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Direct observation of two-photon optical ionizing collisions in crossed lithium atomic beams

P. Polak-Dingels,* Regina Bonanno, John Keller, and John Weiner
Department of Chemistry, University of Maryland, College Park, Maryland 20742

J.-C. Gauthier
Institut d'Electronique Fondamentale, Bâtiment 220, Université de Paris-Sud, 91405 Orsay, France

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We report here the direct observation of a two-step, ionizing "optical collision" between crossed lithium beams in which very-long-range coupling, due to van der Waals' resonance force between identical particles, is followed by photoionization:

$$\mathrm{Li}^*(2p)+\mathrm{Li}(2s)+\hbar\omega\rightarrow\mathrm{Li}^*(3d)+\mathrm{Li}(2s),$$

$$\mathrm{Li}^*(3d)+\hbar\omega\rightarrow\mathrm{Li}^+ + e.$$

Cross-section magnitude and form of the intensity profile are described by a simple three-level model. These results suggest that polarization of the laser field together with collisional two-photon ionization may be used to delineate the shape of individual molecular-state potential curves at long range.

I. INTRODUCTION

Stimulated by early theoretical speculation,[1-6] experimental efforts[7-12] over the past few years have produced a growing body of evidence that intense laser fields applied to a two-body collision may influence the outcome of the event. Among the rich variety of possible collisional interactions, long-range electrostatic forces such as dipole-dipole,[6,10] or dipole-quadrupole coupling[13] have played a crucial role in establishing laser-induced energy transfer. In an early discussion of these processes Yakovlenko[14] drew the distinction between *radiative* collisions and *optical* collisions. An inelastic process which alters initial states of both colliding partners and in which the maximum cross section occurs at a laser frequency equal to the energy difference between atomic states in both partners is termed a radiative collision:

$$A(2)+B(1)+\hbar\omega\rightarrow A(1)+B(2)$$

$$\hbar\omega\simeq B(2)-A(2)\,. \quad (1)$$

By contrast an optical collision occurs when only one partner changes state and the laser frequency is close to an allowed atomic transition of that partner:

$$A(1)+B(1)+\hbar\omega\rightarrow A(2)+B(1)$$

$$\hbar\omega\simeq A(2)-A(1)\,. \quad (2)$$

Gallagher *et al.*[15-17] have shown that the essential nature of the two processes is identical and a unified picture may be drawn from the quasistatic theory of collision broadening. From an experimental viewpoint, however, process (1) creates a new feature in the absorption spectrum while process (2) simply modifies the shape of the isolated absorption profile. The more dramatic appearance of an entirely new peak explains the emphasis on radiative collisions in recent experiments.

Optical collisions possess, however, a dramatic property of their own when they take place between identical particles. Long-range dipole dispersion forces may give rise to an interaction potential which falls off as the inverse cube of the internuclear distance rather than the more familiar inverse sixth power. This special dipole-dipole "resonance" force obtains in collisions between two identical atoms when one of them is in an excited state whose symmetry permits dipole energy transfer to its partner. This electrostatic interaction must perforce be the longest-range coupling between colliding neutral particles with its physical origin discussed long ago by Van Vleck[18] and Margenau.[19] The optical collision line profile is a direct probe of the dispersion force dominant at long range.

We report here observation of resonance dipole forces between $\mathrm{Li}^*(2p)$ and $\mathrm{Li}(2s)$ atoms by means of a two-step, two-photon ionizing collision. In the first step $\mathrm{Li}^*(3d)$ is populated *via* an optical collision

$$\mathrm{Li}^*(2p)+\mathrm{Li}(2s)+\hbar\omega\rightarrow\mathrm{Li}^*(3d)+\mathrm{Li}(2s) \tag{3}$$

followed in the second step by photoionization from $\mathrm{Li}^*(3d)$:

$$\mathrm{Li}^*(3d)+\hbar\omega\rightarrow\mathrm{Li}^+ + e\ . \tag{4}$$

The optical collision line shape is reflected in the observed rate of Li^+ production as a function of laser frequency. As pointed out by Nayfeh,[20–22] in a series of pioneering articles, exploitation of two- and three-photon ionizing collisions is attractive because of inherent efficiency and sensitivity of charged-particle detection.

