

Nonlinear Optical Processes by Van der Waals Interaction during Collision*

S. E. Harris and D. B. Lidow†

Microwave Laboratory, Stanford University, Stanford, California 94305

(Received 24 June 1974)

We describe an optical process where off-diagonal optical excitation of a first atomic species is coupled during collision to a second species. This coupling leads to new types of nonlinear optical processes, and allows large cross sections for inelastic collision between atoms with nonresonant energy levels.

By tuning a laser to the resonance line of an atomic species, a strong time-varying dipole moment is excited at the frequency of the incident laser. Alternatively, by making use of higher resonances, strong dipole moments may be excited at harmonics of the incident frequency.¹⁻³ In this Letter we describe a new type of nonlinear process where dipolar excitation of a first atomic species is coupled during collision to a second species. This dipole-dipole coupling leads to new types of nonlinear optical processes, and may be used to produce large enhancements in both the linear and nonlinear transition probabilities and cross sections of the second species. In particular, the process allows large cross sections for inelastic collision, or optical pumping, between atoms with nonresonant energy levels.

To avoid confusion with more familiar inelastic collision processes we note that we are considering a process where, in essence, energy is conserved by optical photons, as opposed to kinetic processes. From the Lorentz model of an atom, the process may be viewed as one where the phase and frequency of an oscillating atom *A* is transferred to a second atom *B*. The strength of the coupling varies as $1/R^3$ and is only strong when the atoms are relatively close ($R \leq 20 \text{ \AA}$). During this interaction time atom *B* may also accept additional photons from the external electromagnetic field, allowing it to conserve energy to complete a transition. This process does not require real transitions of atom *A*. Off-diagonal, as opposed to on-diagonal, excitation is transferred during collision.⁴

Subject to the approximation that the interatomic spacing is greater than the atomic dimension, the perturbation Hamiltonian which describes this process is given by⁵

$$H' = -e\vec{r}_A \cdot \vec{E} \cos\omega t - e\vec{r}_B \cdot \vec{E} \cos\omega t + [e^2/R^3(t)](x_A x_B + y_A y_B - 2z_A z_B), \quad (1)$$

where $R(t)$ is the relative distance between atoms

and x_A, x_B , etc., are the coordinates of each electron with respect to its nucleus, and \vec{E} is the applied electromagnetic field. The first two terms of the Hamiltonian describe the interaction of each (isolated) atom with the electromagnetic field, while the last term describes the coupling between atoms. The calculation proceeds by expanding the wave function in a basis of product states with time-varying coefficients $c_{ij}(t)$.⁵ Perturbation equations are written as a function of the relative atomic spacing $R(t)$. We assume straight-line atomic paths and integrate over $R(t)$ with a distance of closest approach r_0 ; and finally integrate over r_0 to an inner limit at which the Van der Waals potential remains valid.⁶

To be specific, we will consider the four-photon absorption process shown in Fig. 1; i.e., we wish to calculate the four-photon transition probability of atom *B* between the levels denoted by ω_{00} and ω_{02} . Though, in general, it is necessary to sum over all paths in the atomic system, in order to simplify the formulas, we will assume that the incident frequencies are sufficiently close to each level that a single path is singled out.

In the first three steps of perturbation, atom *A*

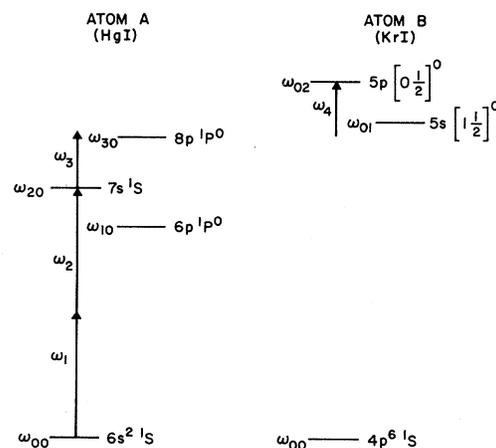


FIG. 1. Energy level diagram for calculation. For the Hg-Kr system, $\omega_1 = \omega_2 = 3129 \text{ \AA}$ and $\omega_3 = \omega_4 = 7342 \text{ \AA}$.

accepts three photons from the electromagnetic field, and develops a mixed state and dipole moment at frequency $\omega_1 + \omega_2 + \omega_3$. In the fourth step of perturbation, this time-varying dipole moment is transferred via the Van der Waals interaction to atom *B*. In the fifth step, atom *B* accepts a photon of frequency ω_4 , to complete the four-photon transition. In the basis of product states, the perturbation sequence is therefore $c_{00} \rightarrow c_{10} \rightarrow c_{20} \rightarrow c_{30} \rightarrow c_{01} \rightarrow c_{02}$. We let $R(t) = (r_0^2 + \bar{V}^2 t^2)^{1/2}$, where \bar{V} is the average velocity and r_0 is the distance of closest approach in a particular collision. Carrying out the perturbation sequence, we find

$$c_{02}(r_0) = \gamma \int_{-\infty}^{\infty} (r_0^2 + \bar{V}^2 t^2)^{-3/2} \exp(j\Delta\omega_5 t) dt, \quad (2)$$

where

$$\gamma = \frac{\mu_{01}^A \mu_{12}^A \mu_{23}^A \mu_{03}^A \mu_{01}^B \mu_{12}^B E_1 E_2 E_3 E_4}{16\hbar^5 \Delta\omega_1 \Delta\omega_2 \Delta\omega_3 \Delta\omega_4}.$$

