Resonance broadening and shifting of spectral lines in xenon and krypton

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Three-photon excitation and multiphoton ionization techniques have been used to measure self-broadening for several resonance lines in xenon and krypton. Tabulations of widths and shifts of the xenon lines at 146.9, 129.6, 119.2, and 117.0 nm were made for pressures between 50 and 900 Torr. Similar measurements were made for the krypton resonance line at 116.5 nm. For pressures less than 500 Torr the widths were found to be in reasonable agreement with theoretical results, which were extrapolated into regions of concentration where the criteria for their validity are at best questionable. We have also found the lines to be shifted to the high-energy side of the unperturbed line. For four of the five lines studied, the blue shifts increased nearly linearly with increasing pressure. In the four cases where the shift could be measured the ratio of shift to width was close to $\frac{1}{2}$. Our experimental technique is very simple, but it has yielded what we believe to be the first resonance broadening data based on absorption under conditions where there is strong trapping of the resonance radiation.

INTRODUCTION

The experimental problems associated with the measurement of self-pressure broadening for resonance lines in atomic gases and vapors are well known. They are associated with the fact that relatively high concentrations are required for pressure-broadening widths to exceed the Doppler widths, while the medium becomes extremely opaque to resonance light with Doppler broadening still dominant. An extreme example will illustrate the problem. Consider the absorption of light near the $3s(J=\frac{1}{2})$ to $3p(J=\frac{3}{2})$ resonance transition in sodium. The latter transition is near 590.0 nm, and has an absorption oscillator strength of 0.655. At room temperature, and slightly higher, the Doppler width is many times larger than the natural width of the line and the absorption coefficient at low concentrations is

$$\kappa(\omega)=\frac{2\pi^2 n(e^2/m_e c)F_{l,u}}{\Gamma_D} \times \exp[-Mc^2(\omega-\omega_r)^2/(2\omega_r^2 kT)] , \quad (1)$$

where M is the atomic mass, $F_{l,u}$ is the absorption oscillator strength, c is the speed of light, k is the Boltzmann constant, T is the absolute temperature, ω_r is the resonant angular frequency, e is the electronic charge, m_e is the electron mass, n is the concentration, and

$$\Gamma_D=\left[\frac{2\pi\omega_r^2 kT}{Mc^2}\right]^{1/2} . \quad (2)$$

An evaluation of Eq. (1) for a few centimeters' thickness of sodium vapor shows that the medium is already opaque at concentrations of 10^{11} cm^{-3}. That is, the effective absorption cross section at line center is $\simeq 10^{-11}$ cm^2. Obviously, the measurement of the absorption line shape at much higher concentrations, where pressure-broadened widths start to exceed Doppler widths, would require very thin samples of the vapor if extreme nonlinearities in the absorption are to be avoided. The latter characteristics explain why almost all measurements of resonance broadening effects have been based on analyzing the emission spectrum of untrapped light resulting from transitions between excited states, where either the upper or lower level is the resonantly broadened state.

At a concentration of $\sim 10^{16}$ cm^{-3} resonance broadening frequently starts to dominate the core of the line, as well as the wings. In this region of concentration, where resonance broadening is just starting to dominate the entire line shape, the time between energy transfer collisions is large compared with the time of collision. For detunings from resonance which are small compared with the reciprocal collision time, the impact theory of resonance broadening is valid. Under these circumstances a large portion of the mechanism for broadening the line is the resonant transfer of excitation energy between collision partners, with accompanying changes in the magnetic quantum number occurring in many collisions. This is different from the mechanism involved in pressure broadening due to a foreign buffer gas where the major effect is due to accumulated phase changes which occur during collisions, resulting in broadening through a loss of phase memory. Most of the theoretical papers[1-6] on self-broadening predict a width and a violet shift which are both proportional to the product of concentration, absorption oscillator strength, and resonance wavelength. With the exception of a theory by Vdovin and Galitskii[4] who (unlike the other authors) deal with collisional recoil effects, the shift is found to be very small compared with the width. The latter workers find a ratio of shift to full width at half maximum (FWHM) close to 0.25. In most

of the more recent theories[2-6] the decay rate of the dipole autocorrelation function is found to be within a few percent of

$$\Gamma_p = 0.61\lambda_r (e^2/m_e c) n F_{l,u} \ , \tag{3}$$

where λ_r is the resonant vacuum wavelength and only $J=0$ to $J=1$ transitions are considered. Equation (3) also gives the width parameter in the Lorentzian line shape predicted for untrapped emission between the resonance state and another unbroadened excited state under conditions of strong trapping of the resonance radiation

$$S_e(\omega) = \frac{\Gamma_p/\pi}{(\omega-\omega_r')^2+\Gamma_p^2} \tag{4}$$

The line-shape function $S_e(\omega)$ of Eq. (4) is only appropriate when Γ_p considerably exceeds the Doppler width of the line.

The rate given by Eq. (3) implies a velocity-averaged cross section for the relaxation which usually satisfies $\sigma_t > 10^{-12}$ cm^2 for strong transitions with $\lambda_r > 100$ nm. Consequently, most of the relevant collisions occur for impact parameters greater than 50 Å. The dominance of such large impact parameters makes the validity of including only dipole-dipole interactions between atoms nearly certain to be an accurate approximation. Such an approximation was used in deriving Eq. (3), thereby accounting for the simple analytical form. With such large cross sections the time of collision is of the order of 10^{-11} sec, which implies that Eqs. (3) and (4) may hold for room temperature xenon while the width of the line in angular frequency units is less than 3×10^{10} sec^{-1}.

