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Calculated pressure broadening and shift for alkali-metal atoms perturbed by rare gases: Two-photon S-S transitions

C. Y. Robert Wu* and William C. Stwalley†
Department of Chemistry, University of Iowa, Iowa City, Iowa 52242
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The broadening and shift of two-photon S-S transitions (e.g., in alkali-metal atoms perturbed by rare gases) are shown to be readily calculable. These calculations employ (a) newly available expressions for alkali-metal–rare-gas long-range potential coefficients C_6, C_8, and C_{10}; and (b) the (herein discussed) appropriate form of impact theory (particularly simple since only a single potential curve is involved and inelastic processes are not usually important). It is demonstrated in particular that the influence of C_8 and C_{10} terms on the broadening and shift is significant though not dominant. Comparison with recent experimental data on the Na–rare-gas pairs shows reasonable agreement for the heavy rare gases.

I. INTRODUCTION

Recently there have appeared several reports about the study of Doppler-free two-photon spectroscopy in alkali-metal (or hydrogenic) atoms, e.g., H-atom[1] $1S$-$2S$ transition; Na-atom[2-6] $3S$-$4D$ and $3S$-$5S$; K-atom[7] $4S$-nD; Rb-atom[8] $5S$-nD (n up to 50), and Ne-atom[9] $3S$-$4D$. Some interesting experiments of Doppler-free two-photon spectroscopy have also been reported in molecules, e.g., CH_3F,[10] NO,[11,12] benzene,[13] and Na_2.[14,15] These experiments yield information on the precision measurements of Lamb shifts,[1] fine structure, hyperfine structure, level shifts,[6] Zeeman[16] and Stark splittings,[17] and collision effects.[18,19] In this paper we present calculations of pressure effects on the S-S two-photon transitions in alkali-metal (and hydrogenic) atoms perturbed by rare gases. In a companion paper,[20] we will examine S-D two-photon transitions, where there are additional experimental results for comparison.

There have been several theoretical studies[21,22] of the pressure effects on the line shapes associated with Doppler-free two-photon spectroscopy. The method utilized is the steady-state rate of two-photon excitation of atom (or molecule) in the prescence of radiative and collisional processes. Our present calculations employ newly available expressions for alkali-metal–rare-gas long-range potentials and the appropriate form of impact theory.

A considerable amount of data have been published on the pressure effects of single-photon D-doublet series of alkali metals perturbed by rare gases and other buffer gases. It is traditional to compare experimental results with those calculated using a full potential with either two or three strictly independent parameters.[23,24] Recently semiempirical and *ab initio* calculations of the interatomic potential[25-28] have become practical; it may now be possible to compare the observed broadening and shift with that calculated from the computed potential. However, it is not necessary to employ such a full potential if (as here) one is only interested in the broadening and shift near the line center. As a general rule, the broadening and shift near the line center depend mainly on the details of the outer part of the potential, i.e., the long-range Van der Waals potentials, as does the shape of the red wing just beyond the impact region.[29] The rest of the potential defines the shape of the far wings of the line.[30,31] Thus, we shall limit our attention to the long-range part of the potential since two-photon excitation is usually carried out under low-pressure conditions—a criterion for impact theory to be valid. Indeed, since the two-photon line can be readily observed Doppler free, collisional effects can be observed at much lower pressures and much nearer the line center than in conventional experiments. The pressure used is typically 10^{-3} torr of the alkali-metal atom added with buffer gas up to 10 torr.

The interaction potential for an S-state alkali-metal atom and rare-gas pair is known to have the form of $-\sum_i C_n/R^n$, where R is the internuclear distance and the C_n are the Van der Waals constants. The constants can be readily evaluated from the results of second-order perturbation theory.[32] To a reasonably good approximation, only the alkali-metal effective principal quantum number and the buffer-gas dipole polarizability need be known.[29]

