I. INTRODUCTION

The study of low-temperature aerosols finds its interest and has applications to stratospheric observations and planetary upper atmospheres’ teledetection. Also fundamental applications to retrieve the optical constants of solids producible only at low temperatures, to test the processes involved in homogeneous nucleation and to determine the surface energy of particles, are of importance. To generate clusters or aerosol particles, several techniques can be used, such as jet expansion, supersaturated solutions, electrospray, and collisional cooling, depending on the nature of the monomers and the required temperature. Collisional cooling offers the advantage of operating in thermal equilibrium with high lifetimes of the aerosol particles reaching up to hours. This enables sufficient detection sensitivity per molecule, especially in combination with optical multiple path cells, for use of the Fourier transform infrared (FTIR) spectroscopy which delivers broad ranging infrared spectra. There are a few articles which describe IR spectra of CO monomers, dimers, and, recently, CO monomers in liquid helium droplets. However, although CO (and other icos) nanoparticles and micro-particles in the aerosol phase are of high interest especially in astrochemical and astrophysical aspects, where the ices are generally measured by thin film spectroscopic methods (e.g., Refs. 13–18 and references therein), corresponding investigations appear to be scarce. In Ref. 19 spectra of crystalline and (partially) amorphous CO nanoparticles have been discussed without size and shape analysis, while in Ref. 20 CO nanoparticles appeared rather as a by-product in the effort to use CO monomers for the calibration of supercooled monomer spectra. In the present work, a much broader variety of particle shapes and sizes are generated by the same collisional-cooling system and investigated by FTIR spectroscopy.

The interpretation of spherical particle spectra has been performed using Mie inversion algorithms with different approaches for the iterated increment. We build in this work a new iterative Mie inversion procedure based on the Kramers–Kronig relations linking the optical constants. Once determined, these optical constants are coupled to a discrete dipole approximation code to generate modeled spectra for arbitrary shapes in order to interpret the recorded particle spectra.

II. EXPERIMENTS

A. CO particle and film generation

The CO nanoparticles were formed in a long-path collisional-cooling cell in Braunschweig which is described in detail in (Refs. 19, 23, and 24). The cooling system includes a multiple-pulse sample-gas injection device for the generation of molecular nanocomposites, which is used in this work for single pulse or repetitive pulse injection of the CO/He probe gas mixtures. The experimental setup is schematically shown in Fig. 1. To cover a broad range of particle sizes and shapes three different sample-gas inlet and particle-formation approaches are used to generate the CO nanoparticles: Pulse injection, continuous injection, and “diffusive nucleation.” In the latter case, the cooling cell was used as a diffusion cloud chamber which was invented by Langsdorf in 1939. Here, a temperature gradient with the bottom of the cell causes a super-
saturated state within the cell with the supersaturation maximum at about 2/3 of the cell height.\(^{28}\) Due to the three-zone (and mirror) heating capability of the cooling cell\(^ {19}\) such a gradient can be adjusted. More technical details and improvement of the technique are planned to be described in a future work.

The infrared spectra was recorded with a Nicolet Magna 550 FTIR spectrometer equipped with a Globar light source, a KBr beam splitter, KBr windows, and an external InSb detector. Optical path lengths of 2.5 and 12.5 m were used. Temperatures were adjusted between 5 and 35 K. The pressure was varied between 1 and 220 mbars. In most cases we used constant buffer-gas densities at temperatures in Kelvins being equal pressures in millibars. The spectra were recorded mostly in a spectral range of 520–7000 cm\(^{-1}\) with an optical resolution of 0.125 and 0.5 cm\(^{-1}\) using a zero filling Happ–Genzel\(^ {29}\) and also a KBr beam splitter, KBr windows, and an external InSb detector of the sensitive cell which has a minimum optical path length of 2.5 m reaches saturation with relatively small CO concentrations although higher concentrations support the generation of bigger spherical particles. Here, the diffusive-nucleation approach carried out to be best suited.

For comparison with aerosols, a CO ice film, produced in an evacuated cryostat, was recorded at Orsay. The film was condensed from the gas phase onto a CsI substrate placed at the end of a cold finger, cooled at 10 K by liquid He transfer. The spectrum was recorded at normal incidence with a Bruker IFS66v spectrometer at a resolution of 0.5 cm\(^{-1}\) and is shown at the bottom trace in Fig. 6.

