

Mass Spectra of the Deuteroethylenes

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Samples of all of the deuteroethylenes have become available in satisfactory purity, and mass spectra have been measured and corrected for isotopic impurities. The mass spectra of *cis* and *trans* dideuteroethylene are nearly identical, and the spectrum of the asymmetrical dideuteroethylene is similar to the symmetrical molecules in the mass range 24 to 30. The probability of removing an H atom from the deuteroethylenes relative to the probability in C₂H₄ is equal to the a priori probability times 1.10, (1.10)², and (1.10)³ in molecules containing 1, 2, and 3 D atoms, and the relative probability of removing a D atom is 0.90 in C₂D₄ and is nearly equal to the a priori probability times (0.90)², (0.90)³, and (0.90)⁴ in molecules C₂HD₃, C₂H₂D₂, and C₂H₃D, respectively. As the factors 1.10 and 0.90 are nearly reciprocals, these ratios can be expressed as positive and negative powers of 1.10. The probabilities of removing 2, 3, or 4 atoms are powers or products of the probability of removing single atoms, and thus are also positive and negative powers of 1.10. Similar relations are found in the previously published data on deuteroacetylenes.

1. Introduction

Studies of the mass spectra of hydrocarbon molecules containing one or more deuterium atoms have shown that in the case of paraffins [1 to 5]² and simple unsaturated molecules [6, 7] the relative probabilities for dissociating hydrogenic atoms from the deuterated molecule relative to the ordinary molecule are not predictable from a priori possibilities alone. In a molecule containing both protium and deuterium, the probability of removing H atoms is increased, and that of removing D atoms is decreased as compared with removing H from the ordinary compound. Schissler, Thompson, and Turkevich [5] describe this by using two parameters, *a* and *b*, which give the relative probabilities of removing H and D from the deuterated compound as compared with removing H from the ordinary compound.

Unfortunately these parameters are different for different compounds and also for the same chemical compound containing different numbers of D atoms. At the present time there is no general theoretical basis for predicting the spectra of deuterated compounds, and the complexity of the problem increases rapidly with the number of carbon and hydrogen atoms in the molecule. For this reason, the availability of samples of all the possible deuterated ethylenes afforded an exceptional opportunity to study the mass spectra of these compounds. The data are useful not only for analytical applications but also to supply additional information on the relation between dissociation probabilities and isotopic structure.

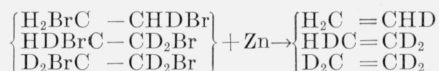
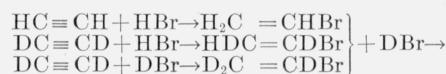
2. Experimental Details

Mass spectra were obtained with a Consolidated 21-103 mass spectrometer. The electron energy was nominally 70 v, with an anode current of 10.5 μ a. The temperature of the ion source was maintained at 250° C. The energy filter at the collector

end was grounded to permit ions resulting from metastable transitions to reach the collector. Other procedures for introducing the samples and obtaining the spectra were conventional.

The ethylene was Phillips Research Grade with a minimum purity of 99.77 mole percent as stated by the manufacturer.

The deuteroethylenes, C₂H₃D, C₂D₃H, and C₂D₄, were prepared by the same general methods described briefly by de Hemptinne, Jungers, and Delfosse [8] and in greater detail by de Hemptinne [9]; i. e., the photochemical addition of hydrogen bromide to acetylene and vinyl bromide. The reactions are briefly summarized as:



Bryce L. Crawford, Jr. of the University of Minnesota very kindly provided a sample of 1,1-dideuteroethylene. The 1, *trans*-2-dideuteroethylene and 1, *cis*-2-dideuteroethylene were part of several samples [10] analyzed for B. S. Rabinovitch of the University of Washington.

As the minimum energy required to form the C₂H₃⁺ ion in ethylene is 3.3 ev greater than that required to ionize the molecule [11], the isotopic purity of the deuteroethylenes was determined by using low-energy electrons in a manner similar to that described by Stevenson and Wagner [12] for deuteroparaffins. Corrections for deuteroethylene impurities were made by using successively corrected patterns. Traces of ethanes were observed in some of the samples, but these did not interfere in the low-voltage measurements. Corrections for the contributions of ethanes were made on the basis of patterns computed on a statistical basis, neglecting the *a* and *b* factors defined above. The measured isotopic purity of the deuteroethylenes was as follows: C₂H₃D, 95 percent; 1,1-C₂H₂D₂, 88 percent;

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²Figures in brackets indicate the literature references at the end of this paper.

