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Measured Stark Widths and Shifts for Neutral Atomic Lines*

Myron H. Miller
Institute for Fluid Dynamics and Applied Mathematics, University of Maryland, College Park, Maryland 20742

and

Roger D. Bengtson
Institute for Fluid Dynamics and Applied Mathematics, University of Maryland, College Park, Maryland 20742
and University of Texas, Austin, Texas 78712 †

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Widths and shifts of Stark-broadened, neutral atomic lines have been measured using a gas-driven shock tube. Stark widths are given for 35 isolated lines or blended multiplets of carbon, oxygen, neon, silicon, phosphorus, sulphur, chlorine, and argon. Shift data are presented for 15 of these features. Electron densities are determined from both H_β profiles and pressure-temperature data. Estimated accuracy is 8–25% for the widths and 15–40% for the shifts. Results are compared with theoretical predictions and other measurements.

INTRODUCTION

The dominant line-broadening mechanism in many laboratory and astrophysical plasmas is the Stark effect due to time- and space-varying microfields.[1-4] Aside from posing an interesting problem in perturbation theory, Stark-broadening is used for determining electron densities in both accessible and remote light sources. Refined radiative transfer calculations, such as those used in stellar elemental abundance determinations,[5,6] can be improved by reliable Stark-broadening data.

Conditions in a radiating source can be qualitatively related to spectral line shapes by classical theoretical treatments.[7] Quantitatively satisfactory theories of pressure broadening treat complex particle interactions by quantum perturbation methods. Recent Stark-broadening theories have been developed by Baranger[8] and by Kolb and Griem.[9,10] Isolated lines from nondegenerate levels were treated by Griem, Baranger, Kolb, and Oertel[11] (GBKO), using the impact for electrons and the quasistatic approximation for ions. Higher-order effects have been incorporated into the theory by Cooper and Oertel (CO).[12] An alternate treatment for isolated lines has been given by Sahal-Bréchot.[13]

Several experiments have tested the GBKO predictions for neutral lines.[14-24] In reviewing some of these measurements, Wiese[2] concluded that the GBKO predictions for neutrals are typically reliable to 10–15%, with occasional discrepancies running as large as 30%. Relatively simple structure makes the lighter elements particularly desirable for testing theoretical broadening models. Prior measurements in the first three periods included helium,[14-17] nitrogen,[18,19] oxygen,[20] sulfur,[21] and argon.[22-24] The present work measures line profiles for several elements in a consistent way.

EXPERIMENTAL METHOD

Precision was optimized by concentrating upon the widest interference-free lines in each spectrum. As a precaution against systematic error, electron densities were deliberately varied by factors of 3 to 6. Two independent methods were used to determine electron densities. Brightness and line-to-continuum ratios were also varied, and optical depths were kept low. Interference from other broadening mechanisms is small because Stark widths typically exceeded Doppler widths by a factor of 30 and exceeded instrumental widths by factors of 2 to 10. Emitter densities were too small (10^{16} cm^{-3}) for significant resonance broadening.[25]

van der Waals interactions contribute no more than 1–3% to the broadening because total pressures were only 50–200 times greater than electron pressures.[1] Demixing, which can be troublesome in zoned light sources,[26] does not occur in the shock tube. It can be shown that thin boundary layers exert negligible influence on the present shock-tube data.

Cold hydrogen was used to drive a conventional 3×4-in. shock tube.[27,28] The steady-state region in the stationary plasmas behind the first reflected shock varied in duration between 50–200 μsec. By suitable selection of initial gas pressure and

composition,[29] we could vary plasma electron densities between $2-14\times10^{16}$ cm^{-3} while restricting temperatures to the range 10 000–12 500 °K. Typical gas mixtures to be shock heated consisted of 99% neon plus 1% spectroscopic additive containing the elements of interest. The additives were usually hydrides, e.g., methane (CH_4) to generate carbon spectra, silane (SiH_4) for silicon, and phosphine (PH_3) for phosphorus. The high vapor pressures of these compounds permitted easy gas handling and gave good brightness to the hydrogen Balmer lines (H_α, H_β) used for plasma-state measurements.

