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Inert-gas collisional broadening and shifts of Rb Rydberg states

Wan-Ü L. Brillet* and A. Gallagher†

Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, Colorado 80309

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The broadening and shift of several Rb $3S$-nS and $3S$-nD transitions perturbed by inert gases have been measured by Doppler-free two-photon absorption and fluorescence detection. The measured shifts are in reasonable agreement with the theoretical predictions, whereas the measured broadening rates are found to be much larger.

INTRODUCTION

Investigations of the interaction between highly excited alkali atoms and ground-state neutral atoms, either foreign gases or alkali, have been carried out for a long time. For foreign-gas perturbers, the earlier experimental measurements of broadening and shift[1-5] concern absorption lines of the principal series and were performed under rather high foreign-gas pressure (a few atmospheres) to overcome the Doppler broadening. The corresponding theory, first formulated by Fermi[6] then refined by Alekseev and Sobel'man,[7] has been recently reconsidered by Omont.[8] For very high levels ($n > 30$), the agreement between experiment and theory was excellent (see, for example, Refs. 7 and 9), although the experimental conditions might not yield the low-pressure limit calculated by the theories. For the intermediate n values, Omont has recently given a theoretical estimate so that it is interesting to obtain more experimental data for this region. Furthermore, the Doppler-free two-photon technique[10-12] allows the experiment to be performed at much lower perturber densities where the impact theory and the binary encounter assumptions are better satisfied. It also allows the excitation of levels of the same parity as the ground level. Self-broadening of the Rb $5S$-nS, nD and Cs $6S$-nD transitions have recently been measured by this technique in a thermionic diode.[13,14] The inert-gas-induced relaxation of Na Rydberg nS and nD states with $n = 5$–40 have also been studied using the trilevel echo technique.[15,16] In the present work, we used the two-photon absorption techniques, with observation of the resulting fluorescence, to investigate the broadening and the shift of several $5\,^2S_{1/2}$-$n\,^2S_{1/2}$ and $5\,S_{1/2}$-$19D_J$ transitions of rubidium by inert gases, and we compared the experimental results to theoretical predictions.

APPARATUS

The experimental arrangement shown in Fig. 1 was designed for line broadening studies in conjunction with the technique of Doppler-free two-photon spectroscopy. The experimental cell consisted of a stainless steel cross closed at each end by a quartz window. Brewster angle windows were used along the laser axis to minimize reflection losses. The center of the cross was heated to a temperature around 190 °C whereas the four windowed ends were water cooled. The cell was coupled to a vacuum system near the windows, so that it could be evacuated to a pressure below 10^{-6} torr, then filled with one of the five inert gases. The gas pressure was varied between 0.2 and 30 torr, and was measured to ±1% with a capacitance manometer. High purity rubidium was placed in the central part of the cell and the metallic vapor diffused toward the cooled parts and condensed on the wall of the tubes before reaching the windows, while the inert gas filled the cell. The rubidium vapor pressure, which was lower than the saturated vapor pressure (2.5×10^{-2} torr at 190 °C), was not measured but remained constant when the temperature was kept constant.

For excitation, we used a single frequency tunable cw dye laser pumped by an Ar^+ laser. The typical output power was 90 mW and the linewidth was about 2 MHz. The laser frequency could be scanned with excellent linearity and reproducibility

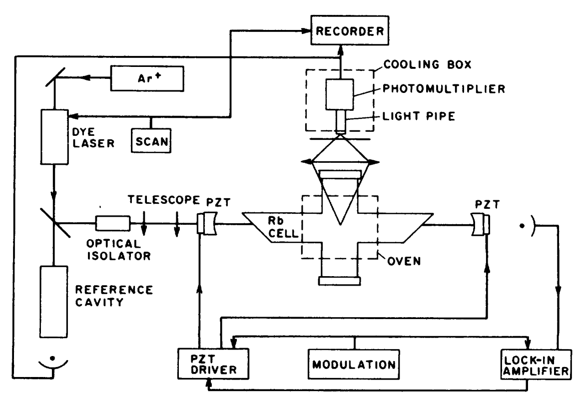

FIG. 1. Experimental arrangement.

