

Isotope separation by optically pumped ionizing collisions*

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We propose a modification of the selective two-step photoionization technique which greatly improves its efficiency. A third species with a strong resonance transition is added to the mix of isotopes which it is desired to separate. Incident optical energy is radiatively and collisionally trapped in this catalytic species. Selective ionization of excited step one species is accomplished by long-range ionizing collisions.

The two-step technique for selective photoionization and dissociation demonstrated by Ambartsumian and Letokhov is capable of great isotopic selectivity and has very general applicability.¹ In the two-step technique, a first photon is tuned to an energy to put a selected atomic or molecular isotope into an excited state, with other species remaining in their ground state. A second photon of energy sufficient to photoionize or dissociate only the selected species is incident on the sample. A principal difficulty with the two-photon technique is the small absorption coefficient seen by the second photon.^{1,2} This results from the small cross section for photoionization or dissociation, and also from the need to work at quite low pressure to avoid isotopic exchange and charge transfer collisions. To ensure photoionization of excited step one species, the transition probability for ionization must be comparable to that for spontaneous decay. Large optical power densities and long optical path lengths (often 10^5 cm) are required; and the number of photons required may be many orders of magnitude larger than the number of isotopic atoms produced.

In this letter we propose³ a modification of the two-step technique which greatly abates these problems. A third species (or optical catalyst) is added to the mix of isotopes which it is desired to separate. This species must have a strong resonance transition to ground at a frequency which causes photoionization of excited, but not of ground-state, isotopic species (i.e., at the frequency of the second photon of the two-step technique). Incident optical energy is radiatively and collisionally trapped in this catalytic species. Selective ionization of excited step one species is accomplished by long-range (large-cross-section) ionizing collisions.

An energy level diagram for the proposed technique is shown in Fig. 1. In the presence of species C (the catalytic species), the transition probability to the continuum of step one excited A atoms (the isotopic species) is equal to the number of ionizing collisions/sec; thus $W_a(t) = N_c^* \sigma_c \bar{V}$, where N_c^* is the density of excited C atoms, σ_c is the cross section for ionizing collision, and \bar{V} is the average velocity. We first calculate σ_c .

We use the semiclassical or impact method of calculating inelastic collision cross sections.^{4,5} In this approximation, the atoms are treated as classical particles following straight-line paths. We work in a basis of product states, with a dipolar interaction matrix element $\mu_A \mu_C / 4\pi \epsilon_0 R^3(t)$, where μ_C is the matrix element of the resonance transition of the C species, μ_A

is the matrix element to the continuum of a (first step) excited A atom, and $R(t)$ is the relative distance between an A and C atom. We take $R(t) = (r_0^2 + \bar{V}^2 t^2)^{1/2}$, where \bar{V} is the average velocity and r_0 is the distance of closest approach in a particular collision. Since the ionizing, or in effect, the dephasing time in the continuum is very short compared to the impact time, the Golden Rule is used to find the probability $|a(r_0)|^2$ of ionization for a particular collision of closest approach r_0 . For an interaction Hamiltonian $|\mu_A \mu_C| / 4\pi \epsilon_0 R^3(t)$, mks units), integrating over $-\infty < t < +\infty$, we find

$$|a(r_0)|^2 = \left(\frac{3}{64} \frac{1}{\epsilon_0^2} \frac{1}{\hbar^2} \right) \frac{|\mu_A|^2 |\mu_C|^2}{r_0^5 \bar{V}} \rho_A(\omega) \\ = \left(\frac{3}{64} \frac{1}{\epsilon_0^2} \frac{1}{\hbar} \frac{1}{\pi} \right) \frac{|\mu_C|^2}{\omega r_0^5 \bar{V}} \sigma_A, \quad (1)$$

where $\rho_A(\omega)$ is the continuum density of states of atom A, $\eta = (\mu/\epsilon_0)^{1/2}$, and ω is the frequency of the second photon. The second equality of Eq. (1) expresses $|a(r_0)|^2$ in terms of the cross section for electromagnetic photoionization σ_A of a (step one excited) A atom. We define ρ_0 as the distance of closest approach r_0 below which $|a(r_0)|^2 > 1$. The cross section for ionizing collision σ_c is then

$$\sigma_c = 2\pi \left[\int_0^{\rho_0} r_0 dr_0 + \int_{\rho_0}^{\infty} |a(r_0)|^2 r_0 dr_0 \right]. \quad (2)$$

Substituting from Eq. (1) and integrating, the first and second terms of Eq. (2) contribute to the cross section in the ratio $1: \frac{2}{3}$. We obtain

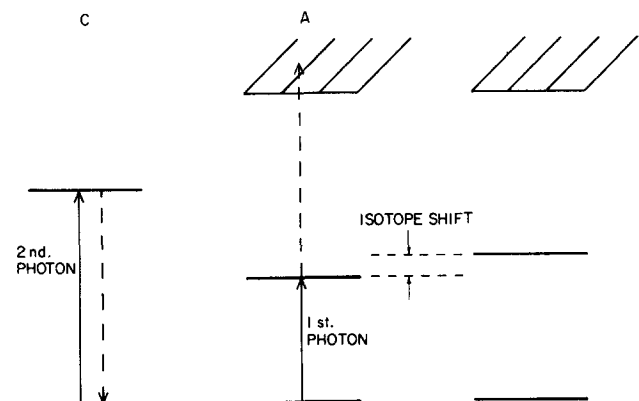


FIG. 1. Schematic of selective photoionizing process. Isotope separation is accomplished by selective excitation of species A, followed by ionization by collision with species C. The dotted lines show energy transfer during collision.

