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Laser-Induced Collisional Processes in Resonant Laser Ablation of GaAs

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Abstract. The transitions between the multiplets of $4^2P \rightarrow 4^2D$ and $4^2P \rightarrow 5^2P$ in Ga have been studied by observing the ions produced in the ablation of a GaAs surface using a tunable dye laser. The asymmetric spectral profiles of the $4^2P \rightarrow 4^2D$ transitions, and the large differences in laser power dependence of the ion yields for the different resonant schemes were observed and analysed. The experimental data are interpreted as resulting from laser-induced collisional processes, especially, from optical collisional excitation and energy-pooling ionisation.

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Recent studies have indicated that higher elemental detection sensitivity and selectivity may be achieved in laser ablation by tuning the wavelength of the ablating laser to a resonant transition line of the atoms under investigation (resonant laser ablation-RLA) [1–3]. Resonant laser ablation in this paper is interpreted to mean laser ablation of neutrals followed by resonant ionisation of the neutrals in the same laser pulse. Resonant enhancements ranging from several times to two orders of magnitude have been obtained. Also, spectral widths, as large as 10 nm [1, 2], have been observed. The close correspondence of the observed resonances and known atomic transition frequencies suggests that resonant excitation and ionisation occur in gas phase atoms ablated from the solid surface by photons in the same laser pulse [3].

Ho-ming Pang et al. [2] proposed a collisional process for the ion formation and the large spectral broadening observed in their experiment, from which they estimated an extremely high density of the neutral plume ablated near the surface of the sample. However, a difficulty in explaining the ionisation mechanism involved in these experiments by the usual thermal collisional processes is that the thermal translational energy of the collision partners is too small for direct ionisation to be significant.

In a recent study [4] on resonant laser ablation of solid GaAs, using a tunable laser of moderate flux ($< 8 \times 10^6$ W cm^{-2}), a highly asymmetrical resonant profile was observed. The line shape of the spectra also varied with laser intensity. These observations suggest that laser-induced collisional processes may play an important role in ion formation during laser ablation. In this paper, resonant ionisation of Ga atoms by direct laser ablation of GaAs using a tunable dye laser are studied for two specific atomic transitions $4^2P \rightarrow 4^2D$ and $4^2P \rightarrow 5^2P$. The spectral profiles and laser power dependence for the two excitation schemes are analysed. Optical collision and energy-pooling ionisation processes are proposed to interpret the experimental data.

1 Experimental Arrangement

The experiments were carried out in a UHV time-of-flight mass spectrometer, which comprised an analysis chamber, an entry chamber for rapid transfer of samples and a one metre time-of-flight (TOF) linear mass analyser of mass resolution approximately 100. The operating pressure was typically $\sim 10^{-8}$ mbar and the ion detector was an electron mutliplier. An MBE grown GaAs sample with a smooth mirror finish surface was fixed with conductive epoxy to a 25 mm diameter stainless steel stub.

The laser arrangement consisted of a Lumonics TE 860-3 XeCl excimer laser (308 nm) pumping a Lumonics EPD 330 dye laser. For resonant excitation to the 4^2D level of Ga, the dye used was Rhodamine 6G and the output was frequency doubled by passing through a KDP crystal mounted on an Inrad autotracker. For the two-photon transition $4^2P \rightarrow 5^2P$ the dye R610 was used.

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The laser beam, with 5 ns pulse duration and bandwidth about 0.01 nm, was directed onto the sample surface at grazing incident angle of $\sim 5°$, and was focused by a lens ($f = 30$ cm) to a diameter of 0.5 mm in the interaction region, resulting in irradiation area on the sample surface about 2.5×10^{-3} cm^2.

The data acquisition system has been described in detail elsewhere [5] and essentially consists of a 12-bit Ortec AD 811 peak-sensing ADC with a gate of variable width and delay coupled to an LSI-11 microprocessor.

