

Multiphoton Ionization of Molecular Cesium with a Tunable Dye Laser*

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This paper reports the observation of the two-photon ionization of molecular cesium as a continuous function of laser wavelength in the 6200–6600-Å region with a tunable dye laser having a 0.18-cm^{-1} linewidth. To the author's knowledge, it serves to illustrate the first extension to neutral molecular species of the important techniques of resonant multiphoton photodetachment spectroscopy. The resulting two-photon photoionization spectrum is interpreted in terms of the vibrational structure of the resonant intermediate molecular state.

I. INTRODUCTION

Recent attention^{1–3} has been focused upon the multiphoton ionization of atomic cesium because of the relatively fewer number of photons required to ionize at available laser wavelengths. This, in principle, provides the most tractable comparison with theory.^{4,5} However, the importance of a molecular component to the studies has been suggested in recent letters,^{6,7} and it may be expected that depending not only upon the molecular- to atomic-concentration ratios, but also upon the relationship of the laser wavelength to potentially resonant intermediate states of Cs_2 , such molecular contributions could dominate multiphoton ionization in cesium. Some corroboration of this point is found in the recent report⁸ of significant two-photon ionization from low-power irradiation at the helium-neon wavelength, 6328 Å, which falls in the Cs_2 6250-Å ($X^1\Sigma_g^+ \rightarrow C$) absorption-band system.

The present paper reports the observation of the two-photon ionization of molecular cesium as a continuous function of laser wavelength and hence as a function of the identity of the resonant intermediate states. To the authors' knowledge, it serves to illustrate the first extension to neutral molecular species of the important techniques of resonant multiphoton ionization spectroscopy introduced by Lineberger and Patterson⁹ in recent studies with a tunable dye laser of the resonant photodetachment spectrum of C_2^- . In extending these techniques spectral resolution has been improved over an order of magnitude with laser linewidths being reduced from about 2.7 to 0.18 cm^{-1} . Signal-to-noise ratios have benefited greatly from the resulting increase in spectral density.

Further system improvements have resulted from the use of space-charge detection of the ions, with the result that the examination of multiphoton ionization spectra is now as readily instrumented as conventional single-photon absorption spectroscopy. This paper presents the details of this technique and reports the results of its use in the investigation of the two-photon photoionization spectrum of Cs_2 .

II. EXPERIMENTAL APPARATUS

As previously suggested,¹⁰ the tunable dye laser was found to be the light source of highest spectral density and thus the most suitable for multiphoton processes which depend upon the square or higher power of the intensity within the atomic or molecular linewidth for absorption. To optimize the peak power the dye laser was operated in the pulsed mode and pumped with a nitrogen laser delivering 50 kW to the dye. Pulse widths were of the order of 15 ns and repetition rates were 8 s^{-1} , as limited by drift times for ions within the space-charge detector. The dye laser was operated with a Cresyl Violet, Rhodamine 6G, Rhodamine B, and HCl mixture and then continuously tuned with a 0.18-cm^{-1} bandwidth through the wavelength range from 6200 to 6600 Å. These wavelengths correspond to the relatively weak 6250-Å ($X^1\Sigma_g^+ \rightarrow C$) absorption band of Cs_2 and were selected as a test of technique. Stronger transitions to intermediate states are to be found in the $1.06\text{-}\mu$ region. Laser power was varied downward from the order of 5 kW during the course of the experiment.

The laser beam was focused into a cesium cell in which space-charge detection of the products

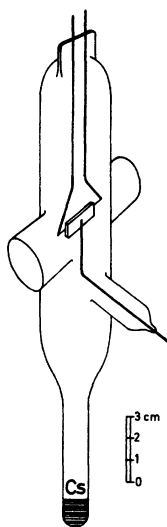


FIG. 1. Schematic diagram of the cesium diode which served as the absorption cell in these experiments.

of photoionization and associative ionization has been shown to extend the sensitivity of classical atomic absorption spectroscopy by several orders of magnitude.¹¹⁻¹⁴ In contrast to the techniques of standard absorption spectroscopy which are based on the measurement of relatively small attenuations of large signals, the method used in this and the previously cited works is based on the detection of positive ions produced either directly or indirectly by the photon absorptions. The positive ions produced in this way enhance the output signal of a thermionic diode containing the absorbing gas by partially neutralizing the negative space charge surrounding the heated diode filament. No external collection voltages are applied to the diode. The relatively long time which the positive ions spend traversing the potential well of the space-charge region provides for the release from that region of 10^4 – 10^6 electrons per ion.¹⁵ Essentially this technique, when coupled with tunable pulsed laser excitation, represents a modernization of early experiments on

