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## Two-Photon Technique for the Dissociative Spectroscopy of Simple Molecules

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A two-photon technique is reported for the measurement of relative cross sections for the photolysis of simple molecules into particular product channels. In a demonstration of this method, two independently tunable dye lasers were used to dissociate molecules of Cs<sub>2</sub> sequentially for wavelengths in the range 445 to 505 nm, and then to excite the resulting products to determine the relative cross sections for the photolysis of the Cs<sub>2</sub> molecules into each of the energetically possible product states.

Historically, it has been the conventional techniques of absorption spectroscopy that have contributed most heavily to the understanding of the structure of simple molecules. However, the successes of these methods have been generally limited to the study of bound states. Comparable studies by conventional means of transitions to repulsive and dissociative states have usually led to featureless absorption continua and, thus, have not resulted in the depth of understanding that has been reached with the well-bound states of molecular systems.

The recent efforts which have developed in laser chemistry and laser isotope separation have tended to refocus spectroscopic interests upon these less tractable dissociative states. For example, if it is intended to activate selectively an isotopic or reactive species, photodissociation of a parent molecule appears, at first, to be a nearly ideal mechanism. Unfortunately, the practical application of such techniques generally requires detailed knowledge of the dissociative

state to be excited, of the states of the products with which it is correlated, and of the dynamics of the dissociation process which determine the extent to which the product channels might be mixed by crossings of the potentials describing long-range forces. The examination of spontaneous fluorescence from the products of laser-induced photolysis provides some of this information but it is generally susceptible to uncertainties in the unique identification of product channels unless the fluorescence lifetimes of the dissociation products are much less than the characteristic times for collisional mixing of the states, as was the case in the classical measurement<sup>1</sup> of the various partial cross sections for the photolysis of H<sub>2</sub>.

The work reported here concerns the demonstration of a sequential, two-photon technique for the study of laser photolysis. It is based on a multiphoton process originally observed in H<sub>2</sub> by LuVan *et al.*<sup>2</sup> and independently demonstrated by Collins *et al.*<sup>3</sup> In particular, it was found in

those works that a multiphoton absorption could occur with high probability through a resonant intermediate state that was unstable against dissociation on the time scale of the multiphoton process. Two-photon ionization spectra of  $\text{Cs}_2$  showing resonances for the absorption to a dissociative state followed by absorption from an excited state of a product Cs atom were reported in 1974.<sup>3</sup> Subsequently such hybrid resonances were reported in Rb,<sup>4</sup> K,<sup>5</sup> In,<sup>6</sup> and Yb,<sup>7</sup> but in all cases the results were limited to resonances which could be excited by multiple photons of the same frequency.

The appearance of the hybrid resonances in dispersion curves of photoionization takes the typical form of a Rydberg series of discrete absorption lines from excited atomic states that are modulated in intensity by the probabilities for the molecular part of the absorption leading to dissociation of the parent dimer. It was suggested<sup>3</sup> in one of the first reports of this phenomenon that the envelope contributed by the molecular part could be isolated and studied as a function of wavelength by use of photons from separately tunable lasers. Furthermore, if the lasers were pulsed, operating for a period short compared with the inverse collision frequency of the dissociation products with the components of the absorbing vapor, the diffuse molecular bands which were found could be uniquely correlated with their dissociation products.

It was the purpose of the work reported here to demonstrate this multiphoton technique by resolving the absorption cross section of  $\text{Cs}_2$ , which appears to be a continuous function of wavelengths in the blue region of the spectrum,<sup>8</sup> into its component cross sections for photolysis into particular product channels. In the absence of thermal excitation of the parent  $\text{Cs}_2$  only four possible products,  $6^2P_{1/2}$ ,  $6^2P_{3/2}$ ,  $5^2D_{3/2}$ , and  $5^2D_{5/2}$ , conserve energy when the illuminating wavelength is greater than 460 nm. The relative cross sections for the production of each were determined in this work in an environment which was essentially free from collisions that might tend to mix the channels for dissociation on the time scale of this experiment. The sensitivity and resolution which were achieved appear to indicate that the multiphoton technique introduced here can be of significant utility to photolytic spectroscopy.

The apparatus used in this work was developed and described by Anderson.<sup>9</sup> Basically, it consisted of two independently tunable dye lasers

pumped by a single pulsed nitrogen laser. The output beams from the dye lasers were aligned to be spatially collinear, but were temporally dispersed so that the one used to dissociate the population of parent molecules arrived first at the absorption cell by about twice the duration of the pulse. Provisions were available for the adjustment of the temporal separation of the pulses but the results were not found to be particularly sensitive to this variable unless the order of the occurrence of the pulses was reversed. As expected, with the reversed temporal sequence the effect was completely absent. The linewidth of the output from the dye lasers was of the order of 0.01 nm and corresponded approximately to the resolution with which the wavelength could be set.

