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ELECTRON-IMPACT BROADENING OF ISOLATED ION LINES*

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Several experiments[1-7] have yielded Stark widths of spectral lines from singly ionized atoms other than helium which exceed theoretically predicted values[8] by factors from 2 to 10. This is in marked contrast to the satisfactory (~±20%) agreement with measured widths of lines from neutral atoms[8,9] and to a similar agreement in case of singly ionized nitrogen[10] and carbon.[11] The purpose of this Letter is to show that most of the reported discrepancies stem from two approximations, namely, the neglect of collision-induced transitions between upper and lower levels of the line and of Coulomb interactions with the perturbed ions.

The shape $I(\omega)$ of a pressure-broadened line obeys (e.g., for radiation polarized in the z direction) in the classical path approximation

$$I(\omega)=\frac{1}{\pi}\mathrm{Re\,Tr}\int_0^\infty e^{-i\omega s}\{Z(0)Z(s)\rho_A\}_{\text{average}}ds, \quad (1)$$

where $Z(s)$ and ρ_A are the dipole moment and atomic density-matrix operators. The trace is over states of the perturbed system and the average over perturber coordinates. Introducing the time-evolution operator $U(s,0)$ and using the iterative solution of the Schrödinger equation accounting for the integrated effect of a perturber approaching the radiator at time s, the average can be written[8] with $Z(0)\equiv Z$ as

$$\{Z(0)Z(s)\rho_A\}=\{Ze^{-iHs/\hbar}U(s,0)ZU^\dagger(s,0)e^{+iHs/\hbar}\rho_A\}\approx Ze^{-iHs/\hbar}Ze^{+iHs/\hbar}\rho_A-(i/\hbar)\{Z[\int_{-\infty}^{\infty}V'(t)dt$$

$$\times e^{-iHs/\hbar}Ze^{+iHs/\hbar}-e^{-iHs/\hbar}Ze^{+iHs/\hbar}\int_{-\infty}^{+\infty}V'(t)dt]\rho_A\}+(i/\hbar)^2\{Z[\int_{-\infty}^{+\infty}V'(t)dt\int_{-\infty}^{t}V'(t')dt'$$

$$\times e^{-iHs/\hbar}Ze^{+iHs/\hbar}+e^{-iHs/\hbar}Ze^{+iHs/\hbar}\int_{-\infty}^{+\infty}V'(t)dt\int_{-\infty}^{t}V'(t')dt'$$

$$-\int_{-\infty}^{+\infty}V'(t)dt\,e^{-iHs/\hbar}Ze^{+iHs/\hbar}\int_{-\infty}^{+\infty}V'(t)dt]\rho_A\}+\cdots. \quad (2)$$

Here H is the Hamiltonian of the unperturbed system and $V'=e^{+iHs/\hbar}Ve^{-iHs/\hbar}$ the interaction Hamiltonian. The zero-order term in the Dyson expansion produces no broadening, and the average of the first-order term vanishes. For monopole-dipole interactions and complete degeneracy ($V'=V$),

the second-order term can be evaluated exactly also for hyperbolic perturber paths,[12] yielding

$$\{Z(0)Z(s)\rho_A\} \approx -2\pi Nvs\int \rho d\rho \tfrac{2}{3}\left(\frac{\hbar v}{e^2}\right)^2\left[1+\left(\frac{m\rho v^2}{e^2}\right)^2\right]^{-1} Z(\vec{R}\cdot\vec{R}e^{-iHs/\hbar}Ze^{+iHs/\hbar}$$
$$+e^{-iHs/\hbar}Ze^{+iHs/\hbar}\vec{R}\cdot\vec{R}-2\vec{R}e^{-iHs/\hbar}Ze^{+iHs/\hbar}\cdot\vec{R})\rho_A+\cdots, \tag{3}$$

with N, v, and ρ being electron density, velocity, and impact parameter, respectively, and $\vec{R}$ the perturbed-electron coordinate vector in atomic units.

