Twophoton excitation of dense sodium vapor near the n d 2 D 5/2,3/2 (n=3,4,5) levels: Na2 13Σ+ g →13Σ+ u excimer emission

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Two-photon excitation of dense sodium vapor near the $nd\ ^2D_{5/2,3/2}$ ($n=3, 4, 5$) levels: $Na_2\ 1\ ^3\Sigma_g^+ \rightarrow 1\ ^3\Sigma_u^+$ excimer emission

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Laser excitation and ionization processes in dense (1–10 Torr) sodium vapor have been studied for laser wavelengths near the two-photon allowed $nd\ ^2D (n = 3, 4, 5)$ and $ns\ ^2S (n = 4, 5, 6)$ states. In particular, the $1\ ^3\Sigma_g^+ \rightarrow 1\ ^3\Sigma_u^+$ excimer emission in Na_2, predicted in 1980 by Konowalow and Julienne and observed recently by Dinev *et al*, was studied here in greater detail. Strong excimer emission ($\sim$830 nm) was observed for two-photon pumping to both sides of the unresolved $4D$ states, and weak excimer emission was seen when pumping near the $5D$ levels. The excimer emission exhibits a complicated pump laser profile with a pronounced "dip" at the $4d\ ^2D$ two-photon resonance. Similarly, [2 + 1] photon ionization via the $3d\ ^2D$ and $4d\ ^2D$ states shows a dramatic decrease as the sodium density increases. These results can be attributed either to depleted $3d\ ^2D$ or $4d\ ^2D$ population due to stimulated electronic Raman scattering (SERS) or to the interference effects recently reported by Malcuit *et al.* and Krasnikov *et al.* and treated theoretically by Manykin and Afanas'ev and by Agarwal. It is argued that both mechanisms are operative. Strong ionization and SERS signals were observed at the *hybrid* resonances corresponding to $3p\ ^2P_{3/2,1/2} \rightarrow 4d\ ^2D$ transitions; however, no excimer lasing at 830 nm was detected. No excimer emission was detected upon two-photon pumping near or at the $3d\ ^2D$ or $ns\ ^2S (n = 4, 5, 6)$ states. Based on these and other observations, the $1\ ^3\Sigma_g^+ \rightarrow 1\ ^3\Sigma_u^+$ excimer emission is attributed to a *molecular* Raman process involving stimulated emission or six-wave mixing via a pathway of the type

$$1\ ^3\Sigma_u^+ \xrightarrow{2h\nu} 3\ ^3\Delta_u \rightarrow j\ ^3\Pi_g \rightarrow (k\ ^3\Pi_u, l\ ^3\Sigma_u^+) \rightarrow 1\ ^3\Sigma_g^+ \rightarrow 1\ ^3\Sigma_u^+ .$$

INTRODUCTION

There have been many recent studies of the interaction of fixed frequency and tunable laser radiation with dense alkali vapors. Resonant excitation of the alkali atoms by one or more photons can lead to strong ionization of the vapor either by multiphoton ionization or collisional ionization between an excited atom and a ground state atom or between two excited atoms. In some cases, associative ionization can dominate. Lucatorto and McIlrath[1] have found substantial ionization in dense ($> 10^{15}$ cm^{-3}) alkali vapors when tuning a laser near allowed resonances. Of particular interest is the production of optically pumped lasers involving alkali dimers. Muller and Hertel[2] and Wang *et al.*[3] have reported infrared laser lines upon two-photon pumping of many high-lying states of Na_2 and K_2. Verma *et al.*[4] reported the first observation of bound–continuum transitions in the laser-induced $1\ ^1\Sigma_u^+ \rightarrow 1\ ^1\Sigma_g^+$ fluorescence of Na_2. These authors (Bahns *et al.*[5]) constructed an optically pumped ring laser oscillator using vibrational levels near the dissociation limit and into the continuum in Na_2. Very recently, Dinev *et al.*[6] reported $1\ ^1\Sigma_u^+ \rightarrow 1\ ^1\Sigma_g^+$ lasing in sodium in which the $1\ ^1\Sigma_u^+$ state was believed to be populated by collisions between two-photon-excited Na($4d$) and Na($3s$) atoms.

Excimer laser emission between the lowest triplet levels (i.e., $1\ ^3\Sigma_g^+ \rightarrow 1\ ^3\Sigma_u^+$) of Li_2 and Na_2 was first predicted by Konowalow *et al.*[7] and more precise calculations were later performed by Konowalow and Julienne.[8] Following this prediction, Dinev *et al.*[9] reported the first observation of excimer laser action in Na_2 centered at $\sim$830 nm due to the $1\ ^3\Sigma_g^+ (v' = 0) \rightarrow 1\ ^3\Sigma_u^+$ bound–free transition. Excimer emission was observed upon two-photon excitation of the atomic $4d\ ^2D$ states. They proposed a mechanism of population of the upper triplet $1\ ^3\Sigma_g^+$ state which involved two-photon excitation of Na ($4d$) atoms followed by collisional energy transfer to dimer triplet states. Figure 1 shows the relevant potential energy curves and transitions involved in the singlet and triplet emissions.

Here, we report further studies of $Na_2\ 1\ ^3\Sigma_g^+ \rightarrow 1\ ^3\Sigma_u^+$ excimer emission in the case of two-photon pumping of dense sodium vapor near the $4d\ ^2D$ excited state. The ex-

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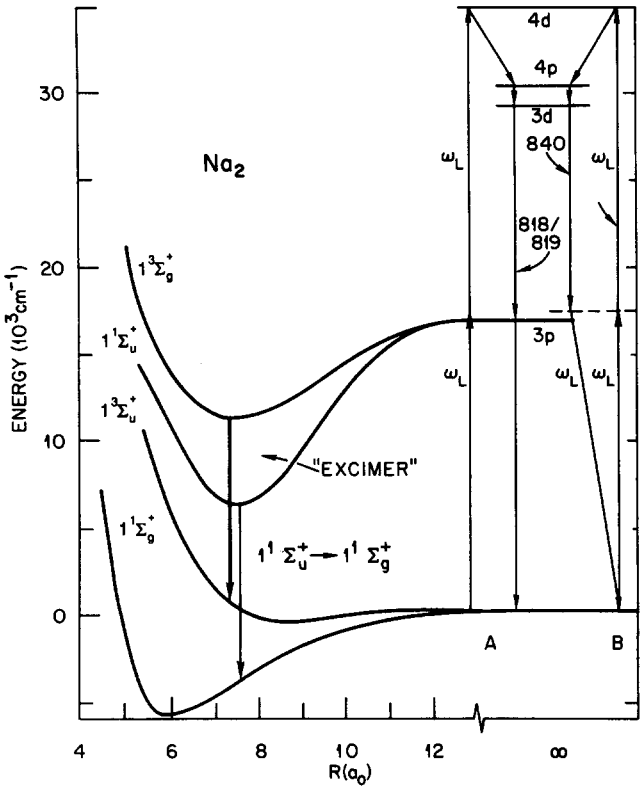

FIG. 1. Term diagram depicting the observed transitions between the lowest singlet ($1\,^1\Sigma_u^+ - 1\,^1\Sigma_g^+$) and triplet ($1\,^3\Sigma_g^+ - 1\,^3\Sigma_u^+$) molecular states for Na_2 and the various atomic processes. A shows the parametric six-wave mixing process which has as one of its branches the $3d \rightarrow 3p$ transition. B shows the six-wave mixing process that accounts for the observed emission at ~840 nm. This wave-mixing process involves a virtual level of sodium at the laser photon energy.

cimer emission is attributed to a stimulated emission process which involves a $1\,^3\Sigma_u^+ \xrightarrow{2h\nu_L} 3\,^3\Delta_u$ excitation of sodium molecules. These studies also include observations of ionization and SERS, and we show that both excimer lasing and ionization is suppressed at the atomic resonance. We attribute the depressed ionization to an interference between the two-photon excitation and parametric four-wave mixing pathways[10,11] to the $4d\,^2D_{5/2,\,3/2}$ levels. The observation that the excimer emission is also suppressed at the $4d\,^2D$ levels may be related to a molecular interference effect.

