

TWO PHOTON PHOTODETACHMENT SPECTROSCOPY: THE  $C_2^-$   $2\Sigma$  STATES

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A tunable dye laser has been used to observe resonant two photon photodetachment of electrons from  $C_2^-$ . These measurements definitely establish the fact that the Herzberg-Lagerquist band system belongs to  $C_2^-$ , and that the ground state of  $C_2^-$  is a  $2\Sigma_g^+$  state. The two photon photodetachment technique is described, and future potentialities are assessed.

### 1. Introduction

While the importance of resonances corresponding to real intermediate states in two photon bound-free processes has been recognized for several years [1, 2], there have been no reports of detailed studies of this phenomena, primarily because an intense tunable light source has not been available. With the advent of pulsed continuously tunable dye lasers the direct study of such processes has become completely feasible. We have investigated resonant two photon photodetachment using a tunable dye laser in a crossed beam photodetachment apparatus. For intermediate negative ion states which lie higher than one half of the vertical detachment energy, but below the single photon photodetachment threshold, the apparent photodetachment signal is the product of the bound-bound excitation function and the relatively smooth single photon photodetachment cross section from the intermediate state. The laser power is sufficiently low that only for near resonant pumping of real intermediate states will there be a detectable photodetachment signal.

A particularly interesting candidate for such studies is the  $C_2^-$  ion, since  $C_2$  has an electron affinity of  $\approx 3.5$  eV [3], and there is indirect evidence [4] of a  $C_2^*$  state lying  $\approx 2$  eV above the ground state. This evidence is a recent observation by Herzberg and Lagerquist [4] of a spectrum (H-L bands) associated with diatomic carbon in their flash discharge apparatus. The spectrum corresponded to a  $\Sigma-\Sigma$  transition, and isotopic substitution definitively established that the molecule contained exactly two carbon nuclei. Precise molecular constants for this system were reported, but the transitions could not be unequivocally assigned to  $C_2$ ,  $C_2^-$  or  $C_2^+$ ; the authors, however, concluded that  $C_2^-$  was the most plausible assignment. This same band system has now been observed for  $C_2$  trapped in rare gas matrices [5, 6] under conditions where it is probable that the band system belongs to  $C_2^-$ , but again this conclusion is not definitive. There are no other negative ions for which there is evidence for a bound electronic excited state in the gas phase.

### 2. Apparatus and procedures

The basic technique [7] is to intersect a 1 keV mass analyzed  $C_2^-$  ion beam with the focused output of a

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pulsed, tunable dye laser and to measure the relative apparent single photon cross section for production of neutral atoms as a function of laser wavelength. Ions are extracted from a discharge in a CO-C<sub>2</sub>H<sub>2</sub> mixture, accelerated to 1 keV, mass analyzed, and focused onto a 15-stage particle multiplier located 20 cm beyond the laser beam crossing region. Beyond the interaction region, but before reaching the multiplier, the ions are electronically deflected into a Faraday cup, so that only the neutral atoms, produced by a charge stripping on the background gas and by laser photodetachment, reach the neutral detector.

With this beam system a focused mass-analyzed C<sub>2</sub><sup>-</sup> beam of 150 nA can be obtained in the interaction region. The background pressure in this region is about  $4 \times 10^{-8}$  torr. As a result of the large number of neutrals reaching the multiplier in a short time, the detector is operated in a linear, charge amplifying mode, rather than as a particle counter.

The light source is a flashlamp-pumped, tunable organic dye laser consisting of a linear xenon flashlamp and a dye cell at the foci of an elliptical cavity<sup>†</sup>. Wavelength selection is achieved with the use of an 1800 lines/mm diffraction grating blazed at 5000 Å in first order as one feedback element in the laser optical cavity. A partially transmitting mirror serves as the output coupler. The laser output is a 300 nsec pulse, with an energy content of 1–10 millijoules/pulse and a line width of 1–3 Å. With the use of rhodamine 6G, cresyl violet acetate mixed with rhodamine 6G, and brilliant sulfaflavine as the laser media, the wavelength region covered by these measurements spanned the range from 5200 Å to 6800 Å. Typical repetition rates were 5 shots/sec.

