Shock-Tube Measurement of the Polarizability of Atomic Hydrogen*

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The electric polarizability of atomic hydrogen has been measured at optical frequencies by shock heating a gaseous mixture of argon and molecular hydrogen to temperatures causing nearly complete dissociation of the latter. Application of Mach-Zehnder interferometry to the shock-heated gas gave measurements of fringe shift across the shock front which were subsequently reduced to obtain the polarizability of the ground state of atomic hydrogen. The resultant value is $\alpha_H = (4.61 \pm 0.07)a_0^3$, for a wavelength of 5870 Å, where a_0 is the first Bohr radius and the error assignment is purely statistical. The shock waves employed were in the Mach number range 10 to 12 in a $\frac{2}{3}$ Ar$-\frac{1}{3}$ H$_2$ mixture (by volume) and produced temperatures of the order of 4600°K at densities high enough to ensure thermal equilibrium. Under these conditions there was negligible ionization or excitation of the argon diluent. In contrast to earlier experiments reported in the literature, the present result is in good agreement with the predictions of the quantum-mechanical time-dependent perturbation theory which gives a value of $\alpha_H = (4.66 \pm 0.01)a_0^3$ for the same wavelength as that used in the experimental work.

I. INTRODUCTION

THE variation with density and composition of the optical properties of a compressible flow provides one of the most useful methods for the quantitative study of gaseous media. At high temperatures the optical behavior of a gas may be modified by internal effects such as dissociation, excitation, or ionization. The present work utilizes this phenomenon to measure the electric polarizability of the ground state of atomic hydrogen. The method was first employed by Alpher and White[1] to measure the electric polarizability of atomic nitrogen and atomic oxygen.

Previous attempts to measure the electric polarizability of atomic hydrogen have been hampered by the difficulty in preparing a known concentration of the atomic species at well-established thermodynamic conditions.

The first reported values are those of Schrauf[2] and Landolt[3,4] in 1863-64. Their method was essentially to take one-half the measured value of the molecular polarizability to obtain a value of $2.73a_0^3$ for the atomic polarizability.

Langer,[5] in 1926, used a discharge tube in conjunction with an interferometer to obtain a value of $(2.7 \pm 0.7)a_0^3$. Van Vleck[6] and Podolsky[7] pointed out that the disagreement between Langer's value and the value $4.5a_0^3$ for the static polarizability as calculated by the Schrodinger theory was probably due to an incorrect evaluation of the amount of atomic hydrogen present in the discharge tube.

Scheffers and Stark,[8] in 1936, used the deflection of a molecular beam by an inhomogeneous electric field due to a transverse force of the form $\alpha E(dE/dz)$. Their result was $(2.0 \pm 0.7)a_0^3$. Scheffers,[9] later reported a correction to the original experimental data leading to a value of $(4.0 \pm 1.4)a_0^3$.

The excellent agreement between the theoretical and experimental Stark effect leads one to support the calculated value of $4.5a_0^3$ for the ground-state, static polarizability of atomic hydrogen. However, the Stark effect can only yield experimental values of the difference in polarizabilities between two states of an atom and is limited to measurements associated with static or low-frequency electric fields.

The experimental result of the present work, which in fact deals with the frequency-dependent or dynamic polarizability at optical frequencies, is in excellent agreement with theoretical calculations using time-dependent quantum-mechanical perturbation theory.[7,10,11]

These measurements are summarized in Table I.

[1] R. A. Alpher and D. R. White, Phys. Fluids 2, 153 (1959).
[2] A. Schrauf, Pogg. Ann. 119, 471 (1863).
[3] H. Landolt, Pogg. Ann. 123, 597 (1864).
[4] H. Landolt, Liebigs Ann. Chem. 213, 75 (1882).
[5] R. M. Langer, Proc. Natl. Acad. Sci. U. S. 12, 639 (1926).