Two resonant excitation schemes were chosen to investigate the ionisation processes in laser ablation of GaAs. The laser wavelength was tuned to the doublet transitions $4^2P \rightarrow 4^2D$ and $4^2P \rightarrow 5^2P$ of Ga, respectively. The difference between the two cases is that the one-photon excitation ($4^2P \rightarrow 4^2D$) is well saturated [6] for the UV laser intensity used here (10^5–10^6 W cm^{-2}), while the two-photon process $4^2P \rightarrow 5^2P$ was far from saturation for the visible laser intensity $< 8 \times 10^6$ W cm^{-2}. In the case of the transition $4^2P \rightarrow 4^2D$, the fundamental beam was directed to the surface of the sample together with the UV component, to produce a sufficiently high atomic density. The Ga ion signal was measured as a function of both laser wavelength and intensity. Both isotopes ^{69}Ga and ^{71}Ga were well resolved in the TOF mass spectra, but no As ion signals were detected.

TOF signals with poor mass resolution and highly energetic ions were also observed when the ablation laser flux was greater than 10^7 W cm^{-2}. Simultaneously, the resonance effects became weak or disappeared entirely. This is likely due to a high density atomic plume being formed in the interaction region, which caused space charge effects and the probable onset of plasma formation. Therefore, throughout the course of the experimental measurements, the mass spectrum was continuously monitored to ensure a constant shape of TOF signals by keeping the laser intensity at relatively low levels.

To avoid the influence of varying surface condition on the experimental results, the sample was carefully handled during the whole period of the experiments. Each time before taking data, the laser was switched on to clean the surface at least for half an hour until stable and reproducible ion signal was observed. The only significant impurity signal is K ions, the size of which was much less than Ga^+ signals.

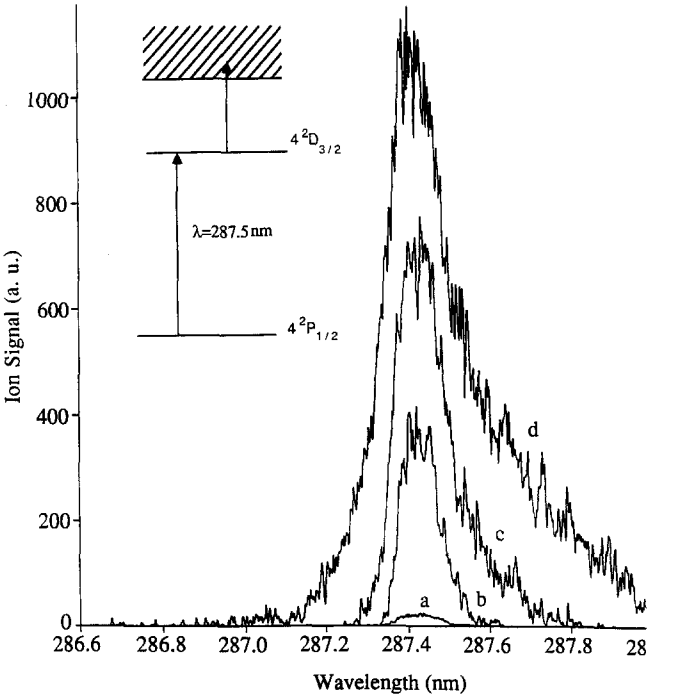

Fig. 1. The ion signal of Ga as functions of UV laser wavelength, λ, and total laser energy E. (*a*) $E = 0.39$ mJ, (*b*) $E = 0.66$ mJ, (*c*) $E = 0.79$ mJ, and (*d*) $E = 0.98$ mJ. The left inset is a partial Grotrian diagram of Ga relevant to the resonant excitation