Consider absorption of light at a large detuning from a resonance line. With the weak coupling between the ground state and an excited state, which is characteristic of three-photon absorption at low power densities, absorption will not occur in the time between collisions, due to the large detuning. For example, if the detuning from resonance is much greater than 10^{11} sec^{-1}, the process of absorption does not even happen during collisions unless the dipole-dipole interaction either produces sufficiently large shifts so that the collision complex comes into transient resonance at some internuclear separation, or the collision is at such small impact parameters that the interaction contains Fourier components sufficiently large to compensate for the energy mismatch. Consequently, with such large detunings from line center only collisions with relatively small impact parameters make a contribution to absorption. In such near collisions the coupling between various states in which one atom is excited and the other is in the ground states is very strong. It is convenient to introduce linear combinations of such product states in order to diagonalize the dipole-dipole interaction at fixed intranuclear separations and orientations. With this set of states, which are energy eigenstates in which relative atomic positions have been regarded as fixed, changes in atomic position provide a coupling between such adiabatic excited states, while the laser couples states with both atoms in the ground state to the excited states. For sufficiently large detunings, collisions must occur at such small impact parameters that the magnitude of the molecular frequency shifts dwarfs the inverse time of collision (shifts go up with b^{-3} while time of collision approximately equals b/v, b is the impact parameter, and v is the mean relative speed) and the adiabatic states are no longer mixed by relative nuclear motion. This is the quasistatic limit, in which no absorption occurs unless the relative atomic positions become such that the adiabatic energy shift produces an exact compensation for the detuning of the laser. In the quasistatic theory a simple mathematical procedure is used in which the absorption is assumed negligible except for times very close to that time at which the adiabatic molecular shift exactly compensates for the detuning of the laser. Transition probabilities are calculated, which are assumed to add incoherently for different "curve crossings." Finally, the proper averaging and summations over collision histories are made in order to arrive at an absorption coefficient. Simplified applications of the above model, in which the dipole-dipole potential curves are angle averaged, lead to energy shifts proportional to R^{-3}. Application of the above concepts then yields an absorption coefficient proportional to $(\omega-\omega_r)^{-2}$.

Vdovin and Galitskii[4] have treated resonance absorption by using many-body theory to calculate the dielectric constant. They find an absorption coefficient at large detunings which varies with detuning just like the wings of the Lorentzian function, which they also derived by using approximations which were valid near line center. Their approximations near line center are much like those used in impact theories, while their far-wing results are closely related to the quasistatic theory. The use of their impact-theory results on the far wing of the line yields exactly the same answer as their quasistatic limit, except it is smaller by a factor of about 0.8. At high concentrations the quasistatic theory results are valid for detunings which are large enough to validate the quasistatic approximation, but not so large as to sample small R values where the dipole-dipole approximation is inadequate.

At high concentrations, the quasistatic theory may become valid before the absorption greatly decreases relative to its value at line center. The total area under an absorption line satisfies a sum rule, which for the case of one-photon absorption, is identical to the following Einstein relation:

$$\int \kappa(\omega) d\omega = \frac{3\lambda_r^2 n \gamma_{u\to l}}{4} \ ,$$

where $\gamma_{u\to l}$ is the spontaneous decay rate for the resonance transition and $\kappa(\omega)$ is the absorption coefficient. Applying the sum rule, we see that, since the actual wings are about 20% higher than the prediction from impact theory, the core of the line must be lower than predicted by this theory. This is suggestive that at higher pressures the impact theory may underestimate the width, and the line shape will deviate from a Lorentzian shape.

The application of three-photon excitation to the measurement of pressure broadening obviously avoids the absorption problem in carrying out an atomic excitation in an optically dense medium. Further, at low pressures where the impact-broadening theory applies, the mechanism for line broadening in three-photon excitation should be very similar to that for one-photon excitation. To our

knowledge there is no detailed theory for three-photon absorption in the presence of resonance broadening effects. However, formulation of the problem for three-photon absorption with plane-polarized light should only differ from one-photon absorption through the strength of the coupling parameter and the replacement of ω by 3ω. For this reason one expects that an absorption profile for three-photon excitation in the impact regime is

$$S_a^{(3)}(\omega)=\frac{\Gamma_p'/\pi}{(3\omega-\omega_r-\Delta_p)^2+(\Gamma_p')^2}\ , \tag{5}$$

where $3\omega=\omega_r$ corresponds to the unperturbed three-photon resonance, Δ_p is the pressure-induced shift, and Γ_p' is an appropriate width similar to Eq. (3). In our own analysis we use Γ_p' to be just the value in Eq. (3), or [2] $\Gamma_p'=0.0229n\lambda_r^3F_{l,u}$.

