Resonance Fluorescence of Benzene. II

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Further study of the resonance fluorescence of benzene with an improved technique is described and the analysis of the spectrum given some time ago by Kistiakowsky and Nelles is amplified and corrected. The new assignment shows that, upon absorption of the 2536A mercury line, only the changes of the quantum number of one (ν_1; $\omega = 990$ cm^{-1}) vibration of the nonexcited benzene molecule are unrestricted in fluorescence. In other vibrations the changes of the quantum numbers are not larger than unity (or two when required by selection rules). This interpretation of the resonance spectrum accounts for most of the line groups measured on the new plates. Five frequencies, besides ν_1, or their multiples can be tentatively identified; they are: 432; 791; 1542; 2557 and 3174 cm^{-1}. The fluorescence of hexadeuterobenzene has also been studied and the spectrum interpreted in the same manner but not as completely as that of benzene. The frequencies observed are: 944 ($\Delta\nu$ unrestricted); 2460. The quenching of the resonance fluorescence of benzene has been investigated with five different gases. This fluorescence is quenched by being changed into high pressure fluorescence. There is very little, if any, loss of electronic excitation energy by benzene molecules on collisions. The quenching action is quite unspecific and appears to increase as the kinetic cross section of the foreign gas molecules. Some new high pressure fluorescence bands have been observed in benzene in the presence of foreign gases. These bands support V. Henri's analysis of the absorption spectrum as consisting of two close electronic levels of the excited molecule. Attempts to excite resonance fluorescence of benzene derivatives have, on the whole, been unsuccessful. Fluorobenzene and toluene, even at 0.01 mm pressure, emit spectra which, by using a spectrograph with a resolving power of better than 25,000, appear nearly continuous. Other derivatives tried have too little fluorescence to study it at low pressures.

Introduction and Experimental Details

SOME time ago, Kistiakowsky and Nelles[2] described experiments dealing with the fluorescence of benzene vapor excited by the monochromatic radiation of the 2536A wave-length. In agreement with the earlier and more qualitative observations of Pringsheim and Reimann,[3] it was found that a lowering of the vapor pressure of benzene produced changes of the spectrum emitted, its structure at low pressures resembling in many ways resonance fluorescence known from studies on diatomic molecules. Although some effort was made in the paper of Kistiakowsky and Nelles (henceforth denoted as I) to give an assignment of the line groups observed, the results were inconclusive and better measurements of the spectrum were clearly needed.

The measurements now presented have been obtained with a technique essentially the same as described previously. In details, however, many improvements were made. The most important of these was the use of the resonance lamp made in one piece out of fused quartz,[4] but otherwise similar to that described in I. The new lamp made it possible to use a much higher current (25–30 amp.) and to maintain better vacuum with a corresponding increase in intensity of the mercury resonance line. In consequence, it became possible to use an efficient system of light blends and to reduce the amount of direct light reaching the spectrograph so far that even after the longest exposures the mercury lines were not very much overexposed and no continuum from the lamp was to be observed on the plates. To get an idea of the efficiency of the optical arrangement chosen, it was found that a strong Raman spectrum excited by the 2536A line was obtained after five minutes' exposure when the resonance tube was filled with liquid water. The exposure time for low pressures of benzene was varied from thirty-five minutes to forty-eight hours and for high pressures from one to thirty minutes depending on the intensity desired.

Two procedures have been used in the study of the quenching of the resonance fluorescence. The one consisted in circulating the quenching gas by means of a high pressure mercury diffusion pump. From the pump the gas passed cold traps for purification, then traps maintained at constant temperature and containing solid benzene for saturation, then the resonance tube and

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[1] Loomis Foundation Fellow.

[2] Kistiakowsky and Nelles, Phys. Rev. **41**, 595 (1932).

[3] Pringsheim and Reimann, Zeits. f. Physik **29**, 115 (1924).

[4] We are greatly indebted to Professor H. S. Taylor of Princeton University for lending us this lamp.

finally, it reentered the pump. In the other procedure, benzene vapor and the other gas were admitted into the resonance tube through fine capillaries from containers maintained at constant pressure. Another narrow tube leading to the pump controlled the total pressure in the resonance tube. The capillaries had been calibrated for gas flow with the substances studied under conditions obtained in the quenching experiments. The total pressure in the resonance tube was also closely followed by means of a heated McLeod gauge. In these and in all previously mentioned experiments the rate of flow was chosen such that only an insignificant fraction of benzene was decomposed during a single passage through the resonance tube.

