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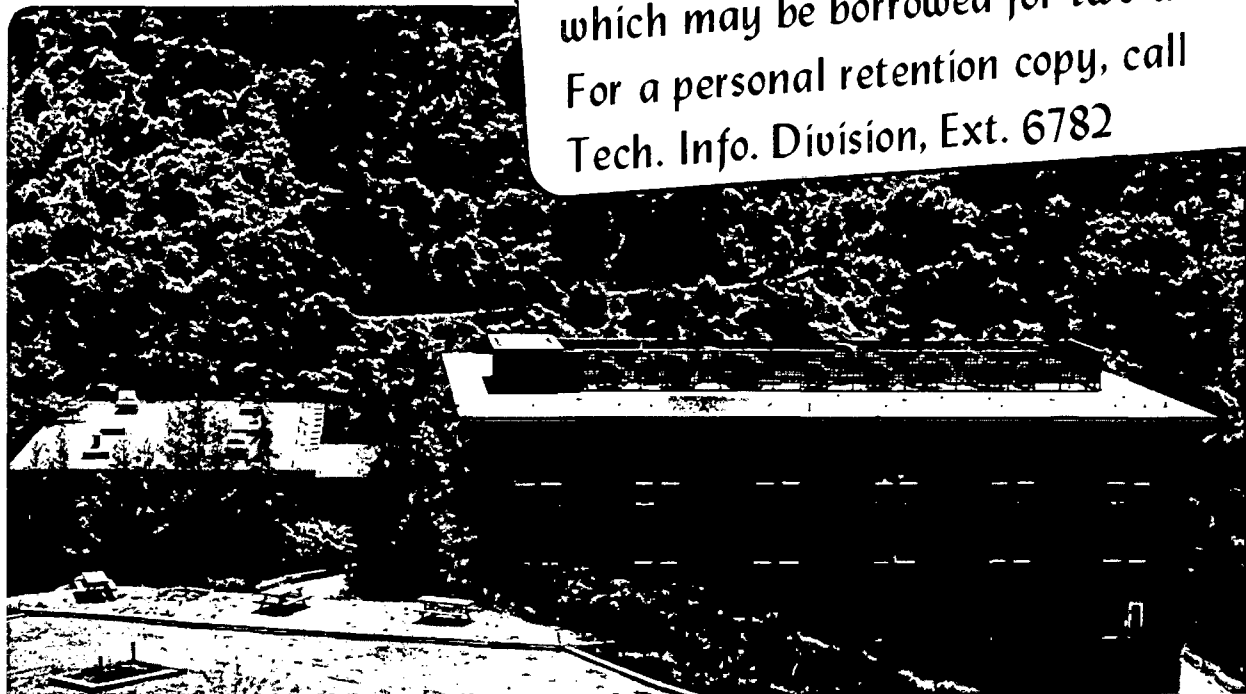RESONANT LIGHT ABSORPTION BY AN EXCITIVE
PENNING IONIZATION COLLISION

James H. Goble, William E. Hollingsworth,
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Resonant Light Absorption by an Excitive Penning Ionization Collision

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Abstract

We have observed the opening of a new channel of excitive Penning ionization by the collision complex absorption of laser light in the system $Ar^*(^3P) + Ca$. Two relatively broad bands at 5958 and 5990 Å were found, corresponding to the production of $Ca^+(5p\ ^2P_{3/2})$ and $Ca^+(5p\ ^2P_{1/2})$, respectively. Preliminary estimates indicate that the laser-assisted Penning ionization cross-section exceeds that of the field-free ionization to $Ca^+(4p\ ^2P_{3/2})$.

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A new category of related phenomena which has generated interest of late is the spectroscopy and dynamics of radiative processes involving the transient species which exists for the duration of a bimolecular collision. These processes are characterized by absorption or emission of light at wavelengths which are not resonant with the constituent elements of the transient species before or after the collision. Such has been the case for the polyatomic systems FNaNa* studied in emission[1] and KBrHgBr studied by absorption.[2] Diatomic transients have been used to study such phenomena as radiative energy[3-5] and charge[4,6,7] transfer, collisional fluoroescence,[4,8] photoassociation,[9,10] and Penning and associative ionization.[11]

