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BENDING FREQUENCY OF THE C_3 MOLECULE*

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ABSTRACT

Ab initio calculations have been carried out to determine a potential curve for the bending motion of C_3. The work was in part motivated by the disagreement between theoretical and experimental values of the entropy of C_3. Three basis sets were used, with (4s 2p), (4s 2p 1d), and (4s 3p 1d) centered on each carbon atom. Both self-consistent-field (SCF) and configuration interaction (CI) (656 configurations) calculations were carried out with the smallest basis. The CI wave functions were obtained by a method which may be viewed as an extension of the pseudonatural orbital technique of Edmiston and Krauss. Using the smallest basis, both SCF and CI calculations yield "normal" bending frequencies, $\sim 320\ cm^{-1}$. It is concluded that electron correlation has little effect on the bending frequency. The larger (4s 2p 1d) and (4s 3p 1d) basis SCF calculations yield much smaller bending frequencies, the latter being $69\ cm^{-1}$, in good agreement with the unusually low experimental value of Gausset, Herzberg, Lagerqvist, and Rosen. The bending potential is predicted to be quite anharmonic. These results are discussed qualitatively in terms of a Walsh diagram and the importance of d orbitals by symmetry considerations.

INTRODUCTION

It is now known that the 4050 Å group in the spectra of comets, first observed in 1881, is due to the C_3 molecule.[1] However, prior to 1942, there was no identification of the molecule responsible for this spectra. Herzberg[2] made the first laboratory observation of the 4050 Å group and suggested that the spectrum was due to CH_2. In 1951 the 4050 Å group was properly identified as being due to C_3 by Douglas.[3] As discussed in Herzberg's recent book,[1] a spectrum of CH_2 was not found until nearly ten years later. In addition to the importance of C_3 in cometary spectra, C_3 has been shown to be a primary constituent of carbon vapors.[4-6]

The most comprehensive study to date of the C_3 spectrum is that of Gausset, Herzberg, Lagerqvist, and Rosen.[7] The most interesting feature of this study is the apparent establishment that C_3 has an extremely small bending frequency, $\nu_2 = 64\ cm^{-1}$. This was a somewhat unexpected result, since the bending frequencies for the adjacent linear molecules CCN, NCN, and BO_2 vary between 300 and 500 cm^{-1}. However, the $1\pi_g$ molecular orbital is occupied in each of these three other molecules and a Walsh diagram suggests that the $1\pi_g$ orbital energy goes up rapidly with decreasing bond angle.[8] Support for the assignment of Gausset and coworkers comes from the work of Weltner and McLeod,[9] who obtained the spectrum of matrix isolated C_3, finding $\nu_2 \approx 70\ cm^{-1}$. The plausibility of the low bending frequency of C_3 is further strengthened by the fact that the bending frequencies of C_3N_2, C_3O_2, and C_3S_2 have also been found to be anomalously low.[10]

There is currently a conflict[11] between the experimental and theoretical values of the entropy of C_3. The experimental values are those of Thorn and Winslow[11] (77.4 entropy units) and Drowart <u>et al</u>.[6] (76.1 entropy units). The

first theoretical calculation of the entropy of C_3 was that of Pitzer and Clementi.[12] They assumed a normal bending frequency of 550 cm^{-1} and obtained an entropy in good agreement with experiment. However, using the recent experimental value[7] ν_2 = 64 cm^{-1}, Strauss and coworkers[13] have calculated the C_3 entropy at 2400°K to be 81.4 entropy units. Thus the low bending frequency significantly raises the entropy, to a value between 4 and 5 entropy units greater than experiments. Possible sources of this discrepancy are

a) The experimental values[6,10] of S°_{2400} are incorrect;

b) The calculations of Strauss and coworkers[12] are misleading;

c) The bending frequency of C_3 is much larger than 64 cm^{-1}.

Very recently, there have been several remeasurements[14,15] of the entropy of C_3. In each case values very close to the earlier experimental determinations were found. A possible explanation of the mass spectrometric data has been suggested by Brewer,[15] who has emphasized the experimental assumption that the ionization cross section is independent of temperature (i.e., vibrational quantum number). If the bending potential were highly anharmonic, such an assumption might lead to a spurious interpretation of experimental data.

Of the three possible sources of error, possibility b) seems the least likely. Several types of potential functions for the bending frequency were used by Strauss and coworkers.[13] The smallest entropy calculated was 79.8 , assuming an extremely anharmonic potential.

The purpose of the present research was to attempt to investigate, by <u>ab initio</u> quantum mechanical calculations, whether in fact the bending frequency ν_2 of C_3 is 64 cm^{-1}. If ν_2 is 64 cm^{-1} for C_3, then it is likely that the experimentally measured entropies of C_3 are in error. In the course of this theoretical

study, both self-consistent-field and multiconfiguration wave functions were obtained using a variety of basis sets. From these wave functions it is possible to obtain considerable insight into the electronic structure of C_3.

