Cluster Growth in Supersonic Jets of CO₂ through a Slit Nozzle

A. Ramos, G. Tejeda, J. M. Fernández, and S. Montero

Laboratory of Molecular Fluid Dynamics, Instituto de Estructura de la Materia, CSIC
Serrano 121, 28006 Madrid, Spain

Abstract. The condensation produced in planar supersonic jets of CO₂ from a 0.13×3.0 mm slit nozzle is investigated quantitatively by means of Raman and Rayleigh scattering. The rotational and vibrational temperatures of the free-monomers bath, the cluster number density $n_c$, and the mean cluster size $\bar{N}$ are obtained for several jets with stagnation pressures $P_0$ from 1 to 3 bar and 295 K stagnation temperature. In a planar jet, the distance to a collision-free regime is larger than in an axisymmetric expansion through a circular nozzle, allowing more clusters to be formed through three- or two-body collisions. Data on the first stage of the nucleation and cluster growth processes in planar expansions are reported here, and are compared with previous data in axisymmetric jets [Ramos et al. Phys. Rev. A 72, 053204 (2005)]. On the basis of Raman spectra we investigate here the formation and evolution of the clusters, and the coexistence of liquid and solid CO₂. An inverse correlation between vibrational temperature of the free monomers and the mean cluster size $\bar{N}$ is also observed, suggesting some kind of cluster-mediated mechanism for the vibrational relaxation in CO₂.

Keywords: Supersonic jets, Carbon dioxide, Clusters, Condensation, Raman and Rayleigh scattering

PACS: 47.40 Ki, 36.40 Mr, 33.20 Fb, 34.50 Ez

INTRODUCTION

Condensation is a phenomenon of interest in many scientific and technical disciplines like life sciences, astrophysics, planetary sciences, meteorology or engineering. Macroscopic theory of homogeneous condensation can be successfully applied to a number of cases, but the comprehension of its molecular fundamentals is still necessary. When a gas is expanded through a nozzle into vacuum its temperature decreases, the gas jet becomes supersaturated and homogeneous condensation occurs. Therefore free jets and molecular beams have been used for years as sources of clusters for experimental studies of condensation. A microscopic explanation of condensation processes in jets remains largely unknown to date, and only empirical expressions have been reported [1].

Just in a few molecular systems like hydrogen, homogeneous condensation has been studied in detail from its very beginning (dimers and trimers) up to the liquid and solid phases [2, 3, 4]. Carbon dioxide is also a suitable system for such studies: It condenses easily and information about its aggregation state and structure can be obtained by spectroscopic techniques. Previous works [5, 6] reported the growth of large clusters in axisymmetric jets. However the study of smaller clusters at the onset of condensation requires warmer and denser jets with a slower evolution of their properties for delaying condensation [1]. Therefore, the use of slit nozzles [7] might be appropriate in order to widen previous investigations on CO₂ homogeneous nucleation.

The present work is aimed at obtaining an overview of the first stages of condensation of CO₂ in free jets from the experimental point of view, by means of non intrusive Raman and Rayleigh scattering. This study provides valuable experimental data for testing existing condensation models and computer programs, to be afforded in a future work.

METHODOLOGY

The jet is composed by a mixture free molecules (monomers) and a aggregated fraction characterized by a distribution of clusters of size $N$ with number densities $n_N$. Defining $n_c = \sum n_N$ for $N \geq 2$ as the number density of clusters, the first two moments about the origin of the distribution and their ratio are [5]

$$\langle N \rangle = \frac{1}{n_c} \sum_{N \geq 2} N n_N, \quad \langle N^2 \rangle = \frac{1}{n_c} \sum_{N \geq 2} N^2 n_N, \quad \text{and} \quad \bar{N} = \frac{\langle N^2 \rangle}{\langle N \rangle},$$ (1)
where the first one stand for the mean cluster size, and the second one for the mean squared cluster size. The total number density $n$ of molecules in the probe volume can be expressed as

$$n = n_1 + \langle N \rangle n_c,$$  

where $n_1$ is the number density of free molecules. Number densities $n$ and $n_1$ can be measured in CO$_2$ by means of Raman spectroscopy, according to the procedure described below.