over a range of 30 GHz ($\Delta\lambda = 0.3$ Å). The laser wavelength was measured to ±0.5 m Å using a lambda meter.[17]

The Doppler-free profile is obtained when atoms absorb simultaneously two photons propagating in opposite directions[10,11] and the absorption varies as the square of the laser beam intensity. To increase the signal size, we placed the rubidium cell inside a nearly hemispherical resonator (~59.7-cm length with mirrors of 30-cm radius), giving a power buildup factor of ~20 and a laser beam waist diameter of ~60 μm. The input mirror had ~5% transmission whereas the rear mirror had high reflectivity (>99.8%). Two lenses making a telescope matched the resonator to the laser cavity, and a Faraday rotor was used as an optical isolator. The two mirrors of the cavity were mounted on piezoelectrical ceramics. One of them had high sensitivity and slow time response, the other had fast response and lower sensitivity. The length of the cavity was thus modulated and a servo loop was used to lock the cavity length to the laser so as to keep the transmission of the cavity maximum as the laser frequency was swept. Modulation and high-frequency correction were provided by the fast PZT while the slow one provided the scan.

Two-photon absorption was detected by monitoring fluorescence ($\lambda < 4200$ Å) corresponding to the $5\,^2S_{1/2}$-$n\,^2P_J$ ($n \geq 6$) transitions. This fluorescence was focused by a lens onto a quartz light pipe placed in front of a cooled photomultiplier and was selected by two Corning 5–57 glass filters.

Experimental data were obtained by scanning the dye-laser frequency sequentially over a given resonance region and then recording simultaneously the output current of the photomultiplier on a chart recorder. The two-photon resonances could be found by means of the lambda meter, their position having been previously accurately measured.[18] For each ns level, one can detect four two-photon absorption lines. The two strongest ones are due to the most abundant (72%) isotope ^{85}Rb and are separated by the hyperfine splitting 3035.73 MHz[19] of the $5s\,^2S_{1/2}$ ground state, the high ns level having a negligible hfs. The outer two components correspond to ^{87}Rb which ground state hyperfine splitting is 6834.68 MHz. As the broadening and shift rates were independent of the hyperfine component,[20] we could choose to record the ^{87}Rb $5\,^2S_{1/2}(F=2)$-$n\,^2S_{1/2}$ line which was well separated from the others, except for $n = 30$ where we chose the strongest component, $5\,^2S_{1/2}(F=3) \rightarrow n\,^2S_{1/2}$ of ^{85}Rb, because of the weakness of the fluorescence signal.

For scan calibration, we added to the signal the transmission peaks of a reference cavity having a free spectral range of 250 MHz. Each scan covered a range of $\simeq 1.3$ GHz and lasted about two minutes. Each resonance was recorded for several pressures of the five inert gases. The shift was measured relative to the reference cavity, and the slow thermal drift of the reference cavity was evaluated and taken into account in the analysis by recording periodically a signal at low gas pressure. Figure 2 shows an example of signals recorded for argon broadening of the ^{87}Rb $5\,^2S_{1/2}(F=2)$-$24\,^2S_{1/2}$ line.