This paper considers laser field-modified Penning ionization. This process, and radiative collisional ionization in general, has generated considerable theoretical interest.[12-15] The work of George and co-workers[15] in particular has indicated that the field-modified systems which Penning ionize in the absence of radiation may enjoy an enhancement of the ionization cross-section in the presence of the laser field. We report here the first observation of a resonant, field-modified excitive channel in the system $Ar*(^3P^o_2)$ + $Ca(^1S)$. The field-free fluorescent channels of this system (both Penning and associative ionization) have been previously reported.[16] The new channel described here,

$$Ar*(^3P^o_2) + Ca + h\nu \rightarrow Ar + Ca^+(5p\ ^2P) + e^-,$$
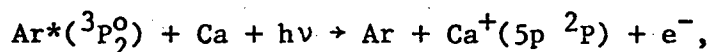
has been previously discussed as a likely one for the study of field-modified collisional ionization.[17] In this process, $h\nu$ equals (approximately) the energy difference between the metastable Ar reagent and the $5p\ ^2P$ state of the ionized Ca product, as illustrated in Fig. 1.

This system has been well studied in the field-free case[16] and is, with one exception, free of any atomic absorptions by reactants or products in the

wavelength region of interest, 5940-6000 Å. The exception is the two-photon

process $Ca(4s^2\ ^1S) \rightarrow Ca(4s5s\ ^1S)$ at 6001 Å which cascades by fluorescence

at 10 345 Å to $Ca(4s4p\ ^1P)$ followed by fluorescence at 4227 Å to the ground

state.

The new channel can be viewed as the excitive photoionization of the

(autoionizing) quasi molecule CaAr* from a continuum state to an excited (and

also unbound) state of $CaAr^+$ that correlates to $Ca^+(5p\ ^2P) + Ar(^1S)$. This

state of Ca^+ has a radiative lifetime[18] of 34 nsec. It decays predominantly

(80%) to the 5s level, which subsequently decays to the 4p doublet at 3737 and

3706 Å . We use these latter emissions to determine the number of 5p ^2P ions

formed (see Fig. 1).

The experiments were performed using the flowing afterglow chemiluminescence

apparatus described previously.[16] Briefly, a d.c. discharge in pure Ar near

1 torr generates $\gtrsim 10^9$ cm^{-3} Ar* $(^3P^o_2,\ 4s[3/2]^o_2)$ in the interaction

region 35 cm downstream from the discharge. Ca (at $>10^{14}$ cm^{-3}) was entrained

in a second flow of Ar around a radiatively-heated crucible containing Ca. In

the interaction region, a conical flame of $Ca^+(4p\ ^2P)$ and neutral Ca fluorescence

(the latter due to various secondary processes) was always present.

A Quanta Ray DCR YAG laser pumped a Quanta Ray PDL-1 pulsed dye laser

yielding tunable radiation of ca. 100 mJ per pulse with a pulse width $\gtrsim$ 10 nsec

at a rate of 10 Hz. The laser dye was Rhodamine 101. The laser bandwidth was

measured to be < 0.7 cm^{-1}, and wavelength scanning was performed by the dye

laser's grating drive without an etalon. Fluorescence at right angles to the

direction of the laser beam and the reagent flow passed first through a broad-

band filter centered at 4000 Å with a bandpass of 800 Å and then through a 0.25 m

monochromator which, without slits, functioned as a tunable bandpass filter

centered at 3740 Å. These measures effectively eliminated scattered radiation

from the Ca oven and the laser beam.

The filtered signal was detected by a dry-ice cooled RCA C31034 photo-multiplier, amplified by a PAR 1120 fast discriminator, and counted by both a gated Ortec 770 counter and an ungated Intel 8253 counter interfaced to a Commodore PET computer. The gated counter was enabled for 1 μsec after about a 10 nsec delay. The ungated counter monitored the background emission $(Ca^+(4p\ ^2P_{3/2}) \to (4s\ ^2S)$ at 3934 Å) which was responsible for 30% of the gated signal. Signal at each wavelength was accumulated for 1200 laser shots, or 2 min.

The raw gated counter signal was processed as follows. The ungated counter signal (2–5×10^6 counts/2 min) times the duty cycle of the gated counter (10^{-5}) was subtracted from the raw gated counter signal. This value was normalized by the ungated signal (to normalize the fluctuations in the Ca density) and by the monitored laser power. The final spectrum[19] is shown in Fig. 2, where error bars represent the statistical uncertainty of the gated counts ($\pm$ one standard deviation). The signal rate was very low for even the most prominent feature. The peak at 5958 Å in Fig. 2b corresponded to a gated count of 78, 18 of which are background, yielding a signal to background ratio of 3.3:1. It was verified that the signal, as weak as it was, did not appear unless both the Ar* and Ca reagents were present.

