The Interaction of Visible and Infrared Radiation with Molecular and Metallic Particles

by

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Abstract

In this thesis, the electromagnetic spectra of both conducting and non-conducting particles are studied. The relationship between particle shape and spectra is explored through both modeling and experiments. Depending on the situation, spectra are modeled using techniques such as the discrete dipole approximation, the vibrational exciton model, various electrostatic methods, or density functional theory. These results are used to not only characterize the particles in the system of interest, but also understand how particle architecture influences its spectrum. Furthermore, it is demonstrated how the consideration of a particle's symmetry, and when appropriate the symmetry of the crystal structure that forms a particle, can greatly simplify the interpretation of spectra.

The main systems studied in this work are Au nanoparticles and molecular aerosol particles composed of either pure C_2H_2 , pure CO_2 , mixtures of pure C_2H_2 and pure CO_2 or co-crystalline $CO_2 \cdot C_2H_2$. The molecular aerosol particles that are studied here were chosen due to their relevance to many planetary atmospheres. Several questions concerning the phase and shape of these molecular particles are addressed and answered.

Finally, the similarities between the electromagnetic response of conducting and nonconducting particles are discussed at several points in this thesis. Hybridization schemes are shown to be a powerful tool for understanding the spectra of complex nanostructures. These schemes involve decomposing complex structures into primitive components. Spectra can then be understood as mixtures of the spectra of these primitive components. For the first time a formalism is developed that allows for such hybridization methods to be extended to non-conducting particles.

Preface

Chapter 2 was published as: Preston, T. C.; Signorell, R. *ACS Nano* **2009**, *3*, 3696-3706. The research program for this chapter was designed by T. C. Preston and R. Signorell. Data acquisition, interpretation and modeling, and preparation of the manuscript were performed by T. C. Preston.

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Other work performed during this Ph.D. study, but not included in this thesis, has been published in the following articles or chapters: (i) Gadermann, M.; Preston, T. C.; Troster, C.; Signorell, R. *Mol. Phys.* **2008**, *106*, 945-953, (ii) Preston, T. C.; Signorell, R. *J. Phys. Chem. C* **2008**, *112*, 17844-17848, (iii) Weiss, A.; Preston, T. C.; Popov, J.; Li, Q.; Wu, S.; Chou, K. C.; Burt, H. M.; Bally, M. B.; Signorell, R. *J. Phys. Chem. C* **2009**, *113*,

20252-20258, (iv) Preston, T. C.; Signorell, R. Langmuir **2010**, 26, 10250-10253, and (v) Firanescu, 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, 2011.

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Acronyms

DDA	Discrete Dipole Approximation
\mathbf{DFT}	Density Functional Theory
EVE	Extended Vibrational Exciton
FDTD	Finite-Difference Time-Domain
GGA	Generalized Gradient Approximation
\mathbf{IR}	Infrared
LO	Longitudinal Optical
NIR	Near-Infrared
\mathbf{PHT}	Plasmon Hybridization Theory
SVE	Standard Vibrational Exciton
TEM	Transmission Electron Microscopy
то	Transverse Optical
UV	Ultra-Violet
\mathbf{Vis}	Visible

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Chapter 1

Introduction

1.1 Background

Gustav Mie's full solution to the interaction of an electromagnetic plane wave with a sphere¹ is the basis for much of our understanding of how light is absorbed and scattered by small particles. In the classic texts of van de Hulst,² Kerker,³ and Bohren and Huffman,⁴ this theory underlies much of the analysis on the interaction of light with small particles. That so much work is devoted to discussing the solution to one problem is indicative not only of the complications and subtleties involved when working with Mie's solution, but also the wealth of information that it contains. In his original paper, Mie used his solution to explain the visually striking colour of gold nanoparticles dispersed in water. The origin of this phenomenon had been a mystery since the 19th century and had even been studied by Michael Faraday.⁵ Due to the ubiquity of small particles in our world, countless other applications of Mie theory have since followed. These range from understanding why milk is opaque and white to the uncommon occurrence of a "blue moon."⁶

One field of study that has benefitted enormously from Mie theory is atmospheric science. Aerosol particles play an important role in the atmospheres of many planets and understanding how they interact with electromagnetic radiation is often of fundamental interest. When an ensemble of aerosol particles is considered to be a distribution of spheres, Mie theory can easily be used to analyze their optical properties. The information obtained from this process aids in not only modeling a planet's radiative balance but also in characterizing the aerosol particles through remote sensing. All of these details allow for a deeper understanding of the role aerosol particles play in cloud formation and various chemical processes (e.g. providing surfaces for heterogeneous chemical reactions).

1.2 Mie Theory and the Electrostatic Approximation

In Mie theory, scattering and absorption by a sphere are determined by first decomposing electric and magnetic fields into spherical harmonics of degree l. By evaluating these fields using the appropriate boundary conditions – a plane wave at infinity and continuity on the surface of the sphere – coefficients can then be obtained to calculate absorption and scattering cross-sections for a sphere. As the process of calculating these coefficients is tedious, they are almost always evaluated using computer programs (see Ref. 4 for an example of such a program).

While the determination of spectra using Mie theory is fairly straightforward, it is often unnecessary. If the dimensions of the particle of interest are much smaller than the wavelength of light impinging on it (Fig. 1.1), then the problem can be considered to be one of electrostatics instead of electrodynamics. This greatly simplifies analysis as it means that it is no longer necessary to simultaneously solve all four of Maxwell's equations and instead one only needs to evaluate Gauss' law (i.e. only one of Maxwell's equations). This approximation, depicted in Fig. 1.1, is often referred to as the electrostatic or long-wavelength approximation (or called the electric dipole limit). It is very common, especially when dealing with infrared (IR) spectroscopy where wavelengths are on the order of micrometers. In this limit, the absorption spectra of both conducting and non-conducting particles will be dominated by surface modes – so-called because with larger l their radial electric field becomes increasingly localized at the surface of the sphere.⁷

One of the most interesting features of the electrostatic limit is that absorption band shapes are invariant with respect to the scale of the particle. Examples of this phenomenon are shown in Fig. 1.2. It is only when the electrostatic approximation begins to fail that changes in band shape can be seen (the 500 and 1000 nm traces in Fig. 1.2). This is also true when dealing with non-spherical particles. Consequently, these bands are extremely useful for characterizing



Figure 1.1: An electromagnetic wave passing over a spherical particle. If the dimensions of the particle are much smaller than the wavelength of light impinging on it then the interaction can be treated within the electrostatic approximation. In this example, the diameter, d, of a sphere is much less than the wavelength of light, λ .

particle shape, as a distribution of sizes will not broaden absorption bands within a spectrum. For instance, the spectrum of an ensemble of cubes with a distribution of side lengths that all satisfy the electrostatic approximation is the same as that of a single cube.

A final point to note is that, when making extinction measurements, the bands that result from the excitation of surface modes will be dominated by absorption within the electrostatic limit (extinction is the sum of scattering and absorption in a spectrum). Scattering will be so minor that it can be ignored. Therefore, the terms extinction and absorption will often be used interchangeably when discussing particles that fall within this limit.

1.3 Plasmons, Vibrons and Phonons

In small particles, surface modes can originate from several different types of excitations. The three which will be discussed extensively in this thesis are plasmons, vibrational excitons (vibrons) and phonons. Fig. 1.3 shows the microscopic origin of plasmons, vibrons and phonons within small, spherical particles. All three of the excitations are collective oscillations that can be excited by an external electromagnetic field. On the microscopic scale, the oscillations are very different. However, the macroscopic effects (surface polarization charges) are all very similar, despite the fact that resonances occur at much different energies.

Plasmons (Fig. 1.3a) occur in conducting materials. They are collective oscillations of the conducting electrons within a metal. In the colloidal gold that was studied by Mie, it was plasmon resonances that lead to the bright, visible colours of the dispersion. Over the



Figure 1.2: Modeled IR extinction for various crystalline CO_2 spheres in the region of the ν_3 band. As the diameter of the sphere, d, approaches the wavelength of light impinging on it, the particle cannot be satisfactorily treated within the electrostatic approximation. In these cases, the shape of the extinction bands change with diameter. Calculations were performed using Mie theory. Traces are offset for clarity.

past 20 years, understanding and controlling the position of plasmon resonances within metallic particles has become an enormous area of research and forms a large subset of the field referred to as "plasmonics."⁸

Similar to plasmons, vibrons (Fig. 1.3b) are also collective oscillations. However, they do not originate from the motion of conduction electrons but rather from the intermolecular coupling of the internal vibrations of molecules.⁹ Vibrons are most commonly observed in molecular crystals. The frequencies of these modes are much lower than those of plasmons. This is because the location of the fundamental vibrational modes of a molecule are found in the IR region of the electromagnetic spectrum. In a molecular crystal, the frequencies of these modes typically do not shift too much relative to the frequencies of t



Figure 1.3: Examples of (a) plasmon, (b) vibron, and (c) phonon surface modes (dipole: l = 1) in spherical particles and their microscopic origin. The wavelengths, λ , indicate approximately where these resonances would occur. All spherical particles are assumed to be much smaller than the wavelength of light exciting the mode. The positive and negative signs are used to indicate surface polarization charges on the spheres.

the vibron modes are also located in the IR.

The phonon (Fig. 1.3c) is another type excitation that is important in the spectra of small particles. Historically, some authors have not always made a distinction between vibrons and phonons. However, the difference is that in the lattice of a molecular crystal, phonons are associated with external vibrations while vibrons are associated with internal vibrations.¹⁰ Therefore, phonons will typically be located at even lower frequencies than vibrons.

1.4 Limitations of Mie Theory

1.4.1 Overview

The discussion of absorption and scattering by small particles in the previous sections has been framed using Mie theory. While this theory is exact, and certainly useful for illustrative purposes, the number of situations in which it can be applied is very limited. The two most common issues with Mie theory are that (i) it is only valid for spherical particles, and (ii) the refractive index of the bulk material that forms the spherical particle needs to be wellcharacterized. The methods used when Mie theory cannot be applied are discussed in Sections 1.4.2 and 1.4.3.

1.4.2 Non-Spherical Particles

There exists only a few analytical expressions for absorption and scattering cross-sections of non-spherical particles. Fortunately, numerical techniques that can be used to evaluate cross-sections of non-spherical particles have progressed enormously since the advent of computers. Two of the most popular methods are the discrete dipole approximation (DDA)¹¹ and finite-difference time-domain (FDTD).¹²

DDA, as implemented with the DDSCAT code,¹³ is used throughout several chapters in this thesis. With this method, the particle of interest is divided into a cubic array of N point dipoles. An example of this process is illustrated in Fig. 1.4. The induced polarization of the *i*th dipole, \mathbf{P}_i , is determined by the relation $\mathbf{P}_i = \alpha_i \mathbf{E}_{\text{loc}}(\mathbf{r}_i)$ where α_i is the polarizability tensor of the dipole (determined from the dielectric tensor using the Clausius-Mossotti polarizability with a radiative-reaction correction)¹⁴ and $\mathbf{E}_{\text{loc}}(\mathbf{r}_i)$ is the local electric field at the position \mathbf{r}_i . This local electric field at the *i*th dipole is equal to the external field at \mathbf{r}_i plus the fields of all the other dipoles in the array at \mathbf{r}_i . Therefore, for an array of N dipoles, $3N \times 3N$ coupled equations need to be solved in order to determine \mathbf{P}_i at each point on the array. Once the induced dipole polarization of each element on the array is determined, extinction, absorption and scattering cross-sections are calculated by using the standard optical theorems.^{15,16} The validity criterion for DDA are discussed in Section 6.3.2.

Similar to Mie theory, both DDA and FDTD use the full set of Maxwell's equations in



Figure 1.4: A cut-corner cube (left) represented by 6699 dipoles (right).

order to determine absorption and scattering cross-sections. However, when the dimensions of a particle satisfy the electrostatic approximation, it is only necessary to evaluate Gauss' law in order to determine the cross-sections. This greatly simplifies numerical calculations. In Chapter 3 (and Appendix A and B) the electrostatic eigenvalue method will be discussed. This is a powerful implementation of an electrostatic approach. The computational advantage of this technique is that integration only involves surface elements instead of volume elements. Both DDA and FDTD require working with volume elements, which makes them much more computationally expensive.

1.4.3 The Requirement of Refractive Index Data

The methods described in Section 1.4.2 all require knowledge of the refractive index of the substance that forms the particle. For many materials such data is not available. In particular, this is an issue for molecular crystals that are only stable at cryogenic temperatures. For instance, there exists no refractive index data for crystalline N_2O as its high sublimation pressure (even at low temperatures) makes it difficult to prepare thin films with stable thicknesses.¹⁷

In situations where no refractive index data is available, modeling must rely on a microscopic particle model. In molecular particles, which are of interest in this work, IR spectra will often be dominated by strong resonant dipole coupling. This effect can be modeled by constructing the particle of interest from unit cells of the molecular crystal. Unlike refractive index data, crystallographic data is much easier to obtain, so information on unit cells is readily available for most molecular crystals. Using this particle model, intermolecular coupling can then be evaluated by treating the vibrational modes of each molecule as oscillators with characteristic frequencies and strengths (i.e. transition frequencies and transition dipole mo-



Figure 1.5: A cut-corner cube constructed using unit cells of a molecular crystal. The positions and orientations of the molecules within the crystal can be used to calculate an absorption spectrum for the particle using the vibrational exciton model.

ments). The response from this system of coupled oscillators can then be used to calculate the IR spectrum of a molecular particle. This approach is referred to in the literature as the vibrational exciton model.^{18,19} The details and implementation are discussed in Chapter 4 where it is used to model the spectra of C_2H_2 particles.

Alternatively, the bulk index of refraction can be modeled using density functional theory (DFT).²⁰ Modeling bulk crystalline systems is completely feasible as the periodicity of the crystal allows one to use cyclic boundary conditions to determine the wavefunctions of the system.²¹ Bulk indices of refraction obtained from this approach can then be incorporated into particle models (as discussed in Section 1.4.2). This method is implemented and discussed in Chapter 6.

1.5 Thesis Overview

The focus of this thesis will be on the optical properties of small particles. Specifically, how the extinction spectra of particles are determined by their shape and composition. This relationship is used to understand systems of plasmonic particles (Chapter 2), the IR spectra of complex dielectric nanostructures (Chapter 3) and characterize particles of relevance to aerosols that exist throughout our solar system (Chapters 4, 5 and 6). For the majority of the examples considered in this work, the dimensions of the particles will satisfy the electrostatic approximation.

In Chapter 2, the growth of gold nanoshells prior to the formation of a continuous metallic layer is studied. These systems consist of gold particles adsorbed on the surface of much larger silica particles. Chapter 2 focuses on the optical properties of these structures. The mode splitting that occurs in the plasmon bands of these structures can be understood by applying plasmon hybridization theory (PHT) in combination with the irreducible representations of various gold clusters.

PHT is discussed in much greater detail in Chapter 3 and the similarities between plasmons, phonons and vibrons, which were briefly discussed in Section 1.3, are revisited. PHT has been used to describe metallic nanostructures as "plasmonic molecules" and, in Chapter 3, this analogy is extended to dielectric nanostructures. While PHT was originally constructed by describing conduction electrons with an incompressible fluid model,²² in Chapter 3 a new hybridization scheme is developed using an alternative formalism (the electrostatic eigenvalue method). The advantage of this method is that hybridization is no longer limited to plasmonic systems. For the first time, excitations within complex dielectric nanostructures (phonons and vibrons) can be understood by analogy to molecular orbital theory.

With a connection between the surface modes of metallic (conducting) and dielectric (nonconducting) particles established, the second of half of this thesis (Chapters 4, 5 and 6) focuses on the study of dielectric particles that are relevant to aerosols that exist throughout our solar system. The examples which are studied here are C_2H_2 aerosols (Chapter 4) and cocrystalline $CO_2 \cdot C_2H_2$ aerosols (Chapters 5 and 6). Characterization is primarily done through a comparison of measured and modeled IR spectra. Nearly all of the techniques discussed in Section 1.4 are used. This is necessary as, unlike the examples in Chapters 2 and 3, most of the phases of interest in Chapters 4, 5 and 6 do not have measured indices of refraction. Through the use of many examples, these chapters illustrate how both particle shape and microscopic structure influence IR spectra.

Chapter 2

Growth and Optical Properties of Gold Nanoshells Prior to the Formation of a Continuous Metallic Layer

2.1 Introduction

Gold nanoshells, particles that consist of a spherical dielectric core coated with a concentric layer of gold, have seen extensive use in applications such as thermal therapy, $^{23-28}$ biological imaging, $^{25,29-31}$ controlled drug release, $^{27,32-34}$ and surface enhanced spectroscopy. $^{35-38}$ The strong dependence of their plasmon modes on the gold shell thickness allows for great control over how these particles absorb and scatter electromagnetic radiation. $^{39-41}$ Specifically, large extinction cross sections at wavelengths in the near-infrared (NIR), important for biological applications, are easily demonstrated.

One of the most popular approaches to construct gold nanoshells involves attaching small gold particles to the surfaces of silica cores and, subsequently, using these sites as nuclei to seed shell growth when a gold salt is reduced in their presence.^{40,42} In this type of a synthesis, it should be possible to control the shell thickness by adjusting the amount of reducible salt present in solution and, as this thickness influences the plasmon modes of the particle,⁴⁰ engineer the particle's electromagnetic response. Ideally, this approach should be guided by a theoretical understanding of the behavior of the spectra for such a particle. By using the



Figure 2.1: The parameter a is used to either represent (a) the gold particle radius or (b) the shell thickness.

analytical solution to the diffraction of electromagnetic radiation by a coated sphere this is indeed possible.⁴³ These results have been discussed in detail elsewhere.^{39–41} The general trend can be summarized as follows: when a shell's thickness is less than the radius of the sphere that it coats - and all other factors are held constant - a blueshift in the particle's plasmon band position will occur as the shell's thickness is increased.

Of course, this is only true if a uniform gold layer is present on the surface of the dielectric core.⁴⁴ Given the manner in which shell growth takes place, one would suspect that this is not always the case. Certainly, there must exist situations where shell formation is incomplete and only islands of gold are present on the surface of the core (e.g. when insufficient reducible salt is added during the growth process). The illustration in Fig. 2.1 compares an incomplete with a complete nanoshell. In the former case, Fig. 2.1a, the electromagnetic response of a particle cannot be described by the model of a sphere coated with a layer of constant thickness.

In this chapter, we examine how the visible and NIR spectra of gold nanoshells behave as a function of the concentration of gold salt added during shell growth. Specifically, we focus our attention on the region where shell formation is incomplete and model how the spectra depend on the morphology of gold present on the surface of the silica sphere. Transmission electron microscopy (TEM) is used to examine the various particle surfaces and determine the parameters which are used in the model. From these images we also discuss the processes through which shell growth occurs in this regime of incomplete shell formation.

2.2 Experimental Section

2.2.1 Materials

Hydrogen tetratchloroaurate(III) hydrate, tetraethyl orthosilicate (TEOS), 3-aminopropyltrimethoxysilane (APTMS), an 80% aqueous solution of tetrakis(hydroxymethyl)phosphonium chloride (THPC), sodium hydroxide, formaldehyde (35 % solution), and potassium carbonate were purchased from Sigma-Aldrich and used as received.

2.2.2 Synthesis of Silica Particles

The silica particles that form the dielectric cores of the gold nanoshells were produced using the method described by Stöber et al.⁴⁵ Ammonium hydroxide (30% solution, 5 mL) was mixed into 50 mL of dry ethanol and, while stirring, TEOS (6.7 mmol, 1.5 mL) was then rapidly added. This solution was stirred overnight. In order to introduce the amine functionality to the surface of the silica particles, APTMS (0.14 mmol, 25 μ L) was then added directly to the reaction vessel and stirring was continued for an additional 24 hours. After this, the solution was gently refluxed for one hour. This solution of APTMS-functionalized particles was then centrifuged (15 minutes, 2000 rpm) and the precipitate was collected and redispersed in 50 mL of ethanol. This process was repeated five times in order to remove any unreacted APTMS from the solvent. TEM gave the average particle diameter to be 229 ± 11 nm (100 particle count).

2.2.3 Synthesis of Colloidal Gold

The gold particles used to decorate the surface of the dielectric cores were prepared using the method developed by Duff et al. 46,47 To 45.5 mL of deionized water, NaOH (0.2 M, 1.5 mL) and a THPC solution (1 mL of a stock solution consisting of 1.2 mL of the 80% aqueous solution of THPC in 100 mL of deionized water) were added. Under vigorous stirring, a solution of hydrogen tetrachloroaurate(III) hydrate in deionized water (25 mM, 2 mL) was then added. This resulted in the rapid formation of a dark orange-brown solution. TEM gave the average particle diameter to be 2.4 ± 0.5 nm and UV-vis absorption spectroscopy gave a broad plasmon shoulder at ~500 nm. Prior to use, these particles were stored in the dark at 4 °C.

2.2.4 Elaboration of the Surface of the APTMS-functionalized Silica Particles with Colloidal Gold Particles

Following the procedure of Pham et al.,⁴² APTMS-functionalized silica particles (0.5 mL) were mixed with colloidal gold (5.0 mL) and left to stand overnight. In all cases, the pH of solution after mixing ranged from 7 to 8. This solution was then centrifuged (30 minutes, 3500 rpm) and the precipitate was redispersed in 5.0 mL of deionized water. This was repeated three times and a light red solution was obtained. TEM images indicated the successful adsorption of gold particles to the surface of the APTMS-functionalized silica particles.

2.2.5 Growth of Gold Nanoshells

The subsequent growth of gold on the particle surface was accomplished using the following process: 42 K₂CO₃ (100 mg, 0.72 mmol) was dissolved in 94 mL of deionized water and a solution of hydrogen tetratchloroaurate(III) hydrate in deionized water (25 mM, 6 mL) was then added. Dilutions of this stock solution were then prepared in deionized water (see discussion for concentrations). In a typical reaction, a 4 mL aliquot of one of these dilutions would be mixed with 200 μ L of the appropriate colloidal gold particle elaborated APTMS-functionalized silica particles and, while stirring, aqueous formaldehyde (35% solution, 10 μ L, 0.13 mmol) would then be rapidly added. Colour changes usually occurred within a couple of minutes. After 30 minutes, the solution was centrifuged (20 minutes, 2500 rpm) and the precipitate was redispersed in 5 mL of deionized water.

2.2.6 Characterization

TEM images were collected using a Hitachi H7600 TEM. Samples were prepared by placing 10 μ L of the solution of interest onto the surface of a formvar/carbon 200 mesh, copper grid (Ted Pella, Inc.). The solvent was then left to evaporate. Ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy was performed using a Varian Cary 50 UV-vis spectrophotometer. All samples were dispersed in water and held in quartz cells during analysis.

2.3 Computational Methods

The electromagnetic response of gold structures considered here are modeled using DDA (see Section 1.4.2 for details on this method). The density of dipoles used were either 27 dipoles per nm³ (when the radii of the structures were 10 nm) or 8 dipoles per nm³ (when the radii of the structures were 20 nm). The dielectric function of gold is taken from a table.⁴⁸ The refractive index of the medium that surrounds the hemispheres is taken to be non-dispersive and set to 1.33 (water). The silica surface is ignored in these calculations. This simplification slightly shifts calculated resonances to shorter wavelengths.^{49,50} Given the large range of wavelengths over which the experimental resonances are found and the small difference in refractive index between the silica core $(n_{silica} = 1.44)^{51}$ and water, this approximation is satisfactory.