Most estimates of the level shift that accompanies line broadening tend to yield a value that is about 5% of the width, and toward the high-energy side of the unperturbed resonance. However, the theory of Ref. 4 includes the effect of recoil on the shift and finds the shift to be nearly 25% of the width, which is more in line with results obtained in the present study, as described below. Measurements of resonance broadening by the observation of untrapped fluorescence associated with transitions between excited states should not exhibit the shift predicted for resonance transitions.[4] Even with the Vdovin and Galitskii theory, none of the earlier studies (which were all based on studies of untrapped radiation emitted in transitions between excited states) should have found appreciable shifts in the observed lines.

Because of its obvious advantage in avoiding the trapping problem, it seems very likely that three-photon excitation must have been tried previously as a technique for measuring self-broadening. However, it has only recently been known[7–12] that if three-photon resonance excitation is attempted with a laser, at elevated pressures, excitation will not be seen, due to a completely destructive interference between the three-photon pumping and one-photon pumping of the same transition by an internally generated third harmonic field.[7–12] In three-photon excitation of an atomic transition with unfocused laser beams, the onset of the latter phenomena can occur at pressures as low as 10^{-5} Torr. However, when the laser beam is reflected back on itself, there is a portion of the three-photon coupling in which two photons are absorbed propagating in one direction and another photon is absorbed propagating in the opposite direction. The latter part of the three-photon coupling has no corresponding part of the third-harmonic field to cancel it, and it provides a perfectly normal source of excitation for the upper state.[12] Possibly, the failure to provide a counterpropagating beam could have led to no signals and resulted in the abandonment of earlier studies.

EXPERIMENTAL APPARATUS

The experimental setup is shown schematically in Fig. 1. The laser used in the study consisted of a Lumonics 861T Series Excimer laser which, with Xe-Cl as the active

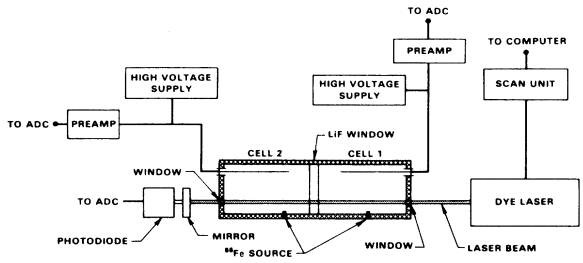

FIG. 1. Schematic of the experimental apparatus used for the study of the resonance broadening of lines in xenon and krypton.

gas, generated approximately 80 mJ per pulse when operated at a repetition rate of 10 Hz. When pumped with the above-mentioned excimer laser, the dye laser (Lumonics EDP 330) generated 4-ns pulses, with an output of several millijoule per pulse. Absolute laser outputs were measured by Scientech Model 36-0001 and Scientech Model 38-0105 energy meters. The bandwidth of the dye laser was $\simeq 0.2$ cm^{-1}. The dye laser was operated unfocused and had a beam diameter of about 2 mm. The gas cells used in the experiment were proportional counters operated in tandem, with each having windows at either end. Each of the two proportional counters operated with a gain such that ionization process yielding fewer than 100 electrons could be measured over a wide range of krypton or xenon pressures. At pressures above a few Torr each counter could be calibrated by normalizing the ionization signals to pulses produced by an internal ^{55}Fe radioactive source. Data acquisition was based on an LSI-11/03 computer and related electronics.

Pressures were measured to an accuracy better than 1% by using a MKS Baratron gauge. In all cases where line shapes were recorded, the cells were filled with high-purity Xe or Kr following pumping the cells to vacuum. A combination of mechanical and diffusion pumps produced a vacuum in the apparatus of less than or equal to 10^{-6} Torr.

In the actual operation of the experiment, a low-pressure sample of the gas under study was introduced into one ionization cell, while that same gas at the desired pressure was used in the other cell. The laser beam passed through both cells and was reflected back through both chambers by a mirror placed near the exit window of the second cell. The dye laser, described above, gave power densities in the ionization cells which were typically 10^7 W/cm^2. With such intensities it was easily possible to measure line shapes by three-photon resonantly enhanced four-photon (five-photon ionization for Xe 6*s*) ionization at pressures above 1 Torr. In the absence of the reflected laser beam no ionization signal could be observed due to the well-established interference effect. A data acquisition computer recorded for each laser pulse the wavelength, the laser output, and the ionization signals from each ionization cell. The low-pressure or "reference" ionization chamber served to locate the unshifted atomic resonance and to give a monitor of the laser linewidth. As the pressure in the first cell was

changed, the gain on the ionization counter could be measured and adjusted to a convenient value by making use of the internal ^{55}Fe radioactive source. Consequently, absolute signals could be measured as a function of pressure. Two typical line shapes are shown in Figs. 2(a) and 2(b) for the Xe 6*s* and Xe 6*s*′ states, respectively, along with smooth curves which represent best-fit Lorentzian functions. Figure 3 shows the line shapes which develop at high pressures, together with the simultaneously observed signal from the low-pressure reference cell. Note that at higher pressures, there is a large blue shift in the position of the line, but nothing dramatic happens to the line shape at the position of the unperturbed line. We believe that the general features of these curves argue strongly against the possibility of blue shifts that are actually small, but appear shifted due to differences between ionization probabilities on the blue and red sides of the resonance. In the higher-pressure cases most of the area under the curves lies on the blue side of the unperturbed line. The high-pressure line shapes shown in Fig. 3 are for the Xe 5*d* resonance, but very similar results were observed for other resonances where the signal from the high-pressure cell and the reference cell could be measured simultaneously.

