PHYSICAL REVIEW A VOLUME 24, NUMBER 2 AUGUST 1981

Calculated pressure broadening and shift for the sodium atom perturbed by rare gases. II. Two-photon $3S$-nS transitions ($n = 6$–9)

C. Y. R. Wu

Department of Physics and Earth and Space Sciences Institute, University of Southern California, Los Angeles, California 90007

W. C. Stwalley

Iowa Laser Facility and Departments of Chemistry and Physics, University of Iowa, Iowa City, Iowa 52242

(Received 29 September 1980)

Our recent treatment [Phys. Rev. A 18, 1066 (1978)] of the broadening and shift of alkali-metal-atom two-photon S-S transitions is applied to the Na $3S$-nS transitions ($n = 6$–9) perturbed by Ar, Kr, and Xe rare gases. Comparison with recent experimental data [A. Flusberg *et al.*, Phys. Rev. A 19, 1607 (1979)] on the Na-Ar pair for $n \leq 7$ shows good agreement. However, for transitions to $n > 8$ the calculated pressure effects no longer agree well with experimental data; presumably the pressure effects cannot be adequately described by a simple two-body long-range impact theory.

Recently we have reported calculation of pressure effects in the two-photon S-S transition of alkali metal atoms in the presence of heavy rare gases.[1] The interaction between an alkali S atom and a rare-gas atom is described using only a two-body long-range interatomic potential. Comparisons between calculated[1] and experimental[2] data were made for the Na $3S$-$5S$ transition perturbed by rare gases. Since then, Flusberg *et al.*[3] have experimentally measured the broadening of Na $3S$-nS (with $n = 5$–20) perturbed by He, Ne, and Ar by utilizing the so-called trilevel echo technique and here we extend our results for comparison with these new experiments.

In a theoretical calculation of pressure broadening for transitions involving large values of n, the scattering is more properly considered to be a three-body problem (Na^+ core, Rydberg electron, rare-gas atom). Omont[4] has used the Fermi potential[5] to describe the interaction between the Rydberg electron and the neutral perturber, and thus treat this high-n limit. In the case of the high-n *nondegenerate* S states of alkali atoms perturbed by either He or Ar, the calculated pressure broadenings agree quite well with the experimental values.[3] However, for low-n levels this theory fails because the Rydberg electron and Na^+ core can no longer be treated independently. On the other hand, our two-body long-range description should be valid near line center, where it is well known that the long-range interatomic potential dominates the pressure effects for Ar, Kr, and Xe when the Rydberg atom is in the lowest-n levels (for He and Ne attraction is very weak and repulsive effects must also be considered). One of the main results of this paper is to show explicitly for the case of Na + Ar the n values where the low-n long-range theory is valid and to define the interesting intermediate range of n (approximately $8 \leqslant n \leqslant 10$) where neither the "high-n" (Ref. 4) nor the "low-n" (Ref. 1) theory is particularly accurate.

Previously[1,6,7] we have also shown that a long-range interatomic potential which includes $-C_8/R^8$, and $-C_{10}/R^{10}$ as well as $-C_6/R^6$, where R is the internuclear distance, is usually necessary in the accurate calculation (for low n) of pressure-induced broadening and shift. The long-range interaction coefficients, i.e., C_m with $m = 6$, 8, and 10, are readily evaluated accurately from the long-range interaction energy expansion for an alkali-like S-state atom with a rare-gaslike S-state atom.[8]

Impact theory has been quite successful in explaining the pressure effects near the Lorentzian-shaped line center since the pressure-induced broadening and shift near the line center often depends mainly on the details of the outer part of the interatomic potential, where only the long-range dispersion potential is important. In Doppler-free spectroscopy, such as two-photon absorption[2] and the trilevel echo effect,[3] the pressure of the alkali metal is typically 10^{-5}–10^{-3} Torr, with added buffer gas up to several Torr. Therefore, data on pressure effects determined by such experimental techniques are ideal for detailed comparison with impact theory, especially for the nondegenerate S states which only involve phase changing (elastic) collisions.

