

## cw All-Optical Triple Resonance Spectroscopy

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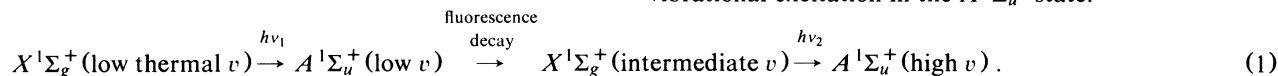
This paper reports for the first time continuous-wave, high-resolution, all-optical triple resonance spectroscopy. Using this technique, one can overcome the spin forbidden nature of a singlet-triplet transition and consequently unperturbed triplet rovibronic levels can be reached from a singlet ground state. This technique also facilitates state-selective population transfer to highly excited vibrational levels, both in the ground state and in excited states.

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Complete understanding of processes involving large internuclear distances (e.g., cold atom collisions) requires accurate knowledge of long-range potentials. Determination of these long-range potentials has been difficult due to the weakness of direct excitation to these levels from thermally populated ground-state levels near an equilibrium internuclear distance. In long-range molecular states most of the amplitude of the vibrational wave function is at large internuclear distances, leading to exceedingly small Franck-Condon factors with ther-

mally populated levels. Spin selection rules and the inversion selection rule (gerade $\leftrightarrow$ ungerade) in homonuclear diatomic molecules impose additional restrictions. For example, *unperturbed* levels of the  $b^3\Pi_u$  state of alkali dimers cannot be reached in a single electronic transition from the ground state. In this paper we report a new continuous-wave high-resolution technique to overcome these difficulties.

With regard to the  $\text{Na}_2 X^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$  system several cw techniques were previously developed to reach high vibrational excitation in the  $A^1\Sigma_u^+$  state:



In 1976 Kaminsky *et al.*<sup>1</sup> developed the modulated-population technique, the fluorescence-enhanced version of which led to increased nonequilibrium level populations in the ground state. Application of this technique to molecular beams by Gerber and Moller<sup>2</sup> and Tiemann<sup>3</sup> has made it possible to use these intermediate levels in the ground state to probe higher and higher vibrational levels in the  $A^1\Sigma_u^+$  state, up to  $v=184$  in the latter case. Using the technique of modulated-gain spectroscopy developed by Schweda, Chawla, and Field,<sup>4</sup> Chawla was able to observe levels up to  $v=105$  in the  $A^1\Sigma_u^+$  state.<sup>5</sup> Recently, Gaubatz *et al.*<sup>6</sup> have reported nearly 100% population switching from a specific rotational level of a vibrational level to an intermediate ground-state vibrational level using the stimulated Raman effect in a molecular beam.

Stimulated-emission pumping (SEP) has been widely used during the last decade<sup>7,8</sup> to study molecular spectroscopy and dynamics involving extreme vibrational excitation. In these experiments, however, pulsed lasers are normally used. The ratio of stimulated-emission rate to spontaneous-emission rate in an arbitrary mode is proportional to the number of photons in this mode. This ratio is typically a factor of  $10^7$  higher for pulsed SEP experiments than for cw SEP experiments.<sup>9</sup> Using cw

lasers, we demonstrate that high resolution can be achieved. Additionally, undesirable side effects of pulsed laser excitation, such as multiphoton processes, can be avoided. The excitation schemes of the all-optical triple resonance (AOTR) technique are illustrated in Fig. 1. The experimental arrangement involved three frequency-stabilized, single-mode tunable dye lasers with 1-MHz linewidth (Coherent Inc. 699-29) pumped by  $\text{Ar}^+$  and  $\text{Kr}^+$  lasers operating with various dyes ranging from rhodamine 590 to LD 700. Typical output powers ranged from 100 to 700 mW depending on wavelength. Normally either the pump or probe laser was modulated for phase-sensitive detection. Standard iodine calibration was used for absolute calibration of wavelengths. The dye laser beams were superimposed in a five-armed stainless-steel cross heat pipe (operated at 1–2 Torr) by optimizing the known optical-optical double resonance (OODR) signals<sup>10,11</sup> of  $\text{Na}_2$  within the dye ranges in question. For detection of the AOTR signal, total fluorescence was detected using a photomultiplier-tube filter set up at one side window. The opposing side window was used for single-fluorescence-channel detection with a Spex 1404 double monochromator.