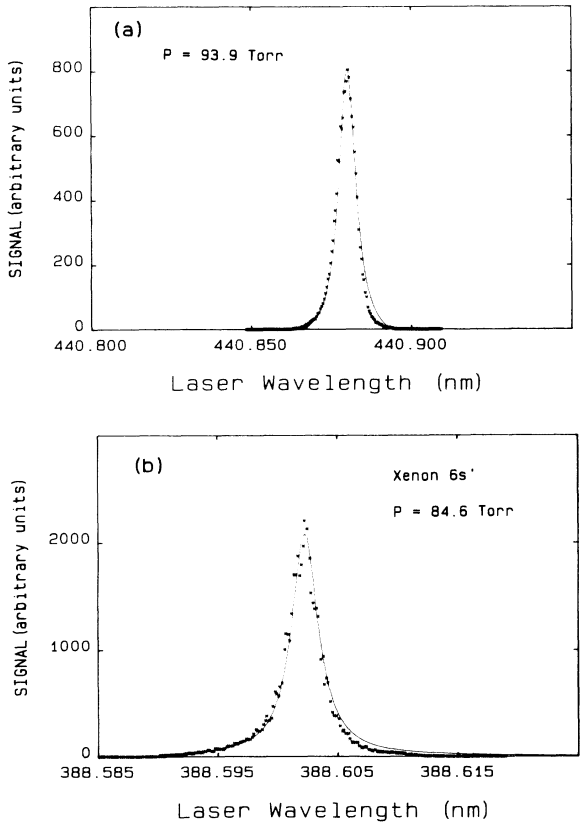

FIG. 2. Measured line shape of (a) the xenon 6*s* resonance line at a pressure of 93.9 Torr and (b) the xenon 6*s*′ resonance line at a pressure of 84.6 Torr. The smooth curve is the best-fit Lorentz function.

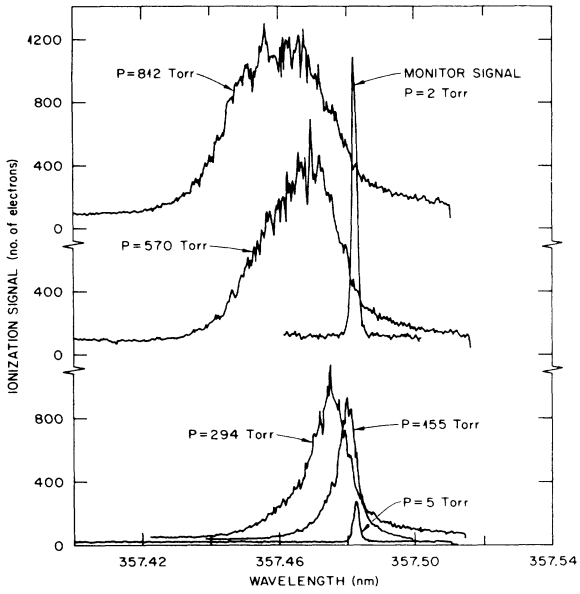

FIG. 3. Pressure-dependent profiles of the $5d[\frac{3}{2}]^{\circ}J=1$ resonance for five values of P_{Xe}. At the upper right is the trace of the low-pressure line profile simultaneously recorded in the second ionization cell (reference chamber) in each experiment. Within experimental error, all profiles are absolute in wavelength and amplitude (reference signal shown at a larger amplification).

EXPERIMENTAL RESULTS

All of our measurements of pressure-broadened line shapes were carried out at absolute temperatures within 2% of 293 K. The usual[11,12] precautions were taken to limit the production of ions to less than a few times 10^5 per laser pulse, so that the detector response could be kept linear, and the line shapes would not be broadened due to space-charge effects. Some tests were carried out in which the power density was varied in an effort to eliminate the possibility of the line shape depending on the efficiency with which the excited state was ionized. No changes in line shape were observed. Theoretical estimates of the pressure-broadened widths were based on Eqs. (3) and (5) which yield the full width at half maximum (FWHM) in wavelength of the dye laser, $\Delta\lambda_{\mathrm{FWHM}}$ in terms of the laser wavelength λ_L, the concentration n, and the absorption oscillator strength as

$$\Delta\lambda_{\mathrm{FWHM}}=0.0214\frac{e^2}{m_e c^2}\lambda_L^3 n F_{l\to u} \ . \tag{6}$$

A rather significant disadvantage in the present experiment resulted from the 0.2-cm^{-1} bandwidth of the dye laser. The rather large laser bandwidth typically dominates the observed widths at pressures below 100 Torr, and makes necessary a significant correction to measured widths even at 200 Torr. In addition line shifts could not be measured well until the shift became comparable with the laser linewidth.

The laser linewidth was included crudely in the theoretical estimates by writing

$$\Delta\lambda_m^2 \simeq \Delta\lambda_L^2 + \Delta\lambda_{\mathrm{FWHM}}^2 , \tag{7}$$

where $\Delta\lambda_m$ is the estimate of the observed linewidth, $\Delta\lambda_{\mathrm{FWHM}}$ was taken from Eq. (6), and $\Delta\lambda_L$, the laser line FWHM, was measured in the second cell to be typically 0.0025 nm.

