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Pressure Effects of Foreign Gases on the Absorption Lines of Cesium. VII. The Shift of High-Member Lines by Various Rare Gases*

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The observed behavior of the shift of the third- and higher-member lines (up to the 25th member) of the Cs principal series produced under various pressures (up to a relative density of ~6) of all rare gases is described. A comparison of the shifts of various lines was made. The red shifts of Cs(3) and Cs(4) are nearly the same for Ar, Kr, and Xe when the relative density (rd) is below 0.6 and become increasingly different when the rd is increased. For He and Ne, the blue shift of the $^2P_{1/2}$ component of Cs(3) is greater than that of the $^2P_{3/2}$ component, while for Cs(4) the shift is greater, although the difference in shift of the two doublet components is much reduced. The slopes of the plots of the asymptotic values of shifts for high-member lines versus rd are 5.85, 0.366, −10.04, −19.6, and −35.0 cm^{-1}/rd for He, Ne, Ar, Kr, and Xe, respectively.

I. INTRODUCTION

In addition to the data for the shift of the first two members of the principal series[1,2] (Papers I and II), [1] similar measurements were carried out for the third up to the 25th members perturbed by Ar and He. The shift produced by Kr and Ne as reported in papers III and IV[1] was extended to much higher relative densities (rd). New behaviors have been noted for certain lines. A comparison of the behaviors of shifts for various lines perturbed by various rare gases were made. For nomenclature, reference is made to our earlier papers.[1]

II. RESULTS

A. Shift of Cs(3)

The plot of the red shift versus the rd for Ar, Kr, and Xe is shown in Fig. 1. One should note that, for rd's less than 1.1, the shifts produced by Ar, Kr, and Xe are nearly the same. The initial nearly linear region for rd less than 0.7 has a common slope of $-1.40\,cm^{-1}$/rd (the minus sign means "red" shift). Above rd 1.1, the curves start to branch out, are slightly inverted S shaped, and do not become nearly linear again until rd = 3.0. One should also note that this transition region, i.e., the range of rd at which the curve is inverted S shaped, took place between roughly the same rd range 0.7–3.0 for all three gases. The slopes of the curves for the second nearly linear region are widely different, with slopes −5.96, −12.1, and $-23.9\,cm^{-1}$/rd for Ar, Kr, and Xe, respectively. The difference of shift of the two doublet components is negligibly small for the three gases.

The corresponding plot for He and Ne is shown in Fig. 2. While the result for He is given here first, that for Ne is merely a part of Fig. 5 in paper IV. It is evident that for both gases the $^2P_{1/2}$ component has conspicuously greater blue shift than the $^2P_{3/2}$ component. Also the range of rd for the first nearly linear part of the graph is longer for the $^2P_{1/2}$ component than for the $^2P_{3/2}$ component for both gases. For He (and Ne), the first nearly linear region for the $^2P_{1/2}$ and $^2P_{3/2}$ components are rd < 0.8 (rd < 1.5) and rd < 0.3 (rd < 0.9) with slopes 2.67 (0.65) and 1.21 (0.42) cm^{-1}/rd, respectively. (The values within the parentheses are for Ne). Beyond these upper rd values, the graph curves upward becoming nearly linear again above rd 3.5 (4.5) and 3.0 (6) with "identical" slopes of 4.24 (1.10) cm^{-1}/rd for the $^2P_{1/2}$ and the $^2P_{3/2}$ components, respectively.

It is interesting to note that for the range of rd observed for both He and Ne, the shift slopes of the second nearly linear part are identical for both components. The two curves are displaced from one another so that the shift of the $^2P_{1/2}$ component is constantly higher than that of the $^2P_{3/2}$ component by about 2.7 (1.6) cm^{-1}.

