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Calculation of Force Constants of Ethylene by a Semiempirical ASMO–SCF Method

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A semiempirial ASMO–SCF calculation involving all valence electrons was carried out for a number of nuclear configurations of ethylene molecule. From the variation of the ground-state energy on the change of various structure parameters, all the diagonal quadratic force constants in the internal symmetry coordinate system were calculated and compared with those obtained from vibrational spectra. A modification of the Dewar and Klopman's formula including two empirical parameters was used to represent the core repulsion energy. It gave reasonable potential energy curves for the stretching coordinates.

INTRODUCTION

In the SCF molecular orbital theory involving all valence electrons, the relative positions of all nuclei in a molecule are taken into account explicitly on evaluating the multicenter integrals. This theory provides accordingly a general and straightforward procedure to predict the equilibrium structure and the force constants of polyatomic molecules through the calculation of ground-state energies for a variety of nuclear configurations. The rigorous treatment of this sort of calculation requires, however, so much labor even for the smallest molecules that the introduction of more or less approximations is inevitable to reduce the calculation to a tractable size. By using the approximation of the neglect of differential overlaps, Pople *et al.* have formulated a semiempirical ASMO–SCF theory for all valence electrons of molecules.[1] These authors' method has given, in spite of its simplicity, a fairly successful result in predicting correct valence angles and bending force constants of a number of simple polyatomic molecules.[2,3] The stretching force constants calculated by this method are too large, however, compared to those obtained from experimental data on vibrational spectra.[3,4]

Since there are many ways of approximations in evaluating the atomic integrals involved in the ASMO–SCF theory, further studies seem to be necessary in order to clarify the influence of various approximations on the reliability of the calculated force constants. It is also worthwhile to look for any systematic way of combining the approximations which can predict force constants and other properties of molecules simultaneously. With these points of view, we have carried out a semiempirical ASMO–SCF calculation of force constants of ethylene based on the method of Yonezawa, Kato, and co-workers which has recently given reasonable values of orbital energies, ionization potentials, electronic transition energies, and ESR hyperfine coupling constants[5,6] for molecules similar to those treated by Pople *et al.* This method is different from that of Pople *et al.* in adopting the one- and two-center electronic repulsion integrals evaluated semiempirically and in taking account of differential overlaps. In the present paper, the calculated force constants are compared with those obtained from the analysis of vibrational spectra and are discussed.

ATOMIC INTEGRALS

Since the detail of the procedure to evaluate the ground-state energy for a given nuclear configuration has already been reported,[5] we outline here only the evaluation of basic atomic integrals. The overlap integrals, S_{rs}, were taken to be the theoretical values for the Slater AO's, the effective nuclear charges being 1.00 and 3.25 for hydrogen and carbon, respectively. The one-center electron repulsion integrals were calculated by the well-known approximation due to Pariser,[7]

$$(rr \mid rr) = a_r^{-1} = I_r - A_r, \tag{1}$$

where I_r and A_r represent the valence state ionization

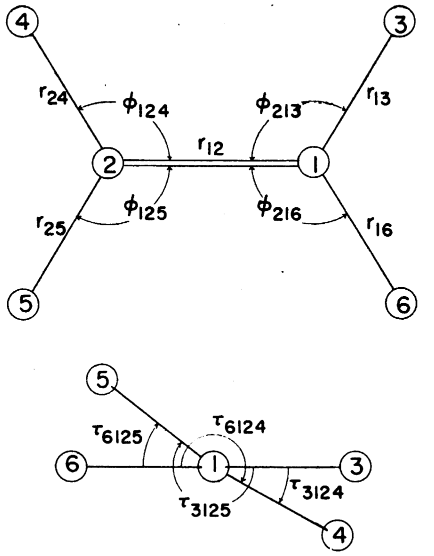

FIG. 1. Internal coordinates.

potential and the electron affinity, respectively, of the atomic orbital (AO) r.[8] For the two-center electron repulsion integrals, we used the Ohno approximation,[9]

$$(rr\,|\,ss)=\tfrac{1}{2}[(a_r^2+R_{rs}^2)^{-1/2}+(a_s^2+R_{rs}^2)^{-1/2}], \quad (2)$$

where R_{rs} is the distance between the nuclei on which the AO's r and s are centered. The multicenter electron repulsion integrals were then calculated by the Mulliken approximation,[10]

$$(rs\,|\,tu)=\tfrac{1}{4}S_{rs}S_{tu}[(rr\,|\,tt)+(rr\,|\,uu)+(ss\,|\,tt)+(ss\,|\,uu)]. \quad (3)$$

