

Principles of Photochemical Separation of Isomeric Nuclides

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About this version. The current author (D.F.Hakala) drafted the original manuscript in 1976 with the other authors. George C.Baldwin was in the Nuclear Engineering Department, and it was his interest in gamma ray lasers (GRASERs) that inspired me to suggest the paper. I was taking a course in Nonlinear Optics and Application from George at the time. He had discussed the possibility, and some concepts of, gamma ray lasers. In part of my thesis, I had done some work showing that I had obtained an isotope separation in ^{18}O using two step photodissociation in Nitrogen Dioxide. Herbert Clark was an undergraduate instructor for me in Physical Chemistry and Nuclear Chemistry and Physics. Robert R Reeves was my Ph.D. thesis advisor. My thesis work had been essentially completed after my second year in graduate school, and I was polishing it up in my third year and doing other projects of interest. Before the paper was completed, I graduated and left to start my first job with RCA. George finished off the paper and presented it in 1978. I had always wanted to finish the paper myself, but I had other priorities. Recently, going through some of my old school notebooks I had saved I came across the draft I had written and decided to finish it now. After covering the basics behind the reasons for spectral differences in a nuclear isomer from its ground state. I then have sections on both bromine-80m and mercury 197m. Bromine is now Section 4.1 and Section 4.2 now covers mercury-197m. Spectra are reproduced from literature values and line broadening by a) natural radiative lifetime, b) doppler shift broadening, and c) the Lorentzian broadening due to collisions(pressure). The spectra and estimated linewidth under various experimental conditions are examined to determine likelihoods of a photochemical separation. Although it was a possible physical option, I did not consider photoionization. In both cases some consideration is given as to how subsequent chemical reaction of the excited species could be used to provide a physical separation of the isomeric nuclides. The original 1976–78 argument is kept; Section 7 separates what has been learned since. Estimated quantities are labeled as such.

Abstract

Photochemical separation of the isomeric states of a single nuclide is one possible route to the nuclear population inversion needed for a gamma-ray laser (graser). As in laser isotope separation, the method depends on spectral differences between the species that exceed both the resolution of tunable lasers and the Doppler width of the absorbing gas. We compare the three sources of such differences between nuclear isomers: the mass difference (10^{-7} – 10^{-5} cm^{-1} , too small to use), the field or isomer shift (typically 10^{-3} – 10^{-1} cm^{-1}), and the hyperfine structure produced by the large spin difference that makes an isomer long-lived (10^{-2} – 10^{-1} cm^{-1} , the dominant effect). For $^{80\text{m}}\text{Br}$ ($I = 5$, 4.42 h), a calculation from measured nuclear moments shows that its six hyperfine components on the $2.714\text{ }\mu\text{m } ^2\text{P}_{3/2} \rightarrow ^2\text{P}_{1/2}$ line are spread over about 6 GHz, with the best-isolated components several Doppler widths (153 MHz at 300 K) from any line of ^{80}Br , ^{79}Br or ^{81}Br . Excited $\text{Br}(^2\text{P}_{1/2})$ atoms can abstract a tertiary hydrogen atom, a reaction that is about 38 kJ/mol endothermic for ground-state bromine, which provides the chemical selectivity. For $^{197\text{m}}\text{Hg}$ ($I = 13/2$, 23.8 h), measured hyperfine constants place the $F' = 11/2$ component of the 253.7 nm line 9.6 GHz (9 Doppler widths at 300 K) from the nearest ^{197}Hg line and 12.5 GHz from any stable isotope, confirming the original estimate; the Lorentzian wings of the other lines then limit single-step selectivity to about 10^3 – 10^4 per atom at practical pressures. Excited $\text{Hg}(^3\text{P}_1)$ is scavenged by HCl as calomel, while ground-state mercury cannot react.

Enrichment is measured from the characteristic radiation of the two states of each nuclide, with corrections for in-growth of the ground state from the isomer.

1. Introduction

A major problem in developing a gamma-ray laser is the rapid separation of an isomeric nuclear state, which would give a population inversion and the possibility of stimulated gamma emission [1, 2]. Aside from its intrinsic scientific interest, photochemical separation of the isomeric states of a single nuclide offers one way to achieve this. The objective here is the isolation or enrichment of a nuclear isomer by selective photoexcitation: atoms or simple molecules containing nuclei in both the ground and the isomeric state are transferred rapidly from a solid target to the gas phase and then separated by photochemical reactions.

Chemical separation of genetically related isomers is not new. In 1939 Segrè, Halford and Seaborg separated the 18-minute and 4.4-hour isomers of ^{80}Br using the chemical activation that follows the highly converted isomeric transition [3]. That method collects the daughter of the isomer; it cannot enrich the isomer itself. Letokhov has proposed laser photochemical separation by two-step photodissociation or photoionization [4], a procedure already used successfully for isotopes [5]. Applied to isomers, it depends on spectral differences between the two nuclear states that arise from (a) their mass difference, (b) their difference in nuclear charge radius, and (c) their difference in nuclear spin. Section 2 estimates each.

2. Spectral differences between nuclear isomers

2.1 Mass effect

Isomers differing in excitation energy E also differ in mass. For $E = 0.1 \text{ MeV}$:

$$E = \Delta m c^2 \Rightarrow \Delta m = \frac{0.1 \text{ MeV}}{c^2} = 1.8 \times 10^{-31} \text{ kg} = 1.1 \times 10^{-4} \text{ u} \quad (1)$$

Vibrational spectra. The mass difference changes the fundamental vibrational wavenumber of a bond to the isomeric atom:

$$\tilde{\nu}_0 = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}, \quad \mu = \frac{m_H m_X}{m_H + m_X} \quad (2)$$

For a diatomic molecule HX with X of mass 100 u and an isomer X' lying 0.1 MeV higher, with a mass-independent force constant k ,

$$\frac{\tilde{\nu}_0}{\tilde{\nu}_0'} = \sqrt{\frac{\mu'}{\mu}} \approx 1 + \frac{1}{2} \frac{m_H}{m_H + m_X} \frac{\Delta m}{m_X} = 1 + 5 \times 10^{-9} \quad (3)$$

For $\tilde{\nu}_0 = 3000 \text{ cm}^{-1}$ this gives $\Delta\tilde{\nu}_0 \approx 1.6 \times 10^{-5} \text{ cm}^{-1}$ for the fundamental. Overtones show more, but are weak because of the $\Delta v = \pm 1$ selection rule. Lasers with bandwidths near 10^{-7} cm^{-1} exist, but the Doppler width of an infrared vibrational band near room temperature is about $4 \times 10^{-3} \text{ cm}^{-1}$, more than two hundred times larger than the shift (Section 2.4).

Electronic spectra of molecules. For excitation to a higher electronic level the (0,0) band shift depends on the change in force constant. If $\tilde{\nu}_0^* = \frac{1}{2}\tilde{\nu}_0$ in the upper state, the zero-point energies give

$$\Delta\tilde{\nu}_A \approx \frac{1}{2} |\Delta\tilde{\nu}_0^* - \Delta\tilde{\nu}_0| = \frac{1}{4} |\tilde{\nu}_0 - \tilde{\nu}_0'| \quad (\tilde{\nu}_0^* = 1/2 \tilde{\nu}_0) \quad (4)$$

about $4 \times 10^{-6} \text{ cm}^{-1}$ for the HX example; transitions to higher vibrational levels of the upper state show more.

Atomic spectra. For free atoms the mass effect enters through the reduced-mass Rydberg constant:

$$\tilde{\nu}_A \propto R_M = \frac{R_\infty}{1+m_e/M} \Rightarrow \frac{\Delta \tilde{\nu}_A}{\tilde{\nu}_A} \approx \frac{m_e}{M} \frac{\Delta m}{M} \quad (5)$$

For mass 100 u at $4 \times 10^4 \text{ cm}^{-1}$ this is about $2 \times 10^{-7} \text{ cm}^{-1}$ (7 MHz) and is negligible beside the effects that follow.