The ρ integral diverges at large ρ, but here $V' \approx V$ is invalid. Since reinstating V' would lead to a rapid decrease in the integrand for perihelion distances ρ' larger than $v'/\Delta\omega'$ (where v' is the velocity at ρ', and $\Delta\omega'$ the angular frequency separation between the levels involved), the integral must be cut off at

$$\rho_{\max} = \rho_{\max}{}'v'/v = (v/\Delta\omega')(v'/v)^2, \tag{4}$$

i.e., at a distance larger by a factor

$$(v'/v)^2 = 1+2(e^2/m\rho_{\max}v^2)^2+2e^2/m\rho_{\max}v^2[1+(e^2/m\rho_{\max}v^2)^2]^{1/2} \tag{5}$$

than for a straight classical path. At small ρ no divergence occurs and the integral could be extended down to $\rho = 0$ (or to $\rho \approx \hbar/mv$ to account for the breakdown of the classical path approximation). However, for close collisions fourth and higher order terms in the Dyson series are no longer negligible. To include them in a gross way the integrand in Eq. (3), which represents the change of $Z(0)Z(s)\rho_A$ due to one collision, should not be allowed to exceed this quantity, and a minimum impact parameter may be defined through

$$\frac{2}{3}\left(\frac{\hbar v}{e^2}\right)^2\left[1+\left(\frac{m\rho_{\min}v^2}{e^2}\right)^2\right]^{-1} Z(\vec{R}\cdot\vec{R}e^{-iHs/\hbar}Ze^{+iHs/\hbar}+\cdots)\rho_A = Ze^{-iHs/\hbar}Ze^{+iHs/\hbar}\rho_A. \tag{6}$$

Below this impact parameter the integrand must then be replaced by the right-hand side of Eq. (6). In this manner there follows from Eq. (3)

$$\{Z(0)Z(s)\rho_A\} \approx -\pi NvsZ\left[\frac{2}{3}\left(\frac{\hbar}{mv}\right)^2(\vec{R}\cdot\vec{R}e^{-iHs/\hbar}Ze^{+iHs/\hbar}+\cdots)\left(1+\ln\frac{1+(m\rho_{\max}v^2/e^2)^2}{1+(m\rho_{\min}v^2/e^2)^2}\right)\right.$$
$$\left.-\left(\frac{e^2}{mv^2}\right)^2(e^{-iHs/\hbar}Ze^{+iHs/\hbar})\right]\rho_A. \tag{7}$$

Substituting into Eq. (1) and inserting, in addition to upper state i and lower state f, the intermediate states $i' \neq f$ and $f' \neq i$ results in the asymptotic line shape as function of the frequency separation $\Delta\omega$ from the line center

$$I(\Delta\omega) \sim \frac{2N}{3v}\left|\frac{\hbar\langle i|Z|f\rangle}{m\Delta\omega}\right|^2\left\{\left[\langle f|\vec{R}|i\rangle\cdot\langle i|\vec{R}|f\rangle+\langle f|\vec{R}|f'\rangle\cdot\langle f'|\vec{R}|f\rangle+\frac{\langle i|Z|i'\rangle}{\langle i|Z|f\rangle}(\langle i'|\vec{R}|i\rangle\cdot\langle i|\vec{R}|f\rangle\right.\right.$$
$$\left.+\langle i'|\vec{R}|f'\rangle\cdot\langle f'|\vec{R}|f\rangle)+\langle i|\vec{R}|f\rangle\cdot\langle f|\vec{R}|i\rangle+\langle i|\vec{R}|i'\rangle\cdot\langle i'|\vec{R}|i\rangle\right]$$
$$\left.\times\left[1+\ln\frac{1+(m\rho_{\max}v^2/e^2)^2}{1+(m\rho_{\min}v^2/e^2)^2}\right]-\frac{3}{2}\left(\frac{e^2}{\hbar v}\right)^2\right\}. \tag{8}$$

Here it was assumed that initially only the upper state of the line is populated, i.e., $\langle i|\rho_A|i\rangle = 1$ was taken as the only nonvanishing matrix element of ρ_A, and the fact was utilized that significant contributions only arise when the $e^{-iHs/\hbar}$ and $e^{+iHs/\hbar}$ matrix elements correspond to the lower and upper states, respectively. (Also, $\langle i|\vec{R}|i\rangle = 0$ for isolated lines.) The first of the two terms involv-

ing the ratio of Z-matrix elements reduces to $\langle i'|\vec{R}|i\rangle\cdot\langle i|\vec{R}|i'\rangle$, while the second ought to be well estimated by $\langle f'|\vec{R}|f\rangle\cdot\langle f|\vec{R}|f'\rangle$, unless profiles of emission and absorption coefficients were different.