Time-resolved spectroscopy was conducted with 15 to 20 absolutely calibrated photomultipliers and a revolving-drum camera. Some photomultipliers were arranged in pairs (line and nearby continuum) to record integrated absolute line intensities for purposes of plasma thermometry. Others were components of a multichannel image dissector that transferred the absolute-intensity (carbon arc) calibrations of the photomultipliers to the film in the drum camera on a shot-to-shot basis.[30] Films were calibrated for relative sensitivity in the conventional way.[27, 28] Because of a somewhat greater susceptibility to reciprocity failure,[31] calibrations in the infrared region were not as repeatable as in the visible, and in consequence, data above 6700 Å are less reliable than at lower wavelengths.

Pressure was measured with quartz transducers. Temperatures were measured redundantly via the absolute integrated intensities of Ne I λ5852 and H_β and by the line-reversal technique[32, 33] applied to the central portions of H_α. These three independent temperatures generally agreed within ±1.5%.[34]

Electron densities were obtained both from pressure-temperature data and from Stark profiles of H_β. Measured temperatures and pressures were used to compute the electron density in gas mixtures of known chemical composition. Computer codes for obtaining iterative solutions[35] to coupled Saha-Boltzmann equations made the appropriate adjustments for the lowering of ionization potentials and truncations of partition functions.[36] Allowance was made for trace concentrations (less than 0.05%) of contaminants evaporated into the hot gas from the shock-tube walls. The fitting of observed H_β profiles to theoretically predicted shapes[37] provided a second measurement of the electron density. Measured H_β intensities were reduced to Stark profiles by applying minor corrections for self-absorption and instrumental broadening, and then averaging the asymmetry of the red and blue half-profiles. Figure 1 compares electron densities measured by the two independent methods.

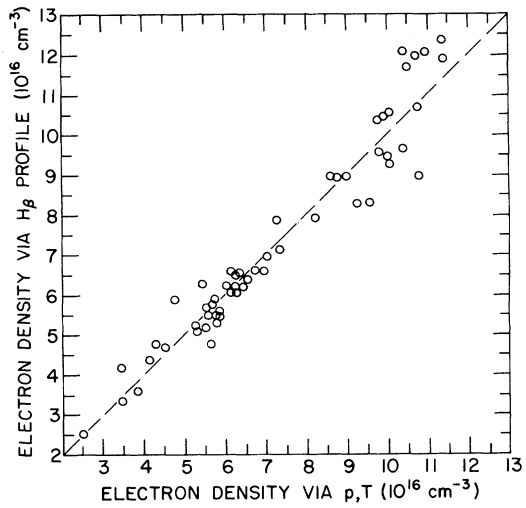

FIG. 1. Comparison of electron densities obtained from H_β profiles with electron densities calculated from temperature and pressure data.

On the average, the two sets of results agree within 3%, with no trends of disagreement detectable in the electron density range $3-12\times10^{16}$ cm^{-3}.

Broadening and shift data were recorded on revolving-drum camera spectrograms covering 1100 Å in wavelength. A mask limited the height of the spectrograph slit image (in the direction of film travel) to give a time resolution of 7–10 μsec at typical writing speeds. Film densities were converted to intensities by means of a recording densitometer and associated digital computer codes.[38]

Instrumental contributions to the line profiles were calculated using tabulated values of the convolution integral.[39] Instrument profiles were obtained from spectra of a neon Osram lamp; for most of our experimental runs the full instrumental half-width was 1.10 Å. Typical Doppler widths (0.1–0.2 Å) were small compared to the total Gaussian component of the instrumental profile. Stark widths were 3–10 times larger than the Lorentzian component of the instrumental profile, so that slit unfolding did not introduce significant error. To check this possibility, Stark widths were plotted against electron density: "Best fits" to the data were linear and, when extrapolated, intercepted the origins of the plots within experimental tolerance. Optical depths occasionally reached 0.20 at the centers of the brightest lines. To eliminate slight distortions due to self-absorption, we used absolute intensity and temperature data to reconstruct profiles to the optically thin limit.[40]

The spectroscopic data films were free of the

Eberhard (adjacency) effect.[41] Emulsion densities seldom exceeded 1.0; peak line intensities were usually not more than 2–4 times greater than the continuum; and constant agitation was used during developing. The astigmatism of the high-aperture spectrograph prevented the use of a multistep filter, so an equivalent procedure was used to test for adjacency problems. Spectrograms were made with an Osram lamp illuminating slits of progressively greater width (100–400μ). Because the lamp emits several narrow lines of varying strength, each exposure produced a number of rectangular images of different density, seen against a local continuum whose density scaled approximately with the slit width. No Eberhard effect could be detected for line-continuum density combinations similar to those encountered in the broadening data.