Using the folded AOTR scheme of Fig. 1(a), we have

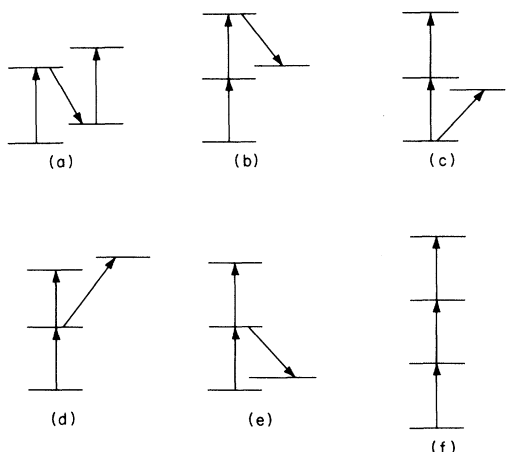


FIG. 1. All-optical triple resonance excitation schemes.

observed a region of the  $\text{Na}_2 A^1\Sigma_u^+$  state where previous data were not available using modulated-gain spectroscopy<sup>4</sup> covering the region  $v=40-61$ . Figure 2 illustrates the following combinations of excitations (L1,L2,L3) while the side fluorescence [laser-induced fluorescence (LIF)] was monitored: (a) Laser-induced fluorescence (L3 only on) of the small thermal population in  $v''=12$ . (b) Optical-optical double resonance (L2 and L3 on) where L2 depletes the small thermal population in  $v''=12$ . (c) Fluorescence enhanced OODR (L1 and L3 on) where the small fraction of fluorescence at the L2 frequency provides enhanced  $v''=12$  population. (d) All-optical triple resonance (L1, L2, and L3 on) where stimulated emission at the L2 frequency provides greatly

TABLE I. Term values (in  $\text{cm}^{-1}$ ) of selected vibrational-rotational levels in the  $A^1\Sigma_u^+$  state of  $\text{Na}_2$ , from the present work (AOTR) and the earlier modulated-gain study (MGS) (Refs. 4 and 5).

| $v$ | $J$ | AOTR       | MGS        |
|-----|-----|------------|------------|
| 55  | 10  | 20 110.066 | 20 110.067 |
| 56  | 10  | 20 186.855 | 20 186.855 |
| 56  | 12  | 20 190.500 | 20 190.567 |
| 57  | 10  | 20 262.816 |            |
| 57  | 12  | 20 266.426 |            |
| 58  | 10  | 20 337.952 |            |
| 58  | 12  | 20 341.559 |            |
| 59  | 10  | 20 412.140 |            |
| 59  | 12  | 20 415.696 |            |
| 60  | 10  | 20 485.533 |            |
| 60  | 12  | 20 489.046 |            |
| 61  | 10  | 20 558.032 | 20 558.047 |
| 61  | 12  | 20 561.521 | 20 561.533 |

enhanced  $v''=12$  population. This AOTR enhancement factor is 60%, 530%, and 2400% for cases where stimulated-emission pumping terminates in ground-state levels  $v''=8, 12,$  and  $21,$  respectively. In the  $v''=21$  case there is virtually no thermal population.

Some results from our AOTR experiment and the earlier modulated-gain experiments<sup>4,5</sup> are given in Table I. The folded AOTR scheme makes it possible to prepare state selectively virtually any ground-state level so that a third laser can be used to probe the desired regions of the  $A^1\Sigma_u^+$  state with high accuracy limited only by the frequency drift of the pump and dump lasers while the final

