Laser gas-discharge absorption measurements of the ratio of two transition rates in neutral argon

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The ratio of line strengths for the two argon transitions, $3p^5(^2P^o_{1/2})4s[1/2]^o_1 \rightarrow 3p^5(^2P^o_{3/2})4p[3/2]_2$ at wavelength 922.7 nm and $3p^5(^2P^o_{1/2})4s[1/2]^o_1 \rightarrow 3p^5(^2P^o_{3/2})4p[5/2]_2$ at wavelength 978.7 nm, is measured in an argon pulsed discharge with the use of a single-mode Ti:sapphire laser. The result 3.29(0.13) is in agreement with our theoretical prediction 3.23 and with a less accurate ratio 2.89(0.43) from the NIST database.

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I. INTRODUCTION

Electronic structure and transition rate data particularly in argon are of importance in applications such as radiation-induced decomposition, astrophysical abundances, biophysics, gas laser physics, as well as the development of theoretical methods of atomic structure. Argon and other noble-gas atoms have been attractive media for applying and testing methods of plasma spectroscopy and especially for testing experimental techniques and theoretical calculations to determine transition rates. Absolute oscillator strengths have been obtained from photoabsorption spectra using the simple Beer-Lambert law (see Refs. [1,2], and references therein), and self-absorption determinations of oscillator strengths [3,4] have been made in noble gases He–Kr. The spectra resulting from electron impact are also used to extract transition rate data [5]. This paper contains further numerous references to previous measurements with other experimental techniques such as pressure broadening profile and lifetime methods. The measurements in the visible part of the argon spectrum are conducted and overviewed in Ref. [6], and the most recent values of transition probabilities included in the NIST database are given in Ref. [7].

It is interesting to note that semiempirical calculations are more successful for the prediction of transition rates between excited states of noble-gas atoms than *ab initio* calculations: actually, in argon we find *ab initio* calculations only for the transitions from the ground state [8] (a review of previous theoretical calculations is provided). Semiempirical calculations in Refs. [9,10] give reasonably accurate values of transition probabilities, despite some mutual discrepancies. In general, a need for improvement of theory remains.

We have recently developed a theory for particle-hole states of closed-shell atoms, which is potentially able to predict energies and transition rates with high precision. Initially, this theory has been tested in neon [11,12]. For transitions between neon excited states, the accuracy of experiments is very good and experiments agree well with our theory. However, for heavier noble-gas atoms, experiments are often prone to systematic errors and the precision is much lower. For example, many absolute transition rates of argon were based on high-pressure arc plasmas and depended on the assumption of local thermodynamic equilibrium of the upper-state populations, which often was satisfied very approximately (see discussion in Ref. [6]). Lifetime measurements using different techniques or even the same technique often yield quite different results. In Ref. [7], a unified set of atomic probabilities for neutral argon is given. The data are included in the NIST database where errors of order 10% are quoted. Although our theory is able to reproduce NIST data, the difference between experiment and theory often exceeds error bars quoted in Ref. [7]. There are two possibilities: (i) the theory is less accurate and needs to be improved and/or (ii) experimental errors are larger and critical, more precise measurements are needed.

We describe a different experimental technique for precise measurements of ratios of transition rates in gas discharges and detail an apparatus realizing this technique in our measurement of the ratio of two argon transitions. After analysis of systematic errors, we present a comparison with our theory and other theories and experiments.

II. AN EXPERIMENTAL TECHNIQUE FOR ACCURATE MEASUREMENTS OF TRANSITION RATE RATIOS IN PULSED DISCHARGES

The essential goal of our experimental technique is to measure the relative absorption rates for two different transitions that start from the same level in a pulsed discharge. The measurement of absorption to determine transition rates is a simple, well-known method of classical spectroscopy. The application of the direct absorption method for precise measurements of transition probabilities in gas discharges where populations of states are difficult to find independently is unusual. Measurement of ratios in a continuum discharge can be problematic, since upper levels are substantially populated. Our unique method relies on the use of pulsed discharges to avoid upper-state populations. Absorption measurements in pulsed discharges with the aim to investigate the dynamics of metastables or their relative population were conducted long ago [13,14]. This method, which is also called the afterglow absorption method, is very sensitive even with the use of discharge lamps where the sensitivity can be limited by background pulsed discharge emission. The use of lasers can enhance the sensitivity and the accuracy of such absorption measurements. We have found no use of pulsed discharges for precise determination of transi-

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tion rate ratios; hence, we would like to describe some unique aspects of our technique in detail.