The occurrence of the desired two-photon process was determined by detecting the cesium ions produced in the vapor by the associative ionization of the populations of states produced from the dissociation products by the delayed laser pulse. The detection was accomplished by including a space-charge-limited diode in the absorption cell. This method has been shown to be very effective for the products of the photoionization of metal vapors and has been used in all of the previous studies in which hybrid multiphoton resonances have been reported.<sup>4-7</sup> Essentially the technique uses the ionization in the vapor as a distributed grid to control a space-charge-limited current flowing between a cathode and an anode arranged to contain the absorbing vapor between them. Sensitivities to the production of one ion per second have been achieved in this manner.<sup>10</sup> In the experiment reported here the detecting diode was operated in cesium vapor at a pressure of 0.13 Torr.

By adjusting the wavelength of the delayed pulse to agree with a known absorption line corresponding to a transition to a Rydberg state of  $\text{Cs}^*$  from a particular one of the possible dissociation products of the parent molecule, the cross section for photolysis into a channel leading to that specific product was isolated for measurement. The relatively narrow bandwidth of that absorption channel ensured that the number of  $\text{Cs}_2^+$  ions resulting from the subsequent associative ionization of the Rydberg atoms exceeded by 1.5 to 2 orders of magnitude the amount of ionization produced by any competing process such as the direct photoionization of the excited states of  $\text{Cs}_2^*$  remaining from the excitation produced by the first laser pulse. It was found that the composite effect of all of the spurious channels leading to

the production of ionization that tended to contribute background signal and noise to the hybrid multiphoton process represented less than 20% of the total signal and, thus, could be readily subtracted without degrading the signal-to-noise ratio. Once corrected in this way, and provided that some care was taken to avoid intensities so excessive that one of the steps in the absorption sequence became saturated, an ion signal was obtained that was found to be linearly proportional to the intensities from each of the two lasers. This resulting signal was then assumed to be proportional to the product of the intensities multiplied by the known transition probability for the excitation of the dissociation product, the probability for the associative ionization of the resulting Rydberg population, and the cross section to be determined for the photolysis of the  $\text{Cs}_2$  into that particular product channel.

In the work reported here the channels for the production of  $6^2P_{1/2}$  and  $6^2P_{3/2}$  atoms were isolated by adjusting the wavelength of the delayed pulse to correspond successively to the transitions to the Rydberg states  $15^2D_{3/2}$  and  $15^2D_{3/2,5/2}$ , respectively. Similarly, transitions to  $20^2F_{5/2}$  and  $20^2F_{5/2,7/2}$  were used, respectively, for the detection of  $5^2D_{3/2}$  and  $5^2D_{5/2}$  products.<sup>11</sup> Each of the component steps in the sequence leading to the ionization of the dissociation products should have depended in  $L \cdot S$  coupling upon quantum numbers  $n$  and  $L$ , but not  $J$ . As a consequence, the overall detection efficiency should have been the same for populations in states differing only in  $J$ , while having been different from the efficiencies for the detection of products in states having other values of  $n$  or  $L$ . Thus, the relative cross sections shown in Fig. 1 for photolysis of  $\text{Cs}_2$  into  $6^2P_{1/2}$  and  $6^2P_{3/2}$  states were obtained by

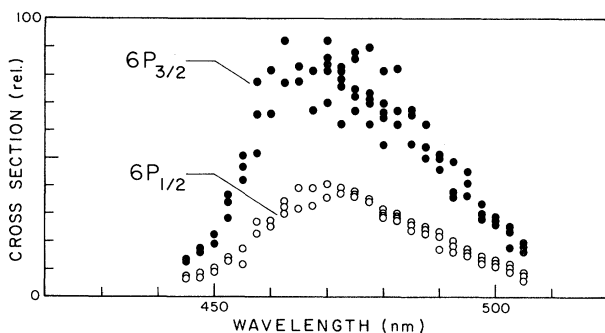


FIG. 1. Relative cross sections as functions of wavelength for the photolysis of  $\text{Cs}_2$  into  $6^2P_{1/2}$  or  $6^2P_{3/2}$  product states of Cs.

simply dividing the bilinear ionization signals described above by the product of the experimentally measured laser intensities. The relative cross sections shown in Fig. 2 for photolysis into  $5^2D_{3/2}$  and  $5^2D_{5/2}$  states were obtained in a similar manner. The relative magnitudes of the resulting curves were significant to  $\pm 20\%$  between each fine-structure component, but the scaling between the  $6^2P$  and  $5^2D$  states was not determined. The scatter between individual measurements reflects the variance observed over a time scale of the order of weeks and may have resulted from the difficulty in maintaining beam alignment.