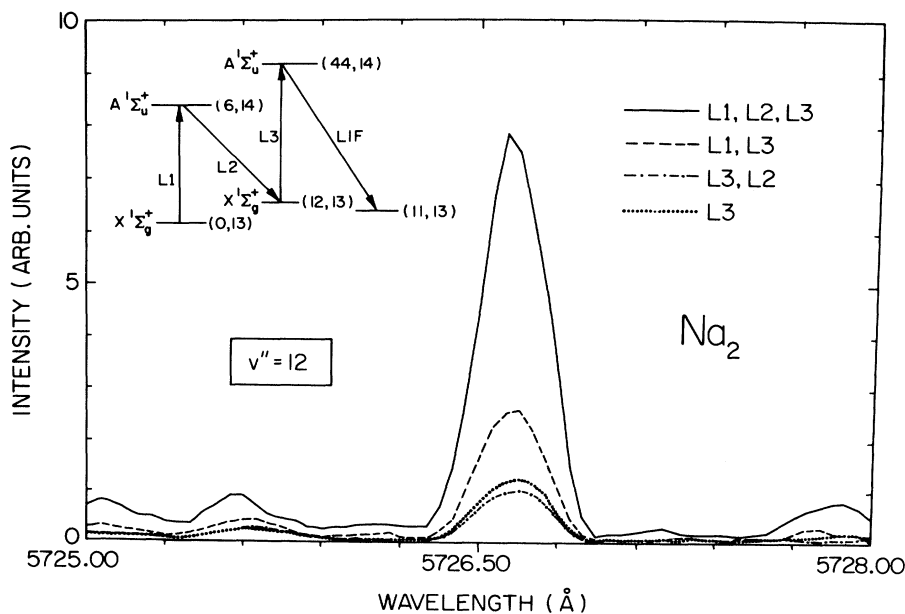


FIG. 2.  $\text{Na}_2 A^1\Sigma_u^+(44,14) \rightarrow X^1\Sigma_g^+(11,13)$  side-fluorescence signal (LIF) for various combinations of lasers 1, 2, and 3 (L1, L2, L3).

probe is scanned. Similar results can, in principle, be obtained using the modulated-gain technique, but one must then construct an optically pumped laser for each dump transition.

We illustrate the AOTR excitation scheme of Fig. 1(b) on  $\text{Na}_2 b^3\Pi_u$  spectroscopy. The unperturbed triplet levels cannot be reached from the ground state directly. The pump laser selectively excites a  $A^1\Sigma_u^+ \sim b^3\Pi_u$  perturbed intermediate level ( $v', J', \Omega'$ ) and the second laser further excites part of this population to a  $2^3\Pi_g$  level ( $v, J, \Omega$ ) (see Fig. 3). The third laser stimulates  $2^3\Pi_g \rightarrow b^3\Pi_u$  emission, detected by a decrease in the side fluorescence. The observed signals are sub-Doppler, leading to a high degree of accuracy equal to the accuracy of laser frequency measurement. Figure 4 illustrates the range of vibration covered in observations of over 350 new  $b^3\Pi_u$  levels (most of them are  $\Omega = 1, 2$  components) using this technique. The new  $b^3\Pi_u$  data together with the improved  $A^1\Sigma_u^+$  data are being used for deperturbation analysis and the results will be reported in detail later in separate papers.<sup>12</sup>

The AOTR excitation scheme of Fig. 1(b) has also been applied to  $A^1\Sigma_u^+$  spectroscopy via the OODR-populated  $4^1\Sigma_g^+$  state. An additional AOTR signal detection scheme involves single-fluorescence-channel detection simultaneous with the frequency scan of the dump laser. This fluorescence is in the  $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  system and monitors the population of the  $A^1\Sigma_u^+$  state produced by the dump-SEP step. Such results could be obtained with OODR followed by Fourier transform spectroscopy but at significantly greater cost.