In this section, we show how line strength ratios can be extracted, why a pulsed discharge has to be used, and why nonmetastable levels, besides metastables, can be used in precise measurements. Further details of our technique are given in the following two sections. Further information on these topics is found in Ref. [12].

In general, the populations of the lower (N_i) and upper states (N_f) are needed for finding the cross section σ_{if} from the absorption coefficient α_{if},

$$\alpha_{if}=[N_i-(g_i/g_f)N_f]\sigma_{if} \tag{1}$$

(here g_i/g_f is the ratio of statistical weights). However, in some cases the upper-state population can be neglected. This happens when the initial state is the ground or long-lived metastable state, and the final, upper states are short lived and relatively unpopulated. In gas discharges, at low current densities, metastable levels are generally much more populated than any other nonmetastable excited levels. Experimentally, we also observed the absorption from some states that have allowed decay modes. The $3p^5(^2P^o_{3/2})4s[3/2]^o_1$ and $3p^5(^2P^o_{1/2})4s[1/2]^o_1$ states, surprisingly, were populated almost as much as metastables at discharge pressures of a few Torr. The long observed lifetimes of these states of the order of 10 μs are explained by radiation capture: many possibilities of emission and absorption of a photon occur before the photon can leave the discharge cell. The observation of these long-lived species in discharges gives the possibility to use them as lower states for absorption measurements. The other excited levels (not belonging to the $4s$ group) quickly decay radiatively without radiation capture and are effectively depopulated in a pulsed discharge as soon as the discharge current disappears. Therefore, in upward transitions that start from the $4s$ levels, the condition $N_i \gg N_f$ is satisfied, and the absorption becomes proportional just to the cross section and the initial density. Thus, by measuring the absorption for two transitions starting from the same level, in our experiment $3p^5(^2P^o_{1/2})4s[1/2]^o_1$, we can find the ratio of cross sections from the ratio of absorptions,

$$\frac{\sigma_{if_1}}{\sigma_{if_2}}=\frac{\alpha_{if_1}}{\alpha_{if_2}}. \tag{2}$$

For a Doppler broadened profile and for monochromatic laser light tuned to the maximum of the profile, the ratio of cross sections is equal to the ratio of line strengths,

$$\frac{\sigma_{if_1}}{\sigma_{if_2}}=\frac{S_{if_1}}{S_{if_2}}=\frac{S_1}{S_2}. \tag{3}$$

Therefore, by measuring the ratio of absorptions for two transitions, we can find the ratio of line strengths S_1/S_2.

If the condition $N_f=0$ is accurately satisfied, the measurement of absorption ratios can be very accurate. For example, the absorption ratio of Cs transition was measured with the accuracy better than 0.1% by Rafac and Tanner [15]. However, in the case of noble gases, especially when we choose the starting level to be a nonmetastable state, a more complicated analysis is required.

In order to satisfy the condition $N_i \gg N_f$ for the lowest excited states, we use a pulsed rather than a dc discharge. In a dc discharge this condition is weaker, because radiatively decaying levels are constantly repopulated by collisions with hot electrons and by decay of higher levels. It is especially true for radiation-capturing levels. A further advantage of a pulsed discharge is the possibility for enhancing the sensitivity of absorption measurements by utilizing the time dependence of absorption. For example, slow fluctuations in laser intensity can be excluded. In addition, the signal-to-noise ratio can be improved using averaging (128-scan in our experiment) on a digital oscilloscope. Without special efforts, an absorption of order 0.1% can easily be detected. Such high sensitivity is useful for fast and precise tuning of the laser to centers of Doppler profiles. The long-term stability of the pulsed discharge is also better: the pulsed discharge has substantially smaller sputtering and thermal effects, since the total charge from the discharge current is much smaller for a pulsed discharge.

