(1.14 eV) than was found (with more limited basis sets) for π ionization of benzene[9] (0.4 eV) or pyridine[10] (0.6 eV). We therefore expect that π excitation to low-lying states in these (and other) larger π-electron systems will cause σ rearrangement of relatively less importance than the already small amount found in ethylene. This will then mean that one can indeed use the fixed core, π-electron approximation as a quantitatively accurate quantum chemical method for such problems (this is implicit in previous work[11,12]). It would be most interesting to see accurate *ab initio* calculations for larger π systems (*e.g.*, naphthalene) using the procedures we used for ethylene: it may be that for such large systems even π excitation to Rydberg states or π ionization would be moderately well represented with the fixed σ-core restriction.

Acknowledgment. M. E. S. acknowledges partial support of this work through a grant from the Petroleum Research Fund, administered by the American Chemical Society. We are also grateful to University Computing Company for a grant from the Chemical Applications Department, which enabled us to perform these calculations. Thanks are due Dr. R. Gilman for a preprint of his paper.[12]

Experimental and Theoretical Comparison of the Electronic Structures of Ethylene and Diborane

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Received January 17, 1970

Abstract: The high-resolution He(I) and He(II) photoelectron spectra of the isoelectronic molecules C_2H_4 and B_2H_6 are compared with each other and the results of near-Hartree–Fock calculations of their spectra using Koopmans' theorem. The agreement with experiment for the first six bands observed for each compound is very good, and lends considerable support to Pitzer's idea that the electronic structure of diborane is derived directly from that of ethylene, but with the $1b_{2u}$ π MO shifted below the first three σ MO's. The relevance of the photoelectron spectra of these molecules to their optical spectra is also demonstrated.

In the last 5 years, two techniques of electronic structure analysis, molecular SCF calculations using gaussian-type orbitals (GTO's) and high-resolution photoelectron spectroscopy, have proved to be of ever-increasing importance, especially when used in concert. In this study, these techniques are applied to the ethylene and diborane molecules, in an effort to trace experimentally and theoretically the correlation between the various orbitals of these two isoelectronic systems. A large number of calculations of the electronic structure of ethylene have already appeared,[2] of course, and the photoelectron spectrum up to 21 eV has been recorded and interpreted in terms of the latest of these calculations.[3] To this, we add the He(II) spectrum of ethylene, and the He(I) spectrum of ethylene-d_4. Nearly as much effort has been expended on theoretical work on diborane,[4] and to this we add a somewhat improved calculation, and the He(I) and He(II) photoelectron spectra.

Photoelectron spectra were recorded using a high-resolution, 127° spectrometer,[5] having a dc capillary discharge lamp operated to maximize the intensities of either the He(I) (21.21 eV) or the He(II) (40.8 eV) resonance line. Under the best conditions, the He(II) line is no more than $^{1}/_{50}$ as intense as that of He(I). Molecular orbital energies of ethylene and diborane in their established ground state geometries were calculated using the POLYATOM programs. The boron and carbon atom basic sets used here are those given in ref 6, except that the seven-term p set was split 5,2 rather than 4,3 as done in that reference. The hydrogen 1s orbital is a five-term fit to a Slater orbital having an exponent of $(1.8)^{1/2}$.[7] Our past experience with such calculations strongly supports the idea that trustworthy estimates of valence shell ionization potentials can be obtained by empirically multiplying the Koopmans' theorem values by 0.92 for first row elements; the theoretical IP's reported here have been so treated. The total energies computed for ethylene and diborane were -78.0188 and -52.7758 au.

The experimental He(II) spectra and the theoretical IP's are compared in Figure 1, and the He(I) spectra showing the IP's up to 21 eV at a higher resolution are given in Figure 2. The lower resolution of the He(II)

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(1) (a) Bell Telephone Laboratories; (b) Ford Motor Company; (c) Rutgers University.

