Experimental Widths and Shifts for $3s$-$3p$ Neon Lines*

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(Received 30 November 1970; revised manuscript received 12 April 1971)

Widths and shifts of several neon red lines were measured as functions of electron densities [$(0.4-2.1)\times10^{17}$ cm^{-3}] and neutral neon densities [$(0.3-2.2)\times10^{19}$ cm^{-3}]. Conditions in a gas-driven shock tube were determined from pressure-temperature data and from the shapes of hydrogen Balmer lines. In each experiment, profiles of neon lines emitted by the plasma were compared directly with the line shapes obtained with a low-pressure neon lamp. Stark broadening and shift parameters were determined with accuracies of 20–30 and 20–25%, respectively. Measured broadening due to neon atoms should be reliable to 35–50%. Theoretical and experimental comparison data are presented.

I. INTRODUCTION

The $3s$-$3p$ lines are the most prominent features of the visible neon spectrum. Strengths of these distinctive red lines have been extensively investigated,[1–3] but first measurements of their Stark widths were reported only recently.[4] The experimental Stark broadening for some multiplets agreed well with the Griem-Baranger-Kolb-Oertel (GBKO) theory.[5] However, observed linewidths for some other multiplets in the same $3s$-$3p$ array were smaller than those predicted[4] by factors of 1.5–1.9. This curious pattern of agreement and disagreement prompted us to investigate the Stark widths and shifts of neon lines belonging to three different multiplets of the $3s$-$3p$ transition array.

When using a gas-dynamic shock tube to measure Stark broadening, one usually treats any competing broadening due to neutral perturbers by enhancing the degree of ionization until Stark broadening clearly dominates. Theoretical approximations can then be used to compensate for the relatively minor broadening due to neutrals. This approach was not feasible for the present work because the $3s$-$3p$ lines are not readily broadened by the Stark effect. Consequently, the broadening of Ne I by Ne I, which is encountered in many laboratory plasmas, and which is theoretically interesting in its own right,[5–7] needed to be known with greater accuracy than appeared to be available from theoretical estimates. To obtain broadening data for both neutral and charged perturbers, thermodynamic conditions were varied over the widest ranges consistent with good plasma homogeneity, useful signal levels, and reasonable optical depths. By concentrating on six noninterfering lines ($6500 < \lambda < 6930$ Å), enough statistics were obtained throughout the range of source conditions to differentiate between the broadening due to the competing mechanisms.

II. EXPERIMENTAL

Except for modifications which improved spectral resolution fivefold, present instrumentation and techniques are similar to those described in an earlier paper.[8] Pressures were recorded by two transducers and temperatures were determined from the integrated energy of optically thin Ne I λ5852 and H_β, and from Planck intensity measured by the reversal technique at 6562 Å.[8–10] For experiments in the range (10 500–12 500) °K, the combined temperature determinations should be reliable to 2–3%.[8–10] Neutral neon densities (90–98% of the plasma neutral densities) were computed from pressure-temperature data with an estimated reliability of 6–8%. Electron densities were obtained by fitting optically thin H_β (or, occasionally, H_γ) profiles to theoretical Stark profiles[11–13] and by employing pressure-temperature data to solve the suitable Saha-Boltzmann equations.[14] The combined results from these two independent determinations are felt to be accurate to 15% in the range $N_e = (0.6-1.5)\times10^{17}$ cm^{-3}, and to 20% elsewhere.[8–10]

Line profiles were photographically recorded by two spectrographs. These employed a fast mechanical shutter to time-resolve the emission from behind first-reflected shocks. A stigmatic 1-m Czerny-Turner (0.24-Å resolution) recorded profiles of the neon red lines, while a second spectrograph (2.4-Å resolution) viewed lower wavelengths to record profiles of H_β or H_γ. A mechanical shutter driven by an exploding wire was situated at a common intermediate focus for both instruments.[15] Exposure times were adjusted between 18 and 50 μsec to maintain optimal photographic image quality as plasma brightness was varied. Photomultipliers inside the spectrographs monitored light incident on the plates, enabling photographic sampling times to be correlated with con-

tinuously recorded diagnostic data from several polychromators.[8-10] Photographic data were discarded whenever the integrated intensity of Ne I λ5852 fluctuated more than ± 15% during an exposure.

