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Long-range interactions of the thallium $7^2S_{1/2}$ state and broadening and shift of the thallium violet and green lines by rare gases^{a)}

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The long-range interaction coefficients (C_6 , C_8 , C_{10}) of the Tl($7^2S_{1/2}$) atom with rare gases are calculated. The pressure-induced broadening and shift of the thallium resonance lines in the presence of rare gases are then calculated using these long-range coefficients and impact theory. We find that higher order van der Waals forces are not negligible compared to the leading $-C_6/R^6$ dispersion force in terms of their contributions to the broadening and shift.

Recently, Cheron, Scheps, and Gallagher reported an analysis of the far wing intensities,¹ and the shift and broadening, of the Lorentzian-shaped line cores of the Tl-rare gas molecules.² Potentials of Tl-rare gas molecules were determined from continuum emission intensities. Long-range interaction potentials were also discussed. While we have carried out some calculations of the pressure-induced broadening and shift for the highly excited S-state alkalis perturbed by a rare gas by using a long-range interaction potential of the form $-\sum C_n/R^n$ ($n=6, 8$, and 10),³ we felt that it may also be interesting to compare the experimentally determined parameters with our calculated values in these Tl-rare gas pairs.

It is well known that at low pressure the shift and broadening near the resonance line center, where only the long-range interaction potential is important, can be calculated by impact collision theory.⁴⁻⁷ A simple analytical expression for the shift and broadening can be obtained for an interaction potential of the simple form $-C_n/R^n$ ($n \geq 3$).⁴⁻⁷ However, in the present case, the contributions from the $-C_8/R^8$ and $-C_{10}/R^{10}$ potential terms are not negligible even in the $R=15$ Å region (the average collision radius is 13 Å); for example, the C_8/R^8 and C_{10}/R^{10} energies for Tl ($7^2S_{1/2}$) + Xe yield about 15% and 3% increases in $|(d/dR)\Delta V(R)|$, respectively. Therefore, a potential which includes $-C_6/R^6$, $-C_8/R^8$, and $-C_{10}/R^{10}$ is necessary in the calculation of broadening and shift. A numerical procedure to integrate over the impact parameter and relative velocity of the colliding pair is employed. The detailed procedure will be described elsewhere.³ The van der Waals constants C_n for the Tl ($7^2S_{1/2}$)-rare gas molecules are calculated according to Ref. 8 and given in Table I. The C_8 values of Tl ($6^2P_{1/2}$)- and Tl ($6^2P_{3/2}$)-rare gas pairs are taken from Ref. 2. It is found that the estimated values⁹ of C_8 and C_{10} for the Tl ($6P$)-rare gas pairs are one or two orders of magnitude smaller than C_8 and C_{10}

for the corresponding Tl ($7^2S_{1/2}$)-rare gas pair. Table II summarizes the constants used in the broadening and shift calculations.

It should be noted that the errors in C_6 , C_8 , and C_{10} values given in Table I represent *only* the truncation error in the asymptotic expansion. It is clear (as discussed in Ref. 8) that actual errors will often be larger, principally, we feel, because of core and core-valence coupling contributions in thallium and because of the neglect of relativistic corrections (noted, for example, for $\langle r^{-2} \rangle$ in the heavy alkali metals in Ref. 8). Thus, it is estimated that reasonable theoretical uncertainties for the Table I values would be $\leq 10\%$. The differences between the $7^2S_{1/2}$ results and the $6^2P_{3/2}$ and $6^2P_{1/2}$ results in Table II should also be good to less than 10% because of the partial cancellation of core and relativistic corrections.

The calculated shifts and widths of the Lorentzian full-width broadenings are given in Table III, where they are compared to the experimental data. The calculated results are in good agreement with experiment; in particular, they all give the same trends in the shift and broadening, e.g., Tl-Kr pairs are always the smallest. A calculation, made assuming only the $-C_6/R^6$ potential is important, is also included in the table. This shows that the contribution of the higher order van der Waals forces should not be ignored.

It is also interesting to note that the $-C_6/R^6$ potential becomes more dominant from Ar to Xe. This is reflected in the ratio of $|\Delta/\gamma|$, which increases from 0.303 to 0.330 for the Ar, Kr, and Xe perturber cases. However, the observed ratio increases from 0.27 ± 0.05 to 0.39 ± 0.04 (not 0.5-0.7).² Since even for a pure $-C_6/R^6$ interaction potential the value of $|\Delta/\gamma|$ is 0.363, we find the data for the particular pair Tl ($7^2S_{1/2}$ - $6^2P_{3/2}$) + Xe ($|\Delta/\gamma| = 0.39 \pm 0.04$) hard to understand.