[6] J. H. Van Vleck, Proc. Natl. Acad. Sci. U. S. 12, 662 (1926).
[7] B. Podolsky, Proc. Natl. Acad. Sci. U. S. 14, 253 (1928).
[8] H. Scheffers and J. Stark, Physik Z. 37, 217 (1936).
[9] H. Scheffers, Physik Z. 41, 399 (1940).
[10] A. Dalgarno and A. E. Kingston, Proc. Roy. Soc. (London) A259, 424 (1960).
[11] W. C. Marlow, Ph.D. dissertation, Stanford University, Stanford, California, June 1963.

TABLE I. Experimental values of the polarizability of atomic hydrogen.

Investigator	Method	Value $\{a_0{}^3\}$
Macroscopic measurements		
Schrauf (1863)	Application of the Biot-	2.73
Landolt (1864, 1882)	Arago law of mixtures	
Batsanov (1961)	of refractivities applied	
	to chemical compounds.	
Langer (1926)	Discharge tube-	2.7±0.7
	interferometer	
Microscopic measurements		
Scheffers & Stark (1936)	Atomic beam in an in-	2.0±0.7
	homogeneous static	
	electric field.	
Scheffers (1940)	Applied a correction to	4.0±1.4
	the 1936 data.	
Present experimental value		$(4.61\pm0.07)a_0{}^3$
Theoretical value[a]		$(4.66\pm0.01)a_0{}^3$
Theoretical value[b]		$4.5a_0{}^3$

[a] The dynamic polarizability for a wavelength $\lambda = 5870$ Å.
[b] The static polarizability for a static electric field.

II. EXPERIMENTAL METHOD

In this work the atomic state of hydrogen was prepared by shock heating a mixture of molecular hydrogen and argon to temperatures causing nearly complete dissociation. The optical properties of the shocked gas were then investigated with a Mach-Zehnder interferometer by observing the fringe shift across the shock front.

The ratio of the polarizability of atomic hydrogen to that of the molecular species is determined from the relation,

$$\frac{\alpha_H}{\alpha_{H_2}} = \frac{1}{2}\left\{1 + \frac{(\eta-1)}{x\eta\beta}\left[\frac{s}{S(\eta-1)} - \left\{(1-x)\frac{\alpha_{Ar}}{\alpha_{H_2}} + x\right\}\right]\right\} . \quad (1)$$

All the quantities on the right of this expression are measured or tabulated. Thus, x, the fraction of H_2 in the original Ar-H_2 mixture, is measured in the preparation of the mixture. The density ratio η across the shock front and the degree of dissociation β are known from shock Hugoniot calculations[12] once the shock Mach number is measured. The fringe shift s is measured from interferograms of the shock front. The polarizabilities for molecular hydrogen α_{H_2} and argon α_{Ar} are determined from tabulated values of their respective refractive indices. The quantity S involves the path length l, the wavelength λ, the initial gas pressure P_1 and temperature T_1, which are measured quantities, and also $n_{H_2}{}^0$, the refractive index of H_2 at standard conditions P_0 and T_0, which is tabulated.

$$S = \frac{l}{\lambda}(n_{H_2}{}^0 - 1)\frac{T_0}{T_1}\frac{P_1}{P_0} . \quad (2)$$

[12] W. C. Marlow, Gas Dynamics RR-463-8, LMSC 6-90-63-39, Lockheed Missiles & Space Company, 1963 (unpublished).
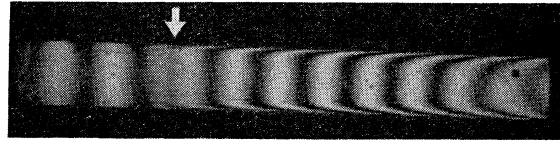
FIG. 1. Boundary layer profile and the flow field behind a Mach 11 shock into a 16-Torr $\frac{2}{3}$Ar—$\frac{1}{3}$H$_2$ mixture. The shock-front location is indicated by an arrow. The channel height is 0.5 cm.