An adjustable occultur mounted on the slits was used to position lines from a low-pressure lamp directly beside the shock-tube spectrum.[15] The lamp lines served as wavelength references for the shift determinations and provided local instrument profiles for unfolding the broadening data. Any small contributions from natural widths and small unresolved isotopes shifts should, to a good approximation, be nulled out by this technique. Shifts between the plasma and lamp neon spectra were measured with a comparator microphotometer. Depending upon the image quality, symmetry, and width of a particular neon profile, the precision of the shift determinations was normally 0.02–0.05 Å.

The characteristic (γ curves) response of photographic emulsions was obtained in the conventional way[16] and was tested for reciprocity failure and Eberhard effect.[17] A computer code converted spectral densities into relative intensities and also employed absolute emission and temperature data to compensate for radiative trapping.[18] Self-absorption at the neon line cores was determined in each experiment from reversal intensities[19] at λ6562 Å. Self-absorption at the profile peaks was typically 5–10%, and exceeded 15% only for λ6678.28 and λ6506.53, where it occasionally reached 20%. To test for possible bias in the photometry, the areas of the experimental profiles (subsequent to their reconstruction in the optically thin limit) were reduced to relative line strengths. These compared satisfactorily with recommended values.[2]

To obtain the (full) half-width W_t due to pressure broadening in the plasmas, the red and blue halves of the measured instrument profile and the measured total profile were each averaged: in the first case to compensate for slight coma, and in the second to wash out the asymmetry due to interactions with ionic perturbers.[5] Both profiles were then fitted [$\ln S(\alpha)$ vs $\ln\alpha$] to the appropriate Voigt shapes, which in turn were treated by tabulated convolution integrals[20,21] to recover W_t. From simplified graphical models of the line and instrument shapes, we estimate that the inability to analytically unfold asymmetrical profiles cannot create as much as 5% repeatable error in the W_t data. Precision of a typical W_t determination is 12–20% (per experiment). The factors limiting precision are, in order of importance, (i) large grain of the fast (Kodak types 2475 and I-F) emulsions, (ii) fitting of total profiles to the proper Voigt shapes, (iii) fitting of measured instrument profiles to appropriate Voigt shapes, and (iv) random error in the measured corrections for self-absorption. More than 30 experiments were conducted, so that this scatter should introduce no more than 4–6 and 10–12% uncertainty into the Stark and resonance broadening parameters, respectively.

Impacts with electrons and neutral particles both impart a Lorentzian shape to a line, the component half-widths being proportional to the respective perturber densities.[5,22] This linear dependence was utilized to experimentally discriminate between Stark and resonance half-widths. Shock-tube test gases were composed of either 0.2–1.4% B_2H_6 or SiH_4 in a neon carrier, or 0.2–1.4% B_2H_6 + 8–12.1% Kr in neon carrier. The readily ionized hydride constituents made it feasible to vary electron densities N_e, neon densities N_n, *and* the degree of ionization over factors of 4–6, as shown in Fig. 1, while the relative hydrogen abundance maintained necessary brightness in the Balmer lines. When we generated shocks with lower neon densities and higher degrees of ionization than those depicted, radiative cooling sharply diminished useful test times and shock-tube flows became far more susceptible to inhomogeneities. At the other end of the N_e-N_n domain, electron densities are limited by energy considerations: The shock tube can produce[9] electron densities in excess of 2×10^{17} cm^{-3} and can provide temperatures needed for good brightness in the neon lines (E_{up} is almost 19 eV), but cannot do both simultaneously.

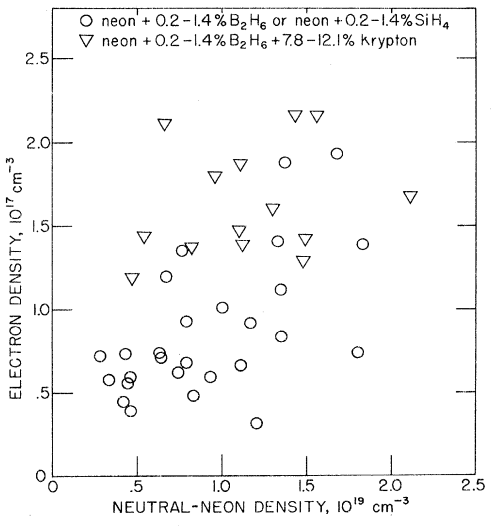

FIG. 1. Electron-density–neutral-neon-density domain utilized for the experiments. For conditions in the upper left-hand quadrant, radiative cooling reduces spectroscopic test times. Neon line brightness declines rapidly for conditions shown in the lower right-hand corner.

