Isotopically Selective Condensation and Infrared-Laser-Assisted Gas-Dynamic Isotope Separation

J.-M. Zellweger, J.-M. Philippoz, P. Melinon,[a] R. Monot,[b] and H. van den Bergh[c]
Institut de Chimie Physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

(Received 18 August 1983)

It is shown that the efficiency of classical gas-dynamic isotope separation can be strongly improved with the aid of a relatively weak cw infrared laser. Irradiation in the collisional region of a free jet of SF_6 diluted in argon with a 20-W CO_2 laser leads to an increase in the overall enrichment factor α from about 1.01 to nearly 2, at conditions that have not yet been completely optimized. Efficient isotopically selective condensation is demonstrated for the first time, the inhibition of homogeneous condensation being due to the selective vibrational excitation of one SF_6 isotopomer.

PACS numbers: 33.80.-b, 28.60.+s, 47.55.Ea, 82.20.Tr

The expansion of a mixture of gases (or isotopomers) through a small orifice can lead to several well established mass separation effects.[1] Among these effects are pressure diffusion, centrifugal separation in a curved nozzle, cross-jet deflection, velocity slip, background invasion, Mach-disk and skimmer interference, and Mach-number focusing. Much of the work on the classical gas-dynamic isotope separation has been abandoned (the curved nozzle being a notable exception[2]) because of the small enrichment factors inherent in the small relative mass differences $\Delta M/M$ between the isotopomers of interest.

Here we report on experiments in which $\Delta M/M$ is strongly increased by isotopically selective condensation. In this process a number $\langle m\rangle$ of argon atoms can be attached to one isotopomer in a mixture, whereas to another isotopomer no argon atoms are attached. The large mass differences generated in this way $[\Delta M \simeq \langle m\rangle \times (40\ \text{amu})]$ can be used to try to improve one or more of the above-mentioned ways of classical gas-dynamic isotope separation.

The model system chosen here is the adiabatic expansion of SF_6 diluted in argon. In the absence of infrared (IR) laser excitation, at a given set of experimental conditions, condensation will be observed for all SF_6 isotopomers. Schematically the formation of van der Waals clusters, which is the onset of this condensation, may be represented by a reaction sequence like

$$SF_6 + Ar \rightleftharpoons SF_6Ar, \tag{1}$$

$$\vdots$$

$$SF_6Ar_{\langle m-1\rangle} + Ar \rightleftharpoons SF_6Ar_{\langle m\rangle}. \tag{2}$$

The excited van der Waals clusters formed by the combination reactions will either be stabilized by collison or decompose. Some $(SF_6)_mAr_n$ clusters are also formed but their concentration decreases with increased dilution of SF_6.

When, however, we "heat" one of the SF_6 isotopomers by exciting it vibrationally with an IR laser, we can inhibit its condensation. For this process to be selective, the SF_6 must be sufficiently diluted in an inert carrier gas so that the laser excitation of one isotope in the collisional region of the free jet expansion is not followed by significant nearly resonant intermolecular vibrational energy transfer which can cause scrambling of the initially selective excitation.

The consequences of exciting one particular isotopomer may be pictured as follows:

$$^{32}SF_6 + h\nu \rightarrow {}^{32}SF_6{}^{\dagger}, \tag{3}$$

$$^{32}SF_6{}^{\dagger} + Ar \rightleftharpoons {}^{32}SF_6Ar^{\dagger}, \tag{4}$$

$$^{32}SF_6Ar^{\dagger} \rightleftharpoons {}^{32}SF_6 + Ar. \tag{5}$$

The larger arrow in Eq. (5) indicates that the $SF_6Ar^{\dagger}$ van der Waals molecule, which contains at least the energy of one IR photon in excess of the van der Waals bond energy, is unstable. Thus the concentration of the $^{32}SF_6Ar_{\langle m\rangle}$ is significantly reduced, whereas the nonexcited $^{33}SF_6$ and $^{34}SF_6$ molecules can condense to, respectively, $^{33}SF_6Ar_{\langle m\rangle}$ and $^{34}SF_6Ar_{\langle m\rangle}$. This isotopically selective condensation is demonstrated in Fig. 1. Figure 1(a) shows the relative intensities of $^{i}SF_5Ar^+$ ions for the $i = 32$, 33, and 34 sulphur isotopes at natural abundance (95.0%: 0.76%: 4.22%). The $^{i}SF_5Ar^+$ signals are taken to be representative of the $^{i}SF_6Ar$ concentrations to a first approximation, thus neglecting contributions from the decomposition of larger cluster ions. In this particular case this neglect does not interfer with the essence of the argument. Figure 1(b) shows the mass spectrum obtained when the $^{34}SF_6$ monomer is excited vibrationally in the collisional region of the free jet expansion at $\lambda = 10.76\ \mu m$, but at otherwise unchanged experimental conditions. The excitation of the $^{34}SF_6$ monomer leads