The method and procedure for the present calculation has been previously described in detail.[1] The difference of the long-range coefficients $\Delta C_m = C_m$ (upper level)$-C_m$ (lower level) for the Na ($3S$-nS)-Ar, -Kr, and -Xe pairs used in the calculation are readily calculated from Ref. 6 and should be accurate to $<10\%$.

TABLE I. Comparison of experimental and calculated absolute rate of broadening $\Delta\nu/N$ (FWHM, MHz/Torr) and shift $\Delta\nu'/N$ (MHz/Torr), for the Na $3S$-nS two-photon transition. A temperature of 400 °C is used in the calculation.

Transition	Na-Ar $\Delta\nu/N$	 $\Delta\nu'/N$	Na-Kr $\Delta\nu/N$	 $\Delta\nu'/N$	Na-Xe $\Delta\nu/N$	 $\Delta\nu'/N$
$3S$-$5S$	89.0 [a] 111.4 ± 8 [b] 119 [c]	−22.6 [a] −35.6 ± 3 [b]	87.6 [a] 99.0 ± 7 [b]	−26.2 [a] −25.3 ± 4 [b]	106.0 [a] 111.4 ± 11 [b]	−29.9 [a] −30.0 ± 2 [b]
$3S$-$6S$	154 158 [c]	−37.4	160.5	−39.9	178.2	−45.4
$3S$-$7S$	239.3 222 ± 15 [c]	−53.6	249.0	−55.7	274.8	−62.6
$3S$-$8S$	353.5 240 [c]	−71.9	364.1	−71.8	401.6	−76.3
$3S$-$9S$	496.8 198 [c]	−86.4	508.5	−80.3	551.8	−76.3

[a] Calculated data at a temperature of 563 K, Wu and Stwalley (Ref. 1).

[b] Experimental data were taken at a temperature of 563 K, Biraben *et al*. (Ref. 2).

[c] Experimental data were taken at a temperature of 400 K, Flusberg *et al*. (Ref. 3). A statistical uncertainty is given explicitly only for $n = 7$, but similar uncertainties should apply to the other n values (Ref. 3).

A temperature of 400 K is used in the present calculation ($n = 6$–9). The calculated results are summarized in Table I, where they are compared to the available experimental data. In Table I we also include the results for the Na $3S$-$5S$ transition which were previously calculated at a temperature of 563 K.

As shown in Table I the calculated absolute rate of broadening and shift increases as n increases. This is because at sufficiently large n, the long-range coefficients are approximately proportional to higher powers[8] of n^* (effective principal quantum number $= n - \delta$, where δ is the quantum defect): $C_6 \propto n^{*4}$, $C_8 \propto n^{*8}$, and $C_{10} \propto n^{*12}$. It is also interesting to note that the ratio of shift to broadening decreases as n increases; for example, in the Na-Xe pair the ratio decreases from 0.28 to 0.14 for the transitions $3S$-$5S$ to $3S$-$9S$. This confirms, as discussed in Reference 8, that the C_8 and C_{10} terms become increasingly important relative to the C_6 term in the long-range interatomic potential as n increases, since, for a pure $-C_6/R^6$ interaction potential, the ratio of shift to broadening is always 0.36 (Refs. 9–11).

Biraben *et al.*,[2] using two-photon Doppler-free spectroscopy, measured the pressure effects on the Na $3S$-$5S$ transition using the rare gases. However, only data on Ar, Kr, and Xe are included here since as noted previously there is evidence that the pressure effects produced by the weakly attractive light perturbers, He and Ne, are mainly determined by the repulsive part of the interatomic potential. Our calculated values[1] showed good agreement with the experiments of Biraben *et al.*[2] Flusberg *et al.*,[3] using the trilevel echo experiment, have measured the collisional broadening of Na $3S$-nS ($n = 5$–20) transitions perturbed by He, Ne, and Ar. Good agreement between our calculated and their experimental values can be seen for the Na ($3S$-nS)-Ar pair with $n \leq 7$ as listed in Table I. Thus, our long-range theory[1] is evidently valid only for $n \leq 7$ when Ar is the perturbing gas. It is possible that the long-range treatment may be valid for higher Rydberg states, for example, in the case of Xe, since Xe has a high polarizability. Unfortunately, experimental data are not available for comparison at the present time.