$$\sigma_c = \frac{5}{3} \pi \rho_0^2,$$

where

$$\rho_0 = \left[\left(\frac{3}{64} \frac{1}{\epsilon_0^2} \frac{1}{\eta} \frac{1}{\hbar} \frac{1}{\pi} \frac{1}{\omega \bar{V}} \right) |\mu_C|^2 \sigma_A \right]^{1/5}. \quad (3)$$

For the Na resonance transition at 5892 Å, $\mu_C = 2 \times 10^{-29}$ C m. Assuming a cross section for electromagnetic photoionization for species *A* of $\sigma_A = 10^{-17}$ cm² and $\bar{V} = 10^5$ cm/sec, we find $\rho_0 = 9$ Å, and $\sigma_c = 4.3 \times 10^{-14}$ cm². Since ρ_0 is quite large, and since the second term of Eq. (2) contributes about as much as the first term to σ_c , the inner limits of the validity of the interaction potential need not be closely examined. Note that $\sigma_c/\sigma_A = 4.3 \times 10^3$. It is not surprising that the cross section for ionization by a species with a strong dipole transition should greatly exceed that for photoionization. In a classical collision of two particles of different size, the cross section for collision is dominated by the larger particle. Equation (3) may also be interpreted in terms of an effective near electric field of atom *C*, acting for an impact time on atom *A*.

We next calculate the density of excited *C* atoms, N_c^* , which is produced by an incident optical power density P/A . We assume that the catalytic species *C* is self-broadened, and that the incident radiation is detuned from line center to allow relatively uniform excitation of the mixture of species. Assuming that nearly all of the incident photons are absorbed by species *C*, the steady-state density of excited *C* atoms is $N_c^* = \tau_R P / \hbar \omega A L$, where P is the incident power, A and L are the area and length of the assumed cylindrical sample, and τ_R is the trapped radiative lifetime of species *C*.

Assuming a species *C* concentration of about 1 Torr, then on line center, the cell will typically be at least 10^5 absorption depths thick. Under these conditions, the principal loss mechanism limiting τ_R is spectral diffusion to the wings of the pressure-broadened line, where the absorption depth is much longer. The problem has been analyzed by Holstein⁶ who shows that for an infinitely long cylinder, the spontaneous (nontrapped) radiative lifetime τ_s is increased by a factor $1/g$, where

$$g = 1.115(\pi k_p R)^{-1/2}, \quad (4)$$

$$k_p = \frac{\lambda_0^2 N_C g_2 \gamma_n}{2\pi g_1 \gamma_p},$$

R is the cylinder radius, k_p is the absorption coefficient on line center, N_C is the ground-state concentration, g_2 and g_1 are the upper and lower level degeneracies, and γ_p and γ_n are the pressure-broadened and natural linewidths of species *C*. If the density of species *C* is increased until pressure broadening exceeds Doppler broadening, then the absorption depth k_p is relatively independent of pressure. For the sodium resonance transition at a temperature of about 2000 °C,

this requires a density of about 7.5×10^{16} atoms/cm³ and for densities above this, $k_p \approx 2 \times 10^6$ cm⁻¹. For a cylinder of 1-cm radius, the radiative lifetime is extended by a factor of 2.3×10^3 , yielding a trapped lifetime of 37 μsec.

The transition probability for an ionizing collision of an excited *A* isotope by an excited *C* atom is then given by

$$W_A(t) = N_c^* \sigma_c \bar{V} = (\sigma_c \bar{V} \tau_{sp} / \hbar \omega L g) P/A, \quad (5)$$

where σ_c and g are given by Eqs. (1)–(4). Again taking Na as the catalytic species, $\sigma_A = 10^{-17}$ cm², and assuming a cell length of 10 cm, we find $W_A(t) = 4.7 \times 10^4 P/A$ (watts/cm²). For efficient isotope separation, species *A* must be ionized before it spontaneously decays to ground. For a species *A* spontaneous lifetime of 100 nsec, this requires $W_A(t) \approx 10^7$. We thus require an incident power density of 214 W/cm². By comparison, if species *C* were not present, to attain the same transition probability for species *A* would require an incident power density of 3.4×10^5 W/cm² [$W_A(t) = (\sigma_A / \hbar \omega)(P/A)$]. The increase in efficiency caused by species *C* is $\sigma_C \tau_{sp} \bar{V} / \sigma_A g L = 1.6 \times 10^3$.

There are two potential limitations of this technique: The first is the possibility of isotopic scrambling collisions between the catalyst *C* and ground-state *A* atoms. Unless there are accidental resonances or curve crossings, this should not be a problem. The second and more severe limitation is the possibility of depletion of all of the desired isotope within a given volume, in a time short compared to the radiative trapping time of the catalyst. Unless additional isotope atoms are flowed into the region of the catalyst, an inherent inefficiency will result.

The short absorption depths of this technique may allow the use of a transverse pumping configuration where the second photon is obtained from an incoherent light source.

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