Let N_r be the number of valence electrons on the AO r, and Z_A be the net core charge of the nucleus A. The core Hamiltonian matrix elements were then approximated as

$$H_{rr}=U_{rr}+\sum_{B\neq A}(B\,|\,rr), \quad (4)$$

$$(B\,|\,rr)=-\sum_{s}{}^{B}\,N_s(rr\,|\,ss), \quad (5)$$

$$U_{rr}=-I_r-(N_r-1)(rr\,|\,rr)-\sum_{r'\neq r}{}^{A}\,N_{r'}[(rr\,|\,r'r')-\tfrac{1}{2}(rr'\,|\,rr')] \quad (6)$$

and

$$H_{rs}=\tfrac{1}{2}S_{rs}[-P(Z_A+Z_B)(rr\,|\,ss)-(B\,|\,rr)-(A\,|\,ss)+H_{rr}+H_{ss}], \quad (7)$$

where P is an empirical parameter and is taken to be 1.40.[6] In Eqs. (4)–(7), it is implied that the AO's r and s are centered on the nuclei A and B, respectively, and the superscript on $\sum$ in Eqs. (5) and (6) indicates that the sum is taken only over the AO's centered on that nucleus. The present treatment is different from the previous one[5] in the introduction of the one-center exchange integrals $(rr'\,|\,rr')$ evaluated according to Hinze and Jaffe,[11] and in the estimation of the off-diagonal core matrix elements, H_{rs} $(r\neq s)$, for which the previous treatment[5] adopted the approximation by Wolfsberg and Helmholz.[12] Furthermore, in order to use the nonzero $(rr'\,|\,rr')$ without violating the invariance of the basic integrals on the rotation of the coordinate axes for p orbitals, the one-center integral $(rr\,|\,r'r')$ for the two different p orbitals centered on the same nucleus, e.g., p_x and p_y, was calculated by

$$(p_xp_x\,|\,p_yp_y)=(p_xp_x\,|\,p_xp_x)-2(p_xp_y\,|\,p_xp_y). \quad (8)$$

By using the above integrals, the molecular orbital ϕ_i was obtained through the SCF calculation as the linear combination of atomic orbitals χ_r,

$$\phi_i=\sum_r C_r^i\chi_r, \quad (9)$$

and the ground-state electronic energy E_{el} was calculated by

$$E_{el}=\sum_{r,s}P_{rs}H_{rs}+\tfrac{1}{2}\sum_{t,u}P_{rs}P_{tu}[(rs\,|\,tu)-\tfrac{1}{2}(rt\,|\,su)], \quad (10)$$

where

$$P_{rs}=2\sum_i^{occ}C_r^iC_s^i. \quad (11)$$

The ground-state energy for a given nuclear configuration is then given by

$$E=E_{el}+\sum E^{AB}{}_{core}, \quad (12)$$

where $E^{AB}{}_{core}$ represents the core repulsion energy between the nuclei A and B, and the sum is taken over all possible pairs of nuclei in the molecule.

CORE REPULSION ENERGY

There have been several ways of estimating the core repulsion energy in the literature. For the π-electron system, Parr and Pariser interpreted it as due to the positively charged holes vacated by the π electrons and evaluated it by the corresponding two-center electron repulsion integrals.[13] On the other hand, the core is just a nucleus for hydrogen and a nucleus surrounded by a closed 1s shell for carbon in the present treatment, and it seems more reasonable, at first sight, to use simply the point charge approximation,

$$E^{AB}{}_{core}=Z_AZ_Be^2/R_{AB}, \quad (13)$$

where e is the electronic charge and R_{AB} is the distance between the nuclei A and B. Segal and Pople *et al.* adopted this approximation and obtained the equilibrium bond lengths agreeing well with the experiments for a number of molecules.[4] The success of Eq. (13) in these authors' method is, however, based on the use of the one- and two-center electron repulsion integrals evaluated theoretically by the Slater 1s and 2s AO's. Since the semiempirical evaluation by Eqs. (1) and (2) gives much smaller values to these integrals than

TABLE I. Internal symmetry coordinates.

