

TEMPERATURE DEPENDENCE OF THE SELF-BROADENED 540.06 nm NEON LINE

P.J. LEO^{a*}, D.F.T. MULLAMPHY^b, G. PEACH^a, V. VENTURI^b
AND I.B. WHITTINGHAM^b

^aDepartment of Physics and Astronomy, University College London
London, WC1E 6BT, UK

^bSchool of Computer Science, Mathematics and Physics
James Cook University, Townsville, 4811 Australia

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Quantum close-coupled calculations of the collisional self-broadening of the 540.06 nm neon line ($3s[3/2]_1-3p'[1/2]_0$) are presented for temperatures from 70 K to 900 K. These calculations are based on the quantum-mechanical impact theory of Baranger and represent the interatomic interaction by adiabatic molecular potentials calculated using model potentials for the electron-atom and atomic core-core interactions. The calculated widths and shifts vary smoothly with temperature and are accurately given across the temperature range by fourth order polynomial fits.

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1. Introduction

The temperature dependence of the width and shift of collisionally broadened atomic spectral lines has long been a subject of experimental and theoretical investigation as this temperature dependence is a sensitive measure of the theoretical model used to describe the line broadening process and of the nature of the potentials used to represent the interaction between the radiating and perturbing atoms. For example, the widely used Lindholm-Foley classical oscillator theory of line broadening (see, e.g. [1]) applied to the Van der Waals interaction $V(R) = -C_6/R^6$ predicts a simple $T^{0.3}$ dependence for the width w and shift d and the temperature-independent ratio $d/w = -0.362$. Recent calculations of collisional self-broadening of non-resonance lines in He [2] and Ne [3-5], based on the quantum-mechanical impact theory of Baranger [6] for non-overlapping lines and in which the interatomic interaction is represented by adiabatic molecular potentials calculated using model potentials for the electron-atom and atomic core-core

*Present address: Atomic Physics Division, PHYS A267, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA.

interactions, have been undertaken for temperatures in the range 70–400 K and predict a far more complex temperature dependence than simple power laws for the widths and shifts. Extension of the calculations to temperatures above 400 K was considered not practicable in general as the convergence of the sums over partial waves was very slow, especially for the shifts, at the high scattering energies needed to accurately perform the integration over the perturber energies significant at high T .

The only existing experimental investigation of the temperature dependence of collisional self-broadening in neon over an extended temperature range is that of Bobkowski et al. [7] who measured the width and shift of the 540.06 nm ($3s[\frac{3}{2}]_1-3p'[\frac{1}{2}]_0$) transition at temperatures of 87, 311, 496, 667, 689 and 864 K and found that, whereas the widths could be fitted to a power law AT^κ with $\kappa = 0.39 \pm 0.04$, the shifts had an irregular behaviour with T .

Fortunately the $3s[\frac{3}{2}]_1-3p'[\frac{1}{2}]_0$ transition is the most suited of all the $2p^53s-2p^53p$ neon lines for an extended theoretical investigation of temperature effects within the quantum-mechanical model used by Leo et al. as the upper level $3p'[\frac{1}{2}]_0$ is represented by a single set of six coupled differential equations and, as $3p'[\frac{1}{2}]_0$ is the strongly isolated highest lying $3p'$ state, all scattering channels to the other $3p'$ states are open at all scattering energies and the complications of closed channels do not occur.

We report here the results of calculations of the widths and shifts of the self-broadened 540.06 nm Ne line for the temperature range 70 K to 900 K. The widths are accurate to four significant figures for all temperatures but the accuracy of the shifts at the high temperatures decreases to only two significant figures as a consequence of the imposed limit of 500 partial waves in the calculations.

