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Letters to the Editor

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Differences in Mass Spectra of H_2 and D_2

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BLEAKNEY, Condon, and Smith[1] refer to unpublished work of J. A. Hipple which indicated a large difference in the yield of monatomic ions produced from H_2 and D_2 by impact with 22-volt electrons. These authors expect such a difference in behavior from a consideration of the Franck-Condon principle and the differences in zero point amplitude of vibration for H_2 and D_2. D. P. Stevenson[2] has recently made a quantitative estimate of the effect, based on these principles. If this theory proves adequate for H_2 and D_2, it may be of importance in estimating isotope effects in mass spectra of other molecules, for instance $C_2H_2D_2$,[3] and CH_3D.[4]

We wish to report a comparison of intensities (maximum ion currents) of H^+ and D^+, relative to H_2^+ and D_2^+, respectively, obtained with the Consolidated Engineering Corporation mass spectrometer (180° type) for a range of electron impact energies. The H_2 (100 percent) and D_2 (97.5 percent D_2, 2.5 percent HD) were found to contain no impurities which could appreciably contribute to $m/e = 1$, 2, or 4. Monatomic and diatomic ion peaks were recorded in close succession by electric scanning, this being repeated over a range of nominal electron energies at intervals of 1 to 6 volts, at constant ionizing current. Nominal values of electron energy were corrected as previously described[4] and the equal appearance potentials of H_2^+ and D_2^+ agreed within 0.5 volt with Bleakney's[5] value for H_2^+. Above 35 volts, secondary electrons were eliminated from the ionizing region. Observed peak heights were corrected for the decrease caused by pressure change during a run. The ratios $r_H = (H^+/H_2^+)$ and $r_D = (D^+/D_2^+)$ were obtained at various energies by interpolation from the ionizing efficiency curves. The results are given in Table I.

Before conclusions can be drawn from the table we must take into account the discrimination characteristics of the particular mass spectrometer. The data of Washburn and Berry[6] indicate that, for the Consolidated instrument, the true relative abundances of ions from n-butane differ from the observed intensity ratios by no more than about 10 percent when the kinetic energy of the ions does not greatly exceed thermal energies and when relatively high ($\sim$1000 volts) values of the ion accelerating voltage (V_{ia}) are used. Our data for H_2 and D_2 around 30 volts should conform to this limit since it is known,[5,7] that the monatomic ions from H_2 produced below 30 volts have very small excess kinetic energy and since V_{ia} was high (3200 volts for H^+, 1600 volts for H_2^+ and D^+, 800 volts for D_2^+) in our experiments. In support of this belief is the fact that we obtained an ion intensity per electron per unit pressure (sensitivity) for D_2^+ which differed from that for H_2^+ by only about 10 percent ($H_2^+ > D_2^+$) in a series of six pairs of careful comparisons.

At electron energies higher than 30 volts, an appreciable fraction of the H^+ ions are known to be formed with excess kinetic energy. However, this excess is so great (at least 5 to 11 volts) that the discrimination against these ions should be sufficient to prevent them from making an

TABLE I.

Electron energy, volts	$r_H = (H^+/H_2^+)$ $\times 100$	$r_D = (D^+/D_2^+)$ $\times 100$	$R^* = r_H/r_D$
30	0.58	0.38	1.5 ±0.2
35	1.04	0.68	1.5 ±0.2
40	1.69	0.93	1.8 ±0.2
45	2.02	1.08	1.9 ±0.2
50	2.37	1.23	1.9 ±0.2
55	2.52	1.30	1.9 ±0.2
60	2.51	1.31	1.9 ±0.1
65	2.50	1.32	1.9 ±0.1
70	2.52	1.32	1.9 ±0.1
75	2.54	1.36	1.9 ±0.1
80	2.60	1.40	1.9 ±0.1
85	2.70	1.42	1.9 ±0.1
90	2.80	1.40	2.0 ±0.1
95	2.88	1.39	2.1 ±0.1
100	2.91	1.31	2.2 ±0.2

* The uncertainties were estimated from the scattering of points on the ionizing efficiency curves and do not include other uncertainties (see text).

appreciable contribution to the maximum height of the H^+ or D^+ peaks; such a behavior for H_2 was observed by Hagstrum and Tate[7] with a mass spectrometer of somewhat similar type. The shapes of our H^+ and D^+ peaks become less symmetrical above 32 volts, indicating some contribution of high velocity ions to the shoulders of the peaks. Thus all of our R values should correspond predominantly to the production of monatomic ions by the single process of excitation of H_2 (or D_2) to H_2^+ (or D_2^+) in its lowest energy state. However, the possibility of smaller contributions from excited states of stable H_2^+ (or D_2^+) cannot be excluded.