2.2 Field (isomer) shift

The nuclear charge radius generally differs between an isomer and its ground state. The resulting shift of every component of a line, the isomer shift, is the atomic analogue of the Mössbauer isomer shift and is written in the same form as an isotope shift:

$$\delta \nu^{g,m} = K \frac{m_m - m_g}{m_g m_m} + F \delta \langle r^2 \rangle^{g,m} \quad (6)$$

where K is the (normal plus specific) mass-shift constant of the transition, F its field-shift constant and $\delta \langle r^2 \rangle$ the change in mean-square charge radius. For heavy elements F is large for transitions that change the number of s electrons at the nucleus, such as the 253.7 nm $6s^2 \text{ } ^1\text{S}_0 \rightarrow 6s6p \text{ } ^3\text{P}_1$ line of Hg, and isomer shifts there are typically 10^{-3} – 10^{-1} cm^{-1} (tens of MHz to several GHz). For a transition within one configuration, such as the bromine $4p^5 \text{ } ^2\text{P}_{3/2} \rightarrow ^2\text{P}_{1/2}$ line used below, the s-electron density hardly changes and the field shift is small; there the hyperfine structure alone provides the selectivity.

2.3 Nuclear spin effects: hyperfine structure

The nuclear spin I couples to the electronic angular momentum J, splitting each level into components of total angular momentum F with energies

$$E_F = \frac{A}{2} C + B \frac{3/4 C(C+1) - I(I+1)J(J+1)}{2I(2I-1)J(2J-1)}, \quad C = F(F+1) - I(I+1) - J(J+1) \quad (7)$$

where A is the magnetic-dipole constant and B the electric-quadrupole constant of the level ($B = 0$ when I or $J \leq \frac{1}{2}$). The allowed components of a line obey $\Delta F = 0, \pm 1$. Herzberg discusses the hyperfine structure of Bi and Pr [6], where components are spread over 0.01–0.1 nm in the visible (about 0.5 – 6 cm^{-1} ; Figure 1). Bismuth is an extreme case ($Z = 83, I = 9/2$); splittings of 10^{-2} – 10^{-1} cm^{-1} are more usual.

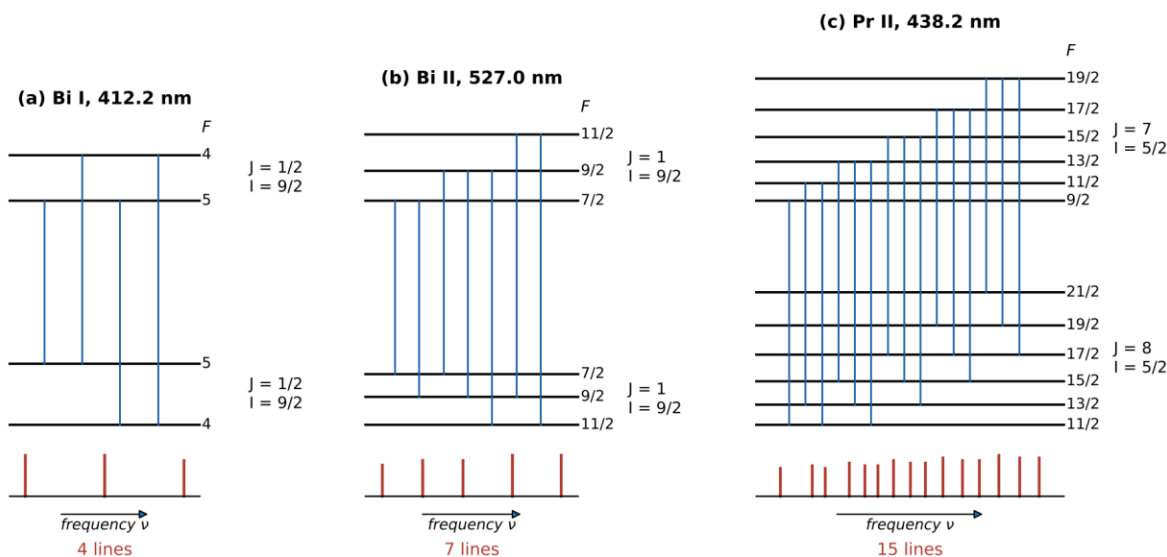


Figure 1. Hyperfine structure of (a) Bi I 412.2 nm, (b) Bi II 527.0 nm and (c) Pr II 438.2 nm, redrawn schematically after Herzberg [6] (4, 7 and 15 components). Level spacings use the interval rule with illustrative constants.

A long-lived isomer usually differs from its ground state by several units of spin, since that is what hinders the gamma transition. Its hyperfine pattern therefore differs in both the number and the positions of its components, and the differences are of the order of the splittings themselves, far larger than the mass effect.

2.4 The Doppler-width criterion

Selective excitation needs the component separation to exceed the Doppler width of the absorbing gas, not only the laser linewidth:

$$\Delta\nu_D = \nu_0 \sqrt{\frac{8k_B T \ln 2}{m c^2}} \quad (8)$$

Effect or case	Size	Doppler FWHM at 300 K	Usable?
Mass effect, HX vibration (3000 cm^{-1})	$1.6 \times 10^{-5} \text{ cm}^{-1}$	$\approx 4 \times 10^{-3} \text{ cm}^{-1}$ (HX, $M \approx 101$)	No
Mass effect, atom ($4 \times 10^4 \text{ cm}^{-1}$)	$2 \times 10^{-7} \text{ cm}^{-1}$	$\approx 5 \times 10^{-2} \text{ cm}^{-1}$ ($M = 100$)	No
$^{197\text{m}}\text{Hg}$ vs ^{197}Hg , 253.7 nm (Section 4.2)	$0.0021 \text{ nm} = 0.32 \text{ cm}^{-1}$ (9.6 GHz)	0.035 cm^{-1} (1.04 GHz)	Yes, by $\sim 9\times$
$^{80\text{m}}\text{Br}$ vs other Br, 2.714 μm (Section 4.1)	$0.015\text{--}0.05 \text{ cm}^{-1}$ (0.45–1.4 GHz) nearest-neighbor gaps	0.0051 cm^{-1} (153 MHz)	Yes, by 3–9 $\times$ (estimate)

Only hyperfine (and, for Hg, isomer-shift) differences clear the Doppler width. Cooling the gas, or using a collimated atomic beam crossed at right angles by the laser, would reduce the width further.

3. From selective absorption to separation

Selective absorption produces an excited species containing the isomeric nucleus. Separation then requires either that this species react chemically in its excited state, or that a second, high-intensity laser drive a further step: photoexcitation, photodissociation or photoionization of molecules, or secondary excitation or photoionization of atoms. Photoions and photodissociation products can be separated mass-

spectrometrically. Excited species often react quite differently from ground-state species; for example $I(^2P_{1/2})$ abstracts hydrogen from alkanes while ground-state $I(^2P_{3/2})$ does not [7].

Selectivity survives only if the excited isomeric atom reacts before it loses its excitation or passes it on. The fraction that reacts is

$$f_R = \frac{k_R[RH]}{k_R[RH] + k_Q[M] + k_T[Br] + A_{rad}} \quad (9)$$

where k_R is the rate constant for reaction with the scavenger RH, k_Q for quenching by other gas M, k_T for resonant transfer of excitation to other bromine atoms (overwhelmingly the stable isotopes), and A_{rad} the radiative decay rate. Because ^{80m}Br is a trace species, transfer to ^{79}Br and ^{81}Br scrambles the selectivity, so the bromine partial pressure must be kept low and the scavenger in large excess. At 10 Pa of scavenger the gas-kinetic collision interval is about 2 μs , while the radiative lifetime of $\text{Br}(^2P_{1/2})$ is of the order of a second, so radiative loss is negligible and the design question is the ratio of k_R to k_Q and k_T .