BASIS SETS

The simplest basis set used was Dunning's (4s 2p) contraction[16] of Huzinaga's (9s 5p) set[17] of primitive gaussian functions for the carbon atom. We refer to this contracted gaussian "double zeta" basis set as (4s 2p) hereafter.

The second basis set used differs from the first in that a set of six d-like functions (d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{xz}, d_{yz}) is added to each carbon atom. Each contracted d function is a linear combination of 2 primitive gaussian d functions. The particular linear combination was chosen[18] to simulate a 3d Slater function with exponent 2.0. This basis set is designated (4s 2p 1d).

In our third basis set, the contraction of Huzinaga's 5p primitive set is "loosened" to 3p. Dunning has shown that this additional flexibility in the p basis is quite important for the N_2 molecule.[16] This final basis set also includes d functions and is labeled (4s 3p 1d).

CONFIGURATION INTERACTION

At the outset of this study, we expected SCF calculations using the (4s 2p) basis to yield an unrealistically large bending frequency. However, based on previous calculations,[19-21] we expected that appropriate multiconfiguration calculations with the (4s 2p) double zeta basis would yield reasonable force constants. For the $^3B_1$ ground state of CH_2, for example, double zeta configuration interaction (CI) calculations predicted[19] a bending force constant of 0.29 millidynes/angstrom. Using a much larger (5s 3p 1d) basis on carbon, CI calculations yielded[21] a similar bending force constant, 0.33 md/Å.

The SCF electron configuration for the electronic ground state of C_3 (C_{2v} symmetry) is

$$1a_1^2\ 1b_2^2\ 2a_1^2\ 3a_1^2\ 2b_2^2\ 4a_1^2\ 3b_2^2\ 1b_1^2\ 5a_1^2 \quad . \tag{1}$$

Following an SCF calculation at each geometry, a CI was carried out including configurations (besides (1)) of three types:

$$1a_1^2\ 1b_2^2\ 2a_1^2\ 3a_1^2\ 2b_2^2\ 4a_1^2\ xy\ 1b_1^2\ 5a_1^2 \tag{2}$$

$$1a_1^2\ 1b_2^2\ 2a_1^2\ 3a_1^2\ 2b_2^2\ 4a_1^2\ 3b_2^2\ xy\ 5a_1^2 \tag{3}$$

$$1a_1^2\ 1b_2^2\ 2a_1^2\ 3a_1^2\ 2b_2^2\ 4a_1^2\ 3b_2^2\ 1b_1^2\ xy \quad , \tag{4}$$

where x and y represent all the orbitals in the basis set which are not occupied in the SCF configuration, that is $6a_1$ - $14a_1$, $1a_2$ and $2a_2$, $2b_1$ - $4b_1$, and $4b_2$ - $10b_2$. There are 247 configurations in this calculation.

Next the reduced first-order density matrix[22] of this 247 configuration wave function is diagonalized. The resulting occupation numbers for a typical geometry are shown in Table I. Table I shows that 10 occupation numbers are quite small, namely the $11a_1$ - $14a_1$, $2a_2$, $4b_1$, $7b_2$ - $10b_2$. Therefore these orbitals were "thrown away" in the ensuing CI, which included all remaining singly- and doubly-excited configurations with respect to (1), with the "chemical" restriction that the carbon 1s orbitals $1a_1$, $1b_2$, and $2a_1$ remained doubly-occupied. 656 configurations were included in the resulting CI calculations. It is seen, then, that the 247 configuration calculation was used to determine a smaller, optimum set of orbitals for a final, larger CI.

This procedure may be regarded as an extension of the pseudonatural orbital method of Edmiston and Krauss.[23] In the Edmiston-Krauss approach, only a single pair of orbitals is replaced in the calculation used to generate pseudonatural orbitals. That is Edmiston and Krauss might have used the SCF configuration (1) plus all configurations of type (4) to determine an optimum set of orbitals. However, in a polyatomic molecule such as C_3, it is possible that any single orbital (e.g., $5a_1$) might be nearly localized, perhaps on the central carbon. In that case the $5a_1$ pseudonatural orbitals might not be suitable for describing correlation effects involving the other SCF valence orbitals. By including excitations from the $3b_2$ and $1b_1$ orbitals as well, we hope to generate a set of orbitals appropriate for the description of electron correlation in the entire valence shell (12 electrons) of C_3. We suspect that the final 656 configuration calculation accounts for $\sim$ 90% of the valence shell correlation energy attainable within our (4s 2p) basis.

C_3 BENDING VIBRATIONAL LEVELS

Four distinct types of calculations were carried out as a function of bond distance and bond angle, retaining a minimum of C_{2v} symmetry. Both SCF and CI computations were done with the (4s 2p) basis, while only SCF studies were made with the larger (4s 2p 1d) and (4s 3p 1d) sets. In the (4s 2p) CI and (4s 3p 1d) SCT treatments, the C-C bond distance was optimized for several bond angles. Somewhat fewer calculations were done of the (4s 2p) SCF and (4s 2p 1d) SCF variety. These calculations are summarized in Table II.