2. Theory

The width w and shift d of the Lorentzian spectral profile for a line involving initial and final emitter states $|j_i K_i\rangle$ and $|j_f K_f\rangle$ respectively (we suppress the quantum numbers (n, L) for convenience) is given by [3]

$$w + id = N \int_0^\infty f(E)S(E)dE, \quad (1)$$

where $f(E)$ is the normalized Maxwellian perturber energy distribution

$$f(E) = \frac{8\pi}{M} \left(\frac{M}{2\pi kT} \right)^{3/2} E \exp\left(-\frac{E}{kT}\right), \quad (2)$$

N is the perturber number density and

$$S(E) = \frac{\hbar^2 \pi}{2M^2 E}$$

$$\begin{aligned} & \times \sum_{l, l'} \sum_{J_i, J_f} (2J_i + 1)(2J_f + 1)(-1)^{l+l'} \left\{ \begin{matrix} J_f & J_i & 1 \\ j_i & j_f & l \end{matrix} \right\} \left\{ \begin{matrix} J_f & J_i & 1 \\ j_i & j_f & l' \end{matrix} \right\} \\ & \times \{ \delta_{l, l'} - \langle j_i K_i l' J_i | S | j_i K_i l J_i \rangle \langle j_f K_f l' J_f | S | j_f K_f l J_f \rangle^* \}. \quad (3) \end{aligned}$$

Here l and l' are the values of the relative emitter-perturber angular momentum \mathbf{L}_R before and after the collision, $\mathbf{J} = \mathbf{L}_R + \mathbf{j}$ is the total angular momentum of the emitter-perturber system, $\langle j K l' J | S | j K l J \rangle$ is the interaction picture scattering matrix in the coupled $\{|j K l J\rangle\}$ representation, $\begin{Bmatrix} a & b & c \\ f & g & h \end{Bmatrix}$ is the $6 - j$ symbol and M is the reduced mass of the emitter-perturber system.

The scattering matrix elements in (3) are determined from the asymptotic behaviour of the radial functions $G_{jKl}^J(R)$ for each scattering channel (j, K, l, J) which satisfy the coupled equations [3]

$$\begin{aligned} & \left[\frac{\partial^2}{\partial R^2} - \frac{l(l+1)}{R^2} + K k_j^2 \right] G_{jKl, j'' K'' l''}^J(R) \\ &= \frac{2M}{\hbar^2} \sum_{j', K', l'} V_{jKl, j' K' l'}^J(R) G_{j' K' l', j'' K'' l''}^J(R), \end{aligned} \quad (4)$$

where (j'', K'', l'') labels the linearly independent solutions of (4) and the Born-Oppenheimer coupling terms have been neglected. The parameter

$$K k_j^2 = 2M \left[E - (E^{(j_c, L)} + \epsilon_j^K) \right] / \hbar^2 \quad (5)$$

is positive for open scattering channels and negative for closed channels. Here E is the total energy of the emitter-perturber system, $E^{(j_c, L)}$ is the energy of the state of the separated atoms to which the molecular state dissociates adiabatically and the fine structure parameter $\epsilon_j^K(R)$ has been assumed to have its asymptotic value ϵ_j^K . The interaction potential matrix elements are

$$\begin{aligned} V_{jKl, j' K' l'}^J(R) &= \sum_{\Omega} (-1)^{j' - j} C(J j l; -\Omega \Omega 0) C(J j' l'; -\Omega \Omega 0) \\ &\times \sum_{\Omega_c, \Omega_K} \sum_{\Omega_L, \Omega_S} C\left(K \frac{1}{2} j; \Omega_K \Omega_S \Omega\right) C\left(K' \frac{1}{2} j'; \Omega_K \Omega_S \Omega\right) \\ &\times C(j_c L K; \Omega_c \Omega_L \Omega_K) C(j_c L K'; \Omega_c \Omega_L \Omega_K) j_c V_A(R), \end{aligned} \quad (6)$$

where Ω denotes the projection of an angular momentum onto the internuclear axis \mathbf{R} , $A \equiv |\Omega_L|$ and $j_c V_A(R)$ are the adiabatic molecular potentials.