The resonance denominators are defined as $\Delta\omega_1 = \omega_1 - \omega_{10}$, $\Delta\omega_2 = \omega_1 + \omega_2 - \omega_{20}$, $\Delta\omega_3 = \omega_1 + \omega_2 + \omega_3 - \omega_{30}$, $\Delta\omega_4 = \omega_1 + \omega_2 + \omega_3 - \omega_{01}$, $\Delta\omega_5 = \omega_1 + \omega_2 + \omega_3 + \omega_4 - \omega_{02}$, and the μ_{ij} and E_i are the matrix elements and applied electric fields as denoted by Fig. 1. In Eq. (2), we have assumed that the dephasing time T_2 of the final level ω_{02} is long as compared to the impact time r_0/\bar{V} . (The impact time is typically $\sim 10^{-12}$ sec, and thus this will almost always be the case for absorption to a discrete level.) The quantity $|c_{02}(r_0)|^2$ is the probability that a collision with closest distance of approach r_0 has resulted in a transition to the final state.

The transition probability to line center ($\Delta\omega_5 = 0$) of atom *B* is then given by

$$W_B(t) = 4\pi N_A \bar{V} \int_{r_{0m}}^{\infty} |c_{02}(r_0)|^2 r_0 dr_0, \quad (3)$$

$$W_B(t) = 8\pi(N_A/\bar{V})r_{0m}^{-2}|\gamma|^2,$$

where N_A is the concentration (cm^{-3}) of *A* atoms, \bar{V} is the average velocity, r_{0m} is the minimum distance at which the dipolar approximation is reasonably valid, and $|\gamma|^2$ has been averaged over angular orientation. By noting the Fourier transform relationship of Eq. (2), one can see that the linewidth of the four-photon transition is approximately \bar{V}/r_{0m} .

If the dephasing time T_2 is short compared to the impact time—for instance, if level ω_{02} were instead the continuum of atom *B* while the intermediate levels remain as above—then $W_B(t)$ is

shown to be given by

$$W_B(t) = \pi^3 N_A r_{0m}^{-3} |\gamma|^2 \rho(\omega), \quad (4)$$

where $\rho(\omega)$ is the density of final states. By noting that near line center $\rho(\omega)$ is, in essence, the dephasing time, it is seen that the ratio of the transition probability of Eq. (4) to that of Eq. (3) is that of the dephasing time T_2 to the impact time r_0/\bar{V} .

As a specific example, we consider four-photon absorption in Kr (atom *B*), with and without the presence of Hg (atom *A*) (see Fig. 1). We choose the first two photons $\omega_1 = \omega_2 = 3129 \text{ \AA}$, such that the sum of these photons equals the nonallowed $6s-7s$ transition of Hg. We choose the second two photons $\omega_3 = \omega_4 = 7342 \text{ \AA}$ to exactly complete the four-photon $4p-5p$ transition in Kr. We assume unity oscillator strength for all transitions except the $6s-8p$ transition of Hg, for which we take $f = 0.1$. The resonance denominators needed to evaluate Eq. (2) are $\Delta\omega_1 = 22105 \text{ cm}^{-1}$, $\Delta\omega_2 = 1 \text{ cm}^{-1}$ (the assumed linewidth of the incident laser), $\Delta\omega_3 = 685 \text{ cm}^{-1}$, and $\Delta\omega_4 = 3369 \text{ cm}^{-1}$. Assuming $r_{0m} = 5 \text{ \AA}$, $\bar{V} = 5 \times 10^4 \text{ cm/sec}$, a Hg concentration of $10^{17} \text{ atoms/cm}^3$, and an incident laser power density of 10^9 W/cm^2 , we find $W(t) = 1.6 \times 10^3 \text{ transitions/sec}$. This transition probability is about 10^4 greater than that for pure Kr.

To observe this effect, it is necessary to avoid a different and often stronger nonlinear process which may alternatively excite the Kr. This latter process is three-frequency summing in Hg to yield $\omega_1 + \omega_2 + \omega_3$, followed by two-photon absorption in Kr ($\omega_4 +$ the sum frequency). This competing process can be avoided by allowing the optical beam at $\omega_3 = \omega_4$ to be incident from the opposite direction to that of the beam at $\omega_1 = \omega_2$, thereby producing a negligible coherence length for the three-frequency summing process.¹ The Van der Waals process will then be the dominant mechanism for four-photon excitation of Kr.

