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

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COMMUNICATION

Photophysical Separation of Conformational Isomers by Microwave Radiation Applied to Molecular Beams

S. BEHRENDT

DEPARTMENT OF CHEMISTRY
CARLETON UNIVERSITY
OTTAWA, CANADA

Summary

A method is proposed by which an experimental quantity of a pure conformer can be stabilized and isolated for the separate study of its reactions. Similarly, isotopic compounds can be enriched on a laboratory scale. Due to the low-temperature feature of the proposed method, microwave spectroscopy can be applied to volatilizable large molecules.

CONFORMATIONAL ANALYSIS

Conformational analysis is not a new subject, but it has been limited to compounds that give rise to very few conformational isomers and that are almost only studied in reactions in which they form different products.

These conformers interconvert rapidly because they are separated by potential-energy barriers of the order of 1 kcal/mole, whereas at least 16 kcal/mole are required for stability at room temperature. Nevertheless, the individual conformers can be distinguished spectroscopically.

If they differ in free energy by at least 0.2 kcal/mole, their spectra can be identified by observing the changes in intensity of the spectral lines of a vapor sample as its temperature is lowered, for lower temperature favors the more stable conformers.

Conformers can be obtained separately if they greatly differ in a physical property that can be utilized for their preparation. The molecular shape of one conformer may be preferred for crystallization. The interaction with an appropriate solvent can cause another conformer to predominate in this solution. When the difference in free energy is large enough, nearly all molecules of a compound convert into the most stable conformer during gradual cooling to sufficiently low temperatures.

Normally, however, the chemistry of conformers is studied in liquid solutions under conditions in which thermal equilibrium provides appreciable concentrations of all conformers and these are distinguished by their characteristic reaction products. The latter are known, being determined in most cases from identical reactions of similar molecules that have the same conformation. These comparison molecules either are so rigid that they have only one conformation, or the desired conformer is statistically favored by bulky, inert substituents which raise the free energies of the competing conformers by several kcal/mole.

MICROWAVE SEPARATION OF A CONFORMER

In this paper, a microwave method is proposed for the isolation of traces of pure conformational isomers, so that the chemical properties of each can be observed separately. This will be useful for any suitable molecular species that consists of a large number of nonequivalent conformers which differ only little in applicable physical properties, have nearly the same free energy, and often form the same reaction products, possibly even interfering with each other's reaction rates.

The photophysical separation of a conformational isomer is performed in the molecular-beam apparatus shown in Fig. 1 as follows. In the source-chamber, the sample is transformed into a molecular beam which passes through the isolating-chamber and then enters the diffusion-chamber. There, the beam is "stored" temporarily while all unwanted conformers are eliminated with the help of selective microwave radiation. From the diffusion-chamber, the molecular beam of the single conformer proceeds into the preparation-chamber, where it can be brought into contact with the molecular beam of a reagent.

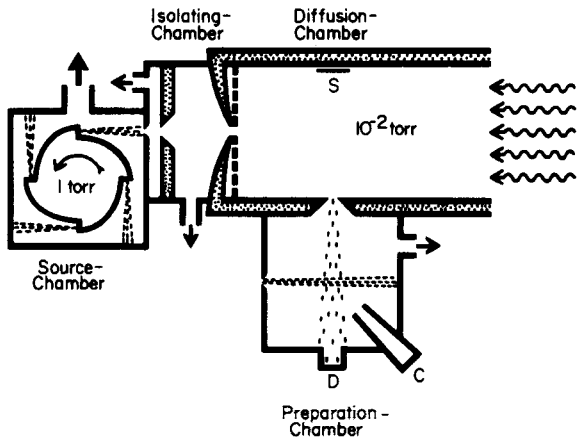

FIG. 1. Scheme (viewed from top) of an apparatus for photophysical separations by microwave radiation.

All compounds to which microwave spectroscopy (*1–4*a) can be applied are suitable for this separation method. Thus, they must reach a vapor pressure of 1 torr without much thermal decomposition, and the permanent dipole moment of the molecules must amount to at least 0.1–1 D, depending on the molecular weight which can range from 30 to 250. Preferably, the larger molecules should also have some rigidity due to multiple bonds or ring structure, and be symmetrical to some extent.