2.4 Results and Discussion

2.4.1 Modeling of Optical Properties

Our study focuses on particles composed of silica cores onto which incomplete gold layers have been grown. As these layers originate from small, roughly spherical seed particles, early stages of growth most likely result in enlarged versions of these precursors (as shown in Fig. 2.1a). When modeling the optical properties of these gold structures, the shape of the individual particles is described as spheres, hemispheres, or droplet-like particles – an intermediate between the spherical and hemispherical shape. The study of the droplet-like shape is motivated by the particles observed in TEM images (see Section 2.4.2). While the optical properties of spherical particles have been extensively studied, $^{1,52-54}$ those of hemispherical particles have only been examined in a few cases.⁵⁵ As the number of individual gold particles on any given silica sphere is quite large, a numerical approach to describe the optical properties would be computationally unfeasible. Therefore, we examine either small clusters of spherical or hemispherical particles. This may appear to be a limitation, but it is actually possible to determine most of the key properties and spectral trends of these larger systems using only a small number of particles.

The clusters of spheres and hemispheres we consider can be classified according to their point groups. Their dimensions are typically much smaller than the wavelength of light impinging on them. Therefore, the electric dipole active modes dominate the spectra. The irreducible representations of these modes are used to label the peaks in the extinction spectra. This approach to label plasmon modes has been taken previously by Mayergoyz et al.⁵⁶ and was used when dealing with so-called plasmonic molecules.^{57,58}

2.4.1.1 Single Sphere or Hemisphere

The optical properties of individual gold spheres are well-known¹ and are only included here for comparison with those of a hemisphere. Fig. 2.2a shows the location of the maximum of the dipole mode, p, as a function of sphere radius. Fig. 2.2c shows a sample spectrum for a constant radius of a = 10 nm. The maximum of the dipole mode shifts to longer wavelengths as the radius increases.

Based on the point group of a hemisphere $(C_{\infty v})$, of the three electric dipole modes, one is non-degenerate (Σ^+) and two are degenerate (II). Fig. 2.2b shows the location of the extinction maximum of these modes as a function of the hemisphere radius, a. An example of the spectra associated with these two modes for a constant radius a = 10 nm is given in Fig. 2.2d. It turns out that at their respective maxima, the extinction cross section of the II modes are about seven times larger than that of the Σ^+ mode. This, combined with the fact that for a randomly oriented hemisphere both II modes will be active, means that the spectra of the gold hemispheres will essentially be dominated by this lower energy mode.

2.4.1.2 A Pair of Spheres or Hemispheres

A pair of spheres belongs to the $D_{\infty h}$ point group. Fig. 2.3a shows the variables s and a which describe the system and the orientation of the polarization that excites the non-denergate mode (Σ_u^+) and the doubly degenerate modes (Π_u). Fig. 2.3b and c show the maxima of the dipole modes as a function of the shortest distance between the surfaces of two spheres, s, for two different radii a = 10 and 20 nm, respectively. Examples of the extinction spectra for s = 1 nm are shown in Fig. 2.3d and e, respectively.

With decreasing separation, s, the Π_u modes show little change in their extinction maxima (small blueshift) while the Σ_u^+ modes strongly redshift. For identical s, the Σ_u^+ mode of the larger spheres (a = 20 nm, Fig. 2.3c) is shifted to longer wavelengths than that of the small



Figure 2.2: (a) Location of the plasmon absorption maximum as function of sphere radius, a. (b) Location of the plasmon absorption maximum as function of hemisphere radius, a, (polarization of incident electric field is indicated with double-sided arrows). (c) Sphere spectrum for a = 10 nm, and (d) Hemisphere spectra for two polarizations for a = 10 nm.

spheres (a = 10 nm, Fig. 2.3b). We also note that the Σ_u^+ modes have much larger extinction cross sections than the Π_u modes. However, in an orientationally averaged sample both Π_u modes are active and their relative contribution thus increases.

For a pair of hemispheres, we assume that the hemispheres lie on a flat surface. Fig. 2.4a shows the orientation and parameters of the two hemispheres used in these calculations. This configuration belongs to the C_{2v} point group and all three electric dipole modes will be non-degenerate. Fig. 2.4a shows the orientation of the polarization that excites these modes together with their labels. Fig. 2.4b and c show the maxima of the dipole modes as a function of separation, s, for radii of a = 10 and 20 nm, respectively. When the spacing, s, is decreased we observe a large redshift in the B_2 modes and much smaller blueshifts in the B_1 and A_1


Figure 2.3: Location of the plasmon extinction maximum for a pair of spheres (shown in (a)) as function of sphere separation, s, for (b) a = 10 nm and (c) a = 20 nm. Traces (d) and (e) show spectra of these modes at a separation, s, of 1 nm and a radius, a, of 10 and 20 nm, respectively. The definition of the modes are shown in (a).

modes. Similar to the case of the paired spheres, the redshift is more pronounced for larger particle radii. Fig. 2.4d and e show the spectra of these modes for a fixed separation s = 1 nm and radii of a = 10 and 20 nm, respectively. Similar to the case of a single hemisphere (Fig. 2.2d) the lowest energy mode – here it is B_2 – possesses the largest extinction cross section and should be readily observable. However, this mode will not be as dominant in an orientationally averaged spectrum as the Π mode of the isolated hemisphere.

In relation to each other, the spectra of the paired sphere (Fig. 2.3) and hemisphere (Fig.



Figure 2.4: Location of the plasmon extinction maximum for a pair of hemispheres (shown in (a)) as function of hemisphere separation, s, for (b) a = 10 nm and (a) a = 20 nm. Traces (d) and (e) show spectra of these modes at a separation, s, of 1 nm and a radius, a, of 10 and 20 nm, respectively. The definition of the modes are shown in (a).

2.4) are very similar, although, when spacing and radii are equal, the low energy B_2 mode of the hemisphere system is found at longer wavelengths than the low energy Σ_u^+ mode of the spherical system. Note that a smaller peak associated with an electric quadrupole moment is visible at shorter wavelengths in the traces that contain the Σ_u^+ mode and B_2 mode in Fig. 2.3 and Fig. 2.4, respectively.

2.4.1.3 A Series of Spheres or Hemispheres

For either spheres or hemispheres, the difference in spectra between the isolated (Fig. 2.2) and paired cases (Fig. 2.3 and 2.4) is quite significant. Therefore, it is worthwhile to investigate the effects of placing additional spheres or hemispheres in the series. This gives an impression of how quickly the spectra converge. For either set of objects, the most convenient way to proceed is by placing all of them along the same axis and maintaining an equal spacing, s, between neighboring members of the series (and for hemispheres maintaining identical orientation). When this is done, the $D_{\infty h}$ and C_{2v} symmetry of the paired case are retained for the spheres and hemispheres, respectively. For the spheres, physical intuition tells us that this will represent a limit on the longest observable wavelength for such a cluster (i.e. when compared to other systems with the same number of spheres and where the shortest spacing between any two spheres is not less than s).

We shall only examine the Σ_u^+ mode in the case of spheres and the B_2 mode in the case of hemispheres as these were found to be the strongest in the paired case and the only modes whose maxima changed significantly (redshifted) when coupled. Fig. 2.5a and b show the location of these modes as the number of objects in the series increases. With each new object that is added to the series a redshift occurs. However, the magnitude of this shift also decreases as more objects are added. Although neither of the series completely converge, in both cases after N = 4 the redshift is quite minor. The redshift in the hemisphere case is more pronounced than that of the case of the sphere. Finally, the maxima of the modes not shown here $(B_1, A_1,$ and $\Pi_u)$, do not change significantly when additional objects are added to the series.

2.4.1.4 Cluster of Four Spheres or Hemispheres

In a situation where spheres or hemispheres are randomly distributed on a surface, such as those that are considered in the Section 2.4.2, a cluster of individual particles might be a better representation than a series of particles. To gain some appreciation of this we examine two such cases; those of four spheres (Fig. 2.6) and four hemispheres (Fig. 2.7). The point group of these arrangements are D_{4h} and C_{4v} , respectively. As s decreases both the spherical and hemispherical configurations have a strong redshift in their lowest energy mode (E_u and E,



Figure 2.5: Location of the plasmon extinction maximum for (a) the Σ_u^+ mode as the number of spheres in a series is increased (or the *p* mode when the number of spheres is equal to one) and (b) the B_2 mode as the number of hemispheres in a series is increased (or the Π mode when the number of hemispheres is equal to one). The spacing between the spheres or hemispheres in the series and radii were held constant at 1 and 10 nm, respectively.

respectively). However, the absolute shift is not as large as in the linear case for N = 4 (Fig. 2.5). More importantly, the overall appearance of the spectra in Fig. 2.6 and 2.7 is very similar to the spectra of the respective pairs in Fig. 2.3 and 2.4. Note again that, similar to the paired sphere and hemisphere cases, a smaller peak associated with an electric quadrupole moment is visible at shorter wavelengths in the traces that contain the E_u mode and E mode in Fig. 2.6 and 2.7, respectively.



Figure 2.6: Location of the plasmon extinction maximum for four spheres (shown in (a)) as function of sphere separation, s, for a system of four hemispheres of radius (b) a = 10 nm and (c) a = 20 nm. Traces (d) and (e) show spectra of these modes at a separation, s, of 1 nm and a radius, a, of 10 and 20 nm, respectively. The definition of the modes is shown in (a).



Figure 2.7: Location of the plasmon extinction maximum for four hemispheres (shown in (a)) as function of hemisphere separation, s, for a system of four spheres of radius (b) a = 10 nm and (c) a = 20 nm. Traces (d) and (e) show spectra of these modes at a separation, s, of 1 nm and a radius, a, of 10 and 20 nm, respectively. The definition of the modes is shown in (a).



Figure 2.8: Location of plasmon extinction maxima as function of base height, b, for a droplet-like structure of radius a = 10 nm.

2.4.1.5 Droplet-like Structure

Fig. 2.8 shows the extinction maxima of the two modes of a droplet-like structure (see inset for details) with a radius a = 10 nm and a varying base height, b. An axis showing the contact angle for the a-to-b ratios is also plotted. The maximum wavelength of the dominant Π mode increases monotonically between the spherical (b = 10 nm) and hemispherical limits (b = 0 nm). Therefore, the hemispherical and spherical clusters which we have considered earlier represent, as an approximation, upper and lower bounds on the maximum wavelength for equivalent clusters made up of these droplet-like structures.

2.4.1.6 Summary of Optical Properties

The systematic calculations performed here tell us where to expect resonances and what their relative strengths are. For a closely spaced system of particles (s < 4 nm), extinction maxima are much more sensitive to changes in spacing than changes in particle radii (i.e. within this region, changing the separation will have a greater effect on the maxima location than an identical change to the radii). Independently of the arrangement of the individual particles there are generally two types of modes: "high energy" modes from 500 to 600 nm and "low energy" modes from 600 to 800 nm. Therefore, for a system of particles randomly distributed across a surface, two plasmon bands should be observable in the extinction spectrum – one

comprising the higher energy modes and the other the lower energy modes. Within the context of the plasmon hybridization model,²² this is simply the splitting of the uncoupled plasmon resonance into higher and lower energy modes.

The comparison of the results for two spheres or hemispheres (Fig. 2.3 and 2.4) with those of four spheres or hemispheres (Fig. 2.6 and 2.7) illustrates that the number of high energy modes goes from two to one and the number of low energy modes goes from one to two (taking into account the degeneracy of some of the modes present). These two cases are examples of a more general phenomenon: as the packing density of randomly placed gold objects on a surface increases, the lower energy band will increase in strength at the expense of the higher energy band. The other effect of the increasing density is that the low energy band redshifts.

2.4.2 Characterization of Particles by TEM

Fig. 2.9 shows TEM images for nanoshell precursors where increasing amounts of the gold salt solution have been reduced in their presence. We first describe the differences between the images qualitatively. For low concentrations of reducible gold salt solution, isolated gold particles are found on the silica surface (Fig. 2.9a-e). As the concentration of reducible salt is increased, these particles grow in diameter, coalesce and eventually form a surface better described as being continuous (Fig. 2.9f-i). This suggests a lower limit on the thickness of a completed nanoshell in the range of 11 to 16 nm (the thickness of the gold shells for the particles in Fig. 2.9f and i, respectively).

During the growth process of the individual gold particles, the most pronounced change appears to occur from Fig. 2.9a to b. Here, not only does the size of the gold particles on the surface increase, as one would expect, but, as is evident by inspection, the number of gold particles greatly decreases. Furthermore, there are large areas of the silica surface that would have contained small gold particles in Fig. 2.9a but are bare in Fig. 2.9b. These observations suggest that the larger particles in Fig. 2.9b do not originate from single seed particles but rather encompass several of these seed particles.

Two dimensional TEM images can be a limitation in elucidating the three dimensional structure of particles. However, the spherical silica surface on to which the particles are bound allows one to view all orientations of the gold particles. In Fig. 2.9b and c the gold particles



Figure 2.9: TEM images for prepared nanoshells. Volume of stock $HAuCl_4/K_2CO_3$ added during coating procedure: (a) 0 mL, (b) 0.25 mL, (c) 0.50 mL, (d) 0.75 mL, (e) 1.00 mL, (f) 1.25 mL, (g) 1.50 mL, (h) 1.75 mL, and (i) 2.00 mL. Corresponding UV-vis extinction spectra are shown in Fig. 2.10.

on the outer edge of the silica spheres, for example, show that the individual particles have droplet-like shapes. This morphology lies somewhere between the spherical and hemispherical shapes discussed in Section 2.4.1. The contact angle of these particles could be measured from the TEM images and values of $125 \pm 8^{\circ}$ (Fig. 2.9b) and $130 \pm 9^{\circ}$ (Fig. 2.9c) were obtained. If we assume that only dispersion forces between gold and silica determine this contact angle we can calculate this value from Young's equation.⁵⁹ For that purpose, we used the surface energies of gold $\gamma_{Au} = 1130 \text{ mJ m}^{-2}$,⁶⁰ silica $\gamma_{Si} = 31 \text{ mJ m}^{-2}$,⁶¹ and the interface energy $\gamma_{Au,Si} = \gamma_{Au} + \gamma_{Si} - 2\sqrt{\gamma_{Au}\gamma_{Si}} = 787 \text{ mJ m}^{-2}$. This leads to a calculated contact angle of 132°, which is in reasonable agreement with the experimental values.

Droplet-like growth has been discussed previously for gold growing on a flat, doped polypyrrole surface.⁶² While the sample preparation in that work was quite different from ours (e.g. gold films were grown by vapor deposition), the surface energies of that system were very similar, suggesting that general dispersion forces play an important role in determining gold particle morphology here as well. The contact angle in that case (128°) was similar to our measurements. In contrast to our study, however, the contact angle could not be measured directly, but was extrapolated to fit X-ray photoelectron spectroscopy (XPS) measurements.

Table 2.1 quantifies the average radius, a, of the gold particles found on the silica surfaces and the percentage of the silica core surface they cover. This data was obtained from TEM images. For cases where the edges of two particles were touching, this was measured and counted as two separate particles. Alternatively, when the coverage of the silica surface by gold was high, the gold hemisphere radius was obtained from the difference between the total nanoshell diameter and the silica core diameter (see Fig. 2.1b). Where both of these results could be applied (Fig. 2.9d and e), results determined in either manner were in agreement. For the situation depicted in Fig. 2.9f-i, only the second method was applicable and the radius a is better interpreted as being the nanoshell thickness. When determining the percentage of surface coverage only the portion of the surface near the center of a silical sphere on a TEM image was used so that the gold particles did not obscure uncoated area and cause an overestimation of the surface coating. The nearest neighbor distance between two particles, s, was not measured directly but instead calculated using the measured coverage of silica by gold. This was done by preparing a plot of area covered versus nearest neighbor distance using values of area and nearest neighbor distance calculated by randomly placing circles with radii of 80 units on a 8000 x 8000 unit grid. In order to avoid artifacts introduced by not using an infinite grid, circles within 1600 units of the grid edge were not included in these calculations.

2.4.3 Characterization of Particles by UV-vis-NIR Spectroscopy

The UV-vis-NIR spectra of the prepared particles are shown in Fig. 2.10 and the positions of the high energy (P_{high}) and low energy (P_{low}) plasmon bands, observed as maxima or shoulders,

Label in	Volume of	Particle radius or	Fraction of silica	Nearest neighbor	Wavelength (nm) of
Fig. 2.9 and	gold salt	shell thickness, a (nm)	surface covered	distances between	plasmon bands
Fig. 2.10	solution (mL)	(see Fig. 2.1)	by gold	gold particles (nm)	P_{high}, P_{low}
b	0.25	9 ± 3	0.31 ± 0.11	3.4 ± 1.1	536, 607
с	0.50	11 ± 3	0.51 ± 0.07	1.5 ± 1.4	550, 625
d	0.75	14 ± 6	0.66 ± 0.13	0.2 ± 0.2	535,644
e	1.00	10 ± 5	0.79 ± 0.14	0	527,684
f	1.25	11 ± 5	0.94 ± 0.05	0	-, 710
g	1.50	17 ± 5	0.93 ± 0.06	0	-, 715
h	1.75	16 ± 3	0.98 ± 0.03	0	-, 715
i	2.00	16 ± 6	0.99 ± 0.01	0	-, 705

Table 2.1: Parameters extracted from TEM images (see Fig. 2.9).

are indicated as well. These values are also listed in Table 2.1. In Fig. 2.10a, the absence of any observable plasmon peak is most likely due to the small dimensions of the gold particles (Fig. 2.9a), the plasmon oscillations of which will be heavily damped. In Fig. 2.10f-i, the fraction of silica covered by gold is larger than that of the densest possible packing of circles on a flat surface (hexagonal packing, ~0.91). Therefore, overlap between gold particles is significant and the spectra are essentially those of completed nanoshells. In Fig. 2.10b-e, we observe a double band structure consisting of P_{low} and P_{high} . In addition, the low energy band, P_{low} , strongly redshifts from trace b to e. The high energy band, P_{high} , exhibits only a minor shift. These spectra correspond to particles where complete shells have yet to form. To explain the origin of this redshift, along with the observed double structure, we use the data extracted from the TEM images (Table 2.1) together with the results from Section 2.4.1.

The radii of the discrete gold particles observed in Fig. 2.9b-e are listed in Table 2.1. Within the uncertainties, these values are all ~10 nm. Despite this similarity in size, we observe a strong redshift of P_{low} . In contrast to this nearly constant radius, the fraction of the silica surface covered by gold increases from 0.31 to 0.79 (Table 2.1). This obviously affects the spacing between gold particles and corresponds to a decrease in the nearest neighbor distance between particles, s, from about 3.49 nm to essentially zero. This indicates that interparticle plasmon coupling between the gold structures is strong and causes the observed redshift.

The high and low energy band description developed in Section 2.4.1.6 provides an adequate explanation as to the observed double structure. As predicted for spherical and hemispherical objects placed on a surface, two distinct bands appear. With increasing coating density the lower energy band (i) redshifts and (ii) increases in strength relative to the higher energy band.



Figure 2.10: UV-vis extinction spectra for nanoshell solutions. Volume of stock $HAuCl_4/K_2CO_3$ added during coating procedure: (a) 0 mL, (b) 0.25 mL, (c) 0.50 mL, (d) 0.75 mL, (e) 1.00 mL, (f) 1.25 mL, (g) 1.50 mL, (h) 1.75 mL, and (i) 2.00 mL. The location of the high energy (P_{high}) and low energy (P_{low}) plasmon bands is indicated using arrows. Corresponding TEM images are shown in Fig. 2.9.

Note again that the same holds for the droplet-like particles as they represent an intermediate between spherical and hemispherical objects. In Fig. 2.10b to e, these two bands are always observed as a maximum or a shoulder. Initially, the high energy band, P_{high} , appears as the main peak while the low energy band, P_{low} , is a shoulder (Fig. 2.10b and c). As the coating density of gold on silica increases, P_{high} becomes a shoulder and P_{low} develops to become the main peak (Fig. 2.10d and e). Not only are the two predicted bands observed – within the correct range of wavelengths predicted from the calculations – but the proper trend is also found: P_{low} strongly redshifts from 607 nm in Fig. 2.10b to 684 nm in Fig. 2.10e and becomes stronger than P_{high} ; which only shifts by a minor amount.

For systems containing large numbers of closely spaced, randomly distributed plasmonic particles predicting the precise location of extinction maxima with DDA is difficult due to computational limitations. However, the fact that the bands in Fig. 2.10b-e fall within the limits established in Section 2.4.1 for gold particles characterized by the TEM images, provides clear evidence that coupling between the latter are responsible for the observed double structure and intensity distribution.

2.5 Summary

The initial growth of gold nanoshells occurs through a combination of gold being plated onto the adsorbed seed particles and a process where these seed particles evolve into a smaller number of larger particles on the silica surface. These particles have a droplet-like shape. Prior to the formation of a continuous gold layer on the silica core, such incomplete nanoshells exhibit high (500-600 nm) and low (600-800 nm) energy bands. Modeling shows that this is the result of interparticle plasmon coupling that occurs mainly between nearest neighbor gold particles adsorbed to the silica surfaces. Model clusters of hemispheres and spheres establish upper and lower bounds for the wavelengths of these bands. The experimental results for incomplete nanoshells with discrete gold particles fall within the predicted limits.

The present results allow for a simple identification of the incomplete growth of nanoshells by UV-vis-NIR spectroscopy. Incomplete growth is an issue in systems where the creation of very thin gold layers is desired. Furthermore, our study provides an explanation as to the origin of the observed optical properties of these systems.

Chapter 3

Vibron and Phonon Hybridization in Dielectric Nanostructures

3.1 Introduction

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 applications⁶³ and for the study of global warming, which strongly depends on how solar radiation interacts with aerosols.⁶⁴ 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 sub-wavelength dimensions. These surface modes typically show a strong dependence on particle morphology.^{4,65} 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. The incomplete Au nanoshells discussed in Chapter 2 are one example of this phenomenon. 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.^{22,66,67} This 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 (as discussed in Section 1.3). 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_L) and transverse optical (ω_T) 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 would be a valuable intuitive aid when designing nanomaterials with a specified infrared response, $^{68-70}$ 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 aerosols⁷¹⁻⁷³ or the study of cosmic dust.⁷⁴⁻⁷⁷

In this work we develop a hybridization scheme which 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. 3.1). This example illustrates the general applicability of the hydbridization scheme and demonstrates how vibrational spectra of complex dielectric nanostructures can be predicted from spectra of primitive building blocks.



Figure 3.1: (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.