We do not regard the apparent change of R with electron energy in the table as significant, since a relative shift of about 1 volt in the absolute values of electron energy used for each related pair of ionizing efficiency curves, would be sufficient to account for the observed differences in R between the low and high ends of the energy range. At these extremes the slopes of the ionizing efficiency curves are rather steep, whereas in the middle range of 50–90 volts, all curves are sufficiently flat to eliminate this source of error.

[1] W. Bleakney, E. U. Condon, and L. G. Smith, J. Phys. Chem. 41, 197 (1937).
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[3] J. Delfosse and J. A. Hipple, Phys. Rev. 54, 1060 (1938).
[4] M. W. Evans, N. Bauer, and J. Y. Beach, J. Chem. Phys. 14, 701 (1946).
[5] W. Bleakney, Phys. Rev. 40, 496 (1932).
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[7] H. D. Hagstrum and J. T. Tate, Phys. Rev. 59, 354 (1941).

Strain in Non-Tetrahedral Carbon Atoms

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IN view of the recent correspondence in this journal[1-3] concerning the non-tetrahedral carbon atom, it seems desirable to call attention to certain results obtained by us which are now being prepared for publication.

Hybridization of s and p orbitals in carbon compounds was originally introduced to provide four atomic orbitals with strong directional properties, it being supposed that the attached groups were placed along the lines of greatest electron density. But, particularly in molecules which are "strained" in the original sense of Baeyer, we may expect that the lines of maximum charge density do not necessarily coincide with the directions of the attached atoms. In this way we are led to a treatment which regards the hybridization ratio λ as a variational parameter. The energy E of a molecule is expressed in terms of λ and $E(\lambda)$ is minimized. This leads to the best possible description of the molecule in terms of the pure valence state approximation of perfect pairing. We have treated the molecules cyclopropane, cyclobutane, and cyclobutadiene along these lines, discussing their stability, strain energy, and the orientation in space of their hydrogen atoms. We have also considered the compounds spiropentane, cyclobutene, and dibenz-cyclobutadiene (diphenylene) with special reference to the earlier treatment of the cyclic C_nH_n and

C_nH_{2n} by Penney.[4] It has also been possible to account qualitatively for the anomalous bond shortening associated with these strained systems[5,6]—anomalous, inasmuch as it is associated with a decreasing force constant.[7-9]

Our chief results for cyclopropane may be summarized as follows:

(i) Each carbon atom is at the corner of an equilateral triangle and the hybridization is such (see Fig. 1) that the
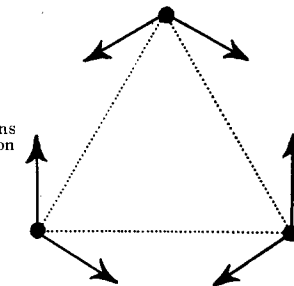

FIG. 1. Arrows denote directions of hybrid orbitals at the carbon atoms of cyclopropane.

two orbitals from any one carbon, in the plane of the ring, make an angle of about 106° with one another. In this way there is obtained a gain of about 5 ev per CH_2 group over a model in which[1] this angle is set at 90°. This means that less overlapping of the wave functions of paired electrons is more than offset by a decrease in strain energy at the carbon atoms.

(ii) The angle of 106° in the plane of the ring implies that the external valence angle should lie near 113°. A recent electron diffraction study[6] of the dichlorocyclopropane molecule gives 112°±4°.

(iii) The bond length is expected to be shorter and the $C-C$ stretching force constant less than the corresponding quantities for, say, ethane.

(iv) The error caused by neglect of resonance in the plane of the ring—a neglect which distinguishes our pure valence state model from the full HLSP treatment—is estimated at approximately 1 ev per CH_2 group. This is important when discussing strain energies.

Since the $C-C$ bonding orbitals are not directed at one another, these bonds may be described as "bent"—a concept which may be usefully employed symbolically to illustrate the effects (i)–(iv) above.

Our predicted HCH angle for cyclopropane (113°) differs appreciably from that of Duffey[1] (180°), and that of Kilpatrick and Spitzer[2] (122°), but is apparently in complete agreement with what is observed for the dichloro compound. Duffey's paper seems to contain no more than a restatement of the implications of Van Vleck's "ω-model," [10] whereas Kilpatrick and Spitzer's treatment, though much more enlightening, involves certain *ad hoc* assumptions which we have managed to avoid.

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[4] Penney, Proc. Roy. Soc. A146, 223 (1934).
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