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The Production and Subsequent Photolysis of Transient Products from the Photodecomposition of Diazomethane at 4.2 °K.[1,2]

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The three isotopic modifications of diazomethane, CH_2N_2, $CHDN_2$ and CD_2N_2 have been photolyzed during deposition in solid krypton at 4.2°K. If light of wave length longer than 3400 Å. is used, sharp absorption features appear in the vicinity of 3000 Å. from photolyzed CH_2N_2 and $CHDN_2$, and it is suggested that these are due to methylene. If this identification is correct the probability is high that the triplet state is the ground state of methylene. Because of the presence of other extremely low-lying excited electronic states in the molecule, the result need not be inconsistent with chemical evidence. Higher energy radiation was found to bleach the sharp features with the simultaneous appearance of well-known CH or CD spectra and a feature at 4240 Å. tentatively identified as belonging to CN_2 or HCN_2. In the case of photolyzed CD_2N_2, there appears to be an altogether different photochemical mechanism taking place in the solid since nothing equivalent to the above sharp structure could be observed. Instead, a series of reasonably sharp 40 cm.$^{-1}$ doublets, which can also be bleached, appears. In the photolysis of all these molecules there are further broad absorption features in the region $\lambda<3300$ Å. which remain unidentified. They could be associated with still larger transient products or could be identical to the species causing the sharp spectra but in more random environments. Their presence further illustrates the complexity of the diazomethane photochemical dissociation process in a solid medium. The region from 2500 to 3500 Å. appears to be a favorable one in which to search for a long wave length flash photolysis spectrum of methylene.

Introduction

Extensive investigations in the infrared, visible, ultraviolet and vacuum ultraviolet have only recently[3] been successful in the identification of a spectrum near 1400 Å. which can without much doubt be attributed to the important molecular fragment methylene. Because of the fact that methylene reacts with many other molecules at a rate comparable to the collision frequency,[4] detection by present flash photolysis techniques is possible only if these are carried to their limit. Even so, no spectrum in the visible or near ultraviolet regions has yet been found in spite of the fact that transitions are predicted in these regions.

This paper describes some results of a series of experiments concerning the trapping of products from photochemical decomposition of some isotopic modifications of diazomethane in solid krypton at liquid helium temperature. The work reveals the apparent complexities associated with this particular problem and presents evidence for the assignment of part of the observed spectrum to an electronic transition of methylene in the near ultraviolet.

Predicted Spectrum of Methylene.—If CH_2 were linear the eight electrons would have the ground molecular orbital configuration[5]

$$K^2(2s\sigma_g)^2(2p\sigma_u)^2(2p\pi_u)^2$$

resulting in three *very* low-lying electronic states $^3\Sigma_g{}^{-1},\Delta_g$ and $^1\Sigma_g{}^+$ in order of increasing energy.[6] The first excited configuration

$$K^2(2s\sigma_g)^2(2p\sigma_u)(2p\pi_u)^3$$

results in two higher excited states, $^3\Pi_g$ and $^1\Pi_g$, which, if compared with NH where similar states are known,[7] should lie about 4 e.v. above the ground state.

If the molecule is highly bent ($90° \lesssim \vartheta \lesssim 130°$), the in-plane $2p\pi_u$ orbital mixes strongly with $2s\sigma_g$, removing the two-fold degeneracy of Π and Δ states. This can lower, probably by about 1 e.v., the energy of the in-plane orbital with respect to the out-of-plane one.[5,8] Eight electronic states, $^1A_1(1)$, $^3B_1$, $^1B_1$, $^3A_2$, $^1A_2(2)$, $^3B_2$ and $^1B_2$, in approximate order of increasing energy would then result. The first two excited states probably have transition energies to the long wave length side of 7000 Å.; and the others very likely lie between 5000 and 2000 Å. Intermediate bending ($\vartheta \gtrsim 130°$) would change slightly the order of the states, in particular it would cause $^3B_1$ to be the ground state of the molecule instead of $^1A_1(1)$. It is highly possible, of course, that some states are linear while others are bent. Because in-plane hybridization favors molecular bending, it is expected that the $^1B_1$ and $^3B_1$ states with one hybrid electron would have larger valence angles than the $^1A_1(1)$ state which has two such electrons.