B. Shift of Cs(4).

Figure 3 gives a comparison of the shift of Cs (4) under various rd's of Ar, Kr and Xe. One will note that the behavior of shift for Cs(4) is very similar to that for Cs(3). For rd below 0.6, the three shift curves practically coincide with an average slope of $-2.6\,cm^{-1}$/rd. Then the curves branch out from rd around 0.62 with a somewhat inverted S shape, and do not become nearly linear again until about rd 2.5. The slopes of the curves for the second nearly linear region are −7.5, −17.5, and $-27.8\,cm^{-1}$/rd, respectively.

Figure 4 gives the corresponding plots for Cs(4)

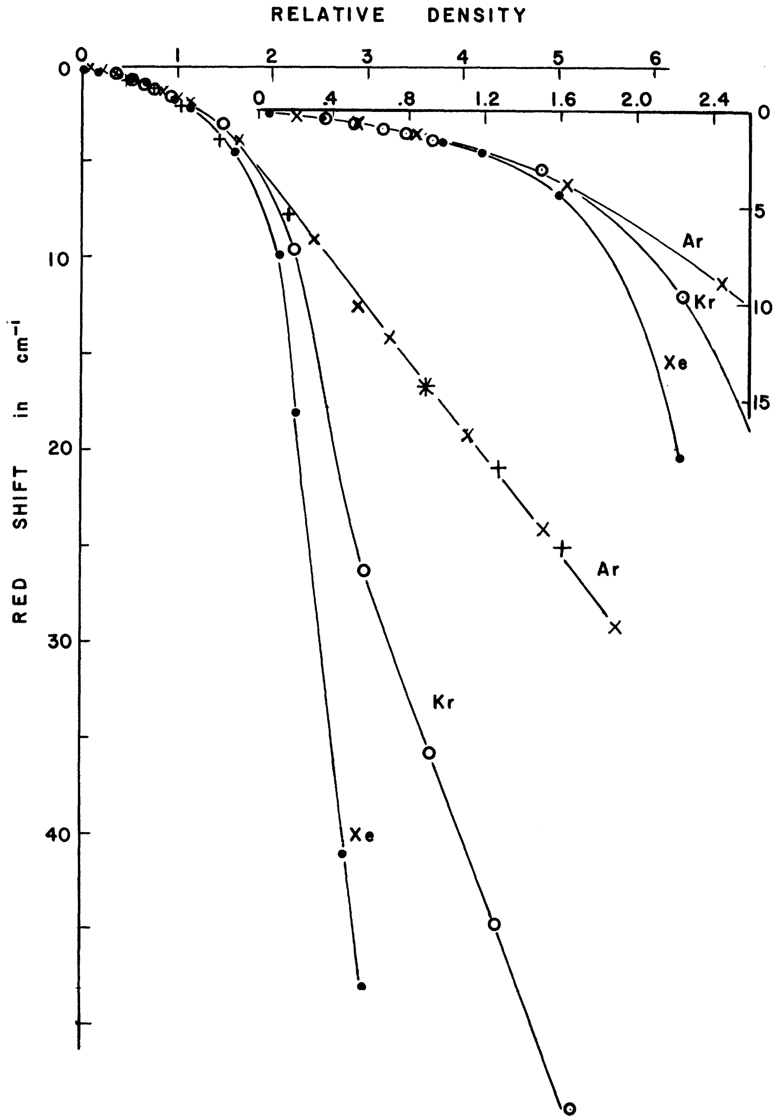

FIG. 1. Red shift of Cs(3) produced by Ar(T=453–512 °K), Kr (T=458–508 °K) and Xe (T=493–537 °K). + and × for Ar $^2P_{1/2}$ and $^2P_{3/2}$ components, respectively; ○ and • for Kr and Xe, respectively, (for the $^2P_{3/2}$ component only). The insert at the upper right corner is an enlargement of the plot for low rd.

in the presence of He and Ne, similar to those for Cs(3) in Fig. 2. While the magnitude of the shift for Cs(4) is increased with respect to the case of Cs(3), the difference of shift for the two doublet components of Cs(4) is much reduced. The plots for both He and Ne have quite similar shape, viz., both graphs curve only slightly upward at around rd = 2. For He, the blue shift of the $^2P_{1/2}$ component is slightly greater than that of the $^2P_{3/2}$ component for rd < 2, but as the rd is increased beyond 2.3 the relative amount of shift for the two components becomes reversed. The approximate slope for the region for rd < 2 is 4.3 cm^{-1}/rd for He (0.83 cm^{-1}/rd for Ne).