The thin boundary layer known to surround shock-tube plasmas[29] can be expected to be of the order of 1 mm in thickness for conditions of the present experiment. Self-reversal dips were regularly observed in the centers of resonance lines, so resolution was ample to detect the effect, should it have been at all strong in the lines presently studied. Voigt profiles could be fitted well to the data, especially for lines where little broadening due to ions is predicted.[1] Our threshold for detecting reabsorption by these direct means is estimated to be 3–5%. Moreover, the effect of reabsorption would be more serious when a line was narrow than when it was broad, yet the data showed no trends that depended upon electron density. The clear evidence for reabsorption in resonance lines is easily reconciled with these findings; reabsorption for resonance radiation is expected to be more serious by 10^3–10^4 times than reabsorption for a line with a 7-eV lower state, depending upon the temperature gradient of the boundary layer.

To further test for freedom from the Eberhard effect, self-absorption, reabsorption, and systematic errors in photographic calibrations, we measured each line profile over factors of 3 to 5 in absolute brightness and over factors of 3 to 10 in the ratio of line-to-continuum intensity.

The brightest features in some spectra were completely blended multiplets. Stark-broadening data for individual lines in these multiplets could be recovered because the interline separations were considerably smaller than the blended multiplet half-widths. To unscramble the blending, we assumed that (i) all lines in a multiplet were broadened equally,[1] and (ii) their strengths were described by LS coupling.

Measured shifts are less reliable than the corresponding widths. To avoid superimposing a densely spaced fiduciary spectrum upon the time-resolved drum-camera data, we utilize narrow lines present in the shock-tube spectra as wavelength references. This procedure decreases the accuracy, not so much because the lines used as wavelength fiduciaries are themselves shifted slightly, but rather because the separations from the nearest available fiduciary were often large enough to generate error in data reduction. Narrow neon lines, e.g., Ne I λ5400, were the most frequently used wavelength standards. Griem's calculated shift parameters[1] were used with measured electron densities to compensate for the small shifts of the standards. This procedure changed the reported shifts for broad neutral lines by 1–15%.

RESULTS AND DISCUSSION

Broadening data for C I λ5052 are presented in Fig. 2, where Stark (full) half-widths $\Delta\lambda$ are plotted against measured electron density. These results were obtained from two distinct data sets.[27, 28] Different slit widths, carbon compounds, and photometric calibrations were employed by the two authors. A large portion of the 15% scatter (σ) in these data is due to the grain of the fast (No. 2475, 103-F) films. The random error ($\sigma/\sqrt{n}$) in the mean value of $\Delta\lambda/Ne$ for these 37 shots is less than 3%. Theoretical predictions of Griem[1] and Cooper and Oertel[12] are indicated by the dashed curves. Red shifts of C I λ5052 are plotted versus the (full) Stark half-width in Fig. 3. Fewer shifts than width data were obtained because the lines required for wavelength standards did not attain useful brightness in all runs. Within experimental

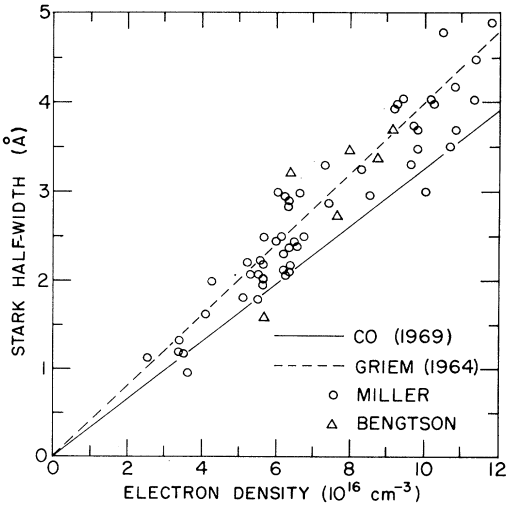

FIG. 2. Stark (full) half-width of C I λ5052 as a function of measured electron density.