Finally, we would like to reiterate that the calculated values of C_n in Table I only involved the valence electron, the relatively small contribution of the core potential¹⁰ having been ignored. However, in our calculation of broadening and shift, only the difference of the van der Waals constants is used. Thus, significant cancellation of the contribution of core potential may be expected.

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TABLE I. The long-range coefficients C_6 , C_8 , and C_{10} (all in a.u.) for Tl ($7^2S_{1/2}$)-X, with their uncertainties listed immediately below. Also listed are the ratios $\beta = C_8/C_6$ and $\gamma = C_6C_{10}/C_8^2$. The symbol (n) means multiply by 10^n . The calculations were performed using the equations and rare gas/hydrogen atom sum values given in Ref. 8. A value of $n^* = 2.194504$ was used for Tl ($7^2S_{1/2}$).

Tl ($7^2S_{1/2}$) + X =	H	He	Ne	Ar	Kr	Xe
C_6	2.584(2)	8.109(1)	1.576(2)	6.471(2)	9.739(2)	1.563(3)
	2.760(0)	0.158(0)	0.298(0)	2.908(0)	5.837(0)	1.343(1)
C_8	3.642(4)	1.158(4)	2.278(4)	9.509(4)	1.430(5)	2.275(5)
	4.043(2)	2.284(1)	4.403(1)	4.630(2)	9.314(2)	2.013(3)
C_{10}	6.447(6)	2.081(6)	4.125(6)	1.727(7)	2.588(7)	4.098(7)
	1.316(5)	8.731(3)	1.431(4)	1.491(5)	2.997(5)	6.554(5)
β	1.410(2)	1.428(2)	1.446(2)	1.470(2)	1.468(2)	1.456(2)
γ	1.256(0)	1.259(0)	1.252(0)	1.236(0)	1.233(0)	1.237(0)

TABLE II. The van der Waals constants (in a.u.) used in the calculation of Tl-heavy rare gas pairs. The symbol (n) means multiply by 10^n .

Perturber	Tl State	C_6	C_8	C_{10}
Ar	$6^2P_{1/2}^a$	6.5(1)	2.4(3)	8.7(4)
	$6^2P_{3/2}^a$	1.05(2)	3.8(3)	1.4(5)
	$7^2S_{1/2}$	6.47(2)	9.51(4)	1.73(7)
Kr	$6^2P_{1/2}^a$	1.0(2)	3.7(3)	1.3(5)
	$6^2P_{3/2}^a$	1.9(2)	6.9(3)	2.5(5)
	$7^2S_{1/2}$	9.74(2)	1.43(5)	2.59(7)
Xe	$6^2P_{1/2}^a$	1.6(2)	5.8(3)	2.1(5)
	$6^2P_{3/2}^a$	3.0(2)	1.1(4)	3.9(5)
	$7^2S_{1/2}$	1.56(3)	2.28(5)	4.10(7)

^a C_6 taken from Ref. 2; C_8 and C_{10} estimated (see text and Ref. 9).

TABLE III. Comparison of the shift Δ/N ($\text{cm}^{-1}/\text{r.d.}$)^a and broadening γ/N (FWHM, $\text{cm}^{-1}/\text{r.d.}$)^a of the Tl resonance lines in the presence of Ar, Kr, and Xe from Expt. (Ref. 2) or calculated here using C_6 only or using C_6 , C_8 , and C_{10} . A temperature of 743 °K is used in the calculation.

Line	Perturber	Expt.		$-\Delta C_6/R^6$		$-\sum_n \Delta C_n/R^n$	
		γ/N	Δ/N	γ/N	Δ/N	γ/N	Δ/N
$7^2S_{1/2}-6^2P_{1/2}$ 377.6 nm	Ar	1.01 ± 0.06^b	-0.27 ± 0.04^b	0.70	-0.25	0.80	-0.25
	Kr	0.91 ± 0.07	-0.23 ± 0.05	0.69	-0.25	0.77	-0.24
	Xe	0.98 ± 0.10	-0.27 ± 0.05	0.77	-0.28	0.83	-0.26
$7^2S_{1/2}-6^2P_{3/2}$ 535 nm	Ar	0.84 ± 0.06^b	-0.27 ± 0.02^b	0.68	-0.25	0.79	-0.25
	Kr	0.72 ± 0.04	-0.25 ± 0.02	0.66	-0.24	0.75	-0.24
	Xe	0.72 ± 0.02	-0.28 ± 0.02	0.73	-0.26	0.80	-0.26

^a1 r.d. = 2.69×10^{18} atom/ cm^3 is the density of an ideal gas at standard temperature and pressure.

^bThe Ar experiments were carried out at a slightly lower temperature (720 °K).

In conclusion, we have shown that the contribution of higher order long-range forces to broadening and shift are not completely negligible compared to the contribution of the leading $-C_6/R^6$ dispersion term.

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