The same procedure, as in the work on benzene, was employed in the study of the fluorescence of hexadeuterobenzene. The latter has been presented to us, very generously, by Professor H. S. Taylor of Princeton University. Because of the limited amount of substance available, only two plates—one at higher and one at low pressure— have been obtained.

The spectrograph used was a thermostated Hilger E-1 instrument.

THE RESULTS AND INTERPRETATION

The pressure range in which the high pressure type of fluorescence begins to give place to the resonance type was reinvestigated. It was found that in I it was estimated as too low. Actually, already at 0.2 mm pressure there are no visible traces of the high pressure fluorescence on the plates and from this pressure down to 0.005 mm no change in intensity distribution of the spectrum emitted can be observed. The use of water or of strong acetic acid as the cooling jacket around the resonance tube produces no changes in the low pressure spectrum and thus it may be safely concluded that it is due to resonance type of fluorescence of benzene molecules excited by the 2536A line. Even the rather improbable supposition that the life of excited benzene molecules is long enough for them to collide with the walls of the resonance tube before emitting fluorescence, is eliminated by the experiments on quenching. An admixture of 0.5 mm of helium to 0.1 mm of benzene, for instance, produces no visible changes

in the intensity distribution of the spectrum, but it increases considerably the diffusion time of the average benzene molecule to the walls.

The plates obtained showed no continuous background and it was possible, therefore, by extending the exposure time, to obtain many more lines and to follow the spectrum further towards the visible. In all, some 450 lines have been measured on the resonance fluorescence plates. In many instances these "lines" are considerably broader and more diffuse than the mercury lines registered on the same plates, although one could expect the reverse to be true. It is therefore very probable that some of the "lines" measured are in reality unresolved rotational line groups and that therefore the wave numbers obtained have little intrinsic significance. This consideration prompted us to abstain from publishing the complete records of the measurements but they may be found in the thesis submitted by one of us (G. R. C.) to Harvard University. It suffices to state here that the new measurements are found to agree with the old (reported in I) to about ± 1 cm^{-1} or better, wherever the comparison is possible. The lines, as the microphotometer tracing published in I will show, are grouped into more or less distinct groups. Each group is to be interpreted as representing one vibrational transition coupled with several rotational transitions. The structure of the latter could be readily predicted if it was not for the fact that the mercury resonance line consists of several hyperfine components and that each of these may be sufficiently broad to cover more than one absorption line in the benzene absorption spectrum. By disregarding the rotational structure for the time being, the vibrational structure of the spectrum can be rather fully interpreted, but the interpretation deviates in several particulars from that presented tentatively in I. In fact, only one progression, termed A in I, could be extended on the new plates. Table I gives the mean of the wave numbers of the two prominent lines in each group (the center of the doublet); the separation of the groups and the separation of the doublet components. Two more members were visually observed but were too weak to measure.

While the figures leave no doubt as to the reality of the progression, the frequency of the

TABLE I. *Resonance series A of benzene.*

ν cm^{-1}	2536A line 39,412.0		38,424.0		37,434.8		36,448.4		35,463.4		34,479.8		33,495.8		32,515.4
$\Delta\nu$ cm^{-1}		988.0		989.2		986.4		985.0		983.6		984.0		980.4	
Doublet separation			5.7		9.7		12.9		15.5		16.6		19.5		20.2

TABLE II. *Resonance series A of deuterobenzene.*

ν cm^{-1}	2536A line 39,412.0		38,469.0		37,525.0		36,583.0		34,708.0
$\Delta\nu$ cm^{-1}		943		942		938		937	

vibration of the normal benzene molecule involved in it can be established, because of the width of the line group, only to a few wave numbers and the magnitude of the anharmonic term only estimated as being quite small.

The benzene-d_6 yielded a similar progression, given in Table II. The "doublet" structure of the groups is not noticeable, one line being prominent in each group. The progression is much shorter because the plate obtained gave a strong continuous background and the groups could be measured only with difficulty. This vibration, as stated in I, can undoubtedly be identified with the Raman frequencies 991 of benzene and 945[5] of deuterobenzene, ν_1 in the notation of Wilson.[6]

In the first publication the attempt was made to look for doublet structure in other line groups and to find progressions involving other frequencies than the above 990 cm^{-1}. The new plates, however, yielded no extension of the previously suggested regularities comparable to that of the A progression. Furthermore, the existence of the doublets in these other line groups appeared at least very doubtful, their structure varying greatly.

