

³¹L. G. Parratt, *Probability and Experimental Errors in Science* (Wiley, New York, 1961), p. 176.

³²G. Gräff, E. Klempt, and G. Werth, *Z. Physik* **222**, 201 (1969).

³³F. Walls, Ph.D. thesis (University of Washington,

1970) (unpublished).

³⁴A. M. Mood, *Introduction to the Theory of Statistics* (McGraw-Hill, New York, 1950), Sec. 7.7.

³⁵J. Orear, Lawrence Radiation Laboratory Report No. UCRL-8417, 1958 (unpublished).

PHYSICAL REVIEW A

VOLUME 4, NUMBER 4

OCTOBER 1971

Moment Analysis of Atomic Spectral Lines*

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(Received 9 April 1971)

The moments of a spectral line are evaluated in a general way and compared with results which invoke standard assumptions of line-broadening theory. Cesium-rare-gas systems are analyzed for a variety of experimental conditions in the hope of extracting useful information about excited-state interactions. The computation uses atomic-beam results for the ground-state interaction and assumes that the excited-state potentials are represented to a first approximation by $V_f = G/R^{12} - D/R^6$. The calculation, which includes a comparison of line shapes, indicates that the following numbers (in cgs units) are reliable for the long-wavelength component of the resonance lines of cesium: with argon, $G = 4.87 \times 10^{-102}$, $D = 4.74 \times 10^{-58}$; with helium, $G = 0.459 \times 10^{-102}$ and $D = -0.614 \times 10^{-58}$. Analysis of the cesium-xenon system yields results which illuminate the practical difficulties associated with an otherwise attractive technique.

I. INTRODUCTION

Realistic calculations of spectral line shapes of gases is a matter of importance in a variety of situations. Significant progress has been made in the case of plasmas, but relatively little has been achieved for the case of (charge) neutral perturbers. The most general formulations of the theory are appropriate for comparison with experiments in which the impact approximation¹ is warranted. Another class of experiments can be analyzed correctly using theories which make the adiabatic approximation.² However, in many cases, especially those in which interesting information about excited-state interactions is available, the computation of line shapes with existing theories cannot be justified. The fact that improvements in the theory are difficult to achieve suggests that something simpler than the line shape itself be studied.

The moments of a spectral distribution have been considered profitably in a number of contexts.³ For example, they have been evaluated for the absorption of light by atoms⁴ and molecules⁵; they have been used to establish error bounds on forces between atoms,⁶ and to study the potentials involved in collision induced absorption.⁷ Moments have been used in line-shape theories,⁸ and to infer intermolecular-force information from experiment.⁹

The use of moments to infer information about interactions and to calculate line shapes is an attractive prospect. Using p moments, it would be

possible, in principle, to obtain p parameters in a realistic model of an excited-state potential. Moreover, since the line shape is the Fourier transform of a correlation function $C(t)$ and since C can be viewed as a power-series expansion in t with coefficients proportional to the moments, a knowledge of the moments would then permit an accurate determination of C for small times.

These prospects raise several significant questions. What is the general quantum-mechanical form for the first few moments, and how is it simplified when various commonly employed approximations are introduced? Is it possible to infer reliable information about interactions from the moments and if so, how much? The present paper seeks an answer to these questions. Specifically, the first three moments are calculated using an adiabatic representation.¹⁰ These results for the diabatic case are then compared with that obtained by making the adiabatic approximation, the quasi-static approximation,² and the approximations used by Fox and Jacobson.¹¹ Then the problem is restricted to a detailed analysis of data on a cesium resonance line when the cesium is pressurized by helium, argon, and xenon.^{12,13} The reliability of the results, which differs in each case, is discussed at the appropriate point and summarized in the conclusions.