B. Experimental results

Within the scope of the present work we produced two classes of particles, smaller ones with diameters below ~100 nm and bigger ones with diameters above ~100 nm. Only the latter show noticeable scattering effects in the recorded spectral range. The temporal evolution of the spectra of the smaller CO particles is shown in Fig. 2. The particles were generated in the pulse-injection mode at varied buffer-gas pressure and constant-temperature conditions [Fig. 2(a)] and at varied-temperature and constant buffer-gas density conditions [Fig. 2(b)]. The maximum of the central band at 2140 cm\(^{-1}\) blueshifts by up to 0.5 cm\(^{-1}\) with increasing pressure [Fig. 2(a)] and decreasing temperature [Fig. 2(b)]. Two further band features appear: A weak shoulder (\(B\)) at the higher-frequency side which only indicates a distinct temporal dependence at the low pressure conditions (25 K, 5 mbars) and a more pronounced band at the transversal optical (TO) mode frequency which shows a striking temporal increase again at low pressures (25 K, 5 mbars). Obviously, an increase in the buffer-gas pressure inhibits the development of the (\(R\)) band which could be a hint that the gas phase is involved in the underlying change of the particles. This pronounced band structure near the frequency of the optical TO mode could also be observed for other van der Waals bonded particles consisting of CO\(_2\) and N\(_2\)O molecules and could be identified due to a change of the particle shape from spherical toward longish structures.\(^ {26,30-32}\) How-
ever, such shape effects have not been observed for experimentally generated CO particles\textsuperscript{19} so far. For the generation of bigger spherical CO particles (with the absence of shape effects) only the diffusive-nucleation mode of the cooling cell carried out to be suitable. Examples of extinction spectra of particles with mean sizes up to micrometers are displayed in Figs. 3 and 4. Especially the two bottom spectra show pronounced scattering features including a base-line increase with frequency and the appearance of Christiansen bands. These spectra are dominated by the spherical shape without strong substructures and as such will provide the basis set of the Mie inversion procedure described hereafter.

There are strong hints that the structure of the particles discussed in this work is crystalline and not amorphous. The band intensity is predominantly distributed within the optical TO and LO modes as is common for the crystalline state\textsuperscript{33} and it does not show a band shape projecting over the TO mode into the lower-frequency region as observed for fully amorphous films and particles of CO\textsubscript{2} and N\textsubscript{2}O.\textsuperscript{33,36,26}

Furthermore, it has to be mentioned that carbon monoxide has two low-temperature solid phases with the transition at 61.55 K.\textsuperscript{35,36} The infrared spectral band shape of the higher-temperature phase is very similar to that of the liquid CO phase with band widths being about three times bigger compared to the lower-temperature phase.\textsuperscript{35} In our experiments, performed at temperatures below 36 K, we did not detect such broader spectral structures and therefore we assume to observe the solid lower-temperature phase only.\textsuperscript{37}

**FIG. 3.** Best fits obtained for the cooling cell experiments by the CO optical constant Mie inversion scheme presented in this article. Top panel: Full span comparison between the fits (gray line) and the recorded (dark line) spectra. Lower right panel: Close-up on the fits in the $^{12}$CO main vibration region. Lower left panel: Retrieved optical constants from the simultaneous inversion of these three spectra using the Mie technique described in the text.

**FIG. 4.** Close-up on the extinction spectra of spherical particles produced with the diffusive-nucleation approach, starting with main sizes below the Rayleigh limit (upper trace) and thus little scattering contribution, up to micron-sized particles with strong scattering effects (middle and lower traces). Note the expanded scale compared to Fig. 2 to display the extended scattering wing contributions. These three spectra are used to perform the Mie inversion.
III. MIE INVERSION

Mie inversion of aerosol extinction spectra is routinely used to predict the aerosol vertical profile in our atmosphere given some aerosol optical constants. It is also used to extract the optical constants directly from extinction measurements of laboratory-produced particles in a collisional-cooling cell as the one used in the present study.

A. A new iterative scheme to extract n and k

The particle size distribution, extinction spectra, optical constants, and Kramers–Kronig relations used in our approach are given in the Appendix for simplicity. Based on the formulations and following the interdependent relations observed between the parameters involved in the extinction spectra, a new iterative scheme to retrieve the optical constants n and k of the ice particles under consideration is developed. We follow basically the procedure presented in Ref. 22, but implement a new iterative correction applied to the k optical constants.