The fact that the shifts of Cs(3) and Cs(4) are nearly the same for Ar, Kr, and Xe when the rd is low, but are quite different when the rd is increased, may be due to the following reason: When the foreign gas pressure is low, the number of foreign gas atoms within the orbit of the upper states is very low, so that the shift of these energy levels due to the polarization of foreign atoms by the core of the Cs atom is small. The shifts caused by the impact of the valence electron with foreign atoms due to the three gases are of the same order of magnitude for such low pressures. When the foreign gas pressure is increased, the number of foreign atoms within the orbits of the upper states becomes more and more appreciable, and the difference of polarization of these foreign gas atoms within the orbit will become increasingly important in changing the energy levels of the upper state. This fact is not true for He and Ne because the interaction potential differences are quite different[2] and

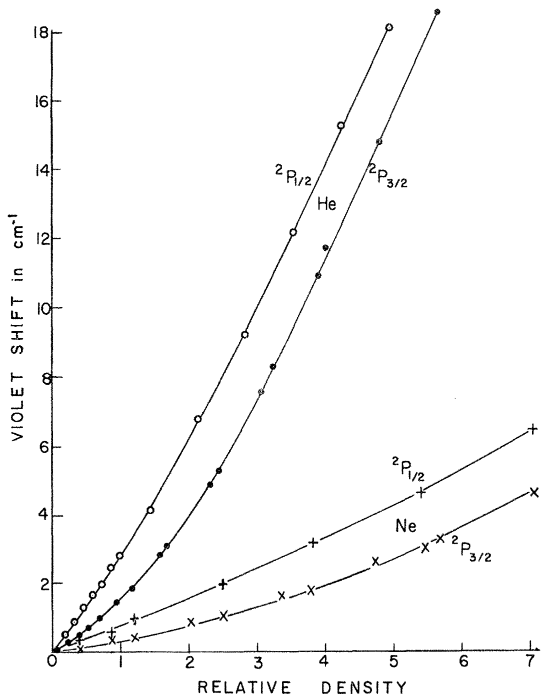

FIG. 2. Violet shift of Cs(3) produced by He ($T = 453$–$475\,°K$). The result for Ne is reproduced from Paper IV for comparison.

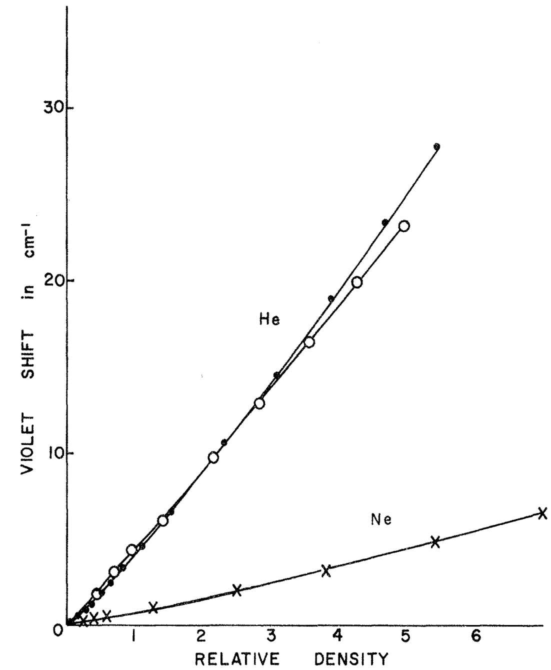

FIG. 4. Violet shift of Cs(4) produced by He ($T = 474$–$523\,°K$). O and ● are for $^2P_{1/2}$ and $^2P_{3/2}$ components, respectively. The result for Ne is reported from Paper IV for comparison.