We will now consider, individually, the data for each of the resonance lines studied. Theoretical widths were based on Eqs. (6) and (7), utilizing absorption oscillator strengths from a paper by Geiger.[13] At the highest concentrations considered experimentally, even the most optimistic estimates of the region of validity of Eq. (6) suggest that it may not apply.

Xenon $5p^6(J=0) \rightarrow 5p^5(^2P_{3/2})6s[\frac{3}{2}]^o(J=1)$ transition

The unperturbed resonance wavelength for this transition is approximately 146.96 nm, thus the dye laser needed to be scanned through the wavelength region near 440.88 nm. A typical line shape, at an intermediate concentration, is shown in Fig. 2(a).

The magnitude of the blue shift in the resonance line is nearly linear in pressure as shown in Fig. 4. The widths and shifts of the lines were determined at concentrations up to 200 Torr by fitting the observations with a Lorentzian, with the resulting peak position being compared to the peak position recorded simultaneously in the reference cell in order to determine the shift. At higher pressures, the quality of such a fit became poor and the widths were then obtained by plotting the smoothed data and simply reading the FWHM and the shift graphically. A display of the data on FWHM versus xenon pressure is shown in Fig. 5. The solid line is calculated from Eq. (7).

At pressures below 300 Torr the agreement between the theoretical estimate of the width and the data is surprisingly good. This agreement is in accord with other studies using emission of untrapped radiation, which have always given widths which agree well with theory for resonance transitions with large oscillator strengths providing

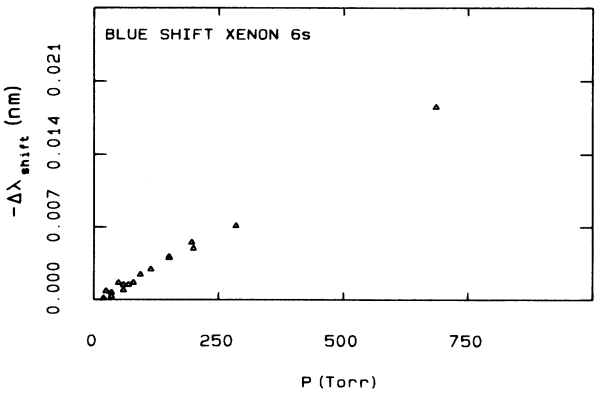

FIG. 4. Graph of the measured blue shift of the xenon 6s resonance line as a function of xenon pressure.

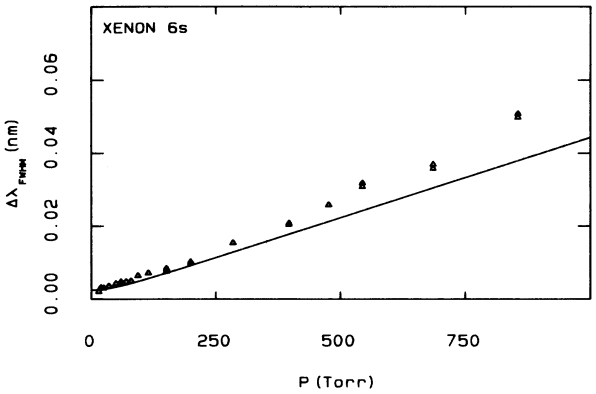

FIG. 5. Graph of the full width at half maximum (FWHM) of the xenon 6s resonance as a function of pressure. The smooth curve is calculated from Eq. (7).

the measurements are made in the region of concentration where the impact theory should apply. In the present case of the Xe 6s level the ratio of shift to width is actually found to be 0.48 ± 0.05. By the time concentrations are increased to a point where the pressure width can be observed, the impact-broadening theories are already questionable in our study.

With a better dye laser, measurements could easily be made at concentrations of 10^{16} cm^{-3}. Such an extension of the method should permit the use of three-photon induced fluorescence, or three-photon resonance enhancements in ionization for tests of theory in many vapors and gases.

In the case of the 6s resonance the ionization of the upper state requires two photons. Correspondingly, it is not possible to rule out completely the possibility of biases in the line shape due to the fact that atomic excited states are being ionized on the blue side of the line, while at high pressures bound molecular states may be formed on the red side. However, we shall see that with higher states, where it should have been possible to increase the laser power to the point either atomic or molecular species would have been ionized with nearly 100% efficiency, the shifts in the lines persist consistently. In addition, the line shapes at high pressure show no dramatic change in shape at the position of the unperturbed resonance. An example of high-pressure line shapes will be presented for the xenon 5d resonance.