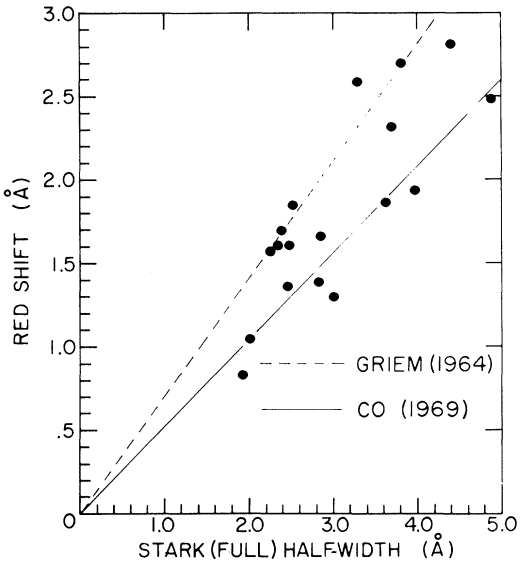

FIG. 3. Red shift versus Stark (full) half-width for C I λ5052.

tolerances, the widths and shifts are linearly related, as predicted by the impact approximation in the absence of Debye shielding.

Measured Stark widths for 35 lines and shifts for 15 lines are given in Tables I and II, respectively. Most data were obtained between 10 200 and 11 800 °K. Wavelengths for completely blended multiplets are "centers of gravity," taking account of relative line strength. Stated tolerances are 50% confidence limits. Generally, one-half of the uncertainty is due to scatter. An exception is the infrared data ($\lambda > 6\,700$ Å), where (i) there is an aforementioned film sensitivity to reciprocity failure, and (ii) gradients (density versus log exposure) are steep enough to hamper accurate reduction of density profiles to intensity profiles.

Comparison data from earlier experiments are available for three sulfur multiplets[21] and an isolated argon line.[24] When adjusted slightly[1] to conform to the current range of electron density (10^{17} cm^{-3}) and temperature (11 000 °K), the sulfur widths and shifts agree within their estimated tolerances (8–15%). The Ar I λ6752 width and shift measured by Bues, Haag, and Richter are both 30% smaller than in the present study (the shift-width ratios in the two experiments agree within 3%). These authors found that arc temperatures determined from linewidth measurements were significantly lower than those obtained by three other independent techniques, thereby suggesting a possible source for the discrepancy with present results.

Comparisons with the GBKO theory are based upon Griem's impact- and ion-broadening parameters,[1] suitably interpolated with respect to temperature and extrapolated to an electron density of 10^{17} cm^{-3}. Griem's parameters for several of the chlorine lines studied have not been utilized because the atomic-level classifications available (when these were calculated) omitted $3d$ and $4s$ perturbing states,[42] which should contribute strongly to the broadening.[43] The average ratio of predicted width to measured width for the 14 lines tabulated by Griem is 1.01 ± 0.02. Standard deviations (8%) and maximum discrepancies (20%) in these ratios are both slightly smaller than in the earlier experiments reviewed by Wiese.[2]

The quality of agreement between present data and the GBKO theory does not appear to vary from element to element, even though $1\frac{1}{2}$ atomic periods are spanned. It should be noted that values of $\Delta E/kT$ for these 14 lines (ΔE is the upper-state energy separation from the strongest perturbing level) are quite similar, lying between extremes of 0.6 and 1.7, so that strong collisions are expected to contribute comparable fractions to widths of all these lines. Turning to the shift data in Table II, GBKO predictions are found to agree with experiment within 20% for all lines except C I λ5380. The anomalous factor-of-5 discrepancy for this line has been traced[44] to the faulty encoding of some atomic data for the computer program used by Griem,[1] namely three important perturbing levels (producing blue shifts) had been neglected. Inclusion of these additional levels would tend also to bring the predicted width of C I λ5380 into closer agreement with our data.

