would be of little use indeed. However, it is a more powerful tool than is indicated by this example alone. Traditionally, Pólya's method has been applied primarily to molecules such as benzene,[6] octahedral and tetrahedral coordination complexes,[7] and polynuclear coordination complexes[7,8] which are characterized by rigid skeletons. The element R_6 is only a single example of internal symmetry operations which occur in nonrigid molecules. In addition to the ring flip–rotation operation, internal symmetry elements which have been investigated include internal rotation (in ethane and metallocene compounds) and inversion (in amines).[9]

Furthermore, the investigation of isomerism in nonrigid molecules has become an important field of chemical investigation. Permutation group properties have been applied to the analysis of these systems, both theoretically[10] and applied.[11,12] In work carried out by Gillespie and his colleagues, the power of the permutation group method has been illustrated for a number of nonrigid systems.[11] They note that monocyclic ring systems, in particular the cyclohexane system, exhibit a dynamic skeletal symmetry which is equivalent to the symmetry of a hypothetical planer ring. They obtain the dynamic skeletal symmetry, group D, by obtaining the product of the permutation group G representing the rigid skeletal system of the ring and the permutation group F representing the flexions: $D = G \times F$.

The advantages of the point group method proposed herein over the permutation group method are similar to those leading to the adoption of point groups for most chemical applications: (a) the symmetry elements bear logical and easily visualized relations to chemical/physical notions of the molecule's properties; (b) the group of symmetry operation can be obtained from the product $G \times F$ in a manner which allows for visualization and description; and (c) the description of the dynamic skeletal symmetry group is independent of the numbering of the skeleton.

It is our hope that the present method of describing the dynamic skeletal symmetries of molecules will serve as a fruitful tool for making the chemist's intuition of internal molecular motions into a theoretically precise notion.

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References and Notes

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Excited States and Photochemistry of Saturated Molecules. I. General Approach and Application to Propane

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Abstract: Following Ruedenberg, we suggest that a useful measure of chemical binding is the two-center, one-electron interference contribution to the energy in the electronic state of interest. Using this conceptual framework, the vertical valence excited states of propane in the optimal ground state geometry are examined using INDO in its original parametrization. The results are compared with available experimental information. The calculations yield bond energies which are consistent with observed decomposition modes for ground states of small alkanes and excited states of propane. Configuration interaction calculations are discussed in the case of propane. Inclusion of all single excitations from the ground state results in considerable rearrangement of the order of excited states; however, the relative bond energies within each state are unaffected.

With the exception of ethane, absorption or electron impact spectra of small ($n \leq 6$) acyclic alkanes contain little discernible information. The broad, essentially featureless spectra[1,2] give little in the way of structural information about the excited state. Recently Lipsky[3] observed that the separation between absorption onset and fluorescence maximum of linear alkanes decreases with increasing chainlength and increases with branching. Based on these results and energy transfer studies, he concluded that these frequencies are related to the extent of nuclear distortion in the excited states. Numerous photochemical studies of small acyclic alkanes have established the striking predominance of two bond cleavages.[4] For energies near or at the absorption onset, those which lead to carbene formation are clearly the most important.

Theoretical speculation about the nature of excited states in small alkanes has largely been limited to methane and ethane. The most complete set of calculations for larger alkanes is that recently carried out by Sandorfy and Salahub[5] using a CNDO/2[6] method modified specifically for the purpose of reproducing excitation energies. While the excitation energies calculated by these authors seem to be in rather good agreement with experimental results, it must be noted that comparison between observed spectra and calculations are difficult for alkanes, as a somewhat arbitrary definition of a lowest excitation energy must be adopted. It is also noteworthy that Sandorfy's calculations do not consistently reproduce important shifts observed due to branching at certain carbon atoms.

Attempts have been made to rationalize photochemical processes using simple MO models;[2,7,8] however, it is apparent that the nature of excited states of alkanes is not yet well understood. This is, in part, due to the difficulty in interpreting experimental data related to these states, and in part due to the lack of accurate quantum mechanical calculations on a sufficient number of these molecules. Of particular interest would be the binding properties and geometries of alkane excited states, for these should be related to the available experimental data on fluorescence and photochemistry of these molecules. Calculations of such properties are rather time consuming at the ab initio molecular orbital level and thus are not easily done. Further, it has been suggested that diffuse, essentially nonbonding Rydberg-like orbitals are essential for an understanding of the electronic *spectra* of at least methane.[9] The existence of such Rydberg states complicates matters experimentally as well as theoretically.