If one now defines a damping constant w through $I(\Delta\omega)\sim|\langle i|Z|f\rangle|^2 w/\pi\Delta\omega^2$ then this quantity, which for a dispersion profile equals its (half) half-width, becomes in terms of radial integrals $R_{n_\alpha l_\alpha}^{\ n_\beta l_\beta}$ of central field wave functions

$$w\approx\frac{2\pi}{3v}\left(\frac{\hbar}{m}\right)^2 N\left\{\frac{3}{2}\left(\frac{e^2}{\hbar v}\right)^2(X-1)+\left[\frac{4l_{i,f}^{\ 2}}{4l_{i,f}^{\ 2}-1}(R_{n_i l_i}^{\ n_f l_f})^2+\sum_{i'\neq f}\frac{l_{i',i}}{2l_{i',i}^{\ \pm 1}}(R_{n_i l_i}^{\ n_{i'} l_{i'}})^2\right.\right.$$
$$\left.+\sum_{f'\neq i}\frac{l_{f',f}}{2l_{f',f}^{\ \pm 1}}(R_{n_f l_f}^{\ n_{f'} l_{f'}})^2\right]\ln\frac{1+Y_{ifi}^{\ 2}}{X}+\sum_{i'\neq f}\frac{l_{i,i'}}{2l_{i,i'}^{\ \mp 1}}(R_{n_i l_i}^{\ n_{i'} l_{i'}})^2\ln\frac{1+Y_{ii'i}^{\ 2}}{X}$$
$$\left.+\sum_{f'\neq i}\frac{l_{f,f'}}{2l_{f,f'}^{\ \mp 1}}(R_{n_f l_f}^{\ n_{f'} l_{f'}})^2\ln\frac{1+Y_{ff'f}^{\ 2}}{X}\right\}. \tag{9}$$

Here X and $Y_{\alpha\beta\gamma}$ are

$$X=\frac{2}{3}\left(\frac{\hbar v}{e^2}\right)^2\left[\frac{4l_{i,f}^{\ 2}}{4l_{i,f}^{\ 2}-1}(R_{n_i l_i}^{\ n_f l_f})^2+\sum_{i'\neq f}\frac{4l_{i,i'}^{\ 2}}{4l_{i,i'}^{\ 2}-1}(R_{n_i l_i}^{\ n_{i'} l_{i'}})^2+\sum_{f'\neq i}\frac{4l_{f,f'}^{\ 2}}{4l_{f,f'}^{\ 2}-1}(R_{n_f l_f}^{\ n_{f'} l_{f'}})^2\right], \tag{10}$$

$$Y_{\alpha\beta\gamma}=m\rho_{\max}^{\ \alpha\beta\gamma}v^2/e^2, \tag{11}$$

with $\rho_{\max}^{\ \alpha\beta\gamma}$ to be estimated from Eq. (4) using for $\Delta\omega'$ the maximum splitting between the levels involved in the $\vec{R}$-matrix elements. (To further ensure symmetry between emission and absorption, $Y_{i'if}$ and $Y_{i'f'f}$ had to be assumed equal to each other and, therefore, practically equal to $Y_{fif}=Y_{ifi}$, because normally levels i and f will be further apart than i and i', etc.) Also, $l_{i,f}$, for example, stands for the larger of the two orbital quantum numbers l_i and l_f, and positive or negative signs are to be used depending on whether, for example, $l_{i'}-l_i=+1$ or $l_{i'}-l_i=-1$. The n_i, etc., are effective quantum numbers, and the radial integrals may, according to Bates and Damgaard,[13] be estimated from

$$R_{n_\alpha l_\alpha}^{\ n_\beta l_\beta}=\tfrac{3}{4}n_{\alpha,\beta}(n_{\alpha,\beta}^{\ 2}-l_{\alpha,\beta}^{\ 2})^{1/2}\varphi, \tag{12}$$

where φ is a correction factor tabulated for s-p, p-d, and d-f transitions.