We start from an initial guess for the real and imaginary parts, n and k, for the refractive index of the particles, using the optical constants determined from a thin film measurements.

A proportional factor \( S(\bar{\nu}_\text{ref}, r_{\text{mean}}, \sigma) \) between the calculated \( \langle C_{\text{ext}}(\bar{\nu}_\text{ref}, r_{\text{mean}}, \sigma) \rangle \) and the measured extinction \( \tau(\bar{\nu}_\text{ref}) \) is evaluated at a reference wavenumber \( \bar{\nu}_\text{ref} \) located in the “purely scattering” part of the spectrum (\( k \approx n \)). The best \( S \) factor is evaluated by minimizing

\[
\chi^2 = \sum_{\bar{\nu}} \left[ \Delta \tau(\bar{\nu}) \right]^2,
\]

\[
\Delta \tau(\bar{\nu}) = \tau(\bar{\nu}) - S(\bar{\nu}_\text{ref}, r_{\text{mean}}, \sigma) \langle C_{\text{ext}}(\bar{\nu}, r_{\text{mean}}, \sigma) \rangle
\]

over a \( r_{\text{mean}}, \sigma \) grid spanning the correct space parameters.

Once minimized, the calculated extinction represents the best fit to the observed spectrum with the given n and k optical constants. Assuming that the model is a “true” representation of the particles (i.e., that we are dealing with spheres here), one can improve the n and k knowledge using the relation established before between \( Q_{\text{ext}}(\bar{\nu}) \) and k.

Other authors have used other relations. Clapp et al. 21 used the Beer–Lambert law \( (\kappa \approx \tau(\bar{\nu}) / \bar{\nu}) \), which is only true for a bulk measurement without interfaces nor scattering. An overall agreement is obtained but the line profiles do not match in detail. Dohm et al. 22 devised a modified approach, using the purely absorbing component of \( \Delta \tau(\bar{\nu}) \) and volume of the particles. It leads to a much better agreement. We propose here another method using the observed dependence of \( Q_{\text{ext}}(\bar{\nu}) \) and k in the Rayleigh regime.

The setting of \( S(\bar{\nu}_\text{ref}, r_{\text{mean}}, \sigma) \) allows us to derive an estimated \( A_i(\bar{\nu}) \) from the observed \( r_{\text{ext}}(\bar{\nu}) \) following

\[
A_i(\bar{\nu}) = \frac{Q_{\text{ext}}(\bar{\nu})}{4x} = \frac{r_{\text{abs}}}{S(\bar{\nu}_\text{ref})} \left[ 1 - \frac{Q_{\text{calc}}(\bar{\nu})}{Q_{\text{ext}}(\bar{\nu})} \right] \frac{1}{8\pi^2 \bar{\nu}^3}
\]

to account for the scattering part of the extinction. We numerically form the function \( A_i(\bar{\nu}) \) by taking the Hilbert transform of \( A_i^{\text{est}}(\bar{\nu}) \), and add the \( A_0 \) constant evaluated at \( \bar{\nu}_\text{ref} \) using as anchor point the value of n(\( \bar{\nu}_\text{ref} \) = 1.3) taken from laser near infrared measurements performed in Ref. 39. The absence of strong bands from the near infrared to the chosen anchor point should ensure us that this value remains near 1.3 to a high accuracy.

Then, \( k_{\text{est}}(\bar{\nu}) \) is evaluated from these \( A_i(\bar{\nu}) \) and \( A_i(\bar{\nu}) \) using the equations presented in the Appendix.

The same is evaluated from \( Q_{\text{calc}}(\bar{\nu}) \) to form \( k_{\text{calc}}(\bar{\nu}) \), thus passing through the same processing. One step in the iteration can be advanced following the equations

\[
\Delta k(\bar{\nu}) = k(\bar{\nu})^{n+1} - k(\bar{\nu})^n = k_{\text{est}}(\bar{\nu}) - k_{\text{calc}}(\bar{\nu}).
\]

Note that one must use this differential form as \( k_{\text{calc}}(\bar{\nu}) \) deviates from the true k optical constant when the aerosol distribution is no longer in the Rayleigh limit. As in the previous studies, the correction is best suited for particles with moderate scattering. The difference is that in our iterative scheme, the solution is the “exact solution” if the considered aerosol distribution falls in the Rayleigh regime. Therefore, the ideal extinction spectra on which to perform such a Mie inversion are the ones in which the contribution to extinction of scattering is significant in the near infrared (allowing a good estimate of S) and low in the vibrational region where main modes are observed (allowing the increment to be closer to the true k value).