1,trans-2-C₂H₂D₂, 97 percent 1,cis-2-C₂H₂D₂, 99 percent; C₂HD₃, 87 percent, C₂D₄, 94 percent.

3. Results

The principal ions in the mass spectra of ethylene and five deuterioethylenes are given in table 1. The relative abundances are tabulated in the conventional manner after correcting for the contributions of ions containing C¹³ in natural abundance. The spectrum of the 1,cis-2-dideuterioethylene is very similar to that of the trans isomer and accordingly is omitted from the table. Also omitted are ions with non-integral values of *m/e*. These "metastable transition" peaks, observed in all of the ethylenes, result from a delay of the order of microseconds in the dissociation of two hydrogenic atoms from the molecule ion. The abundances relative to the molecule ion are about 0.1 percent or less, and in general increase somewhat with increased deuterium substitution.

The total ion abundances of the hydrogen group, Σ*i*_H⁺, the C₁ group, Σ*i*_{C₁}⁺, and the C₂ group, Σ*i*_{C₂}⁺, are given for each molecule at the bottom of the appropriate column. The measured sensitivity (ion current per unit of pressure) of the molecule ion was the same for all of the ethylenes within the estimated error in pressure measurement (about 2%).

TABLE 1. Principal ions in the mass spectra of ethylene and deuterioethylenes for 70-v electrons

<i>m/e</i>	C ₂ H ₄	C ₂ H ₃ D	1,1-C ₂ H ₂ D ₂	1,trans-2-C ₂ H ₂ D ₂	C ₂ HD ₃	C ₂ D ₄
1	6.71	5.81	3.81	3.66	2.10	---
2	0.88	1.17	1.70	1.67	2.47	3.78
3	---	0.26	0.42	0.45	0.26	---
4	---	---	.14	.09	.26	0.64
12	3.17	3.31	3.58	3.33	3.61	3.78
13	4.68	3.34	2.58	1.76	0.97	---
13.5	0.38	0.17	0.11	0.06	.04	---
14	7.83	5.72	6.18	4.03	4.98	6.26
14.5	---	0.28	0.25	0.22	0.22	---
15	0.61	4.38	1.16	8.19	4.05	0.47
15.5	---	---	---	---	0.32	---
16	---	0.42	4.85	0.46	5.13	10.2
17	---	---	0.34	.14	0.28	---
18	---	---	---	---	---	<0.1
24	4.62	4.15	3.75	3.70	3.35	3.04
25	13.5	7.65	4.03	4.07	1.70	---
26	67.5	31.0	15.0	15.5	9.79	10.4
27	67.9	50.6	42.6	41.5	25.8	---
28	100.0	55.6	39.9	41.6	38.2	63.7
29	---	100.0	41.9	40.0	40.8	---
30	---	---	100.0	100.0	22.7	60.8
31	---	---	---	---	100.0	---
32	---	---	---	---	---	100.0
Σ <i>i</i> _H ⁺	7.59	7.24	6.07	5.87	5.09	4.42
Σ <i>i</i> _{C₁} ⁺	16.3	17.2	18.7	17.9	19.0	20.2
Σ <i>i</i> _{C₂} ⁺	253.5	249.0	247.2	246.4	242.3	237.9

3.1. C₂-Group Ions

Two different fragments containing H and D atoms contribute to some of the mass peaks in the C₂ group of the monodeutero- and the dideuterioethylenes. In order to determine the relative probabilities of dissociating two or more protium atoms and one or more deuterium atoms from these molecules,

some assumption must be made concerning the relative amounts of the contributing ions. No assumption need be made in the spectrum of C₂HD₃, as each of the ion peaks has only one possible configuration.