II. CALCULATION OF MOMENTS

A. Diabatic

The spectral density $F(\omega)$ for a line-shape prob-

lem can be written in terms of a time correlation function $C(s)$:

$$F(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} ds e^{-i\omega s} C(s). \quad (1)$$

Here the frequency ω is understood to be measured from the unperturbed line center. The n th moment of the line shape $\langle \omega^n \rangle$ is defined here to be

$$\langle \omega^n \rangle = \int_{-\infty}^{\infty} \omega^n F(\omega) d\omega / \int_{-\infty}^{\infty} F(\omega) d\omega. \quad (2)$$

Using the rules for manipulating Fourier transforms, these moments can be written as

$$\langle \omega^n \rangle = (-i)^n \frac{d^n C}{ds^n} \Big|_{s=0} / C(s) \Big|_{s=0}. \quad (3)$$

Thus we have

$$C(s) = \sum_{n=0}^{\infty} (i)^n \langle \omega^n \rangle s^n / n!.$$

The correlation function is to be calculated from

$$C(s) = \text{Tr}(\rho_0 \int_{-\infty}^{\infty} dt \vec{\mu}(t) \vec{\mu}(t+s)), \quad (4)$$

where $\vec{\mu}$ is the dipole moment of the system and ρ_0 is the density matrix. For the sake of definiteness, consider an isolated spectral line between the initial state i and final state f . In the event that more complicated spectra are of interest the additional sums over final states and averages over initial states can be readily included. [A sum and average over degenerate levels is already implied in Eq. (4).]

The adiabatic representation is convenient for calculation, displays the time dependence, and facilitates comparison of the general results with those obtained using the adiabatic approximation. The adiabatic basis functions satisfy

$$H(t) \phi_a(t) = E_a(t) \phi_a(t), \quad (5)$$

while the functions to be used in (4) satisfy the Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = H(t) \psi. \quad (6)$$

If the solutions of (6) are expanded in terms of the set ϕ , i. e., $\psi = \sum a_i \phi_i$, and if an operator A is de-

finied by $a(t) = A(t) a(0)$, then A satisfies

$$i\hbar \frac{\partial A}{\partial t} = (H - D)A, \quad A(0) = 1, \quad (7)$$

where

$$D = i\hbar \frac{\partial}{\partial t}.$$

Also, in this representation the equation of motion for an operator B is

$$i\hbar \frac{dB}{dt} = BD - DB + i\hbar \frac{\partial B(t)}{\partial t}. \quad (8)$$

Now if at time t , $\psi_j(t) = \phi_j(t)$, then the correlation function (4) can be written as

$$C(s) = \text{Tr}(\rho_0 \vec{\mu}_{if}(t) A^*(t+s)_{fj} \vec{\mu}(t+s)_{jk} A(t+s)_{ki})_t, \quad (9)$$

where each of the matrices is computed using the functions ϕ and $\rho_0 = \rho(-\infty) \delta_{ij}$.

Since $A(t)_{ki} = \delta_{ki}$,

$$C(s) \Big|_{s=0} = \text{Tr}(\rho_0 |\vec{\mu}_{if}(t)|^2)_t, \quad (10)$$

$$-i \frac{dC}{ds} \Big|_{s=0} = \text{Tr}(\hbar^{-1} \rho_0 |\vec{\mu}_{if}(t)|^2 [E_f(t) - E_i(t)])_t, \quad (11)$$

and the mean frequency, according to Eq. (3), is the ratio of (11) and (10). Equation (11) follows directly from the derivative of (9) when the equations of motion for A^* , A , and $\vec{\mu}$ [Eqs. (7) and (8)] are inserted and evaluated at $s=0$. The important feature of Eq. (11) is that no diabatic terms appear¹⁴; the result is identical to that which will be obtained later by making the adiabatic approximation at the outset. The energies which appear in (11) are the solutions of Eq. (5) and they include the interaction energy of the absorbing or emitting atom with all of the perturbers. If the interactions happen to add as scalars, the energies in (11) would be replaced by the one-perturber result multiplied by the number density.

