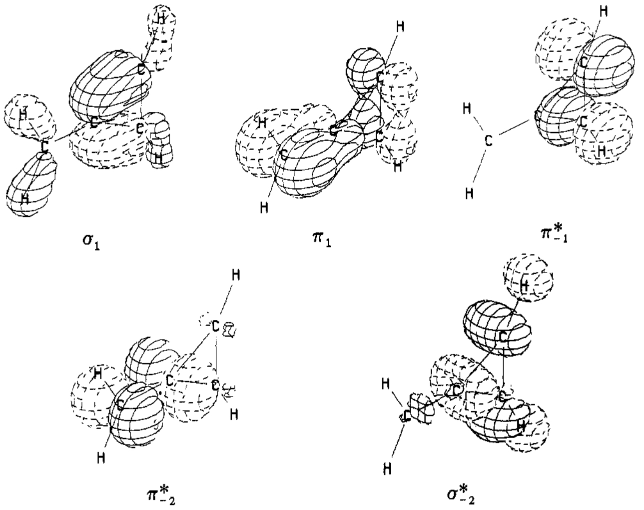
solvent dependence (e.g., δ 3.53 and 8.88 in ammonia-d_3 at −70 °C) which is currently under further investigation.

The ultraviolet (UV) spectrum of **1** in *n*-pentane at −78 °C (Figure 2) displays a broad low-intensity band at 309 nm, a more narrow low-intensity band at 242 nm, and a strong band at 206 nm. All bands disappear at the same rate when the sample is warmed. The long-wavelength band is identified with a $^1B_2$ ($\pi_1 \rightarrow \pi^*_{-1}$, internal charge transfer) transition on the basis of its strong solvent dependence (276 nm in methanol −78 °C) and INDO/S-CI calculations.[5] These calculations, along with the relative intensity (ϵ is estimated to be >3000) and the small solvent dependence (210 nm in methanol), identify the 206-nm band as arising from a $^1A_1$ ($\pi_1 \rightarrow \pi^*_{-2}$) transition. Finally, the approximate relative areas (1.5:0.01:0.2) and energies (6.02, 5.12, and 4.01 eV) of the three UV bands in Figure 2 agree reasonably well with those theoretically predicted[5] (0.62:0.01:0.05 and 6.22, 5.59, and 4.54 eV, respectively) if the small middle band (which is centered at 248 nm in methanol) arises from a $^1B_1$ ($\pi_1 \rightarrow \sigma^*_{-2}$) transition. A second $^1B_1$ transition ($\sigma_1 \rightarrow \pi^*_{-1}$) is also theoretically predicted but is probably obscured by the long-wavelength tail of the 206-nm band.



The most stable form of $C_4H_4^{+\cdot}$ has been considered to be the radical cation of **1**.[6] We have determined that the collision-induced dissociation (CID) spectrum (70 eV, EI) of the *m/z* 52 peak from **1** (*m/z* (relative intensity): 39 (15), 38 (77), 37 (100), 36 (31), 27 (27), 26 (99), 25 (31), 24 (7)) is essentially identical with those obtained for the corresponding ions obtained from benzene and pyridine.[7]

As expected, methylenecyclopropene is a highly reactive compound. On warming, solid samples of **1** (trapped at −196 °C) polymerize to a sparsely soluble white or light yellow film which displays ^{1}H NMR peaks at δ 7.28, 1.10, and 0.05 in 10% acetone-d_6/CS_2. Dilute solutions of **1** in pentane show a half-life of approximately 20 h at −78 °C as determined by monitoring the ultraviolet spectrum.

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Registry No. 2, 90246-24-5; **3**, 23230-90-2; allene, 463-49-0; bromocarbene, 17141-28-5; methylenecyclopropene **1**, 4095-06-1.