The principal disadvantage of the pulsed discharge is the more complicated analysis of systematic errors, basically owing to the finite-time response of the detection system. The various factors that can influence the measurement of the ratio in pulsed discharges need careful analysis: we will consider systematic errors that arise from large absorption and inhomogeneity. When two transitions differ by a factor of at least 3, a larger absorption is recommended for a better signal-to-noise ratio. In such a case the linear relation between absorption and line strength may no longer hold, and instead Beer's law must be used to derive the more general equation:

$$\frac{\ln(I_1/I_{10})}{\ln(I_2/I_{20})}=\frac{S_1}{S_2}. \tag{4}$$

Here I_1/I_{10} and I_2/I_{20} are the reductions in the intensity after passing the absorber for the first and the second transitions, respectively. This nonlinear equation can lead to several systematic errors, which will be considered later.

If we examine NIST transition data [16] for neutral argon, we find many transitions in the range of tunable lasers such as a Ti:sapphire laser, which can be used for the absorption experiments. However, in practice there are some restrictions: first, the pair of transitions has to start from the same metastable level or radiation-capturing level such as mentioned above. Second, the range is greatly restricted by the tunability of the laser: for example, our Ti:sapphire laser has several mirror sets for several ranges of wavelengths. Because the change of mirrors takes many hours to complete, only one mirror set can be used for measurements of ratios at one time. As a result, for our currently installed mirror set, only two pairs of transitions were appropriate. However, our laser could not be tuned for one transition, and we were able to make measurements for only one pair of transitions: one transition at a wavelength 9227 Å and the other at 9787 Å.

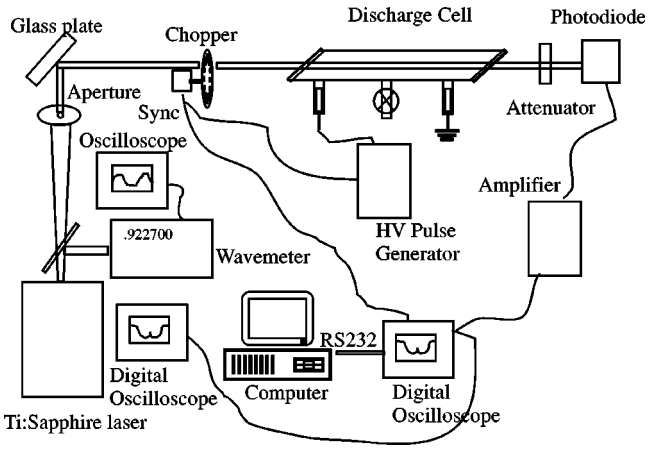

FIG. 1. An experimental setup for conducting measurements of absorption of laser radiation in pulsed discharges.

III. EXPERIMENTAL ARRANGEMENT

The optical and electrical diagrams of the experimental arrangement are shown in Fig. 1. The monochromatic 1-W laser beam generated by the Ti:Sapphire laser is expanded by traveling 8 m between two optical tables to the size of about 5 cm diameter. A variable aperture reduces both the beam's size and its power. To avoid saturation of the transition, the beam intensity is further reduced using a 2% reflection off a glass plate. A chopper periodically interrupts the beam to give a 100% reference absorption. (Because the background emission from a discharge is negligible in our experiment, a closed chopper is equivalent to 100% absorption and an open chopper to 0% absorption.) The beam is then directed through the discharge cell where it undergoes time-dependent absorption in the discharge initiated by HV pulses from the high-voltage (HV) pulse generator. The optical path of the laser beam is terminated on the photodiode. The attenuator in front of the screened photodiode compartment is used to avoid any saturation effects in the detection system.

The signal from the photodetector is amplified and sent to the two digital oscilloscopes for measurement of the absorption. The chopper synchronizes the HV pulse generator and the digital oscilloscopes. The chopper frequency can be varied in some range and is chosen fast enough for the convenience of data acquisition but slow enough for the HV pulser to be able to break down discharge since the power is limited. In addition, the sputtering becomes an issue at fast rates (see also Ref. [12]). The laser is manually tuned to two transitions in sequence. The tuning is performed in two steps. First, using the wavemeter, we find approximately an argon transition, and then fine tuning is achieved with a laser scan by observing the absorption signal on an oscilloscope.

The laser is a commercial single-frequency MBR-110 Ti:sapphire laser, pumped with 7–15 W continuous-wave (cw) coherent argon ion laser.