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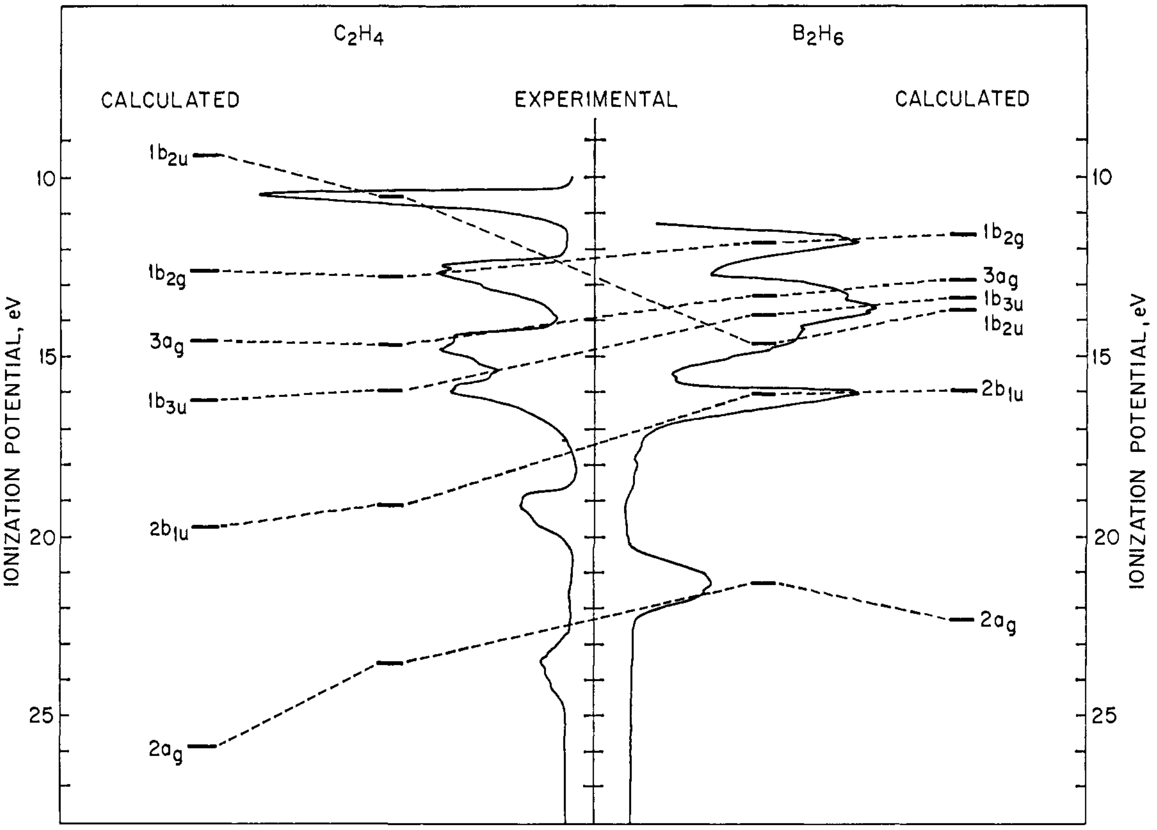

Figure 1. Comparison of the He(II) photoelectron spectra of ethylene and diborane with those calculated using Koopmans' theorem values multiplied by 0.92.

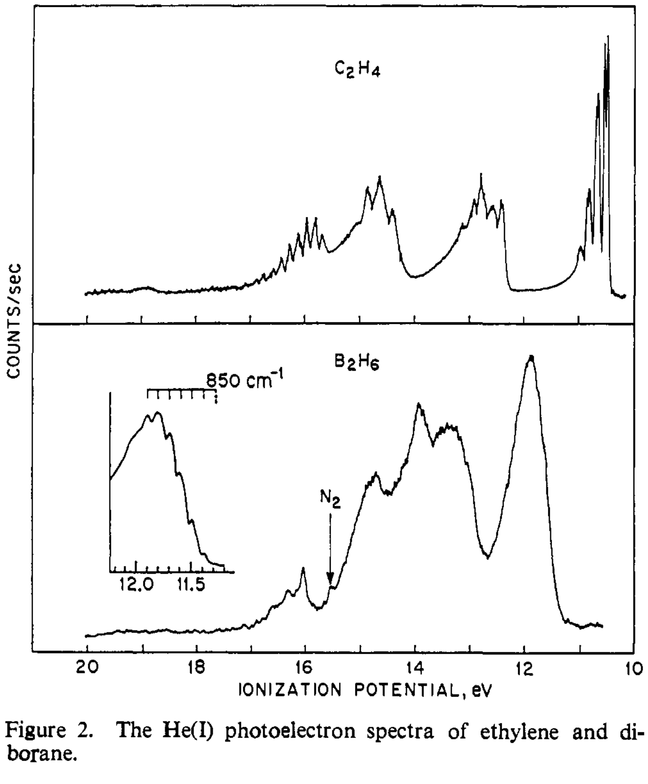

Figure 2. The He(I) photoelectron spectra of ethylene and diborane.