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Experimental Evidence for a C_{2v} ($^2B_1$) Ground-State Structure of the Methane Cation Radical: ESR and ab Initio CI Investigations of CH_4^+ and $CD_2H_2^+$ in Neon Matrices at 4 K

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The electronic ground state and structure of the fundamentally important CH_4^+ cation radical has not been previously established by experiment. Neon matrix ESR results combined with ab initio CI spin-density calculations are presented which provide the first direct experimental evidence for a C_{2v} ($^2B_1$) ground-state assignment. Extremely interesting H/D isotope effects were also observed in this preliminary study. The properties of CH_4^+ are important for several reasons. Its potential significance as an interstellar species and its possible involvement in chemical evolution preceeding the origins of life have been discussed.[1] The early planetary atmosphere presumably contained large quantities of methane, and CH_4^+ is known to be a highly reactive and major radiation product of CH_4. Molecular ions in general are difficult to study experimentally and the short lifetime of CH_4^+ has hindered efforts to obtain direct spectroscopic measurements in the gas phase.[1]

Numerous theoretical studies concerning the equilibrium structure and Jahn–Teller distortion have been reported over the last 20 years that have predicted differing ground-state assignments.[1-9] More recent and extensive theoretical calculations indicate a C_{2v} ($^2B_1$) ground state, which conflicts with earlier theoretical conclusions used to interpret details of photoelectron results.[5,7-9] A recent summary of the photoelectron data has questioned the suggested D_{2d} ground-state assignment.[10] Although valuable information for large alkane cations trapped in matrices such as CCl_3F and SF_6 has been obtained by ESR,[11-13] the failure to detect CH_4^+ by such methods has recently been cited by Symons.[14]

The three independent ion generation methods employed in the experiments were open-tube neon discharge photoionization at 17 eV, electron bombardment, and high-energy neutral-atom bombardment of the neon matrix gas doped with approximately 0.1% CH_4. These generation methods and experimental details of trapping small cation radicals in neon matrices at 4 K have been discussed in recent reports on CO^+,[15] H_2O^+,[16] N_2^+,[17] and

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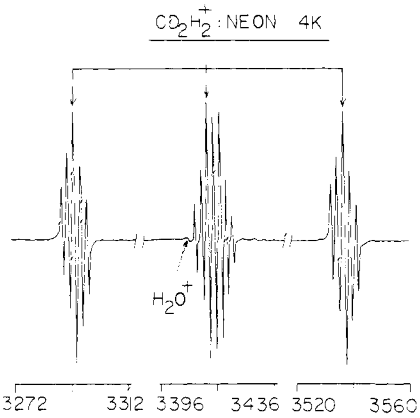

Figure 1. ESR spectrum of $CD_2H_2^+$ isolated in neon matrix at 4 K is shown. The vertical expansion is 4 times greater for the wing quintets relative to the central region. The lowest field component of the background impurity species, H_2O^+ is indicated. Other, very weak lines result from CD_2H and CH_2D radicals. The magnetic field position of g_e occurs at 3421.2 G.

Cd^+.[18] A neon matrix is apparently the only inert medium that can trap small cations having electron affinities greater than approximately 11-12 eV.[15] The large ionization energy of neon (21 eV) is presumably its distinguishing characteristic.

Electron loss from the 3-fold degenerate t_2 orbital of CH_4 can lead to C_{2v}, D_{2d}, and C_{3v} Jahn-Teller-type distortions.[8,10,19] Second-order analysis of the nearly isotropic triplet of quintets ESR spectrum observed for $CD_2H_2^+$ (Figure 1) yields $g_{iso} = 2.0029$ (4), $|A_{iso}(H)| = 121.7$ (3) G, and $|A_{iso}(D)| = 2.22$ (6) G. Multiplication of the D hfs by the appropriate nuclear g factor ratio yields 14.6 (4) G on the H "scale". The quintets result from two equivalent deuteriums ($I = 1$) and the triplet from two equivalent hydrogens. As expected second-order effects of such a large triplet splitting produce two transitions in the central spectral region which appear as partially overlapping quintets. The observation of two groups of two highly inequivalent H-atom positions is consistent only with a C_{2v} assignment. A recent ESR study of BH_4, isoelectronic with CH_4^+, has also reported a C_{2v} structure with $|A_{iso}(H)|$ values of 122 (18) and 10 (11) G.[14]

