Quantitative study of cluster growth in free-jet expansions of CO₂ by Rayleigh and Raman scattering

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

Instituto de Estructura de la Materia, CSIC, Serrano 121, 28006 Madrid, Spain (Received 26 July 2005; published 9 November 2005)

The condensation produced in supersonic expansions of CO₂ is studied quantitatively combining Rayleigh and Raman scattering. The cluster number density n_c and the mean cluster size \bar{N} are obtained for five expansions with stagnation pressures $P_0=1-5$ bars, and temperature $T_0=294$ K, along axial and radial directions; n_c and \bar{N} are determined from the condensation onset up to a terminal size \bar{N}_{∞} , verifying the empirical law $\bar{N}_{\infty} \propto P_0^{2.23}$. A maximum growth rate $d\bar{N}/dt \approx 8 \times 10^8 \text{ s}^{-1}$ is estimated for the 5-bar expansion. The Raman spectra show a coexistence of solid and liquidlike phases in the jet, with a progressive transition from the liquid to the solid fraction as the clusters increase their size.

DOI: 10.1103/PhysRevA.72.053204

PACS number(s): 36.40.-c, 33.20.Fb

I. INTRODUCTION

Clusters, an intermediate stage between the isolated atoms or molecules and the bulk state, display unique and challenging properties, which are mostly due to their large surfaceto-volume ratio [1]. Much theoretical and experimental work has been carried out about nucleation, cluster growth, and accompanying structural changes, as well as their connection with the bulk [2–5].

In addition to the applications of clusters in materials science [6], attention has recently been paid to the interaction of intense laser pulses with clusters generated in supersonic expansions [7]. Due to their small volume and density close to that of the solid, it is more efficient to generate a hot plasma by laser irradiation in clusters than by using gas or solid targets. In this way, nuclear fusion has been produced from deuterium clusters [8], as well as ultraviolet or x-ray bursts from Ar and Kr clusters [9].

The interpretation of experiments involving clusters relies on a good knowledge of their size and spatial distribution. For instance, in the interaction of high-intensity laser radiation with clusters, their density and average size are crucial for the coupling dynamics [10,11], and even the cluster size distribution is important concerning other parameters of the interaction [12].

Supersonic nozzles [13] and free jets [14,15] are widely used as cluster sources, yielding clusters of a broad size range. Their characterization is possible by a number of experimental techniques. Some of them are based on extracting a cluster beam out of the expansion, usually in the terminal stages of the condensation. Mass spectrometry after electron or photoionization provides a high sensitivity and cluster size resolution [16,17]. Nevertheless, it needs corrections for multiple ionization and ionization-induced fragmentation that distort the original size distribution of neutral clusters [18,19]. Scattering methods rely on the interaction of the cluster beam with another beam of atoms or molecules [20,21], or with a buffer gas [22]. Cluster-particle collision models are required for the interpretation of these results.

Diffraction methods can be used within both supersonic nozzles and free jets. Electron diffraction provides informa-

tion on mean size, temperature, and crystal structure of the clusters [23–25]. Small-angle neutron scattering has proved to be a powerful tool allowing for the direct measurement of nucleation rates and the size distribution of clusters produced in Laval nozzles [26,27]. Recently, clusters themselves have been diffracted through a transmission grating [28,29], leading to the determination of size distributions and binding energies of He clusters. All these methods, however, cannot be easily applied to track the evolution of the condensation along the expansion.

In contrast, some optical methods are not restricted by the aforementioned limitation. Rayleigh scattering has been applied to study the condensation in jets [30-32]. However, Rayleigh scattering alone is not sufficient to separately provide information on mean size and cluster number density [33]; therefore some other measurements or assumptions are necessary. Within the approximation of total condensation, relative mean cluster sizes were estimated by Rayleigh scattering jointly with total density data obtained by other techniques [11,34,35]. In more recent works Rayleigh scattering has been combined with infrared absorption spectroscopy [36], and with Mach-Zehnder interferometry [10,33]. In addition to Rayleigh scattering, linear [30,37] and nonlinear Raman [38–40] spectroscopies have also been applied to the diagnostic of clusters. In recent years linear Raman spectroscopy has reached a high competitive level for the quantitative study of supersonic jets [41,42], including the effect of condensation on the flow [43] and the formation of clusters [44].