Symmetry	Coordinate	Description	Increment
a_g	$S_1=(\Delta r_{13}+\Delta r_{24}+\Delta r_{25}+\Delta r_{16})/2$	C–H stretching	±0.1 Å
	$S_2=\Delta r_{12}$	C=C stretching	±0.05 Å
	$S_3=(\Delta\varphi_{213}+\Delta\varphi_{124}+\Delta\varphi_{125}+\Delta\varphi_{216})/2$	CH_2 bending	±0.1 rad
a_u	$S_4=(\Delta\tau_{3125}+\Delta\tau_{3124}+\Delta\tau_{6124}+\Delta\tau_{6125})/2$	torsion	0.2 rad
b_{1g}	$S_5=(\Delta r_{13}-\Delta r_{24}+\Delta r_{25}-\Delta r_{16})/2$	C–H stretching	0.1 Å
	$S_6=(\Delta\varphi_{213}-\Delta\varphi_{124}+\Delta\varphi_{125}-\Delta\varphi_{216})/2$	CH_2 rocking	0.1 rad
b_{1u}	$S_7=(\Delta\tau_{3125}-\Delta\tau_{6124})/\sqrt{2}$	CH_2 wagging	$0.2/\sqrt{2}$ rad
b_{2g}	$S_8=(\Delta\tau_{3124}-\Delta\tau_{6125})/\sqrt{2}$	CH_2 wagging	$0.2/\sqrt{2}$ rad
b_{2u}	$S_9=(\Delta r_{13}+\Delta r_{24}-\Delta r_{25}-\Delta r_{16})/2$	C–H stretching	0.1 Å
	$S_{10}=(\Delta\varphi_{213}+\Delta\varphi_{124}-\Delta\varphi_{125}-\Delta\varphi_{216})/2$	CH_2 rocking	0.1 rad
b_{3u}	$S_{11}=(\Delta r_{13}-\Delta r_{24}-\Delta r_{25}+\Delta r_{16})/2$	C–H stretching	0.1 Å
	$S_{12}=(\Delta\varphi_{213}-\Delta\varphi_{124}-\Delta\varphi_{125}+\Delta\varphi_{216})/2$	CH_2 bending	0.1 rad

the theoretical values, the core repulsion energy in the present method must also be smaller than that given by Eq. (13), in order that its change on a nuclear displacement be just canceled by the corresponding change of E_{el} at the equilibrium nuclear distance. From this reason we adopted initially an extended form of the Parr and Pariser's expression,

$$E^{\text{AB}}_{\text{core}}=\sum_r^{\text{A}}\sum_s^{\text{B}} N_rN_s(rr\mid ss). \qquad (14)$$

On the calculation of force constants, the equilibrium structure of ethylene was initially taken from Allen and Plyler's data.[14] From the internal coordinates shown in Fig. 1, the internal symmetry coordinates were constructed in the same way as in the previous analysis of the vibrational anharmonicity.[15] These coordinates are defined to represent the actual changes of the given structural parameters and are therefore related to the Cartesian coordinates curvilinearly. They are listed in Table I together with their symmetries and descriptions.[16] Distorted configurations of the molecule were then constructed by displacing the nuclei from the equilibrium positions successively along each internal symmetry coordinate, in terms of which the increments were taken as given in Table I. From the ground-state energies for these nuclear configurations, the potential energy curve for each coordinate was obtained, and by fitting it to a polynomial of that coordinate, say S_i, by the least squares method, the quadratic diagonal force constant,

$$K_{ii}=\tfrac{1}{2}(\partial^2E/\partial S_i^2),$$

was evaluated at the minimum of the calculated potential. As the polynomial to be fitted, the quartic function was used in general but the sextic function was also used for the totally symmetric stretching coordinates, S_1 and S_2.