Suppression of two-photon excitation in dense alkali vapors has been a subject of much current interest. Malcuit *et al.*[10] have recently reported suppression of amplified spontaneous emission (ASE) by the four-wave mixing (FMW) process upon two-photon pumping at the $3d\,^2D$ levels in sodium. Their calculations have shown that the ASE is suppressed by destructive interference between the two pathways connecting the ground and $3d\,^2D$ states. Agarwal[11] later quantized the electromagnetic field and showed that when ASE is suppressed, the fields generated in the FWM process constitute what is called a squeezed state of the radiation field. Agarwal[11] further stated that the $3d\,^2D$ state would not be excited under these conditions. More recently, Krasnikov *et al.*[12] have reported a suppression of the two-photon absorption for 3*s*–4*s* in sodium by more than two orders of magnitude. The possible suppression (interference) of two-photon absorption was first suggested theoretically by Manykind and Afanas'ev.[13] The results reported here are the first observation of suppressed *ionization* due to the interference effect in two-photon excitation.

EXPERIMENTAL

Two-photon excitation of the $3d$ and $4d\,^2D_{5/2,\,3/2}$ levels and "hybrid resonances" of sodium was studied using a tunable dye laser (Quanta-Ray PDL-2) with a bandwidth of 0.2 cm^{-1} pumped by the second harmonic (532 nm) of a Nd:YAG laser (Quanta-Ray DCR). The dyes used and their maximum average output powers were: LDS698-65 mW, R610 (basic)—150 mW, and R590-100 mW, respectively. Coumarin 500 pumped by the third harmonic (355 nm) of the Nd:YAG was used to excite the $5d\,^2D_{5/2,\,3/2}$ levels of sodium and had an average output power of 50 mW. A pulse rate of 10 Hz was employed with the pulse length being ~6 ns.

The output of the dye laser was focused by a 15 cm focal length lens into the center of a stainless steel heat pipe containing dense sodium vapor and argon as a buffer gas. The heat pipe was 30 cm in length and had an active length of 15 cm between the cooling coils with quartz windows on either end. The pressure of the heat pipe was controlled by varying the temperature and the buffer gas pressure.

The ionization signal was collected on a biased insulated collector wire which passed through the active region of the heat pipe. The ionization signal (electrons) was observed as a negative voltage due to the electronic flow through a 10k resistor to ground. In some cases the collector voltage was reversed, and positive ions were collected resulting in a positive voltage pulse. The + or − voltage pulse was displayed on an oscilloscope and averaged by a boxcar integrator (Standford Research Systems model SR250), the output of which was recorded on an *x*–*y* recorder. Further details concerning the experimental setup can be found in Ref. 14.

RESULTS

Many nonlinear optical effects (self-focusing, conical emission, etc.) were observed upon strong pumping of sodium vapor at the one- and two-photon resonance levels. We report here only those observations which are new or important to the interpretation of the results for excimer emission between molecular levels.

Figure 2 shows the forward-directed emissions when the focused dye laser is tuned to *near* resonance with the two-photon excited $4d\,^2D_{5/2,\,3/2}$ levels of sodium. Due to the bandwidth of the laser (~0.2 cm^{-1}), both $4d\,^2D_{5/2,\,3/2}$ fine structure levels (separation 0.035 cm^{-1}) are excited. In the region of 790 and 800 nm, directly pumped bound–bound lasing between the two lowest singlet molecular states was observed. Monitoring one of the $1\,^1\Sigma_u^+ \rightarrow 1\,^1\Sigma_g^+$ emission features as a function of pump laser frequency shows that the $1\,^1\Sigma_u^+$ state is populated by cascading transitions from states excited by one- or two-photon excitation from ground state

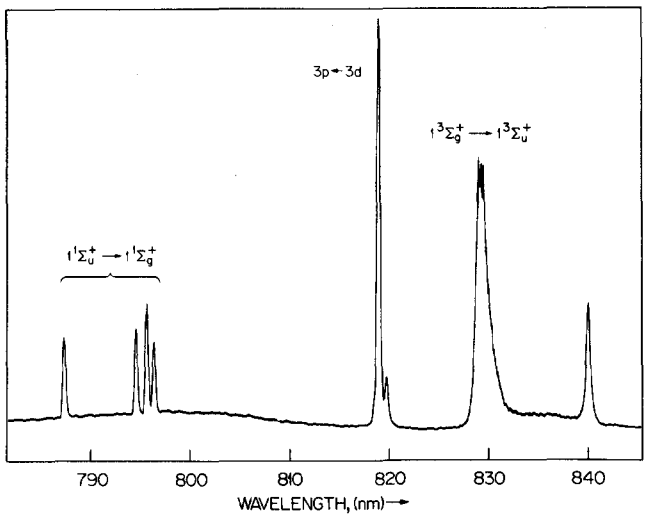

FIG. 2. Forward-stimulated emission in sodium vapor (~7 Torr) produced by two-photon pumping *near* the $4d\ ^2D_{5/2,\,3/2}$ levels. Laser power was 12 mJ/pulse, and the focal length of the lens was 150 mm.

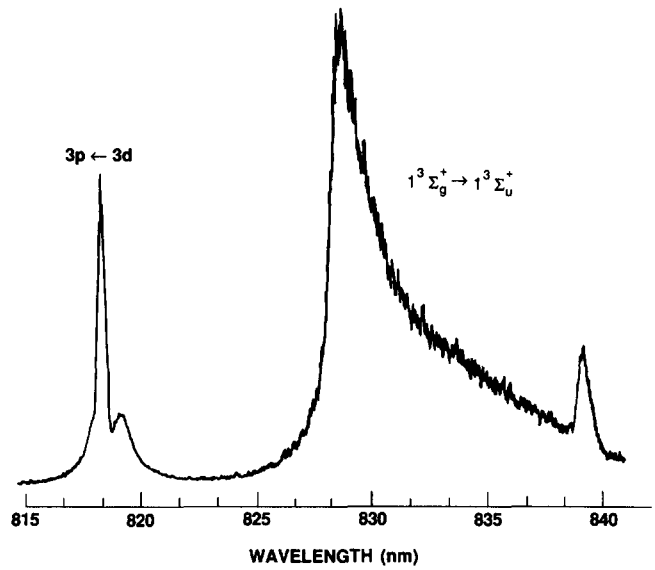

FIG. 4. Forward-directed emissions from heat pipe under optimum conditions for excimer lasing; laser power 19 mJ/pulse and pressure ~10 Torr.

