Experimental Observation of Laser Control: Electronic Branching in the Photodissociation of Na_2

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Control over the product branching ratio in the photodissociation of Na_2 into $Na(3s) + Na(3p)$ and $Na(3s) + Na(3d)$ is demonstrated using a two-photon incoherent interference control scenario. Ordinary pulsed nanosecond lasers are used and Na_2 is at thermal equilibrium in a heat pipe. Results show a depletion in the $Na(3d)$ product of at least 25% and a concomitant increase in the $Na(3p)$ yield as the relative frequency of the two lasers is scanned.

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We report the experimental observation of laser control over a branching photochemical reaction. The reaction studied is the two-photon dissociation of the Na_2 molecule at energies where one Na atom is in its ground state and one Na atom is in the 3*p*, 4*s*, or 3*d* states, i.e.,

$$\mathrm{Na}_2 \xrightarrow{2h\nu} \begin{array}{l} \mathrm{Na}(3s) + \mathrm{Na}(3p)\,, \\ \mathrm{Na}(3s) + \mathrm{Na}(4s)\,, \\ \mathrm{Na}(3s) + \mathrm{Na}(3d)\,. \end{array} \qquad (1)$$

Control is demonstrated over the $Na(3d)/Na(3p)$ branching ratio.

Achieving laser control over dynamical processes has been a long-standing goal of both physicists and chemists. Recent theoretical work [1–3] has shown that this goal may be achieved by manipulating quantum interferences, an area of research known as coherent control. Experimental verification of the basic principles of coherent control have followed [4–12] showing, for example, that total ionization rates can be coherently modulated [6–9] and that current directionality can be phase controlled [7–12]. However, there has only been one very recent report [13] of the *primary* aim of coherent control: to successfully manipulate integral yields into *different competing product channels.* Here we present an experimental demonstration of such control.

Our approach is based upon our recent theoretical prediction [14] that laser induced continuum structure (LICS) [15] can give rise to final channel selectivity. In this arrangement one gives structure to the continuum by optically dressing it with a bound state. We showed theoretically [14] that if we dress the continuum with an initially unpopulated bound state using a laser field of frequency ω_2, while exciting a populated bound state to this dressed continuum using a laser field of frequency ω_1, then a quantum interference arises whose destructive or constructive character depends upon the final channel. (An illustration of this scenario as it applies to Na_2 is shown in Fig. 1.) Theoretical studies [14] further showed that the character of this interference depends on the relative frequency between the two light fields, and that selectivity between the $Na(3p)$ and $Na(3d)$ channels [Eq. (1)] can be achieved by varying ω_1 or ω_2. This effect is virtually independent of the relative phase between the two light fields; i.e., the light fields need not be coherent. Thus, although the control depends on quantum interference, these interferences are not destroyed by incoherence of the incident laser radiation.

The fact that this control scenario does not require laser coherence makes it especially attractive for laboratory use

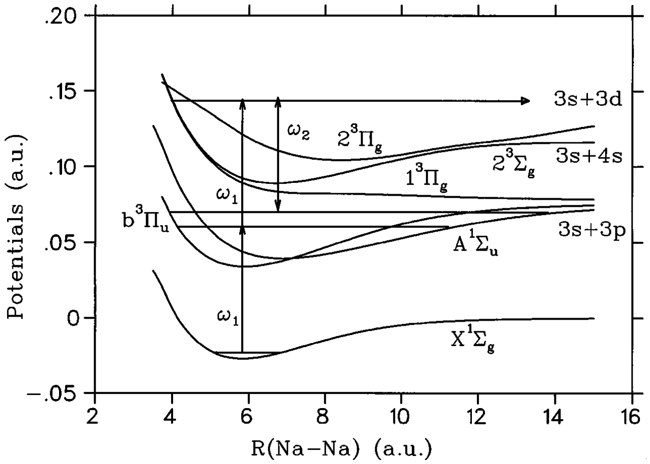

FIG. 1. Incoherent interference control (IIC) scheme and potential energy curves for Na_2. In this scheme a $2\omega_1$-photon excitation interferes with an ω_2 photon. The two-photon process proceeds from an initial sate, assigned here as ($v = 5, J = 37$), via the $v = 35, J = 36, 38$ levels, belonging to the interacting $A^1\Sigma_u/^3\Pi_u$ electronic states, acting as intermediate resonances. The ω_2 photon dresses the continuum with the (initially unpopulated) $v = 93, J = 36$ and $v = 93, J = 38$ levels of the $A^1\Sigma_u/^3\Pi_u$ electronic states.