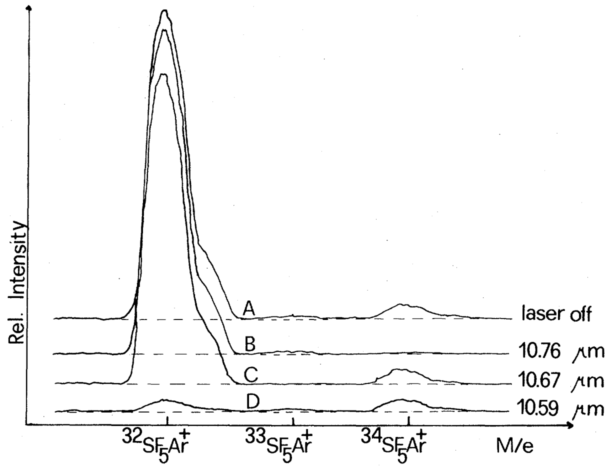

FIG. 1. The isotopically selective condensation of 0.5% SF_6 in argon. $T_0 = 225$ K, $P_0 = 1.5$ bars, and the laser power density is about 20 kW cm^{-2}. (a) No laser, (b) irradiation of $^{34}SF_6$ at 10.76 μm, (c) irradiation of $^{33}SF_6$ at 10.67 μm, and (d) irradiation of $^{32}SF_6$ at 10.59 μm. The irradiation of a single isotopomer in the mixture clearly and selectively inhibits the formation of SF_6Ar clusters for the isotopomer which has been vibrationally excited.

to the selective inhibition of van der Waals cluster formation for this isotopomer, as can be seen by the absence of $^{34}SF_6Ar$, whereas $^{33}SF_6Ar$ and $^{32}SF_6Ar$ are essentially unchanged. Figure 1(c) shows that excitation of $^{33}SF_6$ near 10.67 μm results in the disappearance of $^{33}SF_6Ar$, leaving both $^{32}SF_6Ar$ and $^{34}SF_6Ar$ unchanged. Finally, in Fig. 1(d) it is shown that the vibrational excitation of the $^{32}SF_6$ monomer leads to nearly complete inhibition of $^{32}SF_6Ar$ formation, whereas the $^{33}SF_6Ar$ and $^{34}SF_6Ar$ concentrations remain the same. This decrease in the $^{32}SF_5Ar^+$ signal of about a factor of 25 without a notable change in the $^{33}SF_5Ar^+$ and the $^{34}SF_5Ar^+$ signals underlines the high degree of isotopic selectivity that can be obtained in these experiments.

In the second part of this Letter we report on the absolute measurement of the IR-laser–induced enhancement of the overall enrichment factor α defined by

$$\alpha = \{\bar{X}_E/(1-\bar{X}_E)\}\{\bar{X}_D/(1-\bar{X}_D)\}^{-1}, \qquad (6)$$

where $\bar{X}_E$ and $\bar{X}_D$ are the average mole fractions of the enriched and depleted species near the beam center. In the experiments described below where $^{32}SF_6$ is excited, $\bar{X}_E$ and $\bar{X}_D$ refer respectively to the fractions of $^{34}SF_6$ and $^{32}SF_6$.

At this point it is important to describe the experimental conditions in some detail. The measurements of α are made in a molecular-beam apparatus with three chambers.[3] The first chamber into which the gas mixture is expanded through a 0.1-mm nozzle is pumped by a Roots blower to 10^{-2} Torr. The skimmer by which part of the free jet enters the second chamber is placed 10 mm downstream from the nozzle and has a diameter of 1 mm. The stagnation temperature and pressure are about $T_0 = 233$ K and $P_0 = 1.5$ bars. The free jet is irradiated with a line-tunable cw CO_2 laser which is focused to 0.3 mm full width at half maximum at a distance d downstream from the nozzle exit. d can be varied but was found to be optimal near 0.2 mm under the applied conditions. Experiments in which isotope separation was attained by the IR-laser–induced vibrational predissociation of the van der Waals clusters at larger d in the collision-free part of the free jet expansion are described elsewhere.[4] The molecular beam leaves the second chamber, which is at 10^{-5} Torr, through a collimator of 5-mm diam placed 12 cm downstream from the nozzle. The beam enters the third chamber in which the pressure is about 2×10^{-7} Torr, which contains the quadrupole mass filter (QMS). After passing the ionizer of the QMS the molecular beam is compressed by a turbomolecular pump into a trap containing zeolite at 77 K. The contents of this trap can be transferred to an IR absorption spectrometer and/or a reverse-geometry double focusing mass spectrometer for the analysis of isotopic abundances. The reported values of α are not measured directly by the QMS in the molecular beam as several factors, such as the degree of internal excitation of the molecules, the effect of van der Waals complex formation, and Mach-number focusing, can influence the observed isotopic abundances. The $^{34}SF_5{}^+/^{32}SF_5{}^+$ ratio measured by the QMS in the molecular beam is, however, used for the rough optimization of the laser-enhanced isotope separation. This is shown in Fig. 2, where the effect of laser radiation on α is demonstrated as a function of the percentage of SF_6 in an SF_6/Ar mixture. The values of α measured in the QMS are higher than the real values, but general trends are correct. The highest selectivities are found for the lowest SF_6 percentage. This is expected at low SF_6 concentrations as less scrambling of the vibrational excitation will occur. The best value measured here for α with the laser turned on, using both IR and mass-separation analysis, is $\alpha = 1.6$. With the laser off under otherwise identical conditions, α is found to be ≤ 1.02. The real values of α are