The pulsed laser beam is focused onto the C<sub>2</sub><sup>-</sup> ion beam and the neutral particle multiplier signal is gated on after a delay following the laser pulse appropriate to the C<sub>2</sub> flight time from the interaction region to the detector. The neutral detector is also gated on to sample the stripped neutral signal approximately 1 μsec before the laser-produced neutrals reach the multiplier, thus providing a neutral background correction obtained in a time short compared to the coherence time of the ion beam. A small portion of the laser beam is detected by a fast photodiode, and another gate samples the ion beam current at the time

of laser firing. A 0.35 m monochromator accurate to  $\pm 1$  Å is used to measure the laser wavelength and line width. A typical data run consists of several groups of 100 laser shots at a chosen wavelength; the quantity actually computed is the following:

$$Q_{AP} = \sum_{i=1}^{100} \frac{(AS-AB)_i - LEN}{[IS(i)][LS(i)]} \quad (1)$$

where  $i$  represents the  $i$ th laser firing,  $AS(i)$  is the atom signal for the  $i$ th firing,  $AB(i)$  is the atom noise immediately prior to the  $i$ th firing,  $IS(i)$  is the ion beam signal for the  $i$ th firing,  $LS(i)$  is the integrated laser flux for the  $i$ th firing,  $LEN$  is the laser electrical noise induced in the atom detector.

A small computer is utilized to control the apparatus, acquire these signals, and do the computation indicated by eq. (1). It should be noted that  $Q_{AP}$  is a relative apparent *single photon cross section* for production of neutral atoms, and in general is the sum of photodetachment and photodissociation cross sections. In the present case, however, only photodetachment is energetically accessible. Data are taken in the form shown in eq. (1) because, in almost all cases, the bound-bound part of the two photon photodetachment is saturated or nearly saturated, so that  $Q_{AP}$  is independent of laser flux at our normal operating power levels.

### 3. Experimental results

Fig. 1 depicts the C<sub>2</sub><sup>-</sup> apparent single photon photodetachment cross section in the wavelength region 5300–5450 Å, well below the single photon photodetachment threshold. The signal-to-noise ratio is  $\approx 100$  for a 100 shot integration at the  $\lambda$  5415 peak.

It is immediately clear that these data show a wavelength dependence totally foreign to ordinary bound-free processes. Further, the sharp peaks at  $\lambda$  5415 and  $\lambda$  5363 correspond within  $2 \text{ cm}^{-1}$  to the reported (0,0) and (1,1) band heads for the H–L system. Since the laser line is too broad to resolve rotational structure the cross section has the appearance of an ordinary low resolution optical spectrum. Using the values of  $B_e$  and  $r_e$  obtained by Herzberg and Lagerquist, and assuming thermal equilibrium among the rotational states (a questionable assumption!), then the separation of the P and R branch

<sup>†</sup> Drawings of the dye laser may be found in ref. [8].

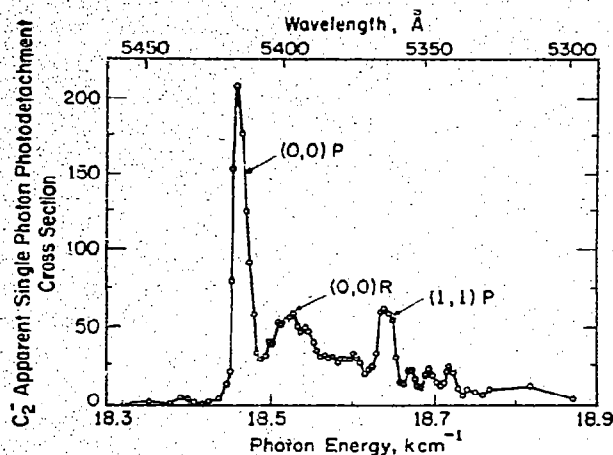


Fig. 1. The  $C_2^-$  apparent single photon photodetachment cross section near the  $\Delta\nu = 0$  sequence of the Herzberg-Lagerquist band system. Single photon photodetachment is energetically impossible for photon energies less than  $\approx 28\,000\text{ cm}^{-1}$ . The indicated P branch peaks appear within  $\pm 2\text{ cm}^{-1}$  of the corresponding P branch band heads of the H-L band system.