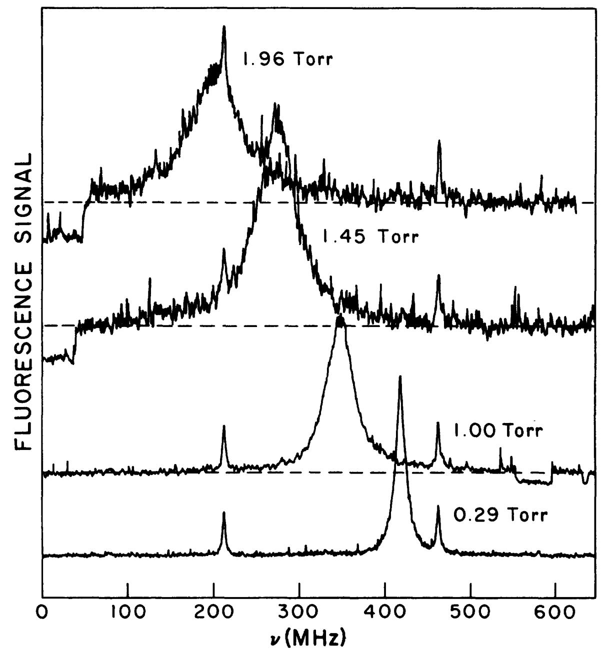

FIG. 2. Recorder trace of $5\,^2S_{1/2}$-$24\,^2S_{1/2}$ signal at pressures of 0.29, 1.0, 1.45, and 1.96 torr argon with different detector sensitivities, as a function of laser detuning ν. The sharp spikes are superimposed signals from a 250-MHz reference cavity.

RESULTS AND DISCUSSION

The pressure broadened Doppler-free lines had a Lorentizian profile, within the experimental accuracy of 1–2%, the laser width of ~2 MHz being negligible compared to the broadened width. The nS state hyperfine structure is expected to be ~20 MHz for $n = 15$, and to decrease rapidly for the higher n. It is also negligible compared to the broadened widths except for the $n = 15$ case for the lowest gas densities used. Owing to absorption of two photons propagating in the same direction, there is a Doppler pedestal underlying the Lorentzian profile.[10] However, it is much broader (width $\simeq$1660 MHz at 460 K) and only affects the Lorentzian by shifting the baseline slightly. One has to note that, because of the two-photon mechanism,

TABLE I. The measured shift rate coefficient $\kappa_{\rm expt}^{\delta}$ of the $5\,^2S_{1/2}$-$n\,^2L_J$ transitions of Rb perturbed by rare gases at 463 K (in 10^{-9} rad sec^{-1} cm^3).

nL	He	Ne	Ar	Kr	Ke
15S	37 ±1.0	3.3±0.15	−62.5±1	−136± 6	−240±10
17S			−67 ±2		
19S	40.7±2	3.5±0.25	−65.0±1	−147±10	−320± 8
24S	30.7±1.5	3.9±0.3	−63 ±2	−125±10	−308± 8
30S	48 ±3	4.1±0.3	−73 ±2	−146± 7	−292±12
34S			−71 ±4		
19D	48.3±1.5	5.2±0.3	−26.2±0.6	−134± 6	−235± 8

the shift and broadening rates measured on the recorded lines in laser frequency units have to be doubled in order to obtain the corresponding rates for the atomic transitions; the latter are reported in the tables and figures.

In Tables I and II, respectively, we give the measured shift and broadening rate coefficients, with their uncertainites, for several $5\,^2S_{1/2}$-$n\,^2S_{1/2}$ transitions of Rb perturbed by the five inert gases. The same results are plotted against the principal quantum number n in Figs. 3 and 4. The broadening and shift rates of the $5\,^2S_{1/2}$-$19\,^2D_J$ transition were also measured and found to be independent of the fine structure (J) component, within the experimental accuracy of 5%. These are plotted in Figs. 3 and 4 at $n=20.8$, since the 19D state has the same effective quantum number as an S state of this n, i.e., the quantum defects are $\delta_s=3.13$ (Ref. 18) and δ_d 1.35.[21] With the exception of the Ar- and Ne-induced shifts, these D-state rate coefficients agree with a smooth average through the S state results (Figs. 3 and 4).

In the study of the broadening and the shift of optical lines involving a Rydberg state, one can ignore the perturbation of the lower level of the transition and only consider the perturbation of the Rydberg state. According to Fermi,[6] the shift is due to two effects. The first one is the scattering of the slow Rydberg electron on the perturbing foreign-gas atom. In the scattering length approximation this shift, also called Fermi shift, can be written in atomic units as [Ref. 8, Eq. (4.1)]:

$$\delta_{sc}=\kappa_{sc}^{\delta}N_p=2\pi LN\,,$$

where L is the scattering length and N is the perturber density. The second effect is the polarization of the perturbing atoms by the positive core of the Rydberg atom. At low perturber density, which is the case in our experimental conditions, this effect has a small contribution and is given in Ref. 7, Eq. (34) and Ref. 8, Eq. (4.2) as (in atomic units):