Although the Rydberg character of excited states of alkanes may be important, there is much to be gained from an examination of pure valence states. Flouquet and Horsley[10] recently analyzed the potential energy surface of the $\tilde{\mathrm{B}}\ {}^1\mathrm{A}_1$ state of water. While the vertical state is largely Rydberg in character, at large OH distances (i.e., in the region of dissociation to OH + H) this state is predominantly an antibonding valence state. Thus, even though Rydberg states are *spectroscopically* important in such molecules, this does not diminish the role valence excited states may play in excited state potential energy surfaces, particularly with regard to dissociation modes. For this reason, in the present work we are less concerned with detailed prediction of spectroscopic assignments than with an understanding of the nature of bonding in valence excited states and the subsequent effect on dissociation. The work of Flouquet and Horsley[10] and the semiempirical results of Segal and coworkers[11] lends credence to this approach.

Since one of our objectives is to obtain binding characteristics of excited states, it is necessary to provide a quantitatively useful approach to chemical binding. Our conceptual definition of a theoretical bond energy is based on the classic series of papers on the subject by Ruedenberg and coworkers.[12] As Ruedenberg pointed out, the essential difference, with respect to covalent binding, between classical electrostatics and quantum mechanics is the way in which the molecular one-electron density is obtained from those of the component atoms or molecular fragments. In the former approach, one simply adds the densities of the isolated atoms in such a way as to obtain a (normalized) molecular density

$$\rho^{\mathrm{CL}}(\mathrm{r}) = \sum_{\mathrm{A}} \rho_{\mathrm{A}}(\mathrm{r}) \qquad (1)$$

while quantum mechanically one first superimposes the component wave functions ϕ_{a} from which the molecular density is obtained.

$$\psi(\mathrm{r}) = \sum_{a} C_a \phi_a(\mathrm{r}) \qquad (2)$$

$$\rho^{\mathrm{QM}}(\mathrm{r}) = \sum_{a}\sum_{b} C_a C_b \phi_a(\mathrm{r})\phi_b(\mathrm{r}) \qquad (3)$$

The latter equation contains terms which are analogous to the classical density ρ^{CL} but contains additional cross terms, $\phi_a\phi_b$: $a \neq b$, which arise from the interference of the superimposed wave functions on different atoms. To isolate this important difference, Ruedenberg suggested a partitioning of the quantum-mechanical one-electron density into two contributions: the quasi-classical density (ρ^{QC}) which is analogous to that obtained from classical considerations and which integrates over all space to the total number of electrons (N); and the interference density (ρ^{I}) which accounts for the interference between atoms and integrates over all space to zero.

$$\rho = \rho^{\mathrm{QC}} + \rho^{\mathrm{I}} \qquad (4)$$

$$\begin{aligned} \int \rho^{\mathrm{QC}} \mathrm{d}V &= N \\ \int \rho^{\mathrm{I}} \mathrm{d}V &= 0 \end{aligned} \qquad (5)$$

Since one-electron properties in general, and the one-electron contribution to the electronic energy in particular, are obtained by integrating the product of ρ and the corresponding operator over all space, the expectation values of such properties $\langle P \rangle$ may be thought of as sums of quasi-classical and quantum-mechanical contributions.

$$\langle P \rangle = \int \rho \hat{P} \mathrm{d}V = \int \rho^{\mathrm{QC}} \hat{P} \mathrm{d}V + \int \rho^{\mathrm{I}} \hat{P} \mathrm{d}V = \langle P^{\mathrm{QC}} \rangle + \langle P^{\mathrm{I}} \rangle \qquad (6)$$

For the one-electron energy, E_1, we have

$$\langle E_1 \rangle = \langle E_1{}^{\mathrm{QC}} \rangle + \langle E_1{}^{\mathrm{I}} \rangle \qquad (7)$$

Ruedenberg developed an analogous partitioning for the two-electron density and corresponding two-electron energy, and then applied his approach to a detailed study of chemical bonding in a series of small molecules. The major conclusion of interest with regard to the present work is that the essence of covalent binding lies in the two-center, one-electron interference contribution to the energy. This implies that one might use such energies at least as a relative measure of bond strengths.