The real refractive index is iterated in the CO case following the Kramers–Kronig relation

\[
n(\bar{\nu})^{n+1} = n_0 + \frac{2}{\pi} \int_{\bar{\nu}_1}^{\bar{\nu}_2} \frac{\bar{\nu}^2 k_{\text{calc}}(\bar{\nu})}{\bar{\nu}^2 - \bar{\nu}^2} d\bar{\nu},
\]

where \( n_0 \) is set to satisfy the anchor point value \( n(\bar{\nu}_\text{ref}) = 1.3 \). As previously said, this applies to the CO ice case (and probably to many other simple ices), but proper extrapolation formula should be used for other substances possessing numerous transitions, to take into account the effect of these transitions arising outside the measured range.

B. Mie inverted CO optical constants

The iterative retrieval of the optical constants detailed previously is coupled to the amoeba function, performing a multidimensional \( \chi^2 \) minimization at each new step, using the downhill simplex method of Ref. 40 over the parameters defining the log-normal distribution, i.e., \( r_{\text{mean}} \) and \( \sigma \). Such a minimization scheme is slow as it requires the evaluation of the function for each point, several times, but has the advantage of using no derivative of the spectra, and thus is less sensitive to the noise.

The imaginary part of the refractive index is initialized using a Lorentz oscillator model for the CO band. The Lorentz parameters are \( \gamma = 1.5 \) cm\(^{-1} \), \( \omega_p = 160 \) cm\(^{-1} \), and \( \epsilon_0 \)

<table>
<thead>
<tr>
<th>Exp No.</th>
<th>( r_{\text{mean}} ) (( \mu )m)</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>0.0032</td>
<td>2.78</td>
</tr>
<tr>
<td>70</td>
<td>0.138</td>
<td>1.99</td>
</tr>
<tr>
<td>75</td>
<td>0.246</td>
<td>2.53</td>
</tr>
</tbody>
</table>

TABLE I. Log-normal minimized parameters corresponding to best-fit results of Fig. 3.
=1.57 and were derived from thin film CO measurements (see Sec. IV A for references). This oscillator is scaled by a factor $\alpha < 1$ to provide the initial conditions to the minimization, a parameter that can also be varied to test the effect of nonlinearity with various initial conditions.

The minimizations show that the $\{r_{\text{mean}}; \sigma\}$ space parameter is partly degenerated when fitting the scattering of a distribution containing particles both in the Rayleigh regime ($x=2\pi n \rho \ll 1$) whereas others are in the scattering regime ($x \approx 1$), and many combinations lead to similar $\chi^2$. Unless $r_{\text{mean}}$ or $\sigma$ can be determined independently or guessed, the constraint does not represent the true log-normal distribution. One can decide to set $\sigma$ above the self-preserving size distribution value obtained by coagulation ($\approx 1.32$, e.g., Ref. 41 and references therein), up to wide distributions with $\sigma \approx 3$, to partly lift the degeneracy. Using our Mie scheme, we performed a simultaneous minimization of the three spectra presented in Fig. 4 without constraining these parameters, in order to retrieve the $n$, $k$ optical constants for CO ice. The $k$ constant is iterated at each step using the mean $\Delta k=(\Delta k_{\text{TO}}+\Delta k_{\text{LO}}+\Delta k_{\text{E}})/3$. The iteration was stopped when the global minimum of $\Sigma \chi^2$ is reached. Results are displayed in Fig. 3 for both the best global fits (upper and lower right panels) and the retrieved $n$, $k$ optical constants (lower left panel). Corresponding $\{r_{\text{mean}}; \sigma\}$ parameters are given in Table I. An even better fit can be reached if each spectrum is inverted individually, but then small variations between the retrieved $n$, $k$ are observed. The simultaneous inversion for the three spectra appears therefore more consistent. Given the underlying assumption that for these experiments only spherical aerosol particles have been generated, the agreement obtained between experimental and modeled spectra, over very different size distributions, seems rather good.