II. DESCRIPTION OF THE EXPERIMENT

The apparatus has been described in previous laser-collision studies,[23,24] but for convenience we summarize the essential points here.

Two atomic lithium beams cross at right angles in the horizontal plane of a cylindrical high-vacuum system. One laser beam enters through an adjacent port between the atomic beam sources. A second laser beam enters from a port opposite the first. Thus the two lasers propagate in opposite directions and are very nearly collinear. All four beams overlap in a well-defined interaction region at the center of the apparatus. A quadrupole mass spectrometer, situated above the collision plane on a vertical axis passing through the interaction region, filters the ion masses produced in the experiment. Signal pulses of mass-selected ions are detected and amplified by a channeltron electron multiplier, integrated over the time of the laser pulse by a charge-sensitive amplifier, and fed to a boxcar averager gated synchronously with the lasers. The laser sources are flash-lamp pumped tunable dye lasers operated at a 10-Hz repetition rate with a pulse duration of about 1 μsec. Laser line width is about 3 cm^{-1}. Hot-wire detectors monitor the lithium beam flux. During a typical run atomic beam density in the collision region is about 10^9 cm^{-3}. Focused laser power density is 2.6×10^7 $\mathrm{W/cm}^2$ in a spot size of about 0.015 mm^2. In the experiments reported here one unfocused laser is tuned to populate the $\mathrm{Li}^*(2p)$ level with power sufficient only to saturate the transition. The second, focused laser is tuned in the vicinity the $\mathrm{Li}^*(2p,3d)$ transition frequency. The quadrupole mass filter is set to pass Li^+ and the ion intensity, produced by photoionization of $\mathrm{Li}^*(3d)$ in the field of the strong laser, is recorded as a function frequency.

III. THEORETICAL DESCRIPTION

The development proceeds in two steps: First, we write down a simple formula for the optical collision cross section by applying standard time-dependent perturbation theory in second order. Secondly, using previously calculated photoionization cross sections for $\mathrm{Li}^*(3d)$, we determine the overall two-photon ionizing rate from coupled rate equations which are then integrated over the time of a laser pulse to find the total ion yield per pulse. The rate equation approach is justified because the two steps, optical collision followed by photoionization, occur with random relative phase in the time development of the overall system wave function. Photoionization takes place essentially in the time between optical collisions not simultaneously with them.[20]

A. Optical collision cross section for a three-level system

We begin by forming appropriate linear combinations of Li atomic-state wave functions to reflect nuclear exchange symmetry,

$$\psi_1^{(g)}=\frac{1}{\sqrt{2}}[\phi_s(1)\phi_p(2)-\phi_p(1)\phi_s(2)]\ , \tag{5}$$

$$\psi_2^{(u)}=\frac{1}{\sqrt{2}}[\phi_s(1)\phi_p(2)+\phi_p(1)\phi_s(2)]\ , \tag{6}$$

where the superscripts g,u have their customary meaning, and subscripts s,p denote the orbital angular momentum of the active electron in atoms (1) or (2). At internuclear separation R the two quasimolecular wave functions interact through the dipole-dipole coupling operator (mks units)

$$H'_{12}=-\left[\frac{e^2}{4\pi\epsilon_0}\right]\left[\frac{2z_1z_2}{R^3}\right], \tag{7}$$

where z_1,z_2 are the space-fixed coordinates of the active electron on atoms 1 and 2. In fact, the collisional perturbation should include two other terms for the x and y coordinates. Including them gives rise to four quasimolecuar states $(\Sigma_{u,g};\Pi_{u,g})$ which elaborates the discussion unnecessarily for the results reported here. Using (5) and (6) to take matrix elements of (7) we find the expression for the energy shifts of states (1) and (2),

$$\Delta E_{12}\left(\begin{smallmatrix} g \\ u \end{smallmatrix}\right)=(\pm)\frac{2(\mu_{12})^2}{4\pi\epsilon_0 R^3}\,, \tag{8}$$

where the *gerade* state is repulsive, the *ungerade* state attractive, and μ_{12} is the transition dipole matrix element between Li(2*s*) and Li(2*p*). Next we make the "fixed atom" assumption in which the initial orientation of the dipole is considered random with respect to the internuclear axis but remains unchanged during the course of the collision. Averaging over initial orientations,[25] one finds

$$\Delta E_{12}=\pm\frac{2}{\sqrt{3}}\frac{(\mu_{12})^2}{4\pi\epsilon_0 R^3}\,. \tag{9}$$

The energy splitting between states (1) and (2) in the case of lithium is depicted in Fig. 1.