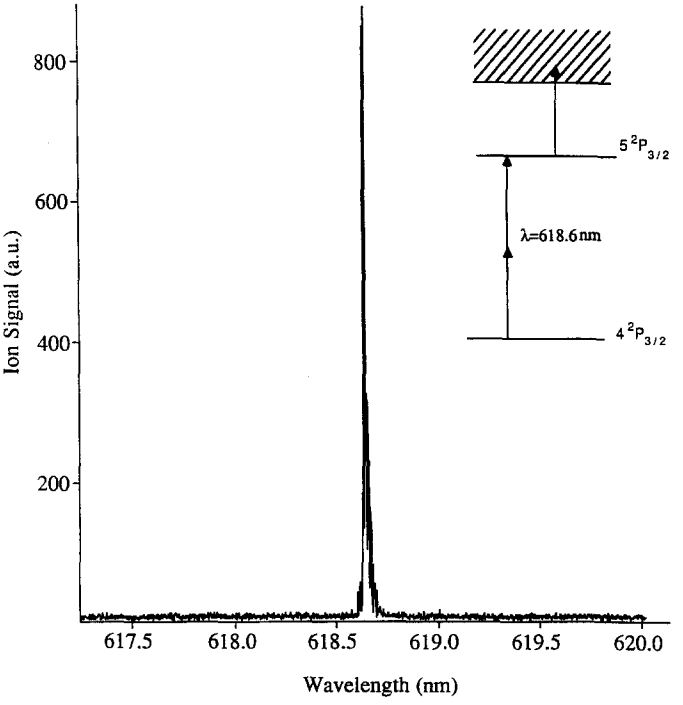

Fig. 2. The ion signal of Ga as a function of laser wavelength for the two-photon resonance with laser energy $E = 97$ μJ. The right inset is a partial Grotrian diagram of Ga relevant to the resonant excitation

2 Results and Discussion

Figures 1 and 2 are Ga ion spectra obtained when the laser wavelength was tuned across the resonant transitions $4^2P_{1/2} \rightarrow 4^2D_{3/2}$ and $4^2P_{3/2} \rightarrow 5^2P_{3/2}$, for the UV one-photon and the visible two-photon excitations respectively. The resonant enhancement of the ion signals is large and no shifts from known atomic transition wavelength were observed within experimental uncertainties. This indicates that, both excitation and ionisation processes occur in the gas phase. Therefore, the production mechanisms of gas phase atoms and their subsequent ionisation can thus be discussed separately.

It can be seen that for the $4^2P_{3/2} \rightarrow 5^2P_{3/2}$ two-photon transition the resonant width of the symmetric profile is only 0.015 nm (FWHM) while for the $4^2P_{1/2} \rightarrow 4^2D_{3/2}$ one-photon transition, considerably larger widths and asymmetric spectra are observed.

In a previous paper [4], an average atomic density in the interaction region was estimated to be about $10^{15}\,\mathrm{cm}^{-3}$. For this atomic density, the Lorentzian width of a pressure broadened line is orders of magnitude less than the present laser linewidth. For the monochromatic UV laser intensity of $10^6\,\mathrm{W\,cm}^{-2}$, the corresponding Rabi frequency for the transition $4^2P \rightarrow 4^2D$ is about 1000 GHz and somewhat less for a finite bandwidth laser. This is consistent with the observed widths. However, the asymmetric profile suggests that other collisional processes should be considered.

It has been shown that long range interactions between collisional partners in the presence of strong laser radiation can produce considerably asymmetric lineshape. This so-called "optical collision" is expressed as follows [7–9],

$$A + B + h\nu \rightarrow A^* + B\,, \tag{1}$$

where the transition of atom A is energetically forbidden without collision. While collisions are known to modify atomic energy levels, a detailed description of optical collisions is given by the dressed quasimolecular model [8] in which the effects of the laser field is taken into account. The frequency shift for an individual collision is predominantly red shifted, and a Van de Waals attractive interaction between the atoms is normally used to describe the collisional process. For the total atomic assembly interacting with the laser, a large asymmetry in the wings of the profile results. In the present experiments, the excitation is well saturated at line centre where the resonant transition need not be assisted by collisions, while the transition probability in the quasistatic wing is still proportional to the laser intensity for one-photon absorption – the total effect produces the very large asymmetric broadening.

Comparing Fig. 1 and Fig. 2 it is seen that no comparable broadening occurs for the $4^2P_{3/2} \rightarrow 5^2P_{3/2}$ excitation. When the laser intensity was increased in the experiment, only a slight broadening of the profile was observed. This can be understood by taking into account the transition probability of the two-photon process which, even at the line center, is far from saturation. For the present laser flux, two-photon optical collisions do not produce a detectable ion signal in the far wing of the spectral line despite similar atomic density as in the case of the $4^2P_{1/2} \rightarrow 4^2D_{3/2}$ transition.

The power dependence of the ion yield measured at line centre of the resonances are shown in Figs. 3 and 4. The observed power indices are 4 ± 0.5 and 9 ± 1 for the two excitation schemes, $4^2P \rightarrow 4^2D$ and $4^2P \rightarrow 5^2P$ respectively. To understand the difference in the power indices, one should consider the three steps to ion formation, namely ablation of neutrals, excitation and ionisation.