The evaluation of the second and third derivatives is rather more complicated. The results are

$$\langle \omega^2 \rangle = \text{Tr}(\hbar^{-2} \rho_0 |\vec{\mu}_{if}(t)|^2 [E_f(t) - E_i(t)]^2) / C(s) \Big|_{s=0} - \text{Tr} \left\langle i\hbar^{-1} \rho_0 \vec{\mu}_{if}(t) \left[\left(\frac{\partial H}{\partial t} \right)_{fj} \vec{\mu}_{ji}(t) - \vec{\mu}_{fj}(t) \left(\frac{\partial H}{\partial t} \right)_{ji} \right] \right\rangle_t / C(s) \Big|_{s=0}, \quad (12)$$

$$\langle \omega^3 \rangle = \text{Tr}(\rho_0 \{ \hbar^{-3} |\vec{\mu}_{if}(t)|^2 [E_f(t) - E_i(t)]^3 - \hbar^{-1} \vec{\mu}_{if}(\ddot{H})_{fj} \vec{\mu}_{ji} - \vec{\mu}_{fj}(\ddot{H})_{ji} \} + i\hbar^{-2} \vec{\mu}_{if} 2[E_f(t) - E_i(t)] [\vec{\mu}_{fj}(\dot{H})_{ji} - (\dot{H})_{fj} \vec{\mu}_{ji}] + i\hbar^{-2} \vec{\mu}_{if} [E_f(t) - E_j(t)] \vec{\mu}_{fj}(\dot{H})_{ji} + [E_i(t) - E_j(t)] (\dot{H})_{fj} \vec{\mu}_{ji} \}) / C(s) \Big|_{s=0}. \quad (13)$$

The terms which contain first derivatives of H do not survive when the average is taken. Thus, the first diabatic terms occur in the third moment. Before discussing these results it will be helpful to

obtain the moments using the adiabatic approximation and the general pressures theory,¹¹ which further assumes that the interactions add as scalars and that the perturbers follow classical paths de-

terminated by the equations of motion.

B. Adiabatic

In the present notation the adiabatic approximation is described by letting

$$A(t+s)_{ij} = \delta_{ij}, \quad \dot{A}(t+s) = 0. \quad (14)$$

Using (14) in (9) and the derivatives of (9) and omitting all of the terms which contain $\partial E/\partial t$, the moments become

$$\begin{aligned} \langle \omega \rangle &= \text{Tr} \langle \hbar^{-1} \rho_0 | \vec{\mu}_{if}(t) |^2 [E_f(t) - E_i(t)] \rangle_t / C(s) \Big|_{s=0}, \\ \langle \omega^2 \rangle &= \text{Tr} \langle \hbar^{-2} \rho_0 | \vec{\mu}_{if}(t) |^2 [E_f(t) - E_i(t)]^2 \rangle_t / C(s) \Big|_{s=0}, \\ \langle \omega^3 \rangle &= \text{Tr} \langle \rho_0 | \vec{\mu}_{if}(t) |^2 [\hbar^{-3} [E_f(t) - E_i(t)]^3 \\ &\quad - \hbar^{-1} \{ \ddot{E}_f(t) - \ddot{E}_i(t) \}] \rangle_t / C(s) \Big|_{s=0}. \end{aligned} \quad (15)$$

Comparison of Eqs. (15) with (11)–(13) indicates that the results are identical except for the terms $(\ddot{H})_{ij}$, $i \neq j$ in $\langle \omega^3 \rangle$.

C. General Pressures

Subject to the assumptions mentioned above the correlation function is given by $C(s) = \exp[-n\phi(s)]$, where

$$\begin{aligned} \phi(s) &= (2m/kT) \int_{-\infty}^{\infty} dv_R \exp[-mv_R^2/(2kT)] \\ &\quad \times \int_{-\infty}^{\infty} dv_\phi \exp[-mv_\phi^2/(2kT)] \\ &\quad \times \int_{-\infty}^{\infty} R^2 dR \exp[-V_i(R)/(kT)] \\ &\quad \times \{ 1 - \exp[i\hbar^{-1} \int_0^s [V_f(t) - V_i(t)] dt] \} \\ &= \langle 1 - \exp[i\hbar^{-1} \int_0^s (V_f - V_i) dt] \rangle. \end{aligned} \quad (16)$$