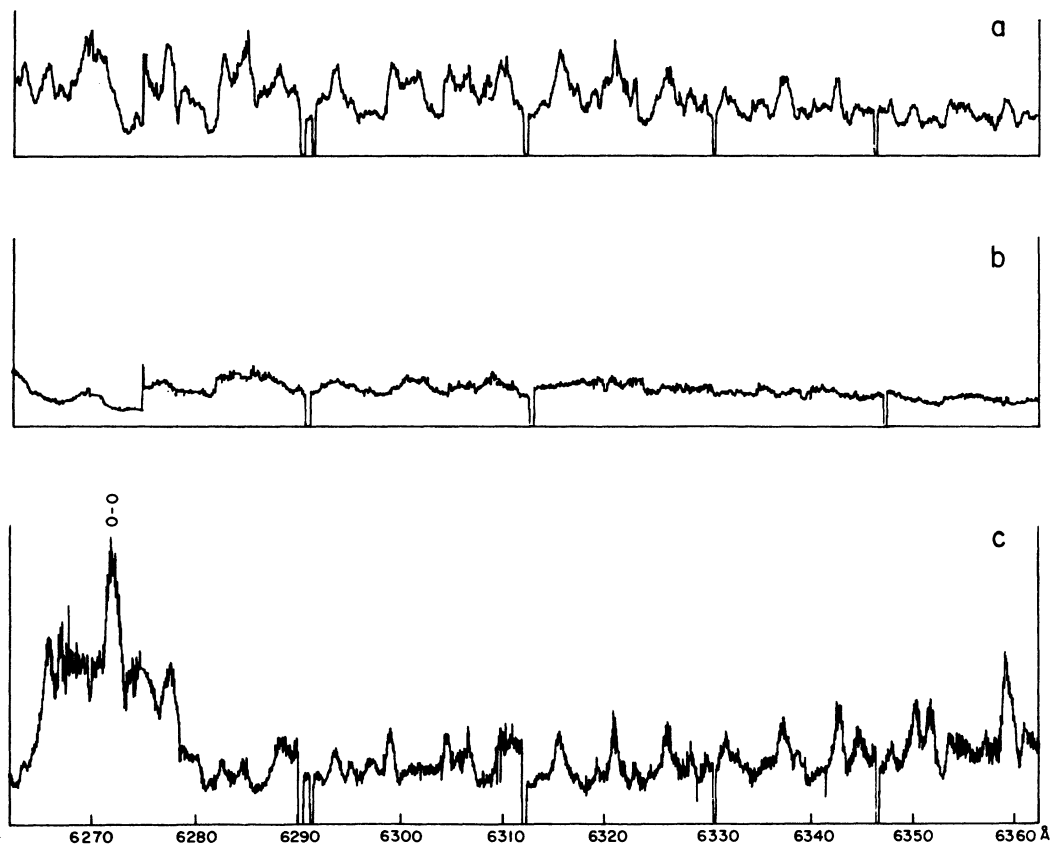


FIG. 2. Photoionization spectra as a function of laser wavelength for the region corresponding to the 6250-Å band system of Cs_2 . Short intervals of negligible signal result from removal of excitation for zero verification. (a) Photoionization current from the cesium diode as a function of laser wavelength. (b) Intensity spectrum of the dye laser beam used to illuminate the cesium diode. (c) Ratio of the photoionization current of (a) less dark current to the square of the laser intensity of (b).