The most obvious point to be seen in Table II is that the energy varies much more rapidly as a function of bond angle for the (4s 2p) SCF and CI calculations than for either the (4s 2p 1d) or (4s 3p 1d) SCF calculations. Note that the optimum bond distance varies little for the different bond angles, with the expected trend, that the bond distance increases with decreasing bond angle. The curvatures of the (4s 2p) SCF and CI bending energies are very similar, implying that the bending frequency is nearly independent of electron correlation.

Rather surprisingly, the (4s 2p 1d) SCF calculations predicts C_3 to be nonlinear, with a bond angle 125°. To verify this point, the bond distance was optimized with the (4s 2p 1d) basis for 120° and 180°. At 120°, the predicted bond distance is 2.431 bohrs and the energy -113.37013 hartrees. At 180°, the optimum bond distance is 2.429 bohrs and the energy is higher, -113.36882. Although C_3 has long been thought[3] to be linear, Gausset, Herzberg, Lagerqvist, and Rosen[7] have allowed that the molecule might be slightly nonlinear, as long as the "slight potential maximum at the linear conformation" is smaller than ν_2. However, our computation (see below) of the vibrational levels from the (4s 2p 1d) calculation shows that several levels occur below the maximum. Thus the (4s 2p 1d) SCF prediction of nonlinearity appears incorrect.

In total energy, the (4s 2p 1d) and (4s 3p 1d) SCF calculations differ relatively little. At 180°, R(C-C) = 2.41 bohrs, the two energies are -113.36851 and -113.38082 hartrees. And both bending potential curves are very flat. However the larger basis predicts C_3 to be linear, as is known experimentally.

In order to more precisely evaluate the usefulness of our four calculations it is necessary to obtain vibrational energy levels for the bending mode. Such calculations have been carried out for the (4s 2p) CI and (4s 3p 1d) SCF cases, which are very different qualitatively. In principle, it is not possible to decouple the bending motion from the symmetric stretch. However, by calculating a minimum energy path for the bending motion, one can approximately determine the vibrational levels. An analogous vibrational calculation for the inversion motion of NH_3 has recently been reported by Stevens.[24] A computer program for the numerical solution of a one-dimensional Schrödinger equation was kindly provided by Mr. Steven M. Hornstein.

Table III gives the a priori vibrational energy levels. The (4s 2p) CI frequency ν_2 is 317 cm^{-1}, much larger than experiment, 64 cm^{-1}. However, the (4s 3p 1d) SCF value of ν_2, 69 cm^{-1}, nearly coincides with experiment. These results are entirely plausible if one considers the C_3 bending frequency as a barrier problem, such as the inversion barrier in NH_3 or the rotational barriers in H_2O_2. In both of these two cases, it has now been established[24-26] that SCF calculations do yield excellent agreement with experiment, but only when very large basis sets are used. It is particularly pertinent to the present work to point out that Stevens[24] found a significant (50%) improvement in the NH_3 inversion barrier in going from a N(4s 2p 1d) to a N(4s 3p 1d) basis set.

Steven's finding is completely analogous to our spurious prediction of a 125° C_3 bond angle with the C(4s 2p 1d) basis. In this light, it seems quite obvious to us that our (4s 3p 1d) SCF calculation is by far the most reliable for the bending frequency. Furthermore, there can now be no doubt that the value $\nu_2 = 64\ cm^{-1}$ obtained experimentally by Gausset et al.[7] is correct.

Figure 1 shows the bending potential of C_3 predicted from our most reliable calculation. The calculated vibrational levels are indicated. Experimentally, Gausset and coworkers observed levels at 132 and 286 cm^{-1}, plus two other levels separated by 144 cm^{-1}, and fit these data to a formula implying the existence of levels at 0, 63.7, 132.6, 206.9, and 286.6 cm^{-1}. As Table III implies, our calculations do not reproduce the positions of these levels, except the first, in any detail. This is primarily due to a "dimple" in the ab initio potential curve between 160 and 180°. Thus the spacings between our first few vibrational levels are 69, 38, 44, 58, and 68 cm^{-1}. Interestingly, our n = 3 and n = 5 levels lie at 151 and 277 cm^{-1}, not too far from Gausset's values. However, we are hesitant to ascribe physical reality to these unusual vibrational spacings.

One feature clearly visible in Fig. 1 which probably does correspond to reality is the anharmonic nature of the bending potential. In fact, except for the dimple between 160 and 180°, the bending potential looks more like a square well. This anharmonicity will of course lower the calculated entropy relative to a more typical potential. However, a value lower than Strauss's limiting value,[12] 79.8 entropy units at 2400°K, is not possible. The remaining discrepancy with experiment, 76.1 - 77.4 , may very well be due to the experimental approximations pointed out by Brewer.[14] A highly anharmonic potential, of course, would tend to place in jeopardy the assumption of independence of ionization cross section with vibtational state.