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since generally available, nontransform limited, nsec dye lasers can be used. In our experiment we use two dye lasers pumped by a frequency-doubled Nd-YAG laser. One dye laser, whose frequency ω_2 was tuned between 13 312 and 13 328 cm^{-1}, was used to dress the continuum with a vibrotational state of the $A^1\Sigma_u/^3\Pi_u$ mixed electronic state [16] of Na$_2$. The other dye laser, whose frequency ω_1 was fixed at 17 474.12 cm^{-1}, was used to induce a two-photon dissociation of the $v = 5, J = 37$ ground state of Na$_2$, through intermediate resonances (assigned as $v = 35, J = 38$ and $v = 35, J = 36$) of the $A^1\Sigma_u/^3\Pi_u$ mixed state. Our ω_1 and ω_2 pulses, both of $\sim$5 nsec duration with the stronger amongst them (ω_2) having an energy of $\sim$3.5 mJ, were made to overlap in a heat pipe containing Na vapor at 370–410 °C. Spontaneous emission from the excited Na atoms [Na($3d$) $\rightarrow$ Na($3p$) and Na($3p$) $\rightarrow$ Na($3s$)] resulting from the Na$_2$ photodissociation was detected and dispersed in a spectrometer and a detector with a narrow bandpass filter.

Figure 2 shows experimental Na(3*d*) and Na(3*p*) emission as a function of ω_2 at a fixed ω_1. Each point represents an average over a few hundred laser shots, each chosen to have an ω_2 pulse energy which deviates by less than 5% from 3.5 mJ. At these energies we estimate our pulse intensity to be $\sim 10^7$ W/cm^2. We see that when the Na(3*d*) yield dips, the Na(3*p*) yield peaks, in accordance with theoretical expectation [17]. The controlled modulation of the Na(3*p*)/Na(3*d*) branching ratio is seen to exceed 30%.

The theoretical calculations [17] of the Na(3*d*) yield resulting from photodissociation of a single initial Na$_2$ bound state are presented in Fig. 3 and contrasted with the experimental results of Fig. 2. The same is done in Fig. 4 for the Na(3*p*) yield. We see two major Na(3*d*) dips, accompanied by Na(3*p*) peaks, in good agreement with the experiment. The calculations were done for the initially unpopulated $v = 93, J = 31$ and $v = 93, J = 33$ levels of the mixed $A^1\Sigma_u/^3\Pi_u$ electronic state, accessed via the $v = 33, J = 31$ and $v = 33, J = 33$ intermediate resonances by the $2\omega_1$-photon process. These v, J values differ slightly from those which we experimentally assigned ($v = 35$ and $J = 36$ and 38), but the line shapes were found to change very little with small changes in v, J. Considering the uncertainties in the theoretical potentials used [17,18], the agreement between theory and experiment [especially in the Na(3*d*) signal] is impressive. Additional computations [14] suggest that the observed experimental substructures may be due to the excitation of numerous additional, as yet unassigned, thermally populated vibrotational Na$_2$ energy levels.

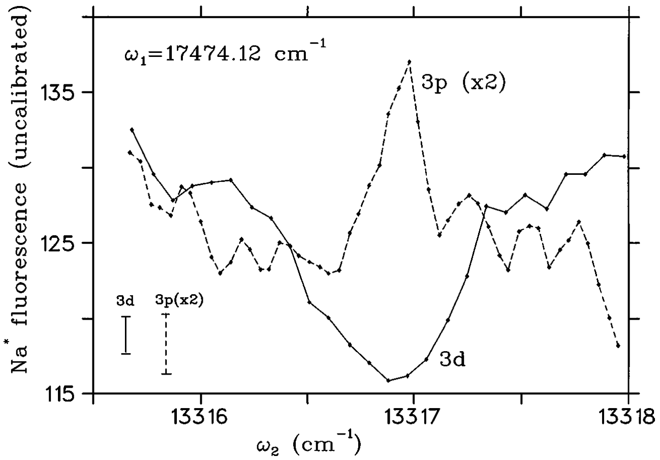

FIG. 2. Experimental Na(3*d*) fluorescence (solid) and Na(3*p*) fluorescence (dashed) (both uncalibrated) for the Na$_2$ $\rightarrow$ Na($3s$) + Na($3d$), Na($3p$) IIC scenario whose details are given in Fig. 1, as a function of the ω_2 frequency. The ω_1 frequency is fixed at 17 474.12 cm^{-1}.