$$\delta_p=\kappa_p^{\delta}N_p=-6.22(\alpha^2v)^{1/3}N\,,$$

where α is the perturber polarizability and v the collision velocity. Figure 3 shows a comparison of our experimental results with the theoretical shift we calculated using the sum of the two above expressions (solid lines). We used the scattering lengths derived from observed total cross sections[22] and the polarizabilities given in Ref. 23. (These values are also tabulated in Ref. 8.) While the disagreements are frequently outside of the experimental uncertainties, it can be seen that there is fairly good overall agreement; only the Ar-induced shift of the 19D state differs from the theory by more than 30%. On the same figure are plotted previous measurements[5] of the shift by He, Ne, and Ar of the Rb principal series absorption lines. These measurements were performed at much higher pressures (a few atmospheres) than here, while Lorenzen and Niemax[24] have shown

TABLE II. The measured broadening rate coefficients $\kappa_{\rm expt}^{\gamma}$ of the $5s\,^2S_{1/2}$-$n\,^2L_J$ transitions of Rb perturbed by rare gases at 463 K (in 10^{-9} rad sec^{-1} cm^3).

nL	He	Ne	Ar	Kr	Xe
15S	5.6 ±0.4	2.95±0.1	14.1±0.3	46.5±2	159±4
17S			12.3±0.6		
19S	5.7 ±0.4	3.32±0.2	10.3±0.9	30 ±1.5	109±3
24S	8.2 ±0.6	3.82±0.2	10.2±0.6	23.3±2	74±5
30S	5.55±0.3	4.04±0.2	10.2±0.9	22.8±1	63±5
34S			10.2±1.2		
19D	5.8 ±0.3	2.86±0.15	9.6±0.9	23.2±1.5	87±4

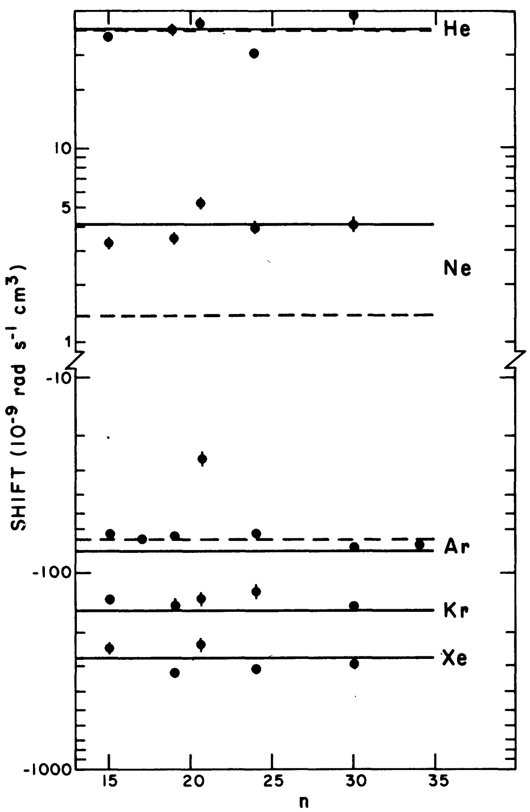

FIG. 3. Shift-rate coefficients of the $5\,^2S_{1/2}$-$n\,^2L_J$ transition of Rb perturbed by rare gases as functions of the principal quantum number n. The points at $n = 20.8$ are from the $19D_J$ states, all others are from the $n\,^2S_{1/2}$ states of the n plotted. Present experiment •, theory of Ref. 3 [Eqs. (4.1) and (4.2)] ——, experiment of Ref. 5 - - -.