Of course, the values of α_{H_2}, α_{Ar}, and $n_{H_2}{}^0$ must be evaluated for the experimental wavelength λ.

III. DISCUSSION

The incident shock wave was formed in a 3-in. diameter circular cross-section shock tube and then converged through a smooth transition section into the final test section, which had a 0.5-cm$\times$3.5-cm rectangular cross section. An interferogram of the boundary layer profile and flow field behind the shock front is shown in Fig. 1. Most of the measurements were made in a $\frac{2}{3}$ Ar-$\frac{1}{3}$ H$_2$ mixture at initial pressures of $P_1 = 6$ to 30 Torr, resulting in Mach numbers of $M_s = 10$ to 12. The temperatures in the shocked gas were of the order of $T_2 = 4000$ to 5000°K, with the degree of dissociation of the order of 70 to 85%.

In the experiment a wide wavelength spectrum of the spark source was used. From intensity-wavelength measurements of this source a mean wavelength for the interferometric system was determined, with due consideration to secondary fringe shift effects associated with dispersion of light from nonmonochromatic sources.[13] From this analysis the effective wavelength was found to be $\lambda = (5870\pm70)$ Å. The details of this analysis are given elsewhere.[11]

Typical fringe shifts (taken from interferograms with horizontal fringes in contrast to the vertical fringe interferogram shown in Fig. 1) due to the atomic hydrogen component in the shocked mixture were around 1 fringe, that due to molecular hydrogen about 0.1 fringe, and that due to argon about 2 fringes. This may be compared with an estimated data reduction uncertainty of ±0.06 fringe.

The effects of vibrational relaxation are negligible under the present experimental conditions. This was substantiated from the fringe shift interferograms themselves and by calculations made by extending Sutton's[14] work to the temperatures and shocked gas conditions of the present experiment.

The density, as determined from the fringe profiles behind the shock, was found to show a slow decay. The space-time location of the shock front was measured and indicated the shock to be weakly attenuated. Normally, the density behind a decelerating shock is found to have a profile which increases with distance

[13] C. W. Curtis, Lehigh University Project NR 061-063 Contract N7 ONR 39302 (unpublished).
[14] E. A. Sutton, J. Chem. Phys. 36, 2923 (1962).

TABLE II. Evaluation of the polarizability ratio α_H/α_{H_2} for $\lambda = 5870$ Å.

P_1 Torr	T_1 °K	M_s	η	β	S	s	α_H/α_{H_2}
			Confidence limits				
±0.16	±0.1	±0.17	±0.046	±0.028	±0.0060	±0.06	
20.0	298.0	11.08	8.754	0.787	0.2011	2.92	0.8139±0.163
20.0	297.7	10.81	8.690	0.739	0.2013	2.86	0.7135±0.171
20.0	297.4	11.40	8.784	0.841	0.2015	2.97	0.9268±0.159
20.0	297.6	11.31	8.782	0.826	0.2014	2.97	0.8350±0.156
20.5	297.9	11.02	8.744	0.776	0.2062	2.99	0.8189±0.165
20.0	298.1	11.35	8.785	0.832	0.2010	2.96	0.8273±0.160
20.0	298.6	10.81	8.690	0.739	0.2007	2.84	0.7756±0.171
20.0	297.4	11.13	8.764	0.796	0.2015	2.96	0.8429±0.167
19.95	297.6	11.16	8.768	0.801	0.2008	2.94	0.8286±0.167
20.0	297.7	11.31	8.782	0.826	0.2013	3.00	0.8673±0.156
20.0	297.7	11.38	8.785	0.838	0.2013	2.99	0.8510±0.156
20.0	297.9	11.50	8.782	0.858	0.2012	2.90	0.7564±0.163
20.15	297.9	11.27	8.781	0.820	0.2027	3.00	0.8492±0.163
20.2	297.9	11.44	8.785	0.848	0.2032	3.00	0.8288±0.160
20.0	295.6	11.26	8.780	0.818	0.2027	3.00	0.8504±0.164
20.0	297.8	11.41	8.786	0.843	0.2012	2.93	0.7896±0.159
20.15	295.9	10.66	8.640	0.711	0.2040	2.89	0.8125±0.189
19.95	296.3	11.30	8.783	0.824	0.2018	3.00	0.8602±0.168
16.05	296.9	10.64	8.730	0.718	0.1619	2.40	0.9273±0.258
16.05	297.4	11.36	8.875	0.845	0.1617	2.34	0.7394±0.207
16.15	297.8	10.56	8.697	0.702	0.1625	2.35	0.8630±0.259
13.0	295.2	11.23	8.956	0.823	0.1319	2.00	0.8510±0.240
12.95	296.1	11.13	8.948	0.815	0.1310	2.00	0.8829±0.231
13.05	295.2	11.07	8.929	0.804	0.1324	2.00	0.8619±0.240
13.05	295.6	11.24	8.956	0.834	0.1323	2.00	0.8408±0.244
13.15	295.9	10.81	8.878	0.757	0.1331	2.00	0.8865±0.240
6.1	294.9	12.10	8.85	0.971	0.0620	0.91	0.7630±0.342