Additional information about the aggregated phase can be obtained by means of Rayleigh scattering. Additive molecular polarizability can be assumed for the actual case because the cluster size is smaller than the excitation wavelength. Thus the polarizability of a cluster of size $N$ is $N$ times the polarizability of a single molecule, and Rayleigh intensity can be expressed as

$$I_R = C (n_1 + \langle N^2 \rangle n_c),$$

where $C$ remains constant for each gas at a fixed experimental configuration. The reduced Rayleigh intensity $I_r$ is defined by the ratio

$$I_r = \frac{I_R}{I_0^R} = \frac{1}{n} (n_1 + \langle N^2 \rangle n_c),$$

where $I_R$ is the Rayleigh intensity of the condensed jet, and $I_0^R = C n_1 = C n$ is the Rayleigh intensity of the uncondensed jet. This reference jet is hypothetical in the sense that cannot be realized experimentally. $I_0^R$ can be obtained from the Raman data as explained below.

From Eqs. (1), (2) and (4), the ratio $\bar{N}$ can be expressed as:

$$\bar{N} = \frac{I_r - n_1/n}{1 - n_1/n}.$$  

Assuming a cluster size distribution of width $\sigma$, for a $\langle N \rangle \gg \sigma^2$ (narrow size distribution) the ratio $\bar{N}$ is a good approximation to the mean cluster size $\langle N \rangle$. Within this approximation, number density of clusters can be obtained from Eq. (2) as

$$n_c = n \left(1 - \frac{n_1}{n}\right)^2 \frac{I_r - n_1/n}{I_r - n_1/n},$$

where all quantities are obtained from the experiment.

**FIGURE 1.** (a) Overview of the experimental setup for studying condensation in supersonic jets. (b) Excitation–collection geometry. Direction $x$: Excitation laser and focusing lens $L_1$. Direction $y$: Scattered light collected by $L_2$ (inside vacuum chamber) and $L_3$. Direction $z$: Supersonic jet. The inset shows the probe volume $a \times b \times c$ inside the jet.
EXPERIMENTAL

Supersonic CO$_2$ expansions at stagnation temperature $T_0 = 295$ K, and stagnation pressures $P_0 = 1$–3 bar have been studied. The jets were generated expanding the gas through a slit nozzle of width $D = 130$ $\mu$m and length $L = 3$ mm (aspect ratio $L/D=23$), into a vacuum chamber specially devised for quantitative Raman spectroscopy. Its vacuum system is based on a 1430 m$^3$/h Roots pump backed by a 70 m$^3$/h rotary pump (see Fig. 1(a)).

A cw-Ar$^+$ laser was employed as excitation source at $\lambda = 514.5$ nm. The laser power was about $\sim 1$ W for Rayleigh scattering, and $\sim 2.5$ W for Raman spectra. Figure 1(b) shows the excitation–collection geometry: The laser beam, parallel to the slit nozzle, was focused onto selected points of the jet by a lens of 35 mm focal length ($L_1$ in Fig. 1(b)), producing a 14 $\mu$m beam waist. The scattered radiation was collected at 90º with respect to the laser beam and the jet axis an projected onto the spectograph entrance slit by means of lenses $L_2$ ($f=50$ mm) and $L_3$ ($f=500$ mm) with a total magnification $\times 10$. The scattered radiation was analyzed with an 1 m additive double monochromator equipped with a 2048 $\times$ 512 pixel CCD detector refrigerated by liquid N$_2$. The Raman spectra were recorded at $\sim 0.7$ cm$^{-1}$ spectral resolution.

The excitation-collection optical system was kept fixed during the experiment, while the nozzle was moved to reach the point of interest in the flow field. The pointing accuracy within the expansion flow field is $\pm 5$ $\mu$m. Relative positions between two points are repeatable to $\pm 1$ $\mu$m, which is the precision of the nozzle motorized stages.