In the computation of the deuteriomethane spectra, the authors assumed that the probability of removing one atom, either H or D, from the deuterio compounds was equal to the probability of removing H from CH₄, and similarly for removing 2, 3, or 4 atoms. This cannot be rigorously true for the ethylenes, for it is seen in table 1 that Σ*i*_{C₂}⁺ decreases regularly with increasing deuterium substitution. It seems reasonable to assume that each of the terms involved in this sum decreases regularly. This is seen to be the case for the loss of four atoms to give C₂⁺. The ratio of relative intensities of C₂⁺ of C₂H₃D to C₂⁺ of C₂H₄ is 0.898; the ratio of C₂⁺ of C₂H₂D₂ (mean of the values of columns 4 and 5 of table 1) to C₂⁺ of C₂H₄ is 0.807; the ratio for C₂HD₃ is 0.725, and for C₂D₄ is 0.658. These four ratios are almost exactly equal to 0.898, (0.898)², (0.898)³, and (0.898)⁴.

TABLE 2. Correction factors necessary to calculate the modified monoisotopic spectra of the deuterioethylenes from ordinary ethylene

Ion	C ₂ H ₄	C ₂ H ₃ D	C ₂ H ₂ D ₂ (average)	C ₂ HD ₃	C ₂ D ₄
C ₂	1	---	0.806 (0.807)	0.724 (0.725)	0.651 (0.658)
ΣC ₂ X ^a	1	(0.898) 0.937	0.878	0.823 (0.851)	(0.770)
ΣC ₂ X ₂	1	0.986	0.972	0.958 (0.948)	(0.944)
ΣC ₂ X ₃	1	0.973	0.946	0.920 (0.935)	(0.895)

^a X represents both H and D atoms.

The first row of table 2 gives these computed ratios, and in parentheses in the second row are the observed ratios. The relative probability of losing 3 atoms from C₂D₄ as compared with C₂H₄ is observed to be 0.770, and it is assumed that the ratio will be (0.770)^{1/4}, (0.770)^{2/4}, and (0.770)^{3/4} in molecules containing 1, 2, and 3 D atoms. Similarly, from the ratio of the C₂D₄ values to the C₂H₄ values one can compute ratios for the loss of 2 and 1 hydrogenic atoms. These data are presented in table 2. In C₂HD₃ the values for these ratios are observed experimentally and are in satisfactory agreement with the computed values. In C₂D₃H and C₂H₂D₂ the computed ratios will be used as correction terms to derive from the C₂H₄ spectrum what might be called the "modified monoisotopic spectra."

The calculations for the individual dissociation probabilities in the C₂H₃D spectrum are illustrated in table 3. In column 2 the abundance of C₂⁺ and C₂H⁺ are the observed values from table 1. It is assumed that [C₂H⁺+C₂D⁺] is equal to the C₂H⁺ abundance of C₂H₄ multiplied by the correction term from table 2, namely, 13.5×0.937=12.65. This value minus the observed abundance of C₂H⁺ from column 2 (7.65) gives the abundance of C₂D⁺ as 5.00. This value subtracted from the 26 peak of C₂H₃D,

31.0 (table 1), gives the abundance of $C_2H_2^+$ as 26.0. Subtracting this from the corrected abundance of $C_2H_2^+$ of C_2H_4 , namely, $67.5 \times 0.986 = 66.5$, gives 40.5 as the abundance of C_2HD^+ . Continuing in this manner, a final value of 55.9 is calculated for $C_2H_2D^+$ as compared with the observed value of 55.6. This agreement is entirely satisfactory.

Columns 3 and 4 of table 3 give the a priori probabilities and the "a priori abundances" of ions of the C_2H_3D spectrum calculated from the C_2H_4 spectrum. These values are quite different from the observed abundances in column 2, and the ratios of the values in column 2 to the values in column 4 give the "weighting factors" of column 5.

TABLE 3. Calculation of individual dissociation probabilities and isotope weighting factors for the C_2 group of C_2H_3D

Positive ion	Relative abundance	A priori probability	A priori abundance from C_2H_4	Weighting factor
C_2	4.15	1	4.62	0.90
C_2H	7.65	$\frac{3}{4}$	10.1	.76
C_2D	5.00	$\frac{1}{4}$	3.38	1.48
C_2H_2	26.0	$\frac{1}{2}$	33.75	0.77
C_2HD	40.5	$\frac{1}{2}$	33.75	1.20
C_2H_3	10.1	$\frac{3}{4}$	17.0	0.60
C_2H_2D	55.6	$\frac{3}{4}$	50.9	1.09
C_2H_3D	100.0	-----	-----	-----