Xenon $5p^6(J=0) \rightarrow 5p^5(^2P_{1/2})6s[\frac{1}{2}]^o(J=1)$ transition

The unperturbed resonance wavelength for the Xe 6s′ transition is near 129.6 nm. Thus the dye laser is scanned through the region near 388.6 nm in recording these line shapes. A typical line shape in the 100-Torr pressure range is shown in Fig. 2(b). If the pressure is increased from 1 Torr upward, the observed width of the line is initially dominated by the laser bandwidth. As long as the pressure-broadened width is small compared with the laser bandwidth, the absolute signal should increase pro-

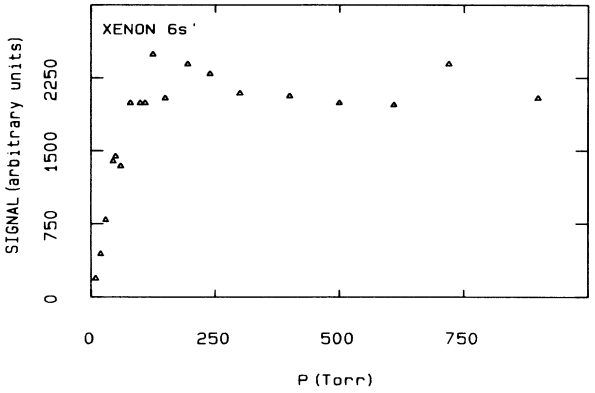

FIG. 6. Absolute ionization signal at line center vs xenon pressure for the 6s′ resonance of xenon. Once the pressure-broadened width becomes much larger than the laser bandwidth, the signal is independent of pressure to our experimental accuracy.

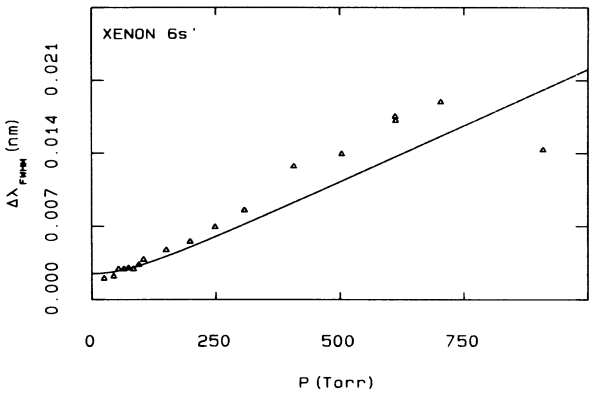

FIG. 8. Width of the xenon 6s′ resonance vs pressure. The smooth line is based on Eq. (7).

portional to the concentration. However, once the pressure-induced width starts to dominate the width to the laser, the number of ionization events should start to be pressure independent. Experimental data on this effect are shown in Fig. 6. The errors involved in retaining known gains as the pressure is changed are believed to be about 25% based on the achievable repeatability of such measurements. Blue shifts which increase approximately linearly with pressure are again observed with this transition. These data are shown in Fig. 7. As in the case of the Xe 6s transition, the agreement between observed broadening and theory is good for pressures below 300 Torr. The comparison between experiment and Eqs. (6) and (7) is shown in Fig. 8. For this level we find the ratio of shift to width to be 0.54 ± 0.05. In this case the excited state can be ionized by one photon, with the photoionization cross section being larger than 10^{-18} cm^2. With power densities a few times larger than 10^7 W/cm^2, the ionization probability becomes close to unity.

Xenon $5p^6(J=0)\rightarrow 5p^5(^2P_{3/2})5d[\frac{3}{2}]^o(J=1)$ transition

The Xe 5d resonance is at 119.2 nm, which corresponds to the laser wavelength of 357.6 nm. The dye laser worked quite well in this wavelength region and some of the best data were obtained near this strong resonance.

In Fig. 9 we again demonstrate the pressure dependence of the absolute ionization signal. Atomic excitation varies linearly with pressure while the pressure broadening is small compared with the laser bandwidth, becoming pressure independent once the pressure-broadened width becomes much larger than the laser bandwidth.

The blue shift for this line is close to linear in the pressure. The latter data are shown in Fig. 10. Actual line profiles of the 5d resonance at several pressures are shown in Fig. 3 above. The ratio of shift to width for the Xe 5d level is found to be 0.53 ± 0.05.

The photoionization cross section of this state is greater than 10^{-17} cm^2, thus with modest power densities nearly 100% ionization of the excited state is achieved. With

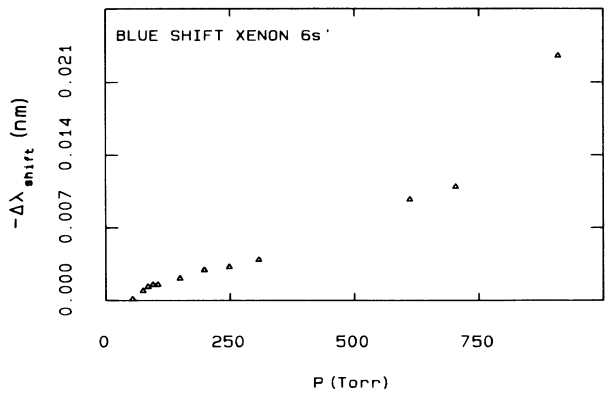

FIG. 7. Blue shift in the xenon 6s′ resonance vs xenon pressure.

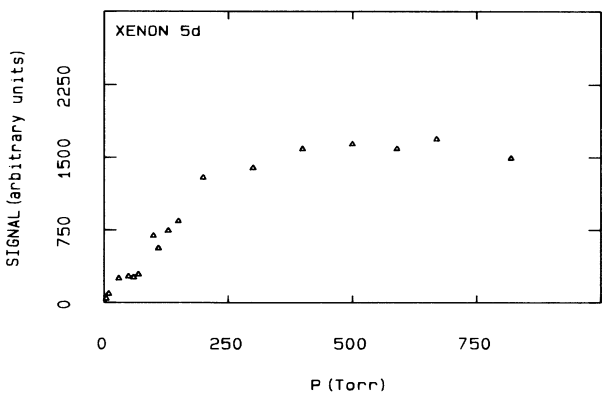

FIG. 9. Absolute ionization signal at line center for the xenon 5d resonance line.

