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Relative noble-gas-induced broadening of the D lines of atomic lithium

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Photon echoes have been employed to measure the relative broadening rates of the lithium D lines perturbed by the noble gases. We find that, for each noble-gas perturber, the D_1-line and D_2-line photon-echo-relaxation rates are identical. Our results are compared with those obtained in line-shape studies of pressure broadening.

We report a precision photon-echo measurement of the relative noble-gas-induced broadening cross sections for the 0.34-cm^{-1} split D lines of atomic ^{7}Li. The ratio of $D_1(2S\text{-}2P_{1/2})$ to $D_2(2S\text{-}2P_{3/2})$ line broadening is interesting because it should be free of many systematic experimental errors. We find that, for all the noble-gas perturbers, the photon-echo-relaxation cross sections (which represent the effect of collisional phase, and velocity and state changes) are the same for both the D_1 and D_2 lines. This result conflicts in some cases with the relative D_1/D_2 broadening measurements obtained using line-shape techniques.[1] Similar discrepancies between echo[2] and line-shape[3,4] measurements of the D_1/D_2 broadening ratio have also been reported in the case of sodium.

The effect of collisions on photon-echo intensity has been discussed elsewhere[2,5–10] and we only quote the relevant results here. As a function of perturber density n the photon-echo intensity I_e behaves according to[5]

$$I_e(n,\tau)=I_e^0\exp[-2nv_rt_e\sigma_{\text{eff}}(\tau)] , \qquad (1)$$

where I_e^0 is the echo intensity in the absence of perturbers (the radiator, i.e., Li; density is assumed constant throughout), $v_r=(8k_BT/\pi\mu)^{1/2}$ is the mean radiator-perturber relative speed, k_B is the Boltzmann's constant, T is the absolute temperature, and μ is the radiator-perturber reduced mass. Here t_e is the time between the first excitation pulse and the echo. In our terminology, $\tau\equiv t_e/2$ will generally be close to but not necessarily exactly equal to the temporal separation between the excitation pulses (see below). The effective relaxation cross section $\sigma_{\text{eff}}(\tau)$ has two components, i.e.,

$$\sigma_{\text{eff}}(\tau)=\sigma_B+\sigma_v(\tau) , \qquad (2)$$

where σ_B is the τ-independent collisional-broadening cross section (the same as that measured in traditional pressure broadening studies) and $\sigma_v(\tau)$ is an effective velocity-changing collision cross section. For a particular τ, $\sigma_v(\tau)$ essentially represents the cross section for collisions which change the radiator's velocity component along the excitation direction by an amount Δv, which satisfies $k\Delta v\tau \gtrsim 1$, where k is the magnitude of the wave vector associated with the echo transition. Collisions which contribute to $\sigma_v(\tau)$ generally also contribute to the pressure-induced shifts in spectral lines.[11] For long τ, σ_v becomes τ independent, and σ_{eff} then represents the total collisional interaction cross section.[5,11] Short- and long-τ measurements of $\sigma_{\text{eff}}(\tau)$ provide, respectively, the value of σ_B and the total collisional interaction cross section. Measurements of $\sigma_{\text{eff}}(\tau)$ at intermediate τ provide information about the probability distribution for the Δv of various magnitude (i.e., the collision kernel).