QUALITATIVE ASPECTS

Since Walsh's papers[27] of 1953, the geometries of simple molecules have been interpreted and predicted using orbital energy or Walsh diagrams. Our *a priori* Walsh diagram for C_3 is seen in Fig. 2. Only the 9 occupied orbital energies are shown, since the virtual orbital energies have no physical significance (in the sense of Koopmans' theorem). Figure 2 "explains" in a simple qualitative way the anomalously low bending frequency of C_3. The four highest orbital energies are nearly constant between the bond angles 120 to 180°. The other two valence orbital energies, $3a_1$ and $2b_2$, nearly balance each other, with the $2b_2$ rising slightly more rapidly with decreasing bond angle. The lowest unoccupied orbital, $1\pi_g$, of C_3 is expected to have the angular dependence predicted by Buenker and Peyerimhoff in their calculations on O_3 and N_3^-. The calculations of Buenker and Peyerimhoff[28] are in fact consistent with Walsh's prediction[8] of an orbital energy rising rapidly with decreasing bond angle. Thus, as remarked previously,[7,8] electronic states in which the $1\pi_g$ orbital is occupied are expected to have much larger bending frequencies than C_3.

It is not as easy to rationalize the anharmonicity of the C_3 bending mode in terms of our orbital energy diagram, Fig. 2. However, there does appear to be a correlation between the increasing steepness of the potential in Fig. 1 and the shape of the $3b_2$ orbital energy as a function of bond angle. For angles greater than 120°, $\in (3b_2)$ is essentially constant, but as the bond angle decreases from 120° the orbital energy moves up steadily.

The orbital energies $\in$ from our (4s 3p 1d) SCF calculations at 2.41 bohrs bond distance are seen in Table IV. There an interesting point may be seen, namely that the $2b_2$ and $4a_1$ orbitals do not become degenerate at 60°, the equilateral triangle geometry. At 60°, the

$2b_2$ and $4a_1$ orbitals should become degenerate components of the 2e' orbitals. Interestingly enough, at 180°, the $1b_1$ and $5a_1$ orbital do become degenerate parts of the $1\pi_u$ orbital. These seemingly inconsistent results are readily understood in terms of the electron configurations for the three symmetries:

$$D_{\infty h},\ 180^\circ \qquad 1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 3\sigma_g^2\ 2\sigma_u^2\ 4\sigma_g^2\ 3\sigma_u^2\ 1\pi_u^4 \quad , \tag{5}$$

$$C_{2v},\ 60\text{-}180^\circ \qquad 1a_1^2\ 1b_2^2\ 2a_1^2\ 3a_1^2\ 2b_2^2\ 4a_1^2\ 3b_2^2\ 5a_1^2\ 1b_1^2 \quad , \tag{6}$$

$$D_{3h},\ 60^\circ \qquad 1a_1'^2\ 1e'^4\ 2a_1'^2\ 2e'^4\ 1a_2''^2\ 3a_1'^2\ 3e'^2 \quad . \tag{7}$$

The important point to be made is that C_{2v} symmetry was assumed in all our calculations; that is, all SCF calculations were based on the single determinant (6). Since (6) becomes (5) at 180° and both single determinants belong to totally symmetric representations ($^1A_1$ for C_{2v} and $^1\Sigma_g^+$ for $D_{\infty h}$), there is a smooth transition between bent and linear molecular orbitals. However, electron configuration (7) has an open-shell structure (the 3e' orbital can hold four electrons) and gives rise[1] to three different electronic states, $^3A_2'$, $^1A_1'$, and $^1E'$. Our $^1A_1$ state of C_{2V} symmetry should be correlated with the totally symmetric $^1A_1'$ state. Unfortunately, for the $^1A_1'$ state SCF wave function arising from electron configuration (7) is a linear combination of two determinants

$$\psi_{SCF}(^1A_1') = \frac{1}{\sqrt{2}}\, 3e_x'\alpha \quad 3e_x'\beta \ + \ \frac{1}{\sqrt{2}}\, 3e_y'\alpha \quad 3e_y'\beta \quad . \tag{8}$$

Or, in terms of the C_{2v} symmetry orbitals

$$\psi_{SCF}(^1A_1') = \frac{1}{\sqrt{2}} 3b_2\alpha \quad 3b_2\beta + \frac{1}{\sqrt{2}} 6a_1\alpha \quad 6a_1\beta \quad . \tag{9}$$

Therefore, when an SCF calculation on the single determinant (6) is carried out for $\theta = 60°$, the resulting wave function is a mixture of $^1A_1'$ and $^1E'$ symmetries. Thus such a calculation is not meaningful. If such a calculation is carried out, the molecular orbitals will not take on the full D_{3h} symmetry and the proper pairs of C_{2v} orbitals (e.g. $2b_2$ and $4a_1$) will not become degenerate.

We have carried out a proper SCF calculation (with the (4s 2p) basis) of type (9) at 60°. The total energy 1s hartrees, compared to hartrees for the single configuration (6). In fact, one expects the coefficient of the configuration $3b_2^2 \rightarrow 6a_1^2$ to smoothly increase as θ goes from 180° (linear) to 60° (equilateral triangle). However, at 180°, this configuration is relatively unimportant (coefficient 0.0103). Table V shows the most important configuration in our 656 configuration wave function for C_3 near equilibrium.