3. Results and discussion

The $3s[\frac{3}{2}]_2$ and $3p'[\frac{1}{2}]_0$ states of neon are represented [3] by three uncoupled and six coupled differential equations respectively. These equations were solved using a modified version [2] of the R-matrix method of Baluja et al. [8] and the solutions fitted to free field boundary conditions to extract the scattering matrix elements.

The adiabatic molecular potentials $j_c V_A(R)$ for the $\text{Ne}^* - \text{Ne}$ system were constructed using a three body model in which Ne^* is treated as a Ne^+ ion plus an active electron and the perturbing neon atom as a polarisable atomic core. Model potentials were used to represent the electron-atom and atomic core-core interactions. The $3p^{1/2} V_{\Sigma}$ and $3p^{1/2} V_{\Pi}$ potentials for $R \leq 20a_0$ and their asymptotic C_6

values are given by Leo et al. [4]. The $3s^{3/2}V_E$ potential has a very weak minimum of $-3.2 \times 10^{-5}E_0$ ($E_0 = \alpha^2 m_e c^2 = 27.212$ eV) at $R = 10.5a_0$ and an asymptotic C_6 value of $55.196E_0a_0^6$ valid for $R > 100a_0$.

In previous calculations of the $2p^53s-2p^53p$ lines the integration over perturber energies in (1) was performed using 86 nodes ranging from $6.65 \times 10^{-5}E_0$ to $8.50 \times 10^{-3}E_0$. Partial wave convergence to six figures was obtained in $S(E)$ for all but the highest few energy nodes, where three to four figure convergence was obtained, by summing over 400 partial waves. However for the increased temperature range of the present investigation this range of energy nodes and number of partial waves was not sufficient. The energy range was extended to $1.40 \times 10^{-2}E_0$ with 21 additional nodes and the partial wave summation expanded to 500 partial waves.

For the temperature range 70–900 K the widths obtained were accurate to at least four significant figures but the poor convergence of $\Im S(E)$ at high E resulted in the accuracy of the shifts decreasing from four significant figures at 500 K to only two figures at 900 K. This slow convergence of the partial wave contributions to the shifts at high E is due to the increasing cancellation of the negative shifts produced by the long range attractive part of the potential by the positive shifts produced by the repulsive part of the potential as the perturber probes more of the small R region.

The widths and shifts were calculated at 1 K intervals and both quantities were found to be smooth monotonic functions of temperature which could be accurately represented by

$$w = 0.138 + 0.912\hat{T} - 1.22\hat{T}^2 + 1.12\hat{T}^3 - 0.464\hat{T}^4,$$

$$d = -0.0613 + 7.79 \times 10^{-3}\hat{T} + 0.114\hat{T}^2 - 0.122\hat{T}^3 + 0.0383\hat{T}^4, \quad (7)$$

where $\hat{T} \equiv T/1000$. This smooth dependence on temperature arises from the weighting of a collision function $S(E)$ whose real and imaginary parts are slowly varying functions of E with relatively broad velocity distribution functions $f(E)$. Whereas $\Re S(E)$ increases steadily with E , $\Im S(E)$ is negative at small E , becomes temporarily positive for the region $4.4 \times 10^{-3}E_0 < E < 7.5 \times 10^{-3}E_0$ and finally positive and increasing monotonically above $1.0 \times 10^{-2}E_0$, indicating that the shifts will eventually become positive at the very high temperatures where the contributions from the repulsive part of the potential are dominant.

Widths and shifts at the temperatures studied by Bobkowski et al. [7] and Lee [9] are given in Table together with their experimental results. Also shown are theoretical results for the widely used approximation in which the Maxwellian average over perturber velocities is replaced by a fixed average perturber velocity $\bar{v} = (8kT/\pi M)^{1/2}$. As expected, the use of an average perturber velocity becomes increasingly inaccurate at higher temperatures where the very broad Maxwellian distribution $f(E)$ weights a large region of $S(E)$.