The principles of the Doppler-free two-photon absorption are well known.[33] In a counterpropagating-beam geometry, an atom, moving at a velocity $\vec{v}$ in a laser field of circular frequency ω in its rest frame, will see a blue shift by an amount $\vec{k}_z \cdot \vec{v}\omega/c$ (where the z axis is defined to coincide with the laser beam) in one beam and see a same amount of red shift in the other. If the atom has to absorb two photons simultaneously to make a transition from the lower state $|1\rangle$ to the upper state $|2\rangle$, then at resonance

$$E_2 - E_1 = \hbar\omega\left(1 + \frac{\vec{k}_z \cdot \vec{v}}{c}\right) + \hbar\omega\left(1 - \frac{\vec{k}_z \cdot \vec{v}}{c}\right) = 2\hbar\omega .$$

Thus the Doppler frequency shift in one beam is exactly cancelled by the other. Therefore, all molecules can participate in the counterpropagating-beam two-photon absorption process independent of their thermal velocity (for simplicity, we ignore transit-time effects). In other words, we are examining a system which has a three-dimensional velocity distribution, yet it is Doppler free. It is important to note that the velocity distribution in different dimensions will give a result for the measured rate of broadening which can be different from that obtained by different experimental techniques.[34]

Thus we now have the necessary information needed as input to the impact-theory calculation of pressure broadening and shift. The appropriate impact-theory formalism is presented in Sec. II. Computational methods and results are presented in Sec. III, and discussed in Sec. IV.

II. IMPACT THEORY

From impact theory[35-39] simple formulas can be obtained if assumptions are made as follows: (i) the interaction is of the form $V = -C_n/R^n$ $(n \geq 3)$; (ii) the path of the colliding atoms is a classical straight line; and (iii) diabatic collisions are not important. Therefore, we can obtain expressions for the broadening (FWHM, in units of Hz) and shift[40] for a system with a three-dimensional velocity distribution. Note that these are defined at the two-photon frequency 2ν; the broadening and shift at the frequency ν would be half these values. They can be expressed as[35]

$$\Delta\nu_n = \frac{\pi^{(n+3)/(2n-2)}}{2}\left[\Gamma\left(\frac{2n-3}{n-1}\right)\Big/\Gamma\left(\frac{2}{n-1}\right)\right] \times \left(\frac{\Gamma(n-1)}{\Gamma(\frac{1}{2}n)^2}\right)^{2/(n-1)} \left(\frac{kT}{2\mu}\right)^{(n-3)/(2n-2)} \times \frac{\langle|\Delta C_n|^{2/(n-1)}\rangle}{\sin[\pi/(n-1)]}, \tag{1}$$

$$\Delta\nu_n' = \tfrac{1}{2}\Delta\nu_n\langle\Delta C_n/|\Delta C_n|\rangle \tan[\pi/(n-1)], \tag{2}$$

where μ is the reduced mass; ΔC_n is the difference in C_n Van der Waals constants between the upper and lower states involved in the optical transition; and $\Gamma(a)$ is the gamma function with argument a.

In reality, the interaction potential between an S-state alkali-metal atom and the rare gas at large internuclear distances is expressed as $-\sum C_n/R^n$, where $n = 6$, 8, and 10. The $-C_8/R^8$ and $-C_{10}/R^{10}$ terms have been found to be important in atomic line broadening, small-angle and low-energy atomic scattering, diatomic energy levels near the dissociation limit, low-temperature gas transport properties, the condensed phase properties of rare gases, etc., and we wish to determine their significance here. As a result of these added terms, the magnitude of the phase shifts becomes

$$\alpha = \int_{-\infty}^{\infty}\left(\frac{\Delta C_6}{\hbar R^6} + \frac{\Delta C_8}{\hbar R^8} + \frac{\Delta C_{10}}{\hbar R^{10}}\right) dt . \tag{3}$$

The time integral is integrated over the instantaneous internuclear distance, $R(t) = (\rho^2 + v^2 t^2)^{1/2}$, where ρ is the impact parameter and v the relative velocity. The broadening and shift can now be expressed as[35]

$$\Delta\nu = N\frac{8}{\sqrt{\pi}}\int_0^\infty\int_0^\infty \left(\frac{\mu}{2kT}\right)^{3/2} e^{-\mu v^2/2kT} \times v^3(1-\cos\alpha)\rho\, d\rho\, dv , \tag{4}$$

$$\Delta\nu' = N\frac{4}{\sqrt{\pi}}\int_0^\infty\int_0^\infty \left(\frac{\mu}{2kT}\right)^{3/2} e^{-\mu v^2/2kT} \times v^3(\sin\alpha)\rho\, d\rho\, dv . \tag{5}$$

No simple analytical expressions can be obtained for Eqs. (3)-(5) for more than one C_n/R^n term.

