

# IR multiphoton excitation of SF<sub>6</sub> molecules subliming from the surface of (CO<sub>2</sub>)<sub>N</sub> nanoparticles in a cluster beam

G.N. Makarov, A.N. Petin

**Abstract.** This work examines IR multiphoton excitation of SF<sub>6</sub> molecules subliming from the surface of (CO<sub>2</sub>)<sub>N</sub> van der Waals clusters (nanoparticles) in a cluster beam (the number of monomers per cluster,  $N \geq 10^2$ ). The SF<sub>6</sub> molecules are captured by clusters when a cluster beam intersects a molecular beam and sublime from the cluster surface after a certain time, carrying information about the velocity and temperature (internal energy) of the clusters. The multiphoton absorption spectra of the SF<sub>6</sub> molecules subliming from the cluster surface are markedly narrower than those of the SF<sub>6</sub> molecules in the parent, gas-dynamically cooled molecular beam, indicating that the vibrational temperature of the molecules subliming from the cluster surface is lower. Therefore, the proposed technique can be used to produce strongly vibrationally cooled molecules, which are of interest for a number of applications, in particular for achieving high-selectivity IR multiphoton excitation and isotopically selective dissociation of molecules.

**Keywords:** molecules, clusters, nanoparticles, molecular and cluster beams, IR multiphoton excitation and dissociation of molecules, IR multiphoton absorption spectra, laser isotope separation.

## 1. Introduction

The study of clusters and nanoparticles is now receiving a great deal of attention [1–7]. (Note that clusters consisting of  $N \geq 10^2$  particles are the same as nanoparticles.) This is due to their unique properties, which allow them to be used in nanotechnology for the fabrication of high-speed miniature electronic devices and large-memory systems, deposition of thin films, engineering of advanced materials and surface processing [1–5]. Moreover, great interest in metallic and composite clusters and nanoparticles is generated by the possibility of using them as novel high-temperature superconductors [6, 8, 9]. These applications

require knowledge of the physical, chemical and thermodynamic properties of such aggregates, including their temperature (internal energy), an important parameter which influences many properties of particles and processes with their participation (see, e.g., review [7] and references therein).

Our recent work [10] has shown that SF<sub>6</sub> molecules captured by large (CO<sub>2</sub>)<sub>N</sub> van der Waals clusters (nanoparticles) when a cluster beam intersects a molecular beam sublime (vaporise) from the surface of the clusters after a certain time, carrying information about the velocity and temperature (internal energy) of the clusters. From the multiphoton absorption (MPA) spectra of the SF<sub>6</sub> molecules subliming from the surface of the clusters, we estimated the temperature of the (CO<sub>2</sub>)<sub>N</sub> nanoparticles in the cluster beam ( $T_{cl} < 150$  K) [10]. At the same time, the study of IR multiphoton excitation of molecules subliming from the surface of cold clusters is of interest per se because this method can be used to produce strongly vibrationally cooled molecules, needed, e.g., for laser isotope separation using selective IR multiphoton dissociation of molecules. The point is that the preparation of molecules with a vibrational temperature  $E_{vib} \leq 150$  K presents serious problems even in gas-dynamically cooled jets and flows [11–13], especially when molecules have a high heat capacity (SF<sub>6</sub>, WF<sub>6</sub>, or UF<sub>6</sub>). At the same time, strong vibrational cooling of molecules is critical for achieving high selectivity of molecule excitation and dissociation in laser isotope separation [14, 15].

In this paper, we examine in detail the spectroscopic and energy characteristics of the IR multiphoton excitation of SF<sub>6</sub> molecules subliming from the surface of (CO<sub>2</sub>)<sub>N</sub> nanoparticles in a cluster beam. We demonstrate that the MPA spectra of such molecules are markedly narrower than those of SF<sub>6</sub> in the parent, gas-dynamically cooled molecular beam, indicating that the vibrational temperature of the subliming molecules is lower. The results obtained are of interest for isotopically selective IR multiphoton excitation and dissociation of molecules and for gaining insight into a number of other atomic/molecular processes in which the vibrational temperature of molecules plays an important role (e.g., chemical reactions or deposition of molecules on cold surfaces, in particular on cluster surfaces) [7, 10, 16, 17].