Ab initio CI spin-density calculations (ref 20 for details) were conducted at the 6-31G* basis set UHF C_{2v} and D_{2d} geometries listed by Pople.[9] For C_{2v}, the two hydrogens in the nodal plane ($\angle HCH = 123°$; C-H = 1.075 Å) of the carbon p orbital containing unpaired electron density had $A = -17$ G; the other two hydrogens ($\angle HCH = 59°$; C-H = 1.164 Å) which are allowed by symmetry to mix with this p orbital had $A = 137$ G. The D_{2d} state, calculated to be only ≈ 900 cm^{-1} above C_{2v}, has four equivalent hydrogens with a theoretical A value of 82 G. The excellent agreement between these theoretical and experimental hfs results further confirms the C_{2v} assignment.

In planar CH_3, all H atoms are in the nodal plane of the carbon 2p orbital containing practically 100% of the unpaired electron and have $A_{iso} = -23.2$ G arising from well-established spin-polarization effects. The small negative deuterium A value for $CD_2H_2^+$, which probably results from a similar spin-polarization mechanism, indicates by a simple ratio estimate that 62% of the spin density resides in the carbon 2p orbital. The two hydrogens with the large positive hfs account for roughly 48% of the spin density thus leaving $\approx 52\%$ in the 2p orbital. This rather crude "difference" estimate shows reasonable agreement with the spin-polarization prediction.

The ESR spectrum of CH_4^+ is an approximately isotropic quintet with $|A_{iso}(H)| = 54.8$ (2) G and $g_{iso} = 2.0029$ (3). It is definitely not a triplet of triplets as would be expected on the basis of $CD_2H_2^+$ results. It is extremely interesting that the weighted average $((2(121.7) - 2(14.6))/4)$ of the $CD_2H_2^+$ A values yield 53.6 G, which is essentially that observed for CH_4^+. Dynamic Jahn-Teller or fluxional behavior could cause rapid averaging of the H environments in CH_4^+. Simple rotational effects alone cannot account for this observation. Presumably, zero point energy differences in $CD_2H_2^+$ prevent such averaging effects at 4 K. Additional theoretical studies are required to explain why the D nuclei prefer the nodal plane positions which according to theory have the shorter bond distance.

Other properties of this important cation radical currently being investigated include ^{13}C hfs, all other deuterated combinations, temperature dependence, preferential orientation effects, a detailed line-shape analysis, and a theoretical treatment of the H/D isotope behavior. Attempts to produce narrower lines for resolution of small anisotropic effects are in progress. Hopefully vibrational studies of CH_4^+ will be conducted by other investigators.

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Registry No. Methane cation radical, 20741-88-2; methane-d_2 cation radical, 61105-67-7.

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Reaction of Sydnones with Ozone as a Method of Deamination: On the Mechanism of Inhibition of Monoamine Oxidase by Sydnones

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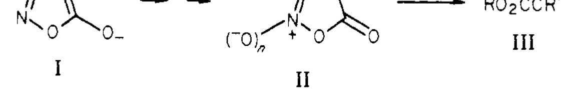
Deaminatively produced carbonium ions are intermediates of high reactivity,[1,2] and they have been utilized for this reason in several methods for the inhibition of enzymes.[3,4] We show herein that such ions can be generated by the reaction of sydnones with ozone.

The oxidation of sydnones (I) generally leads to mixtures of degradation products.[5-8] With oxygen gas as the oxidant (13-21-day reaction period), α-ketoacetate esters (8-30%) were found among the reaction products by Nakajima and Anselme.[8] A reasonable pathway for this conversion involves "diazo" ester intermediates[8] (II, $n = 0, 1$), characteristic of deamination reactions[9,10] (eq 1). We have found, in fact, that benzyldiazoic pyruvic anhydride (IV) (generated from the corresponding ni-



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