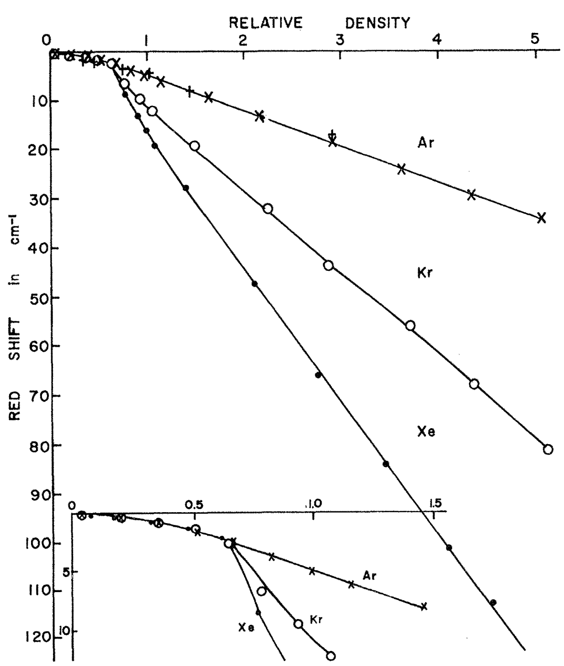

FIG. 3. Shift of Cs(4) produced by Ar ($T = 453$–$512\,°K$), Kr ($T = 458$–$508\,°K$), and Xe ($T = 493$–$537\,°K$). The notation of marks is identical to that of Fig. 1. The insert at the lower-left-hand corner is an enlargement of the plot for low rd's.

the polarizabilities are low. The inverted-S-shaped portion of the plots are indications of the presence of red satellites.

C. Shift of Cs(5) and Higher-Member Lines

The shift of Cs(5) and some of the higher-member lines produced by Ar, Kr, and Xe is depicted in Fig. 5. For the sake of description and comparison, curves for Cs/Ar were drawn also for low-member lines. It is shown that the shift for low-member lines is small, then increases very quickly as the ordinal number of the member is increased and finally reaches an asymptotic value for high members. Thus for Cs(1)/Ar the curve is very close to the abscissa, and the curve for Cs(3)/Ar is quite far apart from it. The increase in slopes for Cs(4), (5), (6) is slowed down more and more so that the curves for Cs(5), Cs(11), and Cs(20) are very close to each other. Similar descriptions can be extended to the case of Kr and Xe except that the magnitude of shift is higher.

Furthermore, Fig. 5 also indicates that one could determine the shift of as high as the 20th member line for argon at rd ~ 3. Because of an increase in broadening for heavier gases, high-member lines diffuse out very fast. Thus at rd ~ 3 one could observe the shift up to the 15th member in Kr and up to only the 11th member in Xe.