Here v_R and v_ϕ are the radial and azimuthal speeds, m is the reduced mass, R the interatomic distance, and V_i and V_f are the interaction energies between one perturber and the absorbing atom in its initial and final state. Taking the appropriate derivatives and noting that $C(0) = 1$, the moments become

$$\begin{aligned} \langle \omega \rangle &= n\hbar^{-1} \langle V_f - V_i \rangle, \\ \langle \omega^2 \rangle &= n^2 \hbar^{-2} \langle (V_f - V_i)^2 \rangle + n\hbar^{-2} \langle (V_f - V_i)^2 \rangle, \\ \langle \omega^3 \rangle &= n^3 \hbar^{-3} \langle (V_f - V_i)^3 \rangle + 3n^2 \hbar^{-3} \langle (V_f - V_i)^2 \rangle \langle V_f - V_i \rangle \\ &\quad - n\hbar^{-3} \langle (V_f - V_i)^3 \rangle - n\hbar^{-1} \left\langle \frac{\partial^2 V_f}{\partial S^2} - \frac{\partial^2 V_i}{\partial S^2} \right\rangle_{s=0}. \end{aligned} \quad (17)$$

The averages required for (17) are the same as that indicated in Eq. (16).

If a reasonable form is assumed for the potentials V_{fi} , they can be written as a power series in time by using the differential equation for the perturber

path as a function of time. Specifically, if $V_i = A/r^p - B/r^q$ and $r(0) = R$, the series is

$$V_i[r(t)] = \sum D_n t^n, \quad (18)$$

where

$$\begin{aligned} D_0 &= V_i(R), \\ D_1 &= v_R (-pA/R^{p+1} + qB/R^{q+1}), \end{aligned} \quad (19)$$

$$\begin{aligned} D_2 &= v_R^2 \left(\frac{p(p+1)}{2} \frac{A}{R^{p+2}} - \frac{q(q+1)}{2} \frac{B}{R^{q+2}} \right) \\ &\quad - v_\phi^2 \left(\frac{p}{2} \frac{B}{R^{p+2}} - \frac{q}{2} \frac{B}{R^{q+2}} \right) - \frac{1}{2m} \left(\frac{pA}{R^{p+1}} - \frac{qB}{R^{q+1}} \right)^2. \end{aligned}$$

Thus the terms in $\langle \omega^3 \rangle$ which contain second time derivatives require the velocity and radial average of D_2 written for the final state minus D_2 as written in (19). Note that D_2 depends on the speeds and the reduced mass m .

The moments calculated using the adiabatic assumption (Eq. 15) become identical in form to the result (17), when the time average is replaced by a spatial average (ergodic hypothesis), ρ_0 is replaced by a Boltzmann factor, and the interactions are considered to add as scalars.

The moments obtained using the quasistatic approximation, i. e., when $\langle 1 - \exp[i\hbar^{-1} \int_0^s (V_f - V_i) dt] \rangle$ in Eq. (16) is replaced by $\langle 1 - \exp[i\hbar^{-1} (V_f - V_i)s] \rangle$, are the same as Eq. (17) except that the last term in $\langle \omega^3 \rangle$ does not appear.

III. INTERMOLECULAR FORCES FROM MOMENT ANALYSIS

The moments of a spectral line should provide a powerful tool for the analysis of excited-state interactions. The fact that the first two moments contain no diabatic effects implies that a systematic study of the moments should permit easy inferences about the gross features of the energy; additional labor should provide detail about the influence of motion, additivity, and inelastic effects. In order to assess the usefulness and reliability of the method a resonance line of cesium¹² perturbed by helium, argon,¹³ and xenon has been studied. In each case the ground-state interaction is assumed to be a Lennard-Jones 6-12 potential with the constants inferred from atomic-beam experiments.¹⁵ Then the final-state constants for a potential of similar form can be obtained from the experimental first and second moments at a given pressure and temperature, and tested against moments of lines measured under other conditions. The objective of such a test is, of course, to determine whether such constants are generally useful and whether higher moments can be employed with confidence.

