acids and pectic acid are not. Evidently the resistance to swelling at high relative humidities at 25° exhibited by the crystallites of sodium pectate and L51 is not related to the behavior of the sample when placed in contact with liquid water.

Acknowledgments.—We wish to express our appreciation to W. D. Maclay, H. S. Owens and R. M. McCready for generously furnishing us with the samples used in this investigation, as well as the analytical data given in Table I. We also wish to thank D. E. Jamison for his help in making some of the BET calculations.

Summary

The equilibrium moisture content at ten relative humidities between zero and 95% are given for seven pectinic and two pectic acids. The moisture content was found to be essentially independent of the methoxyl content.

The free energy change (average about 1600 cal./mole) is considerably higher than found for most proteins.

The BET constants have been calculated. The value of a_1 is nearly the same for all samples and corresponds to approximately one water molecule per galacturonic acid unit.

The variation of the equatorially accentuated X-ray reflection with water content has been determined. These results show that the interchain distance within the crystalline regions increases with increase in water content for all samples, except that having the highest methyl ester content (10.9%). In this latter sample the interchain separation appears to be independent of the water content.

ALBANY, CALIFORNIA RECEIVED JUNE 2, 1947

[CONTRIBUTION FROM THE COATES LABORATORIES, LOUISIANA STATE UNIVERSITY]

The Near Ultraviolet Absorption Spectra of the Vapors of the Monodeuterated Toluenes

BY A. R. CHOPPIN AND C. H. SMITH[1]

The study of the spectra of compounds in which hydrogen is partially or entirely replaced by deuterium is of importance in that it provides data on molecules having the same force constants but different masses and mass distributions. Such data are of assistance in identifying the vibrational forms corresponding to particular frequencies, and provide the additional frequencies which are often needed for the solution of secular equations and the calculation of numerical values for force constants.

Spectral data on deuterium substituted benzene derivatives are rather meager, although such data on benzene itself is extensive.[2,3,4,5] The infrared[6] and ultraviolet[7] absorption spectra of phenol-*d* and aniline-d_2 have been determined, but no report of work on benzene derivatives with nuclear deuteration has been found. This paper presents the results of a study of the near ultraviolet absorption spectra of the vapors of the following compounds: toluene, toluene-α-*d*, toluene-2-*d*, toluene-3-*d*, and toluene-4-*d*.[8] The spectrum of toluene vapor has been extensively investigated by many workers. The latest study is that of Ginsburg, Robertson and Matsen.[9] Such studies of the deuterated toluenes have not been reported.

Experimental

Preparation of Compounds.—Merck "Reagent Grade" toluene was purified by sulfonation, recrystallization of the sodium *p*-toluenesulfonate from saturated sodium chloride solution and regeneration of the toluene by steam distillation of a solution of the sodium *p*-toluenesulfonate in 80% sulfuric acid. The toluene layer was thoroughly washed with sodium hydroxide solution, cold concentrated sulfuric acid and with water. After drying over sodium and distilling over sodium, the middle fraction of the toluene boiled at 110.6 and had a refractive index (n^{20}D) of 1.4965.

Each of the deuterated toluenes was prepared by treating the Grignard reagent, made from the appropriate halogenated toluene, with an equivalent amount of 99.9% deuterium oxide. Volatile components of the reaction mixture were removed by distillation, using an oil-bath. The temperature of the bath was not allowed to rise above 150°. The distillate was fractionated, using a packed eight-inch column, until the temperature of the vapors had risen to 50°. The distillate from the fractionation contained most of the ether and was discarded. The residue from the fractionation was thoroughly extracted with cold concentrated hydrochloric acid in order to remove the remainder of the ether. Then it was

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(1) Ethyl Corporation Research Fellow at Louisiana State University during this research.

(2) Langseth and Lord, *Det. Kgl. Danske Videnskabernes Selskab*, **16**, no. 6 (1938).

(3) Bailey, Hale, Ingold and Thompson, *J. Chem. Soc.*, 931 (1936).

(4) Miller and Crawford, *J. Chem. Phys.*, **14**, 292 (1946).

(5) Bailey, Hale, Herzfeld, Ingold, Leckie and Poole, *J. Chem. Soc.*, 255 (1946).