One obtains a more satisfactory representation of the spectrum by assuming that the same frequency of 990 cm^{-1} is involved in other progressions also. Their shift with respect to progression A is to be interpreted then as showing that these progressions are due to combination transitions, involving, besides an arbitrary change in the quantum number of the ν_1 vibration, a change of one or two in the quantum

numbers of one of the other vibrations in the normal benzene. That this interpretation is qualitatively right is demonstrated best by Fig. 1 which shows a microphotometer record of
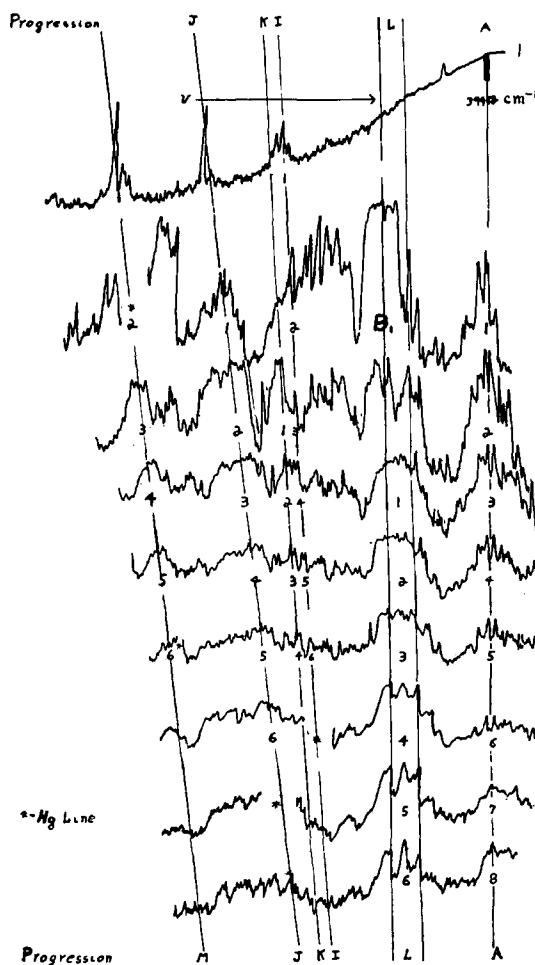

FIG. 1.

[5] Wood, J. Chem. Phys. **3**, 444 (1935).
[6] Wilson, Phys. Rev. **45**, 706 (1934).

TABLE III. *Combination progressions of benzene.*

Series I

ν cm⁻¹	2536A line 39,412		38,979		37,991		37,003		36,014		35,027		34,039
Δν cm⁻¹		432		988		988		989		987		988	

Series J

ν cm⁻¹	2536A line 39,412		37,870		36,876		35,886		34,898		33,910		32,925
Δν cm⁻¹		1542		994		990		988		988		985	

Series K

ν cm⁻¹	2536A line 39,412		36,965		35,970		34,977		33,985
Δν cm⁻¹		2557		995		993		992	

Series L

ν cm⁻¹	2536A line 39,412		36,237		35,238		34,244	33,251		32,259		31,274*		30,289*
Δν cm⁻¹		3174		999		994		993		992		985		985	

Series M

ν cm⁻¹	2536A line 39,412		38,621		37,628		36,638		35,653		34,667		33,684
Δν cm⁻¹		791		993		990		985		986		983	

* Very weak.

the spectrum after it had been cut into sections covering about 990 cm⁻¹ each and these placed one below the other. The structures of all these sections show great similarity, although some new progressions appear on sections further away from the exciting line and others disappear. The new interpretation has another point in its favor, namely, that groups of similar fine structure are now found to belong to the same progressions, while groups belonging to different progressions show, in general, quite different appearances. The complete repetition of the fine structure in succeeding groups is the main guide in selecting progressions given in Table III. Some others could perhaps be added, but in general we find the selection not altogether easy and free from arbitrariness. Concerning series L it should be remarked that although the microphotometer tracing indicates the possibility of extending this progression nearer to the exciting frequency, the two line groups in question have quite a different structure and no 990 cm⁻¹ intervals can be found. Furthermore, in benzene-d_6 these groups are considerably displaced, having even no superficial connection to the L series.