Tabulated predictions for the Stark broadening parameter w were interpolated to find $(1/w)\,\Delta w/\Delta T$.[5] This was used to compute the factor $\phi(T)$, in value between 0.94 and 1.07, for normalizing all data to 11 600 °K. Iteration was necessary to find the Stark and resonance broadening parameters w and w_α which best fit simultaneously to the width data and shift/width data via

$$W_t = w\phi(T)N_e + w_\alpha N_n\,, \tag{1}$$

$$\frac{D\theta(T)}{(W_t - w_\alpha N_n)\phi(T)} = \text{const}\,, \tag{2}$$

where D is the measured red shift and $\theta(T)$ is a temperature-normalizing factor for shifts analogous to $\phi(T)$. The convergence rate for the iteration varied in proportion to the quality of data for different lines, as one would expect if experimental uncertainties were predominantly random.

III. RESULTS AND DISCUSSION

Half-intensity Stark widths of λ6678.28 are shown in Fig. 2 as functions of electron density. Scatter is commensurate with *a priori* estimates. Experimental Stark broadening parameters are compared with literature values in Table I. Standard deviations from analyses of scatter and estimates of possible bias have been included in our 67% confidence limits. Reduced signal-to-noise ratios for relatively faint λ6532.88 and λ6929.47 caused accuracies for these lines to decline substantially.

Although the wavelength regions utilized for the present and the previous[4] Stark broadening measurements do not overlap, both experiments secured data for some lines of multiplets (4), (5), and (6). The arc data were collected near 12 600 °K, and have therefore been reduced 4% for comparison with present (11 600 °K) results. Unless resonance and van der Waals broadening were implicitly taken into account, it would appear that

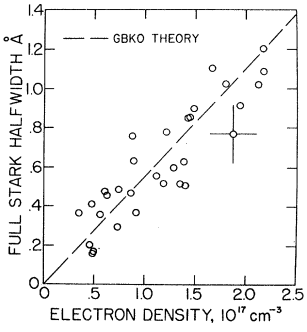

FIG. 2. Stark half-widths $(W_t - w_\alpha N_n)\phi(T)$ of Ne I λ6678.28 shown as functions of shock-tube electron density.

3–7% of the widths measured in the arc and attributed to Stark broadening were in fact due to broadening by neutrals. It is not clear how data from the two experiments might best be scaled to a common wavelength for comparison purposes. Fine-structure splitting[22] spreads each multiplet over several hundred angstroms. A simple wavelength dependence[5] of the form $w/\lambda^2 = \text{const}$ (per multiplet) may be offset by variations in individual transition integrals. When wavelength differences are ignored, the two experiments overlap within claimed tolerances.

Tabulated electron impact and quasistatic ion broadening parameters[5] were suitably interpolated to obtain the total Stark widths ($T = 11\,600$ °K) predicted by the GBKO theory. The typical (10–20%) reliability[8,23] of the GBKO predictions is probably degraded in the present case because Coulomb–*LS*-coupling wave functions are particularly inappropriate for neon,[24] and because strong collisions account for more than 60% of the predicted electron impact widths. Still, experimental uncertainty could be responsible for any of the differences between shock-tube data and (multiplet average) theoretical widths.

Collision-induced transitions between $3s$ and $3p$ states appear to influence significantly the neon line Stark widths and shifts, whereas interactions between a visible neutral line's upper and lower states are usually not significant,[5] and were customarily omitted from the GBKO predictions. By taking the $3s$-$3p$ perturbations into account, the GBKO predictions are transformed into those we denote by GBKO*. This modification causes only a marginal (+6%) change in predicted widths but has a stronger (−15%) effect on shifts.