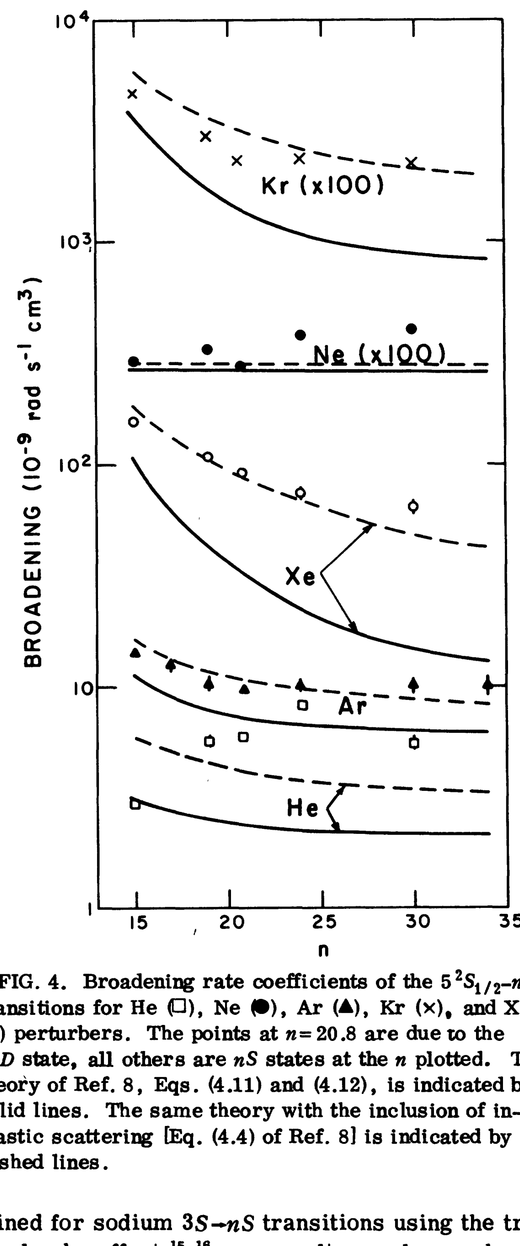

FIG. 4. Broadening rate coefficients of the $5\,^2S_{1/2}$-$n\,^2L_J$ transitions for He (□), Ne (●), Ar (▲), Kr (×), and Xe (○) perturbers. The points at $n = 20.8$ are due to the $19D$ state, all others are nS states at the n plotted. The theory of Ref. 8, Eqs. (4.11) and (4.12), is indicated by solid lines. The same theory with the inclusion of inelastic scattering [Eq. (4.4) of Ref. 8] is indicated by dashed lines.

that some nonlinearity occurs in the Xe-induced shift of Cs for the smaller n values.

Previous studies of alkali lines perturbed by inert gases have shown that as n increases from intermediate to large values the broadening rate decreases toward its asymptotic value. Such behavior is also seen in our experimental broadening rates in the cases of Ar, Kr, and Xe. On the other hand the He points seem to show a maximum near $n = 24$ and the Ne points are increasing with increasing n. No other measurements of inert gas broadening of Rb Rydberg states are available, but we can compare our results to those obtained for other alkalis. Alekseyev *et al.*[9] have measured Cs broadening by Ar, with results (16.3×10^{-9} rad sec^{-1} cm^3 for $n = 15$ and about 12.5×10^{-9} rad sec^{-1} cm^3 for $n > 19$) comparable to what we observe for Rb. Their 25% larger value for high n may be due to Cs self-broadening, whereas in our experiment the Rb self-broadening is completely negligible. Compared to the broadening cross sections obtained for sodium $3S$→nS transitions using the trilevel echo effect,[15,16] our results are larger by about a factor of 4 for Xe, 3 for Kr, and 2 for Ar, He, and Ne. The sodium $3S$-nD broadening cross sections found by the same authors are generally larger than those for the $3S$-nS transitions and are attributed by the authors to the large inelastic collision cross sections measured elsewhere[25,26] for nD states of sodium.

The theoretical estimate of the broadening rates given by Omont[8] for intermediate n values assumes that only elastic collisions contributed to the broadening. The calculation is based on a first-order interaction potential including one term from the Fermi interaction and the other from the polarization effect. After integration over the impact parameter it leads to two additive cross sections for elastic collisions. The calculation neglects the Fermi potential for small impact parameters and the polarization potential for large ones, with the integration limits depending on the relative values of the two corresponding Weisskopf radii. The results we obtained using the appropriate equations [Ref. 8, Eqs. (4.14)–(4.17)] are plotted by solid lines in Fig. 4 where they are seen to be below the experimental points, especially for Kr and Xe.