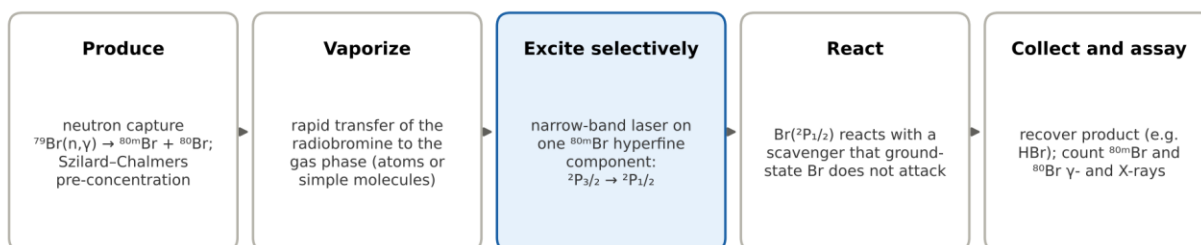


Figure 2. The proposed separation sequence for ^{80m}Br .

4. Candidate systems

4.1 Bromine-80m

Bromine has been studied for photochemical isotope enrichment [11] and has an isomer that lives long compared with chemical processing times. The nuclear properties needed are in Table 1.

Nuclide / state	I^π	Half-life	Magnetic moment μ (μN)	Quadrupole moment Q (b)	Decay
^{79}Br (stable, 50.7 %)	$3/2^-$	stable	+2.106	+0.313	—
^{81}Br (stable, 49.3 %)	$3/2^-$	stable	+2.271	+0.262	—
^{80}Br ground state	1^+	17.7 min	+0.5140	+0.185	β^- 92 %, EC/ β^+ 8 %
^{80m}Br isomer (85.8 keV)	5^-	4.42 h	+1.3177	+0.71	isomeric transition

The moments of both ^{80}Br states were measured by atomic-beam magnetic resonance in the 1960s [12], so their hyperfine structure in the atomic ground state is known in principle. Bromine atoms can be excited on the magnetic-dipole transition between the fine-structure levels of the $4p^5$ ground configuration, $^2P_{3/2} \rightarrow ^2P_{1/2}$ at 3685 cm^{-1} ($2.714\text{ }\mu\text{m}$); atoms in $^2P_{1/2}$ carry 44.1 kJ/mol of extra energy.

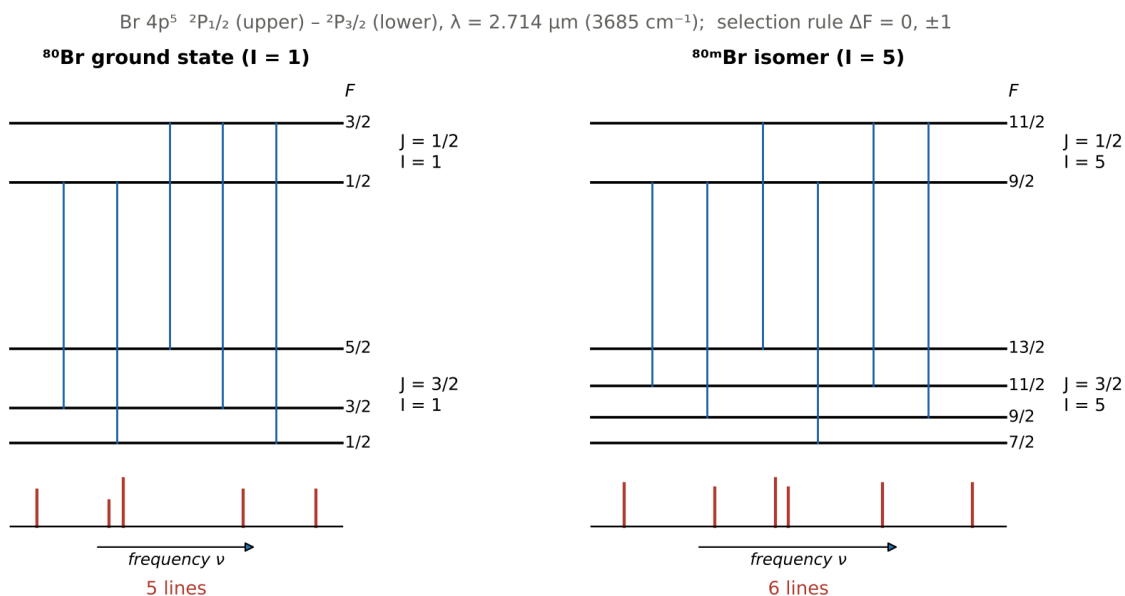


Figure 3. Hyperfine level structure of the $^2P_{1/2} - ^2P_{3/2}$ line for ^{80}Br ($I = 1$; 5 components) and $^{80\text{m}}\text{Br}$ ($I = 5$; 6 components), $\Delta F = 0, \pm 1$ (schematic).

Calculated spectrum. The hyperfine constants of each nuclide follow from those of ^{79}Br by scaling with the nuclear g-factor and quadrupole moment (hyperfine anomalies neglected):

$$A_x = A_{79} \frac{\mu_x/I_x}{\mu_{79}/I_{79}}, \quad B_x = B_{79} \frac{Q_x}{Q_{79}} \quad (10)$$

with $A_{79}(^2P_{3/2}) = 884.8 \ \text{MHz}$ and $B_{79}(^2P_{3/2}) = 384.9 \ \text{MHz}$ [13]. The $^2P_{1/2}$ constant is not available to us and is estimated as $6 \times A(^2P_{3/2})$, between the single-p-hole value of 5 and the measured ratios for chlorine (≈ 5.2) and iodine (≈ 7.7). Relative component strengths for the magnetic-dipole transition are

$$S(F \rightarrow F') \propto (2F + 1)(2F' + 1) \left\{ \begin{matrix} J & F & I \\ F' & J' & 1 \end{matrix} \right\}^2 \quad (11)$$

Nuclide	$A(^2P_{3/2}) \ \text{MHz}$	$B(^2P_{3/2}) \ \text{MHz}$	$A(^2P_{1/2}) \ \text{MHz (est.)}$	Components	Span
^{79}Br	884.8	384.9	≈ 5300	6	$\approx 11 \ \text{GHz}$
^{81}Br	953.8	322.2	≈ 5700	6	$\approx 12 \ \text{GHz}$
^{80}Br	323.9	227.5	≈ 1900	5	$\approx 3 \ \text{GHz}$
$^{80\text{m}}\text{Br}$	166.1	873.1	≈ 1000	6	$\approx 6 \ \text{GHz}$

Table 2. Hyperfine constants used in the calculation (br80_hfs.py).

Calculated hyperfine components at 2.714 μm with 300 K Doppler profiles (FWHM 153 MHz); $A(^2P_{1/2})$ estimated