The generalized impact theory of Cooper and Oertel[12] also incorporates the LS-coupling–Coulomb-approximation assumptions. However, where Griem[1] typically included the 5–7 atomic levels most strongly perturbing the upper state of the lines via dipole interactions and neglected perturbations to the lower state, Cooper and Oertel take account of all allowed dipole and quadrupole transitions acting upon both upper and lower states. The predictions of Cooper and Oertel[45] (CO) shown in Tables I and II cannot be simply regarded, except for their greater refinement, as duplicates of the Griem calculations, since the computational methods used in two treatments are frequently different.[46] In reevaluating the parameters (coefficients "a" in Ref. 1) for inelastic collisions, CO obtained values that were frequently 10% lower than Griem's. This difference should, however, be largely offset by their inclusion of more perturbing levels. It is, therefore, not clear why good (10%) agreement between the two sets of predictions appears (for lines so far compared) limited to He I and C I. The CO predictions

TABLE I. Shock-tube and comparison values for stark widths of neutral atomic lines.

Element [a]	Multiplet	λ(Å)	Present experiment	Other values	Stark half-width Å Griem (GBKO)	Cooper and Oertel [b]	Griem (SE×1.48)
C(11)	$3s^1P^\circ$-$4p^1P$	5380.2	3.0±0.3	···	2.53	2.59	3.30
C(12)	$3s^1P^\circ$-$4p^1D$	5052.1	4.0±0.3	···	3.99	3.27	4.14
C(13)	$3s^1P^\circ$-$4p^1S$	4932.0	4.1±0.5	···	5.23	4.12	4.97
O(10)	$3p^5P$-$4d^5D^\circ$	6157.3[c]	37.2±5.0	···	···	24.00	28.4
O(11)	$3p^5P$-$6s^5S^\circ$	5436.8[c]	27.2±4.0	···	···	22.32	37.9
O(12)	$3p^5P$-$5d^5D^\circ$	5328.9[c]	70.6±10.0	···	···	60.90	91.9
Ne(9)	$3p$ 1-$4dX^\circ$	5338.9[c]	50.4±10.0	···	···	···	···
Ne(13)	$3p$ 2-$4d3^\circ$	5764.4	31.0±4.0	···	···	···	···
Ne(19)	$3p$ 3-$4d4^\circ$	5820.1	23.8±3.0	···	···	···	···
Si(10)	$4s^3P^\circ$-$5p^3P$	5645.7	7.4±0.7	···	7.18	5.10	6.42
		5665.8	7.3±0.7	···	7.18	5.00	6.32
		5690.4	7.7±0.7	···	7.18	5.00	6.37
		5701.1	6.5±0.7	···	7.18	5.00	6.35
		5708.4	7.1±0.7	···	7.18	5.18	6.52
Si(11)	$4s^3P^\circ$-$5p^3S$	5684.5	7.5±0.8	···	7.41	4.02	4.95
Si(16)	$4s^1P^\circ$-$5p^1D$	5948.6	11.6±1.3	···	11.10	8.34	10.0
Si(Ref. 51)	$4s^1P^\circ$-$6p^1D$	5006.1	13.9±1.4	···	···	···	···
P(Ref. 52)	$4s^4P$-$5p^4S^\circ$	5515.9	11.8±2.0	···	···	···	···
S(2)	$4s^5S^\circ$-$5p^5P$	4695.1[c]	5.3±0.7	4.86±0.5 BW[d]	5.25	4.08	4.28
S(4)	$4s^3S^\circ$-$5p^3P$	5278.9[c]	4.8±0.5	4.29±0.4 BW[d]	5.08	2.68	2.81
S(8)	$4p^5P$-$5d^5D$	6751.0[c]	31.8±4.0	34.7 ±2.0 BW[d]	33.4	···	···
Cl(2)	$4s^4P$-$4p^4D^\circ$	8428.3	3.3±0.8	1.82 Ro[e]	···	···	···
		8212.0	3.5±0.8	1.73 Ro[e]	···	···	···
		8194.4	2.1±0.6	1.73 Ro[e]	···	···	···
Cl(3)	$4s^4P$-$4p^2D^\circ$	7878.2	4.2±0.9	···	···	···	···
Cl(4)	$4s^4P$-$4p^2P^\circ$	7717.6	1.7±0.5	···	···	···	···
		7414.1	1.7±0.5	···	···	···	···
Cl(5)	$4s^4P$-$4p^4S^\circ$	7744.9	2.8±0.7	1.56 Ro[e]	···	···	···
		7256.6	2.8±0.7	1.65 Ro[e]	···	···	···
Cl(6)	$4s^4P$-$5p^4P^\circ$	4438.5	7.3±1.1	···	···	···	···
Cl(14)	$4s^2P$-$4p^4S^\circ$	8686.3	1.6±0.4	1.61 Ro[e]	···	···	···
Cl(15)	$4s^2P$-$5p^2P^\circ$	4601.0	5.8±0.7	···	5.00	3.24	3.41
		4526.2	5.7±0.7	···	5.00	3.24	3.41
Ar(11)	$4p[\frac{1}{2}]$-$4d[1\frac{1}{2}]$	6752.8	9.4±1.0	6.6 BHR[f]	9.17	···	···

[a]Classification, unless otherwise denoted, from Ref. 50.