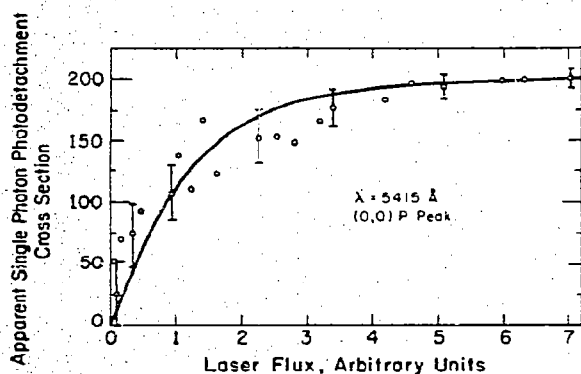


Fig. 2. Laser flux dependence of  $Q_{AP}$  at the  $\Delta\nu = 0$  P branch band head. The solid line is the flux dependence expected for saturation of one step of the two photon process. Data in figs. 1 and 3 are obtained at fluxes such that  $Q_{AP}$  is laser flux independent.

peaks implies a rotational temperature of  $\approx 600^\circ\text{K}$ , a reasonable temperature for our ion source. As a result of the fact that our laser source is relatively intense, the bound-bound transitions are saturated near the line center and  $Q_{AP}$  is laser flux independent for all of the data shown in fig. 1. However, if the laser flux is reduced by means of neutral density filters, the flux dependence characteristic of two photon processes

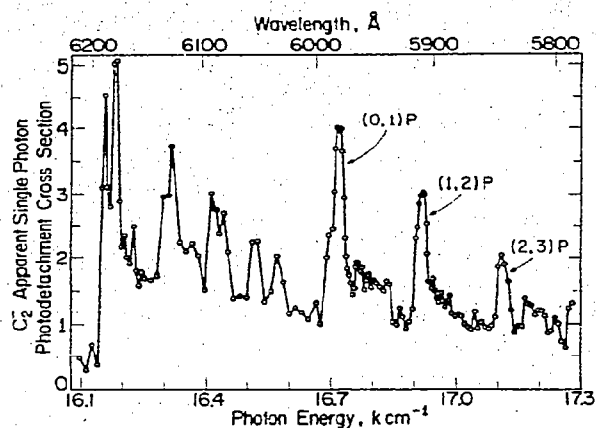


Fig. 3.  $Q_{AP}$  in the region near the  $\Delta\nu = -1$  sequence of the H-L band system. The indicated peaks lie within  $\pm 2\text{ cm}^{-1}$  of the corresponding P branch band head. The features at energies below the (0,1) peak do not belong to the H-L band system, but include at least one other state, possibly a  $^2\Pi$  state. The cross section scale is in the same (arbitrary) units as the data of fig. 1.

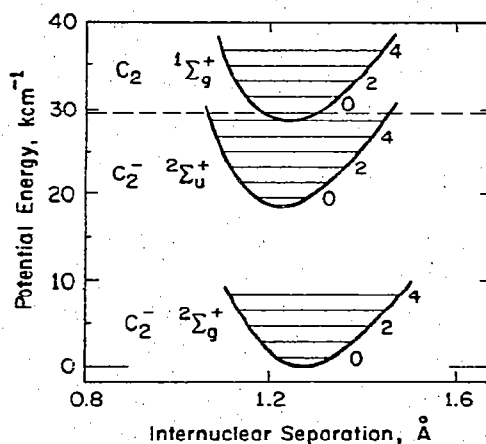


Fig. 4. RKR potentials for the identified  $C_2^-$  states and the  $C_2$  ground state.

can be observed. This fact is clearly seen in fig. 2, which depicts the laser flux dependence of the  $\lambda 5415$  peak. The solid line is a normalized fit to the flux dependence expected under the assumption that the bound-bound transition may saturate, but that the bound-free transition is unsaturated. At our normal laser flux levels ( $\approx 10^{24}$  photons/cm<sup>2</sup> sec) and for the ion residence time in the laser beam ( $\approx 10^{-8}$  sec), the

bound-free cross section would have to be greater than  $10^{-16}$  cm<sup>2</sup> for appreciable saturation effects to occur; the cross section maxima for similar processes are typically  $\approx 10^{-17}$  cm<sup>2</sup>.

