

Principles of Photochemical Separation of Isomeric Nuclides

Abstract

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Introduction:

Aside from intrinsic scientific interest, photochemical separation of the isomeric states of single nuclides offers one possibility of achieving a nuclear population inversion, essential for the development of gamma ray lasers, or GRASERS [1,2]. Just as for isotope separation, photochemical methods of isomer separation depend upon the existence and magnitude of spectral differences between the species to be separated exceeding the resolution of tunable optical sources.

Mercury has already been shown capable of isotopically selective photochemical reaction using 254 nm radiation [3]. These studies have been performed on the even mass number stable isotopes (i.e. 198 and 202) which have zero nuclear spin and one hyperfine component per isotope within the hyperfine structure of the 254 nm line. Mercury 197m, the excited nuclear state, has a half-life of 24 hours, with three hyperfine components due to the nuclear spin splitting effect [4,5]. The ground state, Hg-197g, is also radioactive with a half-life of 64 hours, but the nuclear spin splitting results in a doublet [4,5].

Mass, spin, quadrupole, and nuclear volume effects give rise to shifts and splittings of the optical energy levels of atoms and molecules. In the case of mercury, its optical spectrum has been shown to contain several lines with well-resolved hyperfine structures characteristic of the different isotopic species. The hyperfine structure has been measured for Hg-197m and Hg-197g [5]. Isotopes have been separated by chemical reaction of mercury atoms selectively excited at 254 nm by means of a mercury lamp incorporating a single isotope (or enriched in a specific, single isotope). The excited atoms can react with oxygen to produce isotopically enriched HgO which may be recovered [3].

Separation of Hg-197m:

In a similar manner it should be possible to selectively excite and separate the Hg-197m isomeric state. However, a different source of radiation is needed. The specific wavelength required may be obtained by use of a nitrogen laser pumped tunable dye laser providing a wavelength of 508 nm, which is then frequency doubled to 254nm using a non-linear potassium pentaborate (KPB) crystal and then tuned and scanned to the desired specific wavelength for the selective excitation process. Resolution is on the order of 0.0008 nm using an in cavity etalon with such a laser configuration. One absorption line of the Hg-197m triplet is almost 0.002 nm from the nearest Hg-197g hyperfine component and about 0.0026nm from the nearest hyperfine component of any of the stable Hg isotopes [5]. Therefore it should be possible to recover the Hg-197m state enriched relative to Hg-197g or any of the stable isotopes of Hg. The degree of isomer enrichment can be readily determined by measurement of the characteristic emissions of the radioactive Hg-197m and Hg-197g states. It is noted also that the use of recoil-based radioactive isotope enrichment (the Szilard-Chalmers process) during the preparation of the isomeric species would facilitate the subsequent photochemical enrichment of the isomeric state.

Possibility of Br Isomer Separation:

Another element which has been studied for photochemical isotope enrichment [6], and has isomeric states of reasonable lifetime (relative to times required for chemical processing to recover the enriched material) is bromine. Selective excitation of the molecule Br₂ produces bromine atoms. Reaction of these atoms by hydrogen abstraction with HI can result in a product enriched in the selectively excited isomer or isotope. Br-80 has an excited state, Br-80m, with a half-life of 4.4 hours and a ground state, Br-80g, with a half-life of 17.6 minutes. It should be feasible to separate these species by a selective photochemical reaction. The spectrum of the molecules containing Br-80m has not been measured, but isomer shifts should exist for these species relative to normal bromine. Again measurement of the characteristic emission from the radioactive isomeric and ground state can be used to verify enrichment factors.

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DRAFT OF PHOTOCHEMICAL ISOTOPE SEPARATION OF BROMINE

A major problem in the development of a gamma ray laser (GRASER) apparently is the rapid separation of an isomeric state leading to energy state inversion and the potential for stimulation of gamma emission. The direct objective of the studies proposed here is the isolation or enrichment of a nuclear isomer through selective photoexcitation. It is suggested that atoms or simple molecular species with nuclei in both the ground and desired isomeric states may be separated rapidly from a solid target source by evaporation to the gaseous state, followed by the appropriate photochemical transformations and subsequent reactions proposed below.