Generally, the force constants are required by their definition to be evaluated for the nuclear configuration corresponding to the true minimum of the potential function in the multidimensional space spanned over all vibrational degrees of freedom. The force constant obtained by the Taylor expansion of the potential function with respect to a single coordinate satisfies this requirement in the case either when the Taylor expansion is carried out at the calculated equilibrium configuration or when the contribution from interaction force constants to the potential energy is negligibly small. Since we cannot regard the second of these conditions to be a good approximation, the calculated equilibrium configuration is required to agree with the initially assumed one in order that the first condition is satisfied without the complicated transformation of the origin of the coordinate system. On the use of Eq. (14), the calculated potential minimum was found very close to the origin for the a_gCH$_2$ bending coordinate (S_3),[17] whereas the potential functions for the C=C stretching (S_2) and the a_g C–H stretching (S_1) coordinates showed only monotonous increases on the increase of the bond distances within the investigated ranges. In the curvilinear internal coordinate system, the distance between bonded nuclei changes only on the change of stretching coordinates. Accordingly, the success for the S_3 mode and the failure for the S_1 and S_2 modes in predicting the correct equilibrium configuration suggest that the core repulsion energy estimated by Eq. (14) is appropriate for such comparatively large nuclear distances as those between nonbonded nuclei but is too small for such shorter distances as those between bonded nuclei. With the purpose to obtain reasonable core repulsion energies for both the cases of bonded and nonbonded nuclei, we interpolated Eqs. (13) and (14) by a two-parameter function,

$$E^{\text{AB}}_{\text{core}}=\sum_r^{\text{A}}\sum_s^{\text{B}} N_rN_s(rr\mid ss)+\Big[Z_{\text{A}}Z_{\text{B}}e^2/R_{\text{AB}}-\sum_r^{\text{A}}\sum_s^{\text{B}} N_rN_s(rr\mid ss)\Big]\exp(-\alpha_{\text{AB}}R_{\text{AB}}{}^n), \qquad (15)$$

where the parameter n was fixed to 1.0, 1.5, and 2.0 after several trial calculations. When $n=1$, Eq. (15) becomes identical with that proposed by Dewar and Klopman in the calculation of the heats of formation of a number of hydrocarbon molecules.[18] In the semi-

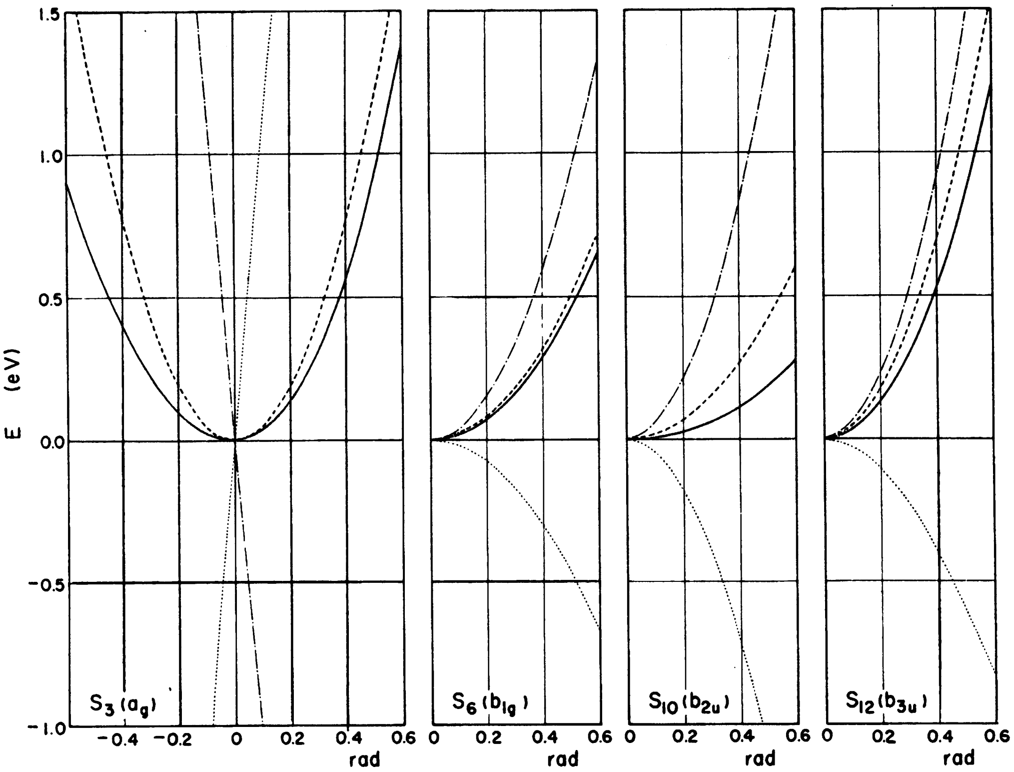

FIG. 2. Potential energy curves for valence angle deformation coordinates: —, E (calculated); - - -, E (experimental); •••, E_{el}; •—•, E_{core}.