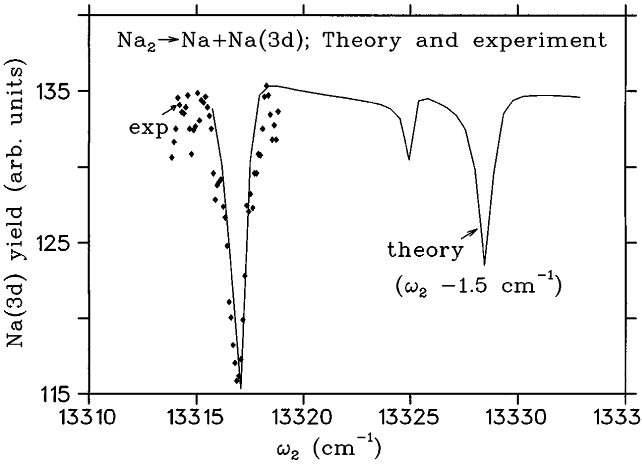

FIG. 3. Comparison of the experimental and theoretical Na$_2$ $\rightarrow$ Na($3s$) + Na($3d$) yields as a function of ω_2. In the calculation, an intermediate $v = 33, J = 31, 33$ resonance is used and ω_1 is fixed at 17 720 cm^{-1}. The intensities of the two laser fields are $I(\omega_1) = 1.72 \times 10^8$ W/cm^2 and $I(\omega_2) = 2.84 \times 10^8$ W/cm^2. The ω_2 frequency axis of the calculated results was shifted by -1.5 cm^{-1} in order to better compare the predicted and measured line shapes.

The Na(3*p*) experimental signal is superimposed on a high background due to population of the Na(3*p*) state by emission from the Na(3*d*) and Na(4*s*) states, and due to direct population of Na(3*p*) from the Na$_2$ molecule by an $\omega_1 + \omega_2$ absorption [not possible energetically for the Na(3*d*) channel]. We also had to overcome radiation trapping effects by monitoring the Na($3p$) $\rightarrow$ Na($4s$) emission off line center. The results shown in Figs. 2 and 4 are obtained by subtracting the contribution of these processes from the observed Na(3*p*) signal. To do so we calibrated the contribution from the Na($3d$) $\rightarrow$ Na($3p$) emission via a separate experiment, where we monitored the Na(3*p*) signal resulting from the direct two-photon excitation of the Na(3*d*) state. The direct $\omega_1 + \omega_2$ contribution was accounted for by measuring the Na(3*p*) signal at different $\omega_1 + \omega_2$ intensities. Because we saturate the one-photon ω_1 resonance, the dependence

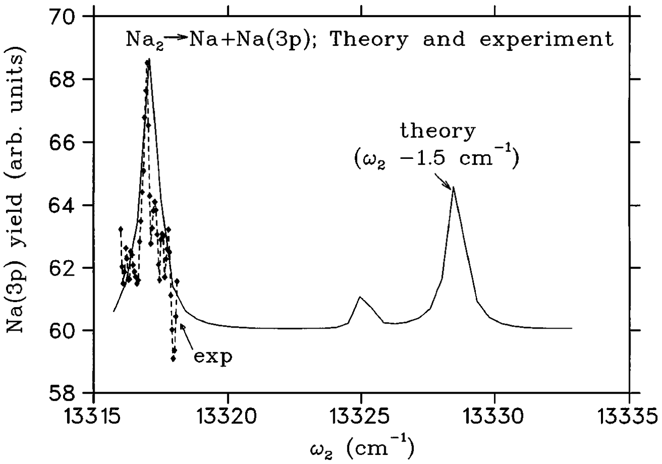

FIG. 4. Comparison of the experimental and theoretical $Na_2 \rightarrow Na(3s) + Na(3p)$ yields as a function of ω_2, with parameters as in Fig. 3.

of the $\omega_1 + \omega_2$ process was found to be linear in the ω_2 intensity. Hence, determining the slope and intercept of this linear dependence allowed us to subtract out its contribution at the experimental ω_1 and ω_2 intensities.