The above considerations show that as long as one of the combining electronic states of methylene is fairly bent, transitions in the near-ultraviolet, visible or photographic infrared should occur. Transitions between two linear states will be vanishingly weak because of the $g \longleftrightarrow u$ selection rule. If the lower state is $^3\Sigma_g{}^-(^3B_1)$ a reasonably intense transition to $^3A_2(^3\Pi_g)$ should occur in the 3000 Å. region, while if the lower state is $^1A_1(1)$ a transition to $^1B_1(^1\Delta_g)$ is expected in the photographic infrared. Two-electron transitions to the $^1A_1(2)$ state or to $^{1,3}B_2$ states are probably weak and the remainder of the absorption transitions are forbidden by selection rules. These considerations are illustrated in Fig. 1. That the lower state of an absorption transition in the solid even at 4.2° K. need not be the ground state has been illustrated

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(1) Supported in part by the National Science Foundation and Office of Ordnance Research, U. S. Army.

(2) Part of this work included in a thesis to be submitted by Maclyn McCarty, Jr. in partial fulfillment of the requirments for the degree of Doctor of Philosophy, Johns Hopkins University.

(3) G. Herzberg, *Nature*, **183**, 1801 (1959).

(4) H. M. Frey and G. B. Kistiakowsky, THIS JOURNAL, **79**, 6373 (1957); T. B. Wilson and G. B. Kistiakowsky, *ibid.*, **80**, 2934 (1958); and refs. given in these papers.

(5) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

(6) G. Herzberg, "The Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 336.

(7) *Ibid.*, p. 556.

(8) K. Dressler and D. A. Ramsay, *J. Chem. Phys.*, **27**, 971 (1957); D. A. Ramsay, "Advances in Spectroscopy," Vol. I, in press.

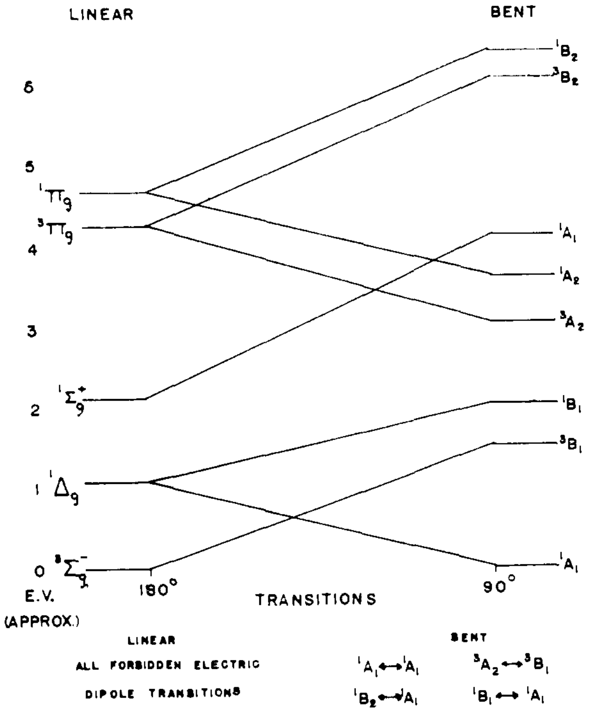

Fig. 1.—Electronic states and transitions of CH_2 in the linear and bent configurations.

in the cases of NH($^1\Delta$)[9] and C_2($^3\Pi_u$),[10] and therefore care must always be taken to assign a ground state in molecules having possible unfilled orbitals. Because of the expected small energy difference between the lowest singlet and triplet states of CH_2, it is very unlikely that the nature of the ground state can be determined by chemical means, and conversely a knowledge of the true ground state of methylene may not be a piece of information useful for the prediction of chemical reactivity of this species. Methylene usually is obtained by photolysis of ketene[4] or diazomethane,[3,11] both of which because of conservation of electron spin angular momentum are expected to produce CH_2 initially in a singlet state regardless of the multiplicity of the ground state.

Experimental

Diazomethane was prepared by adding 50% KOH in isoamyl alcohol to N,N'-dinitroso-N,N'-dimethylterephthalamide, a large sample of which was kindly supplied by E. I. du Pont de Nemours and Co. Gaseous diazomethane is easily separated *in vacuo* from the relatively non-volatile alcohol, and the more volatile impurities, presumably N_2 and C_2H_4, then were removed successfully by slowly condensing the material in a trap at −145° while it was continually being pumped. Deuterium substitution[12] was carried out by exchange near 0° with a large excess of 50% KOD in D_2O solution using as solvent for the diazomethane well-purified anisole to facilitate later separation. The exchange reaction proceeded much more slowly than anticipated, requiring violent agitation of the ingredients for at least 30 min. to introduce 95% deuterium (90% CD_2N_2, 10% $CHDN_2$). Very little diazomethane decomposed during the exchange. The deuterium content was determined from the well-known infrared spectra[13] of these molecules. In the course of these experiments two violent explosions resulted from improper handling of liquid diazomethane, the first occurring when the pure liquid near −40° was slightly disturbed and the second when an attempt was made to freeze the material originally at −78° in the presence of about a gram of solid KOD in D_2O solution (mechanical disturbance from cracking of solid on cooling?). Pure liquid diazomethane at Dry Ice temperature or below appears to be relatively stable if carefully handled and can be distilled *in vacuo* quite easily from a trap at this temperature.