## 2. Experimental setup and measurement procedure

The experimental setup is shown schematically in Fig. 1. A high-intensity pulsed (CO<sub>2</sub>)<sub>N</sub> cluster beam intersected a pulsed SF<sub>6</sub> molecular beam at a right angle. In the beam

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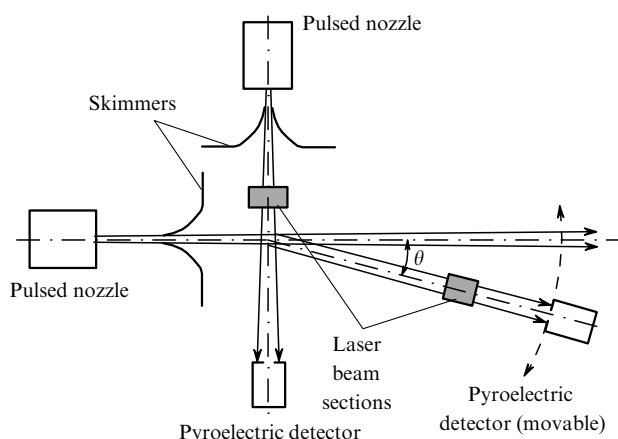
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intersection zone, SF<sub>6</sub> molecules were captured by (CO<sub>2</sub>)<sub>N</sub> clusters. The momentum transfer from the molecules to the clusters [18–20] caused these latter to deflect through some angle  $\theta$ . The cluster beam was produced by a current-loop-actuated pulsed nozzle [21] with a tip hole diameter of 0.75 mm. The valve-on time was 100–120  $\mu$ s (full width at half maximum, FWHM), depending on the gas composition and pressure over the nozzle. The gas pressure over the nozzle was varied from  $\sim 0.5$  to 4.5 atm. The nozzle tip had the form of a 30-mm-long cone with an apex angle of 26°. The generation of cluster beams using pulsed nozzles was examined in detail earlier [22]. Under the conditions of this study, the number of particles in (CO<sub>2</sub>)<sub>N</sub> clusters was  $N \geq 10^2 - 10^3$ . Note that large (CO<sub>2</sub>)<sub>N</sub> clusters have a crystal structure [7, 23].



**Figure 1.** Schematic of the experimental arrangement.

The SF<sub>6</sub> molecular beam was produced by a General Valve pulsed nozzle (electromagnetic valve) with an orifice 0.8 mm in diameter. The valve-on time was 300  $\mu$ s FWHM, and the gas pressure over the nozzle was varied from 0.5 to 2.5 atm.

To separate the molecular and cluster beams from the pulsed jets generated by the nozzles, we used conical apertures (skimmers) with entrance diameters of 3 and 6 mm, placed 30 and 26 mm from the nozzles, respectively. The molecular and cluster beams were detected by uncooled pyroelectric detectors (PEDs) with a time resolution of 5–10  $\mu$ s [12, 14, 15]. The detectors could be mounted at different distances from the nozzles. The distance from the nozzle to the centre of the beam intersection zone was 93 mm for the cluster beam and 90 mm for the molecular beam. The vacuum chamber in which the beams were generated was pumped down to  $\sim 3 \times 10^{-6}$  Torr by a diffusion pump.

In the beam intersection zone, some of the molecules were captured by clusters and, after thermalisation, sublimed from the surface of the clusters, carrying information about their velocity and temperature. The kinetic and internal (quantum state) energies of the molecules provide a measure of the cluster temperature. When the bond energy of monomers in a cluster exceeds the energy of the bonds between cluster and probe molecules, the captured molecules are more likely to sublime from the cluster surface than are the host molecules (atoms). This condition is fulfilled for many combinations of clusters and molecules (atoms), and it

was realised in the experiments described here. The heat (energy) of SF<sub>6</sub> sublimation (5.46 kcal mol<sup>-1</sup> [24]) is lower than the heat of CO<sub>2</sub> sublimation (6.03 kcal mol<sup>-1</sup> [24]). Molecule capture increases the probability of molecule sublimation from the cluster surface because the energy of a captured molecule is transferred to the cluster, raising its temperature [18–20].