The appeal of Ruedenberg's approach is that, on the one hand it ties the very nature of chemical bonding to the basic ingredient of wave mechanics, while on the other hand it is completely general and *not* tied to a particular quantum-mechanical method. Thus, while our initial investigations will make use of the molecular orbital approximation, and a semiempirical method at that, it is readily extended to more sophisticated levels.

Within the molecular orbital (LCAO-MO) approximation, the one-electron two-center interference density is given by

$$\rho^{\mathrm{I}} = \sum_{\mathrm{A}} \sum_{\mathrm{B} \neq \mathrm{A}} \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} P_{\mu\nu}[\chi_\mu \chi_\nu - \tfrac{1}{2} S_{\mu\nu}(\chi_\mu{}^2 + \chi_\nu{}^2)] \qquad (8)$$

where $S_{\mu\nu}$ is the overlap integral between two atomic orbitals χ_μ and χ_ν

$$S_{\mu\nu} = \int \mathrm{d}V_1 \chi_\mu(1) \chi_\nu(1) \qquad (9)$$

$P_{\mu\nu}$ is the electron density bond order matrix

$$P_{\mu\nu} = \sum_{i} N_i C_{\mu i} C_{\nu i} \qquad (10)$$

Table I. Calculated Ground State Bound Energies in Alkanes (eV)[a]

Molecule	C_pH	C_sH	C_tH	C_pC_p	C_pC_s	C_sC_s	C_pC_t
CH_4[b]	4.51 (4.51)[d]						
C_2H_6[c]	4.39 (4.26)[e]			3.83 (3.82)[d]			
C_3H_8	4.40 (4.31)[e]	4.28 (4.08)[e]			3.71 (3.49)[e]		
n-C_4H_{10}	4.40 (4.37)[e]	4.30			3.72	3.59 (3.45)[e]	
i-C_4H_{10}	4.40		4.17 (3.86)[e]				3.61
n-C_5H_{10}	4.40	4.27			3.72	3.60	

[a] The subscripts p, s, t stand for primary, secondary, tertiary, respectively. Experimental values in parentheses. [b] Prototype for CH bonds. [c] Prototype for CC bonds. [d] W. Moore, "Physical Chemistry," 4th ed, Prentice-Hall, Englewood Cliffs, N.J., 1962, p 72. [e] V. I. Vedeneev, L. V. Gurvich, V. N. Kondrat'ev, V. A. Medvedev, and E. L. Frankevich, "Bond Energies, Ionization Potentials, and Electron Affinities," Edward Arnold Publishing Co., New York, N.Y., 1966.

and A and B refer to the centers. The latter sum is over all occupied orbitals and N_i is the occupancy of the ith MO. For closed shells $N_i = 2$ for all i, while for virtual excitations $N_i = 1$ for the two MO's involved in the excitation and 2 for all others. The corresponding two-center, one-electron interference energy is

$$E_1{}^{\mathrm{I}} = \sum_{\mathrm{A}} \sum_{\mathrm{B}\neq\mathrm{A}} \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} P_{\mu\nu}[\langle\chi_\mu|\hat{h}|\chi_\nu\rangle - \tfrac{1}{2}S_{\mu\nu}(\langle\chi_\mu|\hat{h}|\chi_\mu\rangle + \langle\chi_\nu|\hat{h}|\chi_\nu\rangle)] \quad (11)$$

where $\hat{h}$ is the one-electron energy operator.