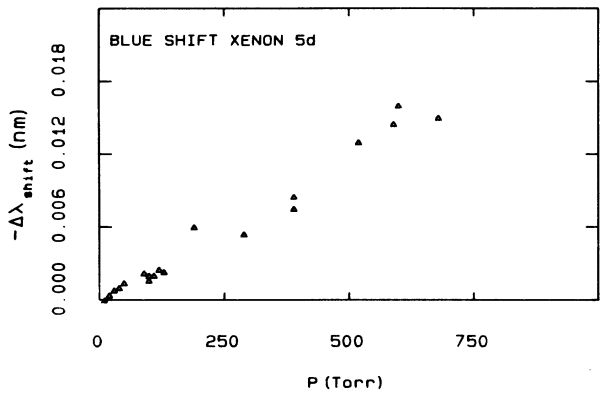

FIG. 10. Blue shift vs pressure for resonance broadening of the xenon $5d$ line.

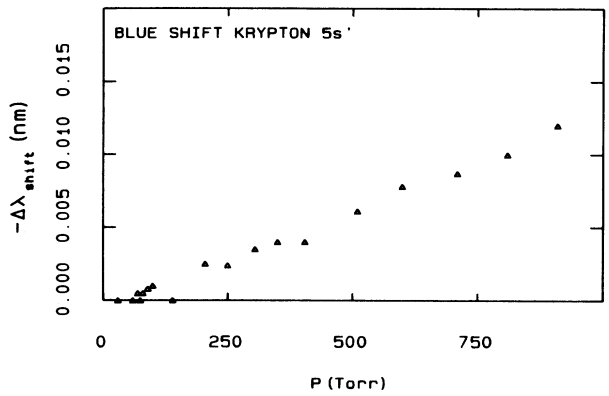

FIG. 12. Blue shift vs pressure for resonance broadening of the krypton $5s'$ transition.

this state we feel assured that the blue shift is not an artifact due to differences in ionization probabilities for atomic excited states relative to Xe_2^*. Figure 11 shows the measured and calculated widths of the $5d$ resonance line. Agreement with Eq. (7) is good for pressures less than 300 Torr.

Krypton $4p^6(J=0)\rightarrow 4p^5(^2P_{1/2})5s[\frac{1}{2}]^o(J=1)$ transition

The data on the Kr $5s'$ and the Xe $7s$ resonances are not as good as those for the other three resonances due to the poor operation of the dye laser at the 116.5- and 117.0-nm three-photon resonances. Due to the poor output of the dye laser, both of the latter resonances were studied with beams focused with a 50-cm focal length lens.

To obtain the shifts and widths shown in Figs. 12 and 13 the dye laser was scanned through the region around 349.5 nm. Figure 12 shows a nearly linear blue shift as the pressure is varied. The widths are in rough agreement with theory at the lowest pressures where the increase in width can be seen above the laser linewidth. The ratio of shift to width is found as 0.54 ± 0.05 for the Kr $5s'$ level.

Xenon $5p^6(J=0)\rightarrow 5p^5(^2P_{3/2})7s[\frac{3}{2}]^o(J=1)$ transition

To obtain data on the Xe $7s$ resonance at 117.02 nm the dye laser was scanned through the region near 351.06 nm. The data here are of lower quality than for any other level due to the poor operation of the dye laser at 351 nm and to the small size of both the widths and shifts. The relatively small size of the width and shift (compared to the laser linewidth) is due both to the small oscillator strength and to the relatively short resonance wavelength. The lack of an adequate signal could be compensated in the first cell by focusing the laser beam and having higher concentrations. This still left a problem with the reference cell, which is important in determining the level shift as a function of pressure. The level shifts were poorly determined, but did appear to be to the violet side of the unperturbed line. The widths are shown in Fig. 14. They are in good agreement with our extrapolation of theory into the high-pressure region where the pressure-broadened width exceeds the laser bandwidth.

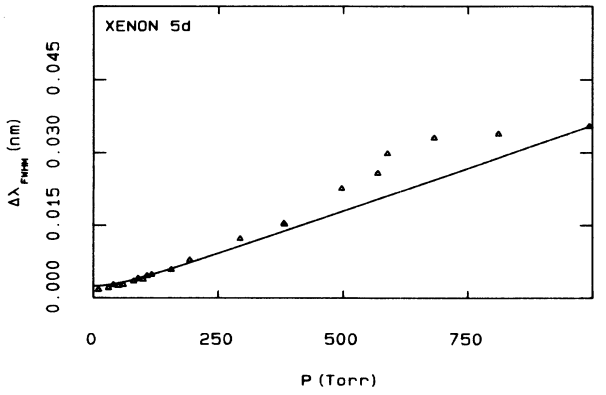

FIG. 11. Width of the xenon $5d$ resonance line vs pressure.

