline and amorphous states), and form complicated multi-component mixtures (Figures 2 and 4). It is a daunting if not impossible task to determine refractive indices experimentally for all those cases (see discussion in ref 8). For metallic systems, where different phases and mixing are often irrelevant and the interest is focused on very few compounds

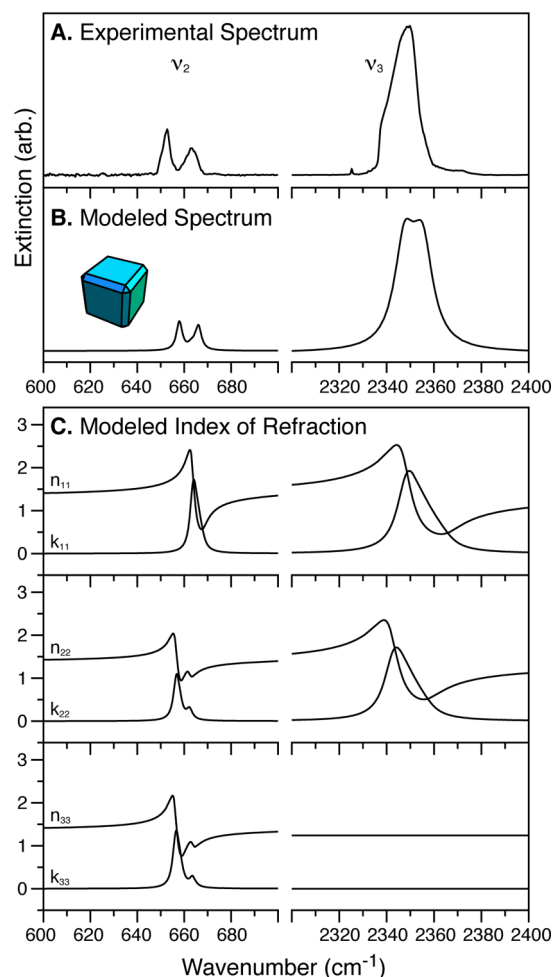


FIGURE 5. Experimental (A) and calculated (B) IR spectra of mixed cocrystalline $\text{CO}_2\text{-C}_2\text{H}_2$ ($\beta\text{-P}2_1/c$ crystal phase) aerosol particles in the region of the bending (ν_2) and the antisymmetric stretching (ν_3) vibrations of CO_2 .⁴⁰ (C) Modeled complex refractive index ($n_{11}+ik_{11}$, $n_{22}+ik_{22}$, $n_{33}+ik_{33}$) along three orthogonal axes of the $\text{CO}_2\text{-C}_2\text{H}_2$ cocrystal in the same spectral region as in panels A and B. The diameters of the experimentally probed particles are approximately 50 nm. The crystal structures and the complex dielectric function were obtained with the ABINIT program.⁶¹ Particle spectra were calculated with DDA.¹⁹

(often Au), this is much less of an issue. Therefore conventional approaches are more widely applicable to simulate plasmon spectra than vibron spectra. We have shown in recent years that a hybrid approach using a combination of molecular and conventional models can be a useful alternative here: vibrational exciton approaches^{37,60} (see below) or solid-state DFT calculations^{40,61} are employed to calculate the frequency-dependent optical properties, which then serve as input for Mie or DDA calculations. Figure 5 shows an example where the complex index of refraction (panel C) was first calculated with DFT and then used as input to simulate the particle IR spectrum with DDA (panel B). The agreement between experimental (panel A) and calculated

spectrum is satisfying.⁴⁰ The calculation reproduces the two characteristic features, i.e. the typical unstructured broad ν_3 band of CO_2 found in mixed CO_2 crystals^{30,33} and the characteristic splitting of the ν_2 band of CO_2 . The combination of DFT with Mie or DDA has clear advantages. Several commercial program packages make this approach easily accessible to everybody, and DFT provides information both on the molecular structures (crystal structure) and on the optical constants. Among the drawbacks is the somewhat limited accuracy of the optical data (frequency shifts etc.) modeled in this way and in particular the fact that solid-state programs provide bulk refractive indices in practice only for ordered molecular structures. The major deficiency, however, is the fact that the combination of DFT with Mie or DDA also fails to predict vibron spectra for ultrafine particles. Clearly a different approach is required here, which is based on a fully molecular description.