To calculate Eqs. (3)-(5), one needs the magnitude of that force for the respective excited- and ground-state alkali-metal atom with the rare gas. Fortunately, several advances have been made in recent years in obtaining the Van der Waals constants of atoms in excited states. One is from relating long-range forces to the interpretation of diatomic spectra near the dissociation limit.[41,42] The Van der Waals constants are then determined from fitting spectroscopic data. However, most of the diatomic spectra studied only involve ground and first excited molecular states; thus they all correlate to the lowest S or P atomic states. One example which leads to a higher atomic state is the $C\ ^3\Pi_u$ electronic state of N_2 which possibly dissociates to $N(^2S) + N(^2D)$,[43] and a C_6 Van der Waals constant has been estimated for this particular transition. No such experiments relevant to the alkali-metal S-S transitions have been carried out, however. Another advance is in the theoretical calculation of long-range forces[14,32,44-48] between highly excited alkali-metal atoms and rare gases. Particularly relevant here are the alkali-metal S-S transitions. In these cases the C_n co-

TABLE I. Difference of the Van der Waals constants ΔC_n (in atomic units) illustrated for the pair of sodium atom (3S-5S) and a rare-gas atom. The C_n values are taken from Ref. 32.

	Na + X = He	Ne	Ar	Kr	Xe
ΔC_6	5.913×10^2	1.147×10^3	4.767×10^3	7.207×10^3	1.163×10^4
ΔC_8	5.698×10^5	1.107×10^6	4.608×10^6	6.961×10^6	1.122×10^7
ΔC_{10}	5.821×10^8	1.134×10^9	4.717×10^9	7.122×10^9	1.146×10^{10}

efficients ($n = 6, 8, 10$) are known. Moreover, there is a single potential-energy curve, so no inelastic or interfering collisional events ordinarily occur. Thus the alkali-metal S-S transitions would seem to be ideal for accurate impact-theory calculations and ripe for experimentation.

III. COMPUTATIONS AND RESULTS

By taking the C_n constants from the literature[32] we are able to calculate the absolute rate of broadening and shift for S-S transitions of alkali-metal atoms perturbed by rare gases. Equations (4) and (5) can be evaluated by a double integration procedure. In all the calculations presented here we vary the lower and upper integration limit for v from $0.01\langle v\rangle$ to $10\langle v\rangle$ with a step size of $0.01\langle v\rangle$; and for ρ from 0.2 to 50 Å with a step size of 0.125 Å. We have found that the result changes less than 1% with ρ having a step size as small as 0.05 Å. Table I summarizes the ΔC_n [C_n(upper) $-$ C_n(lower)] constants of the Na(3S-5S)–rare-gas pairs used in the calculation. Table II shows the calculated broadening and shift for (a) an individual long-range potential term C_6/R^6 by using Eqs. (1) and (2); and (b) the $-\sum C_n/R^n$ potential by using Eqs. (4) and (5). A temperature of 563 °K is used. We calculate a rate of broadening (FWHM) of Na 3S-5S two-photon transition to be 82, 65, 89, 88, and 106 MHz/torr for Na-He, -Ne, -Ar, -Kr, and -Xe pairs, respectively. The ratio of shift to broadening of the corresponding pair is 0.229, 0.232, 0.231, 0.293, and 0.286. As can be seen from Table II, higher-order Van der Waals terms are important as well as the R^{-6} dispersion term. Although $-C_6/R^6$ dominates in the alkali-metal–Kr and –Xe pairs, contributions from $-C_8/R^8$ and $-C_{10}/R^{10}$ are still too large to be ignored.

Table III shows the calculated broadening and shift for the H(1S-2S) and other alkali-metal–rare-gas pairs. It is interesting to note that for the S-S two-photon transition of an alkali-metal atom with rare gases, the broadenings and shifts always show dips in Ne in the trend of increasing with the

TABLE II. Calculated absolute rate of broadening $\Delta\nu/N$ (FWHM, MHz/torr) and shift $\Delta\nu'/N$ (MHz/torr), for the Na 3S-5S two-photon transition. The broadening calculated for a single term $-C_6/R^6$ potential and a two-term $-C_6/R^6 - C_8/R^8$ potential are also included. A temperature of 563 °K is used in the calculation.