The second perturbation comes from the laser field which couples one of the collision states (1) and (2) to the final state (3) of the system

$$\psi_3=\phi_s(1)\phi_d(2)\,, \tag{10}$$

where $\phi_d(2)$ is the atomic wave function of the Li*(3*d*) level. Taking, for example, an optical transition from state (2) to state (3), we write the appropriate coupling expression as

$$V'_{23}=\mu_{23}E\cos\omega t\,, \tag{11}$$

where μ_{23} is the transition dipole between Li(2*p*) and Li(3*d*), and E,ω are the optical field amplitude and frequency. The time evolution of the system wave function is

$$\psi(t)=a_1(t)\phi_1 e^{-i\int\omega_1 dt}+a_2(t)\phi_2 e^{-i\int\omega_2 dt}+a_3\phi_3 e^{-e\int\omega_3 dt}\,. \tag{12}$$

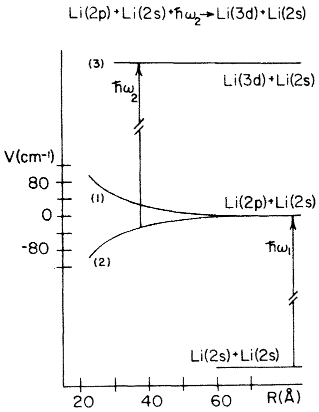

FIG. 1. Three-level-model system showing C_3/R^3 van der Waals' collisional interaction between the ground state and first excited *p* level of lithium followed by optical absorption to the manifold of states correlating to Li*(3*d*) + Li(2*s*). The energy separation between level (3) and levels (1) and (2) is not to scale on the ordinate. Splitting between levels (1) and (2) as a function of internuclear separation was calculated using Eq. (9).

Substituting (12) into Schrödinger's time-dependent wave equation (where H'_{12} and V'_{23} are perturbative terms of the Hamiltonian) and solving the resultant set of time-dependent coupled differential equations for the coefficients a_n, we write the expression for the probability of finding the system in state (3),

$$|a_3|^2=\frac{\pi C_3 E^2(\mu_{23})^2}{6\hbar^3 v R_x^2(\delta\omega)^2}\,, \tag{13}$$

where

$$|C_3|=\frac{2}{\sqrt{3}}\frac{(\mu_{12})^2}{4\pi\epsilon_0}\,,$$

and R_x is the point of stationary phase where the laser field of frequency ω is resonant with the energy difference between states (2) and (3). The term $\delta\omega$ in the denominator is the laser detuning from the Li(2*p*,3*d*) atomic transition, and v is the relative velocity of collision. In writing (13) we have assumed that the region around R_x is traversed twice and that the transition probability to state (3) remains the same for both the incoming and outgoing branches of the trajectory. Finally we calculate the optical collision cross section as

$$\sigma_c=2\pi\int_0^\infty |a_3|^2 R\,dR=\frac{\pi^2 C_3 E^2(\mu_{23})^2}{3\hbar^3 v(\delta\omega)^2}\,. \tag{14}$$

For crossed-beam lithium collisions with relative velocity corresponding to source temperature of ~1000 K,

$$\sigma_c(\mathrm{cm}^2)=1.42\times10^{-17}\frac{I}{(\delta\omega)^2}\,, \tag{15}$$

where I is laser power density in W cm^{-2} and $\delta\omega$ is the detuning in cm^{-1}. Equation (14) agrees with an earlier result of Nayfeh[21] who analyzed the problem in terms of potential curve crossings. Equation (15) is for the particular case of Li-Li collisions, where C_3 and μ_{23} are calculated from a compilation[26] of critically evaluated oscillator strengths.