3.2 Formulation of Hybridization Scheme

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.^{56,78–82} This method is reviewed in Appendix A. Using this approach we demonstrate 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 the geometry depicted in Fig. 3.1a the normal component of the electric field on the outer surface \mathbf{E} and inner surface \mathbf{E}' satisfy the following equations

$$\mathbf{n}_Q \cdot (\epsilon_2 \mathbf{E}^+ - \epsilon_3 \mathbf{E}^-) = 0 \text{ on } S$$
(3.1)

$$\mathbf{n}'_Q \cdot (\epsilon_1 \mathbf{E}'^+ - \epsilon_2 \mathbf{E}'^-) = 0 \text{ on } S'$$
(3.2)

where ϵ_1 , ϵ_2 , and ϵ_3 are the permittivities of the core, shell, and medium, respectively. The direction of the normals \mathbf{n}_Q and \mathbf{n}'_Q are outwards and inwards, respectively, and we set $\epsilon_1 = \epsilon_3 = \epsilon_0$ (a numerical method for solving this problem when $\epsilon_1 \neq \epsilon_3$ is given in Ref. 83). Furthermore, we consider S and S' to be scaled versions of each other throughout this work. The normal components of the electric field at each surface are then

$$\mathbf{n}_Q \cdot \mathbf{E}^{\pm}(Q) = \mp \frac{\sigma(Q)}{2\epsilon_0} + \frac{1}{4\pi\epsilon_0} \left(\oint_S \sigma(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_Q}{|\mathbf{r}_{MQ}|^3} dS_M + \oint_{S'} \sigma'(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_Q}{|\mathbf{r}_{MQ}|^3} dS_M \right) \text{ on } S \quad (3.3)$$

$$\mathbf{n}_{Q}^{\prime} \cdot \mathbf{E}^{\prime \pm}(Q) = \pm \frac{\sigma^{\prime}(Q)}{2\epsilon_{0}} + \frac{1}{4\pi\epsilon_{0}} \left(\oint_{S} \sigma(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_{Q}^{\prime}}{|\mathbf{r}_{MQ}|^{3}} dS_{M} + \oint_{S^{\prime}} \sigma^{\prime}(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_{Q}^{\prime}}{|\mathbf{r}_{MQ}|^{3}} dS_{M} \right) \text{ on } S^{\prime}$$

$$(3.4)$$

These equations along with the boundary conditions 3.1 and 3.2 lead to the following pair of simultaneous linear integral equations for the outer (σ) and inner (σ') surface-charge densities

$$\sigma(Q) = \frac{\lambda}{2\pi} \left(\oint_{S} \sigma(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_{Q}}{|\mathbf{r}_{MQ}|^{3}} dS_{M} + \oint_{S'} \sigma'(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_{Q}}{|\mathbf{r}_{MQ}|^{3}} dS_{M} \right)$$
(3.5)

$$\sigma'(Q) = \frac{\lambda}{2\pi} \left(\oint_{S} \sigma(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_{Q}'}{|\mathbf{r}_{MQ}|^{3}} dS_{M} + \oint_{S'} \sigma'(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_{Q}'}{|\mathbf{r}_{MQ}|^{3}} dS_{M} \right)$$
(3.6)

where $\lambda = (\epsilon_2 - \epsilon_0)/(\epsilon_2 + \epsilon_0)$. If integral equations using the kernels from equations 3.5 and 3.6 are written as

$$\sigma_m(Q) = \frac{\lambda_m}{2\pi} \oint_S \sigma_m(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_Q}{|\mathbf{r}_{MQ}|^3} dS_M$$
(3.7)

$$\sigma'_m(Q) = \frac{\lambda'_m}{2\pi} \oint_{S'} \sigma'_m(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}'_Q}{|\mathbf{r}_{MQ}|^3} dS_M$$
(3.8)

where λ_m and λ'_m are both equal to $(\epsilon_2 - \epsilon_0)/(\epsilon_2 + \epsilon_0)$, it is apparent that these equations also describe the surface-charge density on the two primitives that can be used to construct the shell in Fig. 3.1a (cf. equations A.3 and A.6). Equation 3.7 gives the surface-charge density relationship on the core (Fig. 3.1c) and equation 3.8 gives the surface-charge density relationship on the cavity (Fig. 3.1b). Because of these equivalences and the fact that equations 3.5 and 3.6 are linear it is immediately obvious that the surface-charge density eigenfunctions of a shell can always be constructed from the eigenfunctions of its primitive components.

The eigenvalues for the shell can be determined by expanding $\sigma(Q)$ and $\sigma'(Q)$ using the eigenfunctions of the core and cavity

$$\sigma(Q) = \sum_{m=0}^{\infty} a_m \sigma_m(Q) \tag{3.9}$$

$$\sigma'(Q) = \sum_{m=0}^{\infty} b_m \sigma'_m(Q) \tag{3.10}$$

These can be substituted into equations 3.5 and 3.6 yielding

$$\sum_{m=0}^{\infty} a_m \sigma_m(Q) = \frac{\lambda}{2\pi} \left(\oint_S \sum_{m=0}^{\infty} a_m \sigma_m(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_Q}{|\mathbf{r}_{MQ}|^3} dS_M + \oint_{S'} \sum_{m=0}^{\infty} b_m \sigma'_m(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_Q}{|\mathbf{r}_{MQ}|^3} dS_M \right)$$
(3.11)
$$\sum_{m=0}^{\infty} b_m \sigma'_m(Q) = \frac{\lambda}{2\pi} \left(\oint_S \sum_{m=0}^{\infty} a_m \sigma_m(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}'_Q}{|\mathbf{r}_{MQ}|^3} dS_M + \oint_{S'} \sum_{m=0}^{\infty} b_m \sigma'_m(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}'_Q}{|\mathbf{r}_{MQ}|^3} dS_M \right)$$
(3.12)

Next, by bringing the integrals inside the summation and substituting in equations 3.7 and 3.8 we get

$$\sum_{m=0}^{\infty} a_m \sigma_m(Q) = \lambda \sum_{m=0}^{\infty} \frac{a_m \sigma_m(Q)}{\lambda_m} + \frac{\lambda}{2\pi} \oint_{S'} \sum_{m=0}^{\infty} b_m \sigma'_m(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_Q}{|\mathbf{r}_{MQ}|^3} dS_M$$
(3.13)

$$\sum_{m=0}^{\infty} b_m \sigma'_m(Q) = \frac{\lambda}{2\pi} \oint_S \sum_{m=0}^{\infty} a_m \sigma_m(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}'_Q}{|\mathbf{r}_{MQ}|^3} dS_M + \lambda \sum_{m=0}^{\infty} \frac{b_m \sigma'_m(Q)}{\lambda'_m}$$
(3.14)

When dealing with the case of a spherical shell (Fig. 3.1a) with an inner radius of a and an outer radius of b this pair of equations can be solved exactly. For the primitive components, the eigenvalues of the core are $\lambda_m = (2m+1)$ and the eigenvalues of the cavity are $\lambda'_m = -(2m+1)$. The degree of the spherical harmonics that generate these eigenvalues are m. Using these relations along with the addition theorem and orthogonality of spherical harmonics, equations 3.13 and 3.14 can be simultaneously solved and the analytical formula for the eigenvalues of degree l of a spherical shell is determined to be

$$\lambda_{l\pm} = \mp \frac{2l+1}{\sqrt{1+4l(l+1)(\frac{a}{b})^{2l+1}}}$$
(3.15)

By inserting $\lambda_{l\pm} = (\epsilon_2 - 1)/(\epsilon_2 + 1)$ into equation 3.15 and setting

$$\epsilon_2 = 1 + \frac{\omega_L^2 - \omega_T^2}{\omega_T^2 - \omega^2} \tag{3.16}$$

we can solve equation 3.15 for the surface resonances (eigenmodes) ω and obtain

$$\omega_{l\pm}^{2} = \frac{\omega_{L}^{2}}{2} \left(1 \pm \frac{1}{2l+1} \sqrt{1 + 4l(l+1)\left(\frac{a}{b}\right)^{2l+1}} \right) + \frac{\omega_{T}^{2}}{2} \left(1 \mp \frac{1}{2l+1} \sqrt{1 + 4l(l+1)\left(\frac{a}{b}\right)^{2l+1}} \right)$$
(3.17)

Equation 3.16 assumes that 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 ($\epsilon_1 = \epsilon_3 = 1$). Consequently, equation 3.17 is also only valid for those cases. By using more elaborate dielectric functions in conjunction with equation 3.15 it is possible to obtain other expressions for the eigenmodes of a spherical shell of more general validity.

3.3 Discussion

Equation 3.17 is similar to what was initially presented for metallic shells⁶⁶ 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 anti-bonding and the low energy level (ω_{l-}) as bonding. The anti-bonding mode involves an antisymmetric coupling between the charge on the inner and outer surface of the shell while the coupling between the surfaces in the bonding mode is symmetric. Equation 3.17 illustrates that a simple scale parameter a/b determines how the spectrum changes as a function of inner and outer radius.

Fig. 3.2 shows the energy levels for the dipolar eigenmodes (l = 1 in Equation 3.17) and the corresponding absorption spectra for the ν_3 band of two spherical CO₂ shells with different thicknesses. As a dielectric substance we have chosen crystalline CO₂ (see Appendix B for details of the dielectric function used). This material is an excellent model system as its cubic crystal structure gives it a simple isotropic dielectric tensor. Furthermore, we have measured infrared spectra of various types of icy CO₂ aerosol particles, allowing for a direct comparison with experimental data.^{18,84} Aerosol measurements also offer the advantage that substrate effects do not influence the measured spectra, keeping the example simple. Finally, the understanding of infrared signatures of CO₂ aerosols of various morphologies is crucial for the interpretation of current and future aerosol data from the Mars atmosphere, where CO₂



Figure 3.2: Energy level diagrams (left) and corresponding absorbance spectra (right) for the ν_3 band of spherical CO₂ nanoshells. These were calculated using spherical harmonics of degree l = 1 (dipole). The scale parameters b/a are (a) 1.2 and (b) 2.

is one of the important cloud components.⁷³ 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 anti-bonding mode is higher in energy than the bonding mode is provided in Fig. 3.2. Analogous to molecular orbital theory, the energy increases with an increasing number of nodal surfaces (higher kinetic energy). The anti-bonding mode has two nodal surfaces while the bonding mode has only one. Furthermore, the calculated absorption spectra for spherical CO_2 shells on the right hand side of Fig. 3.2 show that an external electromagnetic field couples much more strongly to the bonding mode than to the anti-bonding mode, which is a consequence of the larger overall dipole moment of the bonding mode. A comparison of Fig. 3.2a to 3.2b shows that as the shell thickness is increased, the splitting between the bonding and anti-bonding 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 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 (longitudinal optical-transverse optical) 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_T while the anti-bonding mode approaches ω_L . This differs from the metallic case where in this limit the bonding mode approaches a frequency of zero and the anti-bonding 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. 3.3a) and CO_2 cubes (lower trace in Fig. 3.3b) 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 while CO_2 ice nanoshells with a cubic shape were prepared by condensing CO_2 onto cubic N_2O templates.⁸⁴ While 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.¹⁸ 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 N₂O 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



Figure 3.3: 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. 3.4. For the two optical modes whose splitting can be resolved experimentally, calculated (experimental) splittings in cm⁻¹ 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).

the absorption spectrum⁸⁵ – a result that is easily verified using the electrostatic eigenvalue method – and it is reasonable to expect a similar type of convergence with a cubic shell. The surface-charge density integrals of both a cube and cubic shell were evaluated numerically⁵⁶ (see Appendix B for further details) and energy level diagrams for the ν_3 and ν_2 bands of cubic CO₂ shells are shown in Fig. 3.4a 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 as hybridization involves a larger number of modes with dipole moments. Despite these details the general result is again straightforward as highlighted in Fig. 3.4: bonding and anti-bonding modes fall into low and high energy bands, respectively,



Figure 3.4: 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 surfacecharge distributions in (a) are associated with these modes. For clarity, only eigenmodes that contribute significantly to the absorption spectra in Fig. 3.3 are listed (in all cases these modes account for at least 96% of the absorbance in the calculated spectra).

with increasing energy for increasing numbers of nodal planes.

In Fig. 3.3a 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. 3.4b) 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 ($|-\rangle$) and antibonding ($|+\rangle$) 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 towards higher wavenumbers for $|\nu''_2-\rangle$ and $|\nu_3-\rangle$ and towards lower wavenumbers for $|\nu''_2+\rangle$ and $|\nu_3+\rangle$. Similiar to the spherical shell, the peaks

of the anti-bonding 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 is highlighted in Fig. 3.5 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 anti-bonding modes shift to lower energies thus reducing the splitting between the two sets of modes. Simultaneously, the intensity of the anti-bonding modes relative to the bonding modes becomes smaller until, finally, they appear only as shoulders in the case of the thickest shells (Fig. 3.5d). While these trends hold for both shapes, Fig. 3.5 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 while 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. 3.3a. 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 since their spectra are dominated by the interplay of molecular structure and finite size (see Ref. 18 for further details).

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 mid-infrared region where most fundamental internal vibrations occur wavelengths range from 2.5 to 25 μ m (4000 to 400 cm⁻¹). Therefore, the quantitative reproduction of absorbance spectra of nanometer sized dielectric particles should



Figure 3.5: 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.

be superior to plasmon spectra of metallic nanoparticles calculated within this approximation. The overall correspondence between the observed and calculated spectra in Fig. 3.3 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 Fig. 3.3 caption). 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.

3.4 Summary

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 usually not 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.

Chapter 4

Infrared Spectroscopy and Vibrational Exciton Modeling of Crystalline, Polycrystalline and Amorphous Acetylene Aerosol Particles

4.1 Introduction

The numerical methods and hybridization schemes discussed in Chapters 2 and 3 can only be used to calculate the spectrum of a particle if the bulk optical constants of the particle's material are known. In this and subsequent chapters, systems will be studied where this is not the case and these parameters are not well-characterized. Therefore, we will primarily rely on the methods introduced in Section 1.4.3 to model spectra.

Acetylene (C₂H₂) aerosols are believed to play a role in the atmospheres of a number of planets and moons, including Neptune's, Uranus', and in the atmosphere of Saturn's moon Titan.^{86,87} Particular interest in atmospheric processes on Titan has been sparked by the similarities to Earth's atmosphere, which is one of the subjects of the ongoing Cassini-Huygens mission.^{87–92} On Titan, C₂H₂ is the third most abundant hydrocarbon after methane and ethane.^{93,94} It is formed from methane by photochemical reactions in the upper atmosphere. The rich photochemistry in the stratosphere leads to Titan's characteristic optically thick haze layer, which has a tremendous influence on the propagation of solar radiation to the surface of the moon. Aerosols of these photochemical products are transported to the lower stratosphere and troposphere where they are believed to influence the formation of methane and ethane clouds and even the formation of Titan's lakes by acting as condensation and crystallization nuclei.^{88,90–92,95,96}

Although much attention has been paid to the properties of other components of Titan's haze, namely the tholins (see Refs. 89,97–99 and references therein), only a few laboratory studies have been performed for hydrocarbon condensates such as C_2H_2 aerosols.^{72,97,100–103} Little progress has been made towards understanding the phase behavior of acetylene aerosols at temperatures relevant to Titan (> 70 K). Bulk acetylene is known to exist in two crystal structures at these temperatures. A low-temperature orthorhombic structure below and a high-temperature face-centered cubic structure above 133 K.^{104,105} In supersonic expansions, cubic as well as orthorhombic acetylene clusters have been identified by Bartell and coworkers using electron diffraction, ¹⁰⁶ by Lee et al. using Raman spectroscopy, ¹⁰⁷ and by Hirabayashi et al. using infrared spectroscopy.¹⁰⁸ The transferability of these results to atmospheric aerosols. however, is limited, possibly because of the small size of the aggregates, but mainly because in a supersonic expansion condensates are formed under non-equilibrium conditions. The only studies on real C_2H_2 aerosols that we are aware of have been performed by Dunder and Miller¹⁰⁰ and in our own research group⁷² using bath gas cooling cells for aerosol formation and infrared spectroscopy for characterization. Dunder and Miller came to the conclusion that C_2H_2 aerosols are formed in the high-temperature cubic structure at temperatures where the low-temperature orthorhombic structure is the most stable. They also excluded "amorphous and mixed crystalline structures" with the rationale that the "vibrational bands would then be substantially broader" than the observed ones. In the absence of an appropriate molecular model to analyze the infrared spectra their conclusions were based on rather hand-waving arguments. Our recent study casts doubt on this interpretation. We found that the acetylene aerosols below 133 K show neither the infrared signatures of the cubic nor of the orthorhombic crystal phase.

In this investigation, we present new infrared spectra of acetylene aerosols together with



Figure 4.1: Experimental infrared spectra of C_2H_2 aerosol particles in the region of the bending vibration ν_5 (left) and the antisymmetric CH-stretching vibration ν_3 (right). The two bands are scaled to the same maximum. a: Spectrum observed for acetylene particles formed at temperatures between 78–110 K. As outlined in the chapter, these particles are polycrystalline (or partially amorphous). b: Spectrum observed for particles formed at 78 K and annealed by condensational heat transfer. As outlined in the chapter, these particles have a crystalline orthorhombic structure.

a detailed analysis of the infrared bands in terms of the vibrational exciton model^{18,109–112} that clarifies a number of issues. When C_2H_2 aerosols are prepared at cryogenic temperatures as reported previously,^{72,100} the spectrum shown in the upper trace of Fig. 4.1 is observed, with the characteristic broad, barely structured band shape of the bending mode (left). We shall demonstrate that the internal structure of these aerosols deviates from perfect crystalline ones. To support our interpretation, we present a new infrared spectrum of crystalline aerosols, which is obtained by annealing the particles (lower trace in Fig. 4.1). Our analysis does not only provide information on the phase of the particles, but also on their shape since both influence the aerosol infrared spectra.

4.2 Experimental

Acetylene aerosols were generated in a bath gas cooling cell at temperatures between 78 K and 110 K (uncertainty ± 1 K), which are typical for the lower atmosphere of Titan, and characterized by rapid-scan infrared spectroscopy in-situ in the cold cell (see Refs. 84 and 113 and references therein for experimental details). Injection of a dilute sample gas $(0.01-2\% C_2H_2 in$ He or in N_2) into a precooled bath gas (He or N_2 at pressures between 500 and 900 mbar) lead to supersaturation of the C_2H_2 gas, and thus to particle formation. Annealing of acetylene aerosols was achieved by condensing ethane onto the C_2H_2 particles ($C_2H_6:C_2H_2=1:1$), which then heat up due to condensation heat transfer before eventually cooling down again. Temperatures between 78 K and 110 K were realized by cooling with liquid nitrogen and additional heating for the higher temperatures. The bath gas cooling cell was equipped with White optics (10 m optical path length) and was connected to the infrared spectrometer (gold-coated mirrors, KBr windows). The vibrational spectra of the aerosols in the region between 600- 5000 cm^{-1} were obtained with a rapid-scan Fourier transform infrared spectrometer (Bruker IFS 66v/S) equipped with a Globar light source, a KBr beam splitter, and a HgCdTe detector at a spectral resolution of 1 cm^{-1} (acquisition time for an individual spectrum 0.5 s, typically 500 spectra were recorded within 45 minutes). By varying the concentration of the gas sample, aerosol particles with sizes between 10 and 500 nm were generated with particle number concentrations between 10^6 and 10^4 cm⁻³ (see Refs. 114 and 115 for a detailed description of size determination). Apart from additional scattering features for the large particles, the same spectral features were observed for the different particle sizes. C_2H_2 (99.6 %), C_2H_6 (99.994%), He (99.999%), and N₂ (99.999%) were purchased from Advanced Gas Technology and Praxair.

4.3 Modeling

The infrared spectra are analyzed in terms of the vibrational exciton model.^{9,18,109,110,116,117} As summarized in Section 1.4.3, this is a quantum mechanical description of the major intermolecular interactions that determine the shape of infrared bands. For acetylene, these are resonant transition dipole coupling and to a lesser extent polarization effects. We have

demonstrated for various aerosols that this model provides a successful description of aerosol infrared spectra.^{18,84,111,112,118–121} It is worth noting that the vibrational exciton model requires no prior knowledge of the index of refraction of the material. This is a crucial advantage over continuum models in combination with classical scattering theory,⁴ which is particulary important for the present case because separate refractive index data are not available for the different phases of acetylene.¹²² To determine the internal structure of non-crystalline aerosol particles, we have performed Molecular Dynamics Simulations combining the intermolecular potential of Garrison and Sandler¹²³ with a harmonic intramolecular potential following the work of Strey and Mills¹²⁴ (Section 4.3.2).

4.3.1 Vibrational Exciton Calculations

With the inclusion of the dominant dipole–dipole interaction and polarization effects the vibrational Hamiltonian has the form (for further details see Refs. 111 and 112):

$$\widehat{H} = \widehat{H}_0 + \sum_{i,j} \mu_i^+ A_{ij} \mu_j \tag{4.1}$$

with

$$A_{ij} = -1/2(\lambda_{ij} + \sum_k \lambda_{ik} \alpha_k \lambda_{jk})$$

where

$$\lambda_{ij} = \frac{(1-\delta_{ij})}{4\pi\varepsilon_0 R_{ij}^3} \left(3e_{ij}e_{ij}^+ - 1\right)$$

 \hat{H}_0 is the Hamiltonian for the uncoupled molecular oscillators. The sum extends over pairs of molecules. μ_i is the dipole moment vector of molecule i, α_k is the polarizability tensor of molecule k, and λ_{ij} are scaled projection matrices. R_{ij} is the distance between molecules i and j, and e_{ij} the unit vector pointing from the center of mass of molecule i to that of molecule j. \hat{H} is diagonalized in the basis of eigenfunctions $|i_m\rangle$ of \hat{H}_0 that correspond to excitations of the vibrational mode m of the molecule i. Within the double harmonic approximation the Hamiltonian is completely defined by molecular transition wavenumbers $\tilde{\nu}_{im}$ and transition dipole moments $\mu_{im} = \langle 0 | \mu_i | i_m \rangle$, and molecular polarizabilities α_k . Shifting the energy zero to the uncoupled ground state energy $\langle 0 | \hat{H} | 0 \rangle$ further simplifies the Hamilton matrix elements (Planck's constant *h*, speed of light *c*):

$$\langle k_m | \hat{H} | l_n \rangle = \delta_{kl} \delta_{mn} h c \tilde{\nu}_{km} - 2\mu_{km}^+ A_{ij} \mu_{ln}$$

$$\tag{4.2}$$

As demonstrated in an early publication, ¹⁰⁹ dipole–coupling between all molecules in an aerosol particle has to be taken into account to converge calculated infrared spectra (it is often wrongly assumed that dipole coupling between nearest neighbours would suffice!). For these large systems the full diagonalization of the Hamiltonian is impractical. Instead we take a time dependent approach to calculate absorption spectra directly from the dipole autocorrelation function. If $\{E_I\}$ is the set of eigenvalues of \hat{H} with corresponding eigenvectors $|I\rangle$ and transition moments $\mathcal{M}_I = \langle 0|\mu|I\rangle$ (overall dipole function $\mu = \sum_i \mu_i$), the absorbance spectrum is proportional to

$$\sigma(E) = \sum_{I} |\mathcal{M}_{I}|^{2} \cdot f(E - E_{I})$$
(4.3)

where f(E) is an appropriate line shape. $\sigma(E)$ is related to the time-dependent dipole autocorrelation function C(t) through the Fourier transformation $(\hbar = h/2\pi)$:

$$\mathcal{C}(t) = g(t) \int \sigma(E) e^{-iEt/\hbar} dE/h = g(t) \sum_{k,m,l,n} \langle k_m | \mu_{km} e^{-i\widehat{H}t/\hbar} \mu_{ln} | l_n \rangle \quad (4.4)$$

ith $g(t) = \int f(E) e^{-iEt/\hbar} dE/h$

 $\sigma(E)$ is obtained by inverse Fourier transformation of $\mathcal{C}(t)$. To calculate $\mathcal{C}(t)$ we employ a second order time-propagation scheme.