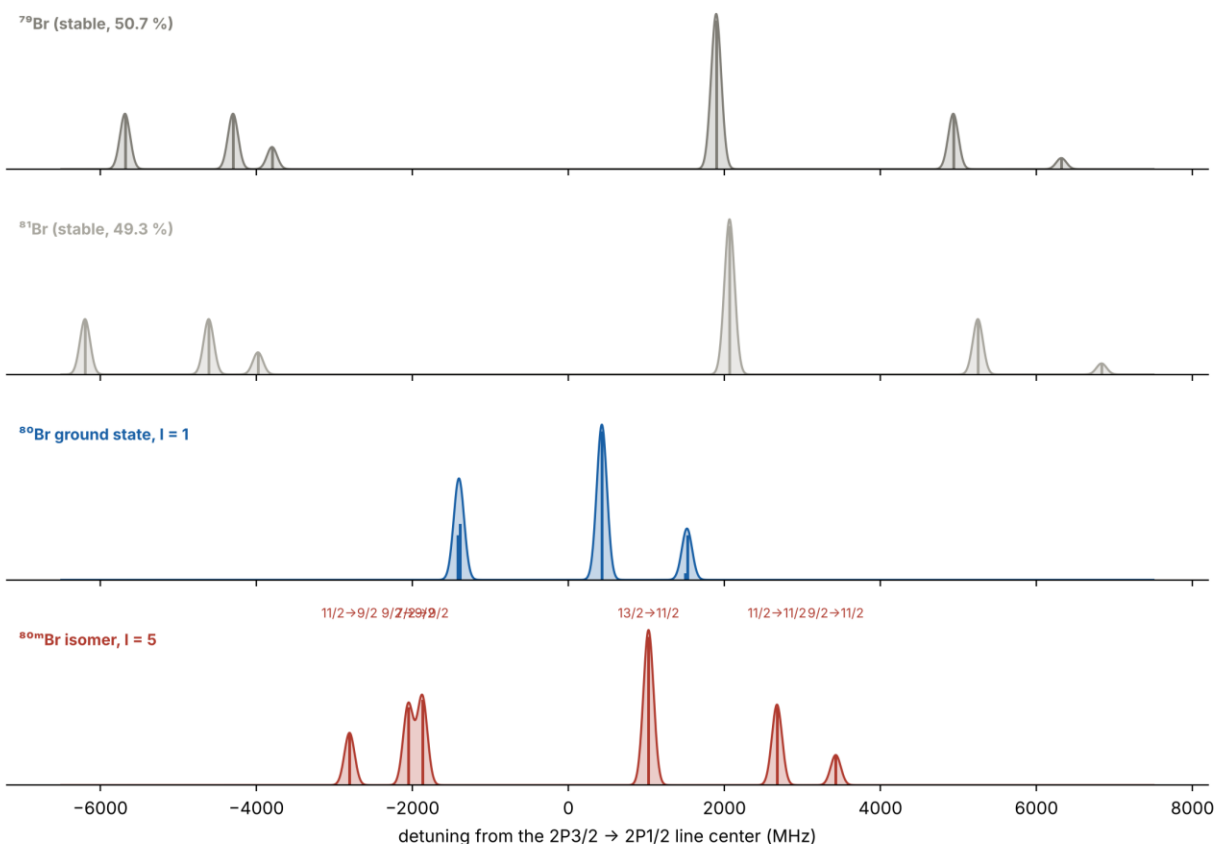


Figure 4. Calculated hyperfine components of the 2.714 μm line for ^{79}Br , ^{81}Br , ^{80}Br and $^{80\text{m}}\text{Br}$ with 300 K Doppler profiles (FWHM 153 MHz), $A(^2P_{1/2})/A(^2P_{3/2}) = 6$. Labels mark $^{80\text{m}}\text{Br}$ components more than two Doppler widths from any other component.

$^{80\text{m}}\text{Br}$ component $F \rightarrow F'$	Detuning (MHz)	Relative strength	Clearance to nearest other Br line, in Doppler widths, for $A(^2P_{1/2})/A(^2P_{3/2}) = 5 / 6 / 7.7$
$11/2 \rightarrow 9/2$	-2806	0.11	2.5 / 6.5 / 11.0
$9/2 \rightarrow 9/2$	-2053	0.17	3.0 / 4.1 / 6.1
$7/2 \rightarrow 9/2$	-1873	0.18	1.8 / 3.0 / 4.9
$13/2 \rightarrow 11/2$	+1027	0.32	2.3 / 3.1 / 0.3
$11/2 \rightarrow 11/2$	+2674	0.17	5.9 / 4.0 / 0.6
$9/2 \rightarrow 11/2$	+3427	0.06	8.2 / 8.9 / 5.6

Table 3. $^{80\text{m}}\text{Br}$ components (detunings for ratio 6) and their isolation from the ^{80}Br , ^{79}Br and ^{81}Br lines.

The result supports the original estimate of a typical 0.03 nm (1.2 GHz) separation. Every $^{80\text{m}}\text{Br}$ component except one is at least 1.8 Doppler widths clear for the central estimate, and the $9/2 \rightarrow 11/2$ component stays more than five widths clear across the whole range of the unknown ratio. Which component is best depends on $A(^2P_{1/2})$, which should be measured on stable bromine before an experiment. Because the stable isotopes outnumber $^{80\text{m}}\text{Br}$ by many orders of magnitude, the Lorentzian wings of their lines (pressure and laser spectral purity), not the Gaussian Doppler profile, set the ultimate discrimination; low pressure and a spectrally clean laser are essential.

Excitation source. The $^2P_{3/2} \rightarrow ^2P_{1/2}$ transition is magnetic-dipole and very weak, so a high-intensity source or a multipass cell is needed. An iodine laser on the analogous iodine transition existed in 1964 [14]; atomic bromine lasers at 3685 cm^{-1} followed in 1979 [15] and later [16], and a tunable single-frequency source at $2.714\text{ }\mu\text{m}$ (for example a difference-frequency or optical parametric source) would now be the natural choice.

Chemistry. Two routes are possible. In the molecular route, selective excitation of Br_2 gives bromine atoms that are scavenged by HI, as in the bromine isotope separation of Leone and Moore [11]; HI reacts with both electronic states of Br, so the selectivity must come from the Br_2 excitation step. In the atomic route the scavenger must react with $\text{Br}(^2P_{1/2})$ but not $\text{Br}(^2P_{3/2})$. Table 4 shows why a tertiary C–H bond is the natural choice.

Reaction $\text{Br} + \text{RH} \rightarrow \text{HBr} + \text{R}$	$D(\text{R-H}), \text{ kJ/mol}$	$\Delta H \text{ for } \text{Br}(^2P_{3/2})$	$\Delta H \text{ for } \text{Br}(^2P_{1/2})$
HI (scavenger, molecular route)	298.3	–68	–112
Toluene, benzylic C–H	375.5	+9	–35
Isobutane, tertiary C–H	403.8	+38	–6
Propane, secondary C–H	412.5	+46	+2
Ethane	420.5	+54	+10
HCl	431.6	+65	+21
H_2	436.0	+70	+26
Methane	439.3	+73	+29

Table 4. Reaction enthalpies at 298 K from standard bond dissociation energies, with $D(\text{H-Br}) = 366.2\text{ kJ/mol}$ and an excitation energy of 44.1 kJ/mol for $\text{Br}(^2P_{1/2})$.

Abstraction of a tertiary hydrogen atom (isobutane) is about 38 kJ/mol endothermic for ground-state bromine, a Boltzmann factor of roughly 10^{-7} at 300 K, but slightly exothermic for $\text{Br}(^2P_{1/2})$. A benzylic hydrogen gives faster reaction but only a +9 kJ/mol barrier against ground-state bromine, a much poorer discrimination. Measured values of k_{R} for $\text{Br}(^2P_{1/2}) + \text{isobutane}$ against its physical quenching rate are the key unknowns for equation (9); the corresponding reactions of $\text{I}(^2P_{1/2})$ [7] provide the model.

Target preparation. $^{80\text{m}}\text{Br}$ and ^{80}Br are made together by neutron capture on ^{79}Br . Recoil separation from an organic bromide, as in the 1939 experiment, where ethyl bromide was irradiated and the radiobromine recovered as sodium bromide [3], concentrates the radioactive bromine relative to the stable target before the optical step.

4.2 Mercury-197m

Mercury undergoes isotopically selective photochemistry at 253.7 nm [8]. Isotopes have been separated by exciting mercury atoms with a lamp containing a single isotope; the excited atoms react with oxygen to give enriched HgO [8]. The even-mass stable isotopes used (for example ^{198}Hg and ^{202}Hg) have zero nuclear spin and a single component each. $^{197\text{m}}\text{Hg}$ (half-life about 24 h) shows three hyperfine components in this line and ^{197}Hg (64 h) a doublet; both have been measured [9, 10, 24]. The original estimate was that one component of the $^{197\text{m}}\text{Hg}$ triplet lies about 0.002 nm from the nearest ^{197}Hg component and about 0.0026 nm from the nearest component of any stable isotope [9]. This section tests that estimate against the measured hyperfine constants and follows it through to a working separation, as was done for bromine in Section 4.1.