Except for the absence of the microwave discharge equipment and the presence of a photolysis source consisting of a Hanovia xenon lamp and a AH-6 lamp in tandem, collimated and focussed on the 1 cm.^{2} deposit area, the experimental arrangement and deposition technique are similar to those described in a previous paper.[14] The ratio of krypton to diazomethane was 75 ± 25 to 1. Taking the minimum value and assuming a maximum of two reactive species produced for each diazomethane molecule, it can be conservatively estimated that statistically 50% of the trapped species have only krypton atoms as nearest and next nearest neighbors. Since diazomethane gas has a tendency to decompose on standing, the desired mixture was obtained continuously by slowly passing high purity krypton at a pressure of 1.5 mm. through a trap containing diazomethane at a temperature of −145°. The vapor pressure of CH_2N_2 at this temperature was found to be approximately 0.02 mm. The total krypton leak rate was 4 ml. STP/min. The mixture flowed through a restriction into the high vacuum chamber where a small fraction of it condensed on a quartz tube at 4.2°K. The remainder was pumped out through two 60 l./sec. diffusion pumps so that a pressure measured by an ionization gauge to be 1×10^{-4} mm. was maintained in the vicinity of the cold finger.

The photolysis was carried out under three different excitation conditions, the full arc of the lamps passing all wave lengths down to the vicinity of 2100° Å.; the lamps with a Pyrex filter passing wave lengths to about 2800 Å. and the lamps with a Corning 7380 filter passing wave lengths greater than 3400 Å. Diazomethane is known to absorb[15] diffusely or continuously in the blue and near ultraviolet with a weak maximum at 3900 Å.; a broad minimum around 3000 Å. and further strong absorption below 2600 Å. Spectra between 2400 and 3000 Å. because of poor light transmission were photographed on a small quartz instrument with plate factor ranging from 27 Å./mm. to 41 Å./min. and those above 3000 Å. on a 2 meter plane grating instrument having a plate factor of 8 Å./mm. Exposure times were about one-half hour.

Matrix Rigidity.—The photolysis was carried out during deposition (and, of course, simultaneously in the solid) in the hope that a higher yield of methylene would be produced because of the ease of surface photodissociation as compared with dissociation within a very rigid medium. This technique which we will call *photodeposition* allows the use of a more rigid solid than those previously used for these studies.[16-19] The necessity for this is indicated since in a molecular nitrogen matrix at 20° K., for example, the free energy of activation for diffusion[20] needs to be only about 1200 cal./

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[9] M. McCarty, Jr., and G. W. Robinson, THIS JOURNAL, **81**, 4472 (1959).

[10] Intense absorption due to the Swan bands ($^3\Pi_g \leftarrow {}^3\Pi_u$) of C_2 trapped in solid rare gases at 4.2°K. persists for at least 4 hr. without apparent decrease of intensity (M. McCarty, Jr., and G. W. Robinson, *J. chim. phys.*, **56**, 723 (1959)). In recent work, however, Dr. D. A. Ramsay has shown that the $^1\Sigma_g^+$ state of gaseous C_2 lies about 600 cm.$^{-1}$ *below* the $^3\Pi_u$ state. Either the $^3\Pi_u$ state has extreme metastability, or intermolecular interactions reverse the order of the states in the solid.

[11] See, for example, R. C. Woodworth and P. S. Skell, THIS JOURNAL, **81**, 3383 (1959), or D. E. Milligan and G. C. Pimentel, *J. Chem. Phys.*, **29**, 1405 (1958), and references given in these papers

[12] We are grateful to Dr. L. C. Leitch of N.R.C., Ottawa, for some illuminating discussions on this matter.

[13] B. L. Crawford, W. H. Fletcher and D. A. Ramsay *J. Chem. Phys.*, **19**, 406 (1951).

[14] G. W. Robinson and M. McCarty, Jr., *ibid.*, **30**, 999 (1959).

[15] F. W. Kirkbride and R. G. W. Norrish, *J. Chem. Soc.*, 119 (1933).

[16] D. E. Milligan and G. C. Pimentel, ref. 9.

[17] W. B. DeMore, Thesis, California Institute of Technology, 1958.

[18] W. B. DeMore, H. O. Pritchard and N. Davidson, THIS JOURNAL, **81**, 5874 (1959).