It is important to note that ρ^{I}, and therefore $E_1{}^{\mathrm{I}}$, may be partitioned further into contributions from each occupied MO.

$$\rho^{\mathrm{I}} = \sum_i \rho_i{}^{\mathrm{I}} = \sum_{\mathrm{A}} \sum_{\mathrm{B}\neq\mathrm{A}} \sum_{i}^{\mathrm{occ}} \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} N_i C_{\mu i} C_{\nu i} \times [\chi_\mu\chi_\nu - \tfrac{1}{2}S_{\mu\nu}(\chi_\mu{}^2 + \chi_\nu{}^2)] \quad (12)$$

Thus if we envision an electronic excitation in terms of removal of an electron from a ground state MO and subsequent placement of that electron in some previously unoccupied MO, it follows that any change in chemical bonding which occurs will be a result of both of those processes. Further, since each MO is, in general, itself a superposition of *all* atomic orbitals, *such an excitation will generally result in a change in the covalent bonding between all pairs of atoms in the molecule.*

While it is reasonable to expect calculated one-electron two-center interference energies to provide a measure of *relative* bond strengths, it is not to be expected that such energies will be *equal* to experimental bond energies. To obtain a more quantitative measure of covalent bonding, we have proposed the following simple procedure.[13] Let $D_{\mathrm{AB}}{}^{\mathrm{e}}$ be the experimental A-B bond energy in some suitable prototype molecule, and $E_1{}^{\mathrm{I}}(\mathrm{A,B})$ be the corresponding A-B one-electron interference energy

$$E_1{}^{\mathrm{I}}(\mathrm{A,B}) = 2 \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} P_{\mu\nu}[\langle\chi_\mu|\hat{h}|\chi_\nu\rangle - \tfrac{1}{2}S_{\mu\nu}(\langle\chi_\mu|\hat{h}|\chi_\mu\rangle + \langle\chi_\nu|\hat{h}|\chi_\nu\rangle)] \quad (13)$$

Then we define N_{AB} as the ratio of $E_1{}^{\mathrm{I}}(\mathrm{A,B})$ and $D_{\mathrm{AB}}{}^{\mathrm{e}}$ such that for the same bond type A-B in other molecules, the theoretical A-B bond energy $D_{\mathrm{AB}}{}^{\mathrm{c}}$ may be obtained from the corresponding interference energy

$$N_{\mathrm{AB}} = -E_1{}^{\mathrm{I}}(\mathrm{A,B})/D_{\mathrm{AB}}{}^{\mathrm{e}} \qquad \text{(prototype)} \quad (14)$$

$$D_{\mathrm{AB}}{}^{\mathrm{c}} = -E_1{}^{\mathrm{I}}(\mathrm{A,B})/N_{\mathrm{AB}} \quad (15)$$

Initially, we propose only to distinguish bonds according to their classical types (e.g., C—C, C=C, C≡C, etc.); however, for excited state equilibrium geometries this may be overly restrictive, and N_{AB} may be more realistically expressed as an explicit function of internuclear distance.

Because of our interest in the geometries of alkane excited states, we have chosen to initiate our study using the semiempirical INDO method in its original parametrization.[14] While the original INDO method has been criticized for its inability to treat excited states of unsaturated molecules properly,[15] we feel that there is ample justification for its use for saturated molecules. Most of the aforementioned criticism has been based on a few CNDO calculations on unsaturated molecules, principally aromatics. The criticism centers around the mixing of σ and π levels by CNDO. Clearly alkanes do not fall into the above category, so there is no a priori reason for assuming that the problems found for aromatic systems will be carried over to saturated ones.

Within the INDO approximations the two-center, one-electron interference energy is given by

$$E_1{}^{\mathrm{I}}(\mathrm{A,B}) = 2 \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} P_{\mu\nu} S_{\mu\nu} \beta_{\mathrm{AB}}{}^0 \quad (16)$$

where $\beta_{\mathrm{AB}}{}^0$ is a semiempirical parameter.[6] As an initial test of the method, the ground state bond energies of the alkanes listed in Table I have been calculated. For all molecules $N_{\mathrm{CH}} = 4.438$, $N_{\mathrm{CC}} = 8.862$, and the ground state geometry has been optimized. The calculated bond energies are listed in Table I and compared with experiment where possible. It is to be noted from these results that the ordering of bond energies reproduces experimental trends and also predicts, on the basis of weakest bond energy, the correct ground state dissociation in each case.