If possible one would like to have a simple picture describing the electron distribution in C_3. To this end a Mulliken population analysis has been obtained from the (4s 3p 1d) SCF wave function for linear C_3, bond distance 2.41 bohrs. In this simple picture the charge on the central carbon is -0.197, while the end carbon atoms are positively charged by +0.098. These are relatively small charges and thus the C-C bonds may be described as covalent. It is interesting to compare these atomic populations with those recently obtained for C_3O_2 by Gelius, et al.[29] From SCF calculations using a smaller basis set, Gelius found the central carbon to have charge -0.68 and the outer carbons +0.59. The electronegative oxygen atoms, each with charge -0.25, are of course responsible for the increased polarity of the C-C bonds with respect to C_3.

A final point worthy of discussion is our finding that the bending frequency of C_3 is predicted by both SCF and CI calculations to be quite normal ($\sim$ 317 cm^{-1}) unless d functions are added to the basis set. The point of interest is that a simple symmetry argument can be given which predicts that d functions will be more important for bent C_3 than for linear C_3. This argument is analogous to that mentioned by Body, McClure, and Clementi[30] with regard to the inversion barrier in ammonia. For $D_{\infty h}$ symmetry, one set of five d functions on each atom in C_3 will yield $2\sigma_g$, $1\sigma_u$, $1\pi_{ux}$, $1\pi_{uy}$, $2\pi_{gx}$, $2\pi_{gy}$, $2\delta_{gx}$, $2\delta_{gy}$, $1\delta_{ux}$, and $1\delta_{uy}$ symmetry orbitals. However, only the first five of these functions are of appropriate symmetry to contribute to the Hartree-Fock wave function, Eq. (5), for linear C_3. For C_{2v} symmetry, the same set of atomic d functions yields $5a_1$, $3a_2$, $3b_1$, and $4b_2$ symmetry orbitals. And twelve of these functions (all but the three a_2) can be utilized in the Hartree-Fock wave function, Eq. (6), for bent C_3. Thus we see that seven additional d functions can contribute to the Hartree-Fock C_3 wave function if the molecule is bent, as opposed to linear. This is one of the more clearcut cases we know of where symmetry necessitates the inclusion of d functions in the basis set for a molecule composed of first-row atoms.

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FOOTNOTES AND REFERENCES

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1. G. Herzberg, The Spectra and Structures of Simple Free Radicals (Cornell University Press, Ithaca, New York, 1971).
2. G. Herzberg, Astrophys. J. 96, 314 (1942).
3. A. E. Douglas, Astrophys. J. 114, 466 (1951).
4. W. R. S. Garton, Proc. Phys. Soc. (London) A66, 848 (1953).
5. J. G. Phillips and L. Brewer, Mem. Soc. Roy. Sci. Liege Ser. 4 15, 341 (1955).
6. J. Drowart, R. P. Burns, G. DeMaria, and M. C. Ingraham, J. Chem. Phys. 31, 1131 (1959).
7. L. Gausset, G. Herzberg, A. Lagerqvist, and A. Rosen, a) Disc. Faraday Soc. 35, 113 (1963); b) Astrophys. J. 142, 45 (1965).
8. A. D. Walsh, Disc. Faraday Soc. 35, 223 (1963).
9. W. Weltner and D. McLeod, J. Chem. Phys. 40, 1305 (1964).
10. W. H. Smith and G. E. Leroi, J. Chem. Phys. 45, 1784 (1966).
11. R. J. Thorn and G. H. Winslow, J. Chem. Phys. 26, 186 (1957).
12. K. S. Pitzer and E. Clementi, J. Am. Chem. Soc. 81, 4477 (1959). See also S. J. Strickler and K. S. Pitzer, page 281 in Molecular Orbitals in Chemistry, Physics, and Biology (Academic Press, New York, 1964).
13. a) A. G. Robiette and H. L. Strauss, J. Chem. Phys. 44, 2826 (1966); b) H. L. Strauss and E. Thiele, J. Chem. Phys. 46, 2473 (1967).
14. P. D. Zavitsanos, "Experimental Study of the Sublimation of Graphite at High Temperature", unpublished report, General Electric Re-Entry and Environmental System Division, Philadelphia, Pa. 19101.