STABILIZATION OF CONFORMERS

The first function of the apparatus is to freeze the conformational equilibrium of the sample, causing the desired conformer to stop interconverting before it can assume a more stable conformation. The sample is quenched in three stages, as described below.

The first stage is translational "cooling" of the molecules: collisions between them are practically eliminated by letting them effuse into vacuum, and the resulting molecular beam is slowed down so that the molecules will carry less translational energy into the diffusion-chamber. This stage takes place in the source-chamber, which is separately pumped and kept barely warm enough to prevent vapor condensation in its interior. This chamber contains a rapidly spinning, hollow rotor which produces mechanically decelerated molecular beams. (Normally, such rotors are rotated in the opposite direction and serve as sources

of tangentially accelerated molecular beams.) The rotor contains sample vapor at 1 torr and has vertical source-canal slits from which these molecules effuse. Every molecular beam thus originating from the spinning rotor is only momentarily aligned with the slits that lead to the diffusion-chamber. When aligned, the beam is defined by the apertures of its source-canal slit and of the vertical collimating slit which leads to the isolating-chamber. The intensity of the resulting beam will be somewhat diminished by the motion of the rotor, which spreads the beam because it decelerates the molecules only in the forward direction without retarding their effusion in other directions.

The second stage provides vibrational cooling for the molecules; it takes place in the isolating-chamber. The main feature of this evacuated chamber is a hollow, silvered partition wall, which contains liquid nitrogen, and which has a vertical slit that lets the molecular beam through without defining it. The partition wall is a cryogenic shield protecting the much colder wall that leads into the diffusion-chamber from thermal radiation and from scattered molecules. Between these two very cold walls, the molecules in the beam reach the ground levels of their more energetic vibrational modes by emitting their excess vibrational energy, with half-lives of typically 10^{-5} sec, as infrared radiation.

The third stage consists mainly of rotational cooling of the molecules. It takes place in the diffusion-chamber, which is thermostatted at 4.2°K and filled with helium gas at 10^{-2} torr. This chamber is the inner part of a cryostat that is built like a double Dewar flask: the inner hollow wall contains liquid helium at atmospheric pressure; of the outer hollow wall, Fig. 1 shows only the section that forms the partition wall in the isolating-chamber. (In some equally effective helium cryostats, the liquid-nitrogen shield is substituted by thermal-radiation barriers which are cooled by the helium gas that slowly boils off within the inner hollow wall. Either design can be used here.) The inner hollow wall has a vertical slit that admits the molecular beam, without defining it, into the diffusion-chamber. Most of the rotational energy of the entering molecules, as well as most of what remained of their translational and of their excess vibrational energies, is then dissipated by repeated collisions with the helium atoms among which the molecules disperse.

ISOLATION OF A STABILIZED CONFORMER

The second function of the apparatus is to isolate the desired conformational isomer from the mixture of conformers that have ceased to

interconvert. This separation takes place in the diffusion-chamber, and is based on accelerating the gaseous diffusion of the chosen molecules by heating them mildly with selective microwave radiation.

The diffusion-chamber is essentially a long flow-cell, with a rectangular cross section, for helium gas at 4.2°K. The circulation of this helium is not shown in Fig. 1. The helium enters by being pumped into the end of the chamber shut off by a porous metallic wall. It permeates this partition wall, establishing in the chamber a slow, laminar flow of helium at 10^{-2} torr, and leaves through the other end (not shown in Fig. 1). The latter end of the chamber is bounded by a transparent pane through which microwave radiation (wavy arrows in Fig. 1) is admitted. (Alternatively, this end of the chamber can enclose the source of the radiation.) The microwave radiation is emitted by directionally coupled klystrons which radiate simultaneously, each generating one of the frequencies that are used, and is beamed at the porous wall which reflects it back. The beam should not be directed at the other walls of the diffusion-chamber in order to avoid heating sample deposited on them.

The microwave spectrum of the conformer (*5*) that is to be isolated must be known in advance. At 4.2°K it will be much simpler and more intense than at room temperature because most molecules will occupy the zero rotational-energy level; the determination of this spectrum is explained at the end of this paper. The molecules are irradiated by microwave radiation of frequencies corresponding to all usable rotational transitions that give rise to strong absorptions. Not usable is any transition, i.e., absorption, due to a conformational interconversion, or which overlaps with an absorption "line" of another conformer, or which is situated in a spectrally unresolved rotation-vibration band.