Readily executed semiempirical formulas[25] were used in two ways to calculate electron impact widths. Predictions utilizing effective Gaunt factors $\bar{g}_n'(kT/\Delta E)$ suggested by Griem[25] are denoted in Table I by SE. Effective Gaunt factors $\bar{g}_n(kT/\Delta E)$ proposed by Van Regemorter,[26] which decline more rapidly than $\bar{g}_n'(kT/\Delta E)$ as mean thermal energies become less than thresholds for inelastic collisions,[25] were employed to calculate the SE° widths in Table I. The present $kT/\Delta E$ regime is below that of an earlier investigation,[8] where it was found that 1.5 SE° would predict experimental widths for several elements within ±25%.

Experimental Stark shifts are compared with theoretical predictions in Table I. Because the shift measurements are less sensitive to photographic image quality, accuracies for the brighter and fainter lines are more nearly the same than was the case for widths. The GBKO* shifts agree better with experiment than do the GBKO shifts. Any competing shifts due to interactions between neutrals are less than our detection threshold,

TABLE I. Measured and predicted Stark widths and shifts for $3s$-$2p$ Ne I lines ($N_e = 10^{17}$ cm^{-3}, $T = 11\,600$ °K).

Multiplet[a]	λ (air)	Stark (full) half-width (Å) This work	Arc expt.[b]	GBKO[c]	GBKO*[d]	SE[e]	SE*[e]	Red shift (Å) This work	GBKO[c]	GBKO*[d]	Shift/(half) half-width This work	GBKO[c]	GBKO*[d]
(4)	6506.53	0.45±0.10	•••	0.50	0.53	0.86	0.57	0.23±0.05	0.36	0.31	0.87±0.20	1.44	1.16
	6382.99	•••	0.33±0.10	0.50	0.53	0.86	0.57	•••	0.36	0.31	•••	1.44	1.16
(5)	6532.88	0.31±0.09	•••	0.42	0.44	0.86	0.57	0.21±0.05	0.29	0.25	1.24±0.39	1.29	1.04
	6163.59	•••	0.25±0.08	0.42	0.44	0.86	0.57	•••	0.29	0.25	•••	1.29	1.04
(6)	6598.95	0.43±0.10	•••	0.55	0.58	0.86	0.57	0.20±0.05	0.35	0.30	0.86±0.24	1.27	1.02
	6678.28	0.52±0.10	•••	0.55	0.58	0.86	0.57	0.25±0.05	0.35	0.30	0.99±0.20	1.27	1.02
	6717.04	0.47±0.10	•••	0.55	0.58	0.86	0.57	0.25±0.05	0.35	0.30	0.96±0.20	1.27	1.02
	6929.47	0.40±0.12	•••	0.55	0.58	0.86	0.57	0.27±0.06	0.35	0.30	1.13±0.29	1.27	1.02
	5852.49	•••	0.56±0.18	0.55	0.58	0.86	0.57	•••	0.35	0.30	•••	1.27	1.02

[a]Reference 3.
[b]Reference 4.
[c]Reference 5.
[d]Predictions of Griem (Ref. 5), modified by the authors to include perturbations from $3s^0$ states.
[e]Reference 25.
[f]Mean value of shift $(N_e)_{av}$/width $(N_e)_{av}$ and (shift/width)$_{av}$.

which is of order 0.03 Å per 10^{19} cm^{-3}.

When observed λ6678.28 shifts D are plotted as functions of W_t, the data (open symbols in Fig. 3) cannot be made to fit well to any straight line that intercepts the origin. These data were reduced to Stark widths and shifts at 11 600 °K (solid symbols in Fig. 3) by allowing w_α to vary so as to minimize deviations in fitting the D-vs-W_t distribution to Eq. (2). The depicted data fit Eq. (2) best when const (slope) = 0.51 and $w_\alpha = 0.18$ Å$\times 10^{-19}$ cm^{-3}. This value is consistent with the ratio obtained from the Stark widths and shifts measured as explicit functions of electron density, i.e., with $[\omega\phi(T)N_e/D\theta(T)] = 0.48$.