With these results we now feel justified in applying the approach described in earlier paragraphs, using INDO. As an initial example of the method, we will consider the propane molecule which has received much attention from experimental photochemists and rather little theoretical attention. In the present work we have limited ourselves to vertical excitations. Later papers will deal more fully with the whole series of small alkanes as well as with geometry relaxation in excited states. Since one of our ultimate goals is to calculate optimal geometries of alkanes in various excited states, the ground state geometries used in investigation of vertical excitations are the INDO optimal geometries. (The INDO ground state geometry for propane is quoted elsewhere.[16]) The effect of the choice of ground state geometry on the ordering of orbitals and states in alkanes will be discussed elsewhere;[17] however, in the particular case of propane it is to be noted that small ground state geometry variations (e.g., standard geometries[18] vs. INDO optimal geometries) have little effect on the conclusions of the present paper.

Table II lists the highest occupied and lowest virtual orbital of propane, since in this particular case the corresponding excitation corresponds to the lowest vertically excited state in the molecule according to INDO. Both orbitals belong to the B_2 representation and may be classified as pseudo-π orbitals, since they have a node in the molecular symmetry plane. (The numbering system and coordinate axes are pictured in Figure 1.) It is important to note that the highest occupied orbital has nodes between adjacent

Table II. Highest Occupied and Lowest Unoccupied Orbitals in Propane[a]

MO	Highest occupied	Lowest unoccupied
AO		
C_1 s	0.0	0.0
p_x	0.0	0.0
p_y	−0.2672	0.2982
p_z	0.0	0.0
C_2 s	0.0	0.0
p_x	0.0	0.0
p_y	0.4248	0.4604
p_z	0.0	0.0
C_3 s	0.0	0.0
p_x	0.0	0.0
p_y	−0.2672	0.2983
p_z	0.0	0.0
H_4	0.0	0.0
H_5	0.2818	0.2690
H_6	−0.2818	−0.2690
H_7	−0.4238	+0.4004
H_8	0.4238	−0.4004
H_9	0.0	0.0
H_{10}	−0.2817	−0.2691
H_{11}	0.2817	0.2691

[a] See Figure 1 for numbering system and coordinate axes. INDO calculated ground state geometry.

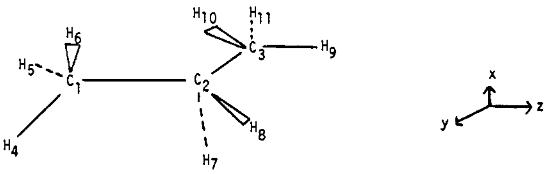

Figure 1. Atom numbering system and coordinate axes for propane.

carbons and therefore is expected to give rise to antibonding interference between these atoms. On the other hand, there are no nodes between the carbons and their adjacent (out-of-plane) hydrogens. Thus this orbital is at once CH bonding and CC antibonding, so removal of an electron should weaken the CH bonds and strengthen the CC bonds. Since more electron density is concentrated in the secondary than the primary CH region, the former bonds will be most affected by electron removal.

It is interesting to note in this regard that the lowest unoccupied MO (Table II) has nodal characteristics exactly opposite to those exhibited by the highest occupied one. It is to be expected, therefore, that placing an electron in this orbital will enhance the trend, that is, a further strengthening of the CC bonds coupled with a further weakening of the secondary CH bonds. That this is indeed the case may be seen from Table III. The net effect of the lowest energy valence excitation is to weaken the secondary CH bonds to the extent that their bond energies are smallest by about 0.6 eV. The out-of-plane primary CH bonds are also weakened considerably while the CC bonds are strengthened. As a result, those latter two bonds are equal in strength in this state.

As we view it, a rational evaluation of photochemical processes for alkanes must begin by collating all knowledge at hand concerning such processes. An electronic description of the ground state is useful since it provides information concerning the nature of chemical bonding in the ground state. The change in electronic description after absorption of a photon of a given energy is necessary, as it is the excited state potential surface which will eventually determine the final disposition of the absorbed energy. Since it is highly unlikely that the state formed by Franck-Condon absorption from a particular ground state will be stable with respect to nearby vibronic states, prediction of photochemistry requires that rate constants for all radiative and nonradiative processes be known for the evolution from the initially occupied state. This last problem has been reviewed recently by Jortner, Rice, and Hochstrasser.[19]

