Optogalvanic study of photodetachment of O^- near threshold

Takanori Suzuki and Takahiro Kasuya
Institute of Physical and Chemical Research, 2-1, Hirosawa, Wako, Saitama, 351-01 Japan
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An optogalvanic signal due to the photodetachment of O^- has been successfully observed using an rf discharge. This signal is shown to be proportional to the photodetachment cross section. The transition strengths determined for various fine-structure levels agree well with the predictions by Rau and Fano [Phys. Rev. A **4**, 1751 (1971)]. An optogalvanic signal due to the photodetachment of O_2^- has also been observed.

I. INTRODUCTION

Optogalvanic spectroscopy of atoms and molecules is now firmly established as a simple and sensitive technique with numerous applications in chemistry and physics. As an application to the study of negative ions, optogalvanic signals resulting from photodetachment have been measured for I^-,[1] CN^-,[2] and Cl^-,[3] using a hollow cathode discharge. The optogalvanic effect due to Cl^- (Refs. 4 and 5) and BCl_3^- (Ref. 4) in rf discharges has been investigated recently with plate electrodes inside the discharge cell. The high concentration of negative ions in the discharge favors the use of optogalvanic detection for their study. The optogalvanic signal associated with photodetachment arises from the significant difference in mobility between negative ions and the detached electrons. In a low-pressure discharge used in the optogalvanic experiment, the negative ions under study are not in an ideal field-free environment. In their study of I^-, Webster *et al.*[1] showed that the field and environmental effects such as Doppler and Stark effects were negligible compared to the laser linewidth of 0.6 cm^{-1}. Photodetachment thresholds for all species cited above have been obtained accurately from the optogalvanic signal.

The magnitude of the optogalvanic signal is usually a function of the type of transitions and the experimental condition of discharges. In a positive column of a low-pressure discharge, the charged particles are mainly lost by diffusion to the walls, resulting in an abundance of electronegative ions at the center of the plasma and negative charging of the walls.[6] In such a discharge, low-energy electrons photodetached from negative ions will not be able to diffuse to the walls unless they have been accelerated to a certain energy. Therefore the optogalvanic signal associated with photodetachment will be expected to be proportional to the number of detached electrons, that is, to the photodetachment cross section, as long as the initial kinetic energy of detached electrons is sufficiently smaller than the average electron energy in the discharge. In this paper, we report the analysis of the magnitude of the optogalvanic signals of O^- in an electrodeless rf discharge of O_2 at low pressure as a new application of optogalvanic spectroscopy to the determination of photodetachment cross sections.

Negative ions of oxygen atoms and molecules have been extensively investigated in order to determine the properties of these ions and as a means to understand the behavior of discharges in electronegative gases.[6] The oxygen discharge at low pressure is usually very noisy because of the presence of negative ions at considerable concentration.[7] We have found that the optogalvanic signal from an rf discharge of oxygen can be obtained with a sufficient signal-to-noise ratio under a critical condition of rf power and gas pressure. In this manner, six thresholds in the optogalvanic signal have been obtained at laser frequencies above 11 607 cm^{-1}, corresponding to O^- atoms undergoing photodetachment at the fine-structure transitions $O^-(^2P_{3/2,1/2}) \rightarrow O(^3P_{2,1,0}) + e^-$.[8] The photodetachment signals due to O_2^- has also been observed at laser frequencies below 11 607 cm^{-1}.

The threshold behavior of photodetachment cross sections has been studied with a negative-ion-beam apparatus.[9,10] Employing a laser as the light source, the photodetachment study on S^- (Ref. 9) and Se^- (Ref. 10) resolved various fine-structure components and determined transition strengths different from those predicted by simple statistical considerations. According to the work of Wigner[11] on threshold laws, the leading term of the photodetachment cross sections near threshold is given by $\sigma \sim k^{2L+1}$, where L is the orbital angular momentum of detached electrons, and k the magnitude of electron's momentum. If a p electron is detached as in O^-, the outgoing electron can be in an s or d wave. Then the behavior is given by the s-wave contribution $\sigma \sim k$, since the d-wave cross section is suppressed by the centrifugal barrier. In their experiments on Se^-, Hotop *et al.*[10] have observed a deviation from the Wigner law even in the vicinity of the threshold. They tried to explain the deviation following the treatment of O'Malley,[12] namely, within the framework of a modified effective range theory, taking account of the long-range interaction (the electron-induced dipole interaction and the electron-permanent quadrupole interaction) between the detached electron and the final-state atom.