[b]Author's estimates using computer code by Cooper and Oertel, Ref. 12.

[c]Blended multiplet.

[d]BW, arc experiment by Bridges and Wiese, Ref. 21.

[e]Ro, theoretical calculations by Roberts, Ref. 43.

[f]BNR, arc experiment by Bues, Haag, and Richter, Ref. 24.

for carbon agree with shock-tube data within estimated tolerances. For other elements, the CO widths are smaller than the corresponding measured widths by factors as large as 1.4.

A number of calculations were made in an effort to clarify this curious pattern of agreement and disagreement. The CO program was run for Si I λ5710 using intermediate-coupling matrix elements,[47] which appear to be more reliable[48,49] than those based on LS coupling. Some relevant matrix elements were changed as much as a factor of 3, but CO predicted a half-width increased by

TABLE II. Shock-tube and comparison values for Stark shifts of neutral atomic lines.

Element (multiplet)	λ (Å)	Red shift Å Present work	Griem	Other	
C(11)	5380.2	0.3 ± 0.3	1.35	0.26	CO[a]
C(12)	5052.1	2.2 ± 0.2	2.78	1.74	CO[a]
C(13)	4932.0	3.0 ± 0.5	3.06	2.29	CO[a]
O(10)	6157.3[b]	16.6 ± 2.0	•••	8.60	CO[a]
O(11)	5436.8[b]	10.8 ± 1.5	•••	10.03	CO[a]
O(12)	5329.9[b]	21.6 ± 2.5	•••	22.00	CO[a]
Ne(9)	5338.9[a]	15.0 ± 3.0	•••	•••	
Ne(13)	5764.4	12.4 ± 1.9	•••	•••	
Ne(19)	5820.1	13.8 ± 2.8	•••	•••	
P(Ref. 51)	5515.9	4.6 ± 1.0	•••	•••	
S(2)	4695.1[b]	2.7 ± 0.4	2.17	2.0 ± 0.3 1.97	BW[c] CO[a]
S(4)	5278.9[b]	2.3 ± 0.3	2.67	0.87	CO[a]
S(8)	6751.0[b]	2.3 ± 0.8	1.91	1.3 ± 2.5	BW[c]
Cl(5)	7256.6	1.1 ± 0.4	•••	0.80	RO[d]
Ar(11)	6752.8	3.1 ± 0.7	3.71	2.3	BHR[e]

[a]CO, author's estimates using computer code by Cooper and Oertel, Ref. 12.
[b]Blended multiplet.
[c]BW, arc experiment by Bridges and Wiese, Ref. 21.
[d]RO, theoretical calculations by Roberts, Ref. 43.
[e]BHR, arc experiment by Bues, Haag, and Richter, Ref. 24.

less than 5%. Neglecting symmetrization,[12] with respect to initial and final perturber states, raised predicted line half-widths a few percent. An arbitrary change in the ρ_{min} cutoff from 1.0 to 1.2 changed the widths by less than 4%. These trial modifications to the CO program bring predictions somewhat closer to the data, but still not within claimed experimental tolerances for the majority of lines.

Strong collisions contribute up to 70% of the calculated widths for the tabulated infrared chlorine lines. Because the strong collision term in the GBKO treatment is regarded as being uncertain by as much as 50%,[1] the considerable differences between GBKO widths predicted by Roberts[43] and the corresponding shock-tube widths may not be significant.