[19] T. D. Goldfarb and G. C. Pimentel, *ibid.*, **82**, 1865 (1960).

[20] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 516–544.

mole for a rapid diffusion to occur. This is 80% of the heat of sublimation of N_2 and there is no assurance that a small species such as methylene can be trapped under such conditions. At the time of writing little appeared to be known about diffusion in solid rare gases and molecular nitrogen in the 4.2–20° K. region but preliminary experiments[21] indicate that 20° K. might be a borderline temperature for the trapping of some species. A good criterion for matrix rigidity here is the presence of CH radicals and these are shown to be trapped in our experiments. The absence of CH could correspond to a lack of matrix rigidity in which case only more bulky transient species are expected to be isolated. Another advantage of the photodeposition technique is that the chance is increased that some of the trapped species will be at substitutional positions in the rare gas lattice rather than in widely varying environments. Uniform environment is necessary for the observation of sharp electronic spectra.[14]

The 2600 Å. Region.—Ten hours of photodeposition using any of the three modes of excitation produced no absorption (except possibly continuous) between 9000 and 4500 Å. However, numerous absorption features whose nature depended rather critically on the type of excitation used were found near 4000, near 3000 and below 2600 Å. to the limit of observation at 2400 Å.

The 2600 Å. region was first discussed by DeMore[17] and DeMore, Pritchard and Davidson (DPD)[18] in an extensive investigation of the photolysis of normal and deuterated diazomethane in rigid media at 20°K. They mentioned that "the possibility exists, though remotely, that these bands are due to a trace of methylene trapped in the film." A similar but not necessarily identical system was discovered independently by the present authors[22] from hydrocarbon discharges as well as from photodeposition of ketene in krypton at 4.2°K.

In the present experiments the spectrum occurred weakly if no filter was used but more strongly if the 7380 filter was used. This observation is consistent with that of DPD who found their system when a Pyrex filter was used but not with the full arc. The separation of the bands derived from CH_2N_2 is about 650 ± 80 cm.$^{-1}$ but because of their breadth it is not certain whether there is an isotope shift or whether the absorbing species is the same in all of these experiments. Even though the parent molecules used to obtain this spectrum are suggestive, it is not possible to identify the 2600 Å. bands conclusively. Our own experiments however do not rule out the possibility that they belong to methylene.

The 3000 Å. Region.—The absorption near 3000 Å. is much more interesting. There appear to be four distinct parts—the relatively broad ($\Delta\nu_{1/2} \approx 40$ cm.$^{-1}$) 3150 Å. CH(CD) band, a series of sharp doublets (40 cm.$^{-1}$ splitting, $\Delta\nu_{1/2} \approx 6$ cm.$^{-1}$) and a few very sharp lines ($\Delta\nu_{1/2} \approx 3$ cm.$^{-1}$) both showing a large isotope effect, and numerous broad features ($\Delta\nu_{1/2} = 10$–40 cm.$^{-1}$). These absorptions will henceforth be called the "CH band," the "sharp doublets," the "very sharp lines" and the "broad features," respectively. The sharp features might be difficult to detect on an instrument of low resolving power.

The "CH band" has been obtained[23,24] on numerous occasions from hydrocarbon discharges in argon, krypton and xenon. It is always accompanied, of course, by the 3900 and 4300 Å. systems[25] of CH. All three of these features in the solid are usually characterized by some slightly longer wave length resonance fluorescence which is excited by the light source used to obtain the absorption spectrum. It should be noted that in these experiments the "CH band" is observed *only* if excitation of $\lambda < 3400$ Å. is used.

The "sharp doublets" and the "very sharp lines" are observed *only* when the 7380 filter is used. *Photolysis with higher energy excitation during deposition or for a duration of about an hour anytime after deposition bleaches these lines completely with the simultaneous, but not necessarily related, appearance of other features, in particular CH.* Photographs in the 3000 Å. region require the use of a Pyrex filter to retard bleaching and in any case only one or at most two photographs can be taken before the sharp features vanish. One interesting aspect of these absorptions is that the most prominent "sharp doublets" occur from photolysis of CD_2N_2 while the "very sharp lines" arise from CH_2N_2 photolysis. The $CHDN_2$ photolysis produces both type of features.

The "broad features" are quite complex and may belong to more than one species. The strongest components are separated by 2150 cm.$^{-1}$ and this progression can be followed to well below 3000 Å. The strongest features appear to be identical in all three isotopic modifications. They can be obtained under any of the three modes of excitation but are best obtained using the 7380 filter.