The present study clearly indicates a deviation from the Wigner law. This has prompted us to attempt to estimate correction terms to the Wigner law arising from the long-range interactions. The high signal-to-noise ratio provid-

ed by the present optogalvanic detection scheme permitted a precise determination of the transition strengths for various fine-structure onsets, as well as a detailed study of the threshold behavior of photodetachment cross section.

II. EXPERIMENTAL PROCEDURE

The experimental setup of the rf optogalvanic detection[13] used in this work is shown in Fig. 1. An rf electric field at 13.56 MHz is applied across a Pyrex discharge tube of 10 mm outside diameter by two copper rings attached to the tube. Commercial O_2 gas (Kanto Chemicals) is continuously supplied to the discharge tube. The gas pressure is measured at the outlet of the discharge tube with a capacitance manometer (Baratron, 220BHS). The measurement of photodetachment in oxygen was carried out under the critical condition of rf power and gas pressure: respectively, 4.8 ± 0.2 W measured at the oscillator output, and 0.084 ± 0.002 Torr at the tube outlet.

The dye LDS 820 (Exciton) was pumped with all lines of an Ar^+ laser. At a pump power of 4 W, a peak output of 250 mW was available from the dye laser equipped with a birefringent filter (BRF). Tuning was accomplished by rotating the BRF with a typical linewidth of 0.7 cm^{-1}. The laser beam was mechanically chopped at a frequency of 3.6 kHz and was subsequently directed and focused onto the center of the discharge tube.

The laser power was monitored by a photodiode (EG&G, PV-100A) which was exposed to a constant fraction of the laser beam. The signal intensity was normalized against the incident laser power by using a ratio meter. Signal linearity was confirmed by attenuating the laser power with various neutral density filters. We observed a slight variation of the normalized output due to residual offsets in the lock-in amplifiers and/or the ratio meter. The variation was within 2% when the outputs of the lock-in amplifiers were reduced by a factor of 2. The signal intensity, the laser power, and the frequency markers from the Ne optogalvanic spectrum and étalon fringe were all digitized by a 12-bit analog-to-digital (A-D) converter and stored in a floppy disk.

Figure 2 shows the optogalvanic signal of O^- as a function of laser frequency. The frequency was scanned at a rate of 0.16 cm^{-1}/s with a lock-in time constant of 1 s. The assignment of the six thresholds (shown by arrows) was straightforward when referred to the photodetachment spectrum of O^- studied with a negative-ion beam apparatus.[8] All six fine-structure onsets could not be recorded with good signal-to-noise ratio in a single scan, because the laser power decreased rapidly at frequencies below 11 750 cm^{-1}. Therefore at least two sets of scans were necessary, as shown by (A) and (B) in the figure. In the scan (A), the laser power ranged from 250 mW around 12 000 cm^{-1} to 150 mW at 11 750 cm^{-1}. As the étalon provides a poor fringe pattern outside the region of scan (A) due to its reduced reflectivity, only the data in the region (A) were considered in the following best-fit analysis.

As shown in the scan (B), the optogalvanic signal is still nonzero at frequencies below the onset of the $^2P_{1/2}\rightarrow{}^3P_2$ transition. Other negative ions abundant in the oxygen discharge at low pressure are O_2^- and O_3^-.[6] This signal is ascribed to the O_2^- photodetachment for which the electron affinity is 0.44 eV,[14] since O_3^- ions with an electron affinity of 1.99 eV (Ref. 15) are not photodetached with the present photon energy. The signal component due to O_2^- is taken to be independent of laser frequency over the limited energy range studied. Thus it is subtracted from the observed optogalvanic signal in the best-fit treatment for our O^- photodetachment analysis.