Our previous efforts have demonstrated that the vibrational exciton approach offers a viable solution.^{11–14,29,37,38,58,60} This is a quantum mechanical model that allows for the prediction of vibron spectra of aerosol particles built from molecules. A detailed quantum mechanical treatment of such large molecular systems is feasible only if the model can be reduced to a few dominant interactions. We have found that essentially one interaction determines when particle properties such as those sketched in Figure 2 dominate the IR spectra. It is the resonant coupling between the oscillating dipoles of all individual molecules that make up an aerosol particle. The corresponding Hamiltonian given in the Supporting Information describes the interaction of each molecular oscillator with the field of all other oscillators, a network of transmitters and receivers with molecules as antennae. For any further details on the model and its implementation, we refer to the Supporting Information or to refs 13, 14, and 29 and references therein. Figure 6 illustrates the differences between the exciton approach and conventional models (DDA) for ultrafine cubic aerosol particles. Obviously, DDA does not capture the unique spectral signature as a function of particle size. Instead it predicts the same spectrum for all sizes, quite incorrectly. In this example, we have reached the size range where molecular structure and quantum effects become important: conventional models and hybrid approaches are no longer valid as the effective range of exciton coupling becomes comparable to particle dimensions. It is a major advantage of the exciton approach that it does not have any principle limits, such as the conventional models for ultrafine particles. It is conceptually simple but successful because it captures the most important interaction. Thereby it provides a molecular level

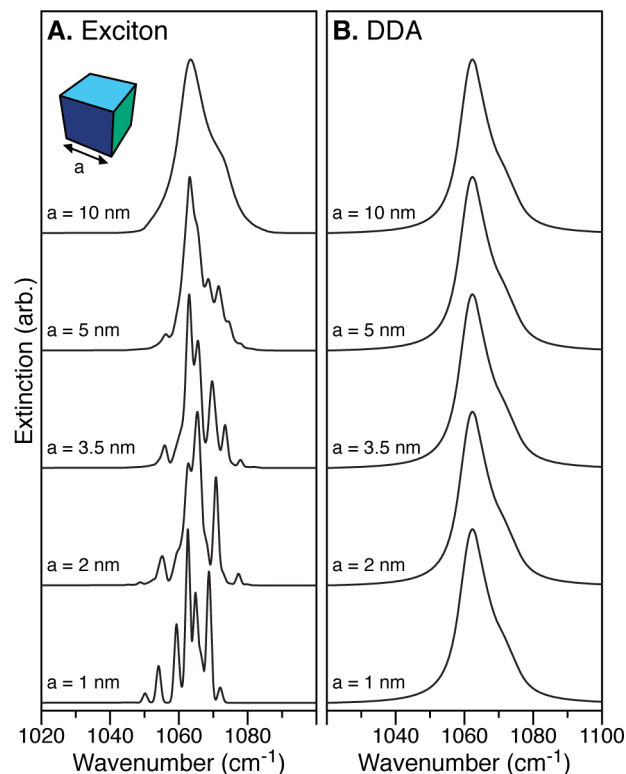


FIGURE 6. Comparison of particle IR spectra calculated with the exciton model (A) and with DDA (B) for crystalline NH_3 particles of various sizes. The particles have a cubic shape with edge lengths of 10 nm, 5 nm, 3.5 nm, 2 nm, and 1 nm from top to bottom. The conventional model (DDA) falsely predicts the same spectrum for all sizes, while the molecular approach (exciton model) captures size effects properly.

understanding of characteristic features in particle vibron spectra (e.g., Figure 4). Still, the molecular structure of the particles and the molecular transition frequencies and molecular transition dipole moments are required as input. This is not an issue for crystalline particles with known structure and known IR bulk or gas phase spectra.^{14,30,33,34} In all other cases, we have to resort to more or less extensive molecular modeling, such as molecular dynamics simulations,^{14,37,38,58} of the particle's internal structure and local transition frequencies and dipole moments.