The 4000 Å. Region.—In addition to the two CH bands, the 4000 Å. absorption region contains a feature at 4240 Å. which appears double (separation ≈ 80 cm.$^{-1}$) and shows no deuterium shift. This band was observed[23] previously at 4235 Å. from the products in solid argon of hydrocarbon discharges containing a trace of nitrogen and is accompanied by fluorescence on its long wave length edge. Like CH, the 4240 Å. band is obtained *only* if excitation with $\lambda < 3400$ Å. is used and appears as the sharp features are bleached. All experimental data have been summarized in Table I.

Discussion

Confident interpretation of the results is hampered by the present lack of information about diffusion and photochemical ejection through the solid at low temperatures. The experiments here yield trapped CH and many earlier experiments[26] have shown that small species similar to CH_2 can be permanently trapped under the very conditions used here. This shows that diffusion in krypton probably is not important at 4.2°K. Unfortunately, similar experiments have not yet been carried out at temperatures above 4.2°K.

The present experiments do show that photochemical ejection of *some* species far from the local environment can take place in solid krypton at 4.2°K. This is evidenced by the production in the solid of CH as well as the species responsible for the 4240 Å. band *after deposition was completed.* Because of the relative lack of broadening in these spectra, it can be deduced that the environment is essentially identical with that in the electrical discharge experiments[23] where it is known that trapping takes place at substitutional sites in a rare gas lattice. It is not known whether whole molecules or only atoms are being ejected through the solid, but a small atom such as hydrogen is expected to present the most favorable case for complete removal from the local environment. One should keep this thought in mind when attempting to evaluate any of the proposed mechanisms listed below.

A reasonable explanation of the data is that CH_2 and CHD are produced with 7380 filtered light from CH_2N_2 and $CHDN_2$, respectively, the spectra of these species being evidenced by the "very sharp lines" in the 3000 Å. region, and possibly by the more intense 2600 Å. features. Since the dissociation limit[27] of CH_2 is about 2860 ± 300 Å.,

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[21] Very slow diffusion of H_2O in N_2 at 20°K. has been reported (M. Van Thiel and G. C. Pimentel, "Infrared Spectra of Intermediate Species in the Photolysis of Hydrazoic Acid, II," ASTIA Document 211 805, Fig. 1).

[22] M. McCarty, Jr., and G. W. Robinson, paper presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June, 1959.

[23] G. W. Robinson and M. McCarty, Jr., The 3rd International Symposium on Free Radical Stabilization, Sheffield, England, September 4, 1958, preprints, p. 58.

[24] M. McCarty, Jr., and G. W. Robinson, ref. 10.

[25] Ref. 6, p. 518.

[26] See, for example, refs. 7 and 12 and references given in these papers.

[27] Arrival at a value for D(CH–H) depends on a knowledge of D(CH_2–H) and L(graphite) which now seem to be established as 101 and 170 kcal./mole respectively, a knowledge of D(C–H) which can, with some reservation, be accepted as the spectroscopic value, 80 kcal./

it is then possible that subsequent excitation by $\lambda < 3160$ Å. is absorbed by methylene and leads to predissociation into CH($^2\Pi$) and H(^2S). There is no doubt, because of energetic considerations, that CH is formed by some secondary photochemical process[28] and whatever primary species is involved must absorb between the 7380 filter cutoff near 3400 and the Pyrex cutoff near 2800 Å. CH radicals produced from CH_2 by secondary photolysis would not be important in most photochemical reactions because of the ordinarily short chemical lifetime of CH_2. The more rapid bleaching effects observed with excitation of $\lambda < 2800$ Å. mean that in this higher energy region further absorption leading to predissociation is taking place. This could be caused by the 2600 Å. absorption, but it should not be forgotten that any continuous and thus undetectable absorption in the region could lead to the same observations. If the identification of the "very sharp lines" is correct the spectrum yields reasonable frequencies for the excited state bending modes of CH_2 and CHD (950–700 cm.$^{-1}$). A precise vibrational analysis is difficult because of the limited spectral region and line multiplicity near the apparent vibrational origins.

Another possible path for formation of CH is through the primary species HCN_2, analogous to N_3 from HN_3 photolysis,[29] and it is possible that part of the observed absorption is therefore due to HCN_2. Secondary photochemical dissociation of HCN_2 could lead to CH (photoejected?) or to CN_2. The latter species is expected to absorb in the 4000 Å. region because of its electronic similarity, except for the absence of one non-bonding electron, to NCO and CO_2^+.[30,31] The species HCN_2 (isoelectronic with NCO and CO_2^+) might also absorb in this region. The 4240 Å. band is therefore tentatively identified with either $CN_2(^3\Sigma^+ \leftarrow {}^3\Sigma^-$ or $^3\Pi \leftarrow {}^3\Sigma^-)$ or $HCN_2(^2\Sigma \leftarrow {}^2\Pi$ or $^2\Pi \leftarrow {}^2\Pi)$.