spectra results in large part from the necessity of using wider analyzer slit widths with the less intense He(II) excitation. Figure 1 illustrates the usual good agreement obtained between calculated and experimental IP's, with the correlation between the orbitals of the two molecules being perfectly straightforward except for one level, the $1b_{2u}$ MO. Qualitatively, the correlation can be understood if one first imagines a proton pulled from each of the carbon atoms of ethylene, and taken to infinity. The carbons thereby become boron atoms, and because of their lower nuclear charge, all occupied MO's are moved upward. The protons are then returned to the dinegative ion, but are inserted into the double bond, thus forming diborane and preferentially stabilizing the π MO, $1b_{2u}$. Looked at in this way, one sees that all of the MO's of diborane are higher in energy than the corresponding MO's of ethylene, except for the π orbital, which is lower. Pitzer's earlier idea that diborane is like ethylene, but with a protonated double bond,[8] seems fully substantiated by these calculations, provided one recognizes that the π MO in diborane is the fourth-highest filled MO, rather than the highest, as it is in ethylene. Experimental verification of the simple idea quoted above is found in the good agreement, band for band, with the observed photoelectron spectra.

Unlike ethylene, only two of the bands of diborane show vibrational structure, Figure 2. The first, with adiabatic and vertical IP's of 11.38 and 11.81 eV, respectively, displays six members of a progression with a characteristic spacing of 850 cm^{-1}. This is most readily assigned to the totally symmetric HBH angle deformation ν_3', which has a frequency of 1180 cm^{-1} in the neutral molecule.[9] The corresponding band at 12.5 eV in ethylene also shows evidence of excitation of the ν_3'

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vibration (among others), the value being 800 cm^{-1} in the ion.[3] Excitation of the ν_3' motion in this state of the ion is consistent with the MO population analysis, which shows the $1b_{2g}$ orbital in diborane to involve the 2p orbitals on boron and only the terminal hydrogen atoms.

Koski, *et al.*,[10] have studied the fragmentation of diborane under electron impact and have obtained values for the first IP, and appearance potentials of various fragments. In general, one expects such values to be up to 1 eV too high. Thus, they give 11.9 eV as both the first IP (0.5 eV too high) and the appearance potential of the $B_2H_5^+$ fragment. Perhaps the appearance potential is also high by 0.5 eV, but it is striking that this value very nearly coincides with that position where the vibrational structure breaks off in the $1b_{2g}$ photoelectron band (inset, Figure 2) indicating a possible dissociative process in this region. In addition to those for $B_2H_6^+$ and $B_2H_5^+$, the threshold for $B_2H_4^+$ formation (12.3 eV) is also found within the $1b_{2g}$ photoelectron band envelope. For comparison, the corresponding ions $C_2H_4^+$, $C_2H_3^+$, and $C_2H_2^+$ also have thresholds within the $1b_{2g}$ band of ethylene.[11]

The second structured band in diborane, $2b_{1u}$, at 16.06 eV shows four members of a 2250-cm^{-1} progression, which we assign to the totally symmetric B–H$_{\text{terminal}}$ stretch, ν_1' (2524 cm^{-1} in the neutral molecule). As expected, the $2b_{1u}$ band of ethylene at about 19 eV also shows evidence of the symmetric C–H stretch (ν_1' $\sim$2500 cm^{-1}, ν_1'' 3019 cm^{-1}). Both of the $2b_{1u}$ orbitals are largely 2s on the heavy atoms with smaller 2p and terminal hydrogen atom contributions.