(6) Williams, Hofstadter and Herman, *J. Chem. Phys.*, **7**, 802 (1939).

(7) Ginsburg, Symposium on "Color and the Electronic Structure of Complex Molecules," Northwestern University, December, 1946.

(8) The nomenclature of the deuterated compounds corresponds to that recommended by the American Chemical Society Committee on Nomenclature, Spelling and Pronunciation, *Ind. Eng. Chem., News Ed.*, **13**, 200 (1935). This is a modification of the nomenclature suggested by Boughton, *Science*, **79**, 159 (1934).

(9) Ginsburg, Robertson and Matsen, *J. Chem. Phys.*, **14**, 511 (1946).

washed, dried and distilled to obtain the deuterated toluene. The deuterated compounds were prepared from the following halogenated compounds: toluene-*α*-*d* from benzyl chloride; toluene-2-*d* from *o*-bromotoluene; toluene-3-*d* from *m*-bromotoluene; toluene-4-*d* from *p*-bromotoluene. When the spectra of these compounds were determined it was evident that toluene-2-*d*, toluene-3-*d* and toluene-4-*d* contained some ordinary toluene. The spectrum of toluene-*α*-*d* was so similar to that of ordinary toluene that it was impossible to detect any small amounts of toluene that may have been present. From the intensities of the 0,0 bands of toluene in the spectra of the three ring deuterated toluenes, it was estimated that the latter contained from 5 to 10% toluene.[10,11]

Spectroscopic Procedure.—The spectra were determined using a Bausch and Lomb Large Littrow Spectrograph with a Hanovia Hydrogen Discharge Tube as the source of the ultraviolet continuum. Absorption cells, varying in length from 20 to 100 cm., were constructed of Pyrex with optically flat quartz end pieces. Spectra were determined at temperatures varying from 20 to 150°. The cells were heated by liquids circulating in an outer jacket. A slit width of two microns and an exposure time of three minutes were used. Eastman Spectroscopic Plates, Type IV-O, developed for five minutes in Eastman D-19 at 18°, proved most satisfactory. Positions of the absorption maxima were determined using a visual wave length comparator equipped with a Variac to control the intensity of the light source. Wave numbers were determined by interpolation between the wave numbers of lines of the iron arc. The iron arc was photographed along with the absorption spectrum by means of a Hartmann diaphragm. Wave lengths of the iron lines were determined by comparison with standard prints.[12] Wave numbers of the iron lines were calculated from these wave lengths using the data of Kösters and Lampe on the refractive index of air.[13]

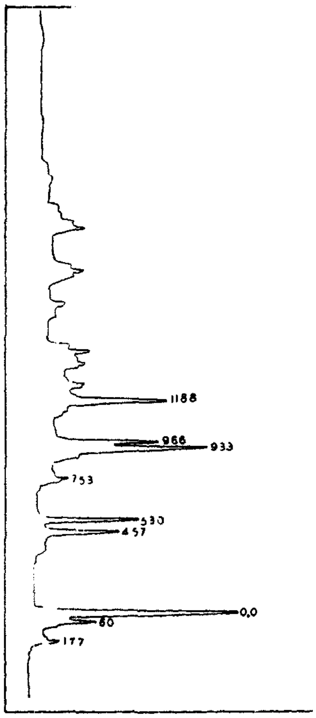

Fig. 1.—Microphotometer trace of the absorption spectrum of toluene.

Intensities were determined by means of a Leeds and Northrup Recording Photoelectric Microphotometer. The absorption does not follow Beer's law; the bands are widened and flattened as the pressure increases. Intensities are reported on a logarithmic scale giving the strongest line of each compound a value of 1000. In determining intensities, account was taken of the presence of continuous absorption and of the overlapping of bands, thus giving the individual bands an intensity more nearly what they would have if they were not overlapped by other bands. Since all of the bands could not be photographed on a single plate or at the same pressure, it was necessary to adopt secondary standards of intensity from among the bands which could be compared directly with the strongest band. The *relative* intensity of the bands is not greatly changed by a change in pressure. In this way a much better approximation to the intensities was obtained than could have been gotten by the use of Beer's law.