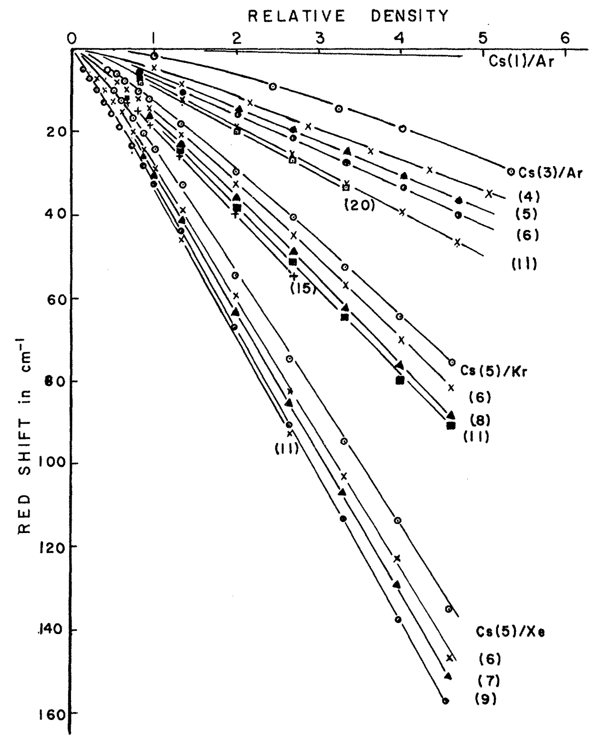

FIG. 5. Red shift of some high-member lines of Cs principal series in Ar, Kr, and Xe.

If one defines "the relative shift" of a line as the ratio of the shift (in cm^{-1}) of that line to the asymptotic value of shift for high members, a very detailed description of the behavior of shift of various lines can be given, such as the case for Cs/Ar

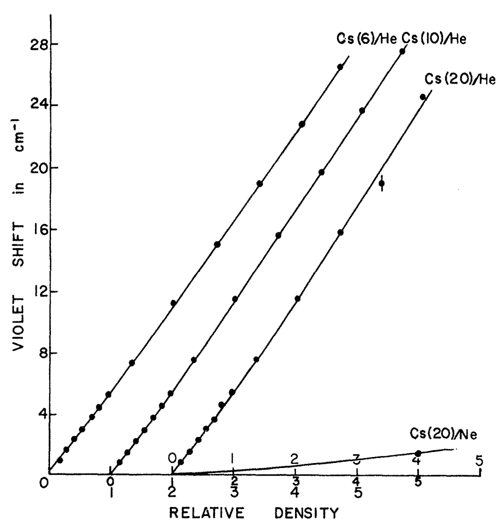

FIG. 6. Violet shift of some high-member lines by He.

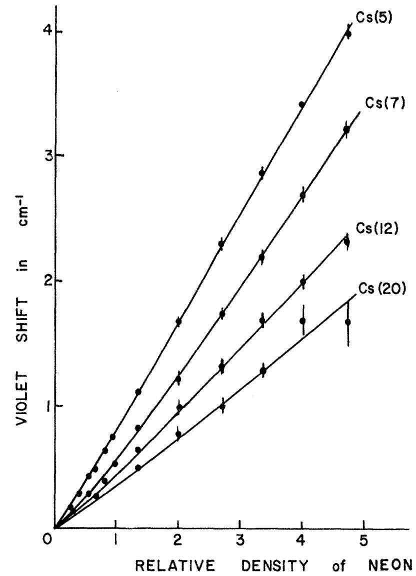

FIG. 7. Violet shift of some high-member lines by Ne ($T-550$ °K). Note that the shift for lower-member lines is greater than that for higher-member lines.

shown in Table I as an example. For rd < 5 the shift of Cs(1) is under 2.5%, 1.5%, and 1% of the asympototic constant shift for high members for Ar, Kr, and Xe, respectively.

Some of the corresponding results for Cs high-member lines in He are shown in Fig. 6. The asymptotic shift for high-member lines is +5.85 cm^{-1} at rd = 1. If one plotted the violet shift versus series members for Cs/He at various rd's one found the curves are quite similar to that shown for Rb/He.[3] When the rd is higher than 5, an indication of a weak maximum at around the 8th member will be seen for both Rb/He and Cs/He.

The measurement of the violet shift of the $^2P_{3/2}$ component of high-member doublets produced by neon was extended from 0.7 to 4.73rd. Some results are shown in Fig. 7. With the range of rd so increased, one could determine the slopes of the plots of $\Delta\nu_m$ versus rd with more accuracy. Consequently, the values for the 5th up to the 20th members in the 3rd column of Table I in Paper IV[1] should be improved, and those for the 4th and the 5th columns be added. A plot of the slope values for various member lines at the first nearly linear region and those for the second nearly linear region are given in Fig. 8. Fig. 8 should supersede Fig. 7 of Paper IV.