B. Photoionization rate

The next step is to calculate the rate of photoionization from the Li*(3d) populated by the optical collision. The rate equations are

$$\frac{d}{dt}[\mathrm{Li}^*(3d)]=[\mathrm{Li}(2s)][\mathrm{Li}^*(2p)]\sigma_c v - A[\mathrm{Li}^*(3d)] - I[\mathrm{Li}^*(3d)]\sigma_p , \tag{16}$$

$$\frac{d}{dt}[\mathrm{Li}^+]=I[\mathrm{Li}^*(3d)]\sigma_p , \tag{17}$$

where the square-bracketed quantities are number densities, A is the spontaneous radiation rate $\mathrm{Li}^*(3d)\rightarrow\mathrm{Li}^*(2p)$, and σ_p is the photoionization cross section from the Li*(3d) excited level. From (16)

$$[\mathrm{Li}^*(3d)]=\left[\frac{[\mathrm{Li}(2s)][\mathrm{Li}^*(2p)]\sigma_c v}{(A+I\sigma_p)}\right]\{1-\exp[-(A+I\sigma_p)t]\} ,$$

which, when substituted into (17), yields

$$\frac{d}{dt}[\mathrm{Li}^*]=\left[\frac{[\mathrm{Li}(2s)][\mathrm{Li}^*(2p)]\sigma_c v I\sigma_p}{(A+I\sigma_p)}\right]\{1-\exp[1-(A+I\sigma_p)t]\} .$$

Finally, integrating over the time of a laser pulse τ and substituting (15) for σ_c we find

$$[\mathrm{Li}^+](\mathrm{pp})=\left[\frac{(2.76\times10^{-29})[\mathrm{Li}(2s)][\mathrm{Li}^*(2p)]I^2\sigma_p}{(A+I\sigma_p)(\delta\omega)^2}\right] \times\left[\tau+\frac{1}{A+I\sigma_p}\{\exp[-(A+I\sigma_p)\tau]-1\}\right] , \tag{18}$$

where pp represents per pulse and where the laser power density I is now expressed in units of photons $\mathrm{cm}^{-2}\,\mathrm{sec}^{-1}$.

Taking the spontaneous radiation rate A from Wiese *et al.*,[26] the photoionization cross section from Manson and Lahiri,[27] and the laser power density from measurement,

$$A=7.44\times10^{7}\,\mathrm{cm}^{-1} ,$$

$$\sigma_p=6.7\times10^{-18}\,\mathrm{cm}^2 ,$$

$$I=7.98\times10^{25}\ \text{photons}\ \mathrm{cm}^{-2}\,\mathrm{sec}^{-1} ,$$

we find that the last term in (18) is negligible. The "red laser" ensures that the Li(2s,2p) transition rate is saturated so that finally we may write

$$\frac{[\mathrm{Li}^+]}{[\mathrm{Li}(2s)]^2}=\frac{(8.28\times10^{-35})I^2\sigma_p}{(A+I\sigma_p)(\delta\omega)^2} , \tag{19}$$

which expresses the ion yield per pulse normalized to atomic beam intensities as a function of laser intensity and detuning from line center. The most important feature of (19) is the inverse square dependence of the detuning. This is a direct consequence of Eq. (9) and is characteristic of collisions between identical atoms. The familiar van der Waals' inverse sixth power law yields a detuning function decreasing as $(\delta\omega)^{-3/2}$. Equation (19) also shows that laser power dependence should increase quadratically for low power but gradually change to a linear form at high power.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the principal result of the experiment. The ion profile maximum is peaked at the Li*(2p,3d) transition frequency. Note that ion intensity at the peak does not increase with laser power due to saturation of the atomic transition, but that broadening in the wings, due to quasimolecular absorption, is dramatic. The effect is more than an order of magnitude above that expected from laser power broadening of the atomic line. For example, at maximum laser power ($I=2.60\times10^{7}\,\mathrm{W\,cm}^{-2}$) the Li(2$p$,3$d$) transition profile is power broadened to about 2 cm^{-1} while the optical collision intensity is still detectable at 125 cm^{-1} into the wing (see Fig. 3). As atomic beam fluxes are reduced the broading effect diminishes and finally disappears. The observed residual spectral profile centered on the atomic line reflects