Frequency calibration was accomplished by simultaneously recording the laser transmission through a Fabry-Perot étalon (Burleigh, TL-38) with a 2.548 cm^{-1} free spectral range and the optogalvanic signal of several favorable transitions in Ne.[16] This procedure permitted a determination of the frequency to an accuracy of ±0.3

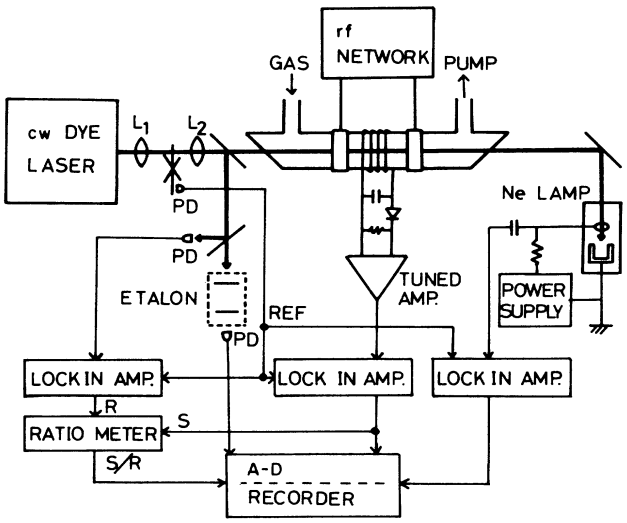

FIG. 1. Experimental arrangement for rf optogalvanic spectroscopy.

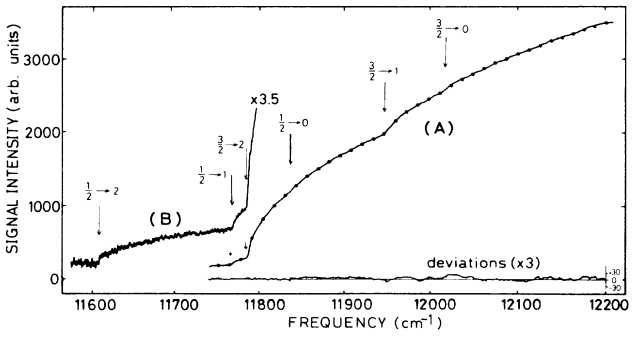

FIG. 2. Optogalvanic spectrum for the photodetachment of oxygen. The six fine-structure thresholds for the $^2P_{J'}\rightarrow{}^3P_J$ transitions are marked by arrows and labeled by $J'\rightarrow J$. Results of the least-squares fit are shown by dots in trace (A) for several data points. The bottom trace shows the deviation of the experimental data and the best fit to theory magnified three times. Trace (B) is recorded with the 3.5 times magnified sensitivity. The optogalvanic signal at frequencies below 11 607 cm^{-1} is due to O_2^- photodetachment.

cm^{-1} over the entire region of concern. Table I lists the threshold transition frequencies obtained from averaging three independent scans. The data are consistent with the high-resolution results previously obtained.[8]

The normalized signal intensity was reproducible to within 3% over a period of hours; slight drifts in the signal intensity were caused by variations either in the O_2 pressure or in the rf power. In order to compensate for any drift, data of reversed scans were collected and averaged.

III. RESULTS AND DISCUSSIONS

The dependence of the optogalvanic signal on the photodetachment cross section will be discussed first within the context of our experiment. With a discharge tube of small diameter and at low pressure, the loss of electrons by diffusion to the walls is estimated to be two orders of magnitude faster than other losses by recombination or attachment.[6] Therefore, a positive column model is applicable, and an estimation for the plasma parameters of our discharge can be made utilizing Thompson's data, which was obtained under a similar noise-free condition in the positive column of a dc discharge at a pressure of 0.04 Torr.[7]

Experimentally, an rf electric field of 20 V/cm is applied across the two electrodes separated by 3 cm. Under the influence of the rf field, the detached slow electrons being oscillating with an amplitude of 5 cm and a peak velocity of 4×10^8 cm/s or a kinetic energy of 45 eV, provided no collisions occur. In fact, the photodetached electrons undergo many elastic collisions with O_2 molecules within a half cycle of rf field. This occurs because the mean free path of the electrons at the gas pressure of 0.084 Torr of our discharge is estimated to be 0.6 cm from the momentum-transfer cross section of 6×10^{-16} cm^2 (Ref. 17) for electrons with 4 eV energy corresponding to the mean electron energy observed in the positive column of the dc discharge of oxygen.[7]