Hybridization Scheme for Complex Particle Architectures

The usual way to predict and engineer the electromagnetic response of particles with complex architectures, or more generally of complex nanostructures, involves full exciton or full DDA calculations. However, there is an alternative approach in cases where the complex nanostructure can be subdivided into simpler subunits whose individual spectra are well-known or easy to calculate. Then a hybridization scheme can be exploited similar to what is known from

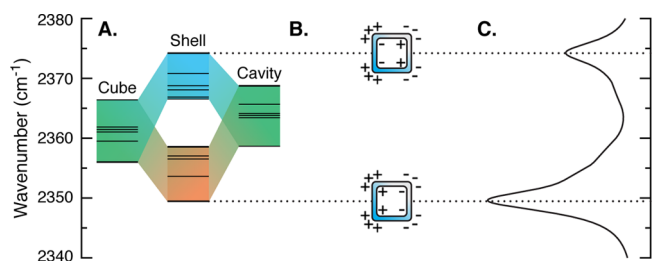


FIGURE 7. (A) Energy level diagram for the antisymmetric stretching vibration of CO₂ for a cube (left), a cubic shell (middle), and a cubic cavity (right). Note that only the most significant eigenmodes are depicted. (B) Sketch of the polarization charges indicating that there are fewer nodal planes in the polarization charge distribution for the energetically lower lying modes. (C) IR extinction spectrum of the shell.

molecular orbital theory. This has originally been shown by Halas, Nordlander, and co-workers for metallic nanostructures⁴⁴ and has recently been generalized by us far beyond metallic systems, in particular including vibron spectra.⁴¹ A short description of the hybridization scheme is included in the Supporting Information.

Figure 7 provides an example for the IR spectrum of a cubic shell. One can think of it as a superposition of a cube and a cubic cavity.⁴¹ The vibrons of the cubic shell are admixtures of those of the cube and the cavity. The modes of the simple subunits (cube and cavity) are well-known and can be used to construct the unknown IR spectrum of the shell. As sketched in Figure 7A, the vibrational energy levels of the shell (middle) are constructed from linear combinations of the known energy levels of the cube (left) and the cavity (right). Hybridization of the cube and cavity results in two classes of vibrational energy levels for the shell. Vibrational modes in the energetically lower lying class have fewer nodal surfaces than those in the energetically higher lying class (Figure 7B). In analogy to bonding and antibonding molecular orbitals, we call them bonding and antibonding modes, respectively. Bonding modes have larger overall transition dipole moments and couple more strongly to the external electromagnetic field. This scheme elegantly explains the characteristic doublet structure of the shell spectrum in Figure 7C. It arises from vibrational transitions from the ground state to the two respective classes of vibrationally excited states, with the more intense absorption band at lower energy. The analogy of the hybridization scheme to molecular orbital theory is quite striking, only with vibrons instead of molecular orbitals. Both simple and intuitive, this approach provides a qualitative understanding of the infrared spectral features of more complex dielectric nanostructures.

Conclusion

This Account demonstrates that molecular models are indispensable for the analysis of infrared extinction spectra of small dielectric particles. While conventional models, such as Mie theory or DDA, are usually sufficient for the analysis of plasmon spectra of metallic nanoparticles, they often fail to capture the spectroscopic signatures in vibron spectra of dielectric nanoparticles.

The combination of molecular models with carefully designed laboratory experiments has helped uncover surprising aspects of vibron spectra and their interpretation. The most prominent is the fact that simple dipole coupling between all molecules that make up a particle determines when and how band profiles in infrared spectra are dominated by particle properties, such as shape, size, or architecture.¹⁴ This discovery allowed us to formulate propensity rules for the occurrence of prominent particle effects in vibron spectra.⁶⁰ Without the need for explicit calculations, they explain why the information about particle shape is lost in spectra of multicomponent particles,³⁰ a result of some consequence for remote sensing, where particle spectra are easily misinterpreted in terms of shape effects. Moreover, the comparison of conventional models with molecular models revealed the existence of a fundamental lower particle size limit below which conventional models fail.¹¹ The effective range of the dipole interaction becomes comparable to the particle dimensions so that the molecular structure and the quantum nature of the vibrations manifest themselves in the spectral features. At this point, the classical description of energies and intensities is no longer quantitatively correct. But this is only the beginning. State-of-the-art experimental approaches, such as 2D infrared pump–probe experiments,⁶² open exciting possibilities to gain new insight. Among the most interesting aspects are the influence of anharmonicities, the delocalization of vibrons, and the role of defects and phonon coupling (lifetimes, coherences).