Using Eq. (17) and assuming that the final state

TABLE I. Moments of the $6^2P_{1/2} - 6^2S_{1/2}$ cesium line pressurized by argon (in cm^{-1}).

Relative Temp density (°K)	Experiment					Theory	
	Shift	Width	$\langle \nu \rangle$	$\langle \nu^2 \rangle - \langle \nu \rangle^2$	$\langle \nu \rangle$	$\langle \nu^2 \rangle - \langle \nu \rangle^2$	
0.81	-0.49	10.8	-0.46	10.5
2.6	344	-0.65	1.8	-1.58	3.72	-1.59	28.0
13.2	374	-5.4	10.2	-7.37	55.0	-7.63	162.0
60.8	410	-32.2	36.5	-34.6	790.0	-34.6	790.0

also has a 6-12 potential, the first moment can be calculated from

$$\langle \omega \rangle = 4\pi m \hbar^{-1} \int_0^\infty R^2 e^{-V_i/kT} (V_f - V_i) dR \quad (20)$$

and

$$J \equiv \langle \omega^2 \rangle - \langle \omega \rangle^2 = 4\pi m \hbar^{-2} \int_0^\infty R^2 e^{-V_i/kT} (V_f - V_i)^2 dR \quad (21)$$

With

$$V_f - V_i = (G/R^{12} - D/R^6) - (A/R^{12} - B/R^6) \\ \equiv \alpha/R^{12} - \beta/R^6,$$

the calculation using the first two moments is straightforward.¹⁶ A quadratic equation for α (or β) results, which leads to a pair of values for G and D .

A. Cesium-Argon

The results for the $6^2P_{1/2} - 6^2S_{1/2}$ line are compared with experiment in Table I. In the calculations $A = 3.68 \times 10^{-102} \text{ cm}^{12} \text{ ergs}$ and $B = 3.30 \times 10^{-58} \text{ cm}^6 \text{ ergs}$. The result of fitting the moments at $\text{rd} = 60.8$ (where rd is relative density) leads to the set of constants $G = 4.87 \times 10^{-102} \text{ cm}^{12} \text{ ergs}$ and $D = 4.74 \times 10^{-58} \text{ cm}^6 \text{ ergs}$, and to the set $G = 3.65 \times 10^{-102} \text{ cm}^{12} \text{ ergs}$, $D = 4.04 \times 10^{-58} \text{ cm}^6 \text{ ergs}$. For the lines with $\text{rd} > 1$, data were available¹² for about 6-8 half-widths on either side of the line center, since the objective of the experiments was an accurate determination of width and shift. As the comparison indicates, the mean frequencies are well calculated while the second moments appear to differ significantly. For $\text{rd} = 0.81$, the data¹³ extend for about 300 half-widths into the red wing and 150 half-widths into the blue wing. The agreement between theory and experiment is excellent, but again the experiments were not done with this comparison in mind.¹⁷ The most

TABLE II. Moments of $6^2P_{1/2} - 6^2S_{1/2}$ cesium line pressurized by helium (in cm^{-1}).

Relative density	Experiment		Theory	
	$\langle \nu \rangle$	$\langle \nu^2 \rangle - \langle \nu \rangle^2$	$\langle \nu \rangle$	$\langle \nu^2 \rangle - \langle \nu \rangle^2$
7.1	2.5	22.5	4.0	76.0
21.2	11.9	227.0	11.9	227.0
40.1	22.1	342.0	23.1	440.0

TABLE III. Comparison of widths and shifts for the cesium-helium system, using the constants of case 1 (in cm^{-1}).

Relative density	Experiment		Theory	
	Width	Shift	Width	Shift
7.1	5.5	1.3	7.80	2.47
21.2	18.0	5.5	20.8	7.2
40.1	35.6	13.0	36.8	13.7

telling reason for caution is the fact that for $\text{rd} = 0.81$ the contribution to the second moment 100 cm^{-1} from line center is as large as that at 8 cm^{-1} . This suggests that inferences from third moments of experimental line shapes will not be feasible without extensive experimental effort, which in turn means that motional and diabatic effects will be difficult to study in this way.