Vibrational excitation of SF<sub>6</sub> molecules was provided by a high-intensity (above  $10^6 - 10^7$  W cm<sup>-2</sup>) tunable pulsed CO<sub>2</sub> laser beam. The pulse energy was within 3 J. Each laser pulse consisted of a peak with a FWHM of about 100 ns and a tail  $\sim 0.6$   $\mu$ s in duration, which accounted for about 50% of the energy. The pulses excited the IR-active mode  $\nu_3$  of the SF<sub>6</sub> molecule (948 cm<sup>-1</sup> [25]). The laser beam intersected the molecular beam at a right angle 75 mm from the nozzle tip (Fig. 1). In studies of the IR multiphoton absorption by SF<sub>6</sub> molecules subliming from the surface of (CO<sub>2</sub>)<sub>N</sub> clusters, the molecules were excited 23 mm from the centre of the beam intersection zone. The beam spot in the excitation zone was  $\sim 10 \times 10$  mm in dimensions. The IR multiphoton absorption of the SF<sub>6</sub> in the molecular beam and the SF<sub>6</sub> molecules subliming from the cluster surface was studied using pyroelectric detection of the absorbed energy [11, 12, 14, 15]. The PED signal induced by the cluster beam and sublimed molecules was amplified ( $\times 100$ ) and fed to a Tektronix TDS-1002 digital oscilloscope. The molecular and cluster beams operated in the single-pulse regime. The detector output was averaged over 16 pulses.

The deflection angle of the clusters that captured molecules (Fig. 1) is given by [26, 27]

$$\tan \theta = \frac{\sin \alpha}{m_1 v_1 / m_2 v_2 + \cos \alpha}, \quad (1)$$

where  $m_1$ ,  $m_2$  and  $v_1$ ,  $v_2$  are the masses and velocities of the clusters and molecules, respectively; and  $\alpha$  is the angle between the molecular and cluster beams. Under the conditions of this study ( $\alpha \approx 90^\circ$ ,  $m_2 \approx 146$  amu,  $v_1 \approx 470$  m s<sup>-1</sup> and  $v_2 \approx 450$  m s<sup>-1</sup>), (CO<sub>2</sub>)<sub>N</sub> clusters that captured single SF<sub>6</sub> molecules deflected by  $\theta \approx 1.8^\circ$  at  $N = 100$  and by  $\theta \approx 0.18^\circ$  at  $N = 1000$ .

The SF<sub>6</sub> molecules captured by clusters were found to sublime from the cluster surface after a certain time. This was inferred from the signal induced in the detector of the cluster beam by the vibrationally excited SF<sub>6</sub> molecules and from the shape of the time-of-flight spectra of the (CO<sub>2</sub>)<sub>N</sub> cluster beam with and without a molecular beam. The molecules subliming from the cluster surface travel predominantly in the cluster beam direction in the laboratory system of coordinates and induce an extra signal at the detector output (Figs 2a, 2b).

The lifetime  $\tau$  of a SF<sub>6</sub> molecule on the surface of a (CO<sub>2</sub>)<sub>N</sub> cluster depends on the energy of SF<sub>6</sub> sublimation (evaporation) and the (CO<sub>2</sub>)<sub>N</sub> cluster temperature, and can be evaluated as [28]

$$\tau = \tau_0 \exp(\Delta E_{\text{ev}} / k_{\text{B}} T_{\text{cl}}), \quad (2)$$

where  $\tau_0$  is the period of van der Waals vibrations of the molecule on the cluster surface;  $E_{\text{ev}}$  is the heat of sublimation (evaporation) per molecule;  $T_{\text{cl}}$  is the (CO<sub>2</sub>)<sub>N</sub> cluster temperature; and  $k_{\text{B}}$  is the Boltzmann constant. Our estimates using literature values of the parameters in (2)