A plot of the shift versus series members for Cs/Ne is quite similar to that shown for Rb/Ne.[3] For Rb/Ne a maximum shift was measured near the 5th (or between the 5th and the 6th member) member, while for Cs/Ne the maximum happened

TABLE I. The relative shifts of the $^2P_{3/2}$ components of various doublets of the Cs principal series by argon with respect to the asymptotic values of shift for high-member lines.

rd	Cs(1)	Cs(2)	Cs(3)	Cs(4)	Cs(5)	Cs(6)	Cs(7)	Cs(8)	Cs(9)	Asymptotic value (cm^{-1})
0.291	0.0215	0.063	0.121	0.208	0.620	0.690	0.801	0.869	0.890	3.0
0.815	0.0216	0.064	0.148	0.556	0.640	0.712	0.811	0.855	0.892	8.2
1.35	0.0217	0.067	0.209	0.554	0.648	0.755	0.827	0.858	0.890	13.5
2.02	0.0218	0.105	0.309	0.601	0.677	0.791	0.842	0.872	0.895	20.2
2.69	0.0221	0.141	0.401	0.635	0.710	0.793	0.843	0.874	0.900	27.0
3.36	0.0228	0.168	0.450	0.650	0.733	0.818	0.856	0.895	0.920	33.8
4.03	0.0235	0.182	0.476	0.671	0.756	0.831	0.873	0.914	0.941	40.1
4.70	0.0244	0.195	0.494	0.683	0.777	0.848	0.880	0.924	0.946	47.3

also close to the 5th (or between the 4th and the 5th member) member. Then the shift gradually decreased approaching an asymptotic value for very high members. For rd = 1, the asymptotic value was $+0.36\,cm^{-1}$.

The authors would like to point out that the shift of the high-member lines is not strictly linearly proportional to rd for all rare gases. As shown in Figs. 5–7, a slight but definite increase in slope at higher rd was detected for both red-shift and violet-shift perturbers. In Fig. 9, the shift of the $^2P_{3/2}$ component of first 20 absorption doublets is plotted for all rare gases at nearly the same rd of about one, and temperature ($T = 277\,°C$).

The pressure shift of very high-member lines was treated theoretically by Fermi[4] and Choudhury.[5] They gave a correct prediction that the shift of high-member lines for a given rd is constant and is independent of the nature of the optical atoms but dependent on the nature of foreign gases, but did not predict the correct dependence of shift on rd when rd is higher than 1 for Ne or higher than 2 for other rare gases.

The first line in Table II gives the slopes of the plots of the observed asymptotic values of shifts versus rd (in cm^{-1}/rd) for Cs high-member lines in various rare gases. The subsequent lines give, respectively, the temperature of the absorption column at which the measurements were made, the ranges of rd of rare gases employed, the upper pressures of rare gases in lb/in^2, the dielectric constant ϵ used in computations of Δ_6 and Δ_σ from Fermi's equations[6] and σ, the effective collision cross section for all atoms in 1 cm^3 at 1 Torr and

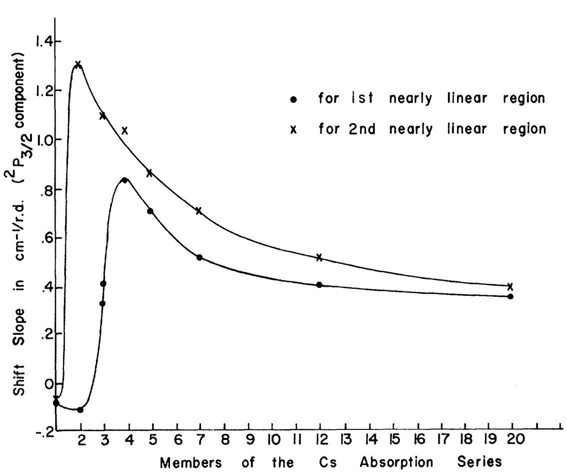

FIG. 8. Slopes of the shift versus rd (Ne) curves for the $^2P_{3/2}$ components of various series lines: • for the initial nearly linear region; × for the second nearly linear region. This graph supersedes Fig. 7 of Paper IV.