W

$$|\psi_{t+\Delta_t}\rangle = e^{-i\widehat{H}\Delta_t/\hbar}|\psi_t\rangle \approx -i\frac{2\Delta_t}{\hbar}\widehat{H}|\psi_t\rangle + |\psi_{t-\Delta_t}\rangle$$
(4.5)

The only parameters in the exciton model are the polarizability tensor α_k , the molecular transition wavenumbers $\tilde{\nu}_{im}$, and the transition dipole moments μ_{im} . The polarizability was

taken from Ref. 125. To determine $\tilde{\nu}_{im}$ and μ_{im} , we have taken two different approaches, which we call in the following standard vibrational exciton (SVE) model and extended vibrational exciton (EVE) model. In the SVE, $\tilde{\nu}_{im}$ and μ_{im} have a fixed value for all molecules in the aerosol particle. The corresponding values for the bending vibration ν_5 and the stretching vibration ν_3 are given in Table 4.1. These are literature values $^{122,126-128}$ that have been further adjusted to one of our experimental spectra. This model does of course not account for the fact that $\tilde{\nu}_{im}$ and μ_{im} can vary for molecules located at different sites in an aerosol particle. To clarify this point, we have also performed the vibrational dynamics calculations with the EVE model where we assigned individual transition wavenumbers and transition dipole moments to each molecule extracted from the explicit potential and dipole moment function described below in Section 4.3.2 (monomer equilibrium bond lengths 129).

Monomer properties										
	$\alpha_{xx} = \alpha_{yy} (\text{\AA}^3)$	α_{zz} (Å ³)	$\tilde{\nu}_{im} \ (\mathrm{cm}^{-1})$	μ_{im} (D)	r_{CC} (Å)	r_{CH} (Å)				
SVE and EVE	2.88^{a}	4.71^{a}								
SVE; ν_5 -band ^b			772.0	0.28^{c}						
SVE; ν_3 -band ^b			3227.5	0.096						
EVE					1.20356^{d}	1.06166^{d}				
Intermolecular potential for EVE^e										
partial charges	q_C (e)	q_H (e)								
	-0.267	0.267								
site–site pair	$\epsilon ~(\rm kJ/mol)$	α (Å ⁻¹)	r_m (Å)	C_6 (Å ⁶ kJ/mol)	$d_1 (Å^{-1})$	$d_6 ({\rm \AA}^{-1})$				
H–H	$3.49818 \cdot 10^{-6}$	0.46866	15.6587	106.670	6.70726	0.607250				
H–C	1.00699	1.61878	2.99965	1255.47	2.06778	2.06751				
$H-COM^{f}$	3.47675	7.15524	2.24017							
C-C	$1.06816 \cdot 10^{-9}$	0.929798	15.5002	1000.99	1.44603	0.620288				
$\mathrm{C-\!COM}^f$	3.48337	1.91559	3.20750							
Intramolecular potential for EVE^g										
	$k_{CC} ~({\rm eV}/~{\rm \AA}^2)$	$k_{HH} \ (eV/ \ Å^2)$	$k_{CH} \ (eV/ \ Å^2)$	$k_{a1} (eV)$	k_{a2} (eV)					
	48.846	18.558	0.105	0.7528	0.5498					

Table 4.1: Parameters for the SVE and the EVE model as described in Section 4.3.

^aPolarization tensor from Ref. 125. ^bSee Section 4.3.1 for transition dipoles and transition moments. ^cNote that ν_5 is degenerate and that the given value is for a single oscillator. ^dAcetylene equilibrium bond lengths from Ref. 129. ^eRef. 123. ^fCOM = centre of mass. ^gRef. 124.

Fig. 4.2 demonstrates that the SVE model and the EVE model essentially lead to the same results for crystalline particles as expected. The local variations in the molecular transition frequences and transition dipole moments are minor for crystalline structures. The main difference between the two sets of spectra are differences in the magnitude of the splitting



Figure 4.2: Infrared spectra of crystalline C_2H_2 aerosol particles with spherical (a and b) and cubic (c and d) particle shapes calculated with the vibrational exciton model. All particles have the cubic crystal structure of the bulk.¹⁰⁵ a and c: Calculations using the SVE model. b and d: Calculations using the EVE model.

between different peaks. Since the SVE model is more efficient than the EVE model, we used the SVE model for all calculations of crystalline particles. In fact, we found a slightly better agreement of the SVE model with experimental spectra of crystalline particles. This is not surprising because the potential used here is rather simple and has not been optimized to provide accurate spectroscopic information, as was done for example with NH_3 and CO particles.^{112,119} EVE calculations were only used for all non-crystalline particles to account for local variations in the transition frequencies and dipoles.

The exciton model allows us to analyze the vibrational wavefunctions in order to better understand from where in a particle spectral features arise. In Section 4.4.3 for example, we interpret the spectral signature in terms of the particles' internal structure. For that purpose, we use the local spectral density, which in essence partitions the overall spectrum into contributions $\sigma_i(E)$ from individual volume elements δV_i .

$$\sigma(E) = \sum_{i} \sigma_i(E) \tag{4.6}$$

Division by the number of molecules N_i contained in the volume element δV_i yields the normalized excitation density

$$\overline{\sigma}_i(E) = \frac{\sigma_i(E)}{N_i} \tag{4.7}$$

which represents the average contribution of individual molecules to the overall spectrum. In the time-dependent approach the $\overline{\sigma}_i(E)$ are obtained from an equivalent partitioning of C(t)(see Ref. 111 for more details).

4.3.2 Potential Model, Internal Structure, and Molecular Dynamics Simulations

To treat aerosol particles with tens of thousands of molecules, intra- and intermolecular potential models must be comparatively simple. Here we used the two-body intermolecular potential of Garrison and Sandler,¹²³ which combines a Morse potential with an inverse r^6 term and an electrostatic part based on partial charges designed to reproduce acetylene's quadrupole moment.

$$U_{inter} = \sum_{a \in A} \sum_{b \in B} \epsilon_{ab} \left(\left[1 - exp \left(\alpha_{ab} \left[r_{m,ab} - r_{ab} \right] \right) \right]^2 - 1 \right) - f_6 \left(d_{6,ab} r_{ab} \right) \frac{C_6}{r_{ab}^6} + f_1 \left(d_{1,ab} r_{ab} \right) \kappa \frac{q_a q_b}{r_{ab}} (4.8)$$

where

$$f_n(x) = 1 - e^{-x} \left(1 + \sum_{i=1}^n \frac{x^i}{i!} \right)$$
(4.9)

a and b represent the sites on molecule A and B respectively and κ is the Coulomb factor. The list of sites and the corresponding parameters are given in Table 4.1.

We combined this intermolecular potential with the intramolecular potential of Strey and $Mills^{124}$ restricting ourselves to the harmonic terms. The weak term coupling variations in the two CH bonds was omitted. The remaining five parameters were fitted to the fundamental transition frequencies of acetylene¹²⁶ (see Table 4.1).

$$U_{intra} = k_{HH} \left(dr_1^2 + dr_2^2 \right) + k_{CC} dR^2 + k_{CH} \left(dr_1 + dr_2 \right) dR$$

$$+ k_{a1} \left(\sin^2 d\Theta_1 + \sin^2 d\Theta_2 \right) + k_{a2} \sin d\Theta_1 + \sin d\Theta_2 \cos \tau$$
(4.10)

 dr_i , dR, and $d\Theta_i$ represent the deviations in the CH bonds, CC bond and HCC angles. τ is the torsion angle defined by the HCC planes.

The potential was used to calculate the input parameters for the EVE calculations (Section 4.4.2), i.e. the transition frequency and dipole moment of each individual molecule in an aerosol particle. Moreover, it also served us to obtain information on the internal structure of the non-crystalline particles. For the crystalline particles, we could simply use the bulk crystal structures from literature.¹⁰⁵ Corresponding structural data, however, are not available for non-crystalline particles. The fully amorphous and partially amorphous particles (Section 4.4.2) were constructed by randomizing orientations and positions of the molecules followed by simulated annealing. The simulated annealing is carried out by classical molecular dynamics using a Verlet algorithm and the above potential.¹¹⁹ Due to the high potential energy of the particles after randomization – half the binding energy, or higher – distributing an initial kinetic energy in the system was superfluous. The building kinetic energy was reduced by 1% within each time step of 0.1 fs. Annealing was performed for times necessary to reduce unphysically high energy configurations, but that did not yet result in the most stable crystalline structure.

4.4 **Results and Discussion**

4.4.1 Annealed Acetylene Aerosols

We begin the discussion with the infrared spectra of the annealed acetylene aerosol particles shown in Fig. 4.1b. The heat needed for annealing was generated by condensation of ethane
onto the C_2H_2 particles (Section 4.2). As outlined in the following by comparison with modelling, the splitting of the ν_5 band into three distinguishable peaks and a ν_3 band appearing as a single absorption peak are consistent with crystalline particles with an almost perfect orthorhombic crystal structure and globular shape.

Crystalline bulk acetylene has been previously studied using infrared spectroscopy, ^{122,130–133} Raman spectroscopy,¹³⁴ x-ray diffraction,¹⁰⁴ and neutron diffraction.¹⁰⁵ X-ray and neutron diffraction identified two crystal structures, a high-temperature (above 133 K) face-centered cubic structure (four molecules per unit cell) and a low-temperature orthorhombic structure (four molecules per unit cell). For the infrared spectra of crystalline bulk acetylene, group theory predicts that, in the orthorhombic case, the ν_5 mode splits into four components, three of which are infrared active, while, in the cubic case, this mode splits into four components, of which two are infrared active. The ν_3 mode splits in both phases into two components. In the orthorhombic phase both are infrared active, while only one is infrared active in the cubic phase. These symmetry considerations, however, do not provide any information on the size of the splittings or the absolute wavenumbers at which the peaks occur. For example, if two components are very close they would appear in the infrared spectrum as a single peak instead of a double peak. Furthermore, the experimental bulk spectra do not clarify this situation since different numbers of distinguishable components are observed in different spectra.^{122,130,132,133} Moreover, in contrast to the situation for bulk spectra additional peaks can occur in particle spectra as a result of the particle shape.¹⁸ Arguments based solely on splitting patterns can thus easily lead to misinterpretations. Thorough modeling is therefore a prerequisite for analyzing the particle infrared spectrum in Fig. 4.1b.

Our analysis is mainly based on the interpretation of the bending vibration since the stretching mode is less sensitive to particle properties as demonstrated below. This is a consequence of the fact that exciton coupling dominates the infrared spectrum of the bending but not the stretching mode. Fig. 4.3 shows for the bending mode a series of calculated spectra in traces a to d together with the experimental spectrum in trace e. The comparison with the experimental spectrum clearly reveals that the agreement with the simulations for particles with an orthorhombic crystal structure (traces c and d) is much better than with the

simulations for particles with a cubic crystal structure. The cubic crystal structure shows essentially two peaks that do not coincide with the experimentally observed peaks. An excellent correspondence, however, is found between the spectra of the particles with an orthorhombic crystal structure (traces c and d) and the experiment. The experimentally observed three–peak structure is nicely reproduced both by the particles with a spherical shape (trace c) and by the polyhedron (trace d). In addition to spherical particles and polyhedra, we also performed calculations for many other particles shapes, including cubes and various elongated particles (not shown). Elongated particles can be excluded. Their spectra show additional pronounced shoulders/peaks that are not observed in the measured spectrum. The spectrum of the cube is similar to the sphere and polyhedron, but again shows additional shoulders not observed here. We found globular particle shapes, such as spherical particles or polyhedra, to agree best with the experiment, so that in what follows we concentrate on these two shapes.

The main differences between the calculated spectra in traces c and d and the experimental in trace e are the slightly less distinct peaks in the experimental spectrum, its somewhat more asymmetric shape, and its higher relative intensity of the peak around 790 cm⁻¹. The less distinct peak structure probably arises from the fact that the prepared particles were not completely crystalline, presumably a consequence of the fast annealing. The simplest way to explore this is to model spectra of imperfect crystals. Fig. 4.4 shows as an example spectra of spherical C_2H_2 particles for which the individual C_2H_2 molecules have been randomly rotated out of their crystalline position within a cone defined by the angle α (see inset for the definition of the cone relative to a C_2H_2 molecule). A systematic broadening of the peaks is indeed found for increasing values of α . A slightly imperfect crystal structure thus explains the less distinct experimental peaks. The asymmetry of the peaks and the relative peak intensities are mainly governed by the shape of the particles as can be seen from the comparison of the sphere's spectrum in Fig. 4.3c with the polyhedron's spectrum in Fig. 4.3d. While the sphere does not lead to any asymmetries in the peaks the polyhedron clearly shows asymmetric contributions very similar to the experiment. The comparison also demonstrates the sensitivity of the relative peak intensities on the exact shape. Since the particles are crystalline it is physically unrealistic to expect any of the experimentally prepared particles to be perfectly spherical in shape. A



Figure 4.3: Calculated (a-d) and experimental (e) infrared spectra of crystalline C_2H_2 aerosol particles in the region of the ν_5 band. a: Spherical particle with a cubic crystal structure. b: Polyhedron with a cubic crystal structure. c: Spherical particle with an orthorhombic crystal structure. d: Polyhedron with an orthorhombic crystal structure. All calculations were performed with the SVE model.

polyhedral morphology better fits with the experiment and is physically more realistic. It is important to note here that we used only a single shape to calculate the spectrum in trace d, whereas the experimentally observed particle ensemble certainly consisted of a distribution over a certain range of globular shapes depending on the annealing conditions. We observed experimental spectra with slightly different peak asymmetries and relative peak intensities than the one depicted in trace d by modifying the annealing conditions which can modify the average shape of the ensemble.

For completeness, Fig. 4.5 shows calculated spectra (traces a and b) together with the experimental spectrum (trace c) of the CH–stretching mode. Since the calculated spectra are



Figure 4.4: Calculated infrared spectra for acetylene particles with a spherical shape. A slightly imperfect crystal structure was simulated by randomly tilting individual C_2H_2 molecules out of their orthorhombic crystalline position by a maximum angle α . All calculations were performed with the SVE model.

almost identical for different particle shapes we only show simulations for two polyhedra with a cubic and with an orthorhombic crystal structure. The cubic structure (trace a) exhibits a single peak while the orthorhombic structure (trace b) shows two overlapping peaks with a splitting of 2.5 cm^{-1} . The interpretation, however, that the simulation for the cubic crystal structure agrees better with the experiment than that of the orthorhombic crystal structure would be incorrect for two reasons. Firstly, our model (as any other model) cannot predict such small band splittings accurately enough to allow us to distinguish between the two crystal structures. In other words, the model only tells us that the maximum splitting in trace b is on the order of a few wavenumbers. The real splitting could range from almost zero to a few wavenumbers. We have performed additional calculations for the bulk using the ABINIT program^{135,136} which predict a splitting of 1.3 cm⁻¹ for the ν_3 band and an orthorhombic crystal structure. Within the expected accuracy of our model, both crystal structures have approximately the same spectrum and would both agree with the experiment. Secondly, as mentioned in connection with Fig. 4.3 and 4.4 above the orthorhombic crystal structure of the particles is probably slightly imperfect. If the molecules in the particles are randomly rotated by a small angle as in Fig. 4.4 the splitting of the ν_3 band disappears for the orthorhombic



Figure 4.5: Calculated (a, b) and experimental (c) infrared spectra of crystalline C_2H_2 aerosol particles in the region of the ν_3 band. a: Polyhedron with a cubic crystal structure. b: Polyhedron with an orthorhombic crystal structure. All calculations were performed with the SVE model.

crystal structure and the two components become indistinguishable (not shown). As a result, we find that the ν_3 mode is not characteristic enough to distinguish between the two crystal structures, which demonstrates the importance of the ν_5 mode for spectral analysis. The reason lies in the exciton coupling, which is clearly the dominant interaction for the ν_5 but not the ν_3 band. This makes the ν_3 band much less sensitive to changes in the crystal structure (and in any other particle property) than the ν_5 band. The importance of exciton coupling is, for example, also reflected in the band width, which is $\sim 7 \text{ cm}^{-1}$ for the ν_3 band in comparison to $\sim 40 \text{ cm}^{-1}$ (Fig. 4.3) for the ν_5 band.

The results of this section clearly show that acetylene particles with an orthorhombic crystal structure can be formed by annealing aerosols below temperatures of 133 K. From the analysis we further conclude that these particles most likely possess a polyhedral morphology. We never observed the formation of particles with a cubic crystal structure after annealing, which is not surprising as the temperature lies below the orthorhombic to cubic transition temperature of 133 K. Moreover, the ν_5 mode turns out to play a key role for spectral analysis while the ν_3 mode shows rather unspecific features.

4.4.2 Non-Annealed Acetylene Aerosols

The spectrum in Fig. 4.1a is observed when acetylene aerosols are formed at temperatures between 78 K and 110 K and no further efforts are made to anneal the particles. A comparison of the ν_5 band with the spectra in Fig. 4.3 reveals that these particles are not crystalline. The broad, rather structureless ν_5 band with its long tail towards lower wavenumbers does not match any of the modeled spectra discussed above. It looks completely different from the ν_5 band of cubic (Fig. 4.3a and b) as well as orthorhombic (Fig. 4.3c and d) particles. The particles in Fig. 4.1a were formed under the same conditions as those reported by Dunder and Miller,¹⁰⁰ who came to the conclusion that the C₂H₂ particles had a cubic crystal structure. However, this conclusion was based purely on qualitative arguments because of the lack of an appropriate model. With the spectra for both cubic and orthorhombic crystalline particles from vibrational exciton calculations the interpretation is clear: acetylene particles formed at these temperatures (without further annealing) possess neither a single orthorhombic nor a single cubic crystal structure.

If not crystalline, what else could the structure of the particles be? The simplest alternative would be completely amorphous particles. At first glance, this seems consistent with the broad ν_5 band observed in Fig. 4.1a. Fig. 4.6a shows our simulation of the spectrum of completely amorphous acetylene particles, which were obtained by annealing of structures with initially randomized molecular orientations and positions as described in Section 4.3.2. The comparison with the experimental ν_5 band in Fig. 4.6f reveals not only a very different band shape but also a much broader band. These differences clearly suggest that the non-annealed aerosols are not completely amorphous.

We next consider partially amorphous and polycrystalline structures. Partially amorphous particles were constructed by first randomly tilting all the molecules in a particle within a cone defined by $\alpha = 60^{\circ}$ (see inset of Fig. 4.4 for definition of cone). Afterwards, the particles were annealed for 40 fs to avoid physically implausible relative positions of molecules. This was performed for both a cubic and an orthorhombic initial structure. The corresponding results are shown in Fig. 4.6b and d, respectively. The polycrystalline particles were generated by randomly placing multiple crystalline inclusions within a particle. The diameter of single



Figure 4.6: Calculated (a-e) and experimental (f) infrared spectra of non-crystalline C_2H_2 aerosol particles in the region of the ν_5 band. a: Completely amorphous particle. b: Partially amorphous particle derived from a cubic crystal structure. c: Polycrystalline particle derived from a cubic crystal structure. d: Partially amorphous particle derived from an orthorhombic crystal structure. c: Polycrystalline particle derived from an orthorhombic crystal structure. All particles were assumed to have a spherical shape, which represents the most likely shape for non-crystalline particles. Note that shape effects are much less pronounced for non-crystalline particles than for crystalline particles. The calculations for the amorphous and partially amorphous particles were performed with the EVE model. The spectra of the polycrystalline particles were calculated with the SVE model.

inclusions was varied between about 10 and 30% of the total particle diameter. We found, however, that the inclusion size, did not strongly affect the overall appearance of the infrared bands so that we show here only the results for the 10% inclusions. Again, this was performed for inclusions with a cubic as well as an orthorhombic crystal structure. Fig. 4.6c and e, respectively, show the resulting spectra. The comparison with the experiment immediately reveals two points. Firstly, the spectra of partially amorphous and polycrystalline particles agree much better with the experiment than those of completely amorphous particles. Although still slightly broader than in the experiment (trace f), their bands are narrower than that of the amorphous particle by almost a factor of two. Secondly, the spectra of partially amorphous and polycrystalline particles constructed from the cubic crystal structure (traces b, c) do not reproduce the experiment as well as those constructed from the orthorhombic crystal structure (traces e, f). This clearly indicates an underlying orthorhombic structure. The agreement of the spectra in traces d and e with the experiment is satisfying in terms of the band shape as the peak, the low frequency tail, and the high frequency shoulder ($\sim 785 \text{ cm}^{-1}$) of the observed spectrum are all reproduced. The major discrepancy between the spectra of partially amorphous and polycrystalline particles is the absence of a pronounced shoulder at 760 $\rm cm^{-1}$ and a slightly more pronounced low frequency tail in the spectrum of the polycrystalline particle. two characteristics that are also found in the experiment. Although this makes polycrystalline acetylene particles more likely, partially amorphous structures cannot be completely ruled out.

Fig. 4.7a and b show the calculated spectra of partially amorphous and polycrystalline particles constructed from the orthorhombic crystal structure in the CH–stretching region. Again, the ν_3 mode does not show characteristic features that would allow one to distinguish between the two types of non-crystalline particles. Both spectra fit equally well with the experiment.

From these observations, we conclude that the commonly found acetylene aerosol particles (Fig. 4.1a) are neither completely amorphous nor perfect crystals. Rather, observed spectral features are in agreement with polycrystalline particles or partially amorphous particles. Similar to the annealed particles discussed in the previous subsection, the crystalline domains of the polycrystalline particles are orthorhombic and not cubic. Likewise, the partially amorphous



Figure 4.7: Calculated (a and b) and experimental (c) infrared spectra of non-crystalline C_2H_2 aerosol particles in the region of the ν_3 band. a: Partially amorphous particle derived from a orthorhombic crystal structure. b: Polycrystalline particle derived from a orthorhombic crystal structure.

particles derive from an orthorhombic and not from a cubic structure. It is also worth noting that the crystalline particles formed by annealing (see previous subsection and Fig. 4.1b) were only stable for a short time (several minutes) after annealing before they converted back to the usually observed polycrystalline or partially amorphous form, showing again the infrared spectrum in Fig. 4.1a. The reason for this remains unclear. It might be a consequence of the particular annealing procedure we employed. Over time, the crystalline ethane shell that forms around the acetylene particles after annealing might destroy the acetylene crystal structure due to lattice mismatch. This scenario is consistent with the fact that distorted crystalline acetylene structures (e.g. polycrystalline) are energetically very close to the orthorhombic structure. Energy differences are estimated to be less than 2 kJ/mol from ABINIT calculations.^{135,136} In other words, by forming distorted structures, the acetylene core could easily compensate the lattice mismatch caused by the ethane shell. A comparison with uncoated crystalline acetylene particles is unfortunately not possible because annealing by condensation was the only way to obtain crystalline acetylene aerosols.

4.4.3 Excitation Densities

The results from Sections 4.4.1 and 4.4.2 reveal that acetylene aerosol particles after annealing (Fig. 4.1b and 4.3d) are crystalline with an orthorhombic crystal structure while non-annealed particles (Fig. 4.1b and 4.7e) are polycrystalline (or partially amorphous) derived from an underlying orthorhombic structure. The size scale of the ordered domains is very different between crystalline and polycrystalline (partially amorphous) particles. In the former case, the domains are equivalent to the particle size, in the latter case they are one third to one tenth as big (see Section 4.4.2). This symmetry breaking in the polycrystalline case modifies the exciton coupling and therefore the mode structure. The excitation density as defined in Eq. 4.7 provides information about this mode structure. Fig. 4.8 and 4.9 show the infrared spectrum (upper traces) and the excitation density (lower traces) of a crystalline orthorhombic particle and of a polycrystalline particle, respectively. The excitation densities are shown as a function of the wavenumber and the particle radius (radius of zero corresponds to the center of the particle) for particles with radii of about 6 nm. Dark colors indicate regions with high vibrational excitation and light colors regions with low vibrational excitation. The excitation density of the polycrystalline particle (Fig. 4.8) shows the strongest excitation density at wavenumbers in the center of the absorption band with decreasing densities towards both sides, consistent with the unstructured infrared spectrum. As a function of the particle radius, the excitation density is more or less uniform. This is consistent with the fact that the excitation density should be the same in all polycrystallites. Since delocalization of the vibrational wavefunctions over the entire particle is not possible in the polycrystalline case no mode structure of the bending mode is visible in the excitation density. The excitation density of the crystalline particle (Fig. 4.9), by contrast, clearly indicates the existence of the three components of the bending vibration (mode structure). It shows three distinct wavenumber regions with high excitation at $\sim 760 \text{ cm}^{-1}$, $\sim 770 \text{ cm}^{-1}$, and $\sim 785 \text{ cm}^{-1}$ corresponding to the three peaks in the infrared spectrum. These modes are more or less delocalized over the entire particle. The disappearance of this three-peak structure for the polycrystalline particle is a consequence of the smaller size scale of the ordered domains, which influences the exciton coupling.