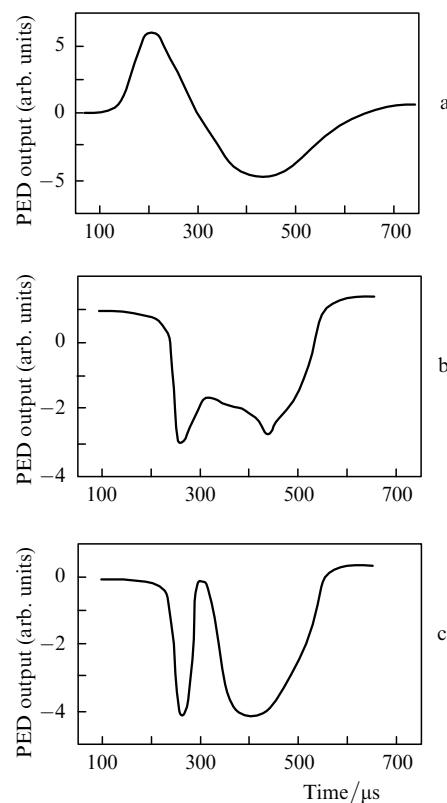
( $\tau_0 \approx 10^{-13}$  s [7],  $T_{cl} = 100 - 120$  K [7, 23] and heat of sublimation  $E_{cv} = 5.46$  kcal mol $^{-1}$  [15]) show that  $\tau$  is from tens to hundreds of microseconds.

It is worth noting here that, since the pyroelectric detection of molecular and cluster beams is based on beam energy measurements and the detector operates at room temperature, molecular beams with molecule energies  $E_b > k_B T_s$  (where  $T_s$  is the surface temperature of the active area of the detector) induce a positive PED signal. Low-energy molecular beams ( $E_b < k_B T_s$ ) and cluster beams induce a negative PED signal [22]. Cluster beams produce a negative signal because clusters striking the PED surface dissociate, and the energy needed for their dissociation is taken from the detector surface. The specific features of the pyroelectric detection of molecular and cluster beams were considered in detail elsewhere [22]. Thus, molecules and clusters induced positive and negative PED signals, respectively. Selective vibrational excitation with a high-intensity CO $_2$  laser pulse markedly raised the internal energy of the SF $_6$  molecules scattered by clusters and, accordingly, the detector output.

### 3. Results and discussion

In our experiments, we measured time-of-flight spectra of the (CO $_2$ ) $_N$  cluster beam and SF $_6$  molecules subliming from the cluster surface and determined the spectroscopic and energy characteristics of IR multiphoton absorption in those molecules and the molecules in the parent molecular beam. The results were analysed with the aim of gaining greater insight into the processes involved. Figure 2 shows the signals induced in the detector at  $\theta \approx 2^\circ$  by the (CO $_2$ ) $_N$  cluster beam in the absence of a molecular beam, by the cluster beam and SF $_6$  molecules subliming from the cluster surface with no excitation and by the cluster beam and subliming SF $_6$  molecules under excitation with a CO $_2$  laser pulse. Note first of all that, as seen in Fig. 2a, the molecules and clusters induce PED signals of opposite polarities, in accordance with earlier results [22]. The ‘molecular component’ of the CO $_2$  beam (positive signal) completely disappears when the SF $_6$  molecular beam is turned on (Figs 2b, 2c), because the molecules and small clusters deflect through large angles. It is seen in Fig. 2b that, in addition to the negative signal from (CO $_2$ ) $_N$  clusters, the SF $_6$  molecules subliming from the cluster surface induce a positive signal. Resonance excitation of SF $_6$  with a high-power CO $_2$  laser pulse markedly increases this signal (Fig. 2c). The extra PED signal due to the excitation of the molecules provides a measure of the energy absorbed by the molecules from the laser beam [12, 14, 15]. Therefore, measuring this signal as a function of the frequency and energy density of the excitation pulse, we can assess the spectroscopic and energy characteristics of IR multiphoton absorption in the SF $_6$  molecules subliming from the surface of (CO $_2$ ) $_N$  clusters.