The dependence of ablation yield on laser wavelength can be ignored. The reason is firstly the energy of the UV laser in the $4^2P \rightarrow 4^2D$ case was several times less than the fundamental beam and would not increases the ablated neutral yield appreciably and secondly, there is no specific absorption structures in GaAs solid [10] in

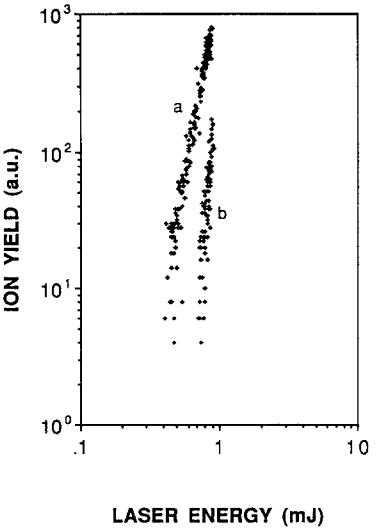

Fig. 3. Laser power dependences of ion yield for one-photon resonance $4^2P_{1/2} \rightarrow 4^2D_{3/2}$ with laser wavelength λ_1 at (*a*) line centre and (*b*) $\Delta\lambda = \lambda_1 - \lambda_0 = -0.5\,\mathrm{nm}$

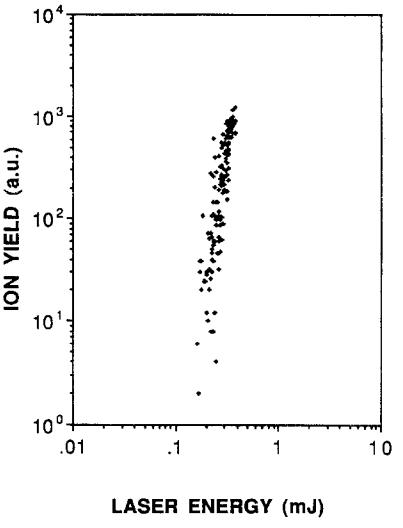

Fig. 4. Laser power dependence of ion yield for two-photon resonance $4^2P_{3/2} \rightarrow 5^2P_{3/2}$ with laser wavelength λ_1 at line centre

the small range of wavelength studied. Furthermore, according to a thermal ablation mechanism [11] applied to our configuration and conditions, the neutral yields produced in the present experiments are expected to have very similar power dependence for the two different laser wavelengths used (575 and 618 nm) [12]. Thus one should consider the subsequent excitation and ionisation processes for the explanation of the difference in the laser power depencence. For the $4^2P \rightarrow 4^2D$ case, the ratio of the number of the excited state to ground state atoms is independent of the laser intensity at line centre because of well saturated excitation, while an I^2 dependence on laser flux (I) for the $4^2P \rightarrow 5^2P$ transition results from the unsaturated two-photon process. It is obvious that the observed difference of the power index between the two cases (~ 5) cannot be accounted for by photoionisation following the resonant excitation, as this type of

process only gives rise to a total difference in the power index of 2. Thus other ionisation mechanisms need to be considered. It should be pointed out that atomic energy level shift under irradiation of strong narrowband pulsed laser tuning around atomic resonance line can greatly influence experimental laser power dependence of photoion yield [13]. However in the present experiment, any such effect will be entirely masked by the large laser linewidth and the normal power law should still be expected for the resonant stepwise ionisation.

The observations mentioned above can be explained on the assumption that ionisation proceeds via energy pooling (EP) collisions. In alkali-metal atomic vapours, these kind of processes have been studied extensively both in theory and experiment [14–17]. EP collisions leading to ionisation has also been suggested [18]. Measurements of the collisional rates by several groups give excitation cross-section of 10^{-14}–$10^{-16}\,\mathrm{cm}^2$ for both homonuclear and heteronuclear collisional systems [19–22], showing that the energy-pooling processes are highly efficient. However very few studies have been reported for IIIB elements, presumably due to the difficulty of preparing the high density atomic vapour necessary to obtain measurable signals. Most recently, Bicchi et al. have reported the experimental observations of EP collisions in indium atomic vapour [23], where the EP processes populated not only the discrete highly excited states but also an autoionisation level.