In this work Rayleigh scattering is combined with linear Raman spectroscopy for the quantitative characterization of cluster growth in supersonic jets of CO₂, reaching a high spatial resolution. The basic quantities measured along the jet are the intensities of Rayleigh scattering, and of rotational and vibrational Raman lines. As shown below these data yield information about cluster size, cluster number density, and spatial and temporal evolution.

II. METHODOLOGY

The following notation will be employed: N is the number of molecules forming a cluster, i.e., its number size; n is the

total number density of molecules regardless of its aggregation state; and n_N is the number density of clusters of size N. Thus, n_1 is the number density of free molecules (monomers), and $n_c = \sum n_N$, for $N \ge 2$, is the number density of clusters.

The total number density of a probe volume of the expansion can be expressed as

$$n = n_1 + \langle N \rangle n_c, \tag{1}$$

where $\langle N \rangle$ is the mean cluster size. The densities *n* and *n*₁ can be measured by Raman spectroscopy as explained in Sec. III.

For clusters much smaller than the wavelength of the exciting radiation, the molecular polarizability behaves additively to a very good approximation. Thus, the Rayleigh intensity I_R scattered by the excited volume is given by

$$I_{\rm R} = C \left(n_1 + \sum_{N \ge 2} N^2 n_N \right), \tag{2}$$

where *C* is a constant including the equilibrium molecular polarizability and several instrumental factors. Since the mean squared cluster size is $\langle N^2 \rangle = (\Sigma N^2 n_N)/n_c$, the Rayleigh intensity becomes

$$I_{\rm R} = C(n_1 + \langle N^2 \rangle n_c). \tag{3}$$

To get rid of the constant *C*, it proves convenient to refer I_R to an expansion free of condensation, where it becomes $I_R^0 = Cn$. The reduced Rayleigh intensity I_r is then given by

$$I_r = \frac{I_{\rm R}}{I_{\rm R}^0} = \frac{n_1}{n} + \langle N^2 \rangle \frac{n_c}{n}.$$
 (4)

 I_r can be measured by combining Rayleigh and Raman scattering data as explained in Sec. IV.

From Eqs. (1) and (4), the ratio N of the first two moments of the cluster size distribution can be expressed as

$$\bar{N} = \frac{\langle N^2 \rangle}{\langle N \rangle} = \frac{I_r - n_1/n}{1 - n_1/n}.$$
(5)

A narrow size distribution will be assumed here; this implying $\overline{N} \approx \langle N \rangle$. Within this approximation the cluster number density becomes

$$n_c = \frac{(1 - n_1/n)^2}{I_r - n_1/n}n.$$
 (6)

The two parameters \overline{N} and n_c , given by Eqs. (5) and (6), depend only on the quantities n, n_1 , and I_r , which are directly obtained from the experiment.

III. EXPERIMENT

Five supersonic expansions of CO₂ at stagnation pressures $P_0=1-5$ bars, and stagnation temperature $T_0=294$ K, have been studied. The expansion chamber of 42×42 $\times 30$ cm³, manufactured in aluminum, has been described elsewhere in detail [37,42]. It contains a movable nozzle controlled by micropositioning devices, as well as an optical system for scattering excitation and collection of the scattered radiation. The nozzle is cylindrical, with a diameter D=0.313 mm and internal length $L\approx 1$ mm. The expansions were maintained stationary by means of a 1400 m³/h Roots pump backed by a rotary pump.

A BeamLok 2080 Ar⁺ laser from Spectra Physics, with improved beam pointing and output power stability, was employed as excitation source at λ =514.5 nm. The laser power was about 1 W for Rayleigh scattering, and 5–8 W for the Raman spectra. The laser beam was focused onto selected points of the jet by a lens of 35 mm focal length, producing a 14 μ m beam waist. The scattered radiation was collected at 90° with respect to the laser beam and the expansion axis.

The scattered radiation was analyzed with a highsensitivity multichannel spectrometer [45], equipped with a 512×512 pixel charge-coupled device (CCD) detector refrigerated by liquid nitrogen. The Raman spectra were recorded at 0.8 cm⁻¹ spectral resolution.