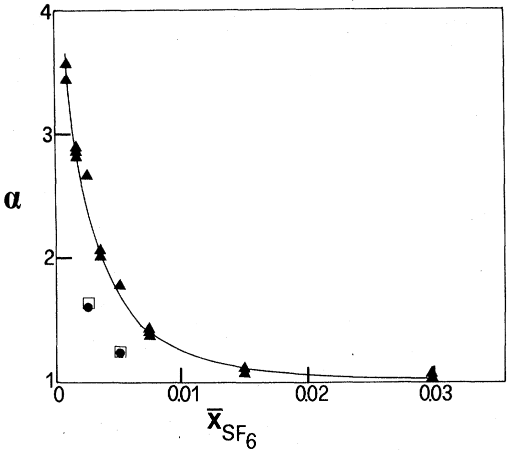

FIG. 2. The overall enrichment factor α as a function of the fraction of SF_6 in argon in the stagnation chamber. Decreasing the SF_6 concentration results in less scrambling of the vibrational excitation and hence higher isotopic selectivity. Triangles are relative measurements made with the QMS in the molecular beam, squares are absolute measurements made by both IR absorption spectroscopy and a double-focusing reverse-geometry mass spectrometer, after condensation of the beam and transfer to these respective apparatus. Circles are measurements with the QMS after the molecules of the beam have collided with several stainless-steel surfaces at room temperature. In these measurements $^{32}SF_6$ is irradiated at 10.59 μm. The center of the free jet is enriched in $^{34}SF_6$ and depleted in $^{32}SF_6$. Stagnation conditions are as in Fig. 1.

reported in Fig. 2 together with those obtained from QMS measurements directly in the molecular beam. Also in Fig. 2 we give two values of α measured with the QMS in which a special collimator to which a small tube had been attached on the high-vacuum side is used. In this tube several "obstacles" hinder the direct traverse of the molecular beam, and the molecules must hit several walls at room temperature prior to being ionized in the QMS ionizer. Clusters are broken up in this tube and molecules leaving it are close to room temperature after a large number of collisions with the walls. With use of this special collimator the QMS values of α are nearly identical to the real values.

It is not trival to establish which of the classical gas-dynamic separation effects mentioned above combines with the isotopically selective condensation to give the observed laser-enhanced separation of isotopomers. Mach-number focusing could be ruled out as a scan across the molecular beam in the third chamber with the QMS showed a nearly constant enrichment over the beam profile. Increasing the argon pressure in the first chamber up to 0.2 Torr increases the isotopic selectivity, indicating that background invasion and the consequent free jet deceleration play an important role. Further investigations along these lines are in progress. It will also be worthwhile to combine the isotopically selective condensation with some of the other gas-dynamic separation schemes.[1] Furthermore we expect to improve the efficiency of the current setup by better focusing of the laser beam in order to concentrate the available power in the most efficient pressure regime of the free jet.

Finally it should be mentioned that the irradiation of the free jet in the collisional zone leads to a "beam widening" effect.[3,5] Some of the vibrational excitation of the SF_6 is degraded to translational motion in vibrational to translational and rotational energy transfer processes. This translational energy is added to the (large) axial velocity and to the (small) perpendicular velocity components of the free jet, thus causing a relatively small increase in the axial velocity but a relatively large increase in the off-axis velocity. This implies a decrease in the speed ratio and a geometrical widening of the jet, which in turn causes a decrease in the particle flux passing through the skimmer. Excitation of one isotopomer in a mixture strongly diluted with argon could thus possibly result in a selective beam widening for this particular isotopomer, and lead to a decrease in its relative abundance near the beam centroid. Under conditions where the effect of selective condensation should be small (i.e., at high T_0 where few van der Waals clusters are formed) we searched for such an effect of selective beam widening. At $T_0 = 375$ K, where no trace of clusters could be detected in the free jet, irradiation of the collisional region of the gas expansion gave a beam-widening effect, and some enhancement of the isotopic selectivity was induced by the laser, indicating the possible existence of the selective beam-widening effect. As some small degree of cluster formation may remain undetected under these conditions, selective condensation cannot be completely ruled out as being responsible for the observed selectivity.

In conclusion, isotopically selective condensation has been observed for the first time in a free jet following the IR laser excitation of one isotopomer in a mixture. A novel way is demonstrated in which IR laser radiation strongly enhances the gas-dynamic separation of isotopes. The method is generally applicable, and besides the separation of sulfur isotopes in SF_6 we have also separated Si isotopes in SiF_4 and Br isotopes in CF_3Br.

The authors are grateful to M. Quack for carefully reading this manuscript, and to the Swiss Fonds National and the Ecole Polytechnique Fédérale de Lausanne for financial support.

(a)Permanent address: Institut de Physique des Solides, Université de Lyon, Villeurbanne, France.

(b)Permanent address: Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

(c)Author to whom correspondence should be addressed.

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