The experimental apparatus has been described elsewhere.[5] Briefly, the 6708-Å photon-echo-excitation pulses are supplied by a N_2-laser-pumped dye laser, are of 4.5-nsec temporal width, 6-GHz spectral width, have a diameter of ≈ 4 mm, and a peak power of a few watts. Li of natural isotopic concentrations was contained in a heat-pipe-type oven with an active region of ≈ 10 cm. The oven was operated simply as a vapor cell at a temperature of 525 ± 15 K. In the course of our measurements, the Li vapor pressure was $\approx 10^{-6}$ Torr. At this vapor pressure echoes were observed on the D_2 line of ^{7}Li and on the degenerate $D_1(^7\text{Li})+D_2(^6\text{Li})$ line. Our D_1 measurements for ^{7}Li actually contain a small contribution from the D_2 line of ^{6}Li. However, since ^{6}Li and ^{7}Li occur naturally in the ratio of approximately 1 : 12, the perturbation of the pure $D_2(^7\mathrm{Li})$ results should be small. Only at higher Li vapor pressures were echoes observed on the D_1 line of ^{6}Li. Excitation pulse separations from $\tau = 9$ to 82.3 nsec were used. The excitation pulses were linearly polarized either parallel or perpendicular to each other. Only that component of the echo signal having the same polarization as the first excitation pulse was detected. Experimentally it is found that $I_\perp / I_\parallel$ is $10^{-2} - 10^{-3}$, where $I_\parallel (I_\perp)$ is the echo intensity when the excitation pulses are polarized parallel (orthogonal). It was found advantageous to keep the excitation-pulse polarization parallel for longer τ, to offset the decrease in signal due to the 27-nsec radiative lifetime of the excited $2P$ state. At shorter τ, the finite switching time (6 – 7 nsec) of a Pockel's cell optical shutter employed in our experiment, necessitated the use of the orthogonal polarization scheme to improve the signal-to-background ratio. Experimental checks, made at several intermediate values of τ revealed that the echo decay rate was independent of the relative excitation-pulse polarizations. Values of $\sigma_{\mathrm{eff}}(\tau)$ are obtained by holding τ fixed and varying n (up to $\approx 2 \times 10^{16}$ cm^{-3}). The echo intensity was observed to decay as a simple exponential in n as expected on the basis of Eq. (1). Using measured values of t_e, $\sigma_{\mathrm{eff}}(\tau)$ was determined by a least-squares fit to the data. The echo signal (measured with a photomultiplier tube followed by a gated current integrator) and the perturber pressure (measured by a capacitance manometer) are monitored by computer.

Simple theory predicts that the photon echo should occur delayed by a time t_e which is equal to twice the separation of the excitation pulses. It is well known, however, that the temporal width of the excitation pulses τ_p can give rise to a small deviation (on the order of τ_p) from this result.[12] In our experiment, we observe another source of variation in t_e. On tuning the laser from the $D_1(P_{1/2})$ to the $D_2(P_{3/2})$ transition, we observed that for some τ the apparent time of the echo changed slightly. We believe that this time change results from quantum-beat-induced modifications to the shape of the echo envelope.[13] For example, destructive interference may reduce the leading half of the echo while constructive interference enhances the trailing half or vice versa. Maximum effective quantum-beat-induced changes in t_e are thus on the order of τ_p. Since the quantum-beat-induced modification of the echo envelope depends on the excited-state hyperfine structure and on τ, one expects the apparent t_e to change (by an amount which depends on τ) when changing from excitation of the D_1 line to excitation of the D_2 line. To avoid a spurious transition dependence of the echo relaxation rate, the measurements presented here were obtained at excitation-pulse separations at which the echo signal, as observed on an oscilloscope, exhibited no temporal variation on switching between fine-structure components.

The values of $\sigma_{\mathrm{eff}}(\tau)$, computed from our measurements assuming $T = 525$ K, are presented in Table I. The quoted uncertainties in Table I are statistical, and *do not* include uncertainty in t_e

TABLE I. Values of $\sigma_{\mathrm{eff}}(\tau)$ (Å^2) [see Eq. (1)] derived from our data at various values of τ. The uncertainty shown is statistical uncertainty in t_e and is not included since it is irrelevant in the determination of the relative D_1/D_2 broadening rates ($T = 525$ K). The gaps in the data are due to the different optical-delay arrangements used in this experiment.

		Pulse separation τ (nsec)							
Perturber	Line	9	27.5	29	42.3	54.5	55.7	67.5	82.3
He	D_1	104(2)		111(2)	119(3)		119(3)		125(3)
	D_2	97(2)		114(3)	118(3)		118(3)		123(5)
Ne	D_1	104(6)	122(5)			134(4)			
	D_2	100(2)	122(3)			136(3)			
Ar	D_1	194(5)		262(6)	277(6)	285(9)		301(11)	
	D_2	189(4)		275(11)	288(8)	292(8)		305(15)	
Kr	D_1	219(7)	287(6)			331(10)			
	D_2	212(5)	289(9)			329(9)			
Xe	D_1	248(5)	326(7)			373(19)			
	D_2	245(5)	332(10)			372(19)			

TABLE II. Comparison of $\sigma_{\rm eff}$ ($\tau=9$ nsec) (Å^2) with the broadening cross sections σ_B obtained from line-shape measurements. Since the absolute size of $\sigma_{\rm eff}$ is of importance here, our listed uncertainties are determined by both imprecise knowledge of t_e and statistical fluctuations of the data.