In order to avoid the perturbation of the clusters by the shock waves of the expansion, all spectra were recorded well within the zone of silence of the jet. The excitation-collection optical system was kept fixed along the measurements, while the nozzle was positioned to reach the point of interest. The accuracy to locate a point within the expansion flow field is about $\pm 10 \ \mu m$. Relative positions between two points are reproducible to $\pm 1 \ \mu m$, which is the precision of the nozzle micropositioning actuators. The spatial resolution of the experiment is determined by the jet region actually seen by the detector of the spectrometer. This is controlled by the CCD readout system and by the laser beam waist. The representative spatial resolution in this work was about 0.05D along the expansion axis z, and across this axis from 0.28D close to the nozzle, up to 3.4D in the farthest measured points, where D is the nozzle diameter.

The Rayleigh intensity $I_{\rm R}$ in the expansion was measured averaging several records at each point. The chamber background signal was collected under identical conditions at evacuated chamber. Subtracting this background from the signal measured in the jet yielded the net signal due to the molecules. The uncertainties in the Rayleigh intensities were below 1% for the expansions at $P_0=3-5$ bars, and below 2% and 6% for the $P_0=2$ and 1 bar jets, respectively.

The total number density *n* at a point of the expansion was measured by integrating the Raman intensity of vibrational bands (*Q* branches) of CO₂: the monomer band at 1388.2 cm⁻¹, and the bands around 1384–1386 cm⁻¹ due to the condensed phases. Some examples of the Raman spectra recorded from the $P_0=5$ bar expansion are shown in Fig. 1, including spectrum (a) at the axial distance z/D=0.64 from the nozzle, prior to the condensation onset. The vibrational Raman intensity can be expressed as

$$I_{\text{Raman}} = \frac{K}{Z_v} n, \tag{7}$$

where Z_v is the vibrational partition function at the vibrational temperature T_v of the gas, and K a coefficient that depends on the exciting irradiance and wavelength, on the scattering geometry, and on the molecular polarizability derivative; K remains constant along the experiment and is de-



FIG. 1. Raman spectra along the axis of a CO₂ expansion showing the monomer Q branch at 1388.2 cm⁻¹, and condensed phase bands within the interval 1381–1387 cm⁻¹. The spectra are scaled to the maximum of the monomer Q branch. The spectral resolution is 0.8 cm⁻¹.

termined by comparison with a static sample of the same gas at known number density. The variation of T_v along the zone of the expansion analyzed changes Z_v by less than 2% [37,43], so Z_v was taken constant. Here Eq. (7) can be safely applied to free as well as to condensed molecules, since the biggest cluster size measured was around 1100 molecules. For this size the effect of the internal field of the condensed phase on the Raman scattering cross section [46] is negligible. The estimated accuracy of the measured number densities is 3% close to the nozzle, and 10% in the farthest section of the jet.

Since the Raman signals from monomers and clusters are spectrally resolved, as shown in Fig. 1, the fraction of free molecules n_1/n can be obtained from the ratio between the intensity of the band at 1388.2 cm⁻¹ (monomers) and the total intensity from 1381 to 1390 cm⁻¹. The uncertainty of the monomer fraction, on the order of 10%, is mainly due to the comparatively weak signal of the condensed phases.

Other local flow quantities can be measured from the Raman spectra [37]. For instance, the rotational temperature T_r of the monomers can be obtained from the CO₂ rotational Raman spectra with accuracy better than 1%. Under the present conditions, these T_r 's are almost in equilibrium with the translational temperature of the monomers [43,47]. Also, the time elapsed as the monomers travel along the jet axis can be inferred from the flow velocity, approximately determined from the Raman data and conservation equations [43]. This flow velocity is increased by the condensation heat released to the jet [43]; for instance, in the $P_0=1$ and 5 bar expansions the flow velocities at z/D=30 are, respectively, around 40 and 90 m s⁻¹ greater than the isentropic velocity of 616 m s⁻¹ at that point [47]. Therefore, the time needed by the monomers to travel a given distance varies within 8% in the five expansions. An estimate of this time is shown in the upper scale of Figs. 2 to 4. However, as the clusters grow, they become slower than the monomers [16] due to the increasing inefficiency of the momentum exchange.