We note that the theoretical values of Omont[4] agree well with experimental data of Flusberg *et al.*[3] for $n \geq 11$ in the Na $3S$-nS transitions perturbed by He or Ar. Thus, it appears that our long-range "low-n" theory is adequate in explaining the pressure effects of Na ($3S$-nS)-Ar collision for $n \leq 7$, while the Omont treatment[4] is valid for values of $n > 11$, and there is an interesting intermediate region where neither theory is particularly accurate.

It should also be noted that for a nondegenerate S state there is only a single asymptotic potential-energy curve, so it is reasonable to assume only phase-changing (i.e., elastic) collisional events occur. Even for $n = 9$, the nearest atomic state ($8d$) is still 154 cm^{-1} away. Indeed, Flusberg *et al.*[3] in their experiment found that this is the case. However, in the Na $3S$-nD transitions inelastic collisions[12-14] and multiple potential-energy curves will contribute to the pressure effects. In this case our simple long-range impact theory[1] will probably be inadequate.

In conclusion, we have calculated the pressure-induced broadening and shift of Na $3S$-nS transitions in the presence of heavy rare gases by using a long-range interatomic potential. We have compared the recently measured data of Flusberg *et al.*[3] for Ar with our calculated results and found good agreement for $n \leq 7$.

ACKNOWLEDGMENTS

The authors would like to thank Dr. S. R. Hartmann for providing data from Ref. 3 prior to publication. Support received from the National Science Foundation and the National Aeronautics and Space Administration is gratefully acknowledged.

---

[1] C. Y. R. Wu and W. C. Stwalley, Phys. Rev. A 18, 1066 (1978).

[2] F. Biraben, B. Cagnac, E. Giacobino, and G. Grynberg, J. Phys. B 10, 2369 (1977).

[3] A. Flusberg, R. Kachru, T. Mossberg, and S. R. Hartmann, Phys. Rev. A 19, 1607 (1979) and references therein.

[4] A. Omont, J. Phys. (Paris) 38, 1343 (1977).

[5] E. Fermi, Nuovo Cimento 11, 157 (1934); and slightly refined by following works, e.g., C. Reinsberg, Z. Phys. 105, 460 (1937); V. A. Alakseev and I. I. Sobelman, Zh. Eksp. Teor. Fiz. 49, 1274 (1965) [Sov. Phys.—JETP 22, 882 (1966)]; G. K. Ivanov, Opt. Spectrosk. 40, 965 (1976) [Opt. Spectrosc. (USSR) 40, 554 (1976)] and references therein.

[6] C. Y. R. Wu, W. C. Stwalley, and T. R. Proctor, J. Chem. Phys. 69, 4238 (1978).

[7] C. Y. R. Wu and W. C. Stwalley, J. Quant. Spectrosc. Radiat. Transfer 20, 211 (1978).

[8] T. R. Proctor and W. C. Stwalley, J. Chem. Phys. 66, 2063 (1977), and references therein.

[9] R. B. Breene, Jr., *The Shift and Shape of Spectral Lines* (Pergamon, New York, 1961).

[10] S. Chen and M. Takeo, Rev. Mod. Phys. 29, 20 (1957).

[11] M. Mizushima, Phys. Rev. 83, 94 (1951).

[12] T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. A 15, 1945 (1977).

[13] T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. Lett. 35, 644 (1975).

[14] R. E. Olson, Phys. Rev. A 15, 631 (1977).