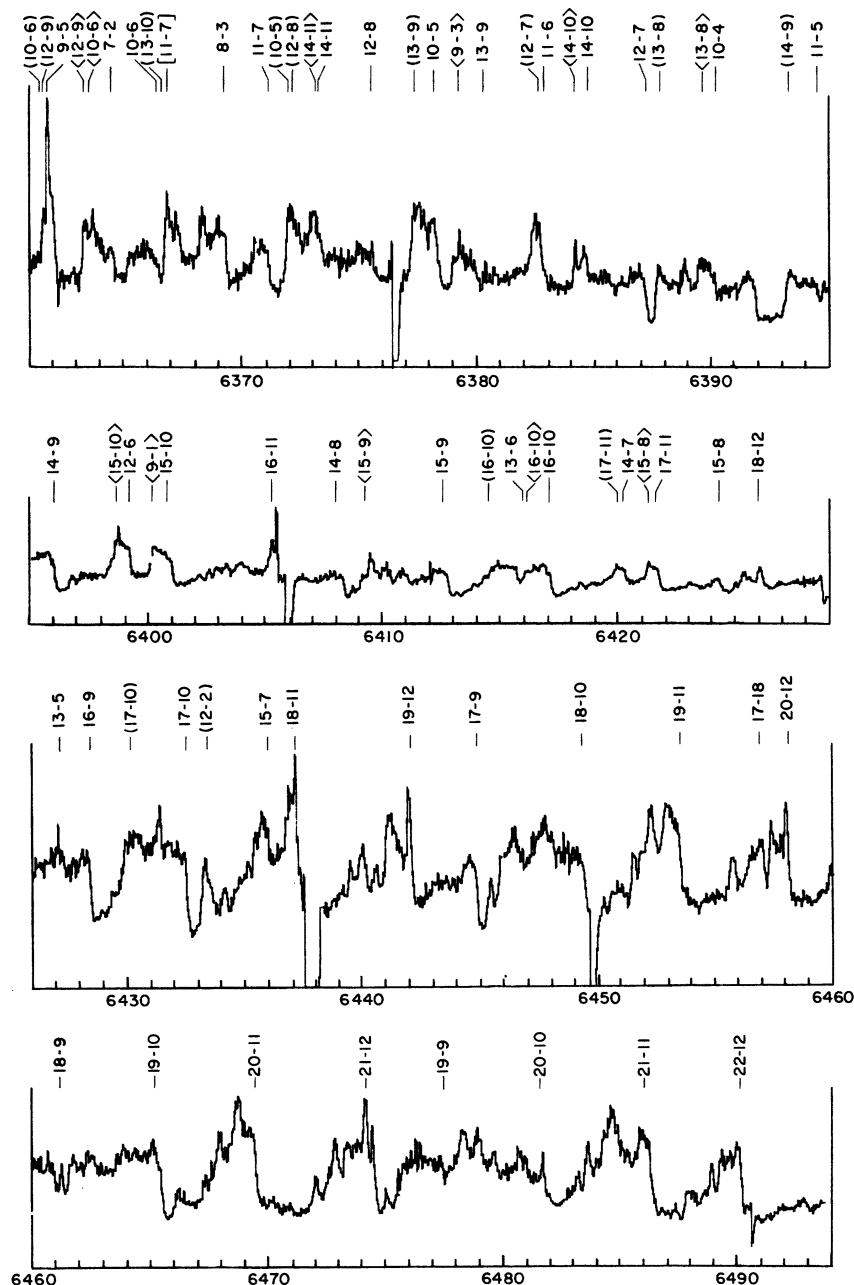


FIG. 3. Photoionization current as a function of laser wavelength for the four consecutive 34-Å segments indicated. The ratio of signal less dark current to the square of the laser intensity is shown. Band heads of the transitions in the 6250-Å system to the intermediate state are identified by the corresponding vibrational quantum numbers shown according to the scheme v'' , v' . The shape of the brackets identifies the red degraded band heads as identified in Ref. 21 with () brackets for heads in the Q branch, < > brackets for heads in the R branch, and [] brackets for heads in the P branch. The vibrational numbers without brackets correspond to the violet degraded band heads. The last two curves have been drawn to a scale three times larger than the previous two curves.

photoionization¹⁸⁻¹⁹ and is now sufficient to allow detection of ion signals as small as a few ions per second.

The particular experimental absorption cell used in these molecular cesium studies is shown in Fig. 1. It was made of Pyrex glass with quartz windows and filled with cesium vapor at a pressure controlled by a two-chamber oven according to standard techniques.¹³ The diode included in the cell consisted of a 0.15-mm-diam tungsten-wire filament and a silver-disk anode, both properly activated with cesium and separated by 1.5

mm. They were aligned so that the conduction path lay transverse to the optical axis. The exact position of the focal volume within the diode structure was not found to be particularly critical, and only required that the positive ions produced by the absorption process under investigation be able to diffuse or drift into the space-charge cloud surrounding the filament.

To obtain the best signal-to-noise ratios, it was necessary to optimize the laser repetition frequency in terms of transit times of the ions. The optimum was found to lie in the range 8-20 Hz,

in agreement with measured²⁰ diffusion coefficients of cesium ions Cs^+ and Cs_2^+ in cesium at the working pressure range corresponding to saturated vapor at temperatures of 490 °K. Under these conditions the number density of cesium atoms was $3.1 \times 10^{15} \text{ cm}^{-3}$, while that of molecular cesium Cs_2 was $7.8 \times 10^{12} \text{ cm}^{-3}$. Optical filament temperatures were of the order of 1100 °K for the detecting diode.

Simultaneous digitization of the diode output signal and input laser intensity was provided by an on-line data-acquisition computer system. It additionally supplied the pulse train necessary to advance the laser wavelength in 0.05-Å steps after the proper sampling time had elapsed. An integration time corresponding to the order of 60 laser pulses per wavelength step was found to provide sufficient signal-to-noise recovery.