Experimental Results.—Tables showing the wave numbers, intensities, and wave number differences (from the 0,0 band) and giving a partial analysis of the bands will be available from the American Documentation Institute.[13a] Figures 1 through 5 give microphotometer tracings of the spectra taken at 5 mm. pressure in a 30 cm. cell. Finer details of the spectra are not visible on these small tracings.

The 0,0 Bands.—The position of the vibrationless transition in toluene is fixed at the

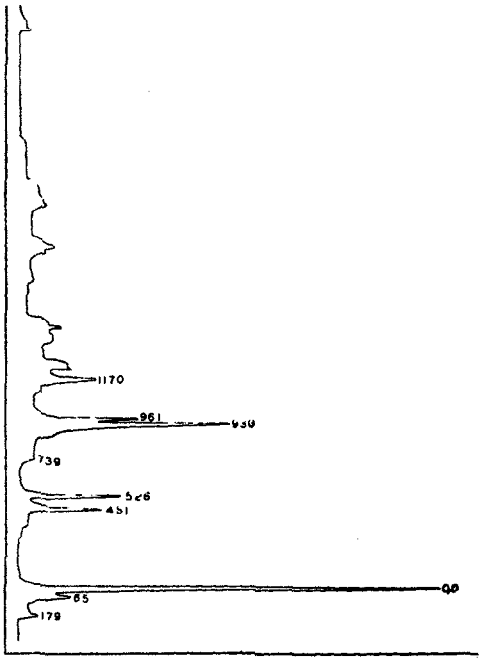

Fig. 2.—Microphotometer trace of the absorption spectrum of toluene-*α*-*d*.

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(10) Due to the small amount of deuterium oxide that was available it was not considered advisable to use up this material in perfecting the experimental technique so as to eliminate the presence of ordinary toluene in the products. The situation is greatly improved now that the United States Atomic Energy Commission has made deuterium oxide more available.

(11) Since these compounds were prepared a technique for preparing pure deuterated benzenes using the Grignard reaction has been published in detail: see Weldon and Wilson, *J. Chem. Soc.*, 235 1946).

(12) Purchased from Adam Hilger, Ltd.

(13) Kösters and Lampe, *Physik. Z.*, **35**, 223 (1934).

(13a) Address American Documentation Institute, 1719 N St., N.W., remitting for Document 2485 $2.40 for photoprints or $0.50 for microfilm.

TABLE I

OBSERVED FUNDAMENTALS

Toluene		Toluene-α-*d*		Toluene-4-d		Toluene-3-d		Toluene-2-d	
Ground	Excited	Ground	Excited	Ground	Excited	Ground	Excited	Ground	Excited
520[a]	457[a]	514[a]	451[a]	516[a]	452[a]	521	458	515	455
624[a]	530[a]	626[a]	526[a]	618[a]	523[a]	620	526	618	526
787[a]	753[a]	776[a]	739[a]	784[a]	744[a]	770	719	786	745
1003[a]	933[a]	1005[a]	930[a]	987[a]	909[a]	816	799?	821?	784?
	966[a]		961[a]		932[a]	875	841	846?	831
1210[a]	1188[a]	1200[a]	1170[a]		961	939	902	955?	900
	979?		978?	1211[a]	1190[a]	1001	967	994	946
1581	1572		1566		1568	1206	1172		953
	3075?		3067?		3071?		1572	1215	1184
							3051?		1572
									3072?

[a] According to the interpretation developed in this article, these frequencies correspond to Class A_1 carbon vibrations.

37478 cm.$^{-1}$ band (strongest of spectrum) by a comparison with the Raman spectrum,[14,15] according to Masaki[16] and Ginsburg, Robertson and Matsen.[17] The corresponding bands in all of the toluenes are as follows (in cm.$^{-1}$)

Toluene	37478
Toluene-α-*d*	37487
Toluene-2-*d*	37513
Toluene-3-*d*	37511
Toluene-4-*d*	37511

The shifts in the position of the 0,0 band are ascribed to the existence of zero-point vibrational energy.