It has recently been proposed by Letokhov¹ that laser photochemical separation employing two-step photodissociation or photoionization may be possible, a procedure successfully used in isotope separation². This technique is based on the concept that the optical properties of isomers differ; this difference may arise from:

- (a) the slight difference in mass of the nuclei; and
- (b) the difference in isomeric nuclear spins.

(a) Mass Effect. Isomers differing in excitation energy E will also differ in mass according to the Einstein relationship $E = \Delta m c^2$. Thus, if the excitation energy is 0.1 MeV, $\Delta m = 1.8 \times 10^{-31}$ kg = 1.1×10^{-4} amu. This slight difference in mass will effect the fundamental vibration frequency ν_0 of a chemical bond involving the isomer and hence the infrared absorption spectrum of the molecule, since $\nu_0 = (1/2\pi) \sqrt{k/\mu}$, where k is the force constant and μ is the reduced mass. For example, consider a diatomic molecule consisting of hydrogen and a hypothetical atom X of atomic weight 100 that possesses an isomer X^1 differing by 0.1 MeV; assuming the force constant k is independent of mass, the ratio of the fundamental vibration frequencies $(\nu_0/\nu_0') = \sqrt{\mu'/\mu} = 1.000000005$. If $\nu_0 = 3000 \text{ cm}^{-1}$,

the difference in frequency between X and X' is $\Delta\nu_0 = \nu_0 - \nu_0' = 1.5 \times 10^{-5} \text{ cm}^{-1}$ for excitation of a single vibrational level; this difference would be increased for multi-level excitation, but such excitation would be quite weak because of the vibrational selection rule limiting the change to a single level. Selective vibrational photoexcitation of the isomeric state would thus require a stabilized infrared laser with bandwidth considerably less than $1.5 \times 10^{-5} \text{ cm}^{-1}$; present lasers do have bandwidths as low as ca 10^{-7} cm^{-1} and frequency reproducibility (stability) of 10^{-11} .

If excitation is to a higher electronic level rather than solely vibrational excitation, the magnitude of the difference in absorbed radiation frequency, $\Delta\nu_A$, will depend on the change in the vibrational force constant with electronic excitation. If the force constant does not change, there will be no mass effect in the (0, 0) transition; if the force constant changes such that $\nu_0^* = \frac{1}{2} \nu_0$, where ν_0^* is the fundamental vibration frequency in the electronically excited state, then $\Delta\nu_A = \frac{1}{4}(\nu_0' - \nu_0) \approx 4 \times 10^{-6} \text{ cm}^{-1}$ for the (0, 0) transition in the case of the diatomic molecule HX cited above; this will also be increased for excitation to higher vibrational levels in the excited state, a process no longer restricted by the vibrational selection rule and hence of much greater probability than for solely vibrational excitation.

If the ground and isomeric nuclear states are in the form of atoms rather than diatomic or polyatomic molecules, then of course there will be no vibrational excitation. A mass effect will still result on the electronic line absorption spectrum; this effect will be extremely small, however. Assuming a hydrogen-like atom, the frequency of absorption for a specific transition is a function of the Rydberg Constant and hence is directly proportional to the reduced mass of the nucleus and the electron; for the atom X of atomic weight 100,

the difference in frequency of absorbed light between the ground state X and isomeric state X' for absorption in the ultraviolet (ca. $4 \times 10^4 \text{ cm}^{-1}$) is $\nu_{A'} - \nu_A \cong 3 \times 10^{-7} \text{ cm}^{-1}$. This difference approaches the resolution of known lasers, and undoubtedly would be masked by nuclear spin effects discussed below.

(b) Nuclear Spin Effects. In both the atom and the molecule, hyperfine structure exists because of nuclear spin coupling. Normally the nuclear spin is that of the ground state nucleus. The electrons outside the nucleus are coupled together and with the nucleus. This is true in each level including the ground state and excited states of the atom. For a given transition between electronic levels of the atom one line appears, but under fine resolution there are a series of lines each dependent on the coupling with the nuclear spin. These closely spaced lines are called the hyperfine structure.