B. Cesium-Helium

In the case of helium and cesium, a difficulty arises in the choice of a parameter to represent the short-range interaction in the ground state. The choice made is consistent with empirical formulas for the position of the well¹⁵ and independent calculations of the interaction.¹⁸ The most interesting feature of the moment analysis is that no solution is available for an excited-state potential which is attractive over some range of intermolecular distances. The pair of potentials inferred from the line at $\text{rd} = 21.2$ for the $6^2P_{1/2}$ level have for case 1

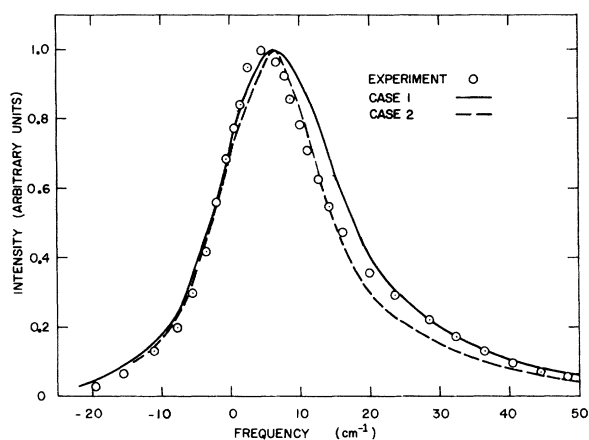


FIG. 1. Comparison of experimental and theoretical line shapes for the cesium $6^2P_{1/2} - 6^2S_{1/2}$ line pressurized by helium at a relative density of 21.2. Intensity, normalized to maximum values of 1.0, is plotted vs frequency ("frequency" here measured in units of wave numbers) from the unperturbed line position. Theoretical lines were calculated using the general pressures theory with constants for cases 1 and 2 which are given in text.

TABLE IV. Moments of $6^2P_{1/2} - 6^2S_{1/2}$ cesium line pressurized by xenon (in cm^{-1}).

Relative density	Experiment				Theory ^a	
	Width	Shift	$\langle \nu \rangle$	$\langle \nu^2 \rangle - \langle \nu \rangle^2$	$\langle \nu \rangle$	$\langle \nu^2 \rangle - \langle \nu \rangle^2$
26.7	-47	66	-84	6000	-84	6000
41.3	-68	81	-115	5400	-129	9300

^aThe calculation was carried out using $A = 12.3 \times 10^{-102}$ erg cm^{12} , $B = 7.9 \times 10^{-58}$ erg cm^6 .

$G = 0.459 \times 10^{-102}$ and $D = -0.614 \times 10^{-58}$ cgs units, and for case 2, $G = 0.734 \times 10^{-102}$ and $D = -0.373 \times 10^{-58}$. The results for the first and second moment are shown in Table II. The implication is not that the van der Waals interaction is absent, but that repulsive forces play a role at much larger distances than previously imagined. The disagreement between the experimental and computed second moments can be attributed, as in the case of argon, to the fact that the low intensities in the wings were not a matter of experimental concern, but contribute strongly to the second moment. In the calculation $A = 0.891 \times 10^{-102}$ cm^{12} erg and $B = 0.426 \times 10^{-58}$ cm^6 erg .

In order to establish whether or not the repulsive R^{-6} term leads to agreement between theoretical and experimental line shapes, a calculation using the general pressures theory was carried out. The results for case 1 are indicated in Table III, and Fig. 1 shows that indeed, either choice yields good agreement with the previously unexplained data of Garrett and Chén.¹²

C. Cesium-Xenon

Finally, the situation was studied for the case of cesium pressurized by xenon. Here the analysis indicates additional difficulties which can be encountered in using moments of lines to infer force information in the absence of other checks. Two lines were studied. In the case of a relative density of 41.3, the model did not yield any solution for G and D . The results of analyzing the other line, $\text{rd} = 26.7$, are shown in Table IV. The agreement of the first moments is satisfactory but the second moments differ significantly.

