Inhibition of formation of SF_6 molecular clusters in a free supersonic expansion

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In this work we present experimental results on the inhibition of formation of sulfur hexafluoride molecular clusters in a free supersonic expansion, due to resonant absorption of intense radiation from a pulsed CO_2 laser. The spatial energy distribution of the molecular beam in the transverse direction was measured with a pyroelectric detector with and without incident radiation. A skimmer placed in the collisional region of the expansion causes a second expansion of the molecular beam which is more divergent when these molecules are vibrationally excited by a CO_2 laser beam perpendicularly crossing the molecular beam before the skimmer. This is due to the inhibition of formation of molecular clusters by the CO_2 laser beam which leads to a lower average mass for the expanding beam particles. In a molecular beam with isotopic species, a selective inhibition of formation of clusters would lead to different spatial distribution for different isotopes in the molecular beam.

Formation and growth of molecular clusters have received considerable attention recently. The physics of weak intermolecular forces responsible for the formation of clusters has been studied for 50 years[1–3] in order to understand phase transitions that are important in the areas of catalysis, combustion, etc. A recent review[4] gives the basic idea of the development attained in this area where the author emphasizes that the knowledge of the properties, formation, and inhibition of formation of molecular clusters is not complete. The observation of atomic and molecular clusters in supersonic expansion[5] using mass spectrometric techniques opened new possibilities to study homogeneous nucleation. Several theoretical models have been developed for atomic[6–10] and molecular beams,[11–13] in this case using classical theories. The laser provides intense electromagnetic radiation and led to new developments in the study of formation and growth of clusters, laser infrared spectroscopy,[14–18] Rayleigh and Mie light scattering[19,20] have been used. Inhibition of SF_6 molecular clusters formation was observed in supersonic free jet[17,18] utilizing resonant radiation from a cw-CO_2 laser.

In this work we report the inhibition of formation of sulfur hexafluoride molecular clusters in a free supersonic expansion due to resonant absorption of intense radiation from a pulsed CO_2 laser. The experimental setup consists of a pulsed valve which connects a high pressure chamber to a high vacuum chamber. In front of the valve orifice a second expansor (skimmer) is placed (28 mm from the valve orifice) in the collisional region of the molecular beam. The spatial energy distribution in the transverse direction is measured with a pyroelectric detector at the center line of the molecular beam, 32 mm from the skimmer entrance. The detector is mounted on a platform which has 1° of freedom perpendicular to the molecular beam axis.

The experimental apparatus is represented schematically in Fig. 1. It is the same as that used in Ref. 21 to characterize SF_6 molecular-beam expansion. According to the results of Ref. 21, the collisional region is within a distance of 50 mm from the valve orifice. A pulsed CO_2 laser beam tuned to the 10P18 line, crosses the molecular beam in the perpendicular direction in the region between the orifice and the skimmer, approximately 8 mm from the valve. With the pyroelectric detector kept fixed at the center line of the molecular beam, the pressure of SF_6 gas in the stagnation chamber was scanned from 1 to 10 atm with the total energy of the molecular beam being measured under various conditions. First, the skimmer was removed and the signal from the detector measured with laser beam *on* and *off*. Second, with the skimmer present in the collisional region, the energy of the molecular beam was determined with laser *on* and *off*. The results are shown in Fig. 2 in which the signals from the detector are normalized to their maximum values at 10 atm. It is observed that without the skimmer, there is no difference between the dependence of the signals on the stagnation pressure with (S_L) and without (S_0) the exciting laser beam. On the other hand, with the skimmer present, it is observed that the pressure dependence is more accentuated when the molecules are excited by the laser beam. To better understand these results, the spatial distribution in the transverse direction was determined by moving the pyroelectric across the molecular beam under different pressure values with and without the laser beam, and with the skimmer

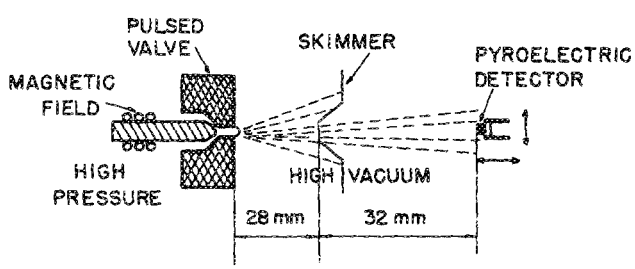

FIG. 1. Schematic of the experimental setup.