Hyperfine structure has been studied extensively. Herzberg discussed studies made on Bi and Pr⁽³⁾. The many lines observed are separated by several tenths to over an angstrom unit (.01 to .1 nm). The splitting of the levels is shown in Figure 1, as given by Herzberg.

For the isomer of interest in this work a large difference in nuclear spin must exist in order for the state to have a significantly long lifetime. This results in a difference in coupling with the electrons and each electronic state. Shifts in the spectral lines of the order of 0.1 nm are thus to be expected (of much greater magnitude than that from the mass effect discussed above), so that relatively easy selective electronic excitation of the isomer compared to the ground state nucleus will be possible.

In each of the cases given above, selective isomeric absorption leads to either a vibrationally or electronically excited nuclear isomeric state. Success of isomeric separation requires that this species react chemically in the excited electronic state, or that a subsequent photochemical process take place

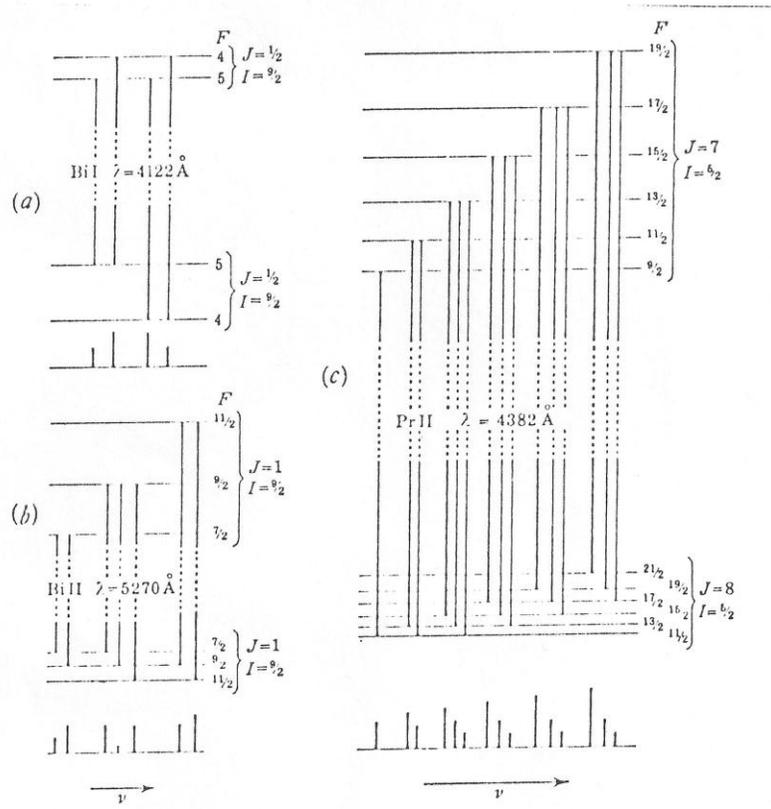


FIGURE 1

Origin of Hyper fine structure (a) Bi, (b) Bi⁺, and (c) Pr⁺

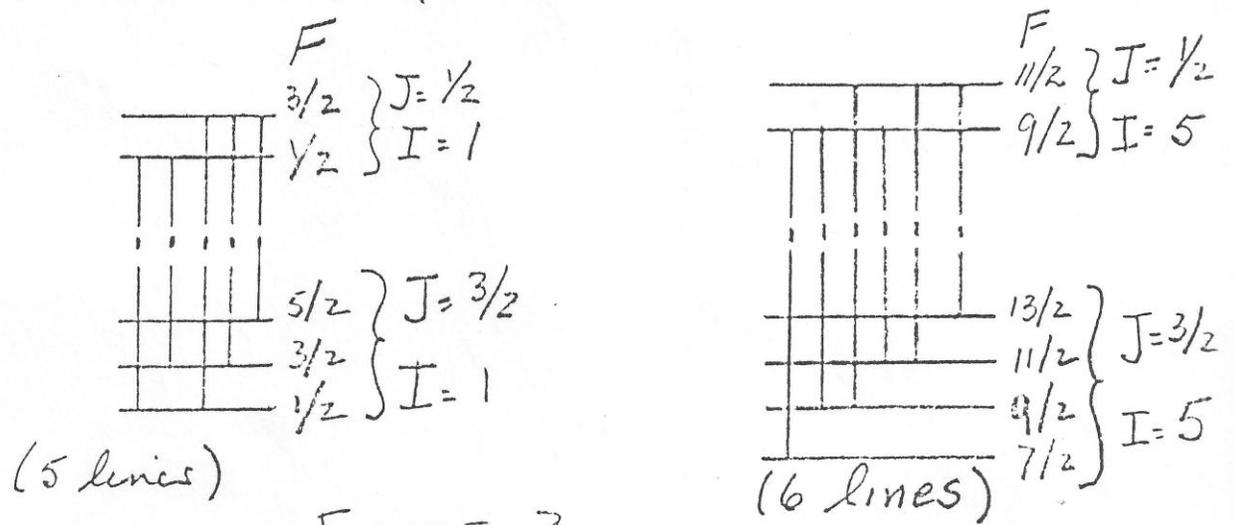


FIGURE 2

POSSIBLE ORIGIN OF LINES FOR $^{80}_{35}\text{Br}$ IN THE GROUND STATE - LEFT, AND ISOMERIC STATE - RIGHT. NOTE $\Delta F = \pm 1, 0$

(for example either further photoexcitation, photodissociation, or photoionization in the case of molecular species or secondary photoexcitation or photoionization in the case of atoms) initiated by a second high-intensity laser. Photoionized atoms or molecules could be separated mass spectrometrically, as could also products of photodissociation. Electronically excited states are known to undergo quite different chemical reactions; a particularly simple example involving excited atoms is the reaction of iodine atoms with alkanes, in which a hydrogen atom is extracted by $^2P_{1/2}$ iodine but not by the ground-state $^2P_{3/2}$ species⁴.

As a first step in this research it is proposed to study the photochemical enrichment of a nuclear isomer without particular regard to the Graser problem itself. One series of experiments is difficult to specify. The halides, however, look most promising.