At each point of interest along the jet, pure rotational and vibrational Raman spectra, and Rayleigh scattering intensity were measured. The spectra were recorded with the same optical configuration to ensure that the sampled volumes in the flow field were identical in all cases. The inset in Fig. 1(b) shows the probe volume The spatial resolution (in $\mu$m) in the present work is $a \times b \times c = 15 \times 500 \times 15$.

Figure 2(a) shows vibrational Raman spectra measured at several distances from the nozzle along the centerline of the $P_0 = 2$ bar jet. At $z/D=0.38$, the closest point to the nozzle, the spectrum shows the Fermi diad at $v_1 = 1285$ cm$^{-1}$ and $v_c = 1388$ cm$^{-1}$ and the first two O–branch lines ($J=2, 4$) for each component at 1283, 1280, 1383 and 1386 cm$^{-1}$ of the CO$_2$ monomer. Cluster signal appears at the 1383–1387 cm$^{-1}$ region resolved from monomer’s.

At each point of interest along the jet, pure rotational and vibrational Raman spectra, and Rayleigh scattering

The total number density $n$ of CO$_2$ molecules was measured by integrating the Raman intensity of the vibrational monomer band (Q branch at 1388 cm$^{-1}$) and the cluster bands (1384–1387 cm$^{-1}$) as follows. The vibrational Raman intensity can be expressed as

$$I_{\text{Raman}} = \frac{K}{Z_v} n,$$  \hspace{1cm} (7)

where $Z_v$ is the vibrational partition function at vibrational temperature $T_v$, and $K$ is a coefficient which depends on the optical conditions of the experiment. Total number density $n$ was obtained from the ratio between the intensity measured in the jet and the intensity of a static sample recorded with the same optical conditions. The estimated accuracy of the measured number densities is 3% close to the nozzle, and 10% in the furthest points.

The monomer fraction $n_1/n$ (free molecules) was obtained, with an uncertainty of $\sim 10\%$, by comparing the intensity of the band at 1388 cm$^{-1}$ (monomer) with the integrated intensity from 1381 to 1390 cm$^{-1}$ (monomer and clusters), excluding the O(2) and O(4) rotational lines.

The rotational temperature, $T_r$, was determined from the ratio of intensities of the Q branches of the 667→2076 cm$^{-1}$ double degenerate vibrational transition, observed as a hotband at 1409 cm$^{-1}$, and the 0→1388 cm$^{-1}$ vibrational transition from the ground state observed at 1388 cm$^{-1}$ [8]:

$$\frac{I_{1409}}{I_{1388}} = 2 \frac{\langle 667|\alpha|2076 \rangle^2}{\langle 0|\alpha|1388 \rangle^2} \exp \left[-\beta \frac{667}{T_r} \right],$$  \hspace{1cm} (8)

where $\beta = 1.4388$ K/cm$^{-1}$, and the transition moments of the polarizability $\langle 0|\alpha|1388 \rangle = 6.79 \times 10^{-42}$ C V$^{-1}$ m$^2$ and $\langle 667|\alpha|2076 \rangle = 7.20 \times 10^{-42}$ C V$^{-1}$ m$^2$.

The rotational temperature, $T_r$, was obtained from the rotational spectrum [9]. The accuracies of the measured temperatures are $\sim 5\%$ for the vibrational and better than $1\%$ for the rotational.

The Rayleigh intensity $I_R$ was obtained by recording the elastic scattering from the jet and subtracting the background signal from the evacuated chamber, under identical instrumental conditions. The uncertainties in the Rayleigh intensities were below 10% for all jets.

As shown in Eqs. (3) and (7), prior to the onset of the condensation, Rayleigh and Raman intensities are proportional to each other, so that the reference Rayleigh intensity $I_R$ can be obtained scaling the measured Raman intensity to the Rayleigh intensity at the closest points from the nozzle. This way, the mean cluster size $\bar{N}$ and the number density of clusters $n_c$ can be obtained by means of Eqs. (5) and (6).
FIGURE 2. Vibrational Raman spectra of CO2 clusters in a free jet from a slit nozzle. (a) Growth of small and large clusters up to \( \bar{N} = 116 \). Axial series with stagnation conditions \( T_0 = 295 \text{ K}, P_0 = 2 \text{ bar} \). Dashed lines mark the monomer O-branch rotational lines. (b) Growth of the liquid and solid-like phases. Pressure series at the axial point \( z/D = 38.46 \). Dashed lines stand for solid and liquid CO2 wavenumbers.