Table III. Singlet Virtual Orbital Excitation Energies and Bond Energies in Propane[a]

State[b]	ΔE[c]	Bond energies, eV			
		CC	CH_4	CH_5	CH_7
Ground ($1A_1$)		3.71	4.39	4.40	4.28
$2A_1$ ($\pi \rightarrow \pi^*$)	14.18	3.98	4.39	3.99	3.36
$1A_2$ ($\sigma \rightarrow \pi^*$)	14.27	3.68	3.95	4.16	3.81
$1B_2$ ($\sigma \rightarrow \pi^*$)	14.49	3.81	4.21	4.09	3.55
$3A_1$ ($\sigma \rightarrow \sigma^*$)	14.57	3.57	4.22	4.05	3.18
$2B_2$ ($\pi \rightarrow \sigma^*$)	14.63	3.74	3.40	4.13	3.80
$3B_2$ ($\pi \rightarrow \sigma^*$)	14.65	3.73	4.41	3.95	2.98
$1B_1$ ($\sigma \rightarrow \sigma^*$)	14.68	3.43	3.96	4.12	3.45

[a] See Figure 1 for atom numbering system. [b] The σ and π notation refers to the absence or existence of a node in the molecular symmetry plane. [c] Excitation energies.

Knowledge of photochemical systems in general, and alkanes specifically, does not even closely approach that needed completely to understand the processes. A complete description of a particular photochemical process for even moderately complicated molecules is at this point an unreasonable expectation. To approach an understanding of such systems, on a qualitative or semi-quantitative level, numerous assumptions must be invoked. The only real tests of most models will be their ability to correlate available data.

A reasonable approach to molecular dissociation in general is to begin with the assumption that dissociation in a particular electronic state occurs in such a way as to break the weakest bond(s) in the molecule. Thermal dissociation of alkanes in their ground electronic states may be consistently predicted in this way. In ethane, for example, the CC bond is weakest, and this molecule dissociates thermally to two methyl radicals. Since photodissociation of the same molecules is strikingly different, an extension of the present hypothesis would be to suppose that these differences are a result of changes in the nature of chemical bonding in the excited valence states.

At an exciting line of 10 eV (Kr) the most important primary processes in propane are[20]

$$C_3H_8 \xrightarrow{h\nu} (CH_3)_2C + H_2 \ (\phi = 0.42)$$

$$\rightarrow C_2H_4 + CH_4 \ (\phi = 0.47)$$

$$\rightarrow CH_2 + C_2H_6 \ (\phi = 0.09)$$

where the relative quantum yields are in parentheses. Loss of H_2 from the secondary carbon and loss of an adjacent CH_3 and secondary hydrogen are essentially of equal importance. Since the lowest absorption *maximum* is at 8.9 eV and since a rather high density of excited states is likely for the alkanes, it is reasonable to assume that 10 eV is sufficient to populate excited states higher than the lowest one. Thus, the above primary processes are not likely to be due solely to threshold excitation. A near-threshold study (159 nm) of the photochemical decomposition of propane has been carried out by Griffiths and Back[21] who observe that the decomposition products are almost solely dimethylcarbene and H_2. If our concept of correspondence between the mode of decomposition and the weakest bond in the molecule is correct, the experimental results imply that the lowest excited electronic state of propane is such that the secondary CH bonds become weaker than the carbon–carbon

Table IV. Singlet Excited States of Propane (SCI)[a]

State	ΔE[b]	Bond energies, eV			
		CC	CH_4	CH_5	CH_7
$1B_2$	13.06	3.74	4.31	4.11	3.11
$2A_1$	13.15	3.81	4.33	4.07	3.18
$1A_2$	13.67	3.65	3.97	4.10	3.90
$2B_2$	13.82	3.58	3.47	4.11	3.93
$1B_1$	14.03	3.51	3.95	3.86	3.84
$3A_1$	14.25	3.70	4.07	4.07	3.46
$2A_2$	14.38	3.62	4.09	3.68	3.95

[a] See Figure 1 for numbering system. [b] Excitation energies.

linkages. It is encouraging, therefore, that our model successfully predicts such a bond energy reversal. These results would imply cleavage of the secondary CH bonds in the lowest excited state of propane in agreement with experimental observations. It is to be noted that the methylene CH bonds are also predicted to be the weakest in the second allowed ($1B_2$) state.