15. L. Brewer, personal communication.

16. T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).

17. S. Huzinaga, J. Chem. Phys. 42, 1293 (1965).

18. T. H. Dunning, J. Chem. Phys. 55, 3958 (1971).

19. S. V. O'Neil, H. F. Schaefer, and C. F. Bender, J. Chem. Phys. 55, 162 (1971).

20. C. F. Bender and H. F. Schaefer, J. Chem. Phys. 55, 4798 (1971).

21. D. R. McLaughlin, C. F. Bender, and H. F. Schaefer, Theoret. Chim. Acta. (in press).

22. R. McWeeny and B. T. Sutcliffe, Methods of Molecular Quantum Mechanics (Academic Press, New York, 1969).

23. C. Edmiston and M. Krauss, J. Chem. Phys. 45, 1833 (1966).

24. R. M. Stevens, J. Chem. Phys. 55, 1725 (1971).

25. A. Rauk, L. C. Allen, and E. Clementi, J. Chem. Phys. 52, 4133 (1970).

26. T. H. Dunning and N. W. Winter, Chem. Phys. Letters 11, 194 (1971).

27. A. D. Walsh, J. Chem. Soc. 1953, 2260, and following 5 papers.

28. S. D. Peyerimhoff and R. J. Buenker, J. Chem. Phys. 47, 1953 (1967).

29. U. Gelius, C. J. Allen, D. A. Allison, H. Siegbahn, and K. Siegbahn, Chem. Phys. Letters 11, 224 (1971).

30. R. G. Body, D. S. McClure, and E. Clementi, J. Chem. Phys. 49, 4916 (1968).

Table I. Natural orbital occupation numbers for the 247 configuration wave function indicated by configurations (1)-(4) in the text. The bond angle was 180° and the C-C bond distance 2.51 bohrs.

$1a_1$	2.0	$1a_2$	0.04447	$1b_1$	1.94480	$1b_2$	2.0
$2a_1$	2.0	$2a_2$	0.00003	$2b_1$	0.01384	$2b_2$	2.0
$3a_1$	2.0			$3b_1$	0.00056	$3b_2$	1.98650
$4a_1$	2.0			$4b_1$	0.00004	$4b_2$	0.04446
$5a_1$	1.94481					$5b_2$	0.00122
$6a_1$	0.01384					$6b_2$	0.00051
$7a_1$	0.00275					$7b_2$	0.00004
$8a_1$	0.00116					$8b_2$	0.00003
$9a_1$	0.00112					$9b_2$	0.00001
$10a_1$	0.00056					$10b_2$	0.00000
$11a_1$	0.00037						
$12a_1$	0.00004						
$13a_1$	0.00001						
$14a_1$	0.00000						

Table II. Summary of calculated C_3 electronic energies as a function of bond angle. In the second and fourth series of calculations, the total energy was minimized with respect to bond distance for each bond angle. The experimental bond distance is 2.413 bohrs.[7]

(4s 2p) Basis, SCF

θ	R(bohrs)	E(hartrees)
180°	2.4	-113.32135
160°	2.4	-113.31817
140°	2.4	-113.30955
120°	2.4	-113.29718
100°	2.4	-113.27989

(4s 2p) Basis, 656 Configurations

θ	R(bohrs)	E(hartrees)
180°	2.492	-113.52215
160°	2.493	-113.51932
140°	2.504	-113.51277
120°	2.511	-113.50561
60°	2.724	-113.40815

(4s 2p 1d) Basis, SCF

θ	R(bohrs)	E(hartrees)
180°	2.41	-113.36851
160°	2.41	-113.36862
140°	2.41	-113.36912
120°	2.41	-113.36979
100°	2.41	-113.36776
80°	2.41	-113.35020

(4s 3p 1d) Basis, SCF

θ	R(bohrs)	E(hartrees)
180°	2.404	-113.380 851
160°	2.404	-113.380 577
140°	2.405	-113.380 358
120°	2.409	-113.380 286
110°	2.412	-113.379 695
100°	2.418	-113.377 748

Table III. Vibrational energy levels in cm^{-1} for the bending of C_3. ΔE indicates the spacing between adjacent vibration levels.

(4s 2p) CI			(4s 3p 1d) SCF		
	E_n	ΔE		E_n	ΔE
0	161	---	0	47	--
1	478	317	1	116	69
2	783	305	2	155	38
3	1080	297	3	199	44
4	1369	289	4	257	58
5	1649	280	5	325	68
			6	401	76
			7	484	83
			8	574	90
			9	672	98
			10	781	108
			11	900	119
			12	1028	128
			13	1164	136
			14	1307	143
			15	1456	150

Table IV. Total and orbital energies (in hartrees) for C_3 as a function of bond angle. The C-C bond distance in all calculations was 2.41 bohrs. The C(4s 3p 1d) basis set was used.

