observed at different temperatures with a variable temperature control, working on the principle of a heat exchanger. The x-irradiated sample of pivalic acid gave an ESR spectrum which resulted from a superposition of spectra from two different radicals. One spectrum contained ten absorption peaks equally spaced and having a Gaussian intensity distribution with ratios of 1:9:36:84:126:126:84:36:9:1. The number of peaks in this spectrum and the intensity distribution agree with the theoretical ESR spectrum expected from a *t*-butyl radical $\dot{C}-(CH_3)_3$, where the unpaired electron interacts equally with the nine hydrogen nuclei through hyperconjugation. The measured hyperfine coupling constant is 22 G and is in reasonable agreement with coupling constants measured for the *t*-butyl radical in the liquid state.[2] The second spectrum of the superimposed spectra was a centrally located resonance having a g value approximately equal to that of the free electron (2.0023).

The x irradiation must break the α-carbon bond to the acid group in order to produce the *t*-butyl radical. If the α-carbon bond is broken in this manner, the other irradiation damage products are most likely CO_2 and H. On warming, the *t*-butyl radical is converted to a second radical as can be seen in Fig. 1. Spectrum *A* obtained at 130°K changes to the spectrum *C* as the temperature of the sample is increased to 250°K. The nature of the second radical has not been determined. The ESR spectrum for pivalic acid completely disappears when the temperature is raised to 273°K.

The ESR spectra for x-irradiated *t*-butyl alcohol at 130°K do not show a well-resolved *t*-butyl radical, as would be expected if the OH bonded to the α-carbon were removed by ionization. The observed spectra are not resolved, but appear to result from the superposition of a seven-component spectrum and a four component spectrum. The radicals formed could then be the isopropyl radical $(CH_3)_2\dot{C}OH$ and the methyl radical $\cdot CH_3$. We have obtained single crystals of *t*-butyl alcohol, and plan to study the spectra from the single crystals. Since the coupling constants of these radicals are essentially isotropic, the ESR should not be orientation dependent.

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† Alfred P. Sloan Fellow.

[1] L. H. Piette and W. C. Landgraf, J. Chem. Phys. **32**, 1107 (1960).

[2] R. W. Fessenden and R. H. Schuler, J. Chem. Phys. **39**, 2147 (1963).

Comments

Comments on the Use of Carbon SCF Atomic Orbitals in Aromatic Molecules

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IN recent work on the electronic states of molecular crystals of aromatic molecules[1] (triplet-exciton, charge-transfer, excess-electron, and hole states) π-electron molecular orbitals have been represented in terms of linear combinations of SCF carbon-atom atomic orbitals (SCF AO), the purpose being to represent properly the tail of the molecular wavefunction. However, it is known that the effective "atomic" orbitals needed in molecules are somewhat less extended in space than the self-consistent field atomic orbitals due to shifts in electron density needed for binding.

To determine the adequacy of this approximation, we have investigated the π-type orbitals of the C_2 molecule recently determined with high accuracy by John Greenshields[2] using the homonuclear diatomic SCF program of Wahl and Roothaan at the Laboratory of Molecular Structure and Spectra of the University of Chicago. Tables I and II display the calcu-

TABLE I. Carbon $2p$ integrals.

	Overlap $(2p\sigma \mid 2p\sigma)$		Exchange $(2p\sigma\, 2p\sigma \mid 2p\sigma\, 2p\sigma)$ in atomic units
Orbital	6 a.u.	7 a.u.	7 a.u.
^3P SCF AO[a]	0.099079	0.054879	0.0013151
^1D SCF AO[a]	0.113259	0.066763	0.0019270
^1S SCF AO[a]	0.135365	0.087553	0.0032735
Single Slater[b] ($\alpha=1.5679$)	0.049680	0.018960	0.00017043
Single Slater ($\alpha=1.625$)	0.040586	0.014627	0.00010261
$1\pi_u$ orbital from $^1\Sigma_g^+$ state of C_2[c,d]			
Complete orbital	0.079864	0.042105	
Only p components	0.079195	0.041827	0.000773679
$1\pi_u$ orbital from $^3\Sigma_u^-$ state of C_2[c,d]			
Complete orbital	0.086592	0.044215	
Only p components	0.084786	0.049854	0.000830581

[a] These are the so-called accurate Bagus–Gilbert sets. P. S. Bagus, T. L. Gilbert, C. C. J. Roothaan, and H. D. Cohen (to be published).

[b] E. Clementi and D. L. Raimondi, J. Chem. Phys. **38**, 2686 (1963).

[c] See Ref. 2.

[d] These orbitals have been transformed to a different axis system for the integration.

Table II. Orbitals used.