Weighting factors for the other deuterioethylenes have been computed in the same manner and are summarized in table 4. As the observed abundances for the C_2 group of ions of 1,1-dideuterioethylene and *cis* and *trans* 1,2-dideuterioethylene are nearly the same, the mean values of the abundances have been used to compute the weighting factors for the $C_2H_2D_2$

molecules. The last two observed weighting factors in each column correspond, respectively, to the b and a factors as defined by Schissler, Thompson, and Turkevich [5]. This notation has been used with subscripts 1 to 4 referring to the number of deuterium atoms in the molecule. As the factors a and b give the respective probabilities of removing one H or one D atom from the deuterium substituted molecule relative to the probability of removing H from C_2H_4 , it has been commonly assumed that the probability of removing two or more hydrogenic atoms will involve the appropriate powers and products of the a and b factors. These powers and products of a 's and b 's are included in table 4. There is in most cases approximate agreement between computed and observed values. It should be noted that experimental errors are magnified in the product terms.

It is seen from table 4 that there is a very regular sequence in the values a_1, a_2, a_3 , and b_1 to b_4 of the following type: $a_2 = a_1^2, a_3 = a_1^3, b_3 = b_4^2, b_2 = b_4^3, b_1 = b_4^4$. Values $a_1 = 1.10$ and $b_4 = 0.90$ give the best fit to the observed values of a_1, a_2, a_3, b_2, b_3 , and b_4 . As b_4 is nearly equal to the reciprocal of a_1 , it is evident that positive and negative powers of a single constant can represent all seven a 's and b 's, and by the relations shown in table 4 can represent all 26 weighting factors. Table 5 is similar to table 4 but with powers of a single constant $K = 1.10$ in place of a 's and b 's. The agreement between observed and computed values is actually better than that found in table 4 based on seven observed weighting factors. It is to be noted that this reciprocal relationship between a and b factors results in the regular sequence that is observed in the intensity of C_2^+ as deuterium

TABLE 4. Summary of the isotope weighting factors for the C_2 group of the deuterioethylenes

Positive ion	C_2H_3D	$C_2H_2D_2^*$	C_2HD_3	C_2D_4
C_2	0.90 $a_1^2 b_1 = 0.78$	0.81 $a_2^2 b_2^2 = 0.77$	0.73 $a_3 b_3^2 = 0.69$	0.66 $b_4^4 = 0.66$
C_2H76 $a_1^2 b_1 = .71$.60 $a_2 b_2^2 = .64$.50 $b_3^3 = .51$	-----
C_2D	1.48 $a_1^2 = 1.30$	1.16 $a_2 b_2^2 = 1.06$.97 $a_3 b_3^2 = .86$.77 $b_4^4 = .73$
C_2H_2	0.77 $a_1 b_1 = 0.66$	0.66 $b_2^2 = 0.53$	-----	-----
C_2HD	1.20 $a_1^2 = 1.19$.94 $a_2 b_2 = .88$.76 $b_3^2 = .64$	-----
C_2D_2	-----	1.43 $a_2^2 = 1.45$	1.13 $a_3 b_3 = 1.07$.95 $b_4^2 = .81$
C_2H_3	0.60 $b_1 = 0.60$	-----	-----	-----
C_2H_2D	1.09 $a_1 = 1.09$	0.73 $b_2 = 0.73$	-----	-----
C_2HD_2	-----	1.21 $a_2 = 1.21$	0.80 $b_3 = 0.80$	-----
C_2D_3	-----	-----	1.34 $a_3 = 1.34$.90 $b_4 = .90$

*Mean values of 1,1- and 1,2- $C_2H_2D_2$

TABLE 5. Isotope weighting factors for the deuterioethylenes compared with the powers of a single constant, $K = 1.10$