C. Comparison with thin film optical constants

The $n$ and $k$ optical constants retrieved from our analysis can be compared to thin film optical constants, although the latter are generally performed using CO monomer deposition at lower temperatures. In Fig. 5 we display the $n$ and $k$ derived by several authors. Compared to our $n$ and $k$ optical constants which are shown in Figs. 5(a)–5(d), and to a lesser extent Fig. 5(e) constants are significantly broader and extend well out of the LO-TO limits, pointing to amorphous samples. We evidenced a similar broadening effect in a previous cooling cell experiment performed on the $^{13}$CO isotopomer where the amorphous phase became dominant for smaller particles and at lower temperatures compared to the experimental conditions applied in this work.

IV. FITTING OF EXPERIMENTAL SPECTRA

Quantum chemistry calculations (e.g., Ref. 42) and the quantum mechanical vibrational exciton model (e.g., Refs. 43, 31, and 44) are powerful to describe the coupling of all the oscillators in the particle and hence, can predict the resultant infrared absorption spectrum. In particular, it is of uppermost importance to describe the infrared spectrum evolution in the regime of high surface to volume molecule ratio for the (small) aerosol particles with appropriate methods.

When particles become, however, big enough, reaching about 100 nm ($\approx 10^{7–9}$ molecules for a typical ice aerosol), a continuum limit of light interaction with the particle can be described by the bulk complex refractive index, adopting the correct shape for the particle (e.g., Refs. 45–48). For the subsequent analysis we are placed above this limit.

A. Limiting cases

The extinction of an ice particle which is small compared to the wavelength of light is influenced by the uniform polarization generated by the incoming light as well as by the surface modes of the particle. In order to better understand the influence of the shape effects in the Rayleigh regime, we display the calculated extinction of randomly oriented CO ice particles with different simple shapes in Fig. 6. For the sphere, needle, and disk, equations can be found in classical textbooks (e.g., Ref. 49). The cube spectrum has been generated using the discrete dipole approximation pre-

FIG. 5. Comparison of the CO optical constants retrieved from our Mie inversion of aerosol spectra (a) with the ones obtained from thin film measurements at 10 K by several authors (b) Ref. 15, (c) Ref. 16, (d) Ref. 17, and (e) Ref. 18. [(b)–(d)] Optical constants extend well over the LO-TO mode, suggesting the amorphous state to be involved for the ices condensed at low temperature directly out of the gas phase on a cold finger. The optical constants in (e) are closest to our result in (a). See text for details.

FIG. 6. Calculated extinction spectra using a classical Lorentzian oscillator for the CO optical constants for various solid particle shapes in the Rayleigh limit. Comparison is presented with spectra of spherical crystalline particles generated in a collisional-cooling cell (upper trace, exp. 65) and of a thin amorphous CO film deposited at 10 K on a CsI substrate (lower trace).
sented in the next section. The spectra were modeled by using the dielectric function determined at 10 K in Ref. 17 and fitted in Ref. 14 by a Lorentz oscillator. The Lorentz parameters are \( \gamma = 1.5 \ \text{cm}^{-1} \), \( \omega_0 = 160 \ \text{cm}^{-1} \), and \( \epsilon_0 = 1.57 \). We could use our retrieved CO optical constants, but for didactic purposes, such a simple oscillator shape was adopted. In this way, the lines and shoulders appearing in the extinction spectra can be fully attributed to shape effects and not to local inflections in the optical constants.

For comparison, an almost scattering free CO extinction spectrum recorded in the collisional-cooling cell is displayed, as well as an extinction spectrum, recorded at normal incidence, of a thin CO ice film deposited at 10 K onto a CsI substrate. As expected, the thin film is best fitted by a disk shape, whereas the particle in the cooling cell is better represented by the spherical shape.

Even with such limiting cases of grain shapes, one can gain insight into the spectra fitting. The appearance of an extinction band near the wavenumber associated with the TO mode (~2138.5 cm\(^{-1}\)) does not contain fully constraining information on shapes, but rather tells us that the shape distribution contains significant amounts of elongated structures in one direction perpendicular to the incoming light. The absence of a well defined mode near the LO mode (~2142.5 cm\(^{-1}\)) is the sign that the shapes are not planar. The more compact shapes should display their dominant absorption peak in the vicinity of the sphere position \( 2\pi r_{\text{TO}}/3 + \bar{v}_{\text{LO}}/3 \), like the cube, for example.