As there is a space-charge sheath field between the plasma and the glass cell, which is several volts in the positive column,[7] slow detached electrons of less than 80 meV energy in the present case cannot penetrate the sheath to escape from the discharge. They stay within the discharge and interact with the rf field until they are heated up to a certain temperature. In other words, photodetached slow electrons are first subjected to energy transfer from the rf field and then thermalize in the electron gas towards a certain steady state independent of their initial velocity. This means that the optogalvanic signal due to photodetachment is proportional to the number of detached electrons and, therefore, to the photodetachment cross section.

TABLE I. Transition wave number for various fine-structure onsets in O^- photodetachment.

O^-	O	This work	Neumark *et al.* [a]
	$^3P_2$	11 607.3±0.6	11 607.53±0.05
$^2P_{1/2}$	$^3P_1$	11 765.8±0.2	11 765.81±0.05
	$^3P_0$	11 834.6±0.3	
	$^3P_2$	11 784.6±0.2	11 784.645±0.006
$^2P_{3/2}$	$^3P_1$	11 942.9±0.2	
	$^3P_0$	12 011.7±0.3	

[a]D. M. Neumark, K. R. Lykke, T. Andersen, and W. C. Lineberger, Phys. Rev. A **32**, 1890 (1985).

An analytical expression for the threshold behavior of the photodetachment cross section has been derived by O'Malley.[12] As the energy of detached electrons is less than 80 meV in our case, the cross section is well approximated by the terms third order in the electron momentum k. The expression for the cross section for the $J=0$ state of the neutral atom in the simplest case of $L=0$ is then given as [Eq. (10) in Ref. 10]

$$\sigma/h\nu = Sk\left[1+\tfrac{4}{3}\beta^2k^2\ln 1.23\beta k + Ak^2(\gamma+\tfrac{2}{3}\pi\beta - A)\right] . \quad (1)$$

In the formula β is defined in terms of the static dipole polarizability α of the final-state atom and the Bohr radius a_0 as $\beta^2=\alpha/a_0$; A represents the scattering length; γ is the modified effective range, S is a constant proportional to the transition strength. Although Eq. (1) does not describe cases for $J>0$, where there is a long-range quadrupole potential, we tried a fit with Eq. (1), interpreting the quantity A as an effective scattering length averaged over the doublet and quartet contributions[10] and assuming a common A for all J states. The observed optogalvanic signal is then interpreted as a sum of onsets, expressed by Eq. (1) for each threshold.

First, the experimental data were fitted to the first term in Eq. (1), corresponding to the Wigner law. The least-squares fit in this approximation was not satisfactory because the increase of optogalvanic signal at higher frequencies was less than expected from the Wigner law, as has been discussed for Se^-.[9]

In the second step, we took account of the second term of Eq. (1) with $\alpha=5.4a_0^3$,[18] corresponding to the electron-induced dipole interaction. The fit improved, but systematic deviations still remained.

As a final step, we used the scattering length A in the third term of Eq. (1) as a fitting parameter. For our data-fitting procedure, we set $\gamma=0$.[10] As a result, the mean deviation was reduced to two thirds of that obtained in the previous analysis, the residual discrepancy shown in the bottom of Fig. 2 being attributable to experimental uncertainties. The scattering length inferred from this procedure was $A=-2.4a_0$. An alternative fit with $\beta=0$ yields comparable mean deviations and step heights for the onsets, but nearly twice as large a scattering length.

It is clear from the analysis discussed above that terms of the order of k^3 have to be taken into account in describing the observed deviation from Wigner law. The scattering lengths obtained from both of the fitting procedures appear to be reasonable, since the momentum-transfer cross section of $\sim1\times10^{-16}$ cm^2 at 10 meV (Ref. 17) gives $A\sim-5a_0$ from the relation $\sigma\sim4\pi A^2$ that holds in the low-energy limit. In other words, the scattering length is difficult to derive simply from our data analysis, as can be understood from the following considerations. The opto-

TABLE II. Transition strength for various fine-structure onsets in O^- photodetachment.