Nuclear and spectroscopic data. The 253.7 nm line is the $6s^2\ ^1S_0 \rightarrow 6s6p\ ^3P_1$ intercombination line. Because the lower level has $J = 0$, it has no hyperfine splitting; all the structure comes from the $^3P_1$ level, which splits into $F' = I - 1, I$ and $I + 1$. Each odd isotope therefore gives three components when $I \geq 1$ and two when $I = \frac{1}{2}$, and each even isotope gives one. Table 5 collects the data used.

Species	I^π	Half-life or abundance	$A(^3P_1)$, MHz	$B(^3P_1)$, MHz	Line center from ^{198}Hg , GHz	Components
^{197m}Hg (298.9 keV)	$13/2^+$	23.8 h; IT 91.4 %, EC 8.6 %	-2328.8	-901	$+2.24 \pm 0.13$	3
^{197}Hg	$1/2^-$	64.14 h; EC to ^{197}Au	+15 387.1	—	+2.09 (estimated)	2
^{196}Hg	0^+	0.15 %	—	—	+4.180	1
^{198}Hg	0^+	9.97 %	—	—	0	1
^{199}Hg	$1/2^-$	16.87 %	+14 757	—	-0.651	2
^{200}Hg	0^+	23.10 %	—	—	-4.805	1
^{201}Hg	$3/2^-$	13.18 %	-5453	-280	-6.410	3
^{202}Hg	0^+	29.86 %	—	—	-10.102	1
^{204}Hg	0^+	6.87 %	—	—	-15.312	1

Table 5. Data for the 253.7 nm line. ^{197m}Hg constants and isotope shift and $A(^{197}\text{Hg})$: Hirsch [24]. Stable isotopes: Schweitzer [23] (converted from mK, 1 mK = 29.979 MHz), with ^{196}Hg from [25]. Decay data: [29]. The ^{197}Hg line center was not found in the sources available here; it is estimated as the ^{197m}Hg value less an isomer shift of 0.15 GHz, similar to that measured for ^{195m}Hg – ^{195}Hg .

As a check, scaling the ^{199}Hg constant by the ratio of nuclear g-factors predicts $A(^{197}\text{Hg}) = 15\,384$ MHz, and scaling the ^{199m}Hg ($I = 13/2$) constant predicts $A(^{197m}\text{Hg}) \approx -2328$ MHz; both agree with Hirsch's measurements to better than 0.5 %. The quadrupole term scaled from ^{201}Hg ($B = -280$ MHz, $Q = 0.387$ b) gives $B \approx -905$ MHz for ^{197m}Hg with $Q = 1.25$ b, again close to the measured -901 MHz.

Hyperfine structure of the 253.7 nm line ($6s^2\ ^1S_0 \rightarrow 6s6p\ ^3P_1$); constants from Hirsch (1961)

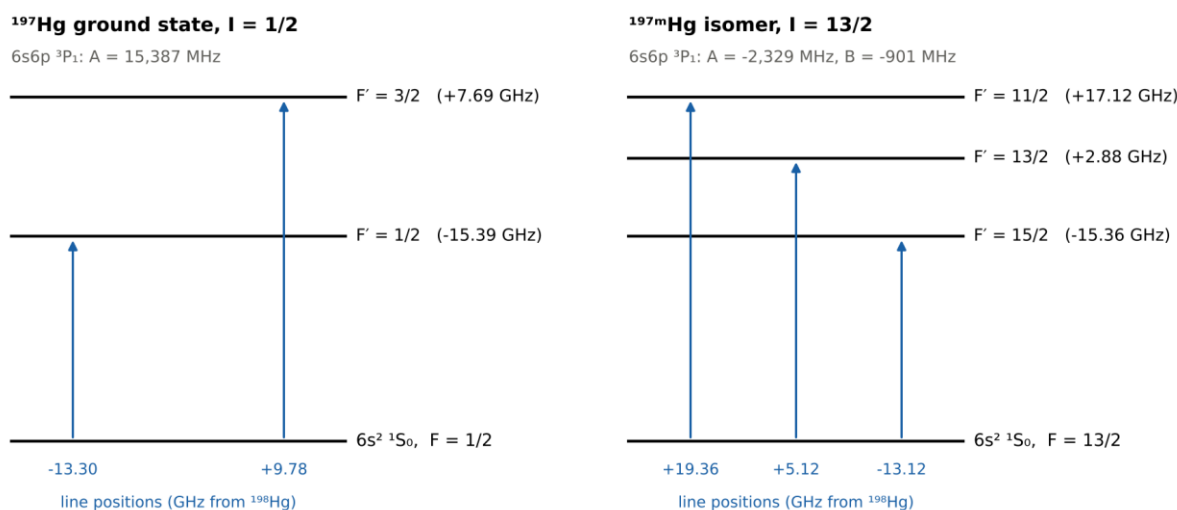


Figure 5. Hyperfine structure of the 253.7 nm line for ^{197}Hg ($I = 1/2$) and ^{197m}Hg ($I = 13/2$). Level labels give the $^3P_1$ hyperfine energies relative to their center of gravity; the numbers under the arrows are the line positions relative to ^{198}Hg .

Calculated spectrum. Combining the line centers with equation (7) gives the components of every species (Figure 6). Relative strengths follow from equation (11); for a $J = 0 \rightarrow J' = 1$ line they reduce to $s(F') = (2F' + 1)/[3(2I + 1)]$. The Doppler width at 300 K is 1.04 GHz.

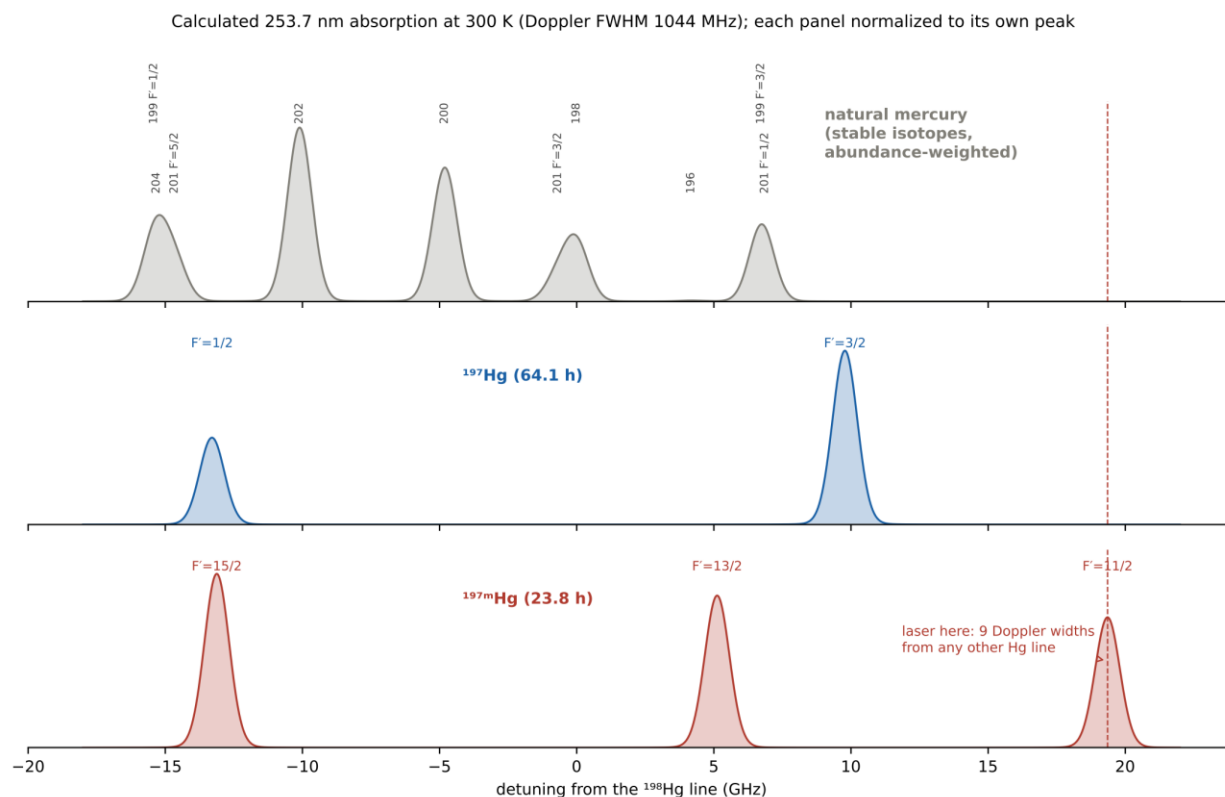


Figure 6. Calculated 253.7 nm absorption of natural mercury, ^{197}Hg and $^{197\text{m}}\text{Hg}$ at 300 K (hg197_hfs.py). The dashed line marks the $^{197\text{m}}\text{Hg}$ $F' = 11/2$ component, which lies above every other mercury line.