A second estimate of the broadening parameter w_α was obtained from the mean value of $[W_t - w\phi(T)N_e]/N_n$, where w is the experimentally determined Stark broadening parameter. Since Stark broadening generally predominated, it is expected that these difference measurements will be decidedly prone to random error. Scatter in the $[W_t - w\phi(T)N_e]$-vs-N_n distribution for λ6678.28, shown in Fig. 4, is indeed serious, but does not preclude a statistically meaningful interpretation of the data. The slope of the best-fit straight line 0.21 ± 0.05 Å/10^{19} cm^{-3} agrees satisfactorily with the estimate $w_\alpha = 0.18$ Å$\times 10^{-19}$ cm^{-3} arrived at above. The mean of these two determinations is compared with theory in Table II. It is estimated that inadequate decoupling of the w_α from the w data may introduce as much as 20–25% bias into the w_α results for all lines except λ6532.88 and λ6929.47: Relatively poor signal levels for these lines aggravate the decoupling problem and repeatable errors of 40% in w_α cannot be ruled out.

Two previous investigations of neon self-broadening[7,27] were conducted with excellent resolution, but neither utilized a thermal light source. Lang[27] and Kuhn and Lewis[7] crossed Fabry-Perot etalons with standard spectrographs to measure the broadening as neon pressure (0-300 Torr) was varied in high-frequency discharges. No estimates of Lang's gas temperature have been provided, but from the fact that the discharge could be run for several hours without external cooling, we surmise that for atoms $300 < T < 400$ °K. An interesting feature of the results (Table II) was that the broadening depended strongly upon whether a line's state was connected to the ground state by part of dipole transitions.[7,27]

The pressure broadening of Ne I λ6074.34, which

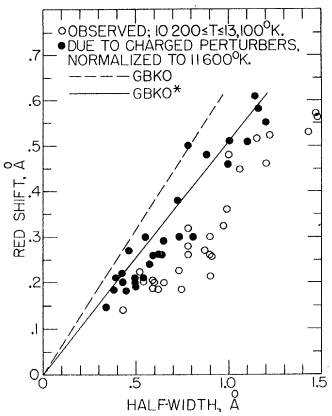

FIG. 3. Measured shifts D vs measured half-widths W_t, and temperature-normalized Stark shifts $D\theta(T)$ vs Stark widths $(W_t - w_\alpha N_n)\phi(T)$ for Ne I λ6678.28.

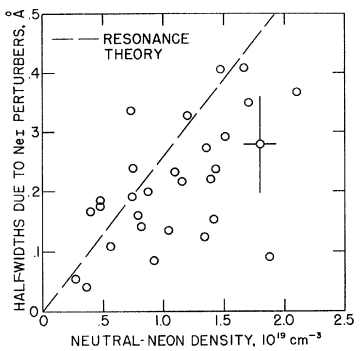

FIG. 4. Resonance broadening half-widths $W_t - wN_e\phi(T)$ of Ne I λ6678.28 shown as functions of neutral neon density.

TABLE II. Half-intensity widths (Å) due to neutral neon ($N_m = 10^{19}$ cm^{-3}).

Multiplet	λ (air)	f_{kl} ($2p \rightarrow 3s$)	This work (11 600 °K)	Kuhn and Lewis[a] (≈ 80 °K)	Meyer *et al.*[b] (≈ 340 °K[c])	Theory ($T = 11\,600$ °K) Lang[d] (≈ 300 °K)[c]	Resonance[e]	van der Waals[f] $3s$ width	van der Waals[f] $\Delta 3s, 3p$ widths
(4)	6074.34	0.012	•••	•••	0.059	0.018	0.02	0.12	0.03
	6506.53	0.012	0.14±0.07	0.079	•••	•••	0.02	0.12	0.03
(5)	6532.88	0.000[g]	0.24±0.12	0.055	•••	0.031	0.00	0.12	0.03
(6)	6598.95	0.162	0.20±0.07	•••	•••	0.140	0.26	0.12	0.03
	6678.28	0.162	0.20±0.07	0.63	•••	0.153	0.26	0.12	0.03
	6717.04	0.162	0.21±0.07	•••	•••	•••	0.27	0.12	0.03
	6929.47	0.162	0.15±0.07	0.62	•••	•••	0.28	0.12	0.03

[a]Reference 7.
[b]Reference 28.
[c]For van der Waals broadening, a factor of 2.9 would be appropriate for scaling these results to $T = 11\,600$ °K (Refs. 5 and 7).
[d]Reference 27.
[e]Reference 30.
[f]Reference 5.
[g]Dipole transitions strictly forbidden between $J = 0$ and $J = 0$.

belongs to the same multiplet as λ6506.53, was recently measured in absorption by a Zeeman scanning technique.[28] The observed width of λ6074.34 (0.059 Å when scaled to $N_n = 10^{19}$ cm^{-3}) was ascribed to van der Waals interactions,[28] from which it would follow that the result could be scaled[7,28] to the present conditions by the factor $\approx (11\,600/340\,°\mathrm{K})^{3/10}$. The λ6506.53 width so obtained, 0.165 Å, would be in satisfactory agreement with the present result (0.14 ± 0.07 Å). The data of Lang,[27] Meyer *et al.*,[28] and Kuhn and Lewis[7] do not agree well, however, even though all of these experiments utilized high-pressure discharges at more or less ambient temperatures.