empirical calculation used in this work, however, reasonable values of the stretching force constants were obtained, as shown in the following, only for the cases where $n \neq 1$. After fixing n to the above values, the parameter α_{AB} was adjusted independently for each of the coordinates S_1 and S_2 to reproduce the correct equilibrium bond distances. On using Eq. (15) with α_{AB} fixed so as to reproduce the equilibrium length of the C–H bond, the contribution from the second term to $E^{AB}{}_{\mathrm{core}}$ was found to be almost negligible at distances larger than 1.5 Å. This result means that the equilibrium H–C–H angle obtained from Eq. (14) is not much changed on the use of Eq. (15) for both the bonded and nonbonded C•••H distances, and that the difference between Eqs. (14) and (15) is not essential for the latter. Accordingly, by assuming a similar situation for the H•••H repulsion, we simplified the calculation by using Eq. (14) for $E^{AB}{}_{\mathrm{core}}$ between nonbonded nuclei.

RESULTS AND DISCUSSION

It has been pointed out that the values of force constants calculated by the polynomial fitting of a potential curve are affected seriously by the spacing and the spread of the representative points of the coordinate.[19] In the present calculation, the uncertainty due to this effect is estimated to be 0.1 and 0.05 mdyn/Å for the C=C and the C–H stretching coordinates, respectively, 0.01 mdyn•Å/rad² for the CH_2 bending and the CH_2 rocking coordinates, and 0.001 mdyn•Å/rad² for the CH_2 wagging and the torsional coordinates. In Table II, the calculated force constants for the CH_2 bending, the CH_2 rocking, the CH_2 wagging, and the torsional coordinates are shown together with those obtained by the analysis of vibrational spectra.[15] For the in-plane coordinates, the bending force constants K_{33} and $K_{12,12}$ were calculated to be larger than the rocking force constants K_{55} and $K_{10,10}$, as expected from the experiment, but the agreement between the calculated and the experimental values of individual force constants was not so good for K_{33}, $K_{10,10}$, and $K_{12,12}$. From the diagonal force constants for the internal symmetry coordinates in Table II, the interaction force constants connecting the equivalent internal coordinates are obtained by the orthogonal transformation of the coordinates given

TABLE II. Angle deformation force constants (in mdyn•Å/rad²).

Force constant	Experimental[15]	Calculated
K_{33} (a_g CH_2 bending)	0.765	0.46
$K_{12,12}$ (b_{3u} CH_2 bending)	0.688	0.50
K_{55} (b_{1g} CH_2 rocking)	0.319	0.28
$K_{10,10}$ (b_{2u} CH_2 rocking)	0.266	0.10
K_{77} (b_{1u} CH_2 wagging)	0.0999	0.082
K_{88} (b_{2g} CH_2 wagging)	0.0735	0.058
K_{44} (torsion)	0.0685	0.063

in Table I. The *trans* and *cis* interaction constants for the C–C–H angles, k_t and k_c, are defined by the terms contributing to the potential energy,

$$k_t(\Delta\phi_{213}\Delta\phi_{125}+\Delta\phi_{124}\Delta\phi_{216})+k_c(\Delta\phi_{213}\Delta\phi_{124}+\Delta\phi_{125}\Delta\phi_{216}).$$

From the normal coordinate analysis of ethylene molecule,[20] it has been established that k_t is important but k_c is not, and the origin of this *trans* interaction has been an interesting problem for the theoretical prediction of force constants of ethylene. The presently calculated value of k_t (0.07 mdyn·Å/rad^2) agrees well with the experimental value (0.065 mdyn·Å/rad^2), whereas the calculated k_c (−0.11 mdyn·Å/rad^2) is much larger in magnitude than the experimental one (0.012 mdyn·Å/rad^2).[15] Thus it seems that any detailed discussion on the interaction force constants requires much more elaborate treatment than the present one.