Effective quantum numbers and angular frequency splittings must be determined from experimental energy values. Errors due to the central field model are minimized by using for the states i' and f' energies, if possible, of levels having the same parent and spin, whose total angular-momentum quantum numbers differ from those of states i and f by the same amounts as the single-electron orbital quantum numbers. The quantities $Y_{\alpha\beta\alpha}$ can, according to Eqs. (4), (5), and (11), be obtained from

$$Y_{\alpha\beta\alpha}=\frac{mv^3}{e^2\Delta\omega_{\alpha\beta}}\left[1+\frac{2}{Y_{\alpha\beta\alpha}^{\ 2}}+\frac{2}{Y_{\alpha\beta\alpha}}\left(1+\frac{1}{Y_{\alpha\beta\alpha}^{\ 2}}\right)^{1/2}\right], \tag{13}$$

and instead of actually averaging over electron velocities, it should suffice to use the mean velocity $\bar{v}=(8kT/\pi m)^{1/2}$.

Widths of lines of singly ionized carbon, nitrogen, sulfur, argon, and calcium for which measured data are available were calculated as described above, including up to 3 levels[14] i' and f' interacting with upper states and lower states, respectively. For most of these levels the logarithmic terms in Eq. (9) turn out to be slightly negative, which indicates that the approximation $V'\approx V$ is valid only marginally. Experience with straight classical path calculations[8] indicates that the strong-collision contributions are virtually unchanged even if $\omega_{\alpha\beta}\lesssim v'/\rho'$, while the weak-collision contributions then become very small. To allow for this, the logarithms were dropped when they became negative. Most of the broadening is accordingly through strong collisions, as was first suggested by Murakawa[3] and Yamamoto.[4] Their effects are reduced, however, by a fac-

Table I. Comparison of calculated (w_{theor}) and measured (w_{exptl}) half-widths for an electron density of $N = 10^{17}$ cm^{-3} at the electron temperatures in the various experiments ($kT = 0.95$,[6] 1.0,[4] 1.1,[1] 1.25, 1.55,[2] 1.65,[10] 2.6,[11] and 2.7[7] eV).

Multiplet[a]	w_{theor} (Å)	w_{exptl}[b] (Å)	Multiplet[a]	w_{theor} (Å)	w_{exptl}[b] (Å)
C II 4	0.30	0.36 (11)	Ar II 6	0.13	0.15 (1)
C II 7	1.2	0.75 (11)	Ar II 6 (2)	0.13	0.14 (5)
C II 8	1.4	1.05 (11)	Ar II 6 (2)	0.13	0.19 (2)
N II 4	0.16	0.08 (10)	Ar II 6 (2)	0.13	0.21 (7)
N II 5	0.14	0.07 (10)	Ar II 7 (2)	0.14	0.13 (5)
N II 18 (2)	0.16	0.13 (10)	Ar II 7	0.15	0.17 (2)
N II 29	0.25	0.10 (10)	Ar II 7	0.12	0.17 (7)
N II 30	0.20	0.29 (10)	Ar II 10	0.12	0.11 (2)
N II 40	1.1	0.69 (10)	Ar II 14	0.19	0.24 (5)
N II 58 (2)	0.41	0.22 (10)	Ar II 14	0.16	0.17 (7)
N II 59	1.4	0.80 (10)	Ar II 31	0.19	0.14 (5)
S II 1	0.18	0.28 (6)	Ar II 109	0.22	0.30 (7)
S II 6 (4)	0.23	0.29 (6)	Ca II 1 (2)	0.07	0.06 (4)
S II 7	0.25	0.38 (6)	Ca II 1	0.07	0.06 (11)
S II 9 (2)	0.16	0.50 (6)			
S II 11	0.30	0.26 (6)			
S II 38	0.22	0.35 (6)			

[a]Number of measured lines or different conditions in parentheses.
[b]References for experimental values in parentheses. See reference list.

tor $1-1/X$ from the straight classical-path hydrogenic result and increased by collision-induced transitions between upper and lower states of the lines. These transitions are made much more frequent by the Coulomb acceleration of the perturbing electrons.