Again, a pair of values of G and D result, but there is no physical reason for preferring one set to the other. A line-shape calculation with the general pressures theory using each is compared with experiment in Fig. 2, and it is clear that neither set yields acceptable results. The constants used, in cgs units, were: case 1, $G = 24.1 \times 10^{-102}$ and $D = 17.1 \times 10^{-58}$; case 2, $G = 14.1 \times 10^{-102}$ and $D = 13.6 \times 10^{-58}$. Thus, constants which reproduce the first two moments of the line under favorable experimental conditions fail to yield a satisfactory line shape.

(It is interesting to note the appearance of a red satellite¹⁹ in one of the calculations at about 100 cm^{-1} . The depth of the well of the difference potential is about 90 cm^{-1} . The well in the other case is 225 cm^{-1} deep.) The disagreement could originate in several places; the point seems to be that a moment analysis can produce useful insights, but cannot be considered as a uniformly reliable way of obtaining force information or calculating correlation functions.

IV. CONCLUSIONS

In Sec. II, the moments of a spectral line were calculated in a general way and compared with the results obtained by invoking standard assumptions of line-broadening theory. The most important aspect of the result was that diabatic effects do not appear in the first or second moments. Analysis of good line-shape data (which was not taken with a moment calculation in mind) indicates that there is little hope of obtaining reliable third moments without extensive experimental effort. However, in the case of the cesium-argon and cesium-helium systems valuable information was extracted about the excited-state potential. The cesium-xenon results confirm the conclusion that the moments of a spectral distribution are very useful in developing an understanding of excited-state interactions, but that results must be critically evaluated by an independent analysis.

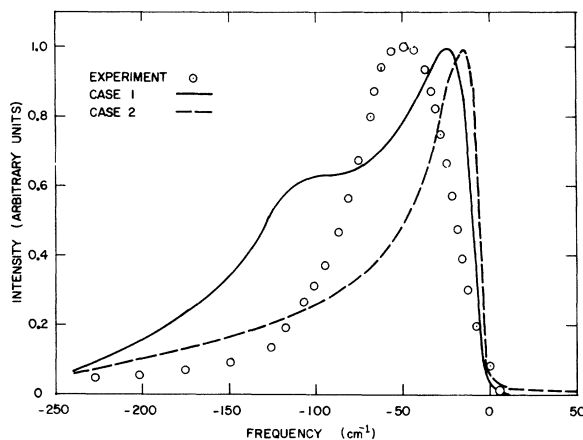


FIG. 2. Comparison of experimental and theoretical line shapes for the cesium $6^2P_{1/2} - 6^2S_{1/2}$ line pressurized by xenon at a relative density of 26.7. Intensity, normalized to maximum values of 1.0, is plotted vs frequency ("frequency" here measured in units of wave numbers) from the unperturbed line position. Theoretical lines were calculated using the general pressures theory with constants for cases 1 and 2 which are given in text.

ACKNOWLEDGMENTS

I am very grateful to Professor S. Y. Chén for furnishing the line-shape data which made this analysis possible. I would also like to thank Dr. C. L.

Chen and Dr. A. V. Phelps for communicating their results to me. Finally, I would like to acknowledge the assistance of A. Atakan who carried out the calculations using the general pressures approach.

*Work supported by the National Aeronautics and Space Administration under Research Grant No. NGL-43-001-006.

¹M. Baranger, Phys. Rev. 112, 855 (1958).

²H. Margenau and M. Lewis, Rev. Mod. Phys. 31, 569 (1959).

³The extensive formal developments and the variety of applications of moment theory preclude a complete accounting. A few references pertinent to the present paper are listed below. See also, R. G. Gordon, in *Stochastic Processes in Chemical Physics*, edited by K. E. Shuler (Interscience, New York, 1969), p. 79.

⁴J. P. Vinti, Phys. Rev. 41, 432 (1932).

⁵R. G. Gordon, J. Chem. Phys. 41, 1819 (1964).