The force constants for the CH$_2$ wagging vibrations, K_{77} and K_{88}, were calculated to have reasonable magnitudes with the correct order, and the calculated and the experimental values of the torsional force constant K_{44} agree well with each other. Since the first derivatives of any internuclear distance R_{AB} with respect to the out-of-plane coordinates S_4, S_7, and S_8 vanish for the equilibrium configuration, only the first derivatives of the core repulsion energy with respect to R_{AB} contribute to the force constants K_{44}, K_{77}, and K_{88}, whereas both the first and the second derivatives contribute to the in-plane force constants. In this respect, the satisfactory result obtained presently for the out-of-plane force constants is not surprising because the inadequacy of the functional form of $E^{AB}{}_{core}$ (R_{AB}) is supposed to be less manifested in the first derivatives than in the second derivatives.

Although the estimation of the cubic and quartic force constants by the polynomial fitting is much more difficult than the case of quadratic constants, the inspection of the energy curves along various coordinates may offer some information on the anharmonicity of a calculated potential function. Figure 2 shows the plot of the calculated potential energy and its components, E_{el} and E_{core}, against the four valence angle deformation coordinates, S_3, S_6, S_{10}, and S_{12}. The corresponding potential energies may be evaluated in the first approximation by multiplying the squares of the coordinates by the quadratic force constants obtained from vibrational spectra.[15] These are also shown in Fig. 2 for the sake of comparison. For the a_g CH$_2$ bending coordinate, S_3, each of E_{el} and E_{core} changes very steeply near the equilibrium position, but they almost cancel each other to give a reasonable energy curve. As expected from the dominant repulsion between the hydrogen nuclei at the geminal positions, the potential energy curve shows the larger curvature in the first quadrant (closure of the H–C–H angles) than in the second quadrant (opening of the H–C–H angles). Unfortunately, we cannot check the validity of the calculated anharmonicity, since the cubic and the quartic force constants for the valence angle deformation coordinates have not yet been estimated from vibrational spectra. For the nontotally symmetric coordinates, S_6, S_{10}, and S_{12}, it is seen that E_{el} attains the maximum value at the origin, but is overcome by the stabilizing effect of E_{core} to give the symmetrical equilibrium structure. In Fig. 3, the experimental and the calculated potential energies and the components of the latter, E_{el} and E_{core}, are plotted against the CH$_2$ wagging coordinates S_7 and S_8. Since the quartic force constants for these coordinates were estimated to be very small,[15] we calculated the experimental potential energies in the same way as those in Fig. 2. From the difference in the change of the internuclear distances, it is expected that E_{core} for a given value of S_7 is much larger than that for the same value of S_8, and the former is in fact more than twice the latter. However, the sign of E_{el} is negative for $S_7\neq 0$ but positive for $S_8\neq 0$, and the net potential energies calculated for the displacements along these coordinates are not much different from each other in agreement with the experiment.

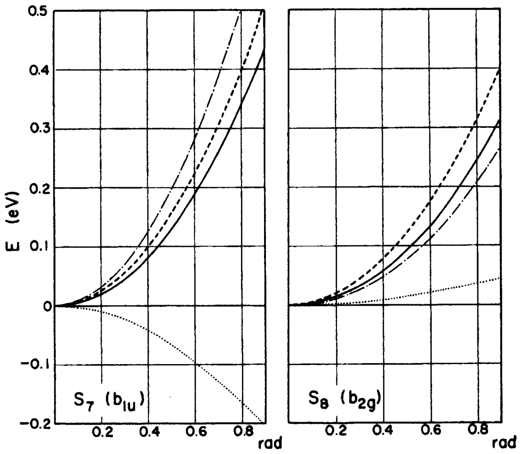

FIG. 3. Potential energy curve for out-of-plane deformation coordinates: —, E (calculated); - - -, E (experimental); • • •, E_{el}; •–•, E_{core}.