RESULTS AND DISCUSSION

Jet properties

Figure 3 shows the quantities measured at points of the CO2 jets (\( P_0 = 1 \) and 3 bar) by means of the Raman spectra. Two more jets are shown as reference: a \( P_0 = 3 \text{ bar} \) CO2 axisymmetric jet through a \( D = 310 \mu m \) cylindrical nozzle [5], and a \( P_0 = 2 \text{ bar} \) N2 planar jet through the same \( 130 \mu m \times 3 \text{ mm} \) slit nozzle used here. Reported reduced distances \( z/D \) are based on \( D = 130 \mu m \) for the slit nozzle, and \( D = 310 \mu m \) for the circular one. Condensation is observed in the axisymmetric CO2 jet but not in the planar N2 one. A vertical dashed line marks onset of condensation of CO2 in the planar jet at \( z/D \approx 3.8 \), the distance where Rayleigh intensity \( I_{LR} \) starts departing from its reference value \( I_{LR}^0 \).

The isentropic flow model predicts number densities \( n \propto 1/z \) for planar jets, and \( n \propto 1/z^2 \) for axisymmetric jets at \( z/D > 20 \). For \( 3 < z/D < 20 \) the measured number density for CO2 planar jets shown in Fig. 3 decays slower than the reference CO2 axisymmetric jet, as predicted by the isentropic flow model. Due to the finite length of the slit nozzle (\( L = 23D = 3 \text{ mm} \) ), the behavior of the measured number densities and temperatures changes from planar to axisymmetric-like for distances \( z/D > 23 \), the length of the nozzle.

As shown in Fig. 3(b) the rotational and vibrational temperatures are strongly affected by the condensation process. For \( 3.8 < z/D < 12 \) the heat released by condensation raises \( T_r \) up to 70 K with respect the N2 jet. Once condensation finishes \( T_r \) keeps decaying as in non condensed jet, but at higher temperature. The behavior of \( T_r \) is qualitatively similar in axisymmetric and planar jets, but the evolution is faster for the axisymmetric one.

The gap between vibrational energy levels of CO2 is larger than the energy involved in molecular collisions in the studied jets. Thus, in the absence of condensation the vibrational degree of freedom tends to “freeze” and its associated temperature \( T_v \) remains almost constant along the jet. Upstream from the condensation onset, vibrational temperatures of all measured jets are constant, but beyond this point \( T_v \) decreases (see Fig. 3(b)). The vibrational cooling enhanced by aggregation is more evident in planar than in axisymmetric jets. The \( T_v \) variation along the condensation process suggests a enhancement of vibrational energy transfer by cluster-mediated collisions.
Clustering

Clustering process can be tracked in the Raman vibrational spectra of Fig. 2, where features associated with clusters of different sizes and condensed phases are shown. Molecules inside clusters perturb each other, shifting the vibrational wavenumbers to lower values. For small clusters this gives rise to a peak (∼1285 cm$^{-1}$) close to that of the monomer, with similar linewidth. Larger cluster increases number of possible configurations and the perturbation, broadening vibrational bands and shifting them towards condensed phase bands. In Fig. 2(a) the weak band at ∼1285 cm$^{-1}$ appears and grows at distances $z/D < 5$. This peak is attributed to dimers [10] and small clusters ($N < 10$). At longer distances $z/D=5$ to 12, the peak at 1285 cm$^{-1}$ decreases while broad bands at 1280–1282 cm$^{-1}$ and 1383–1387 cm$^{-1}$ appear due to the growth of larger clusters of mean size $\bar{N} = 9$ to 116.