from the shock front.[15] Calculations indicate such an effect would not be caused by the converging channel. It might, therefore, be attributed to the relatively large thickness of the boundary layer relative to the channel dimensions as can be seen in Fig. 1. Fortunately, this effect does not perturb the fringe shift measurement directly across the shock front. The same can be said about the boundary layers on the observation windows in their effect on the optical path of the light beam.

The possibility of a contribution to the polarizability measurement from the excited states (vibrational and rotational) of the hydrogen molecule has been considered using the simplest of models. The polarizabilities of the excited states of the molecule were assumed to depend linearly on the excited state internuclear distance and to be limited in range by the ground-state value of the molecular polarizability α_{H_2} and twice the atomic polarizability $2\alpha_H$. The results of this calculation indicated the final reported experimental value $(4.61a_0^3)$ should have been reduced by $-0.01a_0^3$. However, this contribution is considerably smaller than the experimental error and has been ignored.

IV. FINAL RESULTS

The experimental data are given in Table II. The confidence limits of the various parameters are indicated

[15] R. J. Emrich and D. B. Wheeler, Jr., Phys. Fluids **1**, 14 (1958).

at the head of each column. The cumulative error is given for each measured value of α_H/α_{H_2}. The resulting values of the ratio α_H/α_{H_2} are plotted in a histogram in Fig. 2, using cell widths of 0.05. Superimposed on the histogram is a plot of the Gaussian probability distribution. The mean value of α_H/α_{H_2} is found to be

$$\alpha_H/\alpha_{H_2} = 0.8283 \tag{3}$$

and the standard deviation from the mean $\sigma = 0.0466$.

Using the standard deviation of the mean $\sigma/\sqrt{N}$ as the precision index, the ratio α_H/α_{H_2} can then be written
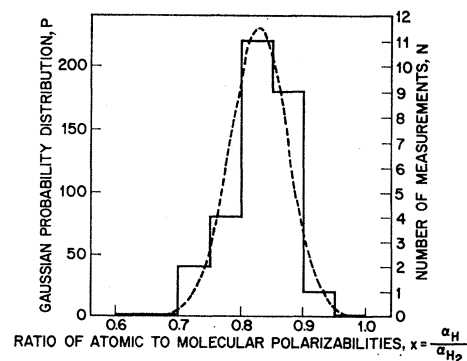

FIG. 2. Histogram of experimental results. Total number of measurements $N = 27$. Mean value $\alpha_H/\alpha_{H_2} = 0.8283$. Standard deviation from the mean $\sigma = 0.0466$. Standard deviation of the mean $\sigma/\sqrt{N} = 0.0090$.

as

$$\alpha_H/\alpha_{H_2} = 0.8283 \pm 0.0090. \tag{4}$$

Taking the value $\alpha_{H_2} = (5.564 \pm 0.028)a_0^3$ for the experimental wavelength of $\lambda = 5870$ Å, the value of the dynamic polarizability of the ground state of atomic hydrogen is found to be,

$$\alpha_H = (4.61 \pm 0.07)a_0^3 \tag{5}$$

with the error assignment on a purely statistical basis.