In each figure the cross sections measured for the fine-structure component of lower energy and lower statistical weight are shown by the open circles. In the case of the  $6P$  states to within experimental error the cross sections appear to be proportional to the product-state degeneracy,  $2J + 1$ , as might have been initially expected. The general similarity of the curves shown in Fig. 1 implies that the photolysis into both  $6P_{1/2}$  and  $6P_{3/2}$  product states occurs through the excitation of a single unstable manifold, either correlated with  $6^2P + 6^2S$ , or predissociating into it.

The case shown in Fig. 2 for the photolysis of  $\text{Cs}_2$  into  $5D$  product atoms is less tractable and even a rough explanation is difficult. Two or possibly three dissociative molecular states seem to be involved. However, such peculiar features as the observed shift toward higher photon energies of the peak of the cross section for the production of the lower energy product imply the existence of complex crossings and predissociations of excited molecular states. In contrast to the occurrence of populations of  $6^2P$  atoms that are proportional to their statistical weights, the  $5^2D$  states are actually inverted. Furthermore,

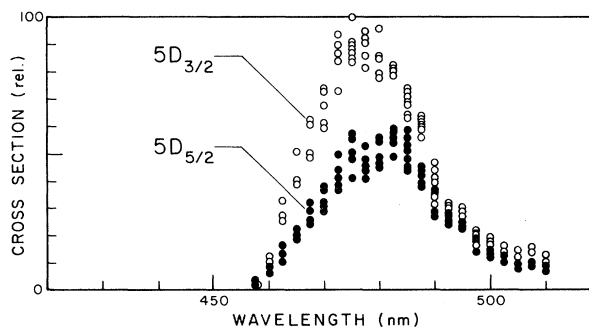


FIG. 2. Relative cross sections as functions of wavelength for the photolysis of  $\text{Cs}_2$  into  $5^2D_{3/2}$  or  $5^2D_{5/2}$  product states of Cs.

if the cross sections are divided by the degeneracies of the product states, the probability per state of producing a  $5^2D_{3/2}$  atom in comparison to a  $5^2D_{5/2}$  becomes as great as a factor of 2.7 larger for the peaks in Fig. 2.

The surprising detail found with this new multi-photon technique in the cross sections for the photolysis of  $Cs_2$  attests to the importance of experimental measurements of these quantities. It is clear that the highly selective photodissociation of  $Cs_2$  into  $5D_{3/2}$  atoms for wavelengths between 470 and 485 nm could not have been anticipated from existing theoretical curves. It appears that the technique introduced here holds the promise of contributing substantially toward the detailed characterization of the repulsive states of simple molecules that are becoming of critical interest and importance in a variety of applications.

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<sup>11</sup>Supplementary data were obtained by exciting the  $5^2D_{5/2} \rightarrow 25^2F_{5/2, 7/2}$  transition with the delayed pulse. As the detection efficiency of the product populations was expected to be proportional to  $n^{-3}$  for  $n \geq 20$ , where  $n$  was the principal quantum number of the Rydberg state, the ionization signals obtained from this transition were multiplied by  $(25/20)^3$ . They were then included in the set from which the relative cross sections shown in Fig. 2 were taken.

## Possibility of Double Sound Propagation in Disparate-Mass Gas Mixtures

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Disparate-mass neutral gases are here predicted to support two different forced-sound modes at moderately high frequencies, a fast and a slow wave. Specific predictions are given for mixtures of xenon and helium.

Forced sound propagation in gases may be studied by considering small disturbances from absolute equilibrium of the form  $\exp[i(kx - \omega t)]$ , where the frequency  $\omega$  is constrained to be real and positive. The dispersion relation which one subsequently obtains for the complex wave number  $k = k(\omega)$  in general has several roots. Usually, one root of the equation will correspond to sound propagation in the  $+x$  direction. That root is identified by its low-frequency behavior: As  $\omega \rightarrow 0$ ,  $\text{Im}(k)$  (proportional to the absorption coefficient) goes to zero, and  $\text{Re}(k)$  (proportional to the dispersion) goes to a positive known constant.

An exception to this simple situation can arise, however. Consider the Navier-Stokes description of a simple monatomic gas. The relevant equations may be written in linearized, nondimensional form, for deviations from equilibrium of the form  $\exp[i(kx - \omega t)]$ , as follows: Conservation equations,

$$n = zU \quad (\text{number-density deviation}), \quad (1a)$$

$$U = z(n + T + P) \quad (\text{flow velocity}), \quad (1b)$$

$$3T = 2n + 2zq \quad (\text{temperature deviation}); \quad (1c)$$