Cluster size can be increased by raising stagnation pressure $P_0$ [1]. Figure 2(b) shows the Raman spectra of large clusters in region close to $\nu_u$ in expansions with $P_0 = 1$, 2 and 3 bar at $z/D = 38.5$, where an almost stationary value of $\bar{N}$ has been reached. The measured mean cluster sizes are 65, 278 and 652 for $P_0 = 1$, 2 and 3 bar respectively. The Raman spectrum shows a broad band at ∼1385.5 cm$^{-1}$ due to the $\bar{N} = 65$ cluster. For $\bar{N} = 278$ cluster band has splitted into two peaks, one close to the band of liquid at 1385 cm$^{-1}$ and a second one, of the crystal, at 1384 cm$^{-1}$ [12]. For larger clusters ($\bar{N} = 652$) liquid and solid-like peaks become narrower and the relative intensity of solid-like phase with respect to the liquid increases.

![Figure 3](image-url)

**FIGURE 3.** (a) Number density $n$ and Rayleigh intensity, and (b) rotational temperature $T_r$ and vibrational temperature $T_v$ measured along the centerline of CO$_2$ jets. Reference expansions of N$_2$ (planar without clustering) and CO$_2$ (axisymmetric with clustering) are shown. Vertical dashed line stand for the onset of condensation in the planar jets.
Figure 4 shows the mean cluster size $\bar{N}$ and free monomer fraction $n_1/n$ along two planar jets with $P_0=1$ and 3 bar, and a $P_0=3$ bar axisymmetric jet. From Fig. 3 we conclude that condensation onset appears further downstream from nozzle than in the axisymmetric jet. Downstream from onset, free monomer fraction $n_1/n$ decreases along the zone of silence. The mean cluster size (see Fig. 4(a)) increases rapidly in the first stages of condensation ($z/D<10$) and then, for $z/D>50$, tends to a constant value $\bar{N} \approx 1000$. However, clustering along axisymmetric jets evolves faster. The onset is closer to the nozzle but the mean clusters size freezes sooner, reaching a constant value $\bar{N} \approx 200$ for $z/D>6$.

CONCLUSIONS

The apparatus for optical diagnostics in supersonic jets developed in our laboratory has been upgraded for its use in planar jets, which show several instrumental advantages with respect to the axisymmetric ones: larger probe volume, less interference with the barrel shock wave, higher sensitivity, and better spatial repeatability nearby the nozzle. However, a more powerful vacuum system is required. The combination of Raman and Rayleigh scattering in the same experiment provides a dataset of rotational and vibrational temperatures, total number density of molecules, free monomer number density, number density of clusters, and mean cluster size along of the jet. Additional details are provided by the ability of Raman spectroscopy to distinguish between condensed phases, tracking its evolution along the jet. This information is aimed at filling the lack of experimental data in this field.

Temperatures and density evolve slower in planar than in axisymmetric jets. Thus, higher temperatures in planar jets delay the onset of the condensation with respect the axisymmetric ones. However higher density induces a steeper and lengthy clustering process than in axisymmetric jets. This slower timescale for condensation might help to obtain accurate experimental data for testing kinetic models of homogeneous nucleation and liquid-solid phase transition.

Evolution of Raman signal in Fig. 2(a) suggests two different aggregation mechanisms depending on the cluster size. In the first step of condensation small clusters grow due to molecule-molecule and molecule-cluster collisions. Three body collision are the main initial mechanism of aggregation, where the third body drains the excess of collisional...
energy and avoids cluster breaking. Once a critical cluster size is reached the cluster-cluster collision becomes more efficient than the molecule mediated ones, and a fast growing of large cluster occurs by coalescence.

Vibrational degrees of freedom of small molecules are frozen for most jets free of condensation. However, vibrational cooling induced by condensation has been clearly observed in the present CO2 jets (Fig. 3(b)). The correlation between vibrational relaxation with size and number density of clusters shows that cluster-mediated collisions are more efficient than molecule-molecule collisions. To our knowledge, this phenomenon is reported here for the first time in a clear way, supported by quantitative data. A detailed interpretation of this process will be the subject of future work.

ACKNOWLEDGMENTS

This work has been supported by the Spanish Ministerio de Ciencia e Innovación (MICINN), Research Projects FIS2007-61430 and FIS2010-22064.

REFERENCES