Along with the ever more accurate information from experimental advances in particle spectroscopy comes the demand for improved models. The development of molecular models for light–particle interaction is doubtless the future direction in the field of small particle spectroscopy. In contrast to conventional models, they provide a molecular level understanding of the observed phenomena, revealing the relationship between molecular structure, particle properties, and infrared signatures. Most notable is the extension to ultrafine particles, a size range of crucial importance, for example, for the nucleation from the gas phase, currently

one of the big issues in aerosol and climate research. From a practical point of view, however, many challenges have to be solved before molecular models can be used more widely. These include issues of system size and computational cost, the question of how to validate the accuracy of calculations performed at a certain level, and of course the development into routine tools that are easy to use.

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. We acknowledge an NSERC graduate fellowship (T.C.P.) and an NSERC E. W. R. Steacie Memorial Fellowship (R.S.).

Supporting Information. The exciton model and the hybridization scheme. This material is available free of charge via the Internet at <http://pubs.acs.org>.

BIOGRAPHICAL INFORMATION

Thomas C. Preston received a B.Sc. in Chemistry at the University of Toronto in 2005, a M.Sc. degree at the University of Western Ontario in 2007 (supervisor, Prof. Silvia Mittler), and a Ph.D. in Physical Chemistry from the University of British Columbia (supervisor, Prof. Ruth Signorell). His doctoral research was focused on the interaction of light with small molecular and metallic particles.

Ruth Signorell studied physics and chemistry at the Swiss Federal Institute of Technology (ETH Zürich) where she received a Ph.D. in high-resolution photoelectron spectroscopy in 1999 (supervisor, Prof. Frédéric Merkt). After a postdoctoral stay at the University of Göttingen (supervisor, Prof. Martin Suhm), she joined the Chemistry faculty at Göttingen in 2002. She moved to the University of British Columbia in 2005, where she was a Professor in the Department of Chemistry until 2012. In 2012, she was appointed as Professor at the ETH Zürich. Her research interests are devoted to the interaction of light with ultrafine aerosols and nanoparticles.

FOOTNOTES

*To whom correspondence should be addressed. E-mail: ruth.signorell@phys.chem.ethz.ch. The authors declare no competing financial interest.