In a system in which the molecules continually exchange energy in collisions, according to the $e^{-\Delta\epsilon/kT}$ factor of the Boltzmann distribution, a separation method can be effective only if the energy that tends to separate the molecules is of at least the same order of magnitude as the thermal agitation which tends to remix them. In helium gas at its boiling-point temperature, kT = (1.38 × 10^{-16} erg/deg-molecule) (4.22 deg) = 5.82 × 10^{-16} erg/molecule. Microwave radiation with a typical wavelength such as 1 cm (30 GHz) has an energy of $\Delta\epsilon = h\nu$ = (6.62 × 10^{-27} erg-sec) (30 × 10^{9}/sec) = 1.99 × 10^{-16} erg per photon; with a wavelength of 1 mm (300 GHz), which is close to the presently attainable upper energy limit of the microwave region, it has 19.9 × 10^{-16} erg per photon.

The molecules from the molecular beam which penetrated into the diffusion-chamber are suspended in the flowing helium. They disperse in it at random, and condense on the walls before the slow gas stream can carry them to the other end of the long chamber. The vertical component of the displacement of the molecules is caused by their diffusion and to a lesser extent by their settling, and is unpredictably influenced by very slow convection currents of the helium. The horizontal component of the displacement of the molecules with reference to the helium stream is caused, in the absence of microwave irradiation, only by their diffusion. Some of the molecules will come into contact and coalesce with other molecules. The resulting molecular agglomerates will diffuse much more slowly than single molecules; when exposed to the selective microwave radiation, they will absorb little or nothing.

The selective microwave radiation tends to raise the rotational energy of the molecules able to absorb it. The rotational relaxation of these molecules is prompt (*6*) because one out of every few of their collisions with the surrounding helium atoms is successful, converting the excess rotational energy into translational energy; helium-4 atoms have no nuclear spin. The continually absorbing molecules are much larger than the helium atoms and will experience an intermediary between propulsion, resembling the photophoresis of aerosol particles (*7*), and jolts, each due to a successful collision. This effect will be superimposed on the normal diffusion of these molecules, accelerating their random motions. Due to this enhanced diffusion in the helium stream, the desired conformer will reach the side walls of the diffusion-chamber earlier and will be deposited on them nearer to the porous wall than the other conformers which will reach the side walls further downstream.

MANIPULATION OF AN ISOLATED CONFORMER

The third and final function of the apparatus is to make available the previously stabilized and isolated conformational isomer in a form suitable for experimentation. Typical conformers stop interconverting directly or by tunneling only at temperatures below 50°K. As this rules out liquid solvents, the chemical reactions of pure conformers can best be studied by a molecular-beam technique.

The pure conformer, deposited on a removable slide (S in Fig. 1) that is fastened to a side wall of the diffusion-chamber, should be used to obtain its infrared spectrum.

The reactions of the conformer are prepared with crossed molecular beams that mix the reactants homogeneously at 4.2°K.

Figure 1 shows an oversimplified outline of the preparation-chamber, which is cooled by liquid helium and evacuated separately. A molecular beam of helium atoms effuses into it from a vertical slit in a side wall of the diffusion-chamber. This slit will not become clogged by condensing molecules during an experiment, because the low pressure in the diffusion-chamber permits it to be about 1 mm wide. The flow rate of the helium gas in the diffusion-chamber must be fast enough so that only molecules of the isolated conformer can join this molecular beam. The flow rate is adjusted with the help of a molecular-beam detector (D in Fig. 1) of the electron-bombardment type. The detector is operated at an electron-accelerating voltage (e.g., 20 V) below the ionization potential of helium (24.5 eV), so that it senses only the organic molecules of the beam (and the residual gases in the chamber). The lower the detector response becomes during the adjustment, the more pure will be the conformer in the beam.