Figure 4.8: Calculated infrared spectrum (upper trace) and excitation density (lower trace) of a polycrystalline particle derived from an orthorhombic crystal structure. The excitation density is shown as a function of the wavenumber and the particle radius. Dark regions: high excitation, light regions: low excitation.

4.5 Summary

Acetylene aerosols or particles coated with acetylene are likely candidates to act as condensation and crystallization nuclei for other substances such as ethane or methane in Titan's lower atmosphere. The phase of these acetylene aerosols is an important factor in determining their effectiveness as condensation/crystallization nuclei. In the present study, we have used midinfrared spectroscopy in combination with vibrational exciton calculations to analyze the phase behavior of acetylene aerosol particles. We found that the bending mode at about 770 cm⁻¹ is extremely useful for the spectral analysis while the CH–stretching mode around 3230 cm⁻¹ does not provide specific phase information.

The infrared spectra of acetylene aerosols formed at temperatures below 110 K show a char-



Figure 4.9: Calculated infrared spectrum (upper trace) and excitation density (lower trace) of a crystalline particle with an orthorhombic crystal structure. The excitation density is shown as a function of the wavenumber and the particle radius. Dark regions: high excitation, light regions: low excitation.

acteristic structureless, broad bending transition with a long tail towards lower wavenumbers (Fig. 4.1a). Our analysis reveals that these particles are polycrystalline or partially amorphous. The polycrystalline domains are orthorhombic in structure not cubic. Similarly, the partially amorphous particles are derived from an orthorhombic structure not a cubic one. Crystalline particles are usually not observed for acetylene, but could be engineered by annealing which resulted in an orthorhombic crystal structure, clearly identified in the infrared spectrum by the three characteristic peaks of the bending vibration (Fig. 4.1b). It is noteworthy that these observations were independent of the aerosol particle size in the size range between about 10 to 500 nm. This is consistent with the results from modeling which also show that the change in size over this range has a negligible influence on the spectral features of the different phases.

In agreement with the bulk phase properties, we never observed any signs of the high– temperature cubic crystal structure below the phase transition temperature. All particles had an orthorhombic structure or were derived from orthorhombic structures. This result is in contrast to an earlier interpretation by Dunder and Miller, ¹⁰⁰ which was based on qualitative arguments rather than modelling. The analysis in terms of the vibrational exciton model demonstrates that such qualitative arguments are insufficient for the interpretation of aerosol infrared spectra.

Chapter 5

Infrared Spectroscopy and Modeling of Co-crystalline $CO_2 \cdot C_2H_2$ Aerosol Particles. Part 1: The Formation and Decomposition of Co-crystalline $CO_2 \cdot C_2H_2$ Aerosol Particles

5.1 Introduction

As discussed in Chapters 3 and 4, C_2H_2 , CO_2 and mixed C_2H_2/CO_2 particles play an important role in the atmospheres of a number of planets and moons.^{71–73,86,87,137} They can directly influence the radiative balance and thus the climate by absorbing and scattering the solar radiation.^{64,86} They are involved in cloud formation either as a major cloud component or as cloud condensation nuclei. Furthermore, the large surface area of aerosol particles can provide reactive sites for various chemical processes.¹³⁸ As atmospheres will contain many molecular species, multicomponent aerosols are often of particular interest.^{139–141} Condensation of different compounds usually happens at various altitudes in planetary atmospheres. This leads to a wealth of possible multicomponent aerosol particle structures such as core-shell structures, inclusions, or in rare cases even the formation of particles with mixed crystalline structures.

 C_2H_2 is known to form a wide range of co-crystals when paired with other small molecules.¹⁴²

As CO₂ and C₂H₂ both exhibit similar sublimation pressures over a wide range of temperatures,¹⁴³ form cubic crystalline phases (Pa3),^{105,144} possess electric quadrupole moments,¹⁴⁵ and are linear molecules of similar dimensions, these two molecules could potentially form a co-crystal. This $CO_2 \cdot C_2 H_2$ phase has indeed been observed. By condensing mixtures of the two gases onto a zinc selenide window, Gough et al. were able to confirm the formation of the $CO_2 \cdot C_2 H_2$ co-crystal using infrared (IR) spectroscopy.^{146–148} This was possible due to the sensitivity of the vibrational frequencies of C_2H_2 and CO_2 to the crystalline environment in which they are found. Significant shifts in most of the IR active bands led to the identification of a mixed $CO_2 \cdot C_2 H_2$ phase. However, the structure of this co-crystal was not established. A surprising observation from this work was that this $CO_2 \cdot C_2H_2$ phase was metastable and over time would decompose into domains of its pure components.^{147,148} This decomposition was also studied using IR spectroscopy. The observed metastability explains why in a recent x-ray diffraction study of various C_2H_2 co-crystals presented by Kirchner et al. it was not possible to prepare $CO_2 \cdot C_2 H_2$ co-crystals.¹⁴² In that work, samples were annealed prior to measurements and this process likely decomposed the $CO_2 \cdot C_2H_2$ phase before it could be properly characterized.

In the current and subsequent chapter we study $\text{CO}_2 \cdot \text{C}_2\text{H}_2$ aerosols. In this chapter, we focus on the experimental formation and decomposition of the $\text{CO}_2 \cdot \text{C}_2\text{H}_2$ aerosols and the analysis of the spectra after decomposition. Similar to Gough et al. we rely on IR measurements for characterization. As we are studying aerosols not thin films, measurements are performed directly in the bath gas cooling cell where the aerosol particles are formed. These in situ measurements avoid any potential complications that might be introduced if the samples were collected on substrates. Furthermore, this setup allows us to record spectra with different architectures (core-shell and mixed) that may be of interest in planetary atmospheres. IR spectra of three different types of aerosol particles are discussed: pure CO_2 and pure C_2H_2 aerosol particles (Section 5.4.1), $\text{CO}_2 \cdot \text{C}_2\text{H}_2$ aerosol particles formed by the condensation of gas mixtures of C_2H_2 and CO_2 (Section 5.4.2), and mixed aerosol particles containing domains of pure C_2H_2 and pure CO_2 formed either by the decomposition of the $\text{CO}_2 \cdot \text{C}_2\text{H}_2$ co-crystal or by the sequential condensation of the two gases (Section 5.4.3). Our discussion primarily focuses on the conditions that allow for the formation of $CO_2 \cdot C_2H_2$ particles and the type of domains present in the particles after the $CO_2 \cdot C_2H_2$ phase decomposes into its pure components.

In Chapter 6 we analyze the spectra of the $CO_2 \cdot C_2H_2$ co-crystalline phase and we examine how the $CO_2 \cdot C_2H_2$ unit cell influences the position and strength of the IR bands using density functional theory. Dielectric functions that describe $CO_2 \cdot C_2H_2$ are constructed from these parameters and incorporated into model particle shapes. This process allows for the spectra of $CO_2 \cdot C_2H_2$ particles to be modeled. A major goal of the work in Chapter 6 is the determination of possible crystal structures for the $CO_2 \cdot C_2H_2$ phase.

5.2 Experimental Section

Mixed $\text{CO}_2 \cdot \text{C}_2 \text{H}_2$ aerosols were generated in a low temperature bath gas cooling cell and spectroscopically characterized in-situ in the aerosol phase by rapid-scan Fourier transform infrared spectroscopy between 600 and 4000 cm⁻¹. The experimental setup was described in Chapter 4. Briefly, aerosol particles were formed via injection of warm sample gas mixtures (0.1-0.3% CO₂ (99.998%) and C₂H₂ (99.6%) diluted in helium (99.999%)) into a pre-cooled bath gas (helium gas at pressures between 500-900 mbar and at a temperature of 78 K). All gases were further cleaned before use in a liquid nitrogen trap. Injection of warm sample gases into the pre-cooled bath gas leads to supersaturation, which in turn results in the formation of aerosol particles. The injection was controlled by magnetic valves, with typical injection times of 500-1000 ms. All infrared spectra were recorded with a spectral resolution of 0.5 cm⁻¹.

For the mixed particles, we employed two different injection schemes. Homogeneously mixed binary aerosols were formed by co-condensation of premixed CO_2 and C_2H_2 gas samples. Core-shell aerosols were generated by sequential injection of the two gases. The time delay between the two sequential injections was 500 ms. This delay was adjusted to ensure optimal coating of the core but avoid any homogeneous mixing of the two substances.

5.3 Computational Methods

In Section 5.4.3, the ν_2 and ν_3 bands of crystalline CO₂ particles are modeled using the bulk optical properties of cubic CO₂ and classical electrostatics.⁴ The dielectric function of CO₂

was constructed using the following expression:

$$\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) \tag{5.1}$$

where

$$\epsilon'(\omega) = \epsilon_{\infty} \left(1 + \sum_{m=1}^{N} \frac{(\omega_{L_m}^2 - \omega_{T_m}^2)(\omega_{T_m}^2 - \omega^2)}{(\omega_{T_m}^2 - \omega^2)^2 + (\omega\gamma_m)^2} \right)$$
(5.2)

$$\epsilon''(\omega) = \epsilon_{\infty} \sum_{m=1}^{N} \frac{(\omega_{L_m}^2 - \omega_{T_m}^2)(\omega\gamma_m)}{(\omega_{T_m}^2 - \omega^2)^2 + (\omega\gamma_m)^2}$$
(5.3)

The number of optical modes was set to three (N = 3). The transverse optical (TO) frequencies (ω_T) of these modes were 655, 661 and 2345 cm⁻¹ with corresponding longitudinal optical (LO) frequencies (ω_L) at 660, 672 and 2377 cm⁻¹, respectively. These modes were based on a fit to refractive index data from a thin film study.¹⁴⁹ The high-frequency dielectric constant was also taken from that work ($\epsilon_{\infty} = 1.54$). When calculating spectra, the damping of each mode (γ_m) is listed in the corresponding figure caption.

All modes and spectra were calculated within the electrostatic approximation (see Section 1.2). With this approach, the wavelength of light is assumed to be much larger than any of the particle dimensions that it is impinging on.⁴ This limit is satisfied for all of the experimentally prepared particles that are considered here. One advantage of using this method is that, in some cases, analytical expressions for the surface modes of an object can be derived. This allows for the concise evaluation of the surface modes over all possible parameters that define an object. The objects considered here are (i) a spherical shell, (ii) a prolate and oblate ellipsoid, and (iii) clusters of spherical particles. These are used as models for the three types of particles that are of experimental interest: (i) core-shell particles, (ii) various elongated or anisotropic particles, and (iii) clusters of closely spaced particles.

Surface modes were determined by examining the expression that defines the polarizability of an object in a uniform electric field. The frequency at which the denominator of the polarizability vanishes corresponds to a surface mode. In the limit of the electrostatic approximation, these surface modes dominate the absorption spectrum of an object. For spherical shells and ellipsoids polarizability expressions are well-known.⁴ In the case of a spherical shell with an inner radius of a and an outer radius of b the condition that the dipole modes satisfy is

$$(\epsilon(\omega) + 2\epsilon_m)(\epsilon_c + 2\epsilon(\omega)) + (a/b)^3(2\epsilon(\omega) - 2\epsilon_m)(\epsilon_c - \epsilon(\omega)) = 0$$
(5.4)

where ϵ_c and ϵ_m are the dielectric functions for the core and medium, respectively. In all calculations these were simply set to one. For an ellipsoid, dipole modes satisfy

$$3\epsilon_m + 3L(\epsilon(\omega) - \epsilon_m) = 0 \tag{5.5}$$

where the geometrical factor L is dependent on whether or not the ellipsoid is oblate or prolate, the direction of the incident polarization of light, and the length of the various ellipsoidal axes. Expressions for this factor are given in Ref. 4.

For clusters of spheres, analytical expressions only exist for a few simple arrangements.¹⁵⁰ In more complicated situations, which are of interest here, a more general method needs to be used. This can be developed as follows: in a distribution of spheres the dipole moment of each sphere is

$$\mathbf{P}_i = \epsilon_m \alpha_i \mathbf{E}_{\text{loc}}(\mathbf{r}_i) \tag{5.6}$$

where $\mathbf{E}_{loc}(\mathbf{r}_i)$ is the electric field at sphere *i* and the polarizability of each sphere, α_i , is

$$\alpha_i = 4\pi a_i^3 \frac{\epsilon(\omega) - \epsilon_m}{\epsilon(\omega) + 2\epsilon_m} \tag{5.7}$$

where a_i is the radius of the sphere. In the absence of an external field, a system of coupled equations for N spheres can be defined by

$$\mathbf{P}_{i} = \epsilon_{m} \alpha_{i} \sum_{j \neq i}^{N} \mathbf{A}_{ij} \mathbf{P}_{j}$$
(5.8)

where

$$\mathbf{A}_{ij} = \frac{1}{4\pi\epsilon_m} \frac{(3\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij} - \mathbf{I})}{|\mathbf{r}_{ij}|^3}$$
(5.9)

and \mathbf{r}_{ij} is the center-to-center distance vector between spheres *i* and *j*, $\hat{\mathbf{r}}_{ij}$ is the corresponding unit vector, and **I** is a 3 × 3 identity matrix.

The system of equations generated by equation 5.8 can be written as an eigenvalue problem in the form of

$$\mathbf{BP} = \mathbf{\Lambda P} \tag{5.10}$$

where

$$\Lambda = \frac{\epsilon(\omega) + 2\epsilon_m}{\epsilon(\omega) - \epsilon_m} \tag{5.11}$$

and the elements of \mathbf{B} are defined by

$$\mathbf{B}_{ij} = \begin{cases} 0, & i = j \\ 4\pi\epsilon_m a_i^3 \mathbf{A}_{ij}, & i \neq j \end{cases}$$
(5.12)

Although there are 3N modes in a system of N spheres, only the strongest optically active modes are considered here (these have been called "in-phase" modes for one-dimensional assemblies).¹⁵⁰ These modes can easily be determined by examining the dipole moments from an eigenvector **P**. It is important to note that other modes (associated with higher order moments) can be important in systems of clustered spheres even if the overall dimensions of the cluster satisfies the electrostatic limit.¹⁵¹ Therefore, several calculations using the above approach were compared to results obtained using Mie theory for coupled spheres.¹⁵² The differences between the coupled Mie theory and electrostatic calculations were found to be minor and, as an approximation, the electrostatic results were judged to be satisfactory.

5.4 Results and Discussion

5.4.1 Pure CO_2 and Pure C_2H_2 Aerosols

Prior to considering aerosol particles composed of the $\text{CO}_2 \cdot \text{C}_2\text{H}_2$ co-crystal, we first summarize the results for pure C_2H_2 (Fig. 5.1a) and pure CO_2 (Fig. 5.1g) aerosols. In Chapter 4, it was shown that pure C_2H_2 preferentially forms orthorhombic, polycrystalline particles under conditions similar to those studied here. This polycrystalline phase makes analysis of the particle shape through the examination of the IR active fundamental modes – the ν_5 bend and the ν_3 anti-symmetric stretch – difficult (see Chapter 4 for a discussion of this issue). However, these polycrystalline particles are likely globular in shape. The bands also show little change in shape over time, suggesting that the particles retain their globular shape over the course of the measurements. In the C₂H₂ orthorhombic phase the ν_5 vibration has three optical modes and the ν_3 vibration has two optical modes. For a particle that is roughly spherical in shape there should therefore be three peaks for the ν_5 band and two peaks for ν_3 band. For the ν_5 band, the approximate locations of the three peaks are indicated in Fig. 5.1a, although the polycrystalline nature of the material makes a precise assignment difficult. For the ν_3 band, the frequencies of the two optical modes are nearly identical (see Chapter 6). Therefore, only one observable peak is expected for this band. Its location is also indicated in Fig. 5.1.

Pure CO_2 aerosols have been extensively studied, ^{84,109,116–118,153–157} and the particles formed under the conditions used here have the same cubic crystal structure as bulk, crystalline CO_2 for similar temperatures (T = 78 K). When studying particles of this phase it is important to note that the two IR active fundamental modes of CO_2 – the ν_2 bend and the ν_3 anti-symmetric stretch – possess significant LO-TO splittings. Consequently, the peaks found in these bands will have a strong dependence on particle shape. This effect has its molecular origin in strong transition dipole coupling (vibrational exciton coupling).^{18,19,109} As we have discussed and verified by modeling in previous publications,^{84,118} the time evolution of these bands is the result of a shape change from cube-like particles to particles with increasingly elongated shapes. The ν_3 band of the cube-like particles features a strong central peak (2361.0 cm⁻¹) with a weak, higher energy side peak (2371.2 cm⁻¹). In the case of elongated particles, a lower energy peak dominates the spectra while a smaller, higher energy peak remains. This lower energy peak is already present in Fig. 5.1g at 2346.9 cm⁻¹. At longer times the absorbance of this peak increases relative to the other peaks in this band. The smaller LO-TO splittings found in the optical modes of the $CO_2 \nu_2$ vibration means that shape-dependent features are more compressed than in the ν_3 band. However, the overall band shapes are similar to those found in the ν_3 band. In Fig. 5.1 only the dominant peaks for each optical mode are indicated.

5.4.2 $CO_2 \cdot C_2 H_2$ Aerosols Immediately after Formation

The initial formation of the $CO_2 \cdot C_2H_2$ co-crystal in the aerosol phase was confirmed through the examination of the positions of several of the fundamental and combination bands of both



Figure 5.1: Experimental IR spectra for aerosols composed of CO_2 and C_2H_2 mixed in various ratios. The mole fraction of CO_2 present in each sample is indicated next to its corresponding trace. The location of peaks associated with pure CO_2 and pure C_2H_2 are indicated with a dashed line while the location of peaks associated with $CO_2 \cdot C_2H_2$ are indicated with a solid line. Details of the exact composition of (a) through (g) are summarized in Table 5.1. All spectra are recorded at time t = 0 s.

 C_2H_2 and CO_2 (Fig. 5.1b-f). Note that all of these spectra show features arising from pure CO_2 and pure C_2H_2 in addition to the features from the co-crystalline phase. Relative to their positions in the respective spectra of the pure aerosols (Fig. 5.1a for pure C_2H_2 and Fig. 5.1g for pure CO₂), the C₂H₂ ν_3 band was shifted by +28.5 cm⁻¹ while the CO₂ ¹³C- ν_3 , $2\nu_2 + \nu_3$ and $\nu_1 + \nu_3$ bands were shifted by -5.3, -11.4 and -9.8 cm⁻¹, respectively. The wavenumbers of these peaks are consistent with what has been reported by Gough et al. for the $CO_2 \cdot C_2H_2$ co-crystal;^{146–148} confirming the formation of the same $CO_2 \cdot C_2H_2$ phase that was found in the thin films from that work. For the optical modes with larger LO-TO splittings in their pure crystalline phases (the CO₂ ν_2 and C₂H₂ ν_5 bands), the band positions of the CO₂·C₂H₂ aerosol differ from those reported by Gough et al. This difference is almost certainly due to a dependence of band positions on particle shape, indicating that a large LO-TO splitting is also present in the $CO_2 \cdot C_2 H_2$ phase. The role of this effect is discussed in detail in Chapter 6. A large LO-TO splitting should also be present in the $CO_2 \nu_3$ band of the co-crystal which, in the cubic CO_2 phase, has the largest LO-TO splitting of any of the modes discussed here. However, this band is not discussed by Gough et al. so there is no thin film reference for comparison (presumably this band was saturated in their spectrum).

In Fig. 5.1, the mole fraction of injected CO₂ is indicated on each trace and Table 5.1 lists the mole fractions of the pure and complexed (co-crystalline) components for each trace. All of these fractions were calculated using the relative absorbance intensities of the C₂H₂ ν_3 band and the CO₂ $\nu_1 + \nu_3$ band for both the pure and complexed substances. These intensities were converted into mole fractions using the relative extinction coefficients calculated by Gough et al.¹⁴⁷

Fig. 5.1 and Table 5.1 both show that while it was possible to prepare $CO_2 \cdot C_2H_2$ aerosols with nearly no pure CO_2 (Fig. 5.1c) it was not possible to prepare $CO_2 \cdot C_2H_2$ aerosols without a significant amount of pure C_2H_2 . This is true even for the cases where a slight (Fig. 5.1d) or large (Fig. 5.1e and f) excess of CO_2 is injected. Despite the expectation that all of the C_2H_2 would be complexed in these situations, there is actually a *decrease* in the amount of $CO_2 \cdot C_2H_2$ relative to the total amount of C_2H_2 present. This result is similar to what was reported by Gough et al.¹⁴⁷ In that work, the authors speculated that pure, crystalline CO_2 ,

	Injected fraction		Aerosol fraction			
	$\chi_{\rm CO_2}$	$\chi_{\mathrm{C_2H_2}}$	$\chi_{\rm CO_2}$ pure	$\chi_{\rm CO_2}$ complexed	$\chi_{C_2H_2}$ pure	$\chi_{C_2H_2}$ complexed
a	0.00	1.00	0.00	0.00	1.00	0.00
b	0.26	0.74	0.18	0.08	0.64	0.10
с	0.35	0.65	0.03	0.32	0.28	0.37
d	0.52	0.48	0.46	0.06	0.40	0.08
e	0.68	0.32	0.67	0.01	0.30	0.02
f	0.77	0.23	0.76	0.01	0.22	0.01
h	1.00	0.00	1.00	0.00	0.00	0.00

Table 5.1: Mole fractions of the injected gases and of the components present in the mixed $CO_2 \cdot C_2 H_2$ aerosols.

which will simultaneously be formed when an excess of CO_2 is used, inhibits the formation of the $CO_2 \cdot C_2H_2$ phase.¹⁴⁷ This type of effect also occurs when attempting to use an excess of C_2H_2 to ensure that all of the CO_2 is complexed, although it is not as significant (compare the amount of complexed $CO_2 \cdot C_2H_2$ present in Fig. 5.1c with 5.1e). In this case, pure C_2H_2 would need to inhibit the formation of the $CO_2 \cdot C_2H_2$ phase.

A surprising result is that the equimolar mixture of CO_2 and C_2H_2 (Fig. 5.1d) contained such a large fraction of pure components relative to those that are complexed. This differs from Gough et al. where the spraying of equimolar mixtures led to the nearly exclusive formation of $CO_2 \cdot C_2H_2$ in thin films.¹⁴⁷ Therefore, the injection of equimolar mixtures into the bath cooling cell was investigated further. It was found that when the pressure of the gas mixture was increased, so too did the amount of co-crystalline $CO_2 \cdot C_2H_2$ that initially formed. For instance, when this pressure was doubled from the conditions used in Fig. 5.1, a three- to fourfold increase in the amount of $CO_2 \cdot C_2H_2$ formed in the aerosol occurred (spectra not shown). An explanation for this dependence may lie in the formation kinetics of the co-crystalline phase. However, these kinetics were not studied in detail. Finally, an analysis of the co-crystalline phase with a 1:1 mixing ratio of $C_2H_2:CO_2$ is provided in Chapter 6.