The "sharp doublets" evidently belong to primary photochemical products and are isotope dependent but not in a simple way. It appears as if the $CHDN_2$ photolysis produces a superposition, with the expected relative intensities, of the doublets from the other two isotopic modifications which, if true, would indicate only one hydrogen. Unfortunately this spectrum is fragmentary in the CH_2N_2 photolysis. These features, because of their sharpness and the 700–800 cm.$^{-1}$ vibrational spacing in CD_2N_2 experiments, can conceivably be due to methylene. Photoisomers or HCN_2-(DCN_2) cannot be ruled out since the present evidence seems to favor different species responsible for the "sharp doublets" and the "very sharp lines."

The observation of what appears to be *a different primary mechanism for photodecomposition of the three isotopic modifications of diazomethane* is rather interesting. The rate of production of the species responsible for the "very sharp lines" appears to be much higher in the CH_2N_2 photolysis compared with the CD_2N_2 photolysis where these features have not yet been observed. The situation in the case of the "sharp doublets" is partially reversed. For $CHDN_2$ photolysis the rates of production of each of these species are comparable since both apparently occur to some extent. Whether this phenomenon is a characteristic of free diazomethane molecules or is caused by a matrix cage effect or a low temperature effect is not known. If it did occur in free diazomethane then *one might expect that the chemistry of photolyzed diazomethane would be drastically affected by the deuterium substitution.* As far as the authors know there has been no work of this kind reported. The fact that a primary photochemical mechanism can be *substantially* changed by isotopic substitution is not exactly unparalleled since it is well known that the transition probability for gas phase predissociation in the cases of CH_3[28,32] and CH_2[3] are probably decreased by orders of magnitude on deuterium substitution. In the present case the relative rates of two competing processes are changed. For such a thing to occur requires of course a rather complex crossing of potential energy surfaces such as might be existent in excited states but not generally in the ground states of molecules.

It is unlikely that the "broad features" arise from a simple hydrogen-containing species because of the lack of a measurable isotope shift for any of this complex structure. It should be stressed however that, in an electronic spectrum, a single feature such as the 4240 Å. band need not show a measurable isotope shift at 8 Å./mm. dispersion even though hydrogen *were* present if the geometry difference in the two electronic states is small (*e.g.*, CH and CD). Because of our earlier theoretical considerations, however, such a situation would be somewhat unexpected in the allowed transitions between low-lying states of CH_2. The expected geometry change therefore tends to rule out the 4240 Å. bands as CH_2 since under these conditions the Franck–Condon principle predicts a progression of bands rather than a single feature.

There is always the possibility, of course, that many of these absorption features belong to the same species in multiple trapping sites.[33] Some of the features may also be caused by photochemical isomerization of diazomethane.[16]

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mole (L. Gerö, *Physica*, **7**, 155 (1940)), the well-known quantities, D(H–H) and the heat of formation of methane, in addition to a knowledge of D(CH_2–H) which is at present unknown. Recent electron impact studies (C. A. McDowell and J. W. Warren, *Discussions Faraday Soc.*, **10**, 53 (1951); A. Langer, J. A. Hipple and D. P. Stevenson, *J. Chem. Phys.*, **22**, 1836 (1954)) have suggested values for D(CH–H) and D(CH_2–H) which are inconsistent with L(graphite) = 170 kcal./mole. If the established values are accepted, then D(CH_2–H) + D(CH–H) = 211 kcal./mole. We feel that a good *guess* for D(CH–H) and its limit of error is 100 ± 10 kcal./mole. This value is certainly consistent with the interpretation in this paper which requires D(CH–H) $\gtrsim$ 102 kcal./mole. On the other hand, if CH is produced only from HCN_2 then this requirement is unnecessary.

(28) The CH radical has been found in the flash photolysis of ketene and was ascribed to a secondary photochemical process (G. Herzberg, *Proc. Chem. Soc.*, 116 (1959)).

(29) The generally accepted mechanism for N_3 formation in the gas phase is through hydrogen abstraction from hydrozic acid but the cage effect in the solid may favor primary loss of hydrogen.

(30) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

(31) R. Holland, D. W. G. Style, R. N. Dixon and D. A. Ramsay, *Nature*, **182**, 336 (1958).

(32) G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956).