$v'' = 0$ and higher levels. For example, Fig. 3 shows the intensity variation of the fourth laser peak reading from the left of Fig. 2 as the pump laser wavelength is varied. A clear rovibrational band structure is seen whose separation is found to be the 159 cm^{-1} vibrational spacing of the ground $1\ ^1\Sigma_g^+$ state. Two-photon excitation to high vibrational levels of two electronically excited singlet molecular states is responsible. Such lasing has been extensively studied.[2–5] The two features near 820 nm in Fig. 2 are due to SERS from $3d\ ^2D_{5/2,\,3/2}$ to $3p\ ^2P_{3/2}$ and $3p\ ^2P_{1/2}$, respectively. This emission is one branch of the parametric six-wave mixing process, $3s \xrightarrow{2h\nu_L} 4d \rightarrow 4p \rightarrow 3d \rightarrow 3p \rightarrow 3s$ [see Fig. 1(A)]. In Fig. 2, the broad band at ~830 nm results from excimer laser emission between the lowest two triplet states of sodium $1\ ^3\Sigma_g^+ \rightarrow 1\ ^3\Sigma_u^+$. The breadth (and to some extent the position) of the excimer emission is dependent upon the laser intensity, the laser frequency, and the alkali density. The broadening occurs to the long wavelength side of the peak. In fact, under optimum conditions the excimer emission can extend out to and somewhat beyond the peak at 840 nm as shown in Fig. 4. However, the excimer emission does not extend below about 828 nm. Figure 4 also shows that under optimum conditions of laser power and sodium density, the excimer peak can be made to be the most intense feature in the spectrum. Another important observation is that the excimer emission only occurs *during* the time the laser pulse is on.

Our measurements of the pump laser threshold for excimer emission and pressure conform fairly well with the observations of Dinev *et al.*[9] Finally, excimer emission is *not* observed when pumping with two photons near the $3d\ ^2D$ or $ns\ ^2S$ ($n = 4, 5, 6$) levels. Also, in accord with the observations of Dinev *et al*,[9] the $1\ ^3\Sigma_g^+ \rightarrow 1\ ^3\Sigma_u^+$ emission is *not* seen in the backward direction.

Dinev *et al.*[9] report considerable structure in the 830 nm feature which is not evident in our spectra. Also, our measurements of the variation of excimer intensity with pump laser wavelength disagree with that of Dinev *et al.*[9] who report that the excimer emission peaks as the pump laser is tuned to the two-photon allowed $4d\ ^2D_{5/2,\,3/2}$ levels. Detailed measurements are shown in Fig. 5. We note a dramatic dip in the excimer emission at the exact position of the $3s\ ^2S_{1/2} \xrightarrow{2h\nu} 4d\ ^2D_{5/2,\,3/2}$ transition. At the density employed for the data in Fig. 5, the excitation profile spans ~1.5 nm. Before discussing possible physical mechanisms for populating the upper $1\ ^3\Sigma_g^+$ excimer level let us address the question of the "dip" in the excitation profile. The excitation of $4d\ ^2D_{5/2,\,3/2}$ atoms can be monitored using the two-photon resonant ionization signal. At low pressure, the ionization signal is due to three-photon ionization, whereas at higher pressure chemi-ionization may also contribute. The measurement of ionization is therefore an approximate detector of $4d\ ^2D$ atoms. Figure 6 shows a strong three-photon ionization signal (a.c. Stark broadened) at low pressure ($p < 1$ Torr). However, as the sodium pressure is increased, this signal is seen to decrease in absolute magnitude as determined by the voltage pulse resulting from current through a

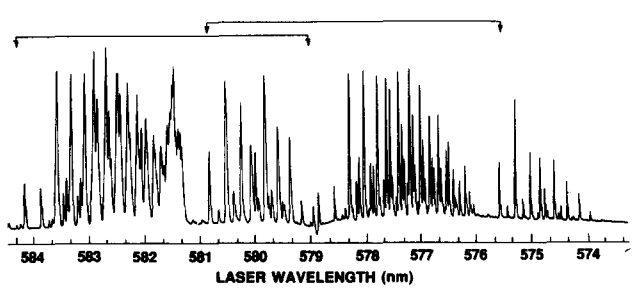

FIG. 3. Singlet–singlet laser emission between $1\ ^1\Sigma_u^+ \rightarrow 1\ ^1\Sigma_g^+$ rovibrational levels. The emission wavelength corresponds to the fourth peak from the left in Fig. 2. The separations of the bands (~159 cm^{-1}), indicated by the arrows, corresponds to the separation of the $1\ ^1\Sigma_g^+$ ground state.

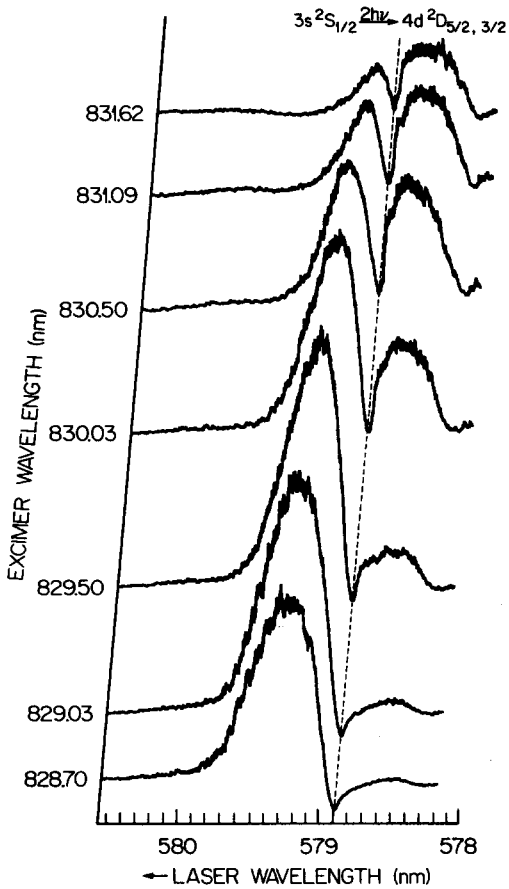

FIG. 5. Excimer emission between the Na_2 $1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$ levels as a function of pump laser wavelength in the vicinity of the two-photon Na $4d\,^2D$ state. The observed dip occurs at the two-photon resonance to the $4D$ state.