$^{197\text{m}}\text{Hg}$ component F'	Position from ^{198}Hg	Relative strength	Nearest other line	Clearance (Doppler widths at 300 K)
11/2	+19.36 GHz	0.286	^{197}Hg $F' = 3/2$: 9.58 GHz (0.0021 nm); nearest stable, ^{201}Hg $F' = 1/2$: 12.49 GHz (0.0027 nm)	9.2 (8.7–9.6)
13/2	+5.12 GHz	0.333	^{196}Hg : 0.94 GHz; $^{197\text{m}}\text{Hg}$ $F' = 3/2$: 1.6 GHz	0.9
15/2	−13.12 GHz	0.381	^{197}Hg $F' = 1/2$: about 0.2 GHz (depends on the estimated ^{197}Hg shift)	≈ 0.2

Table 6. $^{197\text{m}}\text{Hg}$ components and their isolation. The range in the last column covers a ^{197}Hg line center anywhere from 1.6 to 2.6 GHz.

The calculation confirms the 1976 estimate closely: the $F' = 11/2$ component is 0.0021 nm from the nearest ^{197}Hg component and 0.0027 nm from the nearest stable-isotope component, against 0.002 nm and 0.0026 nm in the original paper. It is the only usable component. The $F' = 13/2$ line sits on the wing of ^{196}Hg , and $F' = 15/2$ almost coincides with the lower ^{197}Hg component. Because $F' = 11/2$ lies above every other mercury line, the clearance hardly depends on the estimated ^{197}Hg isotope shift: 8.7–9.6 Doppler widths over a ± 0.5 GHz range. That matches the best bromine component (Table 3) and, unlike bromine, does not hang on an unmeasured hyperfine constant.

Selectivity limited by line wings. Nine Doppler widths of separation would make the Gaussian overlap negligible (below 10^{-90}). What limits selectivity is the Lorentzian wing of the other lines, from the natural

width (1.34 MHz FWHM for $A = 8.4 \times 10^6 \text{ s}^{-1}$ [31]) and from pressure broadening. The single-step selectivity against species x , per atom, with the laser at ν_L is

$$S_x = \frac{\sum_{F_I} S_{F_I}^{(m)} V(\nu_L - \nu_{F_I}^{(m)})}{\sum_{F_I} S_{F_I}^{(x)} V(\nu_L - \nu_{F_I}^{(x)})}, \quad S_{F_I} = \frac{2F_I + 1}{3(2I + 1)} \quad (12)$$

where V is the Voigt profile of each component. Figure 7 and Table 7 give the results.

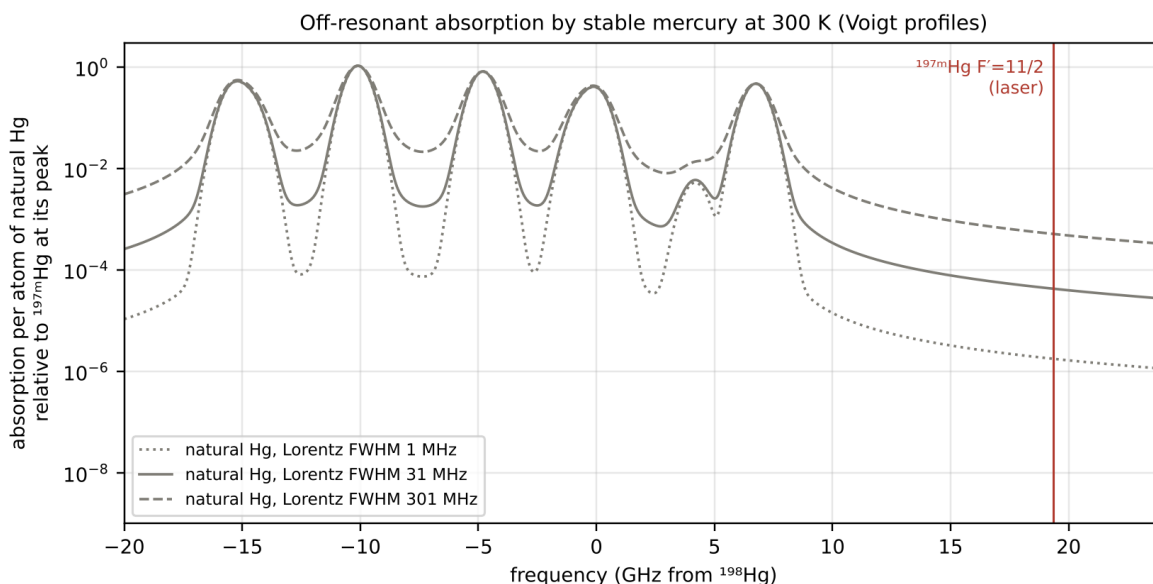


Figure 7. Off-resonant absorption by natural mercury, per atom, relative to the peak absorption of $^{197\text{m}}\text{Hg}$ on its $F' = 11/2$ component, for three Lorentzian widths (natural only, plus 30 MHz, plus 300 MHz of pressure broadening).

Lorentzian FWHM (natural + pressure)	S against ^{197}Hg	S against natural Hg	Corresponds roughly to
1.3 MHz (natural width only)	1.6×10^5	5.7×10^5	collision-free gas or atomic beam
31 MHz	6.6×10^3	2.3×10^4	a few kPa of scavenger
301 MHz	5.5×10^2	2.0×10^3	tens of kPa

Table 7. Single-step selectivity S from equation (12), laser on $^{197\text{m}}\text{Hg}$ $F' = 11/2$, 300 K (hg197_hfs.py). The pressure-broadening column is an estimate; the HCl broadening coefficient of the 253.7 nm line should be measured.

Selectivities of 10^3 – 10^4 per atom mean that the mercury carrier must be kept out of the sample. With ordinary neutron-irradiated mercury, $^{197\text{m}}\text{Hg}$ is a tiny fraction of the stable isotopes, and the wings of their lines would excite more stable atoms than isomeric ones. The preparation route below avoids this.

Absorption strength. The Doppler-limited peak cross section of the 253.7 nm line is $(\lambda^2/8\pi)(g'/g) A \cdot 0.939/\Delta\nu_D \approx 5.8 \times 10^{-17} \text{ m}^2$, or $1.7 \times 10^{-17} \text{ m}^2$ on the $F' = 11/2$ component. A 1 GBq sample of $^{197\text{m}}\text{Hg}$ contains 1.2×10^{14} atoms (about 40 ng); vaporized in 1 L it absorbs 2 m^{-1} on this component, so a multipass cell a few meters in total path absorbs most of the laser. Nanogram quantities vaporize completely at room temperature (the vapor pressure of mercury is about 0.25 Pa), so no heated cell is needed.