(33) E. L. Cochran, V. A. Bowers, S. N. Foner and C. K. Jen, *Phys. Rev. Letters*, **2**, 43 (1959).

TABLE I

ELECTRONIC SPECTRA OF PHOTOLYZED CH_2N_2, $CHDN_2$ AND CD_2N_2 IN SOLID KRYPTON AT 4.2°K.

		λair, Å.	I	$\Delta\nu_{1/2}$, cm.$^{-1}$	ν_{vac}, cm.$^{-1}$	Remarks
CH_2N_2	Sharp lines	3336.3	w	6	29665 ± 5	Obsd. only with 7380 filter, can be bleached
		3274.5	w	3	30531 ± 5	
		3265.6	vw	3	30614 ± 5	
		3261.5	w	3	30652 ± 5	
		3178.7	w	3	31450 ± 5	
		3130.3	w	3	31937 ± 10	
		3099.0	w	3	32259 ± 10	
	CH	4324^a	m	50	23121 ± 15	Obsd. only after bleaching
		3941^a	mw	50	25368 ± 15	
		3174^a	m	40	31497 ± 20	
	4240 Å. band	4248^a	s	30	23535 ± 15	
		4234	s	30	23613 ± 15	
	Broad features	3335	mw	25	29980 ± 15	Many of these more intense with 7380 filter
		3290	w	30	30389 + 15	
		3251	vw	30	30754 ± 15	
		3218	w	30	31069 ± 15	
		3186.7	w	10	31372 ± 10	
		3168	w	40	31561 ± 15	
		3119	mw	40	32051 ± 25	
		2925	mw	40	34180 ± 40	
		2770	mw	40	36090 ± 40	
		2715	mw	50	36820 ± 40	
		2592	ms	60	38565 ± 40	
		2548	s	60	39231 ± 40	
		2507	s	60	39872 ± 40	
$CHDN_2 + CH_2N_2$	Sharp lines	3336.3^b	ms	6	29965 ± 5	Obsd. only with 7380 filter, can be bleached
		3327.3	w	3	30046 ± 5	
		3315.9	vw	3	30150 ± 5	
		3307.8	vw	3	30223 ± 5	
		3273.5^b	w	3	30540 ± 5	
		3268.7	vw	3	30585 ± 5	
		3265.0	w	3	30619 ± 5	
		3260.9^b	vw	3	30658 ± 5	
		3256.8	w	3	30697 ± 5	
		3252.8^c	m	8	30734 ± 8	
	CH and CD	Same as in CH_2N_2 experiments except stronger				
	4240 Å. band	Same as in CH_2N_2 experiments except stronger				
	Broad features	Apparently identical with features from CH_2N_2 except much stronger; scattering prohibited useful photographs below 3120 Å.; 2600 Å. system barely detectable				
CD_2N_2	Sharp lines	3256.2	mw	6	30702 ± 6	Obsd. only with 7380 filter, can be bleached
		3252.1	s	6	30741 ± 6	
		3250.1	vw	6	30760 ± 10	
		3173.9	mw	6	31498 ± 6	
		3170.2	s	6	31535 ± 6	
		3092.0	mw	6	32332 ± 10	
	CD	No measurable shift from CH, in agreement with gas phase spectrum				
	4240 Å. band	No apparent isotope shift				
	Broad features	Apparently identical with features from CH_2N_2 except a little weaker; scattering prohibited useful photographs below 3000 Å. in experiments performed; 2600 Å system barely detectable				

[a] Usually accompanied by emission on long wave length side. [b] Probably identical with CH_2N_2 features. [c] Possibly identical with CD_2N_2 feature.

These experiments point out the complexity of the low temperature diazomethane photolysis and show the difficulties encountered in making an unambiguous simple interpretation of the results in terms of methylene storage. Further work of this kind involving a set of *definitely known species* must certainly be done in order to understand diffusion, photoejection, the cage effect and photoisomerization in these matrices between 4.2 and 20°K. According to the discussion in an earlier section any absorption in the 3000 Å. region which is ascribed to methylene most probably has $^3\Sigma_g{}^-$-$(^3B_1)$ as lower state. The probability is fairly high therefore that the triplet state is the ground state of methylene, but, in addition to these solid phase results, further work on the gas phase spectrum is needed to verify this point. The region from 2500 to 3500 Å. appears to be a favorable one in which to search for a long wave length flash photolysis spectrum of methylene.