Positive ion	C_2H_3D	$C_2H_2D_2$	C_2HD_3	C_2D_4
C_2	0.90 $K^{-1} = 0.91$	0.81 $K^{-2} = 0.83$	0.73 $K^{-3} = 0.75$	0.66 $K^{-4} = 0.69$
C_2H76 $K^{-2} = .83$.60 $K^{-4} = .69$.50 $K^{-6} = .57$	-----
C_2D	1.48 $K^3 = 1.33$	1.16 $K^{-1} = 1.10$.97 $K^{-1} = .91$.77 $K^{-3} = .75$
C_2H_2	0.77 $K^{-3} = .75$	0.66 $K^{-6} = 0.57$	-----	-----
C_2HD	1.20 $K^2 = 1.21$.94 $K^{-1} = .91$.76 $K^{-4} = .69$	-----
C_2D_2	-----	1.43 $K^4 = 1.47$	1.13 $K = 1.10$.95 $K^{-2} = .83$
C_2H_3	0.60 $K^{-4} = 0.69$	-----	-----	-----
C_2H_2D	1.09 $K = 1.10$	0.73 $K^{-3} = 0.75$	0.80 $K^{-2} = 0.83$	-----
C_2HD_2	-----	1.21 $K^2 = 1.21$	1.34 $K^3 = 1.33$	-----
C_2D_3	-----	-----	-----	.90 $K^{-1} = .91$

atoms are added to the molecule. This supports the assumptions used to compute the correction factors in table 2.

These relations can be expressed in terms of one equation containing only one arbitrary constant. The relative probability, $R_{l,m,n}$ of removing l H atoms and m D atoms from an ethylene molecule containing n D atoms and $(4-n)$ H atoms as compared with the probability of removing H from C_2H_4 is

$$R_{l,m,n} = A_{l,m,n} K^{[ln+m(n-5)]}$$

where $A_{l,m,n}$ is the a priori probability.

3.2. Ions in the Mass Range 1 to 18

The more abundant ions in the m/e range 12 to 18 are C^+ , CH^+ , and CH_2^+ , or ions with one or two D atoms instead of H atoms. There are no significant differences in the spectra of *cis* and *trans* 1,2- $C_2H_2D_2$. The larger peaks in the spectra of 1,1- $C_2H_2D_2$ and 1,2- $C_2H_2D_2$ differ in a manner that is consistent with their structure. In the former compound, CH_2^+ and CD_2^+ are large, and in the latter, CHD^+ is the largest peak. However, a small peak at mass 15 in the spectrum of 1,1- $C_2H_2D_2$ must be in large part CHD^+ , ($C_2H_2D_2^{++}$ accounts for only a small fraction of the observed intensity). The peak at mass 16 in the spectrum of 1,2- $C_2H_2D_2$ is not necessarily CD_2^+ , for an ion CH_2D is also to be expected. Ionization processes involving rearrangements of atoms complicate the interpretation of the spectra in this mass range, and a quantitative determination of weighting factors will not be attempted.

The following ions containing three hydrogenic atoms can be identified in spectra of table 1: CH_3^+ of C_2H_4 , CH_2D^+ of C_2H_3D , and CHD_2^+ from the $C_2H_2D_2$ molecules and from C_2HD_3 . Other possible ions of this class are masked by other isomeric ions. A small H_2O background may mask CD_3^+ ions of C_2HD_3 and C_2D_4 .

Doubly charged ions of half-integer mass number can be identified as follows: $C_2H_3^{++}$ of C_2H_4 , $C_2H_3D^{++}$ of C_2H_3D , $C_2HD_2^{++}$ and C_2HD^{++} of $C_2H_2D_2$, and $C_2HD_3^{++}$, $C_2HD_2^{++}$, and C_2HD^{++} of C_2HD_3 . This indicates that doubly charged ions containing 2, 3, and 4 hydrogenic atoms are present in all the spectra, with the ions of even molecular weight masked by singly charged ions.

It is apparent from table 1 that the relative abundance of the C^+ ions increases as the number of D atoms in the molecule increases, in contrast to the variation of C_2^+ ions with increasing deuterium content. If an average value of 3.45 is taken for the C^+ ions of the $C_2H_2D_2$ molecules, then the abundance of C^+ from the deuterated molecules is $(1.043)^x$ times the abundance of C^+ from C_2H_4 where x is the number of D atoms in the molecule.

The sum of the hydrogenic ions decreases progressively from C_2H_4 to C_2D_4 as the number of D atoms increases, but this decrease is not accurately represented by a power sequence. Weighting factors computed for H^+ ions (observed abundances divided by H^+ of C_2H_4 times the a priori probability of removing H atoms) are 1.15, 1.13, and 1.25 for C_2H_3D , $C_2H_2D_2$ (mean value), and C_2HD_3 , respectively. Weighting

factors for D^+ are 0.49 for C_2HD_3 and 0.56 for C_2D_4 . H_2^+ makes a contribution to the mass 2 peaks of C_2H_3D and $C_2H_2D_2$, and this cannot be accurately evaluated. The weighting factor for producing D^+ is somewhat less than 0.50 for $C_2H_2D_2$ and probably less than 0.5 for C_2H_3D . The data do not show any regular trend in weighting factors such as is found for the C_2 group of ions.