Figure 5.2: Time dependent IR spectra for an aerosol composed of CO_2 and C_2H_2 . The mole fraction of CO_2 is 0.35.

5.4.3 $CO_2 \cdot C_2H_2$ Aerosols after the Decomposition of the $CO_2 \cdot C_2H_2$ Co-crystalline Phase

5.4.3.1 Overview

Similar to Gough et al. we observed the decomposition of the co-crystalline $CO_2 \cdot C_2H_2$ phase into pure C_2H_2 and pure CO_2 in all of the prepared $CO_2 \cdot C_2H_2$ aerosols (over a time period of about 12 minutes). Fig. 5.2 shows spectra of $CO_2 \cdot C_2H_2$ aerosols recorded at different times during decomposition. The mole fraction of injected CO_2 for this sample is 0.35. We focus on this sample as, of all the aerosols that were prepared, it contained the largest mole fraction of co-crystalline $CO_2 \cdot C_2H_2$ (Table 5.1). Over the period of time studied in Fig. 5.2 the decomposition of $CO_2 \cdot C_2H_2$ proceeds to near completion. In this section, we focus on the analysis of the IR spectra of the decomposed aerosols at t = 730 s. As the optical properties of the crystalline phases of pure CO_2 and pure C_2H_2 under similar conditions have been previously studied (Section 5.4.1), this is simpler than studying the aerosols immediately after formation (studied in Chapter 6) or prior to the completion of decomposition.



Figure 5.3: Diagrams for possible architectures of aerosol particles after decomposition of the co-crystalline $CO_2 \cdot C_2H_2$ phase: (a) CO_2 domains embedded in a C_2H_2 matrix, (b) CO_2 shell on a C_2H_2 core, and (c) C_2H_2 shell on a CO_2 core.

As the decomposition of co-crystalline $\text{CO}_2 \cdot \text{C}_2\text{H}_2$ proceeds, so too must the phase separation of pure CO_2 and pure C_2H_2 in the aerosol particles. Gough et al. hypothesized that this process results in the formation of "micro crystallites of CO_2 embedded in a softer, deformed matrix of C_2H_2 ." ¹⁴⁸ One interpretation of this type of structure, for aerosol particles, is depicted in Fig. 5.3a. However, there exist many other possible architectures aside from this. For example, core-shell structures (Fig. 5.3b and c). As these structures can be experimentally prepared through the sequentially injection of C_2H_2 and CO_2 , it is straightforward to compare the decomposed aerosol spectra to those of actual core-shell particles. These results will aid in characterizing the decomposed products.

Fig. 5.4 compares the spectra of core-shell structures prepared through the sequential injection of the pure components to the spectrum of the decomposed (t = 730 s) aerosols. Two different types of core-shell particles were prepared: (i) CO₂ shell–C₂H₂ core particles (Fig. 5.4b) and (ii) C₂H₂ shell–CO₂ core particles (Fig. 5.4c). As expected the C₂H₂ ν_5 and ν_3 bands give little information on particle architecture. For these bands, shapes and peak positions across Fig. 5.4a-c are too similar to allow for any differentiation between the various aerosols. The CO₂ bands, by contrast, show distinct differences in band shapes and peak positions. Examination of the CO₂ ν_3 band of the two core-shell structures that were prepared (Fig. 5.4b and c) reveals that, in terms of overall band shape, the spectrum of the CO₂ shell–C₂H₂ core structure provides the better match to Fig. 5.4a. However, the position of the dominant peak in the spectrum of the C₂H₂ shell–CO₂ core structure (2361.0 cm⁻¹) shows slightly better agreement with that of the decomposed aerosol (2357.2 cm⁻¹) than that of the CO₂ shell–C₂H₂ core (2351.1 cm⁻¹). As discussed in Section 5.4.1, all of the shape-



Figure 5.4: Comparison between experimental IR spectra of (a) decomposed $CO_2 \cdot C_2H_2$ aerosols (t = 730 s in Fig. 5.2), (b) CO₂ shells formed on a C_2H_2 core (note the scale factor of three for the CO₂ bands), and (c) C_2H_2 shells formed on a CO₂ core. As the decomposition of $CO_2 \cdot C_2H_2$ in (a) was not 100% complete (see Fig. 5.2 at t = 730 s) small bands associated with residual co-crystalline $CO_2 \cdot C_2H_2$ were subtracted using an appropriate $CO_2 \cdot C_2H_2$ spectrum.

dependent information that is found in the ν_3 band is also present in ν_2 band. However, due to the smaller LO-TO splitting it is more compressed. Therefore, throughout the remaining discussion we focus entirely on the CO₂ ν_3 band.

5.4.3.2 CO_2 Shells with C_2H_2 Cores

For CO₂ shells, the sensitivity of peak positions to shell thickness was studied in Chapter 3. It is possible that the difference in peak positions between the CO₂ bands of Fig. 5.4a and b is a consequence of a small difference in thickness. Note that the mole fraction of CO₂ is smaller in the aerosol whose spectrum is shown in Fig. 5.4b than the aerosol whose spectrum is shown in Fig. 5.4a. This means that, in this case, shells prepared through sequential injection are thinner than any shells formed through decomposition of the CO₂·C₂H₂ phase.

When dealing with the IR absorption spectra of dielectric shells, it is well-known that for constant core size an increase in the shell thickness causes the splitting between the two dominant absorption peaks to decrease. Therefore, it is possible that the CO_2 shells whose spectrum is shown in Fig. 5.4b are too thin to give a good match to the spectrum in Fig. 5.4a. Unfortunately, experimental attempts to prepare thicker shells through sequential injection were unsuccessful. Simply increasing the mole fraction of injected CO_2 in order to prepare thicker shells resulted in spectra which were best characterized as being a mixture of pure CO_2 particles and CO_2 shell– C_2H_2 core particles. Therefore, the possibility of thicker shells was explored through calculations using the analytical expressions for the surface modes of a spherical shell. These calculations allow the ratio of CO_2 to C_2H_2 to be easily varied.

For the spherical shell, the two surface modes of the $CO_2 \nu_3$ band are plotted on the leftside of Fig. 5.5 as a function of the scale parameter b/a, where b is the radius of the outer sphere and a is the radius of the inner sphere. On the right-side of Fig. 5.5 the calculated spectrum for a ratio of b/a = 1.26 illustrates where two of these surface modes would be found in a spectrum. Next, we assume that the spectrum in Fig. 5.4b is that of a spherical shell whose core and shell volumes are determined by the amount of injected C_2H_2 and CO_2 , respectively. When the molar volumes for cubic CO_2 and orthorhombic C_2H_2 are used, ^{105,144} this assumption yields a scale parameter of b/a = 1.08. In order for the lower energy surface mode in Fig. 5.5 to shift by 6.1 cm^{-1} (similar to what is observed when going from Fig. 5.4b to a), b/a would need to change from 1.08 to 1.47. Such a change would require that the mole fraction of CO_2 present in the aerosol increase from 0.24 to 0.72. When moving from Fig. 5.4b to a, the actual increase is from 0.24 to 0.35. Such a large discrepancy between the modeled and experimental results means that the formation of a CO_2 shell-like structure through decomposition is unlikely. Even if other factors are taken into consideration with this model (e.g. using a shell model that is non-spherical or altering the dielectric constant of the core), the requirements of using CO_2 shells to account for the band shapes in Fig. 5.4a will always demand differences in thicknesses that far exceed experimental errors. Therefore, this structure seems unlikely.

5.4.3.3 C_2H_2 Shells with CO_2 Cores

Next we consider whether or not the spectrum of the C_2H_2 shell- CO_2 core (Fig. 5.4c) can be reconciled with that of Fig. 5.4a. As discussed in Section 5.4.1, when pure CO_2 is injected into the cell the shape of the $CO_2 \nu_2$ and ν_3 bands show a strong temporal dependence believed



Figure 5.5: Left side: position of surface modes for the ν_3 band of a spherical CO₂ shell. These modes are plotted as a function of the outer radius, b, divided by the inner radius, a. Right side: a sample spectrum for b/a = 1.26. For the calculated spectrum, the damping constant in the dielectric function was set to 0.2% of ω_T .

to originate from the formation and growth of elongated particles. In the sequential injection of CO₂ followed by C₂H₂ it was found that this type of evolution would halt once C₂H₂ was injected. This was presumed to be due to the coating of CO₂ particles with C₂H₂. During the decomposition of the co-crystalline CO₂·C₂H₂ phase, any growth of CO₂ particles inside a C₂H₂ matrix would be similarly blocked. However, obtaining experimental IR spectra similar to the one in Fig. 5.4a using a sequential injection method again proved difficult. The main discrepancy is that the low energy peak at 2346.9 cm⁻¹ in Fig. 5.4c is not found in Fig. 5.4a. As the position of this lower energy mode is very sensitive to the aspect ratio of the elongated particle, it is possible that the aspect ratio of the particles whose spectrum is shown in Fig. 5.4c is simply too large in comparison to the particles whose spectrum is shown Fig. 5.4a. If the aspect ratio was decreased the low energy peak, located at 2346.9 cm⁻¹ in Fig. 5.3c, could shift into the region between 2355 and 2361 cm⁻¹. This would lead to a better correspondence with Fig. 5.3a.

As it was difficult to experimentally produce particles with specific aspect ratios, the influence of this parameter was modeled using the electrostatic solution to an ellipsoid.⁴ Rod-like particles were modeled using a prolate spheroid (Fig. 5.6a and b) while disc-like particles were modeled using an oblate spheroid (Fig. 5.6c and d). The pure CO_2 aerosol whose spectrum was shown in Fig. 5.1g primarily consists of cube-like particles (i.e. not elongated). Within this ellipsoidal model, these can be taken as a reference for particles with an aspect ratio of one. For the CO₂ ν_3 band, the difference in peak position between the dominant peak in the spectrum shown in Fig. 5.1g and that of Fig. 5.4a is about 3.8 cm⁻¹. For the rod-like particles, such a change occurs when the aspect ratio is increased from 1 to 1.5, while for the disc-like particles the aspect ratio needs to increase from 1 to 2.1. The spectra for these two aspect ratios are plotted in Fig. 5.6b and d, respectively. For the disc-like particle, the ratio of peak heights associated with the two ellipsoidal modes fits much better to the experimental spectrum in Fig. 5.4a than the rod-like particle shape. Furthermore, the splitting between the two surface modes of the disc-like ellipsoid (10.6 cm⁻¹) shows a better correspondence to the observed splitting of 12.5 cm⁻¹ than the rod-like ellipsoid (5.5 cm⁻¹). Therefore, disc-like CO₂ particles with an axis ratio of around 2.1 coated with C₂H₂ could explain the spectrum in Fig. 5.4a.

5.4.3.4 CO₂ Domains in a C₂H₂ Matrix

Next we consider the possibility that the aerosol particles resemble the situation shown in Fig. 5.3a. Unlike the case of the core-shell particles, where sequential injection provides a means to experimentally produce the structures depicted in Fig. 5.3b and c, there is no obvious experimental method that allows for the direct formation of a particle similar in structure to Fig. 5.3a. Therefore, we have to rely entirely on modeling for such particles. As a model we use clusters/assemblies of spherical CO_2 particles. Fig. 5.7 shows the wavenumbers of the strongest optically active modes for one-, two-, and three-dimensional assemblies of spheres. As discussed in Section 5.3, these modes will dominate the spectrum when a cluster of spheres is much smaller than the wavelength of light impinging on it.

The one- and two-dimensional examples in Fig. 5.7 illustrate that interparticle coupling can easily account for the difference in peak position between an isolated particle (Fig. 5.1g) and a system that potentially contains particles that are clustered together (Fig. 5.4a). Furthermore, the band shape of the two-dimensional structure (not shown) is very similar to that of the disc-like ellipsoid, which was shown to have a good correspondence to the shape in Fig. 5.4a. However, the ordered structures in Fig. 5.7 are not satisfactory models of the particle depicted in Fig. 5.3a. Placing the spheres into random positions within a large geometric domain



Figure 5.6: (a) Position of the surface modes for the ν_3 band of a prolate CO₂ spheroid (rodlike particle). (b) A sample spectrum for a prolate CO₂ spheroid defined by b/a = 1.5. (c) Position of surface modes for the ν_3 band of an oblate CO₂ spheroid (disc-like particle). (d) A sample spectrum for an oblate CO₂ spheroid defined by b/a = 2.1. For the calculated spectra, the damping constant in the dielectric function was set to 0.2% of ω_T .



Figure 5.7: Position of the dominant optically active modes for one-, two- and threedimensional assemblies of CO_2 spheres. As the three-dimensional assemblies contain many optically active modes only the position of the dominant peak of each overall spectrum is listed.

(representing the C_2H_2 matrix) is a more suitable approach. This was examined by randomly packing CO₂ spheres into either (i) a larger C_2H_2 sphere or (ii) a larger C_2H_2 cube. These larger structures had dimensions that were 10 to 20 times the radii of the spheres packed inside. When spheres were packed inside at low densities the CO₂ bands resembled that of isolated CO₂ spheres while at high packing densities CO₂ spectra began to resemble those of the domain that the randomly placed spheres were chosen to fill. Therefore, unless these spheres are tightly packed into a disc-like structure, they will not be able to account for the overall band-shape and peak position observed in Fig. 5.4a. This means that a particle model similar to that depicted in Fig. 5.3a is unlikely as a random distribution of separated CO₂ crystallites is insufficient to cause the observed shift.

For completeness we also consider the opposite situation: C_2H_2 domains embedded inside a CO_2 matrix (i.e. the materials in Fig. 5.3a are interchanged). The formation of such particles under these experimental conditions is problematic for two reasons. First, such a growth process would be inconsistent with the study presented by Gough et al.¹⁴⁸ In that work, kinetic data was shown to fit very well with a model of CO_2 domains growing inside of a C_2H_2 matrix. Secondly, the mole fraction of CO_2 present in the aerosols whose spectrum is shown in Fig. 5.4a is 0.35. This gives a total volume of CO_2 present in a particle consisting of domains of pure CO_2 and pure C_2H_2 of about 31%. Such a small volume would mean that the C_2H_2 domains would be very densely packed inside such a particle. This would lead to situations where the CO_2 matrix is broken up into smaller domains throughout the particle. In this case, the above analysis concerning CO_2 domains inside a C_2H_2 matrix would again be valid. As was already discussed, the optical properties of this structure are not consistent with the spectrum shown in Fig. 5.4a.

5.4.3.5 Summary of Analysis

Based on the above analysis, the modeled spectra of disc-like ellipsoids consisting of a CO_2 core and a C_2H_2 shell provides the best match to the observed CO_2 bands of the decomposed $CO_2 \cdot C_2H_2$ aerosols (Fig. 5.4a). The observed and modeled spectra of these particles are shown in Fig. 5.8. No attempt was made to model a distribution of ellipsoids or structural changes at the CO_2 - C_2H_2 interface although this undoubtedly plays an important role in some of the



Figure 5.8: Comparison between experimental (Fig. 5.4a) and modeled spectra after decomposition of the originally co-crystalline $\text{CO}_2 \cdot \text{C}_2\text{H}_2$ particles. The modeled spectrum is that of an oblate CO_2 spheroid (disc-like particle) with b/a = 2.1. Damping was set to 0.45% of ω_T for each mode.

discrepancies between the two spectra. Including either of these effects would broaden the bands in the calculated spectra. The satisfactory correspondence between the spectrum of the disc-like ellipsoid and the experimental spectrum does not necessarily mean that the CO_2 domains are perfectly ellipsoidal, but rather they can be described as being roughly disc-like.

Overall, this type of structure is also consistent with the decomposition mechanism proposed and modeled by Gough et al. (CO₂ particles in a deformed C₂H₂ matrix). Furthermore, the small aspect ratios mean that this model does not require the formation of particles with unrealistic aspect ratios during decomposition (e.g. it would only require the coalescence of several roughly spherical crystallites of CO₂ inside a C₂H₂ matrix). Finally, from Fig. 5.6 it can be seen that the sensitivity of the peak position to the aspect ratio in this region is small, so the presence of a distribution of particles with varying ratios would not be expected to produce a completely broadened, unstructured peak. This is also consistent with what is observed.

5.5 Summary

In the present work, we have investigated the mid-IR spectra of aerosol particles composed of mixed CO_2 and C_2H_2 with various compositions and architectures at cryogenic temperatures. For aerosol particles formed by co-condensation of CO_2 and C_2H_2 we have found the same $CO_2 \cdot C_2H_2$ co-crystalline phase that had previously been observed in thin films.^{146–148} An analysis of this co-crystalline phase is provided in Chapter 6. Similar to the thin films, the co-crystalline particles were found to be metastable and decomposed into pure CO_2 and $pure C_2H_2$ over time. The structure of the particles after decomposition was analyzed. From the different particle structures that were proposed, disc-like $CO_2-C_2H_2$ core-shell ellipsoids with an aspect an aspect ratio of approximately 2.1 seem to be the most consistent with the experimentally observed aerosol particles after decomposition.

Chapter 6

Infrared Spectroscopy and Modeling of Co-crystalline $CO_2 \cdot C_2H_2$ Aerosol Particles. Part 2: The Structure and Shape of Co-crystalline $CO_2 \cdot C_2H_2$ Aerosol Particles

6.1 Introduction

It has previously been established that C_2H_2 and CO_2 can form a co-crystal with a 1:1 stoichiometry.^{146–148} In that series of thin film experiments, this co-crystal was demonstrated to be metastable and decomposed into the solid phases of its pure components. In Chapter 5 the same system was studied as aerosols and a similar behaviour was found: co-crystalline $CO_2 \cdot C_2H_2$ particles initially form and decompose over time into particles with domains of pure C_2H_2 and pure CO_2 . In all of this work, it has been possible to monitor decomposition and formation due to the differences in the infrared (IR) bands of the three phases.

Our aim here is to understand the origin of the IR bands of co-crystalline $CO_2 \cdot C_2H_2$ aerosol particles. There are two principle points to consider: (i) how the type of crystal structure of $CO_2 \cdot C_2H_2$ affects the optical modes of the crystal, and (ii) how particle morphology influences the IR band shapes. The main difficulties are the lack of any crystallographic information and refractive index data for co-crystalline $CO_2 \cdot C_2H_2$. In the absence of experimentally measured indices of refraction, one must rely on a molecular model to calculate the IR absorption spectra for small particles. For that purpose, knowledge of the phase of the particles is essential. However, attempts to obtain crystallographic information on this substance have not been successful.¹⁴² This failure is almost certainly due to the metastability of the co-crystal. Despite this lack of information, there has been speculation on the nature of the phase. It was initially thought that C_2H_2 and CO_2 formed a 2:1 C_2H_2 :CO₂ phase.¹⁴⁶ Additional experiments revised this ratio to 1:1 and the unit cell of the co-crystal was proposed to be face-centered cubic.¹⁴⁷ Aside from some hints obtained from IR spectra, the justification for this structure was based on the fact that both C_2H_2 and CO_2 (i) can form cubic crystals (Pa3 symmetry), (ii) are similar in size, (iii) share the same set of symmetry operations, and (iv) possess electric quadrupole moments without possessing electric dipole moments.

Based on the observations that were mentioned it is reasonable to restrict our attention to unit cells with a 1:1 stoichiometry that are constructed by replacing molecules in either cubic CO_2 cells or cubic C_2H_2 cells. To find energetically favourable crystal structures for $CO_2 \cdot C_2H_2$, we have investigated such cells using density functional theory (DFT), as implemented with the ABINIT code.^{135,136,158} From optimized crystal structures, dielectric functions were calculated. These dielectric functions were then incorporated into a model of the $CO_2 \cdot C_2H_2$ aerosol particles in order to simulate IR spectra. This step was implemented using the discrete dipole approximation (DDA).^{13,15,16} These simulated spectra were then compared to experimental spectra and the validity of modeled crystal structures were evaluated.

Throughout this study we strongly rely on the previous work that has been performed on both pure CO₂ and pure C₂H₂ in their crystalline phases and pure CO₂, pure C₂H₂, and mixed CO₂·C₂H₂ in their gas phases. These systems have been extensively studied due to the simplicity of the molecules involved, their relevance to a broad range of fields and their importance as model systems. As was mentioned above, both C₂H₂ and CO₂ exhibit no permanent dipole moments yet possess quadrupole moments. Measurements put the values of these moments at 4.2 x 10⁻²⁶ to 8.4 x 10⁻²⁶ esu for C₂H₂ and -4.3 x 10⁻²⁶ to -4.57 x 10^{-26} esu for CO₂.¹⁴⁵ With pure CO₂ quadrupole-quadrupole interactions can be used to explain the cubic structure of its crystalline phase as this arrangement is the lowest in energy for such moments.¹⁵⁹ This is not true for C_2H_2 whose low temperature crystalline phase is orthorhombic. Therefore, higher-order electric moments are needed to describe the electrostatic portion of the intermolecular potential of C_2H_2 .^{160–162} When these are included the optimized geometry is based upon the donor-acceptor interaction between a C_2H_2 carbon-carbon triplebond and a C_2H_2 hydrogen. This is clearly seen in the orthorhombic primitive unit cell which consists of two C_2H_2 molecules arranged in a T-shape.

These electrostatic interactions also largely define the molecular configurations seen in gas phase studies of the van der Waals dimers of CO_2-CO_2 , $C_2H_2-C_2H_2$ and $CO_2-C_2H_2$.^{163–171} The configuration of CO_2 dimers is slipped parallel^{163,164,171} while the configuration of C_2H_2 dimers is T-shaped.^{165–167,171} These configurations are both favorable quadrupole-quadrupole interactions and in either of the homodimers the energy difference between the two states is small.¹⁷¹ The $CO_2-C_2H_2$ heterodimer has a structure which is completely predicted by electrostatics – both molecules are parallel with their centers of mass being joined by a perpendicular line.^{168–171} All of these examples illustrate that it should be possible to qualitatively understand the results of $CO_2 \cdot C_2H_2$ optimized cells in terms of electrostatics with an emphasis on quadrupole-quadrupole interactions. The importance of electrostatics in this co-crystal means that the semilocal DFT functional used here should be appropriate for describing structural effects and IR spectra.¹³⁵ However, this functional does not capture dispersion interactions so that calculated lattice energies are not expected to be accurate.¹⁷²

6.2 Experimental Section

The experimental conditions used for the formation of the $\text{CO}_2 \cdot \text{C}_2\text{H}_2$ aerosols were described in detail in Chapter 5. The IR spectra shown here were measured immediately after the injection of the gases into the bath cooling cell. The mole fraction of CO_2 in the aerosol particles is 0.35. As was discussed in Chapter 5, for this fraction, nearly all of the CO_2 is found in the co-crystalline phase. This greatly simplifying analysis of these bands.

6.3 Computational Methods

The procedure used to calculate the IR absorption spectra of particles is described in detail below but can be summarized as follows: the bulk crystal structure of the substance of interest
is optimized using ABINIT. With this optimized structure a dielectric tensor is then calculated. This tensor is then incorporated into a model of the shape of the $CO_2 \cdot C_2H_2$ aerosol particles and, using a discretization method (in our case DDA), the absorption cross-section of the particle is calculated.