⁶R. G. Gordon, J. Chem. Phys. 54, 663 (1971).

⁷J. D. Poll and J. Van Kranendonk, Can. J. Phys. 39, 189 (1961); R. P. Futrelle, Phys. Rev. Letters 19, 479 (1967); and H. B. Levine, *ibid.* 21, 1512 (1968).

⁸R. Kubo, in *Stochastic Processes in Chemical Physics*, edited by K. E. Shuler (Interscience, New York, 1969), p. 101; R. P. Futrelle (unpublished).

⁹H. Margenau and H. C. Jacobson, J. Quant. Spectry. Radiative Transfer 3, 35 (1963).

¹⁰R. M. Herman, Phys. Rev. 132, 262 (1963); H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (Van Nostrand, New York, 1964), Vol. II, p. 413.

¹¹R. L. Fox and H. C. Jacobson, Phys. Rev. 188, 232 (1969).

¹²R. O. Garrett and S. Y. Chén, Phys. Rev. 144, 66 (1966); S. Y. Chén and R. O. Garrett, *ibid.* 144, 59 (1966); S. Y. Chén, D. E. Gilbert, and D. K. Tan, *ibid.* 184, 51 (1969).

¹³C. L. Chen and A. V. Phelps, Phys. Rev. 173, 62 (1968); and C. L. Chen and A. V. Phelps (private communication).

¹⁴H. Margenau, J. Quant. Spectry. Radiative Transfer 3, 445 (1963).

¹⁵R. B. Bernstein and J. T. Muckerman, in *Intermolecular Forces*, edited by J. O. Hirschfelder (Interscience, New York, 1967), Chap. 8.

¹⁶A. D. Buckingham and J. A. Pople, Trans. Faraday Soc. 51, 1173 (1955).

¹⁷The data of Phelps and Chen are relative to the line maximum. The figures in the table are relative to the unperturbed line position. According to Chén and Garrett [Phys. Rev. 144, 59 (1966)] the shift for $\text{rd}=0.81$ is 0.19 cm^{-1} . In order to infer moments the area near line center had to be estimated. This was done by fitting a Lorentz line shape to the available data. The inferred half-width at half-height was 0.35 cm^{-1} , a value consistent with the results of Ref. 12. The moments were calculated assuming a cell temperature of $410 \text{ }^\circ\text{K}$.

¹⁸W. E. Baylis, J. Chem. Phys. 51, 2665 (1969).

¹⁹M. Takeo, Phys. Rev. A 1, 1143 (1970); J. M. Farr and W. R. Hindmarsh, Phys. Letters 27A, 512 (1968); R. P. Futrelle (unpublished); R. G. Breene, Jr., Phys. Rev. A 2, 1164 (1970).

Intermolecular Forces from Atomic Line-Shape Experiments*

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(Received 19 April 1971)

A systematic convergent method of studying intermolecular forces in excited states is detailed. Extensive comparison between theory and experiment indicates that high-resolution line-shape experiments over a wide range of frequencies will permit the inference of parameters in realistic forms of the potential energy. The analysis focuses on the $^2P_{1/2}-^2S_{1/2}$ resonance line of cesium pressurized by helium, argon, and xenon. When the model is used with ground-state potentials inferred from atomic-beam experiments, and when the excited state is described by $V=G/R^{12}-D/R^6$, the following reliable parameters were determined: helium, $G=0.459 \pm 0.060$ and $D=-0.614 \pm 0.061$; argon, $G=6.48 \pm 0.20$ and $D=5.23 \pm 0.05$; xenon, $G=53.6 \pm 5.8$ and $D=19.1 \pm 0.57$, where the units of G are $10^{-102} \text{ erg cm}^{12}$ and of D are $10^{-58} \text{ erg cm}^6$.

I. INTRODUCTION

Information about intermolecular forces between systems in the ground state is available from a

variety of experiments¹; however, line-shape experiments afford the only generally useful probe of excited-state interactions. Extensive effort has been devoted to the study of interactions in the