It is of interest that the ion HD^+ has about the same relative abundance in the different $C_2H_2D_2$ molecules. That is, the abundance is the same whether or not the two deuterium atoms are on the same carbon atom.

4. Discussion

Delfosse and Hipple [6] have previously published the mass spectrum of a *cis-trans* mixture of 1,2- $C_2H_2D_2$. The relative intensities of the $C_2H_2D_2$ and C_2H_4 spectra reported by them are entirely consistent with the results obtained in this research.

An interesting and unexpected feature of the experimental results is that in the C_2 mass range there is no appreciable difference between the mass spectra of 1,1- $C_2H_2D_2$ and *cis* and *trans* 1,2- $C_2H_2D_2$. The weighting factors remain the same whether there are two D atoms on one carbon atom or one on each carbon atom. Appearance potential measurements [11] indicate that production of $C_2H_2^+$ from C_2H_4 involves the production of H_2 rather than atoms of hydrogen, and H_2 is also formed when 3 or 4 H atoms are removed. The present results suggest that the hydrogenic molecule is formed with equal probability whether the two atoms are on the same carbon atom or not. This cannot be explained by the assumption of complete mixing of H and D atoms in the ionization process, for the fragment ions in the C_1 range reflect the molecular structures. There is some rearrangement of hydrogenic atoms, but it is relatively unimportant.

The progressive increase in C^+ and Σi_{C_1} with increasing number of D atoms in the molecule is in marked contrast to the decrease of C_2^+ and Σi_{C_2} as the number of D atoms increases. This interesting difference is not entirely unexpected, as Stevenson and Wagner [4] discuss in a general way the theoretical basis for two opposing effects of heavy isotopes on the probability of dissociation.

The analysis of the data in the C_2 range of the deuterioethylenes as given in tables 4 and 5 shows a very striking relationship between the "weighting factors" for removal of H and D and the number of D atoms in the molecule. The powers of a single constant assigned according to a definite system or pattern account for all 26 weighting factors, at least to a fairly good approximation. A relationship of this kind might be expected in other deuterated hydrocarbons. The only clear case of such a relationship among the molecules already studied is acetylene.

A previous publication [7] gives the mass spectra of C_2H_2 , C_2HD , and C_2D_2 , and from these data the weighting factors given in table 6 for dissociation of H and D have been computed as in table 3 for the

ethylenes. The table shows that powers of a single constant $K=1.13$ represent quite accurately the five weighting factors. The weighting factors for dissociation of H, D, HD, and D_2 from the acetylenes C_2HD and C_2D_2 are related in the same way as they are in the ethylenes $C_2H_2D_2$ and C_2D_4 , except that the constant is 1.13 in the acetylenes and 1.10 in the ethylenes.

TABLE 6. Acetylene weighting factors compared with powers of $K=1.13$

	C_2HD		C_2D_2	
C_2	0.86	$K^{-1}=0.88$	0.79	$K^{-2}=0.78$
C^2H67	$K^{-3}=.69$	----	----
C^2D	1.28	$K^2=1.28$.86	$K^{-1}=.88$

Schissler, Thompson, and Turkevich [5] have found that there is a roughly linear relation between the weighting factors for removing H and D from the methanes and the number of D atoms in the molecule. They report values for the a factor as 1.23, 1.48, and 1.80 in molecules containing 1, 2, and 3 D atoms. These a factors can be quite accurately represented as 1.22, $(1.22)^2=1.49$, and $(1.22)^3=1.81$, corresponding to the relation found in the ethylenes. However, the b factors apparently are not related to each other and to the a factors as they are in the ethylenes. It is to be noted that the researches of two of the authors [3] and of Schissler et al. [15] on the

deuteromethanes are not in good agreement, and in the opinion of the authors the isotopic purity and the isotopic analyses leave much to be desired in both researches. The deuteromethane spectra deserve further research when compounds of better isotopic purity become available. Obviously the computation of weighting factors depends rather critically on the isotopic purity of the mass spectra.

5. References

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