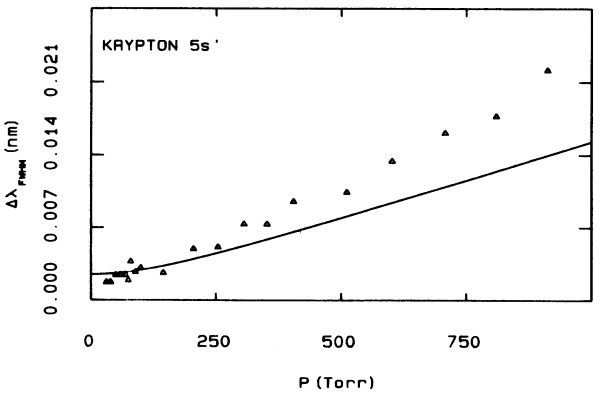

FIG. 13. Width of the krypton $5s'$ resonance line vs pressure.

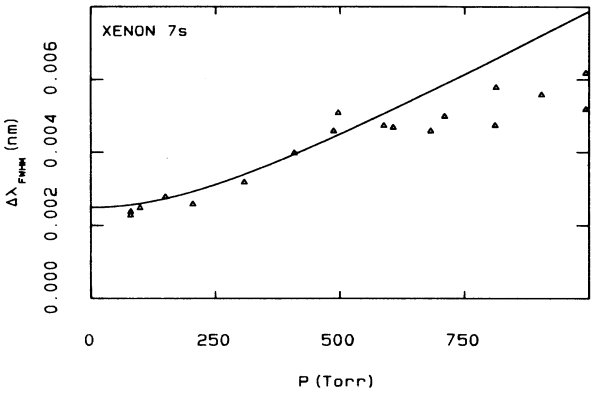

FIG. 14. Width of the xenon 7*s* resonance line vs pressure.

CONCLUSIONS

Previous measurements of resonance broadening have been based on studies of light emitted in transitions between two excited states, one state being the upper state for the resonance transition.[14] According to Vdovin and Galitskii,[4] the previous measurements should not have exhibited a shift, but the observed width should be the same as for resonance absorption. The observations are consistent with this prediction. On the other hand, if one observes the resonance transition, the theory of Ref. 4 predicts a blue shift which depends on the oscillator strength, the concentration, and the wavelength in exactly the same way as the pressure-induced width. The ratio of shift to width was predicted to be 0.24. This shift is five times larger than the result obtained when recoil effects are neglected in the collisions. Most theories have used a classical trajectory method with straight-line trajectories and have thereby neglected recoil effects. The latter theories still yield the correct width but apparently neglect an important factor in calculating the shift. The shifts which have been observed in this study also have a constant ratio (within experimental error) to the width. This ratio averaged over four levels is 0.52 ± 0.05.

For the five levels studied here we have found that the widths calculated from Ref. 2 are systematically about 20% lower then the higher-pressure data. However, the data start at pressures where the impact-theory assumptions are no longer justified over most of the line shape. Previous comparisons between theoretical widths[2] and experiment[14] have given impressive agreement for cases where the pressure was low enough for the impact-broadening theory to be valid. In order to estimate oscillator strengths (and confirm their theory), Berman and Lamb[2] used width data based on flourescence line shapes in which the lower level is the upper resonance level and the pressure is much lower than in our study. The results were so good that in many cases present day oscillator strengths are far closer to their results than were the values known in 1967.

Even though we have used a broad bandwidth dye laser, we have obtained the first absorption data on self-broadening of resonance lines under conditions of strong radiation trapping. It is unlikely that the slightly faster than linear increase in width at the highest pressures is due to differences in ionizing atoms on the blue side of resonance, relative to the ionization of excimers on the red side. We say this because for all resonances except the Xe 6*s*, the ionization of atoms excited on the blue side of resonance should have been nearly 100% efficient. If the ionization was less than 100% efficient for excitation on the red side, the effect would be to narrow the line. Figure 3 demonstrates that nothing dramatic happens to the observed line shape at the position of the unshifted resonance. In fact, at the higher pressures most of the area under the line shapes lies on the blue side of the line.

The fair agreement with low-pressure theoretical widths extrapolated to high pressures is a bit surprising. However, studies of the transport of resonance radiation[15] have already indicated that this might be the case. In the latter studies it is found that the application of the Holstein theory[16,17] of radiation trapping to the prediction of the rate of escape of resonance radiation from a pulse-excited atomic gas agrees very well with theory at pressures as high as 150 Torr. A simple picture applies to radiation trapping. Essentially, the emitted photons go nowhere, unless they are emitted so far on the wing of the line that their mean free path is comparable with the dimensions of the gas cell. Emission on the extreme wing of the line is a very rare event, so that the escape of the radiation may be slowed by several orders of magnitude relative to the spontaneous decay rate for a cell with dimensions of a few centimeters. In a sense, this apparent validity of Lorentzian absorption very far from line center is even more surprising at high pressures than the results found here. Transport equations, like those of Holstein, have been derived[3] from many-body theory where they do not rely on a particle picture of the photon.

There are variations on the present method which could be important. For instance, for excited states which have allowed transitions to another lower excited state, one could monitor the integrated emission of the untrapped radiation as the laser is scanned through three-photon resonance as an indicator of the absorption line shape. There is certainly no problem with signal size with the latter technique. With a good dye laser, measurements of shift and width should be possible from the onset of the dominance of resonance broadening relative to Doppler broadening.

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