In conclusion we wish to express our gratitude to Professor Norman Davidson and Professor George Pimentel[34] for communicating some of their interesting results to us prior to their publication. While there are still some apparent divergences between the observations and interpretations of this work and the work of Pimentel and his co-workers,[16,19] it should be remembered that many of the conditions under which the two sets of experiments were carried out are widely different, especially with regard to the temperature, nature of the matrix and the deposit technique. The fact that a portion of the major conclusion is the same in both cases, namely that methylene can be trapped and its spectrum detected near 3000 Å. in these solids at low temperatures, unfortunately does not lessen the importance of the divergences.

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[34] We wish to thank Professor Pimentel for sending us prior to publication a rough draft of the paper with Dr. Theodore D. Goldfarb entitled "Spectroscopic Study of Photolysis of Diazomethane in Solid Nitrogen." After reading their manuscript we feel that a few clarifying comments are in order.

(a) We have accumulated over the past two years a bulk of data (ref. 26) on *electronic* spectra of small polyatomic free radicals in solid argon, krypton and xenon. There is no indication that low M/R ratios down to about 20 preclude the trapping and storage of easily detectable amounts of these small reactive species at 4.2°K. Because of the less rigid nature of the solid at 20°K. the question is no doubt more important at this temperature. The negative result on the 2620 Å. band at low M/R in Experiment 1 of their paper, while suggestive, we feel does not give compelling evidence for abandonment of our suggestion that the 2500 Å. bands described in our paper belong to methylene.

(b) Their 4182 Å. band might be the same as our 4240 Å. band and, if so, probably is not due to methylene for reasons discussed in our paper.

(c) If it were established that their 3968 and 3174 Å. bands were caused by CH, then we would feel fully confident about the rigidity of the matrix at 20°K. If these identifications are made, the absence of the 4320 Å. CH band is very puzzling since we have found this band to be the easiest of the three to detect.

(d) The fact that we *have* observed numerous ultraviolet absorption features using the 7380 filter is in apparent direct disagreement with the negative results in Experiments 3 and 5 of Goldfarb and Pimentel. This merely emphasizes the differences in the two photolysis techniques. Suppose the infrared absorptions (Class-C bands) are caused by relatively large concentrations (because of the small absorption coefficients in the infrared as compared generally with those in the ultraviolet) of products such as photoisomers formed only in the matrix "cage." If the kinetic energy necessary to overcome the cage effect cannot be imparted to photolysis products of diazomethane with light of $\lambda > 3400$ Å., photolysis with the 7380 filter of *pretrapped* diazomethane would yield only these "cage molecules" which may show only continuous ultraviolet absorption. Higher energy radiation might then be required to produce a quantity of separated fragments sufficient to give the discrete ultraviolet absorptions but in quantities insufficient for infrared detection. Our "photodeposition" technique permits fragments to be formed in the gas phase or on the 4.2° K. surface, and thus lower energy radiation is adequate for fragment separation. The infrared studies show apparently that the "cage molecules" do not form readily in the case of CD_2N_2.

(e) It should be remembered that our results show that secondary photolysis *does* take place in the solid and some species (which we think is methylene) *does* disappear when energy corresponding to $\lambda < 3400$ Å. is employed. Hence it is extremely unlikely that the species responsible for what we have called the "sharp doublets" and the "very sharp lines" could have ever been obtained in detectable quantities by Goldfarb and Pimentel using Pyrex filtered or unfiltered radiation. As a matter of fact their spectra resemble our "bleached spectra" in many respects. Therefore there is little chance that the species producing sharp electronic spectra have anything to do with their Class-C bands which can be produced with high energy radiation. The sharp features which we observe appear fairly faintly and it would be surprising if they could give detectable infrared absorption in any case. Our experience has indicated that a maximum of two atoms other than hydrogen in a molecule is a necessary but not sufficient condition for the production of sharp ($\Delta\nu^1/_2 \lesssim 20$ cm.$^{-1}$) electronic spectra in the solid. For this reason we lean toward the feeling that the sharp features are the ones important in the methylene problem and that all other features belong to species formed on secondary photolysis, to larger fragments, or to fragments in non-uniform environments.

(f) In our work as well as that of Goldfarb and Pimentel the ultraviolet spectra demonstrate the complex nature of photolysis products. There may certainly be other products present which absorb continuously and thus undetectably in these regions. Reactions on warm-up of any or all of these unidentified reactive species could give some ethylene and thus we feel the reported 5% conversion of diazomethane to ethylene (ref. 16) can be accounted for whether methylene were stored in detectable quantities or not. In addition, sufficient methylene for ultraviolet detection may be stored without yielding sufficient ethylene on warm-up for infrared detection. Until further experimentation is performed, we feel that neither the presence nor absence of detectable ethylene infrared absorption on warm-up can be accepted as criteria pertinent to the question of storage and ultraviolet detection of methylene in the solid.