FIG. 2. Total number density *n* and Rayleigh intensity I_R along the axis of CO₂ expansions. Solid lines are best fits. The dashed line is I_R^0 for the 1-bar jet. T_c are the rotational temperatures at the onset of condensation. Top axis indicates the time elapsed for the monomers along the expansion.

IV. RESULTS

The total number density n measured along the axis of the five expansions is shown in the lower part of Fig. 2. Best fits to the experimental density data are depicted as solid lines. A slightly faster drop of the total density with distance is observed the higher is the stagnation pressure P_0 . This effect may be attributed in part to a depletion of the lighter free molecules from the jet axis [48]. The Rayleigh intensities $I_{\rm R}$ are shown in the upper part of Fig. 2, scaled to minimize their differences for z/D < 1. In order to obtain I_r according to Eq. (4), $I_{\rm R}^0$ is derived from the density best fits, scaled to the Rayleigh intensity prior to the condensation onset. As an example, the I_R^0 for the 1-bar expansion is shown as a dashed line in Fig. 2. For the other four expansions $I_{\rm R}^0$ is somewhat different. In Fig. 2 the condensation is revealed by the departure of the Rayleigh intensity $I_{\rm R}$ from the $I_{\rm R}^0$ plot. The onset of condensation occurs between $z/D \approx 1$ and $z/D \approx 2$, closer to the nozzle for higher stagnation pressure P_0 . The rotational temperature of the gas at the beginning of the condensation is included in Fig. 2. These temperatures are far below the triple point of CO₂ (217 K) in all cases.

The monomer fractions n_1/n measured along the jet axis, and their best fits, are shown in Fig. 3. Again, the condensation onset is observed between $z/D \approx 1$ and $z/D \approx 2$, in agreement with the Rayleigh results in Fig. 2. The present values are consistent with estimates of the monomer fraction in CO₂ expansions derived from the condensation energy released to the flow: values of $n_1/n \approx 0.95$ and 0.91 at P_0 = 1 and 2 bars, respectively, were reported [43] at z/D=27using a D=0.3 mm nozzle. In another work with a fairly different setup a CO₂ monomer fraction of around 0.83 was found in a $P_0 \approx 5$ bar expansion [36]. However, this result is not directly comparable to ours, due to the dependence of clustering efficiency on the geometry and size of the nozzle [17].



FIG. 3. Monomer fraction n_1/n along the axis of CO₂ expansions. Continuous lines are best fits. Error bars are two standard deviations. Top axis indicates the time elapsed for the monomers along the expansion.

The cluster number density n_c and the mean cluster size N on the expansion axis are shown in Fig. 4. They have been obtained from Eqs. (5) and (6) using the fits to the total number density *n* of Fig. 2 and to the monomer fraction n_1/n of Fig. 3. The cluster number density n_c (Fig. 4, top) reaches a maximum within one nozzle diameter after the condensation onset, then decreasing slower than the total number density n. Due to the different experimental conditions our results are only qualitatively comparable to the data on cluster densities found in the literature: an Ar expansion through a 0.5 mm conical nozzle was reported to produce $n_c \approx 5$ $\times 10^{19} \text{ m}^{-3}$ at $z/D \approx 6$ with $P_0 \approx 12$ bars [10], and a CO₂ expansion through a 0.7 mm capillary tube generated n_c $\approx 6 \times 10^{17} \text{ m}^{-3}$ at $P_0 \approx 5$ bars [36]. This last work on CO₂ shows that the higher the stagnation pressure P_0 the lower the cluster number density n_c , a conclusion confirmed by the present results. The mean cluster size \overline{N} (Fig. 4, bottom) shows a fast growth up to a near constant size reached at $z/D \approx 20$, with a similar behavior in the $P_0 = 3-5$ bar plots. As far as we can observe the growth rate $d\overline{N}/dt$ decreases monotonically after the condensation onset. For the 5-bar expansion a maximum growth rate of 8×10^8 s⁻¹ is estimated at $z/D \approx 1$, assuming a cluster velocity equal to the isentropic one; this is a good approximation for the very first stage of the condensation. The maximum mean size attained $\bar{N} \approx 1100$ corresponds to a sphere of diameter 4.5 nm, taking 2.317×10^{28} m⁻³ for the number density of the crystal. This estimated size of the biggest cluster is much smaller than the exciting laser wavelength, justifying the additivity of the molecular polarizability in Eq. (2).