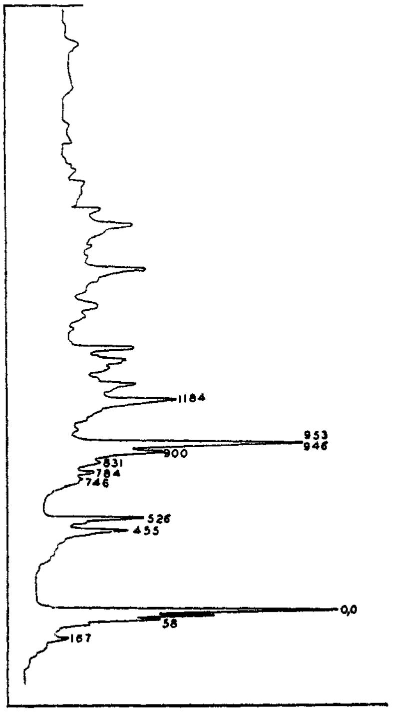

Fig. 3.—Microphotometer trace of the absorption spectrum of toluene-2-*d*.

Difference Frequencies.—On the low frequency side of the 0,0 band of each of the compounds is found a group of strong bands. These bands are interpreted as difference frequencies (1–1 transitions), in agreement with the interpretation of Ginsburg, Robertson and Matsen[17] for toluene.

Fundamental Vibrational Frequencies.—The presence of difference, overtone and combination frequencies renders the identification of fundamentals somewhat difficult. Therefore, the following list must be considered tentative and subject to revision when the Raman and infrared spectra have been studied. Doubtful fundamentals are marked with a question mark. Corresponding lines in the ground and excited states of each compound have been placed on the same line.

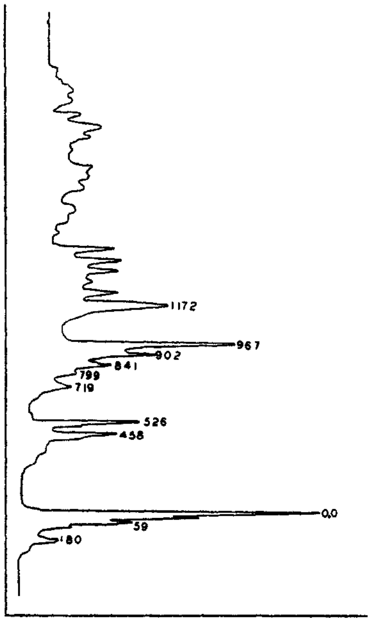

Fig. 4.—Microphotometer trace of the absorption spectrum of toluene-3-*d*.

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(14) Howlett, *Can. J. Res.*, **5**, 572 (1931).

(15) Kohlrausch and Wittek, *Monatsh.*, **74**, 1 (1941).

(16) Masaki, *Bull. Chem. Soc. Japan*, **11**, 346 (1936).

(17) Ginsburg, Robertson and Matsen, *J. Chem. Phys.*, **14**, 511 (1946).

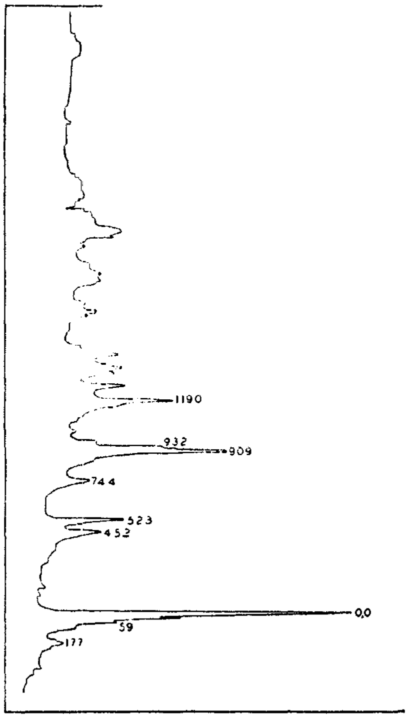

Fig. 5.—Microphotometer trace of the absorption spectrum of toluene-4-*d*.

Theory.—From heat capacity measurements Pitzer and Scott[18] concluded that in toluene the potential hindering methyl group rotation must be extremely small, so that at ordinary temperatures this group has essentially free rotation. In this case, at most positions of the methyl group, the molecule has no symmetry elements. However, on a time average the hydrogens on the methyl group would be smeared out in a cone and the molecule would have C_{2v} symmetry, and at no time would its symmetry vary greatly from C_{2v}. For the following discussion, C_{2v} symmetry is assumed for toluene,[18] toluene-α-*d* and toluene-4-*d*, and C_s symmetry for toluene-2-*d* and toluene-3-*d*.