Semiempirical formulas for widths due to electron impacts have been proposed by Griem[53] for situations requiring ease of computation rather than the utmost reliability. Thermally averaged Gaunt factors[54] for neutrals, $g_n(kT/\Delta E)$, were used to apply these formulas to 17 of the lines presently studied. With the additional approximation of a uniform 10% broadening contribution due to ions, predicted total Stark widths were found to be systematically smaller than those measured by a factor of 1.48. The semiempirical (SE) widths shown in Table I have been scaled by the factor of 1.48; this appears to be statistically significant: Scatter (σ) in the ratio 1.48×SE width/measured width is 24%, while $\sigma\sqrt{n}$ is not quite 6%. The following interpretation suggests itself. For 16 of the 17 calculated widths, the relevant Gaunt factors fall in a fairly narrow range (0.08–1.8). The SE widths, therefore, scale in an approximately linear fashion with the assumed Gaunt factors, which by this interpretation appear to have been too small by a factor of 1.5.

CONCLUSIONS

Griem's calculated Stark shifts and widths agree with the current data somewhat more closely than might have been anticipated from results of prior experimental tests. Present data on lines of similar $\Delta E/kT$ suggest no way to discriminate *a priori* between those cases where predictions approach experiment to better than 10% and other cases where agreement is not better than 20%. Predictions based on refinements to the GBKO treatment do not give improved agreement with our

data. The semiempirical formulas for impact broadening give fairly reliable (25%) predictions if Gaunt factors for neutrals are taken to be 1.5 times greater than literature values. At this time, careful experiments still appear to be the most reliable source of Stark-broadening coefficients. Further experiments would not only provide valuable astrophysical data but might also make a broad enough base to support a "systematic" search for regularities, such as those recently found in sets of atomic transition probabilities.[55]

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Bound States and Quasibound Resonances of Diatomic Systems*

W. E. Baylis†
Joint Institute for Laboratory Astrophysics, Boulder, Colorado 80302
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The importance of quasibound resonances is emphasized, with special reference to alkali–noble-gas systems. A modified WKB method for calculating the distribution and properties of quasibound resonances as well as of bound states is reviewed and applied to calculations of KAr and RbAr ground states. The calculated distribution of states in a Lennard-Jones 6-10 potential agrees precisely with the exact results of Mahan and Lapp. Inclusion of quasibound resonances is found to increase the total number of states by about $\frac{2}{3}$. Tunneling lifetimes much larger than typical collisional destruction times are found for most resonances.

INTRODUCTION

Mahan and Lapp[1] have recently calculated the number of vibrational levels as a function of the rotational quantum number K for ground states of diatomic molecules composed of an alkali atom and a noble-gas atom. Their method is based on an exact solution of the Schrödinger equation valid only for a 6-10 Lennard-Jones potential when the total energy $E=0$. Consequently, it is useful only in calculating the number of bound states ($E<0$) of potential wells which can be adequately approximated by a 6-10 potential; energies of the states are not calculated. As Mahan and Lapp noted, their numbers are lower bounds on the numbers of effectively bound levels because quasibound resonances have not been included.

For many situations, quasibound resonances are as important as bound states. Such resonances, which have $E \geq 0$, may be contained by the "centrifugal barrier," $\hbar^2 K(K+1)/2\mu R^2$, where $2\pi\hbar$ is Planck's constant, K is the rotational quantum number, μ is the reduced mass of the diatomic system, and R is the internuclear separation. Lifetimes as large as or larger than the collisional destruction time of the molecule are typical for alkali–noble-gas systems. Thus, for example, we expect resonances to be nearly as important as bound states in the elucidation of the satellite bands in line-broadened alkali spectra, the problem referred to by Mahan and Lapp.[1] Quasibound resonances are apparently also important in processes such as relaxation of optically oriented alkalis[2] and collisional-narrowing effects in alkali hyperfine transitions.[3] Indeed, whenever knowledge of the equilibrium density or the rate of formation of weakly bound molecules is of interest, it is a mistake to ignore quasibound resonances.[4]

An additional, possibly important property of quasibound resonances is that, in contrast to bound states, they can be formed during two-body collisions. The phenomenon is just that of long-lived "orbiting collisions," which have become of interest in recent years.[5] There are evidently some cases in which orbiting effects are observable even in thermally averaged total cross sections.[6]

There are various well-known methods for calculating bound-state energies for any potential – highly accurate numerical routines[7] for solving the radial Schrödinger equation as well as rapid, simple WKB methods.[8] Quasibound resonances have been treated by a modified WKB method in several