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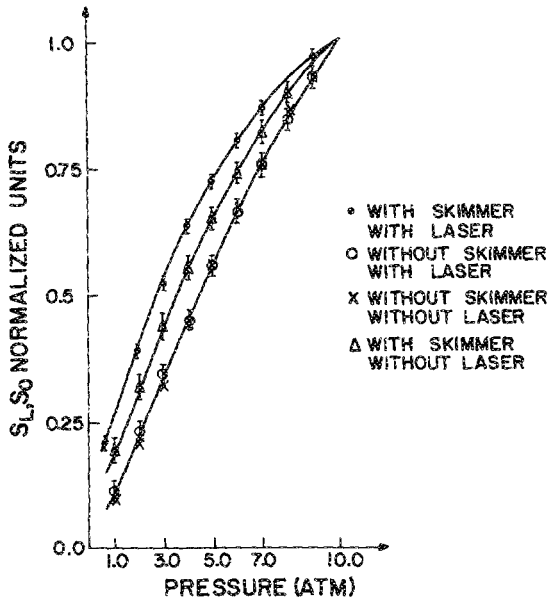

FIG. 2. Pyroelectric detector signal, normalized to the maximum value at 10 atm vs the pressure of the stagnation chamber.

placed 28 mm from the valve orifice. The results are shown in Fig. 3 where the ratio of the signals with laser on (S_L) and without laser (S_0) is plotted against the position of the detector. It can be seen that for pressures above 1 atm, there is spatial broadening of the excited molecular beam relative to the case where there is no excitation (laser off). This spatial spread of the molecular beam can be due mainly to three different physical processes, namely: (A) differences in the mean particle mass of the beam due to inhibition of formation of molecular clusters by the CO_2 laser excitation; (B) expansion temperature effects due to V-T energy transfer due to vibrational excitation from the CO_2 laser and; (C) direct momentum transfer from CO_2 laser radiation photons to the molecules. This effect is, however, discarded because the spread is symmetrical.

To observe the effect of a purely V-T energy transfer, the skimmer was removed so that a second expansion does not occur. In this case there is an increase of the signal when the laser is on but there is no spread of energy as was observed with the skimmer present. We have also measured the mean velocity of the molecules by moving the detector along the axes, and observed that there was no effect of excitation on it. This means that the V-T transfer, in this case, does not cause a measurable expansion of the beam. We are then limited to hypothesis A to explain the phenomenon.

The spatial broadening of the molecular-beam-energy distribution observed is due to a decrease of the effective mass of the particles of the beam when the laser is present. In order to study the pure cluster inhibition effect due to resonant excitation, the skimmer was placed in the collisionless region (57 mm from the valve orifice) so that an expansion effect of the skimmer is avoided. In this way it is possible to determine the equivalent mean mass of the particles in the beam using a theoretical energy distribution function similar to the density distribution given by[22]

$$f(m,T) = A(m/T)\exp[-(mu^2/2l^2kT)y^2], \qquad (1)$$

where A is a constant, m the mass of a particle, m the mean velocity, l the distance from the skimmer, k the Boltzmann constant, T the translation temperature, and y the transverse distance from the center line of expansion. The results are shown in Fig. 4. Assuming identical distributions for $S_L(m)$, $S_0(m)$, and using Eq. (1), we were able to calculate the mean equivalent particle mass for the unexcited particle beam as being 1.23 times the mass of the excited molecular beam. In this calculation, a translational temperature of 200

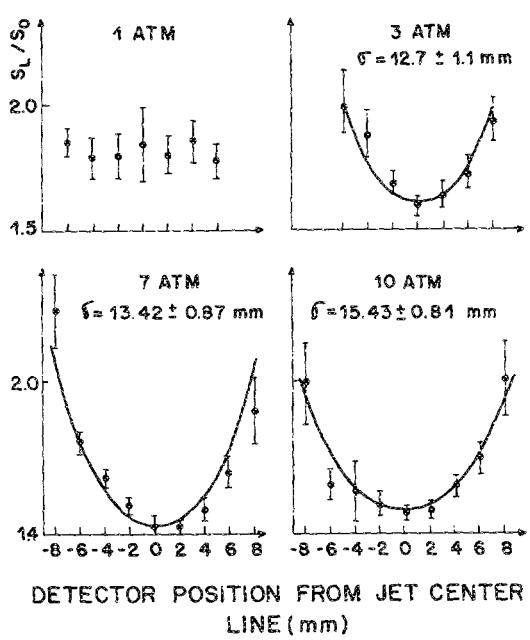

FIG. 3. Dependence of the ratio (S_L/S_0) of the pyroelectric detector signal with laser ON (S_L) over signal with laser OFF (S_0), on the position of the detector across the beam. Skimmer placed in the collisional region.