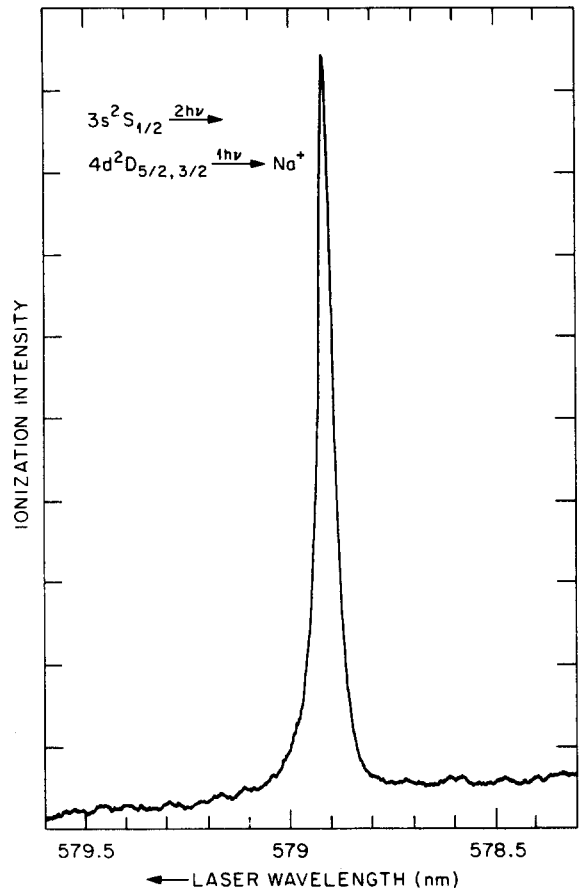

FIG. 6. Resonantly enhanced three-photon ionization of sodium atoms at low pressure ($p \sim 0.8$ Torr).

10 K resistor to ground. At higher pressure (above 1 Torr) the $4d\,^2D$ ionization signal decreases until it is of the order of the molecular ionization signal (Fig. 7). All of the peaks in Fig. 7 are reproducible and are attributed to molecular resonance enhancement at the one, two, or three (autoionization) photon level. The drop in excimer emission on resonance (Fig. 5) therefore appears to be associated with a decrease in the $4d\,^2D$ excitation. Note, however, that considerable two-photon absorption is still observed as evidenced by the strong minimum in the transmitted laser light. The strong two-photon absorption of the input laser and reduced ionization signal appear to be contradictory. One likely explanation is that strong SERS processes occur: for instance, the SERS process responsible for the two peaks at ~ 820 nm in Fig. 2. This emission *peaks* on resonance. These same parametric SERS processes could also account for a partial cancellation of the coherent two-photon excitation process in the manner reported for the $3d\,^2D_{5/2,\,3/2}$ state by Malcuit *et al.*[10] In this connection, we have studied two-photon excitation of the $3d\,^2D_{5/2,\,3/2}$ state of sodium and find strong three-photon ionization signals at low pressure and the disappearance of signal (i.e., less than the molecular signal) at high number density (> 1 Torr). We see *no* excimer emission tuning at or near the two-photon $3d\,^2D$ level. The fact that no excimer emission is seen near the $3d\,^2D$ level will be

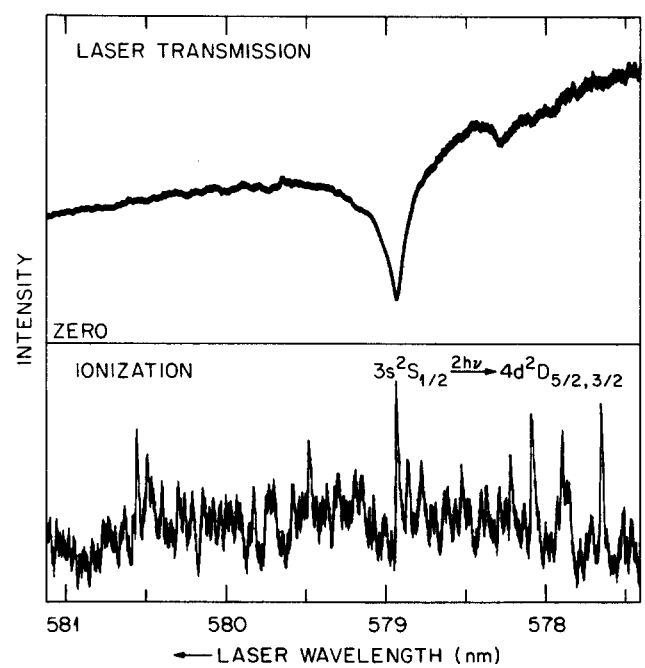

FIG. 7. Resonantly enhanced three-photon ionization of sodium atoms at higher pressure ($p \sim 7$ Torr). The top portion of the figure shows the strong two-photon absorption of the incident laser light that occurs at the $4d$ resonance.

discussed later as one of many major arguments refuting an atomic pathway and favoring the purely molecular excitation mechanism for populating the $1\,^3\Sigma_g^+$ state from which lasing occurs.

We have investigated a second method of strongly populating the $4d\,^2D_{5/2,3/2}$ levels by way of *hybrid* resonances involving $3p$–$4d$ transitions. Figure 8 shows the strong ac Stark-broadened ionizaion signals which are recorded as the laser is tuned around the frequencies corresponding to $3p\,^2P_{3/2} \rightarrow 4d\,^2D_{5/2,3/2}$ and $3p\,^2P_{1/2} \rightarrow 4d\,^2D_{3/2}$ transitions. The $3p$ levels are believed to be populated by energy transfer to ground state atoms through collisions with excited molecules ($1\,^1\Sigma_u^+$ or $1\,^1\Pi_u$) resonantly excited by the laser beam.[3,15] Intense SERS signals corresponding to $3d\,^2D \rightarrow 3p\,^2P_{1/2}$ and $3d\,^2D \rightarrow 3p\,^2P_{3/2}$ transitions are seen as shown in Fig. 9. However, no excimer (830 nm) emission is observed in conjunction with these transitions. A possible explanation might be that a critical threshold of population of $4d\,^2D$ atoms is not reached in this case, but such a population is produced upon direct two-photon pumping near the $4d\,^2D$ state described earlier. A more plausible explanation is that the excimer emission is *not* due to energy transfer from $4d\,^2D$ atoms to ground state molecules thus producing $1\,^3\Sigma_g^+$ sodium excited states as suggested by Dinev *et al.*[9] but rather is due to a molecular stimulated emission process to be discussed below.

Two-photon pumping at and near the $5d\,^2D_{5/2,3/2}$ level produces only weak excimer emission as shown in Fig. 10. Atomic stimulated emission corresponding to $3d \rightarrow 3p$ is strong, however.

Apart from the *dip* on resonance, the remaining key observations regarding the $1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$ laser emission which must be explained are:

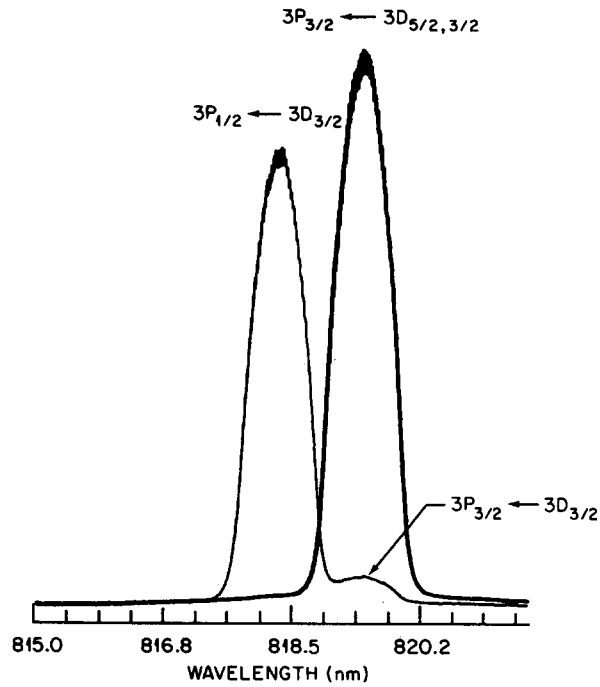

FIG. 9. Wavelength resolved stimulated electronic Raman scattering signal from excited sodium ($3p\,^2P_{3/2,1/2}$) atoms. SERS signals corresponding to $3p\,^2P_{3/2} \leftarrow 3d\,^2D$ transitions result from excitation of $3p\,^2P_{3/2}$ atoms ($\lambda_L = 5689.8$ Å), whereas excitation of $3p\,^2P_{1/2}$ atoms ($\lambda_L = 5684.2$Å) produce SERS signals mainly corresponding to $3p\,^2P_{1/2} \leftarrow 3d\,^2D_{3/2}$.