**B. DDA calculations: Shape aspects**

We experimentally observe many spectra with profiles different from the expected one for spheres. The fact that we are dealing with an ensemble of particles with various shapes, which cannot be determined independent of the spectra, tells us that a direct inversion method on the data to retrieve the shape distribution is probably hopeless due to the high level of degeneracy. However, to gain insight into the dominant shapes contributing to the observed extinction spectra we calculate template extinction spectra for parallel-epipedic shapes with various edge ratios using the determined CO ice optical constants. Computational approaches based on the separation of variables method, T-matrix method, and discrete dipole approximation (DDA) methods are often employed to numerically solve the scattering problem for particles with distinct shapes and/or when the size parameter \( 2\pi r/\lambda \) approaches or exceeds unity. In our case we make use of the DDA program **DDSCAT** (Refs. 50 and 51). The extinction spectra of randomly oriented particles, calculated over 64 different angle orientations, for a given shape, in the Rayleigh regime, are explored. The results of these calculations are displayed in Fig. 7, where numerous sub-structures raise, depending on the particle specific shapes. These spectra provide a basis set to fit the experimental spectra.

Note that the shape behavior studied here for CO can generally be applied to many other experiments. Figure 5 of Ref. 52 for many different ice particles, spanning a large range of vibrational mode intrinsic intensities, is a good example of that. The sharpness and exact positions of the features are dependent on the dipole moment of the transitions, but the observed structures are qualitatively similar.

**C. Fitting the diversity of spectra**

In Fig. 2, the diversity of possible band shapes for various experiments was shown to cover the full span of produced profiles. The six spectra of the 25 K/5 mbar experimental conditions of Fig. 2(a) are included in Fig. 8 (thick lines). The shape evolves with a progressive growth of two bands at ~2141.5 and 2138.5 cm\(^{-1}\). Using the set of DDA calculated spectra, based on our determined CO refractive index data, we performed a decomposition of individual band shapes assuming that these synthetic spectra are the template spectra entering into the final band shape. For that purpose we make use of a positive matrix factorization (PMF) algorithm (a principal component analysis with positive matrices\(^{53} \)) which allows to define the main spectra contributing to the final shape.

This PMF analysis leads to the best combination of our calculated spectra, presented in Fig. 7 for those parallelepipeds that reproduce the experimental spectra best. It gives some indication on the dominant shapes generated in the aerosols. In most cases a combination of two to three shapes is sufficient to produce the fits to the recorded spectra, as shown in Fig. 8. Such an analysis shows that the spectra can be decomposed in a spherical plus an elongated particle component. The obtained fits (dotted lines) and the three first contributing model spectra (thin lines) are shown in Fig. 8.

Although the exciton calculation is by essence a quantum mechanics and thus a more fundamental description, the continuum approach presented here is well compatible with
the observed spectra. It further demonstrates the dominant role of shape effects on the spectral profiles and allows to follow the shape evolution of large aerosol particles.

D. DDA calculations: Bigger particles

In multi-pulse-injection experiments, large particles are formed. Here, both the shape of the particles and scattering of infrared radiation by the particles dominate the spectra in general. To explore the large size effect in the absence of shape effects, the volume attenuation coefficient for a sphere with various size parameters reaching from the Rayleigh to the scattering regimes have been calculated by using our derived optical constants, see Fig. 9. Using these DDA results in combination with the PMF decomposition we are able to elucidate the spectral structure appearing at the lower-frequency side of the LO-TO range. In particular, the band around 2137 cm\(^{-1}\) can be attributed to scattering of bigger particles in the size parameter range of \(x = 1 \pm 1\).

The analysis shows that the particle spectra can be simulated by a distribution of six particle sizes which roughly resembles a log-normal distribution in all three cases. It could also be shown (not depicted in the figure) that the slight shoulder at 2141.5 cm\(^{-1}\) on the left side of the main band is better reproduced by the parallelepped shapes rather than spherical particles, but clearly scattering effect prevails upon shape effects in the large size limit.

V. CONCLUSION

An improved Mie inversion algorithm has been designed and applied to the spectra of spherical CO ice particles generated at low temperatures in a collisional-cooling experiment using the diffusive-nucleation capability of the cooling system. The other operating modes of the cooling cell, pulse injection and continuous flow injection, delivered CO nanoparticles with pronounced shapes deviating from spherical.