A brief description of other essential elements of our experimental setup is provided below; more information about components of this experiment can be found in Ref. [12]. The discharge cell is a quartz tube of diameter 2.5 cm and a length of 30 cm. Two standard electrodes were fused symmetrically in side tubes near each end. The electrodes have large area to reduce unwanted sputtering from the cathode, which can reduce the lifetime of metastables significantly and affect the population distribution in the discharge as we observed in detail in helium [12]. Moreover, for the same purpose, an external ballast volume was added to the cell.

A high-voltage pulse generator produces high-voltage (more than 10 kV to allow fast discharge breakdown) pulses each of a few microsecond width. The circuit is based on a power transistor in the switching mode and a high-voltage transformer.

The detection system consists of a photodiode, an amplifier, and digital oscilloscopes. There is no special requirement on those elements except that the detection system should provide a linear response and the distortion of the wave form of the signal should be minimal. The first requirement is completely fulfilled if the laser intensity does not exceed the saturation limit for a particular diode. The second requirement is approximately satisfied: small distortion of the signal has been observed. This effect is analyzed in detail in the following section.

IV. MEASUREMENT AND ERROR ANALYSIS

To find the ratio of line strengths S_1/S_2 (S_1 is the line strength for the first transition $3p^5(^2P^o_{1/2})4s[1/2]^o_1 \rightarrow 3p^5(^2P^o_{3/2})4p[3/2]_2$ at 922.7 nm, and S_2 is the line strength for the second transition $3p^5(^2P^o_{1/2})4s[1/2]^o_1 \rightarrow 3p^5(^2P^o_{3/2})4p[5/2]_2$ at 978.7 nm), we measure the peak absorption for two transitions and use the formula

$$\frac{\ln(1-V_1/V_{10})}{\ln(1-V_2/V_{20})}=\frac{S_1}{S_2}. \tag{5}$$

Here V_1 and V_{10} are the voltages proportional to the maximum of a pulsed discharge absorption and to the chopper normalization absorption for the transition at $\lambda=922.7$ nm shown in Fig. 2. Similar voltages for the second transition at $\lambda=978.7$ nm also shown in Fig. 2 are V_2 and V_{20}.

Repeating measurements of absorption several times, we have obtained the ratio 3.29 ± 0.04. A small error here indicates the excellent statistics. However, the result can still have systematic errors which need to be estimated and if possible be excluded.

Systematic error can occur from a slow drift in discharge conditions. Though our pulsed discharge is very stable, to account for any slow drift, we alternate measurements of the absorptions for the two transitions.

A second possible systematic error can arise from the uncertainty in wavelength when the laser is manually tuned to the resonances of the transitions by monitoring absorption peaks similar to those shown in Fig. 2. Although the uncertainty of wavelength is random, it gives a systematic decrease in the values of peaks because only at resonance is the absorption signal maximum. If $\varepsilon_1=\langle[V_1(\lambda)-V_1(\lambda_{res})]/V_{10}\rangle_{av}$ and $\varepsilon_2=\langle[V_2(\lambda)-V_2(\lambda_{res})]/V_{20}\rangle_{av}$ are relative average shifts in the absorption signals owing to tuning uncertainty, then the absolute systematic shift in the ratio $\sigma(\varepsilon_1,\varepsilon_2)$ is