Excitation source. The 1976 proposal used a nitrogen-laser-pumped dye laser at 508 nm, frequency-doubled to 254 nm in potassium pentaborate and narrowed with an intracavity etalon to about 0.0008 nm (3.7 GHz). That bandwidth is less than half the 9.6 GHz clearance and would have resolved the $F' = 11/2$ component,

though its wings would add to those of Table 7. Single-frequency continuous 253.7 nm sources, made by frequency-quadrupling ytterbium lasers near 1015 nm, are now standard in mercury laser cooling [30] and would reach the natural-width limit.

Chemistry. Ground-state mercury cannot abstract hydrogen from HCl: with $D(\text{H}-\text{Cl}) = 431.6 \text{ kJ/mol}$ and $D(\text{Hg}-\text{Cl})$ of about 100 kJ/mol , the reaction is endothermic by about 330 kJ/mol . Excitation to $^3\text{P}_1$ adds 471.4 kJ/mol (4.89 eV), which makes it exothermic by about 140 kJ/mol :



Unlike bromine, then, mercury has no thermally accessible ground-state channel, and all the selectivity is optical. This chemistry has been proven at scale. Webster and Zare enriched ^{196}Hg by factors of 2.3–4.2 at 2–5 Torr (270–670 Pa) HCl with butadiene added to scavenge hydrogen atoms [26], and the GTE process raised ^{196}Hg from its natural 0.15 % to 3.4–5.2 % in the calomel at 2 Torr HCl, an enrichment factor of about 23–36 [27]. Both used filtered mercury lamps; the lamp linewidth, not the chemistry, limited their selectivity. The original proposal's oxygen route ($\text{Hg}(^3\text{P}_1) + \text{O}_2$, giving HgO) remains an alternative.

Kinetics. Equation (9) applies with mercury in place of bromine, but the time scale is very different. The $^3\text{P}_1$ radiative lifetime is only 119 ns, against about a second for $\text{Br}(^2\text{P}_{1/2})$, so the scavenger must react within about 100 ns. For a reactive cross section of order $10 \text{ \AA}^2$ (an order-of-magnitude assumption), $k_R \approx 4.5 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$ at 300 K, and half the excited atoms react at about 0.8 kPa (6 Torr) of HCl, 90 % at about 7 kPa. Collisions that do not react still broaden the line, which is why Table 7 is given for 30 and 300 MHz. Two complications of the lamp processes disappear here. Radiation trapping, in which re-emitted 253.7 nm photons excite other atoms, needs a dense absorber, and a no-carrier-added sample has none. Resonant excitation transfer $\text{Hg} + \text{Hg} \rightarrow \text{Hg} + \text{Hg}$ needs mercury collision partners, which are equally scarce. The balance to optimize is therefore reaction against fluorescence (favoring high HCl pressure) against wing excitation of ^{197}Hg (favoring low pressure).

Target preparation. Proton bombardment of gold, $^{197}\text{Au}(p,n)$, produces both mercury-197 states with no stable-mercury carrier. At 12 MeV the measured cross sections are about 35 mb for ^{197m}Hg and 62 mb for ^{197}Hg , an isomeric ratio of about 0.6 at the end of bombardment [28] (values read from that paper's tables; to be confirmed). Mercury is released from the gold by heating and swept into the photolysis cell. Neutron capture on ^{196}Hg is the alternative; it brings stable carrier with it, and the recoil (Szilard–Chalmers) concentration suggested in the original draft would then be needed.

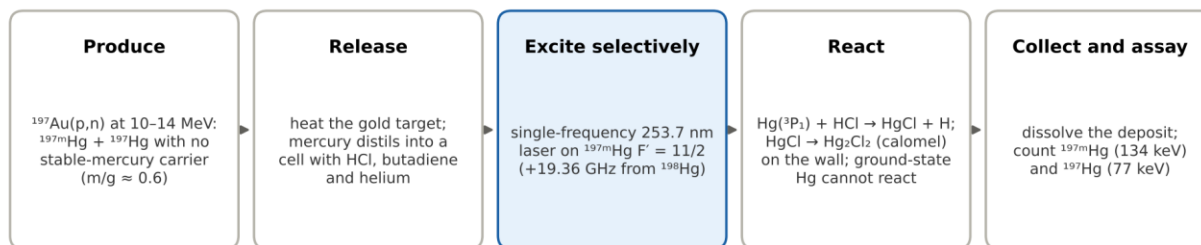


Figure 8. The proposed separation sequence for ^{197m}Hg .

Expected result. Starting from an isomeric ratio of 0.6 and a selectivity against ^{197}Hg of 10^3 – 10^4 (Table 7), one pass would give calomel in which ^{197m}Hg outnumbers ^{197}Hg by several hundred to several thousand to one. That is a population inversion of the isomer over its ground state in the separated product. It persists for

more than a day (Section 5). $^{197\text{m}}\text{Hg}$ is not itself a graser candidate, because its 299 keV energy is far too high for recoilless emission, but it would demonstrate the separation step of the graser scheme.

5. Measurement of enrichment

The enrichment factor of the product relative to the feed, for the isomer m against any other species x , is

$$\beta = \frac{(N_m/N_x)_{\text{product}}}{(N_m/N_x)_{\text{feed}}} \quad (13)$$

For bromine, $^{80\text{m}}\text{Br}$ is measured from its isomeric-transition radiation (37 and 49 keV gamma rays, strongly converted, with bromine K X-rays near 12 keV) and ^{80}Br from its β^- decay and 616 keV gamma ray. Two corrections are needed. First, the isomer decays into the ground state after separation:

$$A_g(t) = A_g(0) e^{-\lambda_g t} + A_m(0) \frac{\lambda_g}{\lambda_g - \lambda_m} (e^{-\lambda_m t} - e^{-\lambda_g t}) \quad (14)$$

so, a sample of pure $^{80\text{m}}\text{Br}$ shows ^{80}Br activity growing to a transient equilibrium of $A_g/A_m = \lambda_g/(\lambda_g - \lambda_m) = 1.071$ within about two hours (Figure 9). Second, as Segrè, Halford and Seaborg showed [3], each isomeric decay ruptures the chemical bond, so the daughter ^{80}Br leaves the product molecule; samples should be counted promptly, or in a closed geometry, so that daughter activity is neither lost nor counted twice.

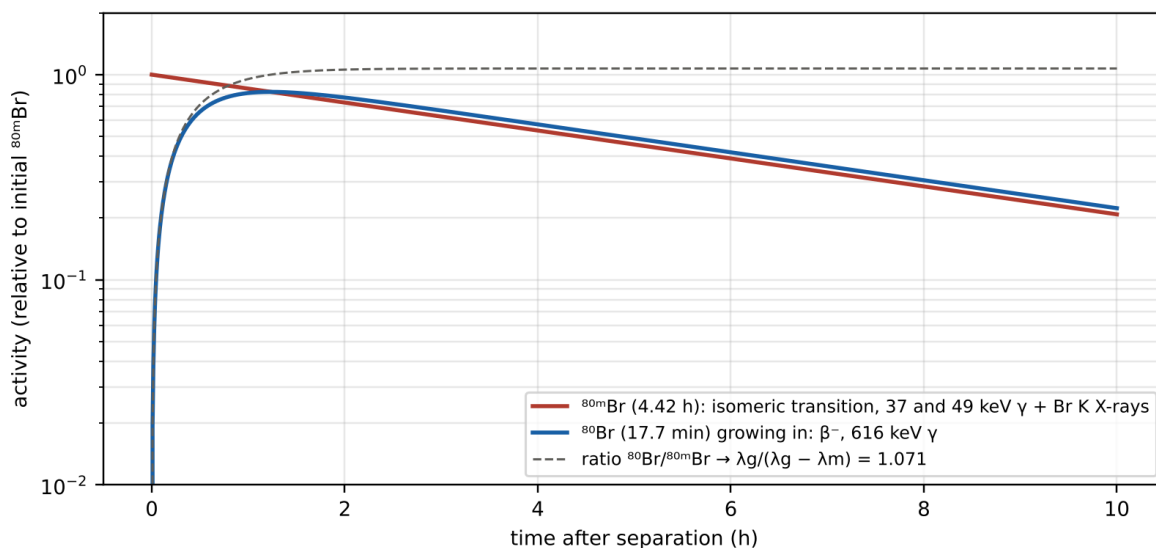


Figure 9. $^{80\text{m}}\text{Br}$ decay and ^{80}Br in-growth after a separation that leaves pure $^{80\text{m}}\text{Br}$.