Most experimental cluster sizes so far reported are terminal mean values in the expansion, \bar{N}_{∞} . They are found to obey the empirical law $\bar{N}_{\infty} \propto (\Gamma^*)^m$ [15,49], with m=2.0 to 2.5. The scaling factor $\Gamma^* = kP_0D_{eq}^qT_0^{-s}$ depends on the equivalent nozzle diameter D_{eq} and on the stagnation condi-



FIG. 4. Cluster number density n_c (top) and mean cluster size \overline{N} (bottom) along the axis of CO₂ expansions. Error bars are two standard deviations. Top axis indicates the time elapsed for the monomers along the expansion.

tions P_0, T_0 , while the constants k, q, s, are characteristics of the gas. This empirical law has been applied mostly to metals and noble gases for a wide range of Γ^* [20,33,50], though some polyatomic gases, like H₂ [11], N₂O [35], and CO₂ [23,36,51] have also been modeled this way. The values of \overline{N} obtained in this work for the farthest axial points are expected to be close to \overline{N}_{∞} , since the growth rate is very low at z/D > 20, as shown in Fig. 4. The mean cluster size at z/D=12.8 is depicted versus P_0 in Fig. 5. These data obey a law $\overline{N} = cP_0^m$, in agreement with the model described above, with the fitted parameters c=24.5 and $m=2.23\pm0.15$. The value of *m* obtained here compares well with m=2.2 to 2.4 reported for CO_2 [23,36,51]. The comparison with the results of [23], shown in Fig. 5, is particularly meaningful since their clusters were generated under similar conditions: $D=0.4 \text{ mm} \text{ and } T_0=300 \text{ K}.$

The distribution of clusters along directions r perpendicular to the expansion axis has also been investigated here. Three representative sections of the $P_0=5$ bar expansion will be discussed. At z/D=2.6 and z/D=6.4 the monomer fraction n_1/n decreases radially as a nearly Gaussian function,



FIG. 5. CO₂ mean cluster size \overline{N} versus stagnation pressure P_0 , at z/D=12.8. The straight line is the best fit discussed in the text.

while at z/D=12.8 it remains almost constant with $n_1/n \approx 0.87$. The corresponding radial distributions of n, n_c , and \overline{N} are shown in Fig. 6. The \overline{N} radial profile at z/D=2.6 shows a shallow minimum on the axis. This may be attributed to the nearly spherical symmetry of the initial stages of the cluster growth, with center at the nozzle. Downstream, the mean cluster size \overline{N} shows up a concentration of the larger clusters on the jet axis. This enrichment is consistent with the separation of species with different masses caused by different perpendicular speed ratios [14,52].

V. DISCUSSION

Raman spectroscopy also provides qualitative information on the phases of the clusters. The $P_0=5$ bar expansion, of which several spectra are shown in Fig. 1, will be discussed as a representative example. The recorded Raman spectra present two main features assigned to the clusters [39]. In the present work we observe how their relative intensities do evolve as the clusters grow. At the beginning of the condensation a band appears at about 1386 cm⁻¹ (Fig. 1, spectrum b), at z/D=1.3, which corresponds to a mean cluster size $\bar{N} \approx 150$. This band shifts toward 1385 cm⁻¹ as the clusters become larger. We assign it to a liquidlike phase by comparison with previous studies in dense CO₂ gas, where the monomer band at 1388.2 cm⁻¹ is reported to shift toward the band of the liquid at 1385 cm⁻¹ as the density increases [53]. Another peak at 1384 cm⁻¹, identified with the crystal [54], begins to show up around z/D=1.6 (Fig. 1, spectrum c), becoming the dominant feature after $\sim 1 \ \mu s$. In the light of the present results it is not possible to conclude whether the coexistence of these liquid and solid phases occurs within the same or in different clusters. This problem has been discussed in the literature with contradictory conclusions [23,51,55–57].