Exponents	^3P SCF AO[a]	^1D SCF AO[a]	^1S SCF AO[a]	$^1\Sigma_g{}^{+}$[b]	$^3\Sigma_u{}^{-}$[b]
2*p*	2.779	2.758	2.789	1.046	1.212
2*p*	6.827	6.858	7.010	1.642	2.178
2*p*	1.625	1.591	1.593	2.777	5.115
2*p*	1.054	0.991	0.908	6.587	...
3*d*				0.985	1.637
3*d*				2.039	2.128
4*f*				2.698	2.152
Eigenvectors					
2*p*	0.17442	0.18740	0.18522	0.32699	0.66938
2*p*	0.00842	0.00792	0.00684	0.55077	0.37488
2*p*	0.45191	0.44628	0.43764	0.18053	0.02850
2*p*	0.43645	0.43929	0.46722	0.01108	...
3*d*				0.00766	0.10659
3*d*				0.06636	0.01191
4*f*				0.01797	0.01382

[a] These are the so-called accurate Bagus–Gilbert sets. P. S. Bagus, T. L. Gilbert, C. C. J. Roothaan, and H. D. Cohen (to be published).

[b] Reference 2.

lated overlap and exchange integrals for the orbitals that have been mentioned in the literature. The exponents and vectors of the normalized Slater orbitals are also listed.

We conclude that exchange integrals calculated using the ^3P SCF AO are approximately 1.5 times too large at 7 a.u., while the single Slater result is low by a factor of approximately 6. The *d* and *f* contribution to the exchange integrals is only 10% to 20%. The use of *p* orbitals of other states of carbon (^1D and ^1S) gives larger errors. For semiquantitative purposes the use of linear combinations of carbon atom SCF atomic orbitals in ^3P state seems to be quite adequate.

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[1] J. L. Katz, S. I. Choi, J. Jortner, and S. A. Rice, J. Chem. Phys. **39**, 1897 (1963); J. Jortner, S. I. Choi, J. L. Katz, and S. A. Rice, Phys. Rev. Letters **11**, 323 (1963); G. C. Nieman and G. W. Robinson, J. Chem. Phys. **38**, 1928 (1963); S. I. Choi, J. Jortner, S. A. Rice, and R. Silbey, J. Chem. Phys. **41**, 3294 (1964).

[2] J. B. Greenshields, "The Electron Structure of Diatomic Molecules. VII. Carbon and Carbon Molecule Ions" (to be published). We are grateful to Greenshields for these results prior to publication.

Announcement

Letters to the Editor

THE Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments, and Errata. The textual material of each Letter is limited to 950 words minus the following: (a) 200 words for each average-sized figure; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Literature references in footnotes, and footnotes to the title or authors' names, are not included in the word count. Other footnotes are counted as textual material. Proof will be sent to authors of all Letters. As in the past, the publication of Notes, Comments, and Errata will await the receipt of proof corrected and approved by the authors. The rapid publication schedule of Communications does not allow the usual time for the return of corrected proof by authors. Authors of Communications are requested to transmit corrections, on the day that proof is received, by telephone or air mail to the Editorial Department of the American Institute of Physics, where the proof will be corrected. The publication of Communications will not be delayed for receipt of authors' corrections.

COMMUNICATIONS

Letters in this category are restricted to reports of preliminary results which are of current and extreme interest to relatively large numbers of workers in the field. It is assumed that in most cases the details of such work, in a completed form, will be published at a later date. Communications are not sent for review, although the Editor will in many cases submit them to readily available experts in order to ascertain their suitability for this section. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Communications accepted for publication by the 1st of Month M will be published in the issue of the 1st of Month $M+2$, and those accepted by the 15th of Month M will appear in the issue of the 15th of Month $M+2$.

NOTES

Letters in this category have the character of short articles, except that, because of the limitation on length, they do not contain an abstract. Notes will be reviewed in the same manner as are articles, and reviewers will be asked to judge them by the same standards as employed for regular articles, except for those differences required by the brevity of Notes. Notes are intended as final publication of the work described in them and are not preliminary reports. It is assumed that work reported in a Note will not be republished in extended form at a later date although, of course, further new work may result in a longer article. A Note accepted by the 1st (15th) of Month M will be published in the issue of the 1st (15th) of Month $M+3$. A backlog of regular articles will not be allowed to delay the publication schedule of Notes.

COMMENTS

Letters in this category include discussion and comments on articles and Letters previously published in *The Journal of Chemical Physics*. Comments by others than the authors of the previously published work being discussed will normally be submitted for review to these authors, and these authors will usually be given the opportunity of submitting a Comment in reply for simultaneous publication. In such cases the publication of both Comments will be delayed until each party has had an opportunity to examine the final statement of the other on the matters under discussion. The Editor may recommend that a single joint Comment by the two parties be published. He will normally consult independent referees when authors are discussing their own work, when there is an unresolved disagreement between the parties, and when there is doubt as to the importance of a Comment. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents.

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Errata are corrections of errors in articles and Letters previously published in *The Journal of Chemical Physics*. If the error which requires correction was not present in the proof approved by the author, the publication charge certification should not be signed. In this case, AIP will not submit a bill for publication charges. The title of an Erratum should begin with the word "Erratum:," followed by the title of the article or Letter being corrected and the reference. Consult recent issues of *The Journal of Chemical Physics* for the form.

J. W. Stout, *Editor*