Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Photophysical Enrichment of Isotopically-Labeled Compounds by Infrared Radiation Applied to Molecular Beams

S. Behrendt[a]
[a] DEPARTMENT OP CHEMISTRY, CARLETON UNIVERSITY, OTTAWA, CANADA

To cite this Article Behrendt, S.(1971) 'Photophysical Enrichment of Isotopically-Labeled Compounds by Infrared Radiation Applied to Molecular Beams', Separation Science and Technology, 6: 1, 43 — 46
To link to this Article: DOI: 10.1080/00372367108055550
URL: http://dx.doi.org/10.1080/00372367108055550

SEPARATION SCIENCE, 6(1), pp. 43–46, February, 1971

COMMUNICATION

Photophysical Enrichment of Isotopically-Labeled Compounds by Infrared Radiation Applied to Molecular Beams

S. BEHRENDT

DEPARTMENT OF CHEMISTRY
CARLETON UNIVERSITY
OTTAWA, CANADA

Summary

A method is proposed by which selective radiant heating of a molecular-beam source could be used to enrich volatile, labeled compounds in the minute quantities that are needed for tracer experiments.

For the isolation of experimental quantities of a labeled component of an organic compound, capillary gas chromatography has been used extensively as it causes no chemical changes. An enrichment that is simpler and much more selective, though it too cannot be applied to traces, could be achieved with a molecular beam formed by selectively irradiated molecules recoiling from the heavy atoms of a matrix gas.

Figure 1 illustrates this with an arrangement of separately thermostatted compartments. R is a sample reservoir partly filled with the condensed compound. S, V, and T are interconnected by aligned apertures and form a molecular-beam apparatus.

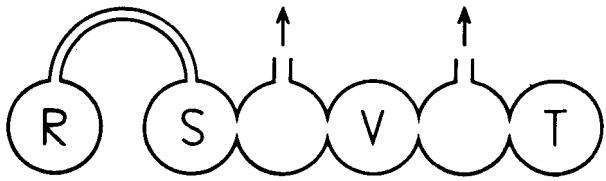

FIG. 1. Scheme of a demonstration apparatus for photophysical enrichment.

From R, sample vapor at a thermally controlled pressure leaks through a capillary into the molecular-beam source-chamber S. The latter contains, as matrix gas, mercury vapor at a pressure of ca. 1 torr that is maintained by some liquid mercury which is thermostatted in it at 126°C. The gas mixture in S is exposed to selective infrared radiation which, as the vibrational isotope effect is quite distinct in rarefied gases, only the labeled molecules can absorb.

The radiation source is not shown in Fig. 1. The simplest one is an incandescent glower using the same but unlabeled compound as a filter. In some cases, a selective radiator can be substituted, e.g., ^{13}CO excited by an electric discharge, with a filter of ^{12}CO. Whenever possible, a laser should be used, because the intensity of the radiation determines the isotopic purity of the labeled compound that will be collected.

Within S, the infrared radiation raises the vibrational-rotational energy of some of the labeled molecules. If this radiation is monochromatic, then it is absorbed by just one vibrational energy level of a molecule, e.g., a stretching vibration. The absorbed energy is next distributed over the molecule by filling lower energy levels, e.g., bending, rocking, wagging, twisting, and deforming vibrations. Most of the resulting vibrational modes will have an energy that is at least as large as the mean translational energy of the molecules. Under the conditions of the experiment, a thus excited molecule will undergo, within its lifetime, some 10^3 collisions with the mercury atoms that are present in huge majority. The multitude of excited vibrational modes makes it highly probable that some of these collisions will be successful, removing the excess energy of the molecule by one vibrational level step at a time. In a successful collision, this vibrational energy is converted into translational energy of both collision partners. The latter rebound and, according to the principle of conservation of momentum, any molecule with a mass smaller than that of a mercury atom must experience most of the resulting acceleration. This molecule momentarily attains a high velocity that may exceed the range of its thermal velocity distribution. Some of the recoiling molecules join the molecular beam which continuously effuses from S.

To reach the cooled target-chamber T, the molecular beam from S must pass through the velocity-selector V which is located between two evacuated collimator chambers.

As a molecular-beam velocity-selector, the conventional mechanical device involving rotating slits could be used. Instead, V is a kinetic

velocity-selector which consists simply of a chamber filled with mercury vapor at a low pressure which is regulated thermally as in *S*.

Every molecule of the molecular beam penetrates into *V* until it is scattered by colliding with a mercury atom. Scattered molecules have very little chance of being scattered back into the beam after further collisions in *V*, and eventually are evacuated from the collimator chambers. The mean penetration range of the molecular beam in *V*, i.e. the mean free path of its molecules, depends on the velocities of the beam molecules and on the pressure of the mercury vapor. The latter is adjusted so that only very few molecules penetrate through *V* and enter *T*, where they are condensed. These molecules, which traversed *V* without colliding with a mercury atom, very probably will have been the fastest ones in the beam and will consist to a large extent of the recoiled labeled molecules.

The yield can be greatly increased by improving the geometry of the apparatus, e.g., as shown in Fig. 2.

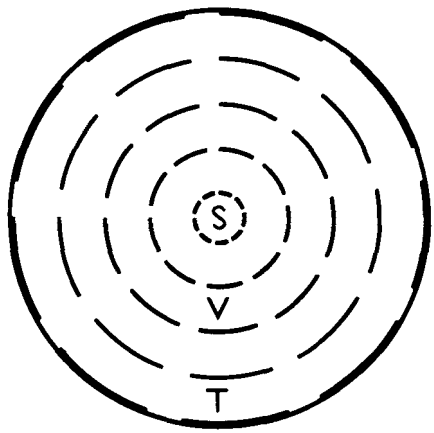

FIG. 2. Cross section of a practical apparatus for photophysical enrichment.

The molecular-beam apparatus shown consists of long, concentric, cylindrical chambers. Matrix gas (mercury vapor or xenon), fresh for each sample, flows through *S*. It is irradiated by a laser beam directed along the axis of *S*. There are source-canal slits along the length of *S*, through which molecular beams effuse. Through *V* flows a permanent gas which cannot be condensed in *T*, e.g., argon. *T*, and the collimator chambers surrounding *V*, are evacuated at their ends.

The labeled molecules are condensed in T, and are later collected from the lengthwise grooves shown within it.

A molecular-beam apparatus of this type can be left to run unattended, until enough enriched compound has been collected.

As radiation is absorbed exponentially, very dilute samples would require enormous radiation intensities that in most cases cannot be attained. Therefore, the concentration of the desired molecules should not be too low. Such molecules can be enriched after preliminary photophysical concentration of the sample. E.g., a very dilute sample of ^{14}C-labeled compound should first be concentrated by photophysical elimination of much of the ^{12}C-labeled compound; afterwards, the ^{14}C-labeled compound can be purified by direct photophysical enrichment.

In principle, the vapor of an isotopically pure compound could be isolated from an isotopic mixture of this compound by its radiation-enhanced diffusion in inert gas, multiplied by zoning or some countercurrent technique.

However, the selective infrared radiation would be utilized too inefficiently for two reasons. For enhanced diffusion, each molecule needs a large number of photons which it absorbs consecutively. Also, as the resulting enrichment is opposed by normal diffusion, many of these photons will be consumed just to maintain any enrichment already achieved.

Received by editor May 18, 1970