Comparison of measured and calculated widths (referred to $N = 10^{17}$ cm^{-3}) in Table I demonstrates that the agreement between measured and calculated values is now in almost all cases well within a factor of 2. Averaged over all lines and plasma conditions, the ratio of calculated and measured widths is 1.1, against an average ratio of 0.5, if previous straight classical-path calculations[8] neglecting lower-state broadening are compared with measured widths. The ratios for C II and N II are now almost uniformly high, which might be due to a systematic error in the electron density determination. Without these data, new and old ratios would come to about 0.9 and 0.25, respectively, and of the remaining 29 measurements all but two yield ratios between 0.6 and 1.2. In any event, average ratios of calculated and measured widths are now close to 1, which should encourage further classical-path calculations of the electron-impact broadening of isolated ion lines accounting for Coulomb effects and upper- and lower-state broadening through monopole-dipole interactions. Possible refinements are then detailed calculations of the velocity average, removal of the approximation $V' \approx V$ (i.e., replacement of the cutoff at large impact parameters by an actual calculation), and inclusion of higher multipole interactions, if necessary. It is unlikely that the combined effects of these refinements would exceed ~20% for the lines considered here. Uncertainties from the approximate treatment of the strong collision term are certainly of the same order, and significant improvement of the theoretical accuracy, therefore, will only be possible if the Dyson series is carried to higher orders. Finally, it remains to be shown (either theoretically or experimentally) that the profiles indeed have dispersion shapes throughout.

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OBSERVATION OF SPIN EXCHANGE BETWEEN THE SINGLY IONIZED Xe^+ GROUND STATE AND THE METASTABLE STATE OF NEUTRAL XENON*

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We have observed spin-exchange collisions between the singly ionized $^2P_{3/2}$ ground state of Xe and the $^3P_2$ metastable state of neutral Xe, both formed and aligned by electronic-impact excitation under space-charge neutralization. Extension to the rf spectroscopy of the ionized ground state of other noble-gas atoms seems promising.

In this Letter we report what we believe is the first observation of spin-exchange collisions between the singly ionized ground state of Xe^+ and the metastable state of neutral Xe, both having P configurations. So far as we know, spin-exchange collision effects have been observed only between an oriented atom and an unoriented atom or an electron, all having zero orbital angular momentum ($L=0$). Dehmelt,[1] using a very elegant ion-storage collision technique, first succeeded in observing spin-exchange collisions between an optically pumped, oriented Cs atom and ionized $(He^4)^+$. This method was used quite recently on $(He^3)^+$, revealing an ultrahigh precession determination of hyperfine structure by this method.[2]

In our experiment, instead of an oriented atom colliding with an unoriented ion, both colliding atoms (Xe^+ ground state and metastable neutral Xe) are formed and aligned by electron impact in the same volume of space. Since both atoms with different states are aligned (not oriented), how one may obtain an observable effect due to spin-exchange collision is not so obvious as in the case of collisions between an oriented atom and an unoriented atom. By a rather qualitative consideration, one can account for the phenomena reported here. First, by electron impact along the field direction, the states

$$|^3P_2, m_J=0, m_s=\pm\tfrac{1}{2}\rangle, \quad |^3P_2, m_J=1, m_s=+\tfrac{1}{2}\rangle,$$

$$|^3P_2, m_J=-1, m_s=-\tfrac{1}{2}\rangle, \quad |^2P_{3/2}, m_J=\tfrac{1}{2}, m_s=+\tfrac{1}{2}\rangle,$$

$$\text{and } |^2P_{3/2}, m_J=-\tfrac{1}{2}, m_s=-\tfrac{1}{2}\rangle$$

are preferentially produced. From production and through subsequent spin-exchange collisions, an equilibrium obtains among these states. The introduction of a radio frequency that redistributes the populations of either the $^3P_2$ or $^2P_{3/2}$ states affects the absorption of linearly polarized light by the $^3P_2$ state.

Using the Born-Oppenheimer approximation, Bethe showed that there is a preferential population of magnetic sublevels of the excited triplet state.[3] In particular, in case of ^1S-^3P excitation, at the threshold energy of excitation, the $M_L=0$ state is populated predominantly. Lamb pointed out that one would not expect the results for the threshold excitation to be in serious error for bombardments a few volts above the threshold.[4] That this is true has been verified for the excitation of the triplet ($^3P_1$) state of He and for the $^3P_2$ metastable states