Herzberg and Teller[19] applied the Franck–Condon Principle to the vibrations of polyatomic molecules during an electronic transition and concluded that, for an allowed transition taking place from the vibrationless ground state, the absorption is intense only when totally symmetrical vibrations are excited in the upper electronic state (the 0,0 band is also intense). For the toluenes of C_{2v} symmetry only the vibrations of class A_1 should appear strongly in the near ultraviolet absorption. However, Ginsburg, Robertson and Matsen[17] assigned one of the stronger lines of the spectrum of toluene (624 cm.$^{-1}$ in the ground state and 530 cm.$^{-1}$ in the excited state) to a Class B_1 vibration. This assignment is supported by the observation of Cleveland[20] that the 624 cm.$^{-1}$ line in the Raman spectrum is depolarized. It agrees with the interpretations of the spectra of fluorobenzene,[21] chlorobenzene,[22] phenol,[23] and aniline.[24] Pitzer and Scott[18] made a complete assignment of the toluene vibrations and assigned the 624 cm.$^{-1}$ line to class B_1.

The authors have developed a different assignment for the toluene vibrations by way of the following steps:

An examination of the spectra of the toluenes shows that, for the excited state, there are no *strong* fundamentals in the region of the hydrogen valence-stretching vibrations. This leads to the assumption that *no hydrogen vibrations appear strongly in the near ultraviolet absorption spectra of the toluenes*. Presumably this statement would hold for other benzene derivatives also. The assumption is reasonable since the absorption largely involves the electrons of the ring carbon atoms.

According to group theory there should be *six* carbon vibrations of class A_1 for each of the toluenes of symmetry C_{2v}. Six strong fundamentals are observed in the excited state of these compounds. This leads to the assumption that *the six strong fundamentals in the excited state of the toluenes of symmetry C_{2v} correspond to the six carbon vibrations of class A_1*. These frequencies are given in Table I. The corresponding ground state frequencies are also given. This assignment differs from the usual one in that the 624 cm.$^{-1}$ line in toluene is assigned to class A_1 instead of Class B_1. Theoretically, the degree of polarization of a Raman line produced by a totally symmetric vibration may vary from total polarization to depolarization. Therefore, the observation that the 624 cm.$^{-1}$ line is depolarized does not exclude the possibility of its belonging to a totally symmetric vibration.

Vibrational Forms.—By a consideration of the frequency changes upon the introduction of deuterium, it is possible to arrive at certain rather hypothetical vibrational forms.

The vibrations at 520 cm.$^{-1}$ and 624 cm.$^{-1}$ in the ground state of toluene are recognized as being due to planar bending of the ring by a comparison with the benzene assignments.[25] The 520 cm.$^{-1}$ frequency is reduced almost equally by substitution of deuterium on the methyl group or on the para carbon atom. This indicates that the methyl group and the para carbon atom form parts of vibrating groups whose amplitudes along the twofold axis are about the same. The only way that this can happen so as to preserve the center of gravity of the molecule is for the ortho and meta carbon atoms to possess a component of vibration in the same direction as the para carbon atom.

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(18) Pitzer and Scott, THIS JOURNAL, **65**, 803 (1943).

(19) Herzberg and Teller, *Z. physik. Chem.*, **B21**, 410 (1933).

(20) Cleveland, *J. Chem. Phys.*, **13**, 101 (1945).

(21) Wollman, *ibid.*, **14**, 123–130 (1946).

(22) Sponer and Wollman, *ibid.*, **9**, 816 (1941).

(23) Matsen, Ginsburg and Robertson, *ibid.*, **13**, 309 (1945).

(24) Ginsburg and Matsen, *ibid.*, **13**, 167 (1945).

(25) Angus, Bailey, Hale, Ingold, Leckie, Raisin, Thompson and Wilson, *J. Chem. Soc.*, 971 (1936).

The mode of vibration must be very similar to that indicated in 1 of Fig. 6.

The 624 cm.$^{-1}$ frequency in toluene is very little affected by substitution of deuterium on the methyl group but is more affected by substitution of deuterium on the para carbon atom. This indicates that the amplitude of the methyl group is very small but that of the para carbon atom is rather large. The mode of vibration must be similar to 2 of Fig. 6.