Due to the high density of states in propane, it is important to investigate the effect of configuration interaction (CI) on the results discussed above. To this end we have carried out CI calculations on all four C_{2v} symmetry types, including all single excitations from the ground state. The results of these calculations are shown in Table IV. Comparison with the SCF results (Table III) prompts the following comments. (a) Inclusion of CI results in considerable reordering of the excited states. All of the excitation energies listed in Table III are decreased, and the spread between the states listed is increased. As expected, the $2B_2$ and $3B_2$ states are strongly interacting. As a result, these two states are significantly split by the CI expansion. (b) In general, the predicted relative bond energies within each state are unaffected by configuration interaction. The lowest two excited states ($1B_2$ and $2A_1$) both predict the methylene CH bonds to be weakest by about 0.6 eV. The (forbidden) $1A_2$ state predicts the CC bond to be the weakest. Thus, even though the order of these three states changes when CI is included, the conclusions concerning bond strengths are the same.

It is important to note that these calculations have been carried out for vertical excitations at the ground state geometry. The resultant calculated bond energies should give an indication of geometric distortions one can expect in these states, particularly with regard to bond stretching. It is clear, however, that quantitative conclusions concerning dissociation must be based on investigation of the potential energy surface in each state. Calculations on the optimal geometries of a number of propane excited states are currently being carried out.[16]

Conclusions

Our model is based on the assumption that excited valence states are important in describing the photodissociation of alkanes. Even if absorption of a photon initially populates a state which is largely Rydberg in character, as the molecule relaxes along a reaction coordinate, that state is likely to become or intersect a state which is strongly valence in character, and the actual dissociation will be described by the characteristics of the valence state. This expectation is supported by the recent work of Flouquet and Horsley.[10] The binding characteristics of both ground and excited states are inferred from the two-center, one-electron interference contribution to the energy of the electronic state of interest.

The following conclusions may be drawn from our results.

(1) At least for saturated hydrocarbons, bond energies calculated from INDO interference energies are in good agreement with experimentally available bond energies and predict the correct modes of thermal decomposition.

(2) For vertical valence excitations from the geometry-optimized ground state of propane, INDO predicts that the secondary CH bonds are most weakly bound in the lowest excited states. This is fully consistent with the experimental observation that the predominant photodissociation at longer wavelengths is $C_3H_8 \rightarrow (CH_3)_2C + H_2$. There are no characteristics of higher states that make them inconsistent with observed photochemistry.[22] However, a more detailed examination of possible reaction coordinates is necessary before specific relationships may be drawn.

(3) Based on (1) and (2) above, we tentatively conclude that the model proposed here is a viable first step toward an understanding of the photochemical decomposition of alkanes. Hopefully, the approach will be applicable to a general molecular system.

Since the calculations discussed here involve only vertical excitations, a necessary next step is an investigation of the geometric relaxation of propane and related molecules in the various excited states. It is likely that the bond energy changes calculated in the present work will at least partially reflect the subsequent relaxation. For example, one would expect a shortening of the CC bonds and a lengthening of the secondary CH bonds in the first excited state of propane. Angular changes are also important since, for example, propane is known to eliminate H_2 rather than 2H near threshhold. The latter changes are more subtle and require a detailed examination of the excited state geometry. Such calculations are currently in progress for a number of propane excited states. These calculations will, in turn, provide a starting point for an investigation of the excited state vibrational manifolds.

If there are limitations to the proposed model, we feel they reside largely in the particular quantum mechanical level at which the concept of interference is applied, rather than in the conceptual model itself. To investigate this expectation, we intend not only to extend the INDO calculations to other alkanes and substituted alkanes, but to investigate nonempirical MO methods as well. Only at the latter level can one realistically begin to introduce Rydberg-like transitions explicitly.