Dipole-dipole interactions between the radiating ($3s$ or $3s'$ lower states) and perturbing ($2p$ or $2p'$) neon atoms should have more effect on linewidths than interactions involving higher-order multipoles.[5] Comparison of the present data with calculated resonance and van der Waals widths does not clearly support this expectation. The tentative identification of w_α as a resonance broadening parameter is not intended to discount consideration of a possible complex interplay between resonance interactions, short-range repulsive forces, and r^{-6} forces.[5,7,29,30]

The impact treatment of resonance broadening[30] predicts that linewidths should be proportional to the absorption oscillator strengths f for transitions connecting the line's lower state with the ground state. Our data on the four multiplet (6) lines (Table II) are in agreement with predictions of this theory, considering experimental tolerances, the estimated[3] 25% reliability of f values, and the inherent uncertainty[5] in the strong-collision term which accounts for 60% of the predicted broadening. In contrast, measured λ6506.73 and λ6532.88 widths do not even qualitatively resemble those predicted theoretically. Measured widths of these lines are similar to those for multiplet (6), whereas theory predicts they should be too small for us to observe. In particular, λ6532.88 should undergo no resonance broadening at all if the atom can be regarded as isolated, since $J = 0$ to $J = 0$ dipole transitions are strictly forbidden. The basic theoretical mode,[29] which has accounted for resonance broadening involving well-isolated singlet and triplet states of He I,[31,32] and appears to account for the relative $3s$-$3p$ neon linewidths observed previously,[7,27] makes no detailed provision for possible mixing of emitter fine-structure states during energetic encounters. Mean thermal energies in the present case are 10–10^2 greater than the fine-structure splitting between $3s$ states,[22] so it seems at least plausible[33] that mixing may cause higher-order terms to assume an inordinate importance.

The possibility that resonance between emitters and perturbers is not the dominant broadening mechanism can be explored to some extent by computing appropriate van der Waals widths. Using the semiclassical treatment with the oversimplification that only upper levels are significantly disturbed,[5,7] one calculates widths that approach the present experiment consistently from below ($3s$ width of Table II). The more realistic assumption that upper and lower levels are both perturbed[5,7] leads one to predict ($\Delta 3p3s$ of Table II) widths which underestimate the present data by factors of 5–7. The pattern of disagreement between the two sets of computed van der Waals widths and the current w_α data is reminiscent of the general trend ($1.3 \lesssim w_{\mathrm{expt}}/w_{\mathrm{upper\ state}} \lesssim 2.5$) obtained when measured foreign gas broadening, e.g., Ca I in neon,[34] Si in argon,[35,36] or in other noble gases, is compared with corresponding predictions.[6,37–40] The relationship between our w_α values and the predicted ($\Delta 3s, 3p$) widths suggests that $\frac{1}{3}$–$\frac{2}{3}$ of the present broadening may be due to van der Waals interac-

tions. With respect to this inference, it should be noted that neither a red shift[6,7,40,41] nor a blue shift[5,7] dependent on N_n was detected in the shock-tube plasmas.

IV. CONCLUSIONS

Widths and shifts of familiar neon red lines were measured in a controlled thermal light source. Stark effect widths (20–30% accuracy) were smaller than the GBKO predictions, and showed no simple trend compared to data from a regulated arc. Stark shifts were 25–45%, or 10–35%, less than expected theoretically, depending upon whether the interaction between $3s$ and $3p$ levels was computed. There is ambiguity regarding the neon-neon broadening mechanism. Some $3s$-$3p$ lines compared favorably with the impact theory of resonance broadening, while other lines in the some array disagreed strikingly. Comparison with other investigations suggest than van der Waals broadening may be responsible for at least a significant fraction of the present neon-neon widths.