It is quite easy to select corresponding lines in groups belonging to one progression, but the decision, as to which of the several possible lines to use for comparison, is quite arbitrary. Therefore the 990 cm⁻¹ frequency is determined in the above progressions with a reasonable degree of accuracy, while the other frequencies may be in error by as much as 20 cm⁻¹. No attempt was made, in selecting progressions of Table III, to choose only frequencies known from Raman spectra because the symmetry character of excited benzene molecules is unknown and thus uncertainty exists concerning selection rules in resonance fluorescence. Actually, the agreement of the frequencies of Table III with Raman data is not perfect but it is probably premature to draw from this conclusions concerning the approximate shape of the excited molecule.

In the spectrum of deuterobenzene only one combination progression could be identified with some certainty, and is given in Table IV.

TABLE IV. *Combination progression of benzene-d_6.*

Series L

ν cm⁻¹	2536A line 39,412		36,944		35,996		35,052
Δν cm⁻¹		2468		948		944	

While the progression is quite short, its reality is well established, the groups being the most prominent in the spectrum. Their fine structure is quite similar to those of the L progression in benzene and therefore we regard both as involving the same vibration. These groups consist of five strong and approximately equidistant lines with 10–11 cm⁻¹ separation. The middle lines of the groups have been given in the tables. The spectrum of benzene-d_6 contains several other diffuse and indistinct groups which can be arranged into 940–950 cm⁻¹ progressions. How-

ever, the origins of these progressions are quite uncertain and the number of members in each is short. It is therefore of little value to give them here.

The benzene-d_6 resonance spectrum, contrary to findings with benzene, shows a rather diffuse anti-Stokes group, with the most prominent lines at 40,163, 40,149 and 40,139 cm^{-1}; thus an absorption band originating from a vibrating state of the normal molecule with about 720–750 cm^{-1} energy must overlap the mercury resonance line.

The most prominent group in the benzene spectrum, denoted as B_1 in the first communication, could not be fitted into any of the progressions. This same group appears also in the spectrum of benzene-d_6, although it has lost here its particular prominence. The separation from the exciting line has been changed from 1187–1216 to 1121–1158 cm^{-1}. This eliminates the possibility of identifying this group with the Raman frequency 1178, since the latter is supposed to be changed in benzene-d_6 to 873 cm^{-1}.[4]

The rotational structure of the resonance spectrum remains quite uncertain. Because progression A of benzene-d_6 and all other progressions of both isotopic modifications do not show a doublet structure, we believe now that undue importance was attached to such appearance of the groups in the first communication. Rather, the "doublets" are due to a more or less "accidental" grouping of rotational lines; however, only photographs taken with a much better resolving power spectrograph than that used here can settle the question.

The quenching of benzene resonance fluorescence has been studied with helium, hydrogen, nitrogen, carbon dioxide and cyclohexane as quenching gases. On raising the pressure of the foreign gas, while that of benzene is kept constant, no appreciable weakening of the total amount of fluorescence emitted has been noticed but instead only a gradual transition to the high pressure type of spectrum. Apparently, as remarked already by Pringsheim, the electronic excitation energy is very seldom lost by benzene molecules on collision and only the rotational and vibrational energies suffer losses and changes. The line groups typical of the resonance fluorescence disappear as such and instead fully de-

veloped high pressure bands appear. Thus no evidence of preferential rotational or of vibrational quenching could be obtained. Because of many experimental difficulties only crude visual observations of the quantitative amount of quenching were made by comparing the intensities of the resonance groups and of the high pressure bands on the same plate and taking several exposures at different pressures of the foreign gas. Different parts of the spectrum seemed to be quenched about equally efficiently. Selecting, for instance, the second (most intense) member of the A resonance progression and the first head of the high pressure bands (O_0 in notation adopted in I) equal intensities were obtained in the presence of helium, hydrogen and nitrogen at $ca.$ 12 mm each, with carbon dioxide at 8 mm and with cyclohexane (and benzene itself) at 5 mm pressure. A choice of other groups and bands would give, of course, different numerical results but they all are of the same order of magnitude. There is thus little selective action in quenching resonance fluorescence of benzene and the effectiveness of molecules increases roughly as their kinetic cross sections. At the same time the total efficiency is quite low, if one attributes to the excited benzene molecule a mean life of the order of 10^{-8} to 10^{-7} second.