In contrast to the cases of the valence angle and out-of-plane deformation coordinates discussed above, the potential curve along the torsional coordinate of ethylene has been the subject of a number of theoretical investigations on the electronic structure.[13,21–25] In comparing the theory with the experiment, however, most of the previous authors referred to the torsional force constant obtained only by applying the harmonic approximation to the indirectly estimated fundamental frequency, 1027 cm^{-1}, in the a_u species. We constructed the experimental potential curve in this work by using the quadratic and quartic force constants obtained from the analysis of the vibrational anharmonicity of ethylene[15] as well as the barrier height for the internal rotation obtained from the reaction rate of the *cis–trans* isomerization of 1,2-dideuteroethylene.[26] This barrier height has been referred to by Charney *et al.*

TABLE III. Parameters in core repulsion energy [Eq. (15)] and stretching force constants.[a]

α_{AB} (in Å^{-n})	Force constant (in mdyn/Å)	Experimental[15]	Calculated $n=1.0$	Calculated $n=1.5$	Calculated $n=2.0$
α_{CC}			1.900	1.844	1.741
	K_{22} (C=C)	5.861	3.5	4.6	5.8
α_{CH}			2.339	2.525	2.650
	K_{11} (a_g C–H)	2.658	2.15	2.70	3.35
	K_{55} (b_{1g} C–H)	2.777	2.05	2.60	3.25
	K_{99} (b_{2u} C–H)	2.676	1.95	2.50	3.15
	$K_{11,11}$ (b_{3u} C–H)	2.683	2.15	2.75	3.40

[a] The calculated and the experimental bond lengths are: $R_{CC}=1.337$ Å and $R_{CH}=1.086$ Å.

in their analysis of the vibrational structure of the ultraviolet spectrum of ethylene.[27]

The torsional potential of ethylene may be expressed in terms of the coordinate S_4 as

$$E(S_4)=V_1(1-\cos S_4)+V_2(1-\cos 2S_4)+V_3(1-\cos 3S_4)$$

$$=K_{44}S_4^2+K_{4444}S_4^4. \qquad (16)$$

The force constants K_{44} and K_{4444} and the barrier height B are then related to V_1, V_2, and V_3 by

$$K_{44}=\tfrac{1}{2}(V_1+4V_2+9V_3),$$

$$K_{4444}=-(V_1/24+2V_2/3+27V_3),$$

and

$$B=2(V_1+V_3).$$

From the numerical values $K_{44}=0.0685$ mdyn·Å/rad^2, $K_{4444}=-0.0039$ mdyn·Å/rad^4, and $B=0.4486$ mdyn·A, we obtained V_1, V_2, and V_3 as 0.2239, -0.02253, and 0.0036, respectively, in mdyn·Å. The resulting experimental curve is shown together with the calculated curves for E, E_{el}, and E_{core} in Fig. 4. As indicated by the relative magnitudes of the quadratic and the quartic force constants, the experimental potential energy curve is quite harmonic except near the top of the barrier, and shows an appreciably smaller curvature at the potential minimum than at the maximum. It is worthwhile to note that the simultaneous fit of the quadratic force constant and the barrier height also requires a potential function which is much less anharmonic than the simple sinusoidal potential which has the same curvature at the minimum and the maximum. On the other hand, the calculated curves for E_{el} and E_{core} appear nearly parabolic and sinusoidal, respectively, and the magnitude of E_{el} increases far more rapidly than that of E_{core} on the increase of the torsional angle. Hence the anharmonicity of the calculated potential function becomes very small, resulting in an excellent agreement between the calculated and the experimental energies over a wide range of the torsional angle. The calculated curve near the top of the barrier is not correct, however, since the interaction between the ground and the excited states is not taken into account in the present treatment.

For the C=C and the C–H stretching coordinates, S_1, S_2, S_5, S_9, and S_{11}, Table III shows the quadratic force constants obtained from the vibrational spectra[15]

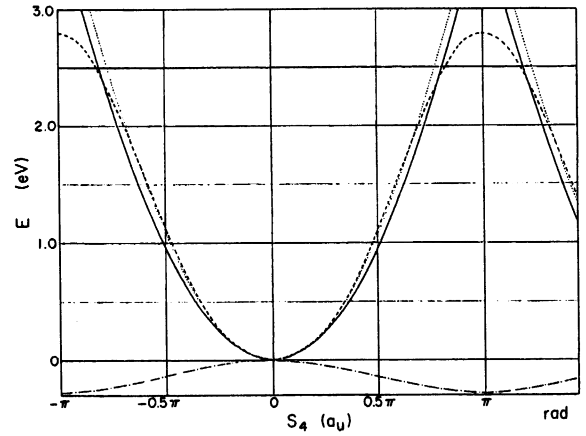

FIG. 4. Potential energy curve for the torsional coordinate: —, E (calculated); - - -, E (experimental); ··· E_{el}; -·- E_{core}.