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Calculations of the Magnetic Moments of Some Benzene Derivatives

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Abstract: We have calculated the magnetic moments in the $^1E_{1u}$ and $^1E'$ states of various benzene derivatives with D_{6h}, D_{3h}, and C_{3h} symmetries using wave functions obtained from the Pariser-Parr-Pople (PPP) method. For the benzene derivatives containing electron-donating substituents, the calculated magnetic moments are in good agreement with the experimental values obtained from our previous MCD measurements both in sign and in magnitude. The magnitudes of the calculated magnetic moments of benzene derivatives having electron accepting substituents are much smaller than those of benzene derivatives containing electron-donating groups, which is consistent with the experimental results that the benzene derivatives with strong electron-accepting functions showed no magnetic circular dichroism for the $^1E' \leftarrow {}^1A_1'$ and $^1E' \leftarrow {}^1A'$ transitions.

The magnetic circular dichroism (MCD) technique has thus far been tested by many authors aiming at making it possible to elucidate complicated electronic spectra and magnetic properties of ions and molecules in their ground and excited electronic states.[1-3] Of much interest in recent MCD work, benzene and its derivatives have been studied because of their intriguing spectral features in their longer wavelength spectral region.[4-10] The vibrational structure observed in the MCD spectrum of the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of benzene itself was analyzed in detail by Shieh,[6] Caldwell,[7] and Douglas[9] and also the effects of substitutions on the sign and magnitude of MCD spectra of the $^1B_{2u} \leftarrow {}^1A_{1g}$ and $^1B_{1u} \leftarrow {}^1A_{1g}$ transitions were investigated.[5,7,8,10] On the other hand, the magnetic circular dichroism of various nonbenzenoid aromatic hydrocarbons[11-13] has also been investigated in our laboratory. In this work, the Faraday A term, which should be expected when either the ground or excited state of a compound is degenerate, was studied and the magnetic moments of degenerate excited states of nonbenzenoid aromatic hydrocarbons were extracted. These values were in good agreement with those calculated using wave functions obtained from PPP and CNDO procedures.[13,14]

It seems also interesting to investigate magnetic circular dichroism of the $^1E_{1u} \leftarrow {}^1A_{1g}$ transitions of benzene derivatives and to obtain the magnetic moments in the $^1E_{1u}$ states. We have already reported the MCD spectra of some benzene derivatives[15,16] with D_{6h}, D_{3h}, and C_{3h} symmetries. The $^1E_{1u} \leftarrow {}^1A_{1g}$ transition of benzene corresponds to the $^1E' \leftarrow {}^1A_1'$ and $^1E' \leftarrow {}^1A'$ transitions in D_{3h} and C_{3h} symmetries, respectively. In the region of these transitions, halogenobenzenes, phloroglucin, 1,3,5-trimethoxybenzene, and 1,3,5-tricyanobenzene showed Faraday A terms. From the observed MCD and uv spectra, A/D values were extracted by use of the method of moments[2] together with B/D values, and these values are shown in Table I. However, 1,3,5-trinitrobenzene, 1,3,5-benzenetricarboxylic acid, and 1,3,5-benzenetricarbonyl chloride indicated no magnetic circular dichroism for these electronic transitions and the magnetic moments in the $^1E'$ states of these molecules seem to be quenched.

It is the purpose of this paper to calculate the magnetic moments in the $^1E_{1u}$ and $^1E'$ states of these benzene derivatives using wave functions obtained from the Pariser-Parr-Pople (PPP) method[17-19] and to explain the experimental results from our previous MCD measurements[15,16] of benzene derivatives.

Calculations of Magnetic Moments

We have calculated the magnetic moments in the $^1E_{1u}$ and $^1E'$ states of benzene derivatives using wave functions determined on the basis of the PPP method including configuration interaction (CI). One-center core and repulsion integrals were evaluated from valence state ionization potentials and electron affinities. Two-center core and repulsion integrals were calculated by use of the Wolfsberg-Helmholtz[20] and Nishimoto-Mataga[21] equations, respectively. For the methoxyl group (OCH_3), we took account of the effect of hyperconjugation using the method offered by Lindner and Mårtensson.[22] We have calculated the electronic transition energies of benzene derivatives and show them in Table II along with the experimental values. The calculated values are in good agreement with the experimental data.

If we use real wave functions, the magnetic moments, μ, in the $^1E_{1u}$ and $^1E'$ states of benzene derivatives are ex-