The above observations taken together conclusively establish the fact that we are indeed observing two photon photodetachment and that the H-L band system definitely belongs to C<sub>2</sub><sup>-</sup>. Furthermore, comparison of the magnitude of the C<sub>2</sub><sup>-</sup> photodetachment signal with that from O<sup>-</sup> indicates that most of the ions in the beam are probably in  $v'' = 0$  of the lower state of the H-L system, and thus that the lower state, a  $^2\Sigma_g^+$  state, should be the ground state of C<sub>2</sub><sup>-</sup>. Accordingly, while Herzberg and Lagerquist [4] conclude that the H-L band system belongs to diatomic carbon, we add that it must be ascribed to a negative ion of  $m/e = 24$ , produced from acetylene, and that the lower state of the system most probably is the ionic ground state.

Further investigations we made in the regions of the  $\Delta v = -1$  sequence, where an order of magnitude higher laser flux can be obtained. These results are shown in fig. 3. The P branch heads of the (0,1), (1,2) and (2,3) bands are detectable and lie within 2 cm<sup>-1</sup> of the position predicted assuming that the peaks belong to the H-L system.

In addition to this structure, however, there are other prominent features to the long wavelength side of the  $\Delta v = -1$  sequence. These features definitely do not belong to the H-L system, nor are they a result of an impurity in our ion beam. It is certain therefore, that these features are characteristic of at least one electronic state other than the  $^2\Sigma$  states of the H-L system. Further studies show that this same pattern of peaks repeats again near  $\lambda$  6800. While much more data will be required to establish the identity of these state(s), it seems likely that a  $^2\Pi_u$  state (analogous to the N<sub>2</sub><sup>+</sup> Meinel upper state) is involved.

Fig. 4 shows RKR potentials for the known C<sub>2</sub><sup>-</sup> states and the C<sub>2</sub>  $^1\Sigma$  ground state. These potentials were calculated by Albritton [9] using the spectroscopic data [4] for the H-L bands, and the measurement by Feldman [3] of the electron affinity of C<sub>2</sub>. Thus, while at this point the electron affinity of C<sub>2</sub> is not as well known as that of O<sub>2</sub> [10] or NO [10],

more accurate molecular potentials are now known for C<sub>2</sub><sup>-</sup> than for any other negative ion.

#### 4. Discussion and conclusions

This experiment has demonstrated that resonant two photon photodetachment is a new technique that can profitably be applied to the study of electronic structure of molecular negative ions, and that the H-L band system can be unequivocally assigned to the C<sub>2</sub><sup>-</sup> ion. In addition, C<sub>2</sub><sup>-</sup> must possess other bound states, probably including a  $^2\Pi_u$  state.

A number of improvements are experimentally possible. For example, the addition of a Lyot filter [11] to the tunable dye laser will reduce the line width to  $\approx 0.01$  cm<sup>-1</sup>, making it easily possible to resolve rotational transitions, and probably possible to resolve the doublet splitting in C<sub>2</sub><sup>-</sup>, for large  $J$ . Further, the brightness of the Lyot filter-dye laser combination is sufficient to saturate bound-bound transitions with oscillator strengths of  $\approx 10^{-6}$ , thus allowing spectroscopic study of many states not normally accessible.

This technique of course is not limited to intermediate states lying energetically more than halfway up to the continuum. By using two light sources, one of which is off resonance, the entire energy range is accessible. This technique may also be applied to many molecular positive ions by observing the neutrals produced by photodissociation from an electronically excited state, provided that single photon photodissociation from the lower state is energetically impossible. Finally, the fact that C<sub>2</sub> has a large electron affinity and that C<sub>2</sub><sup>-</sup> has a strong band system in the visible should soon lead to the discovery of C<sub>2</sub><sup>-</sup> in the atmospheres of cool carbon stars.

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