The cluster temperature has been reported to be higher than that of the monomers [24,38,58]. This is attributed to the condensation heat [59], which is not efficiently released



FIG. 6. Total number density n (top), cluster number density n_c (top), and mean cluster size \overline{N} (bottom), along radial directions at three z/D sections of the 5-bar CO₂ expansion. Error bars are two standard deviations.

to the surrounding bath, rising therefore the temperature of the clusters. Electron diffraction studies on CO_2 clusters [23,24] reported terminal cluster temperatures, independent of the cluster size, of about 110 K, this including the effect of the evaporative cooling. It is not possible to establish the cluster temperature from the present data, but, as a comparison, the bath temperatures T_r at selected points of the $P_0 = 5$ bar expansion are included in Fig. 1.

Finally, it should be pointed out that the approximation assumed in this work, considering the ratio $\langle N^2 \rangle / \langle N \rangle$ as the mean cluster size $\bar{N} = \langle N \rangle$, is a simplification of the actual cluster size distribution. This is well approximated by a lognormal distribution function [60,61], which has been successfully applied to describe the condensation in free jets, from clusters with few molecules [62] up to aggregates of several thousand particles [21]. The ratio between the size \bar{N} given by Eq. (5) and the average size $\langle N \rangle$ of a log-normal distribution with geometric standard deviation σ , can be written as $\bar{N}/\langle N \rangle = \exp(\ln^2 \sigma)$. Metallic particles of diameter larger than 3 nm were found to show a log-normal size distribution with $\sigma = 1.4 - 1.6$ [63]. Though our clusters are smaller and nonmetallic, we employ this σ range to conclude that our mean cluster size \bar{N} is overestimated by about 12–25 % with respect to the log-normal average size. Similar arguments on Ar expansions [33] assuming a Gaussian size distribution led to a comparable overestimation of 20%.

VI. CONCLUSIONS

In this work we have shown that the combination of Rayleigh and Raman scattering within the same experiment, using the same instrumentation and optical configuration, provides an useful nonintrusive methodology for the quantitative diagnostics of molecular condensation in continuous supersonic jets. The information is retrieved here in a more direct way than by other optical or mass selective techniques, and in comparison with other studies with pulsed nozzles the accuracy and reproducibility of our experiment is better. More important is, however, that the use of nonpulsed nozzles allows us to come close enough to the origin of the expansion to observe the complete condensation process, from the onset up to the terminal steady stage.

Primarily, under the assumption of a narrow cluster size distribution, the methodology enables us to measure the cluster number density, as well as the mean size of the growing clusters. But also, a wealth of relevant information on other aspects of cluster growth is obtained. For instance, the superb spatial resolution of the method (few microns), both along the axial and radial directions of the expansion, allows for a precise mapping of cluster sizes and densities. In addition, the spatial resolution along the expansion axis can approximately be transformed into a temporal resolution, yielding an estimate for the local growth rates at a given density and temperature of the monomer bath. Furthermore, the coexistence of gas, cluster, liquid and solid phases and their evolution along the jet can be probed from the corresponding vibrational Raman bands.

The experimental procedure has been tested here on CO_2 , a relatively well-known system, and a good agreement has been found with previous works. It is expected however that the growth rates obtained will be useful for testing condensation models.

The outlined methodology, based on the combination of Rayleigh and Raman scattering, is highly universal as far as the condensing species is concerned. It can be applied to other small molecules like H_2 , N_2 , H_2O , or CH_4 , and their mixtures with noble gases, with no more limitations than in the present work. Furthermore, a much broader range of source conditions than used here can be explored with a modest effort, for instance heating or cooling the nozzle for a wider range of pressures, or using slit nozzles. This can substantially widen the working ranges and may complement to good a measure the information from other techniques.

Last, throughout the present work the resolution of the recorded Raman spectra has been 0.8 cm⁻¹. Since this poses a severe limitation to size-resolved studies of the small clusters, work is in progress at our laboratory in order to improve the spectral resolution by at least one order of magnitude.

ACKNOWLEDGMENTS

This work has been supported by the Spanish Ministerio de Educación y Ciencia, Research Projects No. BFM2001-2276 and No. FIS2004-02576.

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