The frequency at 1003 cm.$^{-1}$ in the ground state of toluene is recognized by its high intensity, high polarization in the Raman spectrum and by its frequency value, as corresponding to the carbon-to-carbon valence-stretching vibration which is totally symmetric in benzene. Agreeing with this mode of vibration, its frequency is little changed in toluene-*α-d* but is reduced in toluene-4-*d*. The vibrational mode corresponds to 3 of Fig. 6.

In studies with vibrating mechanical models, Teets and Andrews[26] observed a mode in which the methyl group vibrated against the remainder of the molecule. Now Lewis and Houston[27] observed the C–C valence-stretching vibration of ethane in the Raman spectrum at 993 cm.$^{-1}$. If the single C–C bond in toluene has the same force constant, the vibrational frequency of the methyl group against the remainder of the molecule is calculated to be 770 cm.$^{-1}$, taking the change in mass into account. This value is very close to the observed frequency of 787 cm.$^{-1}$ in the ground state of toluene. Furthermore this frequency is reduced much more in toluene-*α-d* than it is in toluene-4-*d*, agreeing with the idea that this vibration chiefly involves the methyl group against the ring, as is shown in 4 of Fig. 6.

The 1188 cm.$^{-1}$ frequency in the excited state of toluene is strongly reduced by substitution of deuterium on the methyl group but not by deuterium on the para carbon atom, indicating that the methyl group has a large amplitude but the para carbon atom does not. Form 5 of Fig. 6 gives a satisfactory mode of vibration.

The 966 cm.$^{-1}$ frequency in the excited state of toluene is reduced much more by substitution on the para carbon atom than it is by substitution on the methyl group, indicating a form similar to 6 of Fig. 6.

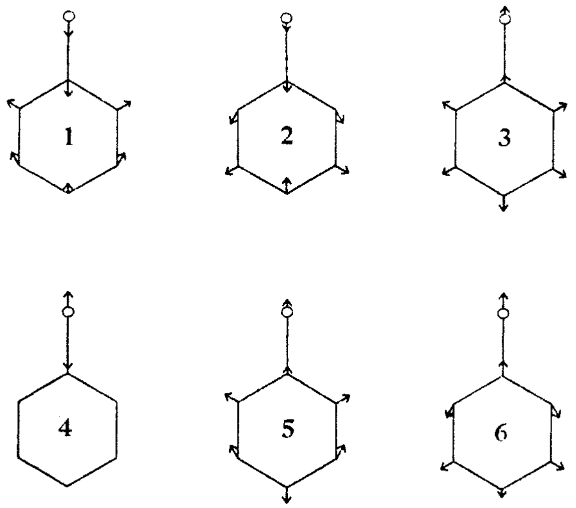

Fig. 6.—Approximate vibrational forms of the toluenes of C_{2v} symmetry. Carbon vibrations of class A_1.

It is realized that these modes of vibration are highly hypothetical. They afford, however, a satisfactory and logical explanation of the data. Both the assumptions and the vibrational forms are to be taken as working ideas, pending further investigations now in progress in this Laboratory.

Toluene-2-d and Toluene-3-d.—These compounds have C_s symmetry and should have eleven totally symmetric carbon vibrations. However, the perturbing effect of deuterium is so slight that the five new vibrations do not appear with such intensity as the six which are totally symmetric in the compounds of C_{2v} symmetry. A greater number of fairly strong fundamentals were found. Additional studies are now being made and will be reported in a subsequent publication.

Summary

The near ultraviolet absorption spectra of the vapors of toluene, toluene-*α-d*, toluene-2-*d*, toluene-3-*d* and toluene-4-*d* have been determined and partially analyzed. It is postulated that the six strong fundamentals in the excited states of the toluenes of C_{2v} symmetry correspond to the six totally symmetric carbon vibrations. The frequencies are correlated with certain hypothetical modes of vibration.

BATON ROUGE, LOUISIANA

RECEIVED JUNE 30, 1947

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(26) Teets and Andrews, *J. Chem. Phys.*, **3**, 175 (1935).

(27) Lewis and Houston, *Phys. Rev.*, **44**, 903 (1933).