This result is in good agreement with the theoretical value

$$\alpha_H = (4.66 \pm 0.01)a_0^3 \tag{6}$$

as calculated using time-dependent perturbation theory[11] and evaluated for the experimental wavelength. Podolsky's calculation[7] and that of Dalgarno and

Kingston[10] are accomplished by expanding the index of refraction (or polarizability) in inverse powers of the wavelength in such a way that the sums over intermediate states are eliminated. The value and error assignment quoted above was obtained by a direct, but laborious, evaluation of the second-order perturbation theory from the well known expression for the polarizability of an atom in the nth quantum state,

$$\alpha_n(\omega) = \sum_{n'} \frac{f(n',n)e^2/m}{\omega_{n',n}^2 - \omega^2}, \tag{7}$$

which includes a sum over a complete set of states and an integration over the continuum states. Here, ω is the applied angular frequency $(2\pi c/\lambda)$, $\omega_{n',n}$ the Bohr frequencies, and $f(n',n)$ the oscillator strengths.

Correlation Effects in Atomic Structure Using the Random-Phase Approximation*

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A procedure for treating correlations in atomic structure is introduced and applied to the calculation of excitation energies, oscillator strengths, and photoionization cross sections. The method is the extension of the Hartree–Fock theory known as the random-phase approximation, which has already been applied to a number of other many-body problems. In this application to atomic physics results are given for the following atoms in column II of the periodic table: beryllium, magnesium, calcium, and strontium. These atoms all have ^1S ground states, and only excitations to ^1P states are considered. The general conclusion of the study is that the values of the oscillator strengths and photoionization cross sections are changed significantly by the correlations, while the changes in the values of the excitation energies are quite small. Wherever comparison with experiment is possible, the inclusion of these correlations improves the agreement between theory and experiment. Their effects are, however, not as marked as in highly degenerate infinite systems or in nuclei.

I. INTRODUCTION

A MAJOR problem in theoretical atomic physics, as in other many-particle problems, is the role of correlations, particularly for observables other than the total energy. The only correlations included in the usual first approximation, the Hartree-Fock approximation, are those arising from the Pauli exclusion principle. The value of the total energy of an atom obtained in this way is, of course, quite accurate, being good to within one percent in most cases. The errors in other quantities can, however, be very much greater.

In the past, two main approaches have been followed in improving this situation in atomic physics problems. The variational approach, in which the electronic

separations are introduced into the wave function, has had good success for two-electron systems, but has not yet proved practical for heavier atoms. The configuration-interaction method, in which linear combinations of Slater determinants are used, has been mainly useful for light atoms. The results show that the wave function improves very slowly as the number of configurations is increased. Little work has been done on the correlation problem for medium and heavy atoms.

In recent years, however, there has been substantial progress in treating correlations in infinite many-particle systems. In addition to developments in perturbation theory, two nonperturbative approaches have been developed and proved useful in several different contexts. These are the Bardeen, Cooper, and Schrieffer theory of superconductivity,[1] and the random-phase

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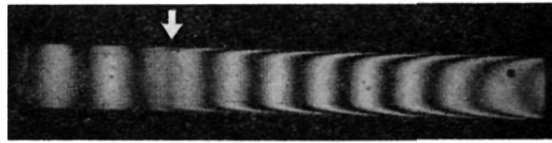[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

FIG. 1. Boundary layer profile and the flow field behind a Mach 11 shock into a 16-Torr $\frac{2}{3}$Ar$-\frac{1}{3}$H$_2$ mixture. The shock-front location is indicated by an arrow. The channel height is 0.5 cm.