For mercury, $^{197\text{m}}\text{Hg}$ is measured from its 133.98 keV gamma ray (33.5 % per decay, from the isomeric transition; also 279.0 keV, 6.1 %, from its electron-capture branch) and ^{197}Hg from its 77.35 keV gamma ray (18.7 %) or its weak 191.4 keV line (0.63 %) [29]. The 77.35 keV line lies among the gold K X-rays ($K\beta$ near 78 keV) that follow electron capture in both states, so a planar germanium detector with peak fitting, or the 191 keV line, is needed. The decay correction is simpler than for bromine because the daughter lives longer than the isomer. Starting from pure $^{197\text{m}}\text{Hg}$, the ratio of ground-state to isomeric atoms grows as

$$\frac{N_g(t)}{N_m(t)} = \frac{b \lambda_m}{\lambda_m - \lambda_g} (e^{(\lambda_m - \lambda_g)t} - 1), \quad b = 0.914 \quad (15)$$

where b is the isomeric-transition branch. The ratio grows by about 2.7 % per hour at first and reaches 1 after 28.6 h (Figure 10), so a separated sample stays inverted for more than a day. As with bromine, the highly converted 165 keV isomeric transition is followed by an Auger cascade that can break the Hg–Cl bond, so samples should be counted promptly or in a closed geometry.

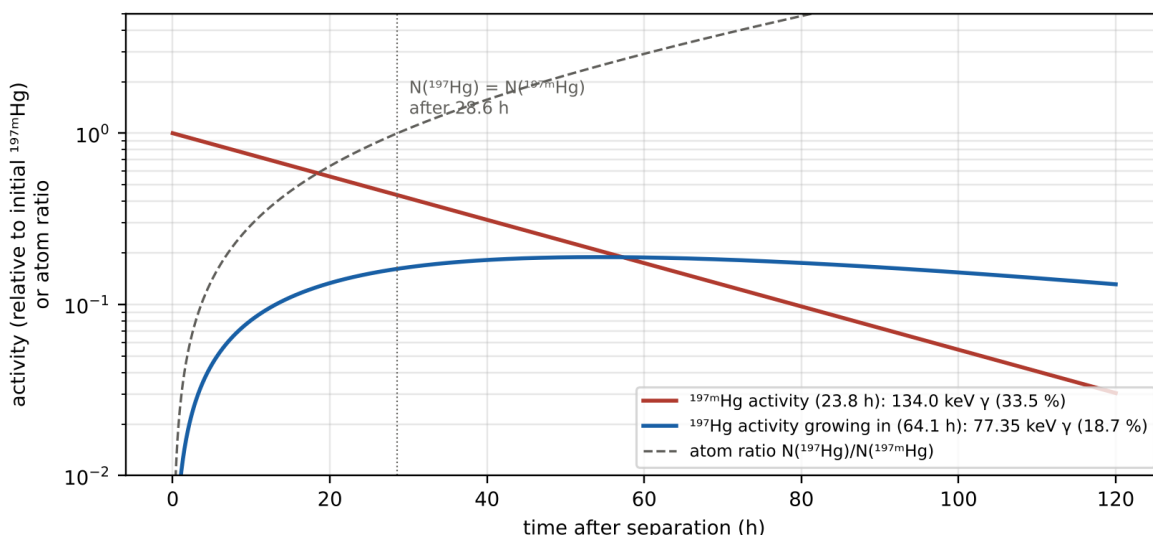


Figure 10. ^{197m}Hg decay, ^{197}Hg in-growth and the $^{197}\text{Hg}/^{197m}\text{Hg}$ atom ratio after a separation that leaves pure ^{197m}Hg .

6. Experimental considerations

1. **Spectroscopy first.** Measure $A(^2\text{P}_{1/2})$ of stable bromine (or the full hyperfine spectrum of the 2.714 μm line) to fix the $^{80\text{m}}\text{Br}$ component to use; Table 3 shows the choice depends on it.
2. **Kinetics second.** Measure the reaction and quenching rate constants of $\text{Br}(^2\text{P}_{1/2})$ with the chosen scavenger, and the rate of excitation transfer $\text{Br}(^2\text{P}_{1/2}) + \text{Br}$, to set pressures through equation (9).
3. **Enrichment demonstration.** With $^{80\text{m}}\text{Br}$ from a Szilard–Chalmers-concentrated source, excite one isolated component and measure β from equation (13), with the decay corrections of Section 5.
4. **Mercury.** With no-carrier-added $^{197\text{m}},^{197}\text{Hg}$ from a proton-irradiated gold target, excite the $F' = 11/2$ component at +19.36 GHz in a multipass HCl cell and measure β against ^{197}Hg . The first quantities to measure are the HCl pressure broadening of the 253.7 nm line and the ^{197}Hg isotope shift, which fix the attainable selectivity (Table 7).
5. **Molecular systems.** Nuclear-spin coupling also changes molecular electronic spectra [17, 18]; a later stage would evaluate molecules such as Br_2 or HBr containing the isomer.

7. Later developments (added 2026)

- **Laser separation of isomers is now routine for radioactive beams.** At CERN-ISOLDE the resonance ionization laser ion source (RILIS) selects one element among many reaction products [19], and with a narrow first excitation step it selects individual isomers by their hyperfine patterns. Isomeric beams of ^{68}Cu and ^{70}Cu were separated in this way [20], and in ^{70}Cu three β -decaying isomers (6^- , 3^- and 1^+) were identified by tuning the laser to each hyperfine pattern in turn, confirmed by Penning-trap mass measurements [21]. This is the principle of Section 2.3, applied to ionization rather than photochemistry.

- **Bromine lasers.** Atomic bromine lasers at 3685 cm^{-1} were demonstrated by 1979 [15] and developed further in the 1980s [16].
- **Mercury isotope photochemistry has become an industrial process.** ^{196}Hg for fluorescent lamps was enriched photochemically by exciting natural mercury in HCl with filtered 253.7 nm lamps [26, 27], the same chemistry proposed here for $^{197\text{m}}\text{Hg}$, and laser cooling and trapping of mercury now uses single-frequency 253.7 nm lasers [30].
- **Gamma-ray lasers.** The prospects and obstacles for a graser were reviewed by Baldwin and Solem in 1997 [22]; isomer separation remains one of the required steps, alongside the problem of line broadening in the solid host.

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Revision notes

- Confirmed from the downloaded originals: Segrè, Halford and Seaborg, Phys. Rev. 55, 321 (1939) [3]; Van Roosbroeck et al. (2004) [21]; Oinonen et al. (2000) [19].
- Estimated, to be replaced by measurement: $A(^2\text{P}_{1/2})$ of bromine (ratio 6 used, 5–7.7 tested); the field-shift range of Section 2.2.
- From standard tables, not re-checked against primary sources here: ^{79}Br hyperfine constants [13], bond dissociation energies (Table 4), the ^{80}Br gamma-ray energies.
- Figures 3–4, 9 and Tables 2–3 are generated by br80_hfs.py and psin_figs.py; Figures 5–7 and Tables 6–7 by hg197_hfs.py; Figures 8 and 10 by psin_figs.py. All are filed with this document.
- Mercury data checked against published values: Schweitzer (1963) [23] for the stable isotopes and Hirsch (1961) [24] for $^{197\text{m}}\text{Hg}$ and $A(^{197}\text{Hg})$. Estimated, to be replaced by measurement: the ^{197}Hg isotope shift (2.09 GHz used, 1.6–2.6 GHz tested), the HCl reaction cross section and pressure broadening. The Au(p,n) cross sections [28] were read from that paper's tables and should be confirmed.