	Na-He	Na-Ne	Na-Ar	Na-Kr	Na-Xe
$(\Delta\nu)_{6/N}$	49.9	45.4	73.3	81.1	95.9
$(\Delta\nu)_{6,8/N}$	66.3	55.6	81.0	86.3	99.6
$(\Delta\nu)_{6,8,10/N}$	82.0	65.0	88.4	87.6	106.0
$(\Delta\nu')_{6,8,10/N}$	−18.7	−15.3	−20.4	−26.2	−29.9
Experimental[a]					
$\Delta\nu/N$	141.3 ± 6	54.7 ± 4	111.4 ± 8	99.0 ± 7	111.4 ± 11
$\Delta\nu'/N$	+32.0 ± 5	+13.0 ± 2	−35.6 ± 3	−25.3 ± 4	−30.0 ± 2
$\Delta\nu'/\Delta\nu$ ratio					
a	+0.23	+0.24	−0.32	−0.26	−0.27
b	−0.229	−0.232	−0.231	−0.293	−0.286
c	+0.02	+0.09	−0.22	−0.18	−0.20

[a] Data were taken at a temperature of 563 °K, Ref. 19(b).

[b] The present work.

[c] Calculated values of Ref. 19 by using the semiempirical potential of Pascale and Vandeplanque (Ref. 25).

TABLE III. Calculated broadening and shift for a two-photon transition of the alkali-metal (or hydrogen) atom perturbed by a rare-gas or hydrogen atom. A temperature of 563 °K is used in the calculation.

	Transition	H		He		Ne		Ar		Kr		Xe	
Atom	Two photon	$\Delta\nu/N$	$\Delta\nu'/N$	$\Delta\nu/N$	$\Delta\nu'/N$	$\Delta\nu/N$	$\Delta\nu'/N$	$\Delta\nu/N$	$\Delta\nu'/N$	$\Delta\nu/N$	$\Delta\nu'/N$	$\Delta\nu/N$	$\Delta\nu'/N$
H	1*S*-2*S*	55	−16	33	−9	39	−11	60	−19	69	−22	82	−26
Li	2*S*-4*S*	178	−42	89	−20	83	−20	118	−32	129	−35	148	−42
Na	3*S*-5*S*	177	−42	82	−19	65	−15	88	−20	88	−26	106	−30
K	4*S*-6*S*	196	−46	90	−20	67	−16	88	−23	89	−25	99	−28
Rb	5*S*-7*S*	199	−48	89	−21	63	−15	81	−21	78	−21	85	−23
Cs	6*S*-8*S*	209	−49	93	−21	64	−15	79	−21	76	−21	82	−23

order of rare-gas series. This feature is similar to that of the first and second doublet series of alkali-metal atoms in the one-photon transition. The results also show that Li atomic lines are more readily broadened than other alkali metals in the presence of buffer gases. However, information regarding pressure effects on Li-atom transitions are generally lacking. The two-photon transition Li(2*S*-4*S*) is experimentally accessible with present laser technology. Further calculations are planned, particularly in response to experimental results. We wish to emphasize that such calculations are relatively simple and that the experiments are clearly also feasible.

IV. DISCUSSION

The comparison between the experimental results[19] and our calculated results is shown in Table II. In the case of the heavier rare gases the agreement is very good, but the comparison in the case of Ar is worse than we expected (see below). The experimental data suggest that the attractive force in the Na-Ar pair is considerably stronger than our calculated long-range forces. The attractive long-range terms considered here are not adequate to describe the pressure effects when weakly attractive He or Ne is the buffer gas, as is found to be the case for one-photon transitions. It is necessary to include repulsive forces for accurate consideration of He or Ne as perturbers.

In Table II the ratio of shift to broadening is also included. The calculated results[19] using the recent potentials of Pascale and Vandeplanque[25] show that their semiempirical potentials may be too repulsive in the long-range region.[49] Moreover, the long-range terms in these semiempirical potentials[25] are thought to be significantly less accurate than the present values. We feel this explains our much better agreement for Kr and Xe, where we expect our long-range (only!) theory to be most accurate.