III. RESULTS

Figure 2(a) shows the photoionization signal from the cesium diode as a function of laser wavelength for the region corresponding to the peak of the Cs_2 ($X^1\Sigma_g^+ \rightarrow C$) absorption band. Figure 2(b) shows one of the principal difficulties of the system, namely, the variability of the dye laser output. In this recording the intensity of the dye laser beam has been digitized simultaneously with the diode signal shown in Fig. 2(a). The effect was that the small-scale variations of intensity of the dye laser were found to be removed from the photoionization signal if the latter was divided by the square of the former, the dark current of both signals having been removed. Figure 2(c) shows the resulting photoionization efficiency obtained in this way by dividing the data. Except for signal-to-noise ratio, the spectrum shown was found to be invariant with respect to variations in laser beam positioning and alignment. It is in good agreement with the extensive analysis of the 6250-Å band system obtained by conventional absorption techniques.²¹

A more detailed examination of this agreement is found in the four segments of Fig. 3, each of which shows a 34-Å region of the photoionization spectrum. Emphasis has been placed upon the longer-wavelength portion of the band, as indicated, because the congestion of structure near the band origin at 6250 Å prevents an adequate resolution of all features by a light source with 0.18-cm^{-1} bandwidth. Transitions from successive vibrational levels are more readily separated in the wavelength region shown. Identification of the vibrational structure has been included in Fig. 3 to the extent that band origins are available from the literature. Particularly good agreement can be seen with the band heads cited by Kusch and

Hessel,²¹ as their criteria for tabulation included the requirement that the structure have a clearly recognizable band head and be degraded either to the red or violet. Complex structures resulting from the overlap of bands corresponding to several different vibrational transitions were not listed in their analyses and no attempt to decompose them has been made in the present work. Such features appear in Fig. 2 without identifying notation. Additional bands, previously unreported, seen to the red of the $\nu = -10$ series are in qualitative agreement with the wavelengths expected from available vibrational spacings.²¹

Fig. 4 gives the observed dependence of the photoionization signal on laser intensity typical of the features of Figs. 2 and 3. Plotted in each case are data without dark current and scaled by a constant to facilitate comparison. For each component examined the slope K was found to be 2, the minimum number of photons required for ionization,²² and provides the justification for the scaling of the spectra of Figs. 2 and 3 by the square of the laser intensity. As would be expected, at these relatively low laser powers no evidence of saturation was observed.

As can be seen from Fig. 3 most of the photoionization signal corresponds to the identifiable structure of the regular absorption spectrum to the intermediate state nearest in energy to the laser wavelength. This is in agreement with the general theoretical expectations^{4,5} which require the multiphoton ionization rate to depend on sums of terms of the form

$$[(E_1 - E_0 - n\hbar\omega)^2 + \Gamma_1^2]^{-1},$$

where E_1 is the energy of a near-lying intermediate state, E_0 is the energy of the ground state,

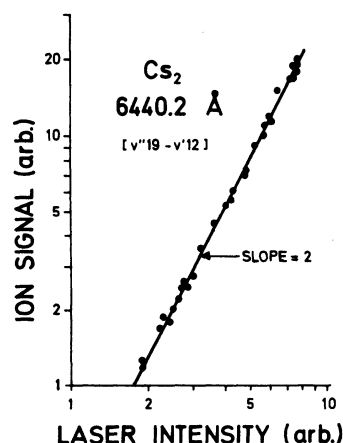


FIG. 4. Photoionization current as a function of the laser intensity for the [19,12] transition, typical of the features shown in Figs. 2 and 3.

Γ_l is the width of the l th state, and n an integer less than the minimum number of photons necessary to ionize the system. Essentially it is the position of the intermediate state in the energy-level scheme with respect to the single-photon energy that contributes the structure to the spectrum seen in the figures. For wavelengths below 6525 Å, the second photon required to ionize the resulting intermediate state for detection adds no further resonances to the spectrum, since it has more than the requisite ionization energy, even assuming the largest of the values for ionization potentials (3.80 eV) reported²² for Cs₂.

The residual base photoionization signal seen in Fig. 1 to underlie the discrete spectra may either be attributed to blurring of the spectra as a consequence of summation over transitions through the large number of close intermediate

states available to the molecular system, or to the multiphoton ionization of the more abundant atomic cesium in the absence of resonant intermediate levels for a two-photon ionization.

This experiment shows two-photon ionization spectroscopy to be a useful tool in the understanding of multiphoton ionization in cesium. Clearly, for laser wavelength in the 6200–6500-Å region the dominant process for such ionization in cesium vapor is the two-photon photoionization through the intermediate C state of the cesium molecule at the equilibrium fractions of Cs₂ corresponding at least to 490 °K. Moreover, because of the highly resonant nature of such excitations through intermediate states, the availability of tunable dye lasers of high spectral density now makes multiphoton ionization spectra as readily obtainable as conventional single-photon spectra.

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