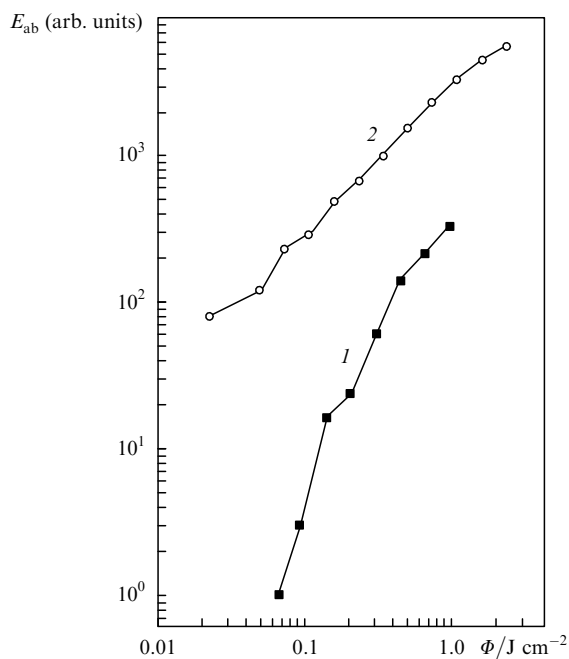
Figure 3 plots the absorbed energy against excitation pulse energy density for SF $_6$  molecules subliming from the surface of (CO $_2$ ) $_N$  clusters and for the SF $_6$  molecules in the parent molecular beam. The data were obtained at an excitation frequency of 945.98 cm $^{-1}$  (10P18 CO $_2$  laser line), which ensured the maximum absorption. The curves are seen to differ in slope. In both cases, the absorbed energy  $E_{ab}$  is a nonlinear function of the excitation energy density  $\Phi$  ( $E_{ab} \sim \Phi^n$ ), with  $n \geq 1.5$  for curve (1) and  $n \geq 1 - 1.1$  for



**Figure 2.** PED signals induced (a) by the (CO $_2$ ) $_N$  cluster beam in the absence of a molecular beam, (b) by the cluster beam and SF $_6$  molecules subliming from the cluster surface with no excitation and (c) by the cluster beam and SF $_6$  molecules subliming from the cluster surface under vibrational excitation with a high-intensity CO $_2$  laser pulse. CO $_2$  and SF $_6$  pressures over the nozzles, 4.5 and 2.25 atm, respectively; distance from the nozzle to the detector of the cluster beam, 200 mm.

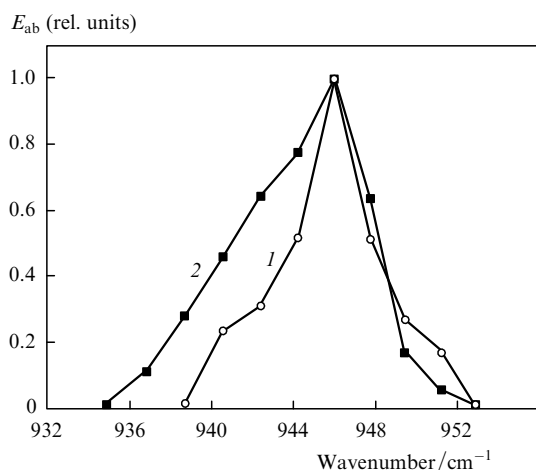
curve (2). Similar  $E_{ab}(\Phi)$  behaviour, with  $n \geq 1$ , was observed in a number of earlier studies of SF $_6$  excitation in gas-dynamically cooled molecular beams and jets [11, 12, 14, 15]. Consequently, curve (1) represents cold and free SF $_6$  molecules. The steeper slope of curve (1) compared to curve (2) attests to a lower vibrational temperature of the molecules [12, 14, 15, 29].  $E_{ab}(\Phi)$  curves similar to those in Fig. 3 were obtained with a variety of CO $_2$  laser lines. From those data, we derived the MPA spectra of SF $_6$  molecules at different excitation energy densities.

Figure 4 shows the IR multiphoton absorption spectrum of SF $_6$  molecules subliming from the surface of (CO $_2$ ) $_N$  clusters and that of the SF $_6$  molecules in the parent, gas-dynamically cooled molecular beam. The spectrum of the SF $_6$  molecules scattered by clusters is considerably narrower on the low-frequency side. As shown earlier [12, 14, 29], the low-frequency wing in the MPA spectrum of SF $_6$  molecules may be suppressed as a result of a reduction in the vibrational temperature of the molecules. Therefore, the present results indicate that the vibrational temperature of the SF $_6$  molecules subliming from the (CO $_2$ ) $_N$  cluster surface is well below that of the SF $_6$  molecules in the parent molecular beam. In earlier studies [12, 29, 30], the vibrational temperature of SF $_6$  molecules in a gas-dynamically cooled pulsed molecular beam was  $T_{vib} \leq 150 - 160$  K, and their rotational temperature was  $T_{rot} \leq 40$  K. Given this, we infer from the spectra in Fig. 4 that the vibrational temper-