It is conceivable that $Ca^+(5s\ ^2S)$ could be formed directly, with the excess energy of the photon going into Penning electron kinetic energy, but since the lifetime of this state is 5 nsec, any formed directly would have completely decayed before gated counting began. Similar lifetime arguments hold for laser enhancement of the 4p level. Emission (at 3159 and 3179 Å) from 4d ^2D levels occurs outside the bandpass of our filter-monochromator. Thus our experiment is sensitive to the 5p ^2P cascade exclusively.

The peak at 5991 Å could be attributed to two-photon excitation of Ar* to the 14d Rydberg levels. Such levels could have long enough radiative lifetimes to ionize Ca to a level with a fluorescence cascade we would ultimately monitor. We have estimated[21] by a quantum-defect calculation the energy levels (to $\pm$ 1 cm^{-1}) for J = 0, 2, and 4 of the ns and nd series (n = 15-20) that could be two-photon connected to Ar* $^3P^o_2$. We find that none of these possible excitations appear in our spectrum, nor would they interfere with the bluer band in Fig. 2. We therefore dismiss this process as a source of our signal.

Perhaps the most remarkable aspect of Fig. 2 is the resonant behavior of the signal. If we view this phenomenon as photoionization of a quasi molecule, we would anticipate, as we scanned the laser from red to blue, to see a stepwise increase in the signal as first the $^2P_{1/2}$ and then the $^2P_{3/2}$ channel opened. Although there is some signal to the blue of each band, it is apparent that a simple photoionization picture is too naive, and that resonant excitation of the 5p ^2P level, with very little kinetic energy going into the ejected electron, is more important in describing the process. (Measurements 100 Å to the red of the long wavelength band satisfied us that no signal was present on the long wavelength side. Onset of signal at the red limit of this band was obscured by the Ca two-photon signal.)

Table I lists the transition resonances and their full width at half maximum bandwidths, along with the anticipated transition frequencies based on asymptotic energy differences of the atomic states. Although we list two maxima for the $^2P_{1/2}$ excitation, the statistics of the data do not warrant the resolution of this band into a doublet; we note the average position (16 691 $\pm$ 5 cm^{-1}) parenthetically in the Table. The maxima occur very close to the asymptotic energy differences, with the $^2P_{3/2}$ signal about 7 cm^{-1} to the blue of its

expected location. This shift is not exceptional, compared to the observed 68 cm^{-1} blue shift of laser-assisted charge transfer.[6] The wide bandwidths of 11-14 cm^{-1} are characteristic of a collision complex absorption,[3a] corresponding to an energy uncertainty due to Harris' fly-by time,[3c] or, equivalently, to the Franck-Condon envelope of a Boltzmann distribution of translational states involved in a free-free transition. We believe that these properties support our premise that we are observing a collision complex absorption process.

It is difficult to make an accurate estimate of the laser-assisted collision cross-section. The field-free cross-section[16] for production of $Ca^+(4p\ ^2P_{3/2})$ is 28 $Å^2$. If we scale this value by the ratio of the peak laser-assisted count rate ($\sim 2-4 \times 10^4\ sec^{-1}$), we can estimate the laser-assisted cross-section to be $\sim 4.6 \pm 2.3 \times 10^3\ Å^2$ at our power density of $\sim 10^7\ W/cm^2$. Cross-sections of similar magnitude have been reported for collisional energy transfer,[3b,4] but at hundreds of times higher power densities. Our scaling ratio should also be corrected by factors accounting for the beam-flame intersection fraction and the relative transmission ratio of the broadband filter-monochromator combination, but such factors are probably close to unity. We therefore cautiously conclude that the field-assisted process has a much higher probability of occurring than does the field-free process at our laser power.

In summary, we have observed a new excitive Penning ionization channel driven by laser excitation of the nascent chemi-ionizing collision complex, Ar* + Ca, yielding $Ca^+(5p\ ^2P_J)$. A small blue-shift of the signal from the expected asymptotic location was observed with a cross-section which exceeded that for the field-free excitation of $Ca^+(4p\ ^2P_{3/2})$.