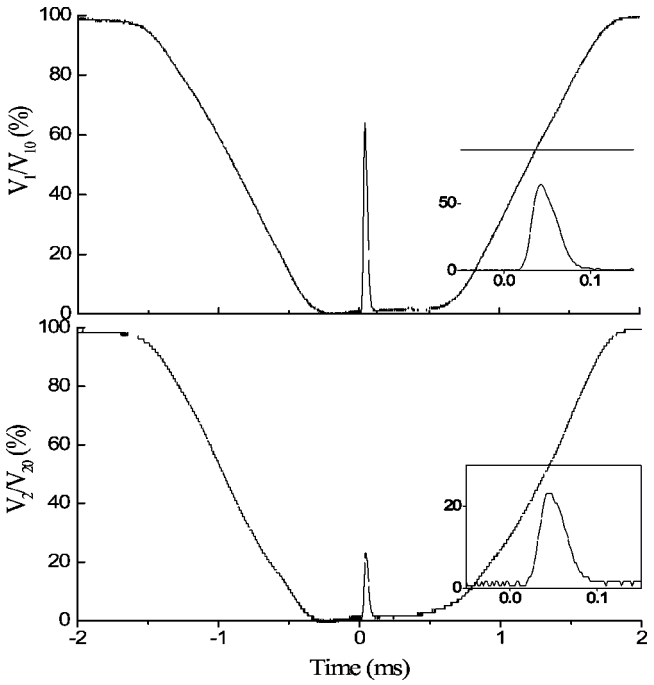

FIG. 2. Absorption signals in a pulsed discharge with chopper modulation for normalization. Absorption of two transitions is measured. The larger peak shown on the upper panel corresponds to absorption at 922.7 nm and the smaller one on the lower panel corresponds to absorption at 978.7 nm. The width of both peaks is about 0.03 ms. The shape of chopper modulation is represented by periodic pulses with width about 2 ms. The absorption peaks and the chopper modulation are synchronized. The insets show that after rescaling, the absorption peaks have the same shapes.

$$\sigma(\varepsilon_1,\varepsilon_2)=\frac{\ln\{[1-(1-\varepsilon_1)V_1/V_{10}]\}}{\ln\{[1-(1-\varepsilon_2)V_2/V_{20}]\}}-\frac{S_1}{S_2}\approx(\varepsilon_2-\varepsilon_1), \tag{6}$$

where this equation was simplified for small absorption. This tuning error is estimated to be about 1.5%.

A significant systematic error arises from a slow response of the detection system. The slow response results in a reduction of actual height of the peak by an unknown coefficient η:

$$\frac{\ln(\eta I_1/I_{10})}{\ln(\eta I_2/I_{20})}=\frac{S_1}{S_2}. \tag{7}$$

If the equations were linear, this coefficient would drop out from the ratio, but for large and significantly different absorptions for the two transitions, it will cause a systematic error in the ratio. Suppose ε is the reduction in the peak height because of a slow time response. Then we can write for the S ratio

$$\frac{\ln[1-(1-\varepsilon)V_1/V_{10}]}{\ln[1-(1-\varepsilon)V_2/V_{20}]}=\frac{S_1}{S_2}+\sigma. \tag{8}$$

This type of the systematic error can be estimated owing to dependence on different levels of absorption. The approximate value of the ratio needed for such an estimate can be taken from our experiment or from other sources because uncertainty in the ratio leads to smaller uncertainty in the estimate of the systematic shift. Comparing measurements of ratios at different discharge currents and, hence absorption, we find that the time response error is about 4% at the level of absorption used in final measurements. This error gives a systematic increase in the ratio by 4%, but the previous error due to tuning decreases the ratio slightly by 1.5% so that the overall systematic error is smaller.

Another systematic effect arises from inhomogeneities in the discharge. So far we assumed that the absorption medium is homogeneous, but in gas discharges this is far from being true. The discharge produces densities of excited atoms with some transverse and longitudinal distributions. The longitudinal distribution does not cause any problem, since for two transitions the ratio at each small length of path stays the same, and eventually the ratio of logarithms of intensities in Eq. (4) will remain the same. The transverse distribution, however, can cause a deviation from the simple Beer's law and requires the analysis of this distribution.

For a cylindrical discharge cell, which we use in our experiment, if r is the distance from the axis, an integration over r is needed,

$$I_{out}=\int I_{in}(r)\exp[-\alpha(r)]2\pi r dr, \tag{9}$$

where $I_{in}(r)$ is the input laser beam intensity, $\alpha(r)$ is the absorption coefficient, and I_{out} is integrated over a detector area output intensity after an inhomogeneous discharge medium. For simplicity in this equation the change in absorption along the laser beam is ignored. It is difficult to find the spatial distribution accurately, although in some simple cases it can be predicted. In the case of a diffusion controlled cylindrical discharge, the distribution for the electron density n_e and for excited-state densities has approximately the form of a Bessel function,

$$\alpha(r)\sim n_e\approx J_0(2.4r/R)\cos(\pi z/L). \tag{10}$$

The expression for the electron density n_e is taken from Ref. [17], p. 67. Using the series expansion of the Bessel function for small argument, $J_0(2.4r/R)\approx 1-\frac{1}{4}(2.4r/R)^2$ we can show that in our experiment with $R=1.25$ cm and $r=0.2$ cm, the maximum change in the absorption over the beam radius r is 3.7% and the change in the integral for small $\alpha(r)$ is only 1.8%. Therefore the effect of the distribution is small. Moreover, if the absorption is not very large, the exponential can be expanded, and the linear dependence of the signal on the absorption coefficient can reduce further the effect of the distribution.