6.3.1 ABINIT

Solid-state DFT calculations were performed with the ABINIT software package ^{135,136,158} using Troullier-Martins pseudopotentials,¹⁷³ the Perdew-Burke-Ernzerhof parameterization of the exchange-correlation functional¹⁷⁴ within the generalized gradient approximation (GGA), and a kinetic energy cutoff for planewaves of 70 Ha. Crystal structures were relaxed using Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization.¹⁷⁵

As implemented with ABINIT, dynamical matrices, high-frequency dielectric tensors, and Born effective charges were calculated using optimized unit cells.²⁰ From these values frequencydependent dielectric tensors were constructed and diagonalized. The form of the dielectric tensors are²⁰

$$\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\beta}}{\omega_{T_m}^2 - \omega^2 + i\omega\gamma_m}$$
(6.1)

where ω_{T_m} is the transverse optical (TO) mode, $\epsilon_{\alpha\beta}^{\infty}$ is the high-frequency dielectric constant, Ω_0 is the unit cell volume, $S_{m,\alpha\beta}$ is the mode-oscillator strength and γ_m is the damping constant for the optical mode m. For a diagonal dielectric tensor, the real longitudinal optical (LO) modes of the lattice will be the roots of equation 6.1.¹⁷⁶

6.3.2 DDA

Absorption spectra for particles were calculated using DDA as implemented with the DDSCAT code.¹³ This method was described in detail in Section 1.4.2. Particles modeled here were constructed using an inter-dipole separation, d, of 0.2 nm. This spacing was chosen so that all particles satisfied the validity criterion for DDA.¹⁶ These are (i) the number of dipoles chosen is sufficient to accurately represent the shape of the particle chosen and (ii) the condition $2\pi d|m|/\lambda < 1$, where m is the complex index of refraction and λ is the wavelength of light, is always true. The dimensions of any particle modeled here are much smaller than the wavelength

of light impinging on them (e.g. if a particle with a cubic shape was modeled the length of its sides would be less than 100 nm).

6.4 **Results and Discussion**

6.4.1 The Optical Modes of Orthorhombic C₂H₂ and Cubic CO₂

Prior to considering $CO_2 \cdot C_2 H_2$ co-crystals, we first examined the applicability of solid-state DFT to molecular crystals composed of either pure CO_2 or pure C_2H_2 . The phases chosen for these crystals corresponded to those found in aerosol particles of the respective pure substances (when prepared under similar conditions to the $CO_2 \cdot C_2 H_2$ particles discussed here). The phases are cubic (CO_2) and orthorhombic (C_2H_2).^{105,144}

Unlike the metastable $\text{CO}_2 \cdot \text{C}_2\text{H}_2$ co-crystal, there exists crystallographic and refractive index data for both cubic $\text{CO}_2^{144,149,177-179}$ and orthorhombic C_2H_2 .^{105,122} Cubic CO_2 has been extensively studied and several thin film experiments have extracted refractive index data in the mid-IR. In Table 6.1, we have listed LO and TO modes for the two IR active fundamental modes of CO_2 – the ν_2 bend and the ν_3 anti-symmetric stretch. These were taken from the most recent of the studies listed above.¹⁴⁹

Crystalline C_2H_2 has two phases (orthorhombic and cubic) that have been characterized using x-ray^{104,180} and neutron¹⁰⁵ diffraction. These phases have also been studied using IR^{122,128,130–132,134} and Raman¹³⁴ spectroscopy. Despite this breadth of work, only Khanna et al.¹²² have presented refractive index data for orthorhombic C_2H_2 (no refractive index data exists for cubic C_2H_2 in the mid-IR). C_2H_2 has two IR active fundamental modes and in the orthorhombic phase the ν_5 bending vibration gives rise to three optical modes (all orthogonal) and the ν_3 antisymmetric stretching vibration gives rise to two optical modes (both orthogonal).

The experimental wavenumbers of the optical modes of the solids listed in Table 6.1 were determined by fitting refractive index data from the referenced thin film experiments. In this fitting process each optical mode was modeled with a single Lorentzian oscillator (e.g. the ν_2 band of CO₂ was fitted with two oscillators). For CO₂ this process was straightforward as its cubic crystal structure leads to an isotropic dielectric tensor ($\epsilon_{11} = \epsilon_{22} = \epsilon_{33}$). This is not

Table 6.1: Experimental and calculated LO and TO modes (cm^{-1}) and high-frequency dielectric constants for crystalline C_2H_2 and CO_2 . Experimental and calculated modes (cm^{-1}) for gas phase C_2H_2 and CO_2 . For the calculated crystalline modes, values without brackets are harmonic while values inside of brackets are corrected. See Section 6.4.1 for details on the procedure used to calculate this correction. For orthorhombic C_2H_2 , all optical modes within a band are orthogonal.

	C ₂ H ₂ gas phase		С	C_2H_2 orthorhombic phase			CO_2 gas	phase	CO_2 cubic phase			
	Expt. 184	Calc.		Expt. ¹²²	Calc.		Expt. 184	Calc.		Expt. ¹⁴⁹	Calc.	
ν_3	3289	3344.7	ω_{T_1}	3223.1	3273.1 (3217.4)	ν_2	667	650.9	ω_T	654.8	643.4(659.4)	
			ω_{L_1}	3228.1	3287.4 (3231.6)				ω_L	660.0	645.0 (661.0)	
			ω_{T_2}	3223.1	3273.3 (3217.5)				ω_T	661.0	$647.1 \ (663.2)$	
			ω_{L_2}	3228.1	3287.5 (3231.8)				ω_L	670.5	657.9(674.0)	
ν_5	730	736.5	ω_{T_1}	745.4	791.6 (785.1)	ν_3	2349	2344.3	ω_T	2345.0	2345.2 (2349.9)	
			ω_{L_1}	753.4	806.7 (800.1)				ω_L	2377.0	2373.9(2378.6)	
			ω_{T_2}	756.2	766.1 (759.5)							
			ω_{L_2}	787.8	$802.6\ (796.0)$				ϵ^{∞}	1.54	1.73	
			ω_{T_3}	769.2	793.5(787.0)							
			ω_{L_3}	777.0	807.4 (800.9)							
			ϵ_{11}^{∞}	1.96	1.98							
			ϵ_{22}^{∞}	1.96	1.98							
			ϵ_{33}^{∞}	1.96	1.69							

the case for orthorhombic C_2H_2 which is a biaxial crystal ($\epsilon_{11} \neq \epsilon_{22} \neq \epsilon_{33}$). Furthermore, the thin film measurements of Khanna et al. were performed on polycrystalline samples. Therefore, it was necessary to use a directionally averaged index of refraction when fitting that data.¹⁸¹ Additionally, we have listed the high-frequency dielectric constants for cubic CO₂ and orthorhombic C_2H_2 in Table 6.1 so that the summarized data can readily be used to construct dielectric functions with damping constants being added in an ad hoc manner, as is typical.¹⁸²

The parameters for the dielectric function of cubic CO₂ and orthorhombic C₂H₂ were calculated using the known crystallographic coordinates (after the structure was relaxed with ABINIT).^{105,144} Except for the optical modes associated with the C₂H₂ ν_5 band, the error between the calculated and observed frequencies was always less than 3%. As all of the ABINIT calculated frequencies are harmonic, correction terms were determined by taking the difference between the observed and calculated gas phase frequencies. This difference was then used to correct the calculated crystal frequencies. After this correction the error between the calculated and observed crystalline modes was lowered to less than 1%. This meant that the C₂H₂ ν_3 , the CO₂ ν_2 and the CO₂ ν_3 bands would be able to satisfactorily reproduce both position and shape in the modeled IR spectra of particles. The larger error in C₂H₂ ν_5 modes (up to 5.8%, even after the correction) meant that any dielectric function constructed using the calculated frequencies does not satisfactorily reproduce the band shape, although the band position is within the listed errors. This discrepancy likely originates from the fact that the prepared C_2H_2 samples are not perfectly orthorhombic and contain a significant amount of disorder (see Chapter 4 for a discussion of this problem). This effect is more noticeable in the $C_2H_2 \nu_5$ band than the $C_2H_2 \nu_3$ band due to the larger transition dipole moment of ν_5 vibration. Therefore, it appears that, after correction, the optical modes associated with all but the $C_2H_2 \nu_5$ band should be reliable in gauging the validity of a modeled crystal structure against measured IR spectra. In Section 6.4.3, the correction terms determined here are also used to correct the calculated modes for the various $CO_2 \cdot C_2H_2$ co-crystals.

6.4.2 Structure of $CO_2 \cdot C_2H_2$ Co-crystal

Currently, there exists no crystallographic information on the $\text{CO}_2 \cdot \text{C}_2\text{H}_2$ co-crystal. Knowledge of this phase is, of course, essential when modeling the optical properties of particles using a microscopic model. As Chapter 5 shows clear evidence that a co-crystalline phase is formed under the present experimental conditions, possible crystal structures were investigated using ABINIT and the proposed 1:1 mixing ratio of C_2H_2 : CO_2 .¹⁴⁷

For the starting structure, half of the C_2H_2 molecules in a cubic C_2H_2 cell were replaced with CO₂ molecules (Fig. 6.1a, α -P2₁/c). This structure was chosen as both CO₂ and C_2H_2 form cubic crystal structures.^{105,144} Both the position of the center of mass and the alignment of the principle axes of the CO₂ molecules were identical to the C_2H_2 molecules that they replaced in the unit cell. Six different cells can be prepared using this procedure. However, all are equivalent so choosing which C_2H_2 molecules are replaced is unimportant and only one unit cell needs to be considered. Additionally, it was found that replacing half the CO₂ molecules in a cubic CO₂ cell with C_2H_2 molecules gave equivalent final structures to the C_2H_2 cubic cell starting point. The C_2H_2 and CO₂ lattice parameters for the starting structures were taken from the literature.^{105,144}

The results of all the optimizations are summarized in Table 6.2 and the final unit cells are



Figure 6.1: $CO_2 \cdot C_2 H_2$ co-crystals that are formed when cell (a) is relaxed. The details and restrictions used in the various optimization procedures are discussed in Section 6.4.2. After this process, the unit cells were rebuilt using the highest possible symmetry. These cells are shown in Fig. 6.2.

Table 6.2: Cell parameters and lattice energies calculated using DFT within the GGA. See the main text for details on how the $CO_2 \cdot C_2H_2$ cells were obtained. Illustrations of the $CO_2 \cdot C_2H_2$ unit cells are shown in Fig. 6.2.

Phase	Lattice energy	Space group	Lattice	paramet	ers (Å)	Cell angles (°)		es (°)	Cell volume $(Å^3)$
	(kJ/mol)		a	b	c	α	β	γ	
Orthorhombic C ₂ H ₂	13.3835	Cmca	6.8138	6.1743	6.2192	90	90	90	261.65
Cubic C_2H_2	12.0100	Pa3	6.3543	6.3543	6.3543	90	90	90	256.57
Cubic CO_2	9.9677	Pa3	6.0457	6.0457	6.0457	90	90	90	220.97
$\beta - P2_1/c \operatorname{CO}_2 \cdot \operatorname{C}_2 \operatorname{H}_2$	8.2271	$P2_1/c$	6.5098	6.5098	6.5098	90	90	90	275.87
$\gamma - P2_1/c \operatorname{CO}_2 \cdot \operatorname{C}_2 \operatorname{H}_2$	10.8429	$P2_1/c$	7.3479	6.1736	6.1987	90	108	90	267.33
α -P2 ₁ CO ₂ ·C ₂ H ₂	10.9326	$P2_1$	6.9066	6.6240	5.6905	90	108	90	247.59
α -P4/mbm CO ₂ ·C ₂ H ₂	10.9695	P4/mbm	6.2077	6.2077	7.1157	90	90	90	274.20

depicted in Fig. 6.2. The lattice energy, $E_{lattice}$, was calculated using the relation

$$-E_{lattice} = \frac{1}{N} \left(E_{crystal} - \sum_{j=1}^{N} E_j \right)$$
(6.2)

where N is the total number of molecules in the unit cell, and $E_{crystal}$ and E_j are the static total DFT energy at T = 0 K for the molecules in the unit cell and the free molecule j, respectively. The calculated energies and cell parameters for cubic CO₂, cubic C₂H₂ and orthorhombic C₂H₂ are also listed in Table 6.2. Experimental values for the lattice energies of the pure substances are typically two- to three-times greater than the values listed in Table 6.2. ^{160,162,183} This discrepancy was expected as it is well-known that GGA functionals provide a poor description of van der Waals interactions. ^{135,172} Despite this deviation, these functionals do provide a very good description of vibrational properties, ¹³⁵ our primary interest in this work.

In the first optimization (Fig. 6.1b, $\beta - P2_1/c$), lattice parameters could only change under the restriction that they remained equal (a = b = c). Cell angles were simply held constant $(\alpha = \beta = \gamma = 90^{\circ})$. The purpose of this restricted optimization was to ensure that the originally proposed 1:1 C₂H₂:CO₂ face-centered cubic cell¹⁴⁷ was maintained. In the second optimization (Fig. 6.1c, $\gamma - P2_1/c$), no restrictions were placed on the cell. This unit cell remains in the same space group as both $\alpha - P2_1/c$ and $\beta - P2_1/c$, however the lattice constants are now all unequal and one of the cell angles is no longer equal to 90°. This unit cell is obviously no longer face-centered cubic.

In both $\beta - P2_1/c$ and $\gamma - P2_1/c$ C₂H₂ is located on sites with C_i symmetry. Therefore, we



Figure 6.2: $CO_2 \cdot C_2H_2$ unit cells obtained by relaxing the cell shown in Fig. 6.1a. Unlike the corresponding cells in Fig. 6.1b-e, these unit cells satisfy the symmetry requirements and cell parameters listed in Table 6.2.

anticipate that the ν_2 mode of C_2H_2 (the symmetric stretch) will not be IR active. This means that these cells cannot be the actual $CO_2 \cdot C_2H_2$ cell as this band is experimentally observed to be IR active (see Section 6.4.3). To address this issue, cells with different symmetries were examined by 'breaking' the symmetry of either α -, β - or γ - $P2_1/c$ and relaxing the cells for a second time. This was done by either displacing molecules from their equilibrium positions or by changing the primitive cell vectors. The amount of change introduced with either of these methods was typically small. Also note that this procedure was by no means comprehensive. Of all the structures that were obtained during this process only two had higher lattice energies than γ - $P2_1/c$. These were α - $P2_1$ and α -P4/mbm. The unit cell of α - $P2_1$ was the lowest in symmetry (monoclinic, $P2_1/c$) and C_2H_2 is now located on sites with C_1 symmetry. Consequently, the $C_2H_2 \nu_2$ mode is IR active. The unit cell of α -P4/mbm actually had a higher symmetry (tetragonal, P4/mbm) than the other cells studied here. While its $C_2H_2 \nu_2$ mode is not IR active, this co-crystal is included here as it had a similar lattice energy as γ - $P2_1/c$ and α - $P2_1$ (it is slightly higher).

An analysis of the arrangement of the molecules in these unit cells is essential for identifying which intermolecular interactions are primarily responsible for changes in bond force constants. This will aid in understanding the shifts in modes that occur between the pure and mixed crystal phases as it will help identify the key interactions that are likely present in the true $CO_2 \cdot C_2 H_2$ cell. For simplicity, we will focus on the simple electrostatic interactions discussed in the Introduction for homo- and heterodimers of $C_2 H_2$ and CO_2 .

The quadrupole moments of C_2H_2 and CO_2 are opposite in sign, so the chosen starting structure α - $P2_1/c$, which is optimal for the case of all molecules having moments of the same sign, should not be at an energy minimum. Indeed, during all of the optimizations, molecules rotate out of their initial alignments and attempt to form alternating sheets of pure C_2H_2 and pure CO_2 . These sheets are constructed as pairs of molecules attempt to form the energetically favorable T-shape, homodimer configuration. When no restrictions are in place (γ - $P2_1/c$, α - $P2_1$, α -P4/mbm) these sheets also slide against each other as C_2H_2 and CO_2 from adjacent sheets attempt to form the energetically favorable parallel heterodimer.

The result of these dilational and rotational motions are clearly seen in Fig. 6.1. When viewed down their b-axes in Fig. 6.1, the angle between the a and c axes has substantially changed from 90° for γ -P2₁/c, α -P2₁ and α -P4/mbm. The molecules in these cells have all rotated towards the plane defined by the b and c axes. If the formation of T-shape homodimers and parallel heterodimers truly is driving the transformation of the cells forward, then cell α -P4/mbm represents the completion of this process. The molecules in this unit cell are in both of these arrangements with little distortion. This co-crystal also has a higher lattice energy than β -P2₁/c, γ -P2₁/c or α -P2₁. In contrast, for the molecules in γ -P2₁/c and α -P2₁ this motion appears to become hindered during the transformational process as the arrangement of molecules into the T-shape homodimers and parallel heterodimers is not optimal. From the IR response calculated below it becomes clear that the amount of distortion has a large influence on the positions of the modes.

6.4.3 Analysis of IR Spectra and Optical Modes of $CO_2 \cdot C_2H_2$

Due to the absence of index of refraction measurements from the previous $CO_2 \cdot C_2H_2$ thin film studies, a direct comparison between calculated and experimental dielectric functions was not possible. Instead, the validity of the $CO_2 \cdot C_2H_2$ unit cells discussed above was evaluated through (i) a comparison of the calculated and experimental spectra of particles (Fig. 6.3) and (ii) a comparison of the calculated and experimental TO modes (Table 6.3). The experimental TO modes used in Table 6.3 were taken from the thin film measurements of Gough et al. $^{146-148}$ For the calculated spectra in Fig. 6.3e-h, dielectric functions were generated using the procedure outlined in Section 6.3.1. These functions were incorporated into a truncated cube particle model (see inset of Fig. 6.3 for a depiction of the particle shape). The experimental spectra of pure CO₂ (see Chapter 5 for a discussion of this), pure C₂H₂ and CO₂·C₂H₂ particles are shown in Fig 3a-c, respectively. Due to the difficulty in preparing CO₂·C₂H₂ particles without the presence of pure C₂H₂, pure C₂H₂ bands were subtracted from Fig. 6.3c using Fig. 6.3b. The dip in the C₂H₂ ν_3 band in Fig. 6.3d indicates that this process was not ideal. Finally, the relative positions of the experimental and calculated spectra are such that the experimental and calculated gas phase modes coincide for each band. This positioning corrects the calculated wavenumbers in a manner identical to that used in Section 6.4.1 for the modes of pure crystalline CO₂ and C₂H₂ (i.e. the upper abscissa represents the corrected wavenumbers for the the calculated bands while the lower abscissa represents the harmonic wavenumbers for the calculated bands).



Figure 6.3: Experimental IR spectra for aerosol particles composed of (a) pure CO₂, (b) pure C₂H₂, (c) CO₂·C₂H₂ and (d) CO₂·C₂H₂ where bands associated with pure C₂H₂ have been subtracted. IR spectra calculated using a truncated cube particle model (see inset) and the dielectric functions generated using (e) β -P2₁/c, (f) γ -P2₁/c, (g) α -P2₁ and (h) α -P4/mbm. For each optical mode damping was set to a percentage of the ω_T of that mode. These were: 0.45, 0.40, 1.00, 0.15 and 0.04 % for the CO₂ ν_2 , CO₂ ν_3 , C₂H₂ ν_5 , C₂H₂ ν_3 and C₂H₂ ν_2 bands, respectively.

Table 6.3: Experimental and calculated TO modes (cm⁻¹) for $CO_2 \cdot C_2H_2$ co-crystals (see Fig. 6.2 for unit cells). Modes in brackets have been corrected (see Section 6.4.1). Italicized modes are not IR active. The experimental ν_3 ¹²CO₂ mode, which was not reported in Ref. 146–148, was determined from the position of the ¹³CO₂ mode in $CO_2 \cdot C_2H_2$ and the observed isotopic frequency ratio between the ν_3 modes in ¹³CO₂ and ¹²CO₂ in crystalline CO₂. % Error is equal to (|Calc. - Expt.|/Expt.) × 100%.

	Expt. ^{146–148}	β -P2 ₁ /c		γ -P2 _{1/}	'c	α -P2	L	α -P4/mbm		
		Calc.	% Error	Calc.	% Error	Calc.	% Error	Calc.	% Error	
$C_2H_2 \nu_2$	1964	1983.9 (1957.0)	$1.01 \ (0.36)$	1977.7 (1950.8)	0.70(0.67)	1981.4(1954.5)	0.89(0.48)	1974.8 (1947.9)	0.55(0.82)	
		1990.8~(1963.9)	1.36(0.00)	<i>1987.9</i> (<i>1961.0</i>)	1.22(0.15)	1988.5~(1961.6)	1.25(0.12)	1986.4~(1959.5)	1.14(0.23)	
$C_2H_2 \nu_3$	3256	$3305.4\ (3249.7)$	$1.52 \ (0.19)$	$3282.6\ (3226.9)$	0.82(0.89)	3296.2 (3240.5)	1.23(0.48)	3274.3 (3218.6)	0.56(1.15)	
		$3305.6\ (3249.9)$	$1.52 \ (0.19)$	3282.8 (3227.1)	0.82(0.89)	3296.5(3240.8)	1.24(0.47)	3274.3 (3218.6)	0.56(1.15)	
$C_2H_2 \nu_5$	740	739.4(732.9)	0.08~(0.97)	752.4(745.8)	1.67(0.79)	758.8(752.3)	2.54(1.66)	757.9 (751.4)	2.42(1.54)	
		753.2(746.6)	1.78(0.89)	769.4(762.9)	3.97 (3.09)	767.3(760.8)	3.70(2.81)	$783.8\ (777.3)$	5.92(5.04)	
	752	782.9(776.4)	4.11(3.24)	$792.1 \ (785.6)$	5.34(4.47)	773.5(766.9)	2.86(1.99)	798.0(791.5)	6.12(5.25)	
		783.4(776.9)	4.18(3.31)	794.7(788.1)	5.68(4.81)	777.4(770.9)	3.38(2.51)	798.0(791.5)	6.12(5.25)	
$CO_2 \nu_2$	649	$640.0\ (656.1)$	1.39(1.09)	$636.8 \ (652.9)$	1.88(0.60)	637.0 (653.1)	1.84(0.63)	$636.3 \ (652.3)$	1.96(0.51)	
		640.3(656.4)	1.34(1.14)	637.7 (653.7)	1.75(0.73)	$638.4\ (654.5)$	1.63(0.85)	637.6~(653.7)	1.75(0.73)	
	658	646.0 (662.1)	1.82(0.62)	642.3 (658.4)	2.39(0.05)	639.9 (656.0)	2.75(0.30)	$640.1 \ (656.2)$	2.72(0.27)	
		$647.4\ (663.4)$	1.62(0.83)	$642.6\ (658.7)$	2.34(0.11)	$640.0\ (656.1)$	2.74(0.29)	$640.1 \ (656.2)$	2.72(0.27)	
$CO_2 \nu_3$	2340	2337.4(2342.0)	$0.11 \ (0.09)$	2336.9(2341.6)	0.13(0.07)	2338.1 (2342.7)	0.08(0.12)	2342.1 (2346.8)	0.09(0.29)	
		2342.7 (2347.4)	$0.12 \ (0.32)$	$2343.9\ (2348.6)$	$0.17 \ (0.37)$	$2342.0\ (2346.7)$	0.09(0.29)	$2342.1 \ (2346.8)$	0.09(0.29)	
Mean % Err	or		1.57(0.95)		2.06(1.26)		1.87(0.93)		2.34(1.63)	

Previous work on pure CO_2 and pure C_2H_2 particles has demonstrated that particle shape can be determined through the analysis of vibrational bands (see Chapters 3 through 5 and Refs. 18,72,117,118,156). Therefore, it should be possible to gain insight into $CO_2 \cdot C_2 H_2$ particle shape and simultaneously evaluate the validity of the dielectric functions that have been calculated here. However, for $CO_2 \cdot C_2H_2$, such an approach is complicated by several factors. First, there is no transition with an LO-TO splitting as large as the ν_3 band of CO₂ in pure CO_2 . This means that shape dependent features of the spectrum will be more compressed and difficult to interpret (within the electrostatic limit, shape dependent peaks will have maxima in the region bound by LO and TO modes).⁴ Second, the low symmetry of the $CO_2 \cdot C_2H_2$ unit cells results in an increased number of non-degenerate optical modes in the co-crystals when compared to the cubic CO₂. This will further complicate analysis as each band will now contain a larger number of peaks. Third, the low symmetry of these co-crystal unit cells means that analyzing a wide array of particle shapes with these calculated dielectric functions will be an enormous task. This is because, in general, there is no clear way to orient the polarization axes of the dielectric tensor relative to the symmetry axes of any arbitrary particle. However, there are cases when this is not a concern. For instance, any spherical particle shape or any particle shape whose symmetry group is cubic (e.g. cube, truncated cube, octahedron, tetrahedron, etc.). In these situations, only one irreducible representation will possess a net electric dipole moment that is non-vanishing. Consequently, when calculating the absorption spectrum of a distribution of such particles with random alignments, the orientation of the polarization axes of the dielectric tensor relative to the symmetry axes of the particle is unimportant. Finally, with the previous work on CO_2 the growth of the particles over time and the resulting changes to the spectrum provided insight into particle morphology. With $CO_2 \cdot C_2H_2$ decomposing into pure CO_2 and pure C_2H_2 over time this type of information is not present (Chapter 5). Due to these factors, in Fig. 6.3 we do not attempt to model any further $CO_2 \cdot C_2 H_2$ particles beyond a truncated cube. The influence of further particle shapes is, however, considered briefly in Section 6.4.4 and Fig. 6.4.