REFERENCES

- Faraday, M. Experimental Relations of Gold (and Other Metals) to Light. *Philos. Trans. R. Soc. London* **1857**, *147*, 145–181.
- Mie, G. Beitrag zur Optik Trüber Medien, Speziell Kolloidaler Metallösungen. *Ann. Phys.* **1908**, *25*, 377–445.
- Odom, T. W.; Schatz, G. C. Thematic Issue: Photonics. *Chem. Rev.* **2011**, *6*, 3667–3994.
- Gao, S; Ueno, K.; Misawa, H. Plasmonic Antenna Effects on Photochemical Reactions. *Acc. Chem. Res.* **2011**, *44*, 251–260.
- Bardhan, R; Lal, S.; Joshi, A.; Halas, N. J. Theranostic Nanoshells: From Probe Design to Imaging and Treatment of Cancer. *Acc. Chem. Res.* **2011**, *44*, 936–946.
- Gordon, R; Sinton, D.; Kavanagh, K. L.; Brolo, A. G. A New Generation of Sensors Based on Extraordinary Optical Transmission. *Acc. Chem. Res.* **2008**, *41*, 1049–1057.
- Bohren, C. F. *Clouds in a Glass of Beer: Simple Experiments in Atmospheric Physics*; Wiley: New York, 1987.
- Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; Wiley: New York, 1998.
- Pierrehumbert, R. T. *Principles of Planetary Climate*; Cambridge University Press: Cambridge, U.K., 2010.
- IPCC, 2007: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Solomon, S.; Qin, D.; Manning, M.; Marquis, M.; Averyt, K.; Tignor, M. M., Eds.; Cambridge University Press: Cambridge, U.K., 2007.
- Signorell, R. Infrared Spectroscopy of Particulate Matter: Between Molecular Clusters and Bulk. *Mol. Phys.* **2003**, *101*, 3385–3399.
- Firanesco, G.; Hermsdorf, D.; Ueberschaer, R.; Signorell, R. Large Molecular Aggregates: From Atmospheric Aerosols to Drug Nanoparticles. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4149–4165.
- Sigurbjörnsson, Ó. F.; Firanesco, G.; Signorell, R. Intrinsic Particle Properties from Vibrational Spectra of Aerosols. *Annu. Rev. Phys. Chem.* **2009**, *60*, 127–146.
- Firanesco, G.; Preston, T. C.; Wang, C. C.; Signorell, R. Vibrational Excitons: A Molecular Model to Analyze Infrared Spectra of Aerosols. In *Fundamentals and Applications in Aerosol Spectroscopy*; Signorell, R., Reid, J. P., Eds.; CRC Press: Boca Raton, FL, 2011; Chapter 2.
- van der Hulst, H. C. *Light Scattering by Small Particles*; Wiley: New York, 1957.
- Kerker, M. *The Scattering of Light and Other Electromagnetic Radiation*; Academic Press: New York, 1969.
- Mishchenko, M. I.; Hovenier, J. W.; Travis, L. D. *Light Scattering by Nonspherical Particles: Theory, Measurements, and Applications*; Academic Press: San Diego, CA, 2000.
- Purcell, E. M.; Pennypacker, C. R. Scattering and Absorption of Light by Nonspherical Dielectric Grains. *Astrophys. J.* **1973**, *186*, 705–714.
- Draine, B. T.; Flatau, P. J. User Guide for the Discrete Dipole Approximation DDSCAT 7.0. <http://arXiv.org/abs/0809.0337v5>, 2008.
- Califano, S.; Schettino, V.; Neto, N. Lattice Dynamics of Molecular Crystals. In *Lecture Notes in Chemistry*; Berthier, G., Dewar, M. J. S., Fischer, H., Fukui, K., Hall, G. G., Hartmann, H., Jaffé, H. H., Jortner, J., Kutzelnigg, W., Ruedenberg, K., Scrocco, E., Eds.; Springer-Verlag: Berlin, 1981.