(a) pumping near the $4d\,^2D$ level of sodium vapor produces the most intense excimer emission;

(b) pumping at or near the $3d\,^2D$ level produces no discernible $1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$ emission and pumping at or near the $5d\,^2D$ level produces weak excimer emission;

(c) pumping any of the $4s$, $5s$, or $6s$ levels produces no excimer emission; and

(d) the excimer emission time profile follows that of the pump laser.

Our rationalization of these observations will depend heavily on arguments regarding the ion-pair character of Rydberg states of the alkalies such as those made in the last

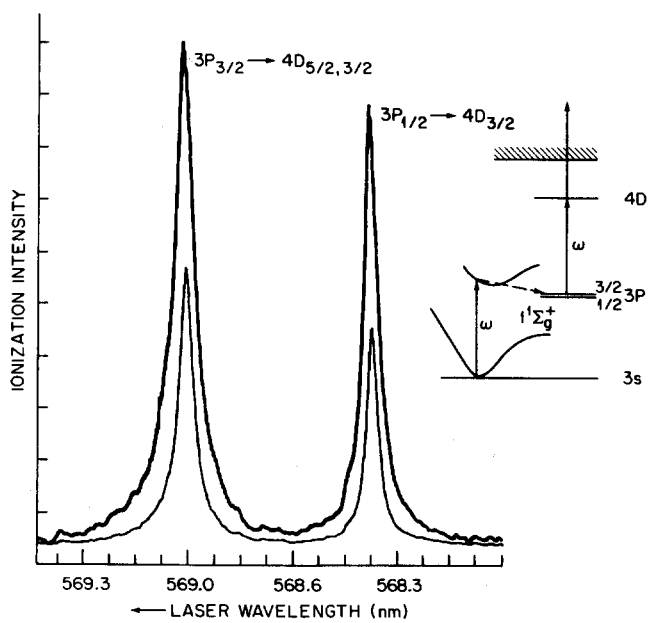

FIG. 8. Two-photon ionization of sodium atoms via *hybrid* resonances of the $3p$–$4d$ transitions ($p \sim 7$ Torr). Collisions between excited Na_2 molecules and ground state atoms populate the $3p$ levels.

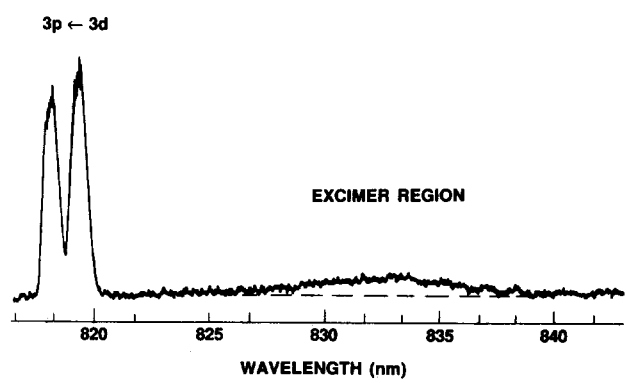

FIG. 10. Forward-stimulated emission in sodium vapor (~ 7 Torr) produced by two-photon pumping near the $5d\,^2D_{5/2,3/2}$ levels. Note that weakly discernable excimer emission is observed.

few years by Konowalow and co-workers.[16–20] We will argue largely by analogy with results of these works and with the, as yet, unpublished research on K_2. These papers argue that individual molecular Rydberg states of the alkalies are likely to have rather unconventionally shaped potential energy curves (containing multiple minima or "shelves") largely due to strong mixing of covalent and "ion-pair" configurations in their wave functions. Such perturbed Rydberg states have a substantially enhanced electric dipole transition moment, hence an enhanced emission probability, in the internuclear separation regions where their wave functions are characterized by a large admixture of ion-pair character. The relative *strength* of the ion-pair character, the long-range internuclear separation at which the ion-pair effects become prominent, and the *range* of internuclear separations over which the ion-pair effects remain prominent depend sensitively on the match of energy of the molecular state in question with that of the hypothetical ion-pair state of the same symmetry which corresponds asymptotically to the atomic ion-pair Na^+–Na^-. (Na^- may be a bound negative ion state or merely a resonance which is stabilized in the field of Na^+.) We assume that the asymptotic energies of the Na^+–Na^- states lie in the order Na^+–Na^- $3s^2\,{}^1S$, $3s3p\,{}^3P$, $3s3p\,{}^1P$, $3s4s\,{}^3S$, $3s4s\,{}^1S$, etc., which is the same *order* as the energies of the magnesium atomic states. We assume that the *molecular* ion-pair states may be formed from the atomic ion pairs in the usual way. All $^1\Sigma^+$ states of Na_2, which lie below the lowest Na^+–Na^-(^1S) ion-pair asymptote at about 37, 093 cm^{-1} above ground state atoms, will have a substantial ion-pair component. The nearer the asymptote of the $^1\Sigma^+$ state in question is to the ion-pair asymptote at 37, 093 cm^{-1}, the larger is the internuclear separation at which the ion-pair interaction becomes palpable (from the point of view of colliding atoms) and the wider the range of separation over which the ion-pair interaction is important. Likewise, the $^3\Pi$ and $^3\Sigma$ states which lie below the Na^+–Na^-(^3P) ion-pair asymptote will exhibit ion-pair effects, and so on.

We are now in a position to address the key observations raised above.

We postulate that the excitation in the vicinity of the $4d$ atomic level is actually a combination of atomic $4d \overset{2h\nu}{\leftarrow} 3s$ and molecular $^3\Delta_u \overset{2h\nu}{\leftarrow} {}^3\Sigma_u^+$ and $^1\Delta_g \overset{2h\nu}{\leftarrow} {}^1\Sigma_g^+$ excitations, since some fraction of Na $3s$ atoms will combine to form $^1\Sigma_g^+$ and $^3\Sigma_u^+$ molecules. It is this combination of atomic and *molecular* transitions which may account for the observed excitation profile. (Let us ignore singlet states at the outset since we wish to explore possible mechanisms to populate the $1\,{}^3\Sigma_g^+$ state.)