	60°	80°	100°	120°	140°	160°	180°
E(total)	-113.26216	-113.36055	-113.37770	-113.38028	-113.38034	-113.38055	-113.38082
$1a_1$	- 11.3316	- 11.3535	- 11.3641	- 11.3689	- 11.3714	- 11.3728	- 11.3734
$2a_1$	- 11.3276	- 11.2947	- 11.2648	- 11.2493	- 11.2428	- 11.2404	- 11.2398
$1b_2$	- 11.3269	- 11.3531	- 11.3639	- 11.3688	- 11.3713	- 11.3728	- 11.3733
$3a_1$	- 1.3658	- 1.2706	- 1.2046	- 1.1641	- 1.1409	- 1.1289	- 1.1253
$2b_2$	- 0.7256	- 0.7966	- 0.8563	- 0.9016	- 0.9329	- 0.9515	- 0.9576
$4a_1$	- 0.7098	- 0.6168	- 0.5697	- 0.5500	- 0.5429	- 0.5406	- 0.5401
$1b_1$	- 0.5817	- 0.5324	- 0.5030	- 0.4870	- 0.4793	- 0.4760	- 0.4752
$5a_1$	- 0.5188	- 0.5035	- 0.4930	- 0.4851	- 0.4794	- 0.4762	- 0.4752
$3b_2$	- 0.3811	- 0.4525	- 0.4832	- 0.4958	- 0.5016	- 0.5042	- 0.5050

Table V. Most important configurations for C_3, $\theta = 180°$, R(C-C) = 2.51 bohrs.

Spatial Configuration	Coefficient	Energy Criterion
1. $1a_1^2\ 1b_2^2\ 2a_1^2\ 3a_1^2\ 2b_2^2\ 4a_1^2\ 3b_2^2\ 5a_1^2\ 1b_1^2$	0.94745	--
2. $5a_1\ 1b_1 \rightarrow 1a_2\ 4b_2$	0.10942	-0.00902
3. $5a_1\ 1b_1 \rightarrow 6a_1\ 2b_1$	0.06849	-0.00584
4. $5a_1^2 \rightarrow 6a_1^2$	0.05573	-0.00348
5. $1b_1^2 \rightarrow 2b_1^2$	0.05573	-0.00348
6. $1b_1^2 \rightarrow 1a_2^2$	0.07444	-0.00327
7. $5a_1^2 \rightarrow 4b_2^2$	0.07444	-0.00327
8. $4a_1\ 3b_2 \rightarrow 7a_1\ 5b_2$	0.03554	-0.00277

FIGURE CAPTIONS

Fig. 1. Minimum energy path for the bending motion of C_3. The figure is a result of the (4s 3p 1d) SCF calculations.

Fig. 2. Oribtal energies of C_3 as a function of bond angle. The C-C bond distance was 2.41 bohrs in all calculations.