- Nehl, C. L.; Grady, N. K.; Goodrich, G. P.; Tam, F.; Halas, N. J.; Hafner, J. H. Scattering Spectra of Single Gold Nanoshells. *Nano Lett.* **2004**, *4*, 2355–2359.
- Jain, P. K.; Lee, K. S.; El-Sayed, I. H.; El-Sayed, M. A. Calculated Absorption and Scattering Properties of Gold Nanoparticles of Different Size, Shape, and Composition: Applications in Biological Imaging and Biomedicine. *J. Phys. Chem. B.* **2006**, *110*, 7238–7248.
- Coronado, E. A.; Schatz, G. C. Surface Plasmon Broadening for Arbitrary Shape Nanoparticles: A General Probability Approach. *J. Chem. Phys.* **2003**, *119*, 3926–3934.
- McMahon, J. M.; Gray, S. K.; Schatz, G. C. Calculating Nonlocal Optical Properties of Structures with Arbitrary Shape. *Phys. Rev. B* **2010**, *82*, No. 035423.
- Disselkamp, R.; Ewing, G. E. Large CO₂ Clusters Studied by Infrared Spectroscopy and Light Scattering. *J. Chem. Phys.* **1993**, *99*, 2439–2448.
- Gough, T. E.; Wang, T. The Influence of Morphology on the Vibrational Spectra of Crystalline Aerosols: SF₆ and CO₂. *J. Chem. Phys.* **1996**, *105*, 4899–4904.
- Wagner, R.; Benz, S.; Möhler, O.; Saathoff, H.; Schnaiter, M.; Leisner, T. Influence of Particle Aspect Ratio on the Midinfrared Extinction Spectra of Wavelength-Size Ice Crystals. *J. Phys. Chem. A* **2007**, *111*, 13003–13022.
- Devlin, J. P.; Yinnon, C. A.; Buch, V. Spectroscopic Evidence for Cyclical Aggregation and Coalescence of Molecular Aerosol Particles. *Phys. Chem. Chem. Phys.* **2009**, *11*, 7819–7825.
- Signorell, R. Verification of the Vibrational Exciton Approach for CO₂ and N₂O Nanoparticles. *J. Chem. Phys.* **2003**, *118*, 2707–2715.
- Signorell, R.; Kunzman, M. K. Isotope Effects on Vibrational Excitons in Carbon Dioxide Particles. *Chem. Phys. Lett.* **2003**, *371*, 260–266.
- Jetzki, M.; Bonnamy, A.; Signorell, R. Vibrational Delocalization in Ammonia Aerosol Particles. *J. Chem. Phys.* **2004**, *120*, 11775–11784.
- Bonnamy, A.; Georges, R.; Hugo, E.; Signorell, R. IR Signature of (CO₂)_N Clusters: Size, Shape and Structural Effects. *Phys. Chem. Chem. Phys.* **2005**, *7*, 963–969.
- Signorell, R.; Jetzki, M.; Kunzman, M.; Ueberschaer, R. Unraveling the Origin of Band Shapes in Infrared Spectra of N₂O–¹²CO₂ and ¹²CO₂–¹³CO₂ Ice Particles. *J. Phys. Chem. A* **2006**, *110*, 2890–2897.
- Firanesco, G.; Luckhaus, D.; Signorell, R. Phase, Shape, and Architecture of SF₆ and SF₆/CO₂ Aerosol Particles: Infrared Spectra and Modeling of Vibrational Excitons. *J. Chem. Phys.* **2008**, *128*, No. 184301.
- Signorell, R.; Jetzki, M. Vibrational Exciton Coupling in Pure and Composite Sulfur Dioxide Aerosols. *Faraday Discuss.* **2008**, *137*, 51–64.
- Sigurbjörnsson, Ó. F.; Firanesco, G.; Signorell, R. Vibrational Exciton Coupling as a Probe for Phase Transitions and Shape Changes of Fluoromethane Aerosol Particles. *Phys. Chem. Chem. Phys.* **2009**, *11*, 187–194.