The calculated widths and shifts do not agree with the measurements of Bobkowski et al. or of Lee. The calculated widths are 38–64% smaller than the measurements of Bobkowski et al. This difference is greater than that found for the other $2p^53s-2p^53p$ neon transitions studied earlier [3, 4] but consistent with the trend found there that the theoretical widths with very few exceptions lie

TABLE

Widths and shifts (in units of 10^{-21} MHz m³/atom) for the $3s[{}^3_2]_1-3p'[{}^1_2]_0$ transition in Ne. Theoretical results are given for integration over a perturber velocity distribution (Vint) and for a fixed perturber velocity (Vbar). The numbers in brackets indicate the change produced by the addition of the last 50 partial waves.

Temp. [K]	Widths			Shifts		
	Vint	Vbar	Exp.	Vint	Vbar	Exp.
77	0.2000	0.1931	0.237 ± 0.016^a	-0.0606	-0.0644	-0.0729 ± 0.0023^a
87	0.2081	0.2026	0.294 ± 0.030^b	-0.0603	-0.0606	-0.105 ± 0.042^b
273	0.3158	0.3428	0.272 ± 0.024^a	-0.0531(2)	-0.0560(1)	-0.0843 ± 0.0057^a
311	0.3324	0.3561	0.468 ± 0.024^b	-0.0513(2)	-0.0550(2)	-0.081 ± 0.012^b
496	0.3986	0.4175	0.609 ± 0.030^b	-0.0418(4)	-0.0461(3)	-0.063 ± 0.030^b
667	0.4438	0.4861	0.639 ± 0.054^b	-0.0338(7)	-0.0464(6)	-0.108 ± 0.078^b
689	0.4486	0.4993	0.734 ± 0.060^b	-0.0329(8)	-0.0466(6)	-0.099 ± 0.048^b
864	0.4790	0.5901	0.660 ± 0.180^b	-0.0264(10)	-0.0137(8)	-0.012 ± 0.054^b

^aRef. [9], ^bRef. [7].

below the experimental widths. The measured widths of Lee at 77 and 273 K are, respectively, 19% above and 14% below the calculated widths. The theoretical shifts are all significantly smaller than the measured shifts, the differences ranging from 21–230%, and there is no theoretical support for the anomalously large shifts measured by Bobkowski et al. at 667 and 689 K.

The current calculations have demonstrated that the formalism and calculational techniques developed by Leo et al. [3, 4] for self-broadening of neon can be used to obtain widths and (to a lesser extent) shifts up to temperatures of 900 K. Such calculations should be possible for other $2p^53s-2p^53p$ transitions but there is little point doing these calculations until experimental studies at elevated temperatures are undertaken.

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References

- [1] G. Peach, *Adv. Phys.* **30**, 367 (1982).
- [2] P.J. Leo, G. Peach, I.B. Whittingham, *J. Phys. B, At. Mol. Opt. Phys.* **28**, 591 (1995).
- [3] P.J. Leo, D.F.T. Mullamphy, G. Peach, I.B. Whittingham, *J. Phys. B, At. Mol. Opt. Phys.* **28**, 4449 (1995).
- [4] P.J. Leo, D.F.T. Mullamphy, G. Peach, V. Venturi, I.B. Whittingham, *J. Phys. B, At. Mol. Opt. Phys.* **29**, 4573 (1996).
- [5] P.J. Leo, D.F.T. Mullamphy, G. Peach, V. Venturi, I.B. Whittingham, *J. Phys. B, At. Mol. Opt. Phys.* **30**, 535 (1997).
- [6] M. Baranger, *Phys. Rev.* **112**, 855 (1958).

- [7] R. Bobkowski, A. Bielski, E. Lisicki, J. Szudy, J. Wolnikowski, *Acta Phys. Pol. A* **67**, 601 (1985).
- [8] K.L. Baluja, P.G. Burke, L.A. Morgan, *Comput. Phys. Commun.* **27**, 299 (1982).
- [9] M. Lee, private communication, 1997.