One result of the quenching studies, which is of some interest, is the finding of several new high pressure bands. These are located near the exciting line, in a region where benzene shows very strong absorption. Their reabsorption is of course the reason why they have not been noticed when, as usual in earlier work, higher pressures of benzene vapor were used, rather than a mixture of very little (0.1 mm) benzene vapor with much foreign gas. The first head of the new bands is at 38,609 cm^{-1} and is followed by other band heads of decreasing intensity in 160 cm^{-1} intervals. Another progression of identical spacing but lower intensity starts at 83 cm^{-1} to the red from the first one. The whole band group thus has an appearance identical with that of the well-known absorption and fluorescence groups of benzene. As the latter, the new band group is repeated to the red in 990 cm^{-1} intervals by other band groups of identical structure. These are mixed with the more intense bands of the main emission spectrum of benzene and only the first

head of the second group can be observed in the microphotometer tracing of the first communication at 135 cm^{-1} to the violet from the O_0 head. The disentanglement of these two progressions clarifies somewhat the high pressure fluorescence spectrum of benzene and shows it to consist of two progressions, each with the 990 interval, one starting at 38,609, the other at 37,481 cm^{-1}. Each member of the progression has the structure as described above and no other bands can be observed in fluorescence excited by the 2536A mercury line. One can interpret the entire spectrum as being due to emission by nonvibrating molecules from two excited electronic levels. This attitude is in conformity with the views of Henri who has interpreted the absorption spectrum with the help of two electronic levels, one at 37,483, the other at 38,612 cm^{-1}, thus with energies identical with those needed to explain the fluorescence spectrum. The difference in intensities of the two band-group progressions in emission one can attribute to the circumstance that the 2536A line coincides with a band belonging to the 37,483 electronic state. On the other hand, Pringsheim has reported that the appearance of the fluorescence spectrum is not affected by a change in the exciting wave-length and this is rather against the outlined interpretation. One way is to regard the upper of the two initial levels as belonging to the same electronic state but with one quantum of vibrational energy of a 1129 cm^{-1} frequency of the excited molecule. It is then necessary to assume that the energy of this vibration is much less readily lost in inelastic collisions than that of the other vibrations of the excited molecule which are known from the absorption spectrum. Neither interpretation is altogether satisfactory.

With benzene-d_6 a spectrum is obtained which is quite similar to that of ordinary benzene. The origin of the strong progression (now with a 945 cm^{-1} interval) is at 37,710 cm^{-1} and that of the faint system at 38,790 cm^{-1}.[7] Both origins are, thus, displaced to the violet, because of a larger zero-point energy of the benzene and benzene-d_6 molecules in their normal, rather than in the excited states. The 160 cm^{-1} frequency of

the ordinary benzene appearing within each band group is changed in benzene-d_6 to 143 (± 1 cm^{-1}) and the weaker of the two such progressions is now displaced to the red by 80 cm^{-1} from the other one.

Although, thus, the two molecules show very similar structure in the band groups, a detailed interpretation of it in terms of molecular vibrations appears to us at present impossible. Assuming tentatively that the entire structure of the band groups is produced by transitions from the same initial level to different levels of the normal molecule, one has to use at least two low frequency vibrations to account for it. Several choices are possible. Thus, for the light benzene, one can use any one of the following pairs: 160 and 83; 80 and 83; 83 and 77, etc. However, as Dr. Wilson has kindly pointed out to us, it is extremely unlikely that there are two vibrations in benzene of quite such low frequency. Furthermore, the selection rules for vibrations ν_4 and ν_{16} of his interpretation, which should have the lowest frequencies of all, are such that, notwithstanding several attempts, it has not been possible to explain the observed structure. It seems more likely at present that only one (160 or $\frac{1}{2}$160 cm^{-1}) frequency of the normal molecule is involved and that the appearance of two progressions is due to electronic multiplicity or the presence of low frequencies in the upper state.

Four benzene derivatives have now been studied in an attempt to produce resonance fluorescence. Fluorobenzene and toluene at ordinary pressures and with illumination by the 2536A line emit a strong fluorescence consisting mainly of a continuum (see a tracing in the earlier communication) with a few faint and indistinct bands. Upon lowering the pressure to about 0.01 mm the appearance of the spectrum hardly changes at all and, if anything, the bands become even fainter.