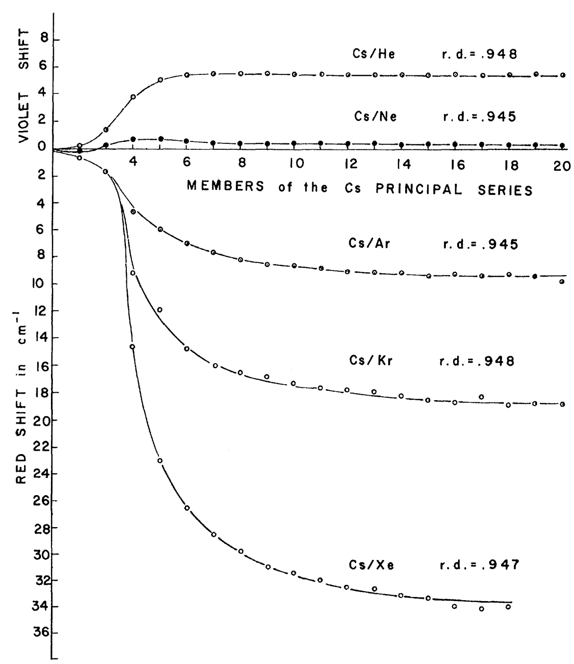

FIG. 9. Plots of the shifts versus series members for various gases at nearly the same rd and temperature ($T = 277\,°C$).

TABLE II. The slope of the plots of the observed asymptotic values of shift versus rd (in cm^{-1}/rd) for Cs high-member lines in various rare gases, and other data.

Cs	He	Ne	Ar	Kr	Xe
$\Delta(cm^{-1}/rd)$	5.85	0.366	−10.04	−19.6	−35.0
Temp. (°C)	277	277	277	185–231	277
Range of rd	0–5	0–5	0–5	0–3.5	0–1[a]
Upper Pressure (p.s.i.)	140	140	140	100	40
$(\epsilon-1)\ 10^{-6}$	67	123	504	768	1238
Δ_ϵ (red)	− 0.184	−0.339	− 1.39	− 2.11	− 3.41
Δ_σ	6.03	0.705	− 8.65	−12.5	−31.6
$\sigma\ cm^2/cm^3$	15.0	0.205	30.8	64.3	411
σ by other	11.7[b]	0.23[c]	42[b] 25.2[c]	121.3[d]	412[e]
authors	15.5[c,f]	0.24[f]	23.7[f]		

[a] Δ increases more than linear with rd for values higher than 1.
[b] E. Amaldi and E. Segre, Nuovo Cimento 11, 145 (1934).
[c] C. Füchtbauer, P. Schultz, and A. F. Brandt, Z. Physik 90, 403 (1934).
[d] C. Füchtbauer and H. J. Reimers, Z. Physik 95, 1 (1935).
[e] C. Füchtbauer and F. Gossler, Z. Physik 93, 648 (1935).
[f] T. Z. Ny and S. Y. Ch'en, Phys. Rev. 51, 567 (1937).

0 °C. The results of σ depend on the accuracy of the values of ϵ which should be used. The ϵ values in Table II are for gases at 1 atm and 25 °C only. The dielectric constants are known to decrease with temperature and to increase with pressure and with the frequency of the oscillating field.[7] The ϵ values need to be corrected for temperature, and therefore should be smaller. Consequently, the Δ_ϵ values appearing in Table II should be a little too high. Nevertheless, our values would be more accurate than those reported by other workers previously.

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[2] G. D. Mahan, J. Chem. Phys. 50, 2755 (1969).
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[7] X. Landolt-Bornstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin 1951), Vol. 1, Pt. 3, p. 896.