The following analysis, indicates that the observations in Figs. 3 and 4 may be explained by assuming that the ions produced in this experiment result mainly from collisional processes between the excited atoms, i.e., EP ionisation, expressed schematically as follows,

$$\mathrm{Ga}^* + \mathrm{Ga}^* \rightarrow \mathrm{Ga}^+ + \mathrm{Ga}(4^2P)\,, \tag{2}$$

where Ga^* stands for the atom in the 4^2D or 5^2P excited states.

For a pair of atoms both in the 4^2D or in the 5^2P level, the total internal energy is sufficient to produce a final state with one atom returning to the ground level and the other emerging above the ionisation potential through an inelastic collision. The internal energy excess may be taken away by the ejected electron.

For collisional ionisation of a pair of atoms in the same excited level, the collisional ionisation rate R per unit volume (in unit $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$) [21] can be expressed as follows

$$R = (1/2)kN_e^2\,, \tag{3}$$

where k is the ionisation rate coefficient in $\mathrm{cm}^3\,\mathrm{s}^{-1}$, N_e the density of the excited atoms and a factor of $1/2$ introduced for the homonuclear system considered here.

If the neutral yield N in the ablation process is assumed to have the following laser power dependence in both $4^2P \rightarrow 4^2D$ and $4^2P \rightarrow 5^2P$ excitation schemes,

$$N \propto I^n\,, \tag{4}$$

where n is the power index of the ablation processes, then the total power dependence of the ion yield in EP ionisation process is

$$R \propto (N_e)^2 \propto (NI^m)^2\,, \tag{5}$$

where m is the power index for the resonant excitation process. For $4^2P \rightarrow 4^2D$ resonant excitation, the saturated excitation condition was satisfied at the line center for the laser power used. Thus $m = 0$ and we have

$$R_{4^2P\rightarrow 4^2D} \propto I^{2n}\,. \tag{6}$$

For $4^2P \rightarrow 5^2P$ resonance the two-photon unsaturated excitation results in $m = 2$, and the total power dependence is

$$R_{4^2P\rightarrow 5^2P} \propto I^{2n+4}\,. \tag{7}$$

From (6) and (7), the resultant difference in the slope of the two log–log curves is 4. This value falls within the experimental observations of 5 ± 1.5 (assuming maximum uncertainties). Following this analysis, the power index for the ablation process should be

$$n = 2.25 \pm 0.5\,. \tag{8}$$

We also measured the laser power dependence for $4^2P \rightarrow 4^2D$ excitation at a detuning $\Delta\lambda = \lambda_l - \lambda_0 = -0.5\,\mathrm{nm}$, where λ_0 is the undisturbed atomic transition wavelength and λ_l the laser wavelength. The results are shown as curve (b) in Fig. 3. The measured power law for the ion signals at the line wing is $I^{11\pm1}$, quite different from $I^{4\pm0.5}$ measured at line center (curve (a)). Consider a two-step process for ion formation in the line wing. Firstly, the Ga atoms in the ground state absorb a photon ($\lambda \neq \lambda_0$) during a collisional event. The production rate of excited Ga atoms is proportional to $N_e \propto N^2 I$ for the unsaturated transition rate in line wing. Then two such excited atoms collide to produce an ion and a ground state atom by the EP process, resulting in the following power law for the signals in the line wing,

$$R \propto N_e^2 \propto I^{4n+2}\,. \tag{9}$$

From the obtained value of n (8) and comparing (6) and (9), the resultant index difference for curves (a) and (b) in Fig. 3 will be $2n + 2 = 6.5 \pm 1$, which fits well to the measured value of 7 ± 1.5. Thus the observed power law agrees with the optical collision explanation.

3 Conclusions

The present experiment has studied the influence of laser-induced collisional processes, i.e., optical collision excitation and probable energy-pooling ionisation, on the ion production during laser ablation of GaAs under moderate laser intensity. The greatly enhanced ion yields, the observed spectral profile and the laser power dependence are well explained by this model. It should also be mentioned that direct photoionisation from the excited states is an efficient ionisation channel in the present experimental conditions, which suggests that the cross-section of energy-pooling ionisation may be very large. Further experiments are now in progress to confirm the role of EP ionisation in laser ablation using tunable lasers.

Due to the relative ease of preparing atomic vapours of high density in laser ablation, it is hoped that various collisional processes between atoms may be studied using the laser ablation technique. It may also be possible to apply this type of resonant enhancement to trace analysis of atoms and molecules in solid samples.

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