One possible cause[8] of the present discrepancy with calculated broadening rates could arise from resonances which occur when the phase shift η_0' of the Rydberg electron scattered by the foreign-gas atom is close to the quantity $\pi\delta$, or more precisely its fractional part, where δ is the quantum defect. For Rb ns levels δ is equal to 3.13, and the fractional part of 0.13 can be compared to η_0'/π. In Table III we tabulate the values of η_0'/π, derived from total electron scattering cross sections, for $15s$ and $30s$ levels as a function of the distance R of the electron from its atomic core. One can see that these values of η_0'/π are quite different from the critical value of 0.13 and this effect is unlikely to be important in the present case.

TABLE III. Electron scattering phase shifts.

			η_0'/π		
n	R/n^{*2}	k (a.u.)	Ar	Kr	Xe
	$\frac{1}{5}$	0.253	−0.021		
	$\frac{1}{2}$	0.146	0.006	0.028	0.049
15	1	0.084	0.017	0.046	0.075
	1.5	0.049	0.017	0.040	0.068
	1.8	0.028	0.012	0.028	0.048
	$\frac{1}{5}$	0.112	0.012	0.041	0.064
	$\frac{1}{2}$	0.065	0.018	0.045	0.075
30	1	0.037	0.015	0.034	0.059
	1.5	0.022	0.010	0.022	0.039
	1.8	0.012	0.006	0.014	0.024

Another possible cause of the present discrepancy is that inelastic collisions also contribute significantly to the broadening rate. For Rb nS states, only one experiment has reported quenching rate coefficients[27] for $n = 16$ perturbed by He, their value is 2.3×10^{-9} cm^3 sec^{-1}, which is 40% of the broadening rate coefficient we observe for the $15S$ state. The quenching rate coefficients measured[28] for Rb np states ($n = 12$ to 22) by He and Ar are about 1 and 0.2×10^{-9} cm^3 sec^{-1}, respectively. Quenching rate coefficients measured[29] for Na nS states ($n = 6$ to 11) increase rapidly with increasing n, and imply a magnitude of $\sim1\times10^{-9}$ cm^3 sec^{-1} for He and Xe perturbers in our n region. These quenching rates are about two orders of magnitude smaller than the elastic rate for heavy inert gases. The inelastic rates are much larger for nearly hydrogenic levels like Na nD ($n = 5$–15) states[25,26] and Rb nF ($n = 9$–21) states[27] due to angular momentum mixing into nearly degenerate levels; this could affect our $19D$ state results.

According to the theory,[8] the contribution of inelastic collisions to the broadening rate is negligible if the adiabaticity criterion is satisfied, that is, if

$$\Delta E_{ij} \gg v/n^*, \quad \text{or} \quad \Delta n^*/n^{*2} \gg v\,,$$

where ΔE_{ij} is the energy gap between adjacent levels, n^* the effective quantum number, and v the collision velocity. This is generally the case for isolated levels. In Rb, due to the values of the quantum defects [$\delta_s = 3.13$ (Ref. 18), $\delta_d = 1.35$, $\delta_f = 0.02$ (Ref. 21)], the ns levels, for large n, are fairly close to the $(n-2)D$ and $(n-3)F$ levels. In the present experimental conditions, v is at least equal to 2.0×10^{-4} a.u. (Xe), whereas $\Delta n^*_{sd}/n^{*2}$ decreases from 15×10^{-4} to 2.3×10^{-4} and $\Delta n^*_{sf}/n^{*2}$ from 7.8×10^{-4} to 1.2×10^{-4} between $15s$ and $34s$ states. Thus, although the experimental results in the previous paragraph indicate that the inelastic rate coefficients are negligible for the heavier inert gases on Na S states and Rb P states, this indicates that the adiabaticity criterion is not satisfied for the Rb S states and they may behave differently. For sudden collision ($\Delta E_{ij} \gg v/n^*$), the broadening rate coefficient due to inelastic collisions is given by [Ref. 8, Eq. (4.4)]: $\kappa^{\gamma}_{sc} = 4L^2/n^*$, which corresponds to a free electron having the mean velocity of the atomic state.[7] The dashed lines on Fig. 4 show the results of calculations including κ^{γ}_{sc}. One can see that, although using this full inelastic rate coefficient is not justified at the smaller n, the discrepancy with the experiment is considerably reduced. This supports our conviction that inelastic collisions are probably contributing significantly to the inert gas broadening of Rb nS states.