Among our motivations was to explore the nucleation behavior of CO aerosols, only possible with the present low-temperature cooling cell. The large aerosol particles we produce also enable us to determine the CO ice optical constants, free of substrate interfaces and complementary to thin films. The DDA models offer the possibility to predict the shape effects on the spectra and to get nucleation tendencies.

The retrieved CO optical constants were therefore used to calculate template spectra for other particle geometries, forming a basis set to deconvolve more complex spectra involving nonspherical distributions of particles.

In that way, a qualitative shape analysis of the observed particles could be realized. Moreover, the presented ap-
proaches serve as a useful guideline for the interpretation of experiments with ice particles of other substances.

In this article we focused on pure CO aerosols. Direct application to real icy particles in space and planetary atmospheres requires some chemical diversity to be added. Low-temperature FTIR investigation of ice mixtures condensed as thin films is extensive in the astrophysical community. The most ubiquitous interstellar ices are made of H$_2$O, CO, and CO$_2$, whereas ice rich environments (dense interstellar clouds) components comprise CH$_3$OH, CH$_4$, NH$_3$, as well as other less abundant species. In this respect, the least complex ice system valuable to explore in further investigations with our technique described in this paper would be a H$_2$O/CO or H$_2$O/CO$_2$ aerosol mixture at relevant interstellar low temperatures.

APPENDIX: INVERSION PARAMETERS RELATIONS

1. Particle extinction spectra

The particle size distribution in such supersaturation experiments is generally fairly well represented by a log-normal probability function:

$$p_{LN}(r, r_{\text{mean}}, \sigma)dr = \frac{1}{\sqrt{2\pi} \ln(\sigma)} \exp \left[ - \frac{(\ln(r/r_{\text{mean}}))^2}{2(\ln(\sigma))^2} \right] dr,$$

where $r$ is the radius of the particle, $r_{\text{mean}}$ the median of the distribution, and $\ln(\sigma)$ the standard deviation. Assuming that the particles are nearly spherical, using Mie theory, and the known optical constants of the material forming the particles, one can therefore calculate the mean extinction cross section for the ensemble of particles (e.g., Ref. 22) given by

$$\langle C_{\text{ext}}(\tilde{\nu}, r_{\text{mean}}, \sigma) \rangle = \int_0^\infty 2\pi r Q_{\text{ext}}[\tilde{\nu}, r, n(\tilde{\nu}), k(\tilde{\nu})] p_{LN}(r, r_{\text{mean}}, \sigma) dr,$$

where $\tilde{\nu}$ is the wavenumber, $n(\tilde{\nu})$ and $k(\tilde{\nu})$ the real and imaginary parts of the complex refractive index characterizing the material, and $Q_{\text{ext}}$ the extinction efficiency of the particle. In practice the integral is evaluated over an interval where $p_{LN}$ contributes significantly.

The transmittance of the cell enclosing these particles can then be evaluated by

$$\ell T(\tilde{\nu}) = \exp[-\tau(\tilde{\nu})] = \exp \left[ - \langle C_{\text{ext}}(\tilde{\nu}) \rangle \int_0^L \eta ds \right],$$

where $\tau(\tilde{\nu})$ is the optical depth, $\eta$ is related to the number density of spheres (cm$^{-3}$), $L$ is the cell optical path length (cm), and $S$ a scaling factor associated with a column density (cm$^{-2}$).

In practice, it is extremely difficult to independently measure the size distribution of particles produced in a cooling cell, due to their inherent short lifetime outside the supersaturation conditions, and therefore the mean extinction cross section has to be properly scaled by the scaling factor $S$ to be compared to experimental spectra.

If the intrinsic optical constants of the material forming the particles are known, one has in principle to deal with three free parameters, $S$, $r_{\text{mean}}$, and $\sigma$.

2. Optical constant relations

The optical constants $n$ and $k$ behavior of a material are related by the Kramers–Kronig relations. The real part $n$ of the refractive index is linked to the imaginary part $k$ by the causal equation

$$n(\tilde{\nu}) = n(\infty) + \frac{2}{\pi} \int_0^\infty \frac{\tilde{\nu}' k(\tilde{\nu}')}{\tilde{\nu}'^2 - \tilde{\nu}^2} d\tilde{\nu}'.$$

This relation and its modification to include the effects of finite bandwidth (real experimental world) measurements are used to derive $n$ from an estimated $k$.