The reagent is admitted into the preparation-chamber as a molecular beam which enters through a vertical slit and effuses across the beam of the conformer. Most molecules of either beam do not collide with molecules of the other beam, and condense on the surfaces within the chamber. A reagent molecule that collides with a helium atom is scarcely deflected when they rebound. When a reagent molecule and a molecule of the conformer collide, they will coalesce and then move in the resultant direction. Some of these molecular aggregates will be deposited on the removable bottom of the collector (C in Fig. 1), and can later be analyzed by infrared spectroscopy.

For infrared spectroscopy, the deposits at S and at C must be removed from the apparatus without warming up. Their infrared spectra can then be obtained by techniques such as low-energy electron scattering (*8*) or inelastic electron tunneling (*9, 10*), which require only a monomolecular layer of sample.

The reaction in the deposit at C should be allowed to occur only within the infrared spectrometer so that its starting time will be known. The spectrometer must then be thermostatted at a temperature well above 4.2°K, e.g., by liquid neon. Only a limited number of successive infrared spectra of the reacting deposit will be available for the determination of reaction rates, because any type of infrared spectroscopy gradually destroys a pure conformer.

It is not advisable to simplify the apparatus by omitting the prepara-

tion-chamber. In principle, one could study a reaction of the conformer with, e.g., a pure conformer of another compound, by condensing a monomolecular layer of the reagent on the deposit at S and later submitting the resulting surface to infrared trace analysis. In reality, such a uniform coating is not attainable in the diffusion-chamber, and the concentration of the reaction products in the heterogeneous sediment will be too low for their indentification by infrared spectroscopy.

MICROWAVE ENRICHMENT OF ISOTOPIC COMPOUNDS

The enrichment of isotopically labeled compounds by selective infrared irradiation of their vapors (*11*) fails whenever the vibrational isotope effect is not distinct enough. Polar isotopic compounds can, in this case, be enriched by a more expensive microwave method, because the rotational spectrum of a molecule is distinctly affected by the isotopy of every one of its atoms that is not located at its center of gravity.

A well-known method for this is molecular-beam electric-resonance, in which polar molecules in the zero rotational state are isolated and exposed to monochromatic microwave radiation while being selectively converged on a very cold obstacle; only the molecules that absorb and thus change their rotational state can bypass the obstacle. However, this method can be applied only to very simple molecules and is not productive enough for preparative use: the molecular beam must effuse from a pinhole instead of from a slit, and is attenuated first by velocity selection and then by rotational-state selection.

Preparative enrichment of labeled compounds on a laboratory scale could be obtained with the apparatus shown in Fig. 1 simplified by using a stationary molecular-beam source and by omitting the preparation-chamber. The diffusion-chamber should be filled with neon at a pressure of at least 10^{-2} torr and be thermostatted by liquid neon. For many compounds, the rotational relaxation of a molecule occurs at its first collision with an atom of a noble gas (*6*); a direction could be superimposed upon the enhanced random diffusion of these molecules by using the Doppler effect, so that radiation can be absorbed only by molecules momentarily moving along a beam from an accurately adjusted backward-wave oscillator.

The microwave enrichment of some isotopes on a commercial scale will become feasible after the development of a tunable electronic source of intense submillimeter radiation. This could enhance the diffusion of polar molecules with an exceptionally small moment of inertia in vapors

that are not undercooled. E.g., a chlorine isotope could be enriched by microwave-enhanced diffusion of hydrogen chloride in a large excess of argon at over 10^{-2} torr, multiplied by zoning or some countercurrent technique, in an apparatus kept at the temperature of boiling hydrogen chloride.

ROTATIONAL SPECTRA AT LOW TEMPERATURES

The molecular-beam technique that provides a flow of dilute sample in the form of supersaturated vapor stabilized temporarily at an extremely low temperature will be useful for microwave spectroscopy, which must then be performed with large optical components instead of with a waveguide, in three cases. Volatilizable large molecules will become accessible to microwave spectroscopy (at higher temperatures, their weak microwave absorption is distributed over far more rotational lines which are then split too many times for individual detection). The assignment of rotational transitions in a conventionally obtained microwave spectrum will be easier when spectra of the sample taken at progressively much lower temperatures become available for comparison. The microwave spectra of nonequivalent conformers that are to be photophysically enriched will become individually distinguishable by the normal procedure—described in the introductory section—because the gaseous sample can be cooled to sufficiently low temperatures.

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