**Figure 3.** Absorbed energy  $E_{ab}$  as a function of the excitation pulse energy density  $\Phi$  for (1) SF<sub>6</sub> molecules subliming from the surface of (CO<sub>2</sub>)<sub>N</sub> clusters and (2) SF<sub>6</sub> molecules in the parent molecular beam. The molecules were excited at 945.98 cm<sup>-1</sup> (10P18 CO<sub>2</sub> laser line). The SF<sub>6</sub> pressure over the nozzle was (1) 2.25 and (2) 1.1 atm, and the CO<sub>2</sub> pressure over the nozzle was 4.5 atm (1). The distance from the nozzle to the detector of the cluster beam, 212 mm; from the centre of the beam intersection zone to the detector, 119 mm (1); and from the nozzle to the detector, 90 mm (2).

ature of the SF<sub>6</sub> molecules subliming from the (CO<sub>2</sub>)<sub>N</sub> cluster surface is  $T_{vib} < 150$  K, and, hence, the temperature of the (CO<sub>2</sub>)<sub>N</sub> nanoparticles in the cluster beam is  $T_{cl} < 150$  K [10].



**Figure 4.** IR multiphoton absorption spectra of (1) SF<sub>6</sub> molecules subliming from the surface of (CO<sub>2</sub>)<sub>N</sub> clusters and (2) those in the parent, gas-dynamically cooled molecular beam. Excitation energy density, 1 J cm<sup>-2</sup>; SF<sub>6</sub> pressure over the nozzle, 2.25 atm (in both cases). The distance from the nozzle to the detector of the cluster beam, 212 mm; from the centre of the beam intersection zone to the detector, 119 mm (1); and from the nozzle to the detector, 90 mm (2). The spectra are normalised to the peak absorbed energy.

In addition, the finding that the vibrational temperature of SF<sub>6</sub> molecules subliming from the surface of clusters is rather low compared to that of the molecules in the parent beam suggests that captured SF<sub>6</sub> molecules reside on the surface of the (CO<sub>2</sub>)<sub>N</sub> nanoparticles for a time long enough to reach thermodynamic equilibrium with the clusters. Therefore, they can be thought of as miniature molecular thermometers that carry real information about the temperature of the nanoparticles.

#### 4. Conclusions

The present results show that SF<sub>6</sub> molecules captured by (CO<sub>2</sub>)<sub>N</sub> van der Waals clusters when a cluster beam intersects a molecular beam sublime from the cluster surface after a certain time, carrying information about the velocity and temperature of the clusters. We studied the IR multiphoton excitation of such molecules and obtained IR MPA spectra of SF<sub>6</sub> molecules subliming from the cluster surface. The spectra are markedly narrower than those of SF<sub>6</sub> molecules in gas-dynamically cooled molecular beams, indicating that the vibrational temperature of the molecules subliming from the cluster surface ( $T_{vib} < 150$  K) is lower than that of the molecules in the parent beam. This finding correlates well with electron diffraction data on the temperature of large ( $N \geq 10^3$ ) (CO<sub>2</sub>)<sub>N</sub> van der Waals clusters generated in nozzle sources with no carrier gas ( $T_{cl} \approx 100 - 120$  K) [23].

The possibility of producing strongly vibrationally cooled molecules via sublimation from the surface of cold clusters is of interest for achieving high-selectivity IR multiphoton excitation and dissociation of molecules and also for laser separation of heavy element isotopes. One drawback to this approach is the low concentration of strongly vibrationally cooled molecules in comparison with the molecule concentration in the parent beam. In particular, it can be inferred from the absorbed energy data in Fig. 3 that the concentration of SF<sub>6</sub> molecules subliming from the surface of (CO<sub>2</sub>)<sub>N</sub> clusters is about one order of magnitude lower than the molecule concentration in the parent beam. Note, at the same time, that the molecule concentration in the former case can be raised by optimising molecule capture at clusters (e.g., using denser cluster beams). Strongly vibrationally cooled molecules are also needed to probe a number of other atomic/molecular processes, such as chemical reactions and surface processes, in particular those on cluster and nanoparticle surfaces.

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