There is one version of the type of process described in this Letter which may have application to the development of short-wavelength lasers, and to other types of optical pumping. In this process, atoms are first collected in an upper level of atom *A*. This collection may be accomplished by an electron discharge, or other techniques. An incident laser frequency is then chosen with a photon energy which conserves energy with a level of a second species which it is desired to pump. For example, in the notation of Fig. 1, population might be collected in the Hg $7s$ level. A laser of wavelength 5886 \AA is then

applied to the system. This wavelength is chosen to exactly connect the 5s level of Kr with the 7s of Hg. Equation (3) applies, with the quantity $|\gamma|^2$ now given by $(1\mu_{23}^A || \mu_{30}^A || \mu_{01}^B || E | / 2\hbar^2 \Delta\omega_1)^2$. $\Delta\omega_1 = 4054 \text{ cm}^{-1}$ is the difference between the applied optical frequency and the Hg 7s-8p transition. At an incident power density of 10^9 W/cm^2 , an excited mercury concentration of 10^{17} atoms/cm³, and $\bar{V} = 5 \times 10^4 \text{ cm/sec}$, we find a Kr transition rate of 2.6×10^7 transitions/sec. This transition rate corresponds to an effective cross section for inelastic collision $[W(t) = N_A \sigma_{\text{eff}} \bar{V}]$ of $\sigma_{\text{eff}} = 72 \text{ \AA}^2$. This cross section varies linearly with the power density of the applied 5886- \AA field. One application of this type of pumping process may be selective rapid ionization of inner-shell electrons, thereby creating an inversion with regard to these levels.⁸

From a somewhat different point of view, we have described a process where by using one or more photons of an external electromagnetic field, large effective cross sections for inelastic collision can be attained without the usual requirement of energy resonance of the atomic species. Experiments to demonstrate these ideas will be

undertaken in our laboratory.

*Work jointly supported by the U. S. Office of Naval Research and the Advanced Research Projects Agency.

†D. B. Lidow gratefully acknowledges support from the Fannie and John K. Hertz Foundation.

¹J. F. Young, G. C. Bjorklund, A. H. Kung, R. B. Miles, and S. E. Harris, *Phys. Rev. Lett.* **27**, 1551 (1971); R. B. Miles and S. E. Harris, *IEEE J. Quantum Electron.* **9**, 470 (1973).

²R. T. Hodgson, P. P. Sorokin, and J. J. Wynne, *Phys. Rev. Lett.* **32**, 343 (1974).

³S. E. Harris and D. M. Bloom, *Appl. Phys. Lett.* **24**, 229 (1974); D. M. Bloom, James T. Yardley, J. F. Young, and S. E. Harris, *Appl. Phys. Lett.* **24**, 427 (1974).

⁴P. R. Berman, *Phys. Rev. A* **6**, 2157 (1972), and **5**, 927 (1972).

⁵L. I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1968) 3rd ed., p. 260.

⁶*Progress in Quantum Electronics*, edited by J. H. Sanders and S. Stenholm (Pergamon, New York, 1972), Vol. 2, Pt. 3.

⁷C. E. Moore, *Atomic Energy Levels*, U. S. National Bureau of Standards, National Standard Reference Data Systems—35 (U. S. GPO, Washington, D. C., 1971), Vols. 2 and 3.

⁸M. A. Duguay and P. M. Rentzepis, *Appl. Phys. Lett.* **10**, 350 (1967).

Radiative Decay of the 2^3S_1 and 2^3P_2 States of Heliumlike Vanadium ($Z = 23$) and Iron ($Z = 26$)*

Harvey Gould, Richard Marrus,† and Peter J. Mohr

Department of Physics and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

(Received 1 July 1974)

Lifetimes of the M1 decay $2^3S_1 \rightarrow 1^1S_0$ and of the decay $2^3P_2 \rightarrow 1^1S_0$ have been measured in the two-electron ions V^{+21} and Fe^{+24} . The measured lifetimes are $\tau(2^3S_1) = 16.9(7)$ nsec for V^{+21} and $\tau(2^3S_1) = 4.8(6)$ nsec for Fe^{+24} . The 2^3P_2 lifetimes are compared with a calculation that considers relativistic corrections and hyperfine-structure effects. It is found that for V^{+21} , hyperfine effects contribute appreciably to the lifetime. For Fe^{+24} we obtain $\tau(2^3P_2) = 0.11(2)$ nsec.

The study of radiative decay from the 2^3S_1 and 2^3P_2 levels of the two-electron system offers an opportunity to test the theory of forbidden decay in a system where precise, unambiguous calculations of decay rates can be made. In this paper, we describe some measurements designed to extend existing experimental information on the rates of these decays to the two-electron atoms V^{+21} and Fe^{+24} . We develop a theory for the 2^3P_2 rates which takes into account leading-order relativistic corrections and hyperfine effects. Our results on vanadium show the first evidence for the influence of the hyperfine inter-

action on the radiative decay of an energy level belonging to the two-electron system.

Experimental work on the 2^3S_1 levels of the two-electron system has established the single-photon nature of the decay in $Ar^{+16,1}$ and ordinary helium.² The theory of this decay has been examined by several authors³ and detailed calculations of the rates have been made by Drake⁴ and by Johnson and Lin⁵ using somewhat different starting points. Measurements of this decay rate have been made on Ar^{+16} , $Ti^{+20,6}$ and $Cl^{+15,7}$. The measured rates in Cl and Ar differ from theory by several times the quoted error, whereas the