A convenient isomer, from the nuclear standpoint, would be bromine where a long-lived (4.4 hour) isomer exists ($^{80}_{35}\text{Br}$). The bromine atoms could be electronically excited by a tuned high intensity bromine laser corresponding to the transition between the ground state and the first excited state ($^2P_{1/2}$ (upper) \rightarrow $^2P_{3/2}$ (lower)). The atoms produced in the excited $^2P_{1/2}$ state by the absorption of the laser line will preferentially react with certain organic gases to produce products.

A high-intensity iodine laser involving the transition between these same electronic states has been developed⁵; a necessary part of this proposed research is the development of the comparable bromine laser or satisfactory substitute. Similarly, preferential reactions of excited ($^2P_{1/2}$) iodine atoms with various alkanes have also been studied⁴, and the same types of reactions involving excited bromine atoms will also be investigated in this work.

The nuclear spin of the atom is 1 for the $^{80}_{35}\text{Br}$ isotope which may also be in the long lived isomeric state with a high spin (5-). The electronic levels of the atom would correspond to the same values modified only by the mass difference and nuclear spin coupling. See Figure 2.

The spacing of the lines will not be uniform but a typical separation of 0.3\AA may be expected. The overlap of all six lines of the isomeric state with the 5 lines of the nuclear ground state should be minimal. The isomer may be selectively excited to the reactive $^2\text{P}_{1/2}$ state by a laser. Collection of the product, such as HBr, should show a high X-ray intensity proportional to the enrichment of the isomer.

Such a result would ~~cl~~minate the first phase objective of the program.

The molecular aspects of the program may be considered. Extensive discussion of nuclear aspects are discussed by Herzberg⁶ and by Dunn in a general review⁷. The nuclear spin coupling produces significant differences in the electronic spectra and changes in the nuclear spin due to the presence of the isomer may result in many cases where a reactive excited molecule can be formed. A secondary objective will be evaluation of possible molecular systems for study.

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