The Stark shifts and widths reported here are factors of 40–60 smaller than those for neon $3p$-$3d$ red lines,[8] which are nearly as strong as the $3s$-$3p$ lines and have slightly (10%) higher excitation potentials.[42] Wavelength separations between the broad and narrow neon red lines offer a particularly simple means of measuring electron densities in homogeneous plasmas with excitation temperatures 1–2 eV. The comparative curves of growth for the two sets of lines should serve as sensitive electron density indicators even when the emitting medium contains uncertain temperature gradients.

ACKNOWLEDGMENTS

The authors wish to thank T. D. Wilkerson for his support and encouragement in this work. Conversations with H. R. Griem, G. L. Hammond, and R. D. Bengtson greatly advanced our work.

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*Research supported in part by National Aeronautics and Space Administration Grant No. NGR-21-002-007/6 and a grant from the Minta Martin Fund. Computer time was provided through NASA Grant No. NsG 398 to the Computer Science Center of the University of Maryland.

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PHYSICAL REVIEW A VOLUME 4, NUMBER 3 SEPTEMBER 1971

Generalized Impact-Parameter Method for Low-Energy Molecular Collisions

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(Received 29 October 1970)

A generalized impact-parameter method (not based upon perturbation theory) which is capable of describing the evolution of a collision system throughout the entire interaction region is developed. The method is then applied to the collision of a proton and a hydrogen atom at low (chemical) energies. The results obtained suggest that static calculations such as those using molecular potential-energy surfaces do not represent a very real picture of a dynamic process like a collision. Furthermore, the model does not assume linear trajectories for the atoms. This is shown from the calculations to be of importance in such low-energy collisions, the trajectories being far from linear. The model is capable of generalization to collisions in which more than two atoms are involved, such as the three-body reaction $A+BC \rightarrow AB+C$.

I. INTRODUCTION

A considerable amount of activity is currently evident in the theory of reactive molecular collisions.[1–3] Although interest in this field is ultimately aimed at the understanding of the physical "mechanism" of chemical reactions, much current work is more closely directed towards the interpretation of the results of molecular-beam studies.[4–7] Typical calculations of this sort include the following two main steps: (1) the assumption of some potential-energy surface describing the interaction between the colliding species; (2) some kind of trajectory calculation which is carried out to evaluate the angular distribution of products, differential cross sections, etc. Let us discuss what is involved in these two steps of calculation, beginning with the second.

In the first place, the whole idea of a trajectory implies a semiclassical model in which the atoms move along "classical" trajectories which are determined by some potential [step (1)]. Presuming that such a potential can be found, then step (2) requires the solution of the classical many-body problem, which is quite feasible by present-day computer techniques. Step (2), therefore, can be regarded as being possible, even if it does require substantial amounts of computer time to evaluate the large number of trajectories at different impact parameters necessary to calculate angular distributions, etc. Step (1), on the other hand, has not been properly treated. Common approaches to potentials are as follows: (a) If the system is sufficiently simple (for example, atom-atom collisions) the potential surface may be taken, for thermal collisions, to be the static (velocity independent) ground-state potential-energy surface or some analytic approximation to it; (b) for more complicated cases, some model potential[8–12] (or even set of model potentials[5] may be assumed, the general characteristics of the process being described by this potential. At the present state of development of such calculations, it is perhaps unfair to criticize, but it would appear to us that one can achieve no more understanding of the details of a given process than one puts in by suitably "doctoring" the model potential which one employs. Even if one accepts the idea of a model potential, it must be admitted that the nonuniqueness of the results obtained by suitably choosing a variety of parameters is scarcely satisfactory. A further criticism, and undoubtedly a much more serious one, of this whole method of calculation, is that the validity of assuming a static potential-energy surface in the first place as an "interaction potential" is somewhat questionable. Certain of the results obtained in this paper cast some light on this problem.

The interest of the present authors in reactive molecular collisions derives from previous work in the theory of molecular processes in general[13,14] and a concurrent interest in techniques for describing the evolution of a quantum system in time.[15] Our interest in semiclassical calculations therefore relates to the model one might use to calculate a given trajectory, rather than the calculation of many trajectories to evaluate quantities of interest to molecular-beam specialists. Apart from the