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*Permanent address: Department d'Astrophysique Fundamental Observatoire de Meudon, 92190, Meudon, France.
†Quantum Physics Division, National Bureau of Standards.

[1]E. Amaldi and E. Segre, Nature (London) 133, 141 (1934); Nuovo Cimento 11, 15 (1934).
[2]C. Füchtbauer, P. Schulz, and A. F. Brandt, Z. Phys. 90, 403 (1934).
[3]C. Füchtbauer and P. Gössler, Z. Phys. 93, 648 (1934).
[4]C. Füchtbauer and H.-J. Reimers, Z. Phys. 95, 1 (1935).
[5]T. Z. Ny and S. Y. Ch'en, Phys. Rev. 51, 567 (1937).
[6]E. Fermi, Nuovo Cimento 11, 157 (1934).
[7]V. A. Alekseev and I. I. Sobel'man, Zh. Eksp. Teor. Fiz. 49, 1274 (1965) [Sov. Phys.—JETP 22, 882 (1966)].
[8]A. Omont, J. Phys. (Paris) 38, 1343 (1977).
[9]V. A. Alekseyev, M. A. Mazing, P. D. Serapinas, I. I. Sobelman, and L. A. Vainstein, in *Abstracts of the Fifth ICPEAC, Leningrad, 1967,* edited by I. P. Flaks and E. S. Solov'ev (Nauka, Leningrad, 1967).
[10]L. S. Vasilenko, V. P. Chebotaev, and A. V. Shishaev, Zh. Eksp. Teor. Fiz. Pis'ma Red 12, 161 (1970) [JETP Lett. 12, 113 (1970)].
[11]B. Cagnac, G. Grynberg, and F. Biraben, J. Phys. (Paris) 34, 845 (1973).
[12]F. Biraben, B. Cagnac, E. Giacobino, and G. Grynberg, J. Phys. B 10, 2369 (1977).
[13]K. H. Weber and K. Niemax, Opt. Commun. 31, 52 (1979).
[14]K. H. Weber and K. Niemax, Opt. Commun. 28, 317 (1979).
[15]A. Flusberg, R. Kachru, T. Mossberg, and S. R. Hartmann, Phys. Rev. A 19, 1607 (1979).
[16]R. Kachru, T. W. Mossberg, and S. R. Hartmann, in *Abstracts of the Eleventh ICPEAC* (The Society for Atomic Collision Research, Kyoto, 1979), p. 946.
[17]J. L. Hall and S. A. Lee, Appl. Phys. Lett. 29, 367 (1976).
[18]S. A. Lee, J. Helmcke, and J. L. Hall, Opt. Lett. 3, 141 (1978).
[19]S. A. Ochs and P. Kusch, Phys. Rev. 85, 145 (1952).
[20]A. Omont, J. Phys. (Paris) 34, 179 (1973).
[21]C. E. Moore, *Atomic Energy Levels*, Vol. II, Natl. Bur. Stand. (U.S.) Circ. No. 467 (U. S. Government Printing Office, Washington, D.C., 1949).
[22]H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon, Oxford, 1969), Vol. I, pp. 544 and 556.
[23]A. Dalgarno and R. E. Kingston, Proc. R. Soc. London Ser. A 259, 424 (1960).
[24]J. Lorenzen and K. Niemax, Z. Naturforsch 32a, 853 (1977).
[25]T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. Lett. 35, 644 (1975).
[26]T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. A 15, 1945 (1977).
[27]M. Hugon, F. Gounand, P. R. Fournier, and J. Berland, J. Phys. B 12, 2707 (1979).
[28]F. Gounand, P. R. Fournier, and J. Berland, Phys. Rev. A 15, 2212 (1977).
[29]T. F. Gallagher and W. E. Cooke, Phys. Rev. A 19, 2161 (1979).