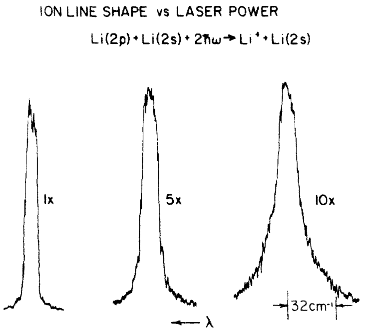

FIG. 2. Ion line shape vs laser power. Note that the peak intensity, corresponding to the Li($2p,3d$) atomic transition, is saturated at all three laser powers but that in the wings, corresponding to the quasimolecular absorption, increases dramatically. Maximum laser intensity is $\simeq 1.3\times 10^7$ W/cm^2.

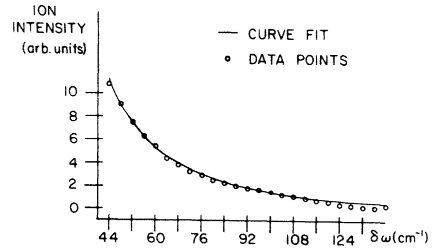

FIG. 3. Comparison of the blue-wing line shape to the function $F(\delta\omega)=a(\delta\omega)^{-3/2}+b(\delta\omega)^{-2}$. Ratio of b/a for best fit was calculated to be 8/1 showing that intensity profile decreases essentially quadratically with detuning from the Li($2p,3d$) atomic line. Laser intensity is $\simeq 2.6\times 10^7$ W/cm^2. Note that conditions of atomic beam and laser field intensity are greater in this figure than in Fig. 2.

only the linewidth of the laser and a small contribution from power broadening.

Another discernable feature in Fig. 2 is the slight asymmetry of the line shape toward the blue wing. This may be due to a C_6/R^6 dispersion interaction between the manifold of states correlating to Li$^*(3d)$ + Li$(2s)$ and those correlating to Li$^*(2p)$ + Li$^*(2p)$. The energy level of the excited pair of atoms in the $2p$ level at inifinite internuclear separation is only 0.18 eV below Li$^*(3d)$ + Li$(2s)$. As internuclear separation decreases, the two manifolds will "repel" each other, thus effectively shifting state (3) in Fig. 1 to higher energy. Transitions from states (1) and (2) will therefore be shifted to the blue. A detailed analysis of the line-shape asymmetry using the quasistatic theory of line broadening is clearly possible and desirable.

Figure 3 shows in detail a portion of the blue wing. To verify a $(\delta\omega)^{-2}$ dependence, the intensity profile was fit to a function of the form

$$F(\delta\omega)=a(\delta\omega)^{-3/2}+b(\delta\omega)^{-2}\ ,$$

and the coefficients a,b were varied to obtain best agreement by the method of least squares. The best-fit ratio of b/a is 8/1 clearly demonstrating that the wing intensity reflects a C_3/R^3 interaction rather than the more usual C_6/R^6 van der Waals law.

The magnitude of the cross section, given by Eq. (15), shows that the resonance interaction gives rise to very large optical collision cross sections. At a detuning of 100 cm^{-1} and a laser intensity of 7×10^7 W cm^{-2}, for example, the cross section is about 10^{-13} cm^2. A recent study[28] of resonance stark tuning in dipole-dipole collisions of alkali Rydberg states has also found remarkably large cross sections.

Finally one may speculate on the use of laser polarization to populate specific m_J atomic sublevels before collision takes place. Under crossed-beam conditions one may expect that nonstatistical population of m_J sublevels will lead to preferential population of Σ or Π quasimolecular states. The simplest physical situation is an adiabatic transformation of m_J to Λ in which the elements of the transformation matrix are the Clebsch-Gordan coefficients. This effect would be clearly reflected in the ion intensity profile and may be used to directly measure van der Waals constants in state-specific detail.

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*Present address: Laser Physics Branch, Naval Research Laboratory, Washington, D.C. 20375.

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