One should not think of the excitation process as the two-photon excitation of a (relatively) isolated ground state atom to form a $4d$ atom followed by a collision with another ground state atom to form an excited molecule. This process would require a conveniently located third body to carry away the energy of bond formation of the excited molecular state. This takes more time to move the nuclei to approximately their equilibrium inter-nuclear separation than the experiment tells us is required for the onset of lasing. These crude kinetic arguments, together with the *molecular* appearance of the excitation profile, suggest that the excitation process is indeed molecular in nature. We conjecture that the starting material comprises pairs of spin-aligned ^2S Na atoms in the $1\,{}^3\Sigma_u^+$ energy continuum that are in a state of collision at separations in the immediate vicinity of the repulsive wall. Figure 11 shows that those separations corresponding to the classical turning points of low energy continuum states of Na_2 line up very nicely with the minima of the potential curves which we claim are likely participants in the deexcitation cascade which populates the $1\,{}^3\Sigma_g^+$ state. Thus, no appreciable time need be wasted in nuclear motion to bring the excited molecules into a propitious Franck–Condon region.

If the two-photon "$4d$" excitation is actually $3\,{}^3\Delta_u \overset{2h\nu}{\leftarrow} 1\,{}^3\Sigma_u^+$ as we assert, then there appear to be many open channels which connect $3\,{}^3\Delta_u$ with the lasing $1\,{}^3\Sigma_g^+$. Figure 11 shows one of the likely pathways: $3\,{}^3\Delta_u(4d+3s) \rightarrow 3\,{}^3\Pi_g(4p+3s) \rightarrow 3\,{}^3\Sigma_u^+(4s+3s) \rightarrow 1\,{}^3\Sigma_g^+(3p+3s) \rightarrow 1\,{}^3\Sigma_u^+(3s+3s)$. These molecular transitions correspond asymptotically to the allowed atomic transitions $4d \rightarrow 4p \rightarrow 4s \rightarrow 3p \rightarrow 3s$, so the probability of molecular transitions should be appreciable over a wide range of internuclear separations as well. The second step of an alternative path-

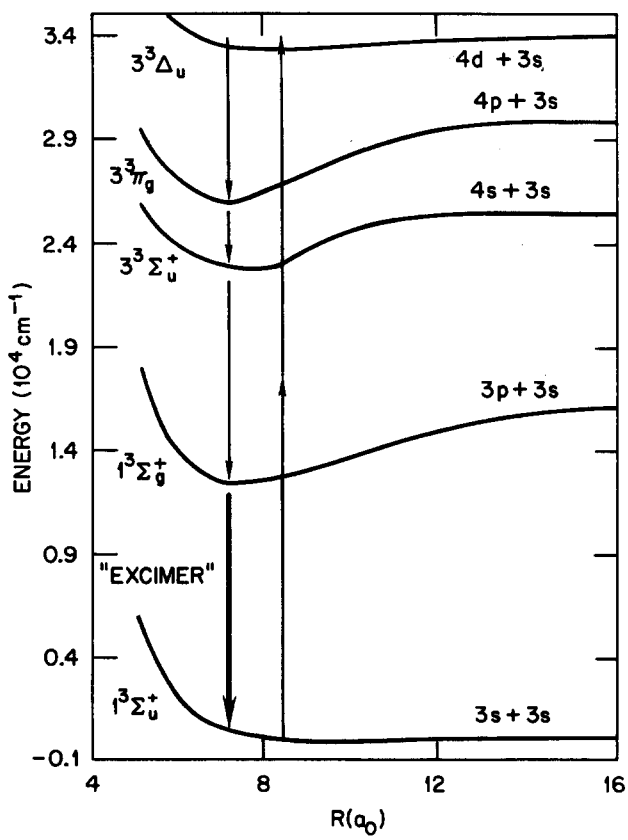

FIG. 11. Schematic of a likely decay cascade following the two-photon excitation $3\,{}^3\Delta_u \overset{2h\nu}{\leftarrow} 1\,{}^3\Sigma_u^+$.

way $3\,^3\Delta_u(4d+3s) \rightarrow 4\,^3\Pi_g(3p+3p) \rightarrow 3\,^3\Sigma_u^+(4s+3s) \rightarrow 1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$ involves a transition which is not allowed asymptotically and, by analogy with the corresponding transition in Li_2,[17] the corresponding transition moment is likely to have several zeros as a function of internuclear separation. Therefore, the pathway involving $3\,^3\Pi_g(4p+3s) \rightarrow 3\,^3\Sigma_u^+$ is invoked. States corresponding to the $3d+3s$ asymptote are also unlikely to serve to populate the lasing $1\,^3\Sigma_g^+$ state. Figure 12 depicts the states of Na_2 corresponding to the Na $3d$ + Na $3s$ interaction calculated by Jeung[23] and our estimate of the $Na^+(^1S)$–$Na^-(^3P)$ ion pair interaction curve. Note that the $^3\Sigma^+$ and especially the $^3\Pi$ curves appear to be perturbed in the region where the ion-pair interaction curve lies nearby while the $^3\Delta$ curves are unaffected, as expected. Let us assume that the two-photon process exciting the $3d$ level is actually $1\,^3\Delta_u \overset{2h\nu}{\leftarrow} 1\,^3\Sigma_u^+$. The only dipole allowed emissions from $1\,^3\Delta_u$ are $1\,^3\Delta_u \rightarrow 2\,^3\Pi_g$ and $1\,^3\Delta_u \rightarrow 1\,^3\Delta_g$. The dipole moment function for both transitions are zero asymptotically and are likely to be small everywhere except possibily in the region where the $^3\Delta_u$ state has its minimum. If that were so, the positions of the relevant curves suggest that the $1\,^3\Delta_u \rightarrow 1\,^3\Delta_g$ transition is more likely than the $1\,^3\Delta_u \rightarrow 2\,^3\Pi_g$ one. However, the $^3\Delta_g$ state is unlikely to populate the lasing $1\,^3\Sigma_g^+$ state. The only state to which $1\,^3\Delta_g$ can emit is the $1\,^3\Pi_u$ state which lies *deeper*[7,20–23] than the $1\,^3\Sigma_g^+$ state over a substantial range of internuclear separations which include much of the $1\,^3\Delta_g$–$1\,^3\Pi_u$ Franck–Condon region. Thus, the $1\,^3\Delta_u \rightarrow 1\,^3\Delta_g$ step is unlikely to lead to the $1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$ step.

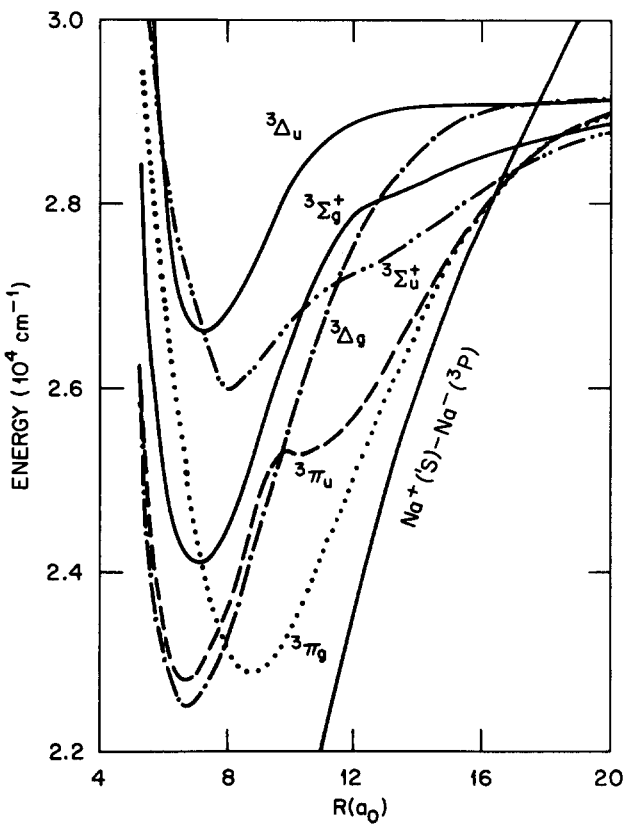

FIG. 12. The molecular states corresponding to Na($3d$) + Na($3s$) after Jeung (Ref. 24). Note the perturbation of the $^3\Pi$ and $^3\Sigma^+$ curves by our estimate of the ion-pair curve which corresponds to $Na^-(^3P) + Na^+(^1S)$.