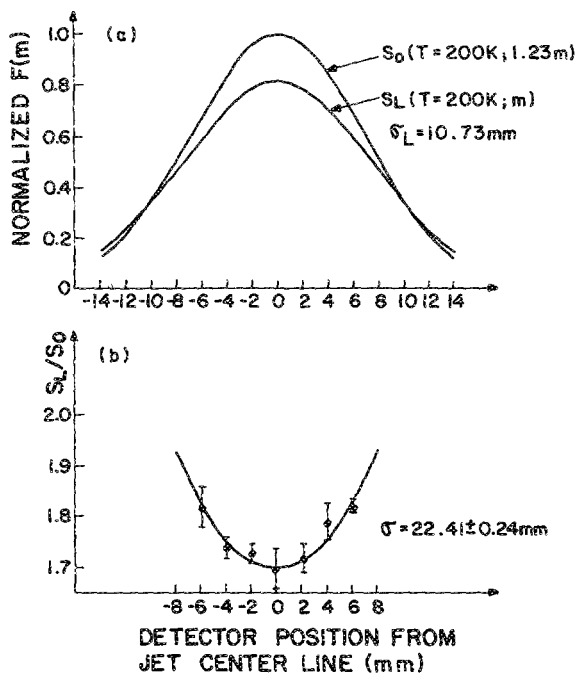

FIG. 4. (a) Theoretical curves from Eq. (1) for masses m and 1.23 m; (b) dependence of the signal ratio (S_L/S_0) on the position of the detector with the skimmer placed in the collisionless region.

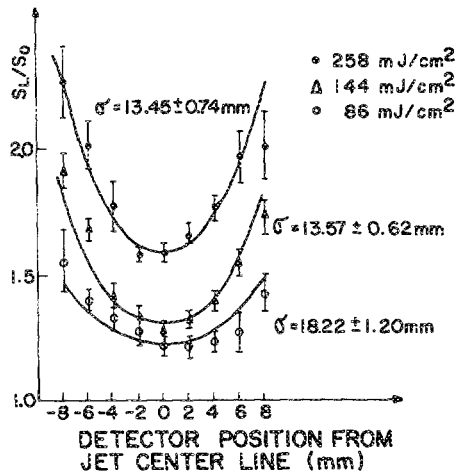

FIG. 5. Dependence of the ratio (S_L/S_0) on the position of the detector across the beam for three different laser fluences with the skimmer in the collision region.

K was measured independently using measurements of time of flight[21] of molecules by moving the detector along the expansion line. These measurements were independent of the excitation state of the molecules. As can be seen, the spread of the molecules due to inhibition of cluster formation is enhanced because of expansion effects when the skimmer is located in the collisional region. The effect of the laser fluence, tuned to the maximum absorption of the Q branch of the SF_6 molecules is shown in Fig. 5.

The conditions in which these experiments were performed are such that there is no condensation of SF_6 molecules but it is possible to have the formation of dimers, trimers, etc.[12] Pressure values in the stagnation chamber, and distances from the expansion orifice were critically chosen such that only small clusters (dimers, trimers, etc.) were allowed to be formed.

In conclusion, we presented an experimental verification of inhibition of SF_6 molecular cluster formation in a free-molecular-beam expansion due to resonant absorption of a CO_2 laser radiation. In addition, we propose an original method to estimate the mean mass of the particles in a free-molecular-beam expansion. The broadening of the spatial energy distribution function due to the selective cluster inhibition could lead to a new laser-assisted gas-dynamic molecular-isotope separation process.

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A parameter study of streamer propagation in SF_6

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In a recent paper a model was presented which described the main features of streamer propagation in SF_6. In this communication the sensitivity of the model to changes in the input parameters is discussed. Each parameter is varied within the limited range expected from experimental determinations. It is predicted that streamers can only propagate within a limited range of streamer channel diameters, and that the charge in the streamer head varies considerably with channel diameter. Results are also presented which predict that the streamer velocity is only weakly dependent on pressure in the range 50–500 kPa.

SF_6 is an important gas used in electrical insulation and has recently been the subject of many studies concerning its fundamental discharge properties.[1–3] In particular, a recent study[1] explains many of the unique features of streamer propagation in SF_6 using a model incorporating a wide range of data taken from the literature.[2] The sensitivity of the predicted streamer properties to variations in the model parameters is of interest to engineers working with SF_6 insulation equipment and researchers measuring the properties of SF_6; this sensitivity is discussed in this paper.

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