- 37 Firanesco, G.; Signorell, R. Predicting the Influence of Shape, Size, and Internal Structure of CO Aerosol Particles on Their Infrared Spectra. *J. Phys. Chem. B* **2009**, *113*, 6366–6377.
- 38 Preston, T. C.; Firanesco, G.; Signorell, R. Infrared Spectroscopy and Vibrational Exciton Modeling of Crystalline, Polycrystalline, and Amorphous Acetylene Aerosol Particles. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7924–7933.
- 39 Preston, T. C.; Wang, C. C.; Signorell, R. Infrared Spectroscopy and Modeling of Co-crystalline CO₂·C₂H₂ Aerosol Particles. I. The Formation and Decomposition of Co-crystalline CO₂·C₂H₂ Aerosol Particles. *J. Chem. Phys.* **2012**, *136*, No. 094509.
- 40 Preston, T. C.; Signorell, R. Infrared Spectroscopy and Modeling of Co-crystalline CO₂·C₂H₂ Aerosol Particles. II. The Structure and Shape of Co-crystalline CO₂·C₂H₂ Aerosol Particles. *J. Chem. Phys.* **2012**, *136*, No. 094510.
- 41 Preston, T. C.; Signorell, R. Vibron and Phonon Hybridization in Dielectric Nanostructures. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 5532–5536.
- 42 Preston, T. C.; Signorell, R. Preparation and Optical Properties of Metallodielectric Core-Shell-Corona Particles. *J. Phys. Chem. C* **2008**, *112*, 17844–17848.
- 43 Preston, T. C.; Signorell, R. Growth and Optical Properties of Gold Nanoshells Prior to the Formation of a Continuous Metallic Layer. *ACS Nano* **2009**, *3*, 3693–3706.
- 44 Prodan, E.; Radloff, C.; Halas, N. J.; Nordlander, P. A Hybridization Model for the Plasmon Response of Complex Nanostructures. *Science* **2003**, *302*, 419–422.
- 45 Jensen, T.; Kelly, L.; Lazarides, A.; Schatz, G. C. Electrodynamics of Noble Metal Nanoparticles and Nanoparticle Clusters. *J. Cluster Sci.* **1999**, *10*, 295–317.
- 46 Mock, J. J.; Barbic, M.; Smith, D. R.; Schultz, D. A.; Schultz, S. Shape Effects in Plasmon Resonance of Individual Colloidal Silver Nanoparticles. *J. Chem. Phys.* **2002**, *116*, 6755–6759.
- 47 Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *J. Phys. Chem. B* **2003**, *107*, 668–677.
- 48 Wang, H.; Brandl, D. W.; Nordlander, P.; Halas, N. Plasmonic Nanostructures: Artificial Molecules. *Acc. Chem. Res.* **2007**, *40*, 53–62.
- 49 González-Galindo, F.; Määttä, A.; Forget, F.; Spiga, A. The Martian Mesosphere as Revealed by CO₂ Cloud Observations and General Circulation Modeling. *Icarus* **2011**, *216*, 10–22.
- 50 Buch, V.; Delzeit, L.; Blackledge, C.; Devlin, J. P. Structure of Ice Nanocrystal Surface From Simulated Versus Experimental Spectra of Adsorbed CF₄. *J. Phys. Chem.* **1996**, *100*, 3732–3744.
- 51 Wagner, R.; Möhler, O.; Saathoff, H.; Schnaiter, M.; Leisner, T. New Cloud Chamber Experiments on the Heterogeneous Ice Nucleation Ability of Oxalic Acid in the Immersion Mode. *Atmos. Chem. Phys.* **2011**, *11*, 2083–2110.
- 52 Signorell, R.; Jetzki, M. Phase Behavior of Methane Haze. *Phys. Rev. Lett.* **2007**, *98*, No. 013401.
- 53 Wang, C. C.; Lang, E. K.; Signorell, R. Methane Gas Stabilizes Supercooled Ethane Droplets in Titan's Clouds. *Astrophys. J. Lett.* **2010**, *712*, L40–L43.
- 54 Cardini, G.; Schettino, V.; Klein, M. L. Structure and Dynamics of Carbon Dioxide Clusters: A Molecular Dynamics Study. *J. Chem. Phys.* **1989**, *90*, 4441–4449.
- 55 Buch, V.; Bauerecker, S.; Devlin, J. P.; Buck, U.; Kazimirski, J. K. Solid Water Clusters in the Size Range of Tens-thousands of H₂O: A Combined Computational/Spectroscopic Outlook. *Int. Rev. Phys. Chem.* **2004**, *23*, 375–433.
- 56 Devlin, J. P.; Joyce, C.; Buch, V. Infrared Spectra and Structure of Large Water Clusters. *J. Phys. Chem. A* **2000**, *104*, 1974–1977.
- 57 Beu, T. A.; Buck, U. Vibrational Spectra of Ammonia Clusters From n=3 to 18. *J. Chem. Phys.* **2001**, *114*, 7853–7858.
- 58 Firanesco, G.; Luckhaus, D.; Signorell, R. Size Effects in the Infrared Spectra of NH₃ Ice Nanoparticles Studied by a Combined Molecular Dynamics and Vibrational Exciton Approach. *J. Chem. Phys.* **2006**, *125*, No. 144501.
- 59 Kunzmann, M. K.; Bauerecker, S.; Suhm, M. A.; Signorell, R. Spectroscopic Characterization of N₂O Aggregates: From Clusters to the Particulate State. *Spectrochim. Acta A* **2003**, *59*, 2855–2865.
- 60 Bonnamy, A.; Jetzki, M.; Signorell, R. Optical Properties of Molecular Ice Particles from a Microscopic Model. *Chem. Phys. Lett.* **2003**, *382*, 547–552.
- 61 ABINIT code, a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (URL <http://www.abinit.org>).
- 62 Hamm, P.; Lim, M. H.; Hochstrasser, R. M. Structure of the Amide I Band of Peptides Measured by Femtosecond Nonlinear-Infrared Spectroscopy. *J. Phys. Chem. B* **1998**, *102*, 6123–6138.