3. Kramers–Kronig relations and extinction

The extinction efficiency for a sphere in the Rayleigh limit ($x \ll 1$) is given by

$$Q_{\text{ext}}(\tilde{\nu}) = 4\pi \text{Im} \left( \frac{\epsilon(\tilde{\nu}) - 1}{\epsilon(\tilde{\nu}) + 2} \right), \quad \epsilon(\tilde{\nu}) = \epsilon_r(\tilde{\nu}) + i \epsilon_i(\tilde{\nu}),$$

$$\epsilon(\tilde{\nu}) = n(\tilde{\nu})^2 + k(\tilde{\nu})^2 = n(\tilde{\nu})^2 - k(\tilde{\nu})^2 + i2n(\tilde{\nu})k(\tilde{\nu}),$$

where $x = 2\pi r\tilde{\nu}$ is the size parameter and $\epsilon(\tilde{\nu})$ the dielectric function of the material.

In their approach of the Mie inversion theory, in Ref. 38 is shown that paired functions satisfying the Kramers–Kronig relations and directly connected to the extinction coefficient $Q_{\text{ext}}$ can be formed.
Reorganizing the above equations, one obtains
\[
e(\tilde{\nu}) = \frac{1 + 2A(\tilde{\nu})}{1 - A(\tilde{\nu})},
\]
and the dielectric function (and therefore the optical constants)
can be evaluated as follows:

\[
\begin{align*}
\epsilon_i(\tilde{\nu}) &= \frac{3(1 - A_i(\tilde{\nu}))}{(1 - A_i(\tilde{\nu}))^2 + A_i(\tilde{\nu})^2 - 2}, \\
\epsilon_o(\tilde{\nu}) &= \frac{3A_i(\tilde{\nu})}{(1 - A_i(\tilde{\nu}))^2 + A_i(\tilde{\nu})^2}, \\
n(\tilde{\nu}) &= \sqrt{\frac{\epsilon_i(\tilde{\nu})^2 + \epsilon_o(\tilde{\nu})^2}{2}}, \\
k(\tilde{\nu}) &= \sqrt{\frac{\epsilon_i(\tilde{\nu})^2 + \epsilon_o(\tilde{\nu})^2 - \epsilon_i(\tilde{\nu})}{2}}.
\end{align*}
\]

In practice the extinction coefficient is measured only on a finite wavenumber interval and therefore
\[
A_i(\tilde{\nu}) = \frac{2}{\pi} \left[ \int_{\tilde{\nu}_l}^{\tilde{\nu}_h} \frac{\tilde{\nu}^2 A_i(\tilde{\nu})}{\tilde{\nu}^2 - \tilde{\nu}^2} d\tilde{\nu} + \int_{\tilde{\nu}_h}^{\tilde{\nu}_b} \tilde{\nu} A_i(\tilde{\nu}) d\tilde{\nu} \right] + \int_{\tilde{\nu}_b}^{\infty} \tilde{\nu} A_i(\tilde{\nu}) d\tilde{\nu},
\]
\(\tilde{\nu}_l\) and \(\tilde{\nu}_h\) defining the low and high wavenumber limits, respectively.

The visible to near infrared spectra of ices generally do not present strong transitions and the influence of ultraviolet transitions through the high wavenumber interval can be approximated to first order by a constant. For the CO case treated here, the same is true for low wavenumbers as the next transitions fall below 100 wavenumbers, well apart from the mode considered here. One can therefore approximate the above integral by
\[
A_i(\tilde{\nu}) = A_0 + \frac{2}{\pi} \int_{\tilde{\nu}_l}^{\tilde{\nu}_h} \tilde{\nu}^2 A_i(\tilde{\nu}) \tilde{\nu} d\tilde{\nu}.
\]

To determine this constant, one can use an anchor point measured (or fixed) in a region where the imaginary part of the refractive index \(k \approx n\) and far away from any strong transitions. In this case \(A_0 \approx 1 - 3/(2 + n^2)\).

Note that in the case of other substances, for which a large number of low (and/or high) wavenumber vibrational modes exist, proper extrapolation formula should be used (e.g., Refs. 38 and 22 and references therein).

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