One last feature of note in the photoelectron spectra are the relative intensities in the He(I) and He(II) spectra. As is readily seen by comparing Figures 1 and 2, the most prominent intensity effect in diborane is the relative fourfold increase in the intensity of the ionization from the $2b_{1u}$ MO, on changing the excitation from He(I) to He(II). An identical effect is apparently evident for the $2b_{1u}$ band of ethylene, but the interpretation is complicated by the discrimination of our analyzer against the slow photoelectrons released in the He(I) spectrum. The significance of these intensity changes is not at all clear, but in this case, they lend support to our supposition that the bands at 19 eV in ethylene and 16 eV in diborane are closely related.

Finally, we wish to discuss several features of the optical spectra of these molecules, and how they relate to the photoelectron spectra. Merer and Mulliken[2] have pointed out the close similarity of the spacing and intensities of the more prominent vibronic lines in the $1b_{2u}$ photoelectron band of ethylene, and that of the $\pi \rightarrow 3s$ Rydberg transition in the optical spectrum. There are also evident in the optical spectrum certain poorly resolved lines in the $\pi \rightarrow 3s$ region, which Wilkinson and Mulliken[12] have called the d bands, and tentatively assigned as part of the $\pi \rightarrow 3s$ transition. These d bands would then result from the excitation of $4\nu_4'$, the ν_4' motion being very anharmonic. Because the d bands are much better resolved in the optical spectrum of ethylene-d_4, we have investigated the $1b_{2u}$ photoelectron band of this molecule, and indeed we find the d bands are present in their expected positions. This adds further weight[13] to the assignment of the d bands as part of the $\pi \rightarrow 3s$ Rydberg envelope.

The question of the location of $\sigma \rightarrow \pi^*$ transitions in ethylene is one of current interest, and relates directly to the optical spectrum of diborane. In ethylene, the weak $\sigma \rightarrow \pi^*$ transitions are undoubtedly covered by the much stronger $\pi \rightarrow \pi^*$ band. However, in diborane, we have seen that the originating π MO is considerably depressed with respect to the uppermost σ levels, so that one would expect the $\sigma \rightarrow \pi^*$ transitions of diborane to fall at much lower energies than the $\pi \rightarrow \pi^*$. Our virtual orbital calculations of the diborane optical spectrum place the first three $\sigma \rightarrow \pi^*$ transitions ($1b_{2g}$, $3a_g$, $1b_{3u} \rightarrow 1b_{3g}$) at 8.55, 9.66, and 10.33 eV, respectively, whereas the $\pi \rightarrow \pi^*$ band ($1b_{2u} \rightarrow 1b_{3g}$) is predicted to come at 11.86 eV. The first three bands are forbidden by symmetry, and the $\pi \rightarrow \pi^*$ has a predicted mixed oscillator strength[14] of 0.516. In the same approximation, the $\pi \rightarrow \pi^*$ band of ethylene has a mixed oscillator strength of 0.48. Experimentally,[15] a very weak band is observed in diborane at 6.8 eV, which we assign to the lowest $\sigma \rightarrow \pi^*$ transition, $1b_{2g} \rightarrow 1b_{3g}$, and two very strong bands appear at 9.2 and 10.3 eV, each about 1.3 times as strong as the $\pi \rightarrow \pi^*$ of ethylene. The lower of these is probably the $\pi \rightarrow \pi^*$ band of diborane ($1b_{2u} \rightarrow 1b_{3g}$), and the higher, the strongly allowed $3a_g \rightarrow 3b_{1u}$, $\sigma \rightarrow \sigma^*$ band.

Since completing this work, it has come to our notice that two other photoelectron studies have been carried out on diborane. One of these[16] involves work done on a commercial instrument[17] of essentially similar design and resolution capabilities to our instrument. A helium(I) source only was available and so IP's above 21.21 eV could not be detected. Both B_2H_6 and B_2D_6 were studied and the results and interpretation of the electronic structure are in agreement with our work.

The second study[18] was performed using a retarding field system for electron energy analysis. The spectrum produced using such an instrument should be the integral of our spectrum. The results and the authors' interpretation are not in agreement with ours. The first point to be made is that though a resolution of 10 meV f.w.h.m. is claimed for an electron of about 5-eV

Table I. Ionization Potentials of B_2H_6

Adiabatic IP, eV[a]	Vertical IP, eV	Orbital	Calculation[b]
11.38 ± 0.01	11.81 ± 0.01	$1b_{2g}$	11.6
<12.7	13.3	3_{ag}	12.9
<13.6	13.9 ± 0.1	$1b_{3u}$	13.4
<14.5	14.7 ± 0.1	$1b_{2u}$	13.8
16.06 ± 0.01	16.06 ± 0.01	$2b_{1u}$	16.0
20.2 ± 0.1	21.4 ± 0.1	2_{ag}	22.3

[a] Measured to the center of the lowest vibrational component where possible, otherwise to the estimated start of the band. [b] 0.92 of the Koopmans' theorem values.