Perturber	Line	$\sigma_{\rm eff}$ ($\tau=9$ nsec) ($T=525$ K)	σ_B (Ref. 1) ($T=628$ K)
He	D_1	104(13)	83(3)
	D_2	97(12)	83(3)
Ne	D_1	104(14)	100(4)
	D_2	100(13)	94(3)
Ar	D_1	194(25)	158(8)
	D_2	189(24)	138(7)
Kr	D_1	219(28)	203(9)
	D_2	212(27)	189(9)
Xe	D_1	248(31)	256(10)
	D_2	245(31)	219(8)

TABLE III. Ratios of the noble-gas-induced broadening cross sections of the ^{7}Li D_1 and D_2 lines. Values on left (right) are from the present work (the line-shape measurements of Ref. 1).

Perturber	$[\sigma_{\rm eff}(D_1)/\sigma_{\rm eff}(D_2)]$	$\sigma_B(D_1)/\sigma_B(D_2)$
He	1.01(4)	1.00(5)
Ne	1.01(3)	1.06(5)
Ar	0.98(3)	1.14(7)
Kr	1.01(3)	1.07(7)
Xe	1.00(4)	1.17(5)

since it is irrelevant (as long as t_e does not vary on changing from one transition to another) for computation of the relative broadening rates. We estimate that the fractional uncertainty in the absolute value of $\sigma_{\rm eff}(\tau)$ which results from imprecise knowledge of t_e is approximately $\tau_p/4\tau$. This uncertainty arises primarily from the inability to define t_e precisely when using excitation pulses of finite duration. Our shortest-τ measurements of $\sigma_{\rm eff}$ are compared in Table II with measurements of σ_B obtained by Lwin using line-shape techniques. The uncertainty listed in Table II for $\sigma_{\rm eff}$ *includes* the uncertainty in t_e. Apparently, for $\tau=9$ nsec, $\sigma_{\rm eff}\simeq\sigma_B$.

Since the ratio

$$R(\tau)\equiv\sigma_{\rm eff}^{D_1}(\tau)/\sigma_{\rm eff}^{D_2}(\tau)$$

does not appear to vary systematically with τ, we have averaged $R(\tau)$ over τ and presented it in Table III along with Lwin's value of $\sigma_B(D_1)/\sigma_B(D_2)$.[1] The fact that $R(\tau)$ is essentially τ independent implies that both σ_B and σ_v [see Eq. (2)] have a similar fine-structure dependence. Our photon-echo measurements indicate that the D_1 and D_2 lines are broadened at essentially the same rate for all the noble-gas perturbers. Lwin, however, finds that Ar and Xe broaden the D_1 line significantly more than the D_2 line. Similar results have been obtained in sodium where echo measurements indicate that Ar, Kr, and Xe broaden the Na D_1 and D_2 lines identically, but line-shape measurements[3,4] indicate that the D_1 line is more strongly broadened. With He or Ne perturbers echo and line-shape measurements concur that the D_2 Na line is more strongly broadened than the D_1 line.

We suspect that both echo and line-shape measurements are "correct," but are sensitive to different parts of the collisional interaction. The photon echo is Doppler free, and effectively measures the collisionally broadened line very near its center, i.e., within roughly $(1/4\pi\tau)$ Hz of the line center or within approximately 9 MHz for $\tau=9$ nsec. The impact approximation should be quite good in this region, and $\sigma_{\rm eff}$ should be primarily determined by the outer portions of the interatomic potential. The line-shape measurements are performed considerably further into the wings of the collisionally broadened line where, as recently demonstrated,[4,14] the impact approximation is already beginning to fail (as evidenced by asymmetry in the observed line shapes). These measurements could be expected to show the effect of close collisions where differences between the various possible interatomic potentials are more pronounced. Since echo measurements of collisional broadening have only begun to be extensively utilized, however, as yet unappreciated systematic errors in the echo results cannot be ruled out. It will be interesting to see how the discrepencies between echo and line-shape measurements are resolved.

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