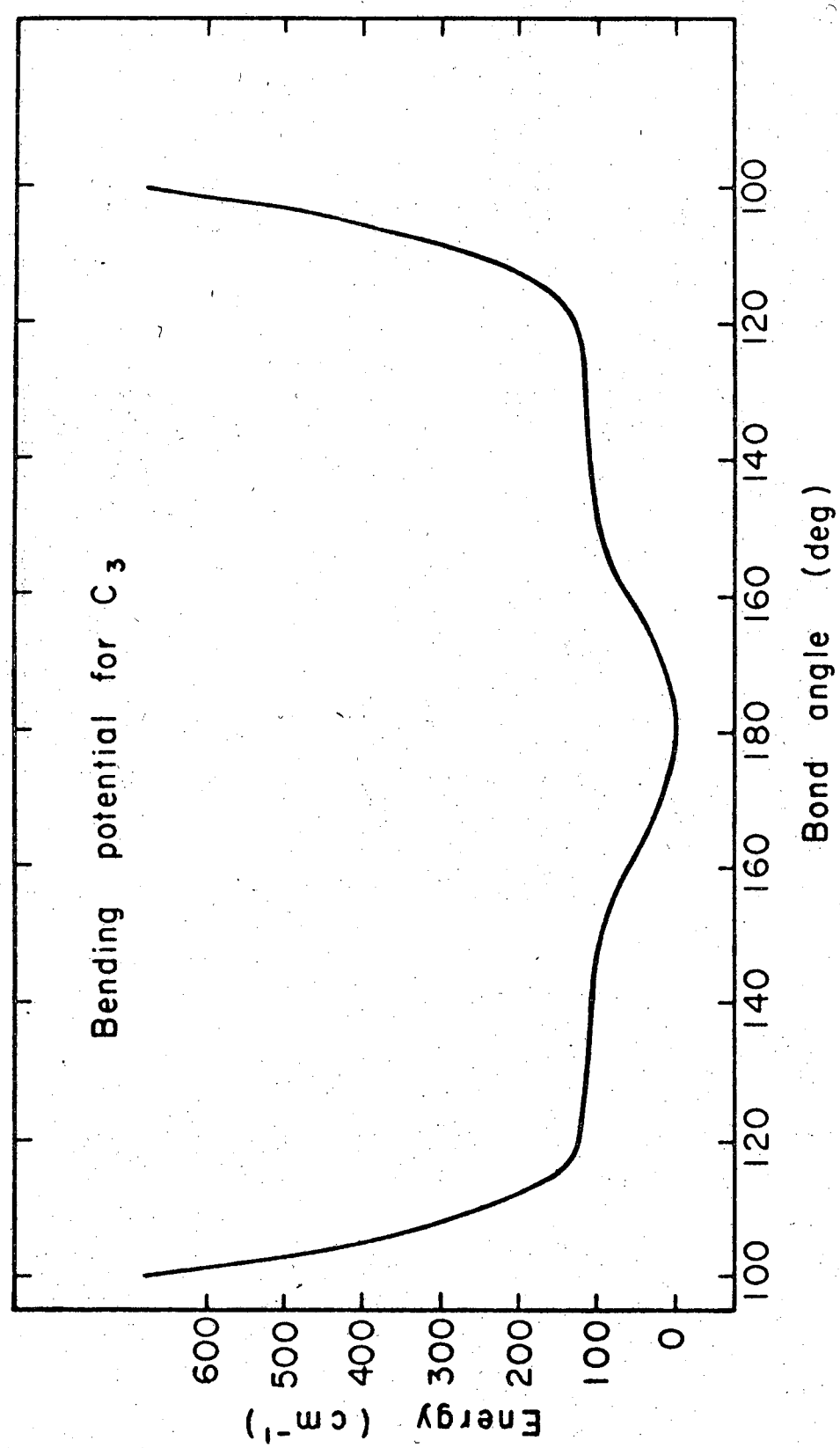

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Fig. 1

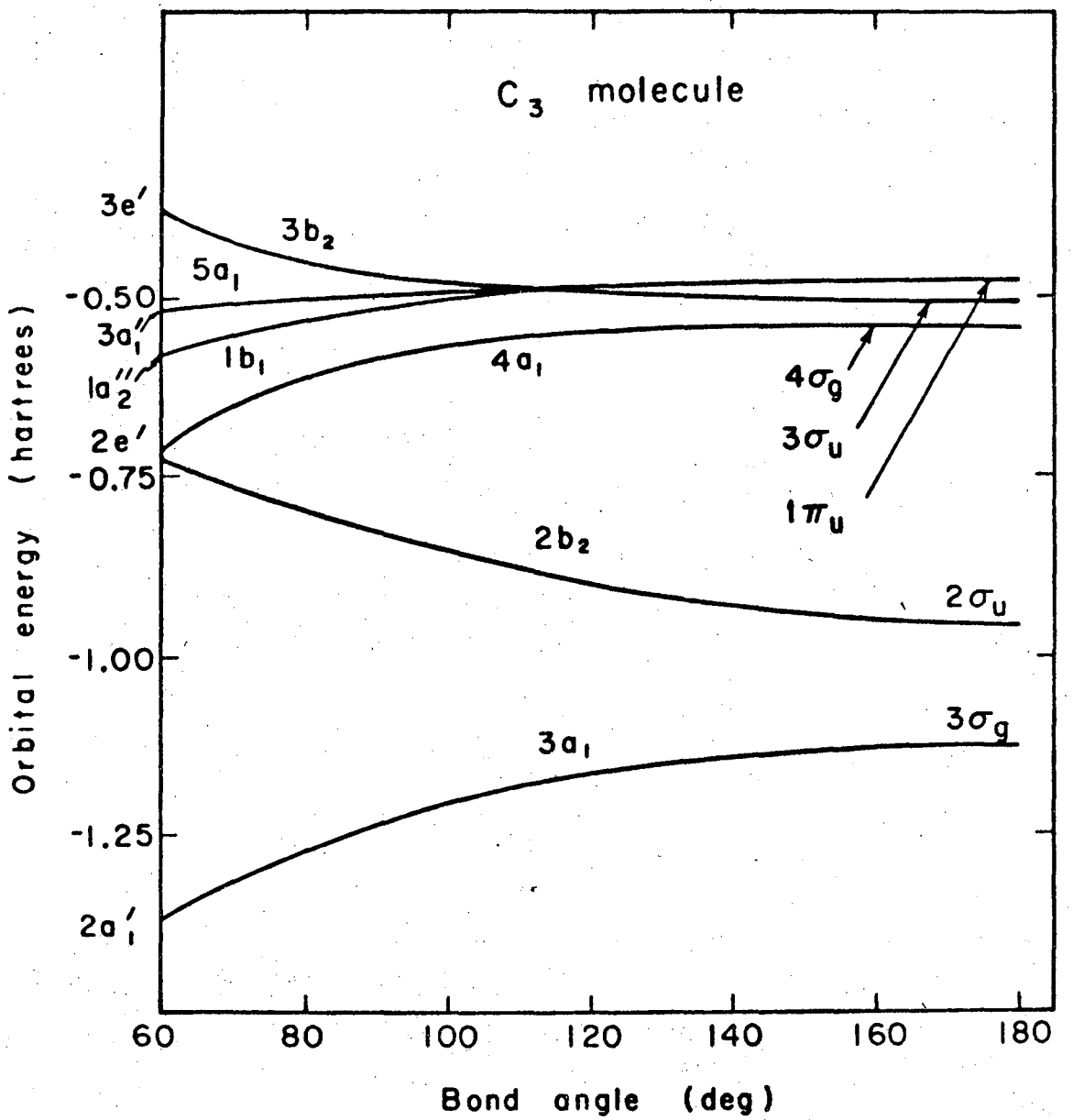

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Fig. 2

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