O^-	O	This work[a]	Rau and Fano[b,c]	Statistical[b]
$^2P_{1/2}$	$^3P_2$	8.2±0.3	20τ (8.5)	50τ (23.2)
	$^3P_1$	17.7±2.2	36τ (15.4)	30τ (13.9)
	$^3P_0$	4.7±1.6	16τ (6.8)	10τ (4.6)
$^2P_{3/2}$	$^3P_2$	100±2.2	100	100
	$^3P_1$	30.3±1.5	36	60
	$^3P_0$	6.2±1.4	8	20

[a]Depicted errors are 3σ.

[b]$\tau = e^{-177.13/kT(\mathrm{cm}^{-1})}$, and values in parentheses are calculated for $\tau = 0.428$ ($T = 300$ K).

[c]A. R. P. Rau and U. Fano, Phys. Rev. A **4**, 1751 (1971).

galvanic signal involves error components due both to variations in laser power and to changes in the discharge parameters. We have attempted to estimate the influence on the fitting parameters caused by these systematic errors. For this purpose, we have adjusted the data assuming that these systematic effects lead to a linear variation in sensitivity of 2%. By fitting the adjusted data, we infer transition strengths altered by less than 1%, but a scattering length changed by as much as 20%.

As illustrated by the discussion above, the transition strengths are not sensitive to small errors in the data. Table II lists the relative transition strengths for the various fine-structure transitions averaged over two independent scans. They agree well with predictions of Rau and Fano,[19] where the Boltzmann factor was evaluated for a $^2P_{1/2} \rightarrow {}^2P_{3/2}$ splitting of 177.13 cm^{-1} (Ref. 8) and a wall temperature of 300 K.

The contribution of O_2^- ions accounts for 2% of the optogalvanic signal at 12 000 cm^{-1}, as is seen from the figure. We assume the optogalvanic signal due to O_2^- is also proportional to the photodetachment cross section, since the kinetic energy of 1 eV for detached electrons is still smaller than the mean electron energy in the discharge. The concentration ratio of molecular to atomic ions of oxygen $[O_2^-]/[O^-]$ in our rf discharge then can be estimated to be 0.1 based on the cross sections of 4×10^{-18} cm^2 (Ref. 20) and 0.8×10^{-18} cm^2 (Ref. 21) for detachment of O^- and O_2^-, respectively, at this photon energy. This compares well with that obtained by Thompson under a similar noise-free condition, reflecting a critical ion balance at this discharge condition.[7]

We now consider the possibility of optical saturation of the optogalvanic signal. The photodetachment cross section of O^- is 6.3×10^{-18} cm^2 at 17 000 cm^{-1}.[20] The rate of photodetachment for a laser power of 200 mW and beam diameter of 1 mm is then estimated to be 5×10^{10} $cm^{-3}\,s^{-1}$ for the O^- concentration of 4×10^8 cm^{-3}.[7] The production and loss rates of O^- ions in the positive column have been found to be $\sim4\times10^{12}$ $cm^{-3}s^{-1}$ for the dissociative attachment reaction and the associative detachment reaction.[6] As the photodetachment rate estimated above is two orders of magnitude lower than this value, we see that optical saturation effects are unimportant in the present case. The absence of any appreciable power dependence of the optogalvanic signal when examined with the 2.5-W output of the Kr^+ laser (647 and 676 nm) further confirms this analysis.

The optogalvanic signal of O^- was also observable in other types of discharges. In the dc discharge of a Ti hollow cathode, the optogalvanic signal from the photodetachment of O^- was observed in the positive column together with an intense optogalvanic signal arising from atomic oxygen in the vicinity of the cathode surface. In microwave discharges, both the O^- and O signal were observed.[22] The maximum signal-to-noise ratio for O^- detection was obtained in an rf discharge, in which the optogalvanic signal due to O atom was hardly observed in the energy range studied.

The simple experimental system of optogalvanic detection should provide a versatile method of obtaining the photodetachment signals for other electronegative species. These studies are expected to be useful not only in determining quantitative results for photodetachment cross section but also in elucidating fundamental processes occurring in discharges.

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