For the C₂H₂ ν_3 band, the experimental difference in peak position between pure C₂H₂ (3230.2 cm⁻¹) and CO₂·C₂H₂ (3258.7 cm⁻¹) is 28.5 cm⁻¹. This shift is the largest among the IR active fundamental modes of both C_2H_2 and CO_2 . Furthermore, the small LO-TO splitting for the optical modes of this band (typically around 5 cm⁻¹) means that particle shape will have little effect on peak position. Therefore, the position and shape of this band is approximately independent of particle morphology and predominantly influenced by the configuration of the $CO_2 \cdot C_2H_2$ unit cell. Furthermore, the large difference in the position between pure C_2H_2 (Fig. 6.3b) and $CO_2 \cdot C_2H_2$ (Fig. 6.3d) for this band indicates its high sensitivity to the configuration of the unit cell and should therefore be an excellent probe of the unit cell structure.

Relative to the calculated $C_2H_2 \nu_3$ TO modes in orthorhombic C_2H_2 (Table 6.1), all of the calculated $C_2H_2 \nu_3$ TO modes in the $CO_2 \cdot C_2H_2$ co-crystals are blue-shifted. This trend is consistent with what is experimentally observed. However, the magnitude of the predicted shift was found to vary significantly between co-crystals. The shifts for both γ -P2₁/c and α -P4/mbm are small, while for β -P2₁/c and α -P2₁ they are much larger. Overall, in both Fig. 6.3 and Table 6.3 we see that the IR response of the β -P2₁/c co-crystal provides the best match to the experimental $C_2H_2 \nu_3$ mode in the $CO_2 \cdot C_2H_2$ cell. Examination of the cocrystal cells in Fig. 6.1 and 6.2 reveals that the structural factor of primary influence on this shift is the configuration of the T-shape $C_2H_2-C_2H_2$ interaction. The greater the disruption of this T-shape, the greater the shift. The interaction between the electronegative carboncarbon triple bond and the electropositive hydrogen atom has a tremendous influence on the force constant of CH stretches. In the case of pure C_2H_2 , the orthorhombic cell is built in such a way that every hydrogen faces an electronegative carbon-carbon triple bond in a nearly optimal T-shape geometry (it is slightly distorted). All of the co-crystal configurations deviate in varying degrees from this configuration. The larger the deviation, the stronger the blue-shift in the corresponding spectrum. Based on this analysis and the large experimental shift it seems likely that the true co-crystal contains C_2H_2 in a T-shape configuration that has been heavily distorted from the one in the orthorhombic unit cell of pure C_2H_2 .

A similar analysis should be possible for the CO₂ ν_3 band, where the OC force constant is reduced due to the intermolecular interaction between an electronegative oxygen with an electropositive oxygen. However, with a difference of only 11.5 cm⁻¹ in the experimental band positions for pure CO₂ (2361.0 cm⁻¹) and CO₂·C₂H₂ (2349.5 cm⁻¹) and a much larger LO- TO splitting for the optical modes found in this band (relative to those found in the $C_2H_2 \nu_3$ band) this type of analysis is not straightforward. In the calculated IR response for all of the $CO_2 \cdot C_2H_2$ co-crystals there is a small redshift in the $CO_2 \nu_3$ TO modes relative to those found in cubic CO_2 . Table 6.3 shows that the error between the observed and calculated TO modes in this band is the smallest of any the bands considered here. Examination of Fig. 6.3 reveals that it is very difficult to differentiate between the various $CO_2 \cdot C_2H_2$ unit cells based on this band. All of the changes due to unit cell configuration are simply far too minor.

A similar result is also found when analyzing the CO₂ ν_2 band shifts. The calculated IR response for the CO₂·C₂H₂ co-crystals differs only slightly from the calculated response for pure, cubic CO₂. Relative to the calculated TO modes for cubic CO₂, the TO modes of the co-crystal are all red-shifted (with the exception of one of the β -P2₁/c modes). The calculated TO modes of the co-crystals are also all split. These two trends are consistent with what is observed. The splitting between the ν_2 modes in this co-crystal is larger than any of the other structures and, when the spectrum of a β -P2₁/c particle is calculated, two distinct peaks are observed in its CO₂ ν_2 band (Fig. 6.3e). This splitting is consistent with the experimental band (Fig. 6.3d) and is not observed in the other calculated CO₂ ν_2 bands (Fig. 6.3f-h).

In Section 6.4.1 it was found that for orthorhombic C_2H_2 the amount of error in the calculated optical modes of the ν_5 vibration was much larger than any of the other IR active fundamental bands in either orthorhombic C_2H_2 or cubic CO₂. This meant that, when incorporated into a particle model, a dielectric function constructed using the optical modes in this band would not be able to satisfactorily reproduce experimental particle spectra. Therefore, basing any conclusion solely on this result is not advised. However, it is still worthwhile to make some statements on the calculated wavenumbers for this band. When the experimental spectra of pure C_2H_2 (Fig. 6.3b) and $CO_2 \cdot C_2H_2$ (Fig. 6.3d) in this region are compared, there clearly must be a red-shift in the corresponding optical modes. This is found for the TO modes of $\beta - P2_1/c$, $\gamma - P2_1/c$ and $\alpha - P2_1$ but not for those of $\alpha - P4/mbm$, whose TO modes are all blue-shifted from those found in pure orthorhombic C_2H_2 (compare the calculated TO modes in Table 6.1 to those in Table 6.3). Examining the C_2H_2 ν_5 band in the $CO_2 \cdot C_2H_2$ spectra (Fig. 6.3), hints that the spectrum of the $\alpha - P2_1$ particle provides the best agreement with the experimental band in terms of overall shape and position.

Finally, we consider the $C_2H_2 \nu_2$ band, which is observed to be IR inactive in orthorhombic C_2H_2 but IR active in the $CO_2 \cdot C_2H_2$ co-crystal. Clearly, the site symmetry of C_2H_2 in the actual co-crystal must allow for this mode to be IR active. Of all the modeled co-crystals, this only holds for α -P2₁. However, this does not mean the α -P2₁ is the correct co-crystal, only that β -P2₁/c, γ -P2₁/c and α -P4/mbm are not. In fact, β -P2₁/c, γ -P2₁/c and α -P4/mbm may be closer to the actual structure of the co-crystal than α -P2₁. Simply moving one of the C₂H₂ molecules out of its symmetry site in any one of the unit cells in these co-crystals makes this band IR active without a large change to the overall unit cell structure. Therefore, the importance of this band in characterizing the crystal structure should not be overemphasized as it is sensitive to very small changes in crystal structure.

The results of this section can be summarized as follows: First, a $1:1 C_2H_2:CO_2$ unit cell seems very likely. Any other stoichiometry would lead to large discrepancies between the calculated and observed $CO_2 \cdot C_2H_2$ band intensities in Fig. 6.3, specifically to the ratio of the C_2H_2 to CO_2 intensities in the co-crystal spectra. Second, the C_2H_2 - C_2H_2 configuration in the co-crystal unit cell is heavily distorted from the T-shape observed in orthorhombic C_2H_2 . Therefore, despite its high lattice energy, a unit cell such as $\alpha - P4/mbm$ is unlikely. Third, relative to how they are arranged in a cubic CO_2 unit cell, CO_2 molecules are moved towards a T-shape configuration in the co-crystal. However, comments on this change are not as definitive as those concerning the C₂H₂-C₂H₂ interaction as the observed and calculated frequency shifts are small. Fourth, as expected, only the α -P2₁ co-crystal yields an IR active C₂H₂ ν_2 band. However, many co-crystals with this property were obtained during the symmetry breaking process (see Section 6.4.2). Therefore, this property is not a definitive indicator of the correct unit cell. Overall, inspection of Fig. 6.3 in the region of the $C_2H_2 \nu_3$ and ν_5 and the $CO_2 \nu_2$ and ν_3 bands reveals that the IR spectrum of the β -P2₁/c particle (Fig. 6.3e) provides the best correspondence to the experimental spectrum (Fig. 6.3d), while the α -P4/mbm particle provides the poorest correspondence. The comparison of the experimental and calculated TO modes in Table 6.3 shows that the corrected TO modes of the α -P2₁ co-crystal have the lowest overall percent error. In summary, the $\beta - P2_1/c$ and $\alpha - P2_1$ unit cells are the most promising candidates for the $CO_2 \cdot C_2H_2$ unit cell. These two unit cells appear to correctly capture most the molecular configurations that exist in the actual co-crystal cell. In fact, since the energies of the unit cells are so similar, the $CO_2 \cdot C_2H_2$ particles may contain contributions from multiple unit cells.

6.4.4 Influence of Shape on the IR Spectra of $CO_2 \cdot C_2H_2$ Particles

We further explore the influence of particle shape on spectra by calculating the spectra for three further shapes with octahedral symmetry – a cube (Fig. 6.4a and d), a truncated octahedron (Fig. 6.4b and e) and an octahedron (Fig. 6.4c and f). As discussed in Section 6.4.3, the orientation of the polarization axes within such particles is unimportant when considering a spectrum that has been averaged over all particle orientations. This greatly simplifies analysis. We only consider spectra generated using the dielectric function of the β -P2₁/c and α -P2₁ phases as these gave the best overall correspondence to the observed spectrum and TO modes (see Section 6.4.3).

Fig. 6.4 reveals that there is little difference among the set of spectra belonging to the same crystal phase. This was expected for bands with small LO-TO splittings (the C₂H₂ ν_3 and ν_2 bands and the CO₂ ν_2 band). However, even the CO₂ ν_3 band, which has the largest LO-TO splitting, only shows a weak shape dependence when compared to particles composed of the pure CO₂. In pure cubic CO₂ the calculated LO-TO splitting is 28.7 cm⁻¹ while for β -P2₁/c and α -P2₁ the largest LO-TO splittings in this band are 19.6 and 23.0 cm⁻¹, respectively. Similar comments apply to the C₂H₂ ν_5 band. For the pure orthorhombic crystal the largest calculated LO-TO splitting is 36.5 cm⁻¹ whereas for β -P2₁/c and α -P2₁ the largest LO-TO splittings are 19.7 and 19.9 cm⁻¹, respectively. These results partially reflect the fact that in the co-crystal the densities of both C₂H₂ and CO₂ molecules are much lower than that of their respective pure crystalline forms. As a result of this lower density, transition-dipole coupling is reduced. This will lead to a decrease in LO-TO splitting and, consequently, shape effects will become less important.

The presence of non-degenerate optical modes in the $CO_2 \nu_3$ band of the co-crystals furthre complicates spectra (relative to cubic CO_2). This effect has its origin in the low symmetry of the co-crystal unit cells. In general, it appears as if it is very difficult to comment on particle



Figure 6.4: IR spectra calculated using a cube (a and d), a truncated octahedron (b and e) and an octahedron (c and f). The dielectric functions used are those of β -P2₁/c (a-c) and α -P2₁ (d-f). Damping constants for the optical modes are identical to those listed in the caption to Fig. 6.3.

shape using the IR active bands of $CO_2 \cdot C_2H_2$. Unlike particles of the pure substances, the shape dependence is simply too weak and complicated to gain any insight. Furthermore, as discussed in detail in Section 6.4.3, the low symmetry of the co-crystal unit cells makes the consideration of wide array of particles shapes an enormous task.

6.5 Summary

IR spectroscopy reveals that co-condensation of CO_2 and C_2H_2 in a bath gas cooling cell initially leads to the formation of co-crystalline $CO_2 \cdot C_2H_2$ aerosol particles. The co-crystalline form is metastable and decomposes over time. As a consequence of this, its crystal structure is unknown. The present contribution uses DFT calculations (as implemented with ABINIT) to determine possible structures for these co-crystals as well as corresponding dielectric functions (in the mid-IR region). Aerosol IR spectra are calculated from these dielectric functions using DDA. Using several different crystal structures found with DFT, β -P2₁/c and α -P2₁ (see Fig. 6.2 for unit cells) agree best with the experimental observations in the IR. Both of these cells have a 1:1 ratio of CO₂ to C₂H₂. As the energies of the unit cells are very similar, it is possible that several polymorphs crystallize when the aerosol particles form. A more detailed determination of the crystal structure(s) would require a thorough crystallographic study. However, this poses a serious challenge due to the metastability of the co-crystalline phase. Calculated IR spectra show little dependence on the particle shape, in contrast to what is observed for pure crystalline CO₂ and C₂H₂ particles. The lack of shape sensitivity has its origin in the the low symmetry of the co-crystal unit cells and the smaller LO-TO splitting when compared to the pure crystalline CO₂ and C₂H₂.

Chapter 7

Conclusion

This thesis has presented a study of the electromagnetic response of small particles for visible and IR wavelengths. While the systems studied in Chapters 2 through 6 have each had their own separate and unique challenges, when the methods used throughout thesis are considered as a whole, a broad program for modeling the spectra of small particles emerges. Unlike most of the previous work that exists in the literature, these methods can even be extended to systems where crystal structures and optical constants are not known.

Beginning in Chapter 2, the optical properties of incomplete Au nanoshells were successfully modeled using clusters of Au spheres and hemispheres. While it was necessary to use the discrete dipole approximation (DDA) in order to model these spectra, all of the results could easily be interpreted using plasmon hybridization theory (PHT). This allowed for the high and low energy bands in the observed spectra to be understood in terms of mode-splitting that results from the low symmetry of the coupled Au structures.

While PHT is a powerful method for understanding the spectra of complex nanostructures, it is only valid for metallic systems. This limitation was overcome in Chapter 3, where a more generalized hybridization scheme was developed. Unlike PHT, this new method could be applied to both conducting and non-conducting particles. In that chapter it was then used to provide an intuitive understanding (through analogy to molecular orbital theory) of the infrared (IR) spectra of complex dielectric nanoshells.

Chapters 4 through 6 dealt with particles composed of materials whose bulk indices of refraction were unknown. Understanding these spectra required a wide array of molecular level modeling techniques. In Chapter 4, the vibrational exciton model was used to model the IR response of crystalline, polycrystalline and amorphous C_2H_2 particles. This method provided insight into the phases of these particles and corrected an earlier mischaracterization.¹⁰⁰

Chapters 5 and 6 dealt not only with the IR response of particles composed of co-crystalline $CO_2 \cdot C_2H_2$, but also with the formation and decomposition of these particles. Unlike the systems in Chapter 4, where the crystal structure of cubic and orthorhombic C_2H_2 were known and could be used as a starting point for further investigation, there exists no crystallographic information on the $CO_2 \cdot C_2H_2$ co-crystal. Therefore, it was necessary to use density functional theory (DFT) to model this structure. The feasibility of several $CO_2 \cdot C_2H_2$ co-crystals was evaluated based on the correspondence of their modeled IR spectra to the observed IR spectra. From this comparison, reasonable co-crystal structures were then proposed. Additionally, the architecture of the decomposed $CO_2 \cdot C_2H_2$ aerosols was determined using primarily the IR active fundamentals of CO_2 .

In summary, the methods and examples presented in this thesis enable not only a qualitative interpretation of the absorption spectra of small particles (composed of a broad range of substances) but also the accurate modeling of these spectra. It has been shown that the relationship between particle architecture and spectra can be easily understood, even for very complicated systems. In particular, the computational methods and intuitive constructs presented here are of great utility for interpreting the spectra of molecular crystalline particles. Finally, the importance of combining experimental approaches with theory to reach a better understanding of the interaction of light with nanoscale particles has been repeatedly demonstrated.

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Appendix A

Formulation of an Electrostatic Eigenvalue Problem

In this Appendix the formulation of the electrostatic eigenvalue problem is briefly reviewed by considering the simple cases of a core (Fig. 3.1c) and a cavity (Fig. 3.1b). A detailed account of this problem can be found elsewhere.^{56,79} For simplicity we set the permittivities $\epsilon_1 = \epsilon_3 = \epsilon_0$. For the core (Fig. A.1), the surface-charge density $\sigma(Q)$ eigenvalue problem can be constructed by taking the outward normal component \mathbf{n}_Q of the electric field \mathbf{E} at point Qon the particle surface S where \mathbf{r}_{MQ} is the vector going from surface point M to surface point Q

$$\mathbf{n}_Q \cdot \mathbf{E}^{\pm}(Q) = \mp \frac{\sigma(Q)}{2\epsilon_0} + \frac{1}{4\pi\epsilon_0} \oint_S \sigma(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_Q}{|\mathbf{r}_{MQ}|^3} dS_M \tag{A.1}$$

and inserting it into the boundary condition obtained from Gauss's law

$$\mathbf{n}_Q \cdot (\epsilon_2 \mathbf{E}^+(Q) - \epsilon_0 \mathbf{E}^-(Q)) = 0.$$
(A.2)

After some manipulation this leads to the homogeneous integral equation

$$\sigma(Q) = \frac{\lambda}{2\pi} \oint_{S} \sigma(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_{Q}}{|\mathbf{r}_{MQ}|^{3}} dS_{M}$$
(A.3)

where $\lambda = (\epsilon_2 - \epsilon_0)/(\epsilon_2 + \epsilon_0)$. For integral equations of this type the spectrum of eigenvalues is discrete with real values $|\lambda| \ge 1.^{56}$



Figure A.1: A particle (core) of arbitrary shape defined by a surface S.

A convenient way to deal with the problem of the surface-charge density on a cavity (σ') is to change the direction of the surface normal from outwards (\mathbf{n}_Q) to inwards (\mathbf{n}'_Q) . Equation A.1 then becomes

$$\mathbf{n}_Q' \cdot \mathbf{E}'^{\pm}(Q) = \pm \frac{\sigma'(Q)}{2\epsilon_0} + \frac{1}{4\pi\epsilon_0} \oint_{S'} \sigma'(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}_Q'}{|\mathbf{r}_{MQ}|^3} dS_M \tag{A.4}$$

Inserting this into the boundary condition

$$\mathbf{n}_Q' \cdot (\epsilon_2 \mathbf{E}'^+(Q) - \epsilon_0 \mathbf{E}'^-(Q)) = 0 \tag{A.5}$$

leads to the integral equation

$$\sigma'(Q) = \frac{\lambda'}{2\pi} \oint_{S'} \sigma'(M) \frac{\mathbf{r}_{MQ} \cdot \mathbf{n}'_Q}{|\mathbf{r}_{MQ}|^3} dS_M \tag{A.6}$$

where $\lambda' = (\epsilon_2 - \epsilon_0)/(\epsilon_2 + \epsilon_0)$.

Appendix B

Calculation of Spectra using the Electrostatic Eigenvalue Method

In Chapter 3, spectra were calculated using eigenvalues and eigenfunctions obtained from the numerical evaluation of either equations 3.5 and 3.6 (spherical shells – Fig. 3.2a and b), equation A.3 (cube – Fig. 3.3b), or the equations discussed in Ref. 83 for a shell in the situation where $\epsilon_1 \neq \epsilon_3$ (cubic shell – Fig. 3.3a and 3.5, and spherical shell – Fig. 3.5). These equations were evaluated using the dielectric functions for CO₂ and N₂O (parameters described below). The procedure for these types of calculations is discussed in detail elsewhere. 56,80,82,83 A comparison of some these spectra to those calculated using multilayer Mie theory 43,185 (the exact solution to the problem in the case of the spherical shell) and DDA (see Section 1.4.2 for details on this method) are presented in Fig. B.1 and B.2. In both the Mie theory and DDA calculations, particle dimensions were never more than 10 nm (i.e. well within the electrostatic limit). Agreement among all methods is excellent.

For CO_2 a frequency dependent dielectric function in the form of

$$\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) \tag{B.1}$$

where

$$\epsilon'(\omega) = \epsilon_{\infty} \left(1 + \sum_{m=1}^{N} \frac{(\omega_{L_m}^2 - \omega_{T_m}^2)(\omega_{T_m}^2 - \omega^2)}{(\omega_{T_m}^2 - \omega^2)^2 + (\omega\gamma_m)^2} \right)$$
(B.2)

$$\epsilon''(\omega) = \epsilon_{\infty} \sum_{m=1}^{N} \frac{(\omega_{L_m}^2 - \omega_{T_m}^2)(\omega\gamma_m)}{(\omega_{T_m}^2 - \omega^2)^2 + (\omega\gamma_m)^2}$$
(B.3)

was constructed using parameters that best-fit refractive index data from a thin-film study.¹⁴⁹ Three optical modes were included (N = 3) in this function. The TO frequencies (ω_T) of these modes were 655, 661 and 2345 cm⁻¹ with corresponding LO frequencies (ω_L) at 660, 672 and 2377 cm⁻¹, respectively. The high-frequency dielectric constant was $\epsilon_{\infty} = 1.54$. The damping of each mode (γ_m) was not based on a fit and instead was simply set to 0.2% of ω_T for each mode.

The calculations involving cubic CO_2 shells included a dielectric function for the N₂O cubic core. As none of the optical modes of N₂O overlap with those of CO_2 ,⁸⁴ this function was simply set to a constant value of 1.6129.¹⁸⁶ It was found that if this dielectric constant were ignored (i.e. simply set to one) the eigenmodes of the cubic shell would not change significantly but the relative heights of the bonding and anti-bonding modes in Fig. B.2 would. Therefore, its inclusion was necessary for the accurate modeling of the infrared spectra.



Figure B.1: Comparison of spectra of spherical CO_2 shells calculated using multilayer Mie theory (a and c) and the electrostatic eigenvalue method (b and d). The ratio of outer-to-inner radii are 1.2 (a and b) and 2 (c and d). For the numerical implementation of the electrostatic eigenvalue method shells were constructed from 1536 surface area elements.



Figure B.2: Comparison of spectra of cubic CO_2 shells and CO_2 cubes calculated using DDA (a and c) and the electrostatic eigenvalue method (b and d). The thickness of the CO_2 shell was such that its volume was equal to the volume of its cubic core. For the DDA calculation 18167 dipoles were used for the cube and 35147 dipoles were used for the cubic shell and its cubic core. For the numerical implementation of the electrostatic eigenvalue method the cube was constructed from 3072 surface area elements and the cubic shell was constructed from 6144 surface area elements. All edges and corners were rounded.