Thus far we have calculated pressure effects in the *S*-*S* two-photon transitions of alkali-metal atoms by using the available alkali-metal–rare-gas long-range interaction potentials. In particular we have given results for nS-$n'S$ (where n is the lowest occupied orbital for each alkali-metal atom and $n' = n+1$ or $n+2$) two-photon transitions. Similar calculations for the two-photon transitions involving more highly excited *S* states (Rydberg states) of alkali-metal atoms in the presence of rare gases can be readily performed. However, at sufficiently large n^*, where n^* is the effective principal quantum number, the interactions relevant to pressure broadening cease to be the simple long-range interactions used here. In particular, repulsive "exchange" forces extend to larger distances and the perturber atom begins to directly feel the positively charged core and the slowly moving valence electron separately. Furthermore, nonadiabatic processes will also be more important because of the density of nearby states. The experimental studies on the high members of the principal series of alkali-metal atoms have normally been carried out at higher pressures, up to several hundred atmospheres. The pressure effects were found to be proportional to the buffer-gas density, dependent on the nature of perturbing gases, but independent of the nature of absorbing atoms.[36] With high-resolution laser spectroscopy, similar studies can be performed at very low buffer-gas pressure where it is then possible to examine the role the higher terms of Van der Waals potential play. For example, as discussed in Ref. 32, for sufficiently large n^* the Van der Waals constants are approximately proportional to high powers of n^*: $C_6 \alpha n^{*4}$, $C_8 \alpha n^{*8}$, and $C_{10} \alpha n^{*12}$. In other words the C_8 and C_{10} terms will become increasingly important relative to the C_6 term in the long-range Van der Waals potential. Thus, it may be particularly interesting to study these effects in the highly excited atomic states.

To make these arguments more quantitative, we note that an approximate criterion exists for the distance at which exchange forces become about 10% of the long-range attraction:

$$R_{\rm LR}=2(\langle r^2\rangle_A^{1/2}+\langle r^2\rangle_B^{1/2}),$$

where $\langle r^2\rangle_A^{1/2}$ is the rms distance in the outermost orbital on atom A.[41(b),42] Clearly line broadening resulting from collisions within $R_{\rm LR}$ are inadequately described by the present calculations. For the various alkali-metal–rare-gas possibilities

$$\langle r^2\rangle^{1/2}_{\rm alkali} \gg \langle r^2\rangle^{1/2}_{\rm rare\ gas}$$

and, moreover,

$$\langle r^2\rangle_{\rm alkali} = \tfrac{1}{2}n^{*2}(5n^{*2}+1)\simeq \sqrt{\tfrac{5}{2}}\,n^{*2}.$$

Thus $R_{\rm LR}$ (alkali-metal–rare-gas) $\simeq \sqrt{10}\,n^{*2}$.

The expression $\Delta C_6/R_{\rm LR}^6$ then gives a rough magnitude for the maximum shift from line center consistent with long-range forces alone (assuming $\Delta C_8/R_{\rm LR}^8<\Delta C_6/R_{\rm LR}^6$ and using $R_{\rm LR}$ for the upper state with larger n^*). Since for alkali-metal–rare-gas interactions[32]

$$C_6\simeq \tfrac{5}{2}n^{*4}\alpha_{\rm RG},$$

where atomic units are used and where $\alpha_{\rm RG}$ is the rare-gas polarizability, and since C_6 for the upper state is much greater than for the lower, this maximum shift from line center (in atomic units) should be $\sim \alpha/400n^{*8}$, where n^* is for the upper S state. For the Na(5s) state in Table II, $R_{\rm LR}=42.2a_0=22.4$ Å and the corresponding maximal shifts for the five rare gases (He, Ne, Ar, Kr, Xe) are 4, 8, 35, 40, and 80 cm^{-1}, respectively. It is thus not surprising that the He and Ne experimental results do not agree with the long-range (only) theory presented here, while Kr and Xe show excellent agreement.

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*Present address: Dept. of Physics, University of Southern California, Los Angeles, California 90007.

†Also Dept. of Physics.

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