The other possible cascade pathway $1\,^3\Delta_u \rightarrow 2\,^3\Pi_g \rightarrow 3\,^3\Sigma_u^+ \rightarrow 1\,^3\Sigma_g^+$ cannot be ruled out entirely. However, we deduce from Jeung's calculations[23] that the $3\,^3\Sigma_u^+$ state lies *higher* than the $2\,^3\Pi_g$ state over a wide range of separations, and so the $2\,^3\Pi_g \rightarrow 3\,^3\Sigma_u^+$ emission may be unlikely. (Since Jeung[23] used different basis sets and computational approaches to describe the low-lying state[22] of Na_2—including $2\,^3\Sigma_u^+$—and higher lying[23] ones—including $2\,^3\Pi_g$—conclusions are, of necessity, somewhat tenuous.) Nevertheless, neither $^3\Delta$ state formed from Na $3d$ + Na $3s$ is likely to help populate the lasing $1\,^3\Sigma_g^+$ state.

Let us assume that the initial two-photon excitation is indeed atomic in nature, and that in addition to the $^3\Delta$ and $^3\Pi_g$ states we have already discussed, $^3\Pi_u$, $^3\Sigma_g^+$, and $^3\Sigma_u^+$ states could be formed by collision with ground state atoms. While the $2\,^3\Pi_u$ state may emit to the $1\,^3\Sigma_g^+$ state, it is more likely to emit to the $2\,^3\Pi_g$ state within the $3s+3d$ manifold. Our previous experience with Li_2 suggests[19] that the $2\,^3\Pi_u \rightarrow 2\,^3\Pi_g$ transition dipole moment is *extremely* large in this region (we estimate 13–18 a_0) where these states have a substantial ion-pair component. Since these Π states are nearly degenerate in this region, they will have a substantial Franck–Condon overlap and emission probability. Thus, the $2\,^3\Pi_u$ state is unlikely to lead to the $1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$ lasing transition. Lastly the Σ^+ states, which will comprise about 20% of the molecules formed from Na $3d$ + Na $3s$ collisions, cannot be ruled out as a potential populator of the $1\,^3\Sigma_g^+$ state. We note, however, that the $Na^-(^3P)$–$Na^+(^1S)$ ion pair state, which as a Σ component is likely to have high emission probability at large internuclear separations. Any $1\,^3\Sigma_g^+$ formed at large internuclear separations will be highly susceptible to thermal dissociation.

In summary, we assert that the two-photon excitation process $1\,^3\Delta_u \overset{2h\nu}{\leftarrow} 1\,^3\Sigma_u^+$ is highly unlikely to produce the $1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$ lasing transition, and the odds are against the process $3d \overset{2h\nu}{\leftarrow} 3s$ followed by $3d$ + $3s$ collisions leading to that lasing transition.

Now let us address the question of why the two-photon excitation to $4s$, $5s$, $6s$ gives no lasing. If the excitation process is $3\,^3\Sigma_u^+ \overset{2h\nu}{\leftarrow} 1\,^3\Sigma_u^+$ then the lack of lasing is not easy to understand since $3\,^3\Sigma_u^+ \rightarrow 1\,^3\Sigma_g^+$ should be a relatively strong emission. An examination of Jeung's potential curves, however, shows that of the triplets corresponding to the $4s+3s$ asymptote, the $2\,^3\Sigma_g^+$ state lies *lower* than the $3\,^3\Sigma_u^+$ state so the process $3\,^3\Sigma_u^+ \rightarrow 2\,^3\Sigma_g^+$ is possible. The $2\,^3\Sigma_g^+$ state lies lower than the repulsive $2\,^3\Sigma_u^+$ state which corresponds to $3p+3s$ asymptotically. Thus, any $3\,^3\Sigma_u^+ \rightarrow 2\,^3\Sigma_g^+$ will not lead to the lasing $1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$ transition. However, our intuition suggests that the $3\,^3\Sigma_u^+ \rightarrow 1\,^3\Sigma_g^+$ should be relatively strong. In summary, we cannot presently account for the observed inefficacy of the

$4s \overset{2h\nu}{\leftarrow} 3s$ pump by arguments involving possible molecular emission processes. It appears, therefore, that the answer must lie in the initial excitation process. That the 5*s* and 6*s* excitations also fail to populate the upper state of the $1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$ transition reinforces the notion that the excitation process is the root cause.

It is relatively easy to accept why the so-called $5d \overset{2h\nu}{\leftarrow} 3s$ excitation which we take to be $5\,^3\Delta_u \overset{2h\nu}{\leftarrow} 1\,^3\Sigma_u^+$ would be less effective than the $4d \overset{2h\nu}{\leftarrow} 3s$ excitation (see Fig. 10) in populating the $1\,^3\Sigma_g^+$ state, since there are probably more dissipative channels connected with the $5\,^3\Delta_u$ state than the $3\,^3\Delta_u$ state. Note, in particular, that all of the $^3\Pi$ and $^3\Sigma^+$ states which correspond to the $5d + 3s$, $6s + 3s$, $5p + 3s$, and $4d + 3s$ asymptotes are expected to have even more substantial ion-pair perturbations than those shown in Fig. 12. Thus, these highly excited $^3\Pi$ and $^3\Sigma$ states are likely to undergo transitions at large internuclear separations to states which are just barely bound and which are, therefore, subject to facile thermal dissociation. In summary, the "5*d*" excitation has many dissipative channels in addition to the four-wave channel $5\,^3\Delta_u \rightarrow 3\,^3\Pi_g \rightarrow 3\,^3\Sigma_u^+ \rightarrow 1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$ which is likely to foster lasing.

Finally, the last feature of Fig. 2 is the narrow emission at ~840 nm which has been assigned as a satellite of the excimer emission by Dinev *et al.*[9] Detailed studies in this work show that the 840 emission is directed along the pump laser beam, and its frequency corresponds to $\nu_{3d-3s} - \nu_{\text{laser}}$. This is a special six-wave mixing process involving a virtual state of sodium at the laser photon energy as shown recently by Wang *et al.*[24] (see Fig. 1B). Similar studies involving this atomic parametric process were carried out earlier by Jackson and Wynne[25] using counterpropagating two-color experiments. Wang *et al.* further showed that superheating the alkali vapor resulted in a spectrum where the $1\,^1\Sigma_u^+ - 1\,^1\Sigma_g^+$ lasing in the region of 790 to 800 nm disappeared due to thermal dissociation of ground state sodium dimers. The excimer and 840 nm emissions were not affected by superheating of the alkali vapor. These studies of Wang *et al.*[24] and the results reported here show that the 830 nm excimer peak does *not* involve atom–molecule energy exchange as proposed by Dinev *et al.*[9] in populating the $1\,^3\Sigma_g^+$ state.