This behavior seems very hard to understand because, using instruments of about the same resolving power as the spectrograph here used, Henri[8] and others have obtained well-developed banded absorption spectra. It is possible, of course, that from the levels reached upon absorption of the 2536A line, transitions to more

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[7] This was obtained by adding 945 wave numbers to the frequency of the first head of the *second* group of this progression.

[8] Henri, J. de phys. et rad. 9, 249 (1928).

numerous vibrational levels of the normal molecule are consistent with the Franck-Condon rule than is the case in absorption by the nonvibrating molecule. Even allowing this, one does not see why sharp band heads typical of absorption should not be visible in fluorescence.

The fluorescence of chlorobenzene and ethyl benzene was too faint to be followed into the region of low pressures.

In conclusion, it is a pleasant duty to thank Dr. E. B. Wilson for many valuable suggestions and criticisms.

Raman Effect of Acetylenes

II. Diiodoacetylene, Liquid Acetylene and Deuteroacetylenes[1]

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An apparatus consisting of eight discharge tubes for Raman work has been designed which is more convenient than the usual helical design of these light sources. It is possible to arrange these eight tubes concentrically around a Raman tube of any diameter. Cylindrical filters of any dimensions can be interposed with great convenience. The vibration Raman spectra of C_2I_2: 191.3, 310.2, 627.0 688.2 and 2109.4; liquid C_2H_2: 381.6, 618, 631, 1762, 1959 and 3338; gaseous C_2H_2: 1973.8 and 3373.7; gaseous C_2HD: 1851.2 and 3334.8; gaseous C_2D_2: 1762.4 and 2700.5 cm^{-1} have been observed and are interpreted in the usual manner on the basis of symmetry considerations. Striking differences in the spectra of liquid and gaseous acetylene (C_2H_2) indicate a serious distortion of the molecules in the liquid state. The extent of this disturbance seems to change completely the symmetry of the molecules of the liquid which are no longer linear as in the gaseous state. Certain Raman lines are accompanied by faint satellites which fit a rotation formula and may be due to rotation effects. The free energies of C_2HD and C_2D_2 were calculated and the free energy change of the reaction $C_2H_2 + C_2D_2 \rightleftharpoons 2C_2HD$ has been evaluated and the equilibrium constant determined for a series of temperatures.

I. INTRODUCTION

OUR study of acetylenes has been continued with still further improvements in technique. The compounds used are C_2I_2 in alcohol and acetone solution; gaseous and liquefied C_2H_2 (at $-80°C$); gaseous deuteroacetylenes: C_2D_2 and C_2HD.[3]

II. EXPERIMENTAL PROCEDURE

A new set of Ne-Hg discharge tubes

The helical tubes used as light sources in our former researches[4] were inconvenient in respect to the possibility of inserting into the helix, Raman tubes of various diameters. Obviously the internal diameter of the helix determines the maximum thickness of the Raman tubes and the various filters needed at times. The new arrangement shown in Fig. 1 admits any size Raman tube and any number or thickness of cylindrical filters. The greater number of discharge tubes adds to the intensity of illumination. Two such tubes are fed by a 200/7000-volt 3-kva transformer. The whole set-up is sufficiently flexible to have motion in all directions. A cylindrical reflector is used.

[1] Part of this work was reported at the Cleveland meeting of the A. C. S., September 1934.

[2] This article is based upon a thesis presented to the faculty of the Graduate School of the University of Minnesota by Charles E. Morrell in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[3] We are greatly indebted to Professor H. S. Taylor for a generous supply of C_2D_2 prepared under his direction at Princeton University by Dr. J. C. Jungers, C. R. B. fellow from Louvain. The liquid acetylene was prepared from a sample of very pure calcium carbide obtained through the courtesy of Mr. E. C. MacQuigg from the Union Carbide and Carbon Chemicals Corp. to whom we express our thanks. The gas C_2HD was loaned us kindly by Professor L. H. Reyerson of the School of Chemistry of the University of Minnesota.

[4] Glockler and Davis, J. Chem. Phys. **2**, 881 (1934) and Phys. Rev. **46**, 535 (1934); Glockler and Morrell, Phys. Rev. **46**, 233 (1934) and **47**, 569 (1935).