To confirm that the observed Na(3*d*) dip and Na(3*p*) peak structures are indeed due to incoherent interference control, i.e., the interference between the ω_1 and ω_2 induced optical processes, we ran the following checks.

(1) We verified that what we are seeing is a *strong field* effect by changing the ω_2 power. Reducing the power by a factor of ~50 resulted in the complete vanishing of the dip and peak structures.

(2) We verified that the observed structures are due to the *combined* action of the two lasers by delaying the ω_1 pulse relative to the ω_2 pulse. A delay of ±19 nsec, guaranteeing no overlap between the pulses, completely eliminated the Na(3*d*) dips.

(3) We rotated the planes of polarization of the two lasers and noted no change in the observed Na* fluorescence. This indicates that the observed peaks and valleys are not due to the polarization of the sodium atoms. It also demonstrates that the Na atoms resulting from the dissociation are unpolarized.

(4) Real time measurements of the rise and decay of the Na(3*d*) and Na(3*p*) signals were performed. If the observed structures are due to an accidental secondary transfer of population from the Na(3*d*) to the Na(3*p*) state then such a mechanism would be reflected in the time dependence of the Na(3*d*) signal. Specifically, if a (collisional or other relaxational) mechanism was in effect at one ω_2 frequency and not at another, thus giving rise to the observed Na(3*d*) dip and Na(3*p*) peak at that particular ω_2 frequency, we would see a faster decay of the Na(3*d*) signal at that frequency relative to the other. Our findings show an *identical* decay curve for the Na(3*d*) signal at *all* ω_2 frequencies probed. The only thing which changes is the area under the decay curve. This indicates that it is the actual production of the Na(3*d*) [Na(3*p*)] state which is affected by changing ω_2, and not its subsequent decay [buildup].

(5) We shifted the ω_1 frequency (by −0.19 and −0.40 cm^{-1}) and examined the effect of such shifts on the dependence of the Na(3*d*) and Na(3*p*) yields on ω_2. Since the two-photon ω_1 absorption is mediated by a (saturated) intermediate one-photon resonance, the ω_2 dependence of the Na(3*d*) and Na(3*p*) structures should move by an amount equal to the ω_1 shift. This is indeed the case, as demonstrated in Fig. 5, where the ω_2-dependent structures are seen to redshift, respectively, by 0.23 and 0.37 cm^{-1}. These values are, within our frequency resolution of ±0.04 cm^{-1}, in perfect accord with the above expectations. A similar shift of the Na(3*p*) peaks was also observed, thus verifying the optical origin of the effect.

In summary, we have experimentally demonstrated laser control of branching photochemical reactions using quantum interference phenomena. In addition, we have overcome two major experimental obstacles to the general implementation of optical control of reactions: (a) we have achieved control using incoherently related light sources, and (b) we have affected control in a bulk, thermally equilibrated, system.

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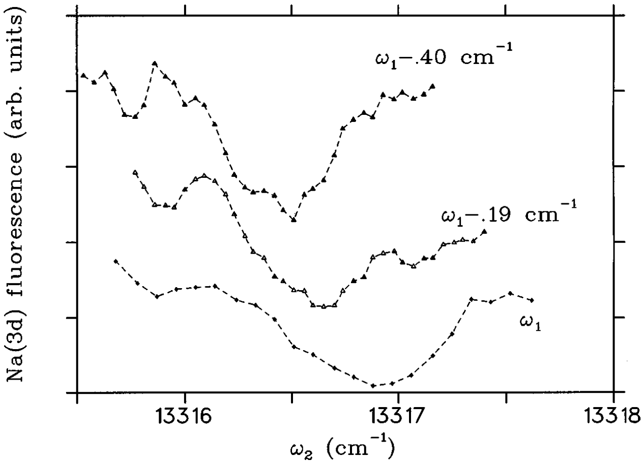

FIG. 5. The Na(3*d*) fluorescence as a function of ω_2 for three different ω_1 frequencies. The lowest trace corresponds to an ω_1 value of 17 474.12 cm^{-1}. The upper traces result from redshifting the ω_1 frequency by 0.19 and 0.40 cm^{-1}. We observe a redshift in the ω_2 dependence of the Na(3*d*) yield of, respectively, 0.23 and 0.37 cm^{-1}, each being, without experimental uncertainty of ±0.04 cm^{-1}, identical to the respective ω_1 shift. Note that the other substructures of the Na(3*d*) line shapes show similar shifts.

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