The observed AOTR signals exhibit power broadening

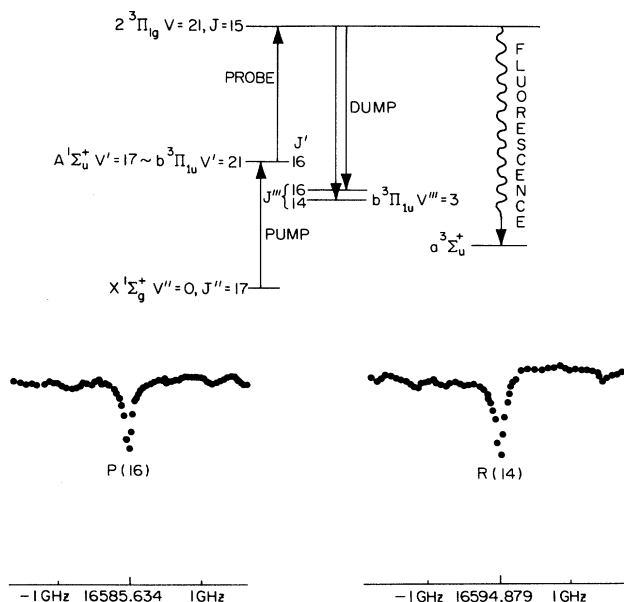


FIG. 3. A perturbation-facilitated OODR-SEP spectrum.

to varying degrees depending on the transitions involved. Since the Rabi frequencies<sup>14</sup> depend on both the electric dipole transition moment and the field strength for each of the three transitions, the typical sub-Doppler line-widths observed (FWHM) vary from 100 to 500 MHz. The theoretical analysis of triple resonance was presented by Petuchowski, Oberstar, and DeTemple<sup>15</sup> and by Bialynicka-Birula and Bialynicka-Birula.<sup>16</sup> Since the cw lasers used in our experiments involve relatively low laser powers, most contributions from Raman-type processes are small.

In summary, we have demonstrated a new cw, sub-Doppler, all-optical triple resonance technique. It has several powerful features. Population can be moved flexibly from the thermally populated region of the ground state to virtually any other region of the ground state. Spin-forbidden transitions can be studied by using perturbation-facilitated all-optical triple resonance techniques. In the OODR-SEP type of AOTR the need for resolved fluorescence measurements (following OODR excitation) using grating devices is removed, since the SEP step allows for the higher accuracy of frequency measurement. Generally one can achieve higher resolution in triple resonance spectroscopy with cw lasers than with pulsed lasers, and also eliminate the undesirable side effects of pulsed-laser work caused by higher peak powers, e.g., multiphoton processes. It is easy to extend the concept of cw triple resonance techniques to other multiple resonance techniques, each step adding more flexibility in terms of preparing molecules state selective-

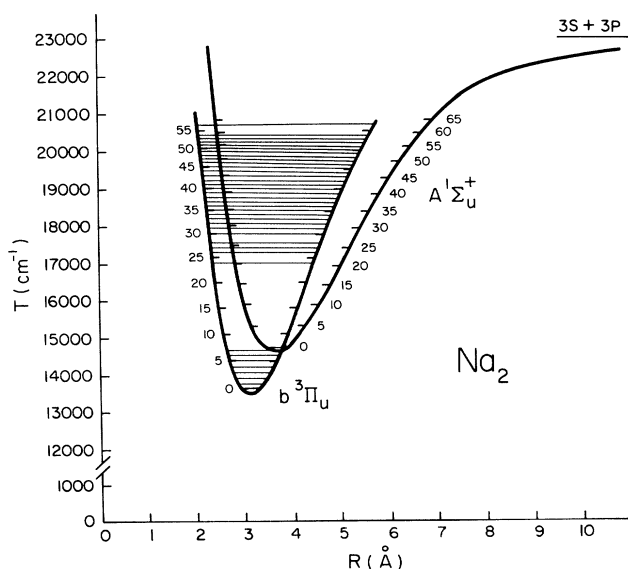


FIG. 4. Vibrational levels of the  $\text{Na}_2 b^3\Pi_u$  state newly observed by the perturbation-facilitated OODR-SEP technique. Vibrational levels  $v = 6-17, 21, 25, 28,$  and  $34$  were studied previously (Ref. 13) through their perturbations of the  $A^1\Sigma_u^+$  state.

ly, e.g., in long-range levels. Application of cw all-optical triple resonance to molecular beams is a very powerful technique for preparing molecules state selectively for dynamics studies. State-selective photodissociation has recently been observed in our laboratory in collaboration with Professor P. D. Kleiber and J. X. Wang using this technique.

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