Taking into account the above statistical and systematic errors, we obtain the accuracy of the measurement of the ratio about 4%. The final value of our ratio is 3.29 ± 0.13.

V. COMPARISON WITH CALCULATIONS AND OTHER MEASUREMENTS

The comparison of the ratio of line strengths is given in Table I. Our measured ratio of line strengths 3.29 ± 0.13 is in

TABLE I. The ratio of the two line strengths at 922.7 nm and 978.7 nm.

Source	Ratio
Experiment	
This work	3.29 ± 0.13
Wiese *et al.* [7]	2.9 ± 0.4
Theory	
Savukov [12]	3.23
Lilly [9]	3.51
Garstang and Blerkom [10]	4.62

excellent agreement with the value 3.23 obtained from our mixed configuration-interaction and perturbation-theory calculations [12]. Both measured and theoretical ratios agree also with the ratio $2.89 \pm 15\%$ calculated from the experimental transition rates of Ref. [7]. Our results are close to semiempirical calculations by [9]. However, the ratio 4.62 from semiempirical calculations of Ref. [10] based on a similar principle as calculations in Ref. [9] disagree substantially with our result. One obvious problem with semiempirical approaches is that energies cannot define completely the wave functions which are very sensitive to the accuracy of calculations. In addition, transition amplitudes have additional corrections which are not accounted by the effective Hamiltonian. For example, random-phase approximation corrections are due to shielding by the atom of an external photon field. Those corrections are substantial in Ar and heavier noble-gas atoms and must be included to reach a good precision.

VI. CONCLUSIONS

We have measured an accurate ratio of line strengths for two argon transitions. For this measurement we developed a different experimental technique based on a pulsed discharge and a laser absorption measurement. This technique can be applied for measurements of other ratios in noble-gas atoms. The agreement of our measurement and calculations is excellent.

[1] W.F. Chan, G. Cooper, X. Guo, G.R. Burton, and C.E. Brion, Phys. Rev. A **46**, 149 (1992).
[2] W.F. Chan, G. Cooper, X. Guo, and C.E. Brion, Phys. Rev. A **45**, 1420 (1992).
[3] N.D. Gibson and J.S. Risley, Phys. Rev. A **52**, 4451 (1995).
[4] R.C.G. Ligtenberg, P.J.M. van der Burgt, S.P. Renwick, W.B. Westerveld, and J.S. Risley, Phys. Rev. A **49**, 2363 (1994).
[5] S.L. Wu, Z.P. Zhong, R.F. Feng, S.L. Xing, B.X. Yang, and K.Z. Xu, Phys. Rev. A **51**, 4494 (1995).
[6] A. Hirabayashi, S. Okuda, Y. Nambu, and T. Fujimoto, Phys. Rev. A **35**, 639 (1987).
[7] W.L. Wiese, J.W. Brault, K. Danzmann, V. Helbig, and M. Kock, Phys. Rev. A **39**, 2461 (1989).
[8] E.N. Avgoustoglou and D.R. Beck, Phys. Rev. A **57**, 4286 (1998).
[9] R.A. Lilly, J. Opt. Soc. Am. **66**, 245 (1976).
[10] R.H. Garstang and J.V. Blerkom, J. Opt. Soc. Am. **55**, 1054 (1965).
[11] I.M. Savukov, W.R. Johnson, and H.G. Berry, Phys. Rev. A **66**, 052501 (2002).
[12] I.M. Savukov, Ph.D. thesis, University of Notre Dame, 2002.
[13] A.V. Phelps, Phys. Rev. A **99**, 1307 (1955).
[14] A.V. Phelps and J.L. Pack, Rev. Sci. Instrum. **26**, 45 (1955).
[15] R.J. Rafac and C.E. Tanner, Phys. Rev. A **58**, 1087 (1998).
[16] Available online at http://physics.nist.gov/cgi-bin/AtData/main_asd.
[17] Y.P. Raizer, *Gas Discharge Physics* (Springer-Verlag, Berlin, 1991).