An emission centered at 855.5 nm was also observed in this study while tuning near the $5d\,^2D$ levels. This emission was first reported by Shahdin *et al.*[26] and originally assigned as the $1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$ transition. Since the 855.5 nm peak cannot be due to the lowest triplet transition, its origin is unknown. However, we have found that the 855.5 nm light is forward directed, and its frequency increases as the laser frequency decreases, which suggests this emission may be part of an atomic wave-mixing process similar to the 840 emission or part of a stimulated molecular or wave-mixing process between higher lying electronic states. It is conceivable that the 855.5 nm emission is part of the cascade terminating upon the $1\,^3\Sigma_g^+$ state.

Finally, at this point we have purposefully avoided referring to the 830 nm emission as part of a six-wave mixing process. Wave mixing is a parametric process which terminates on the state from which it originates. Since the 830 nm emission is very broad, this would require six-wave mixing over a range of internuclear separations corresponding to various points on the repulsive $1\,^3\Sigma_u^+$ curve. This is not an impossibility and may be attractive in view of the fact that the 830 nm emission is forward directed, which is indicative of a wave-mixing process. Direct proof of this mechanism would involve the observation of the other three emissions. Other emissions are seen in these studies, but inspection of Fig. 11 shows that some of the expected transitions probably lie at very long wavelength. Exact predictions of these wavelengths are difficult (Fig. 11 represents only one suggestion).

CONCLUSIONS

We have presented a detailed study of the $Na_2\ 1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$ excimer emission and proposed a mechanism for populating the upper $1\,^3\Sigma_g^+$ excimer laser state. We propose a purely molecular pathway of the type $1\,^3\Sigma_u^+ \overset{h\nu_L}{\rightarrow} \rightarrow 3\,^3\Delta_u \overset{h\nu_1}{\rightarrow} 3\,^3\Pi_g \overset{h\nu_2}{\rightarrow} 3\,^3\Sigma_u^+ \overset{h\nu_3}{\rightarrow} 1\,^3\Sigma_g^+ \overset{h\nu_{ex}}{\rightarrow} 1\,^3\Sigma_u^+$. Strong excimer emission was observed while pumping with two photons *near* the $4d\,^2D$ levels only. A second method (involving hybrid resonances) was also examined by tuning the laser near the 3*p*–4*d* transitions. Although strong ionization and SERS signals were recorded, no excimer emission was observed.

In addition, observations of the suppression of the direct two-photon excitation of the $3d\,^2D$ and $4d\,^2D$ levels in dense sodium vapor are reported. The suppression of multiphoton ionization is taken as further evidence for the model of Malcuit *et al.*[10] for the cancellation of two-photon excitation.

We have completed identical, and in some regards, more detailed measurements on lasing of K_2 at ~1.1 μm (bound–bound emission in this case), and the results completely coincide with our results presented here for Na_2. Bound–free excimer lasing has also been observed in Li_2 upon two-photon pumping *near* the $3d\,^2D$ state. Although we cannot prove yet that these emissions are due to $1\,^3\Sigma_g^+ \rightarrow 1\,^3\Sigma_u^+$, the energies and general shape of the emissions correspond to those calculated by Konowalow and Julienne[8] for Li_2 and Konowalow (unpublished) for K_2. These results will be published later but provide some confidence to the interpretation and validity of the results presented herein.

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[1] T. B. Lucatorto and T. J. McIlrath, Appl. Opt. **19**, 3948 (1980).
[2] W. Muller and I. V. Hertel, Appl. Phys. **24**, 33 (1981).

[3]Z. G. Wang, L.-J. Qin, L.-S. Ma, Q.-Q. Lin, and I.-S. Cheng, Opt. Commun. **51**, 155 (1984).
[4]K. K. Verma, J. T. Bahns, A. R. Rajaei-Rizi, and W. C. Stwalley, J. Chem. Phys. **78**, 3599 (1983).
[5]J. T. Bahns, K. K. Verma, A. R. Rajaei, and W. C. Stwalley, Appl. Phys. Lett. **42**, 336 (1983).
[6]G. S. Dinev, I. G. Koprinkow, and I. L. Stefanov, J. Phys. B **19**, 2735 (1986).
[7]D. D. Konowalow, M. E. Rosenkrantz, and M. L. Olson, J. Chem. Phys. **72**, 2612 (1980).
[8]D. D. Konowalow and P. S. Julienne, J. Chem. Phys. **72**, 5815 (1980).
[9]S. G. Dinev, I. G. Koprinkov, and I. L. Stefanov, Opt. Commun. **52**, 199 (1984).
[10]M. S. Malcuit, D. J. Gauthier, and R. W. Boyd, Phys. Rev. Lett. **55**, 1086 (1985); R. W. Boyd, M. S. Malcuit, D. J. Gauthier, and K. Rzazewski, Phys. Rev. **35**, 1648 (1987).
[11]G. S. Agarwal, Phys. Rev. Lett. **57**, 627 (1986); see also G. S. Agarwal and F. Rattay, Phys. Rev. A **37**, 3351 (1988).
[12]V. V. Krasnikov, M. S. Pshenichnikov, and V. S. Solomatin, JETP Lett. **43**, 148 (1986).
[13]E. A. Manykind and A. M. Afanas'ev, Zh. Eksp. Theor. Fiz. **52**, 1246 (1976) [Sov. Phys. JETP **25**, 828 (1967)].
[14]S. M. Hamadani, J. A. D. Stockdale, R. N. Compton, and M. S. Pindzola, Phys. Rev. A **34**, 1938 (1986).
[15]Qin Lijuan, W. Zugen, Z. Kechang, and Z. Yishan, Chin. Phys. **6**, 988 (1986).
[16]D. D. Konowalow and J. L. Fish, J. Chem. Phys. **76**, 4571 (1982).
[17]D. D. Konowalow and J. L. Fish, J. Chem. Phys. **77**, 435 (1983).
[18]D. D. Konowalow and J. L. Fish, J. Chem. Phys. **84**, 463 (1984).
[19]L. B. Ratcliff, J. L. Fish, and D. D. Konowalow, J. Mol. Spectrosc. **122**, 293 (1987).
[20]D. D. Konowalow and M. E. Rosenkrantz, J. Phys. Chem. **86**, 1099 (1982).
[21]W. J. Stevens, M. M. Hessel, P. J. Bertoncini, and A. C. Wahl, J. Chem. Phys. **66**, 477 (1977).
[22]G. H. Jeung, J. Phys. B **16**, 4231 (1983).
[23]G. H. Jeung, Phys. Rev. **35**, 26 (1987).
[24]Z. H. Wang, H. Schmidt, and B. Wellegehausen, Appl. Phys. B **44**, 41 (1987).
[25]D. J. Jackson and J. J. Wynne, Appl. Phys. B **28**, 238 (1982).
[26]S. Shahdin, B. Wellegehausen, and Z. G. Ma, Appl. Phys. B **19**, 195 (1982).