TABLE I

Anticipated and observed transitions for laser-assisted excitive Penning

ionization of calcium by metastable argon

Ca State	5p $^2P_{1/2}$	5p $^2P_{3/2}$
λ (Å)	5991, 5988	5988
ν Observed (cm^{-1})	16687, 16695 (16691 ± 5)	16780
ν Expected (cm^{-1})	16695.19	16773.44
Bandwidth (cm^{-1})	5.6, 13.9	11.3

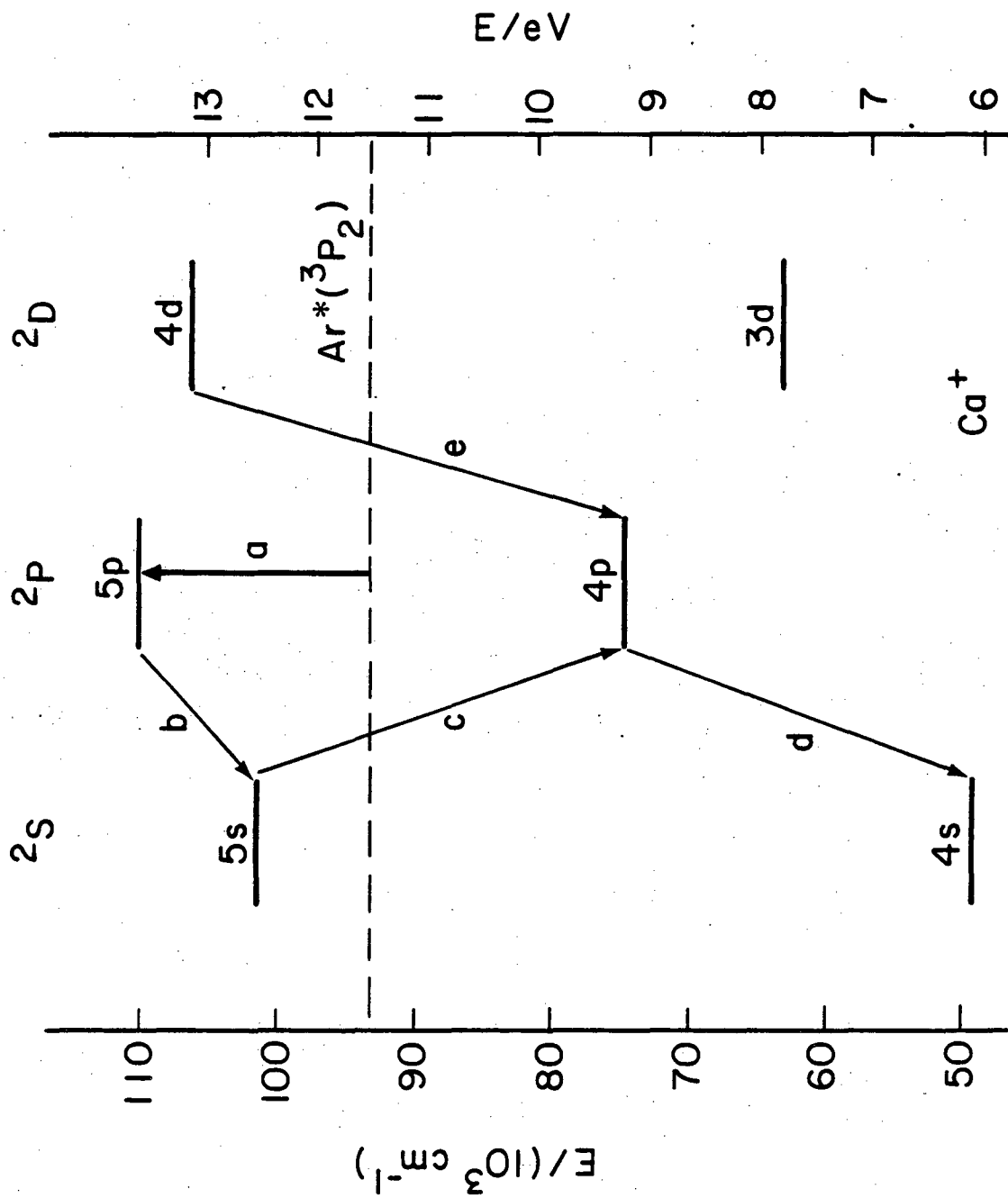## Figure Captions

Figure 1.   Energy level diagram for $Ca^+ + Ar$ relative to $Ca(4s^2\ ^1S) + Ar(^1S)$. The dashed line locates the energy of $Ar^*(^3P^o_2)$. Wavelengths (in Å) of the transitions are: (a) 5958, 5988; (b) 11 836, 11 947; (c) 3706, 3737; (d) 3934, 3968; (e) 3159, 3179, 3181. Energy level values are from Ref. 20.
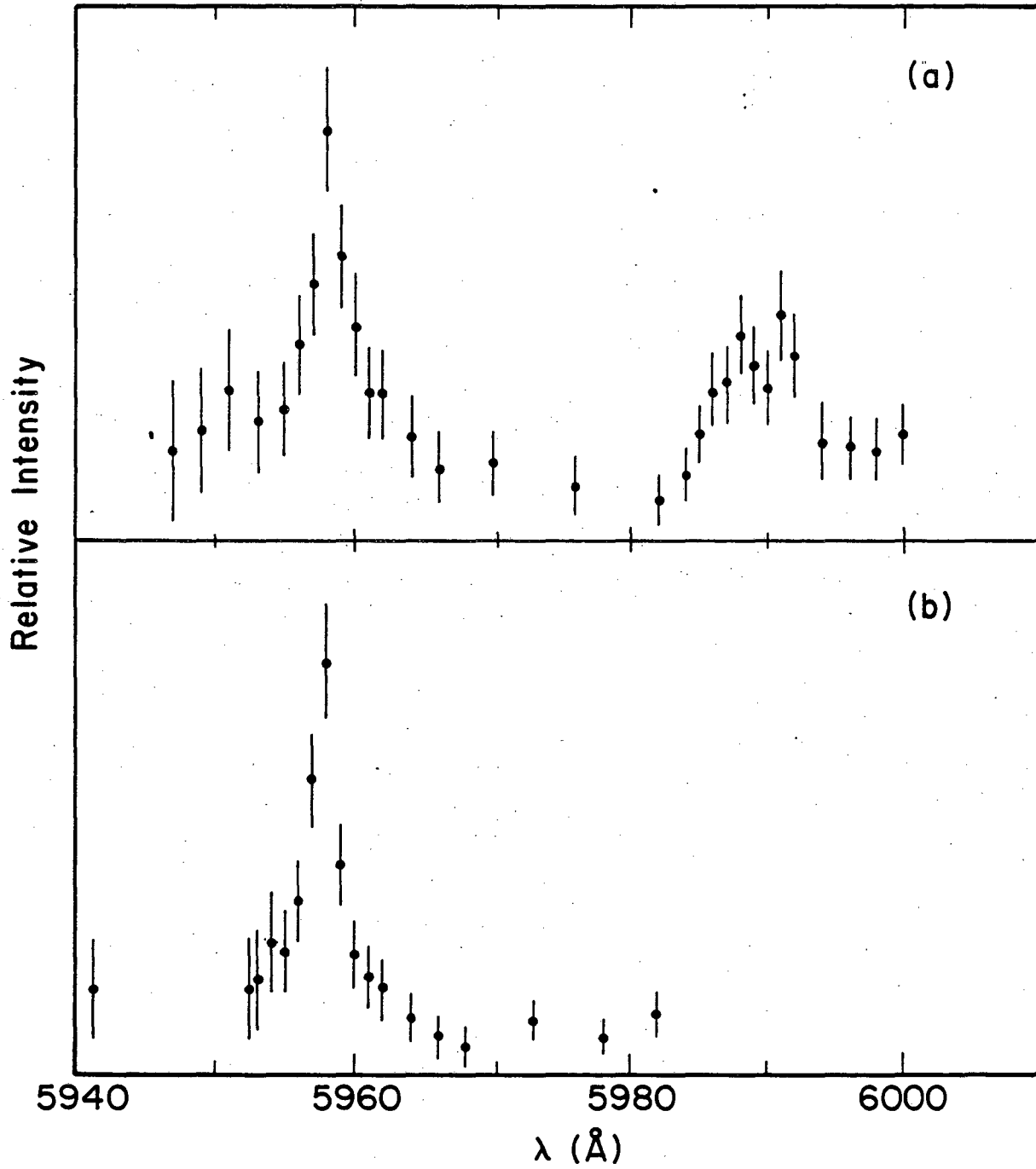
Figure 2.   Laser excitation spectrum of $Ca^+(5p\ ^2P)$ fluorescence resulting from $Ca + Ar^* + h\nu$ collisions. (a) Complete excitation spectrum. (b) Second scan of blue portion of spectrum to illustrate the degree of reproducibility. Error bars represent $\pm$ one standard deviation due to counting statistics.

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19. Not shown is the signal at 6001 Å from the 4227 Å fluorescence cascade of the two-photon excitation of Ca. Although our bandpass filter/monochromator arrangement should, in principle, interdict this signal, the fluorescence is so strong that scattered light within the monochromator produced a signal several times stronger than the data shown in Fig. 2.

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