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energy (electron ejected from argon by He(I)), there is no sign of any of the clear vibrational structure observed on the first and fourth bands in our spectrum, where a resolution of only 20 meV is employed.

The second point to note is that on the basis of two sharp steps observed in their spectrum (quoted as 12.728 ± 0.001 eV and 12.803 ± 0.005 eV) the authors reverse the assignment of the 3_{ag} and $1b_{2u}$ orbitals (3_{ag} and $1b_{3u}$ in their notation). These two sharp peaks are not observed in our spectrum, the second vertical IP being 13.3 eV (see Table I), and it is believed[19] that they are due to an HCl impurity (first IP 12.74 ± 0.01 eV and 12.82 ± 0.01 eV; a spin-orbit doublet[20]). Besides removing any reason for reversing the orbital assignment this also implies that their error limits must be $\geq \pm 0.002$ eV on the first HCl peak, not ±0.001 eV, and ≥ 0.007 eV on the second peak, not ±0.005 eV.

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Circular Dichroism of Nucleoside Derivatives. VIII. Coupled Oscillator Calculations of Molecules with Fixed Structure

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Abstract: A method of calculating rotational strengths by a bond–bond coupled oscillatory theory is described. The technique is applied to a variety of specially chosen molecules to check the theory at various levels of approximation. Good agreement with experiment, particularly in the case of the cyclonucleosides, suggests that coupled oscillator theory accounts for most of the observed optical activity in the pyrimidine nucleosides. The calculation is particularly useful for structure determination because of its simplicity and complete dependency on bond orientations within a molecule.

In a recent survey[1] on ORD and CD of aromatic compounds it was noted that very few of the theoretical aspects of Cotton effects attributed to electronic transitions in symmetric aromatic chromophores bonded to an array of chemical groups with transitions in the far-uv region have been investigated. While it is generally accepted that the Rosenfeld equation[2] gives the correct quantum mechanical result for the optical rotatory dispersion of any optically active molecule and the theories of Condon, Altar, and Eyring[3] and of Kirkwood[4] provide expressions governing the relationship between optical rotatory strengths and chemical structure, the extension of these theories to more complex chromophores remains to be conceived. Some progress along these lines has been made recently by several investigators employing the one-electron theory of optical rotation. Caldwell and Eyring[5] have calculated the sodium D-line optical rotation of 1-methylindan. More recently, Moscowitz[6] has employed qualitative one-electron concepts to explain the enhancement of the ^1L_b Cotton effect when the benzene ring is substituted with oxygen or nitrogen. Kuriyama, *et al.*,[7] and DeAngelis[8] have published quadrant rules for predicting the absolute configuration of aromatic compounds based on symmetry rules that arise in the one-electron theory.

Nevertheless, there is some evidence that the coupled oscillator mechanism can make significant contributions to these Cotton effects. Höhn and Weigang have demonstrated that "dynamic coupling" terms can be dominant in appropriate ketone molecules.[9] In previous papers of this series,[10] the π–π^* nature of the absorption spectra of the ribonucleosides (and some 300 closely related derivatives) has been established in the 190–300-nm range. To assign absolute configurations to these molecules, resort has been made to the Kirkwood–Tinco[11] polarizability expression for the rotational strength. This treatment utilizes bond polarizabilities to bring in the effects of the vicinal group upon the planar chromophore. The chromophore electronic transition moment was either calculated from simple LCAO MO theory or obtained from experimental data. This moment was then coupled to each bond of the vicinal group *via* a dipole–dipole interaction potential. The magnitudes of the calculated rotational strengths were sufficiently large to encourage further pursuit of a coupled oscillator interpretation of the CD data.

In the present communication we give an improved scheme to obtain coupled oscillator rotational strengths of nucleosides, as well as all other molecules containing

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