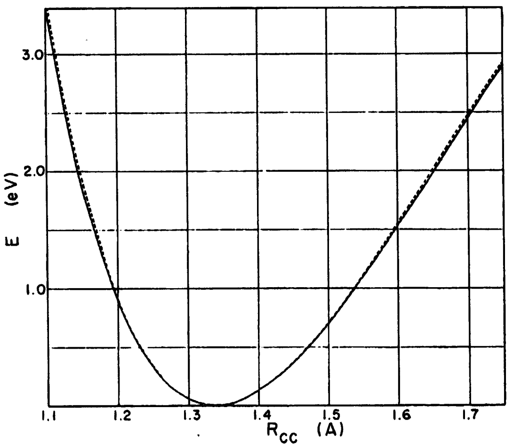

FIG. 5. Potential energy curve for the C=C stretching coordinate: —, E (calculated); - - -, E (experimental).

and the corresponding constants calculated in this work. The parameters α_{AB} and n in Eq. (15) are also given in Table III. It is seen that the force constants attain reasonable values when n is 1.5 and 2.0 for the C–H and the C=C bonds, respectively, but the equilibrium bond lengths and the force constants cannot be fitted to the experimental values simultaneously by fixing n for the C=C and the C–H bonds to the same value. The potential curves calculated by using the best values of n are compared with the experimental curves in Figs. 5 and 6 for the C=C stretching and the a_g C–H stretching coordinates, respectively. The experimental curve for the C=C stretching coordinate represents a Morse-type function,

$$E(S_2)=(K_{22}/a^2)[1-\exp(-aS_2)]^2, \tag{17}$$

where the parameter a is taken to be 2.0 Å^{-1}. This function has been assumed in estimating the cubic and quartic force constants from the spectroscopic data.[15] The effect of truncating the Taylor expansion of Eq. (17) at the quartic term becomes so large for $S_2 >$ 0.3 Å that the curve based on a quartic function is not adequate as the experimental curve to be compared with the calculated. For the a_g C–H stretching coordinate, such the effect of truncation was found to be small in the range -0.6 Å$< S_1 <$0.6 Å, and the experimental curve in Fig. 6 was calculated by the quartic function

$$E(S_1)=K_{11}S_1^2+K_{111}S_1^3+K_{1111}S_1^4,$$

where the value of K_{11} was that given in Table III, and according to the previous estimation of the vibrational anharmonicity,[15] K_{111} and K_{1111} were taken to be -2.159 mdyn/Å^2 and 1.007 mdyn/Å^3, respectively.

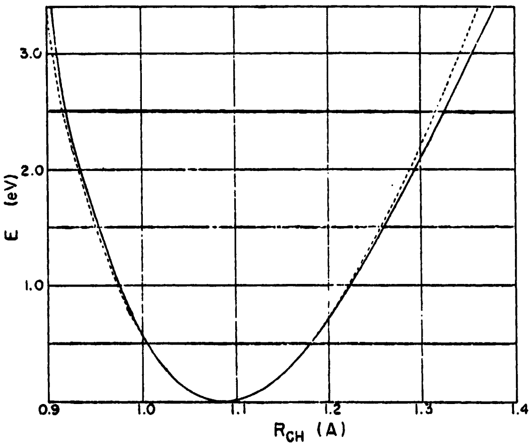

FIG. 6. Potential energy curve for the a_g C–H stretching coordinate: —, E (calculated); - - -, E (experimental).

The agreement between the experimental and the calculated potential energies throughout the investigated range of the bond length indicates that the use of E_{core} including two empirical parameter is fairly successful for predicting the anharmonicity of the bond stretching potential. It may thus be interesting to see if the parameters used for ethylene can fit also the bond lengths and the force constants of other molecules, especially acetylene and ethane.

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[1] J. A. Pople, D. P. Santry, and G. A. Segal, J. Chem. Phys. **43**, S129, S136 (1965).

[2] J. A. Pople and G. A. Segal, J. Chem. Phys. **44**, 3289 (1966); D. P. Santry and G. A. Segal, *ibid.* **47**, 158 (1967); J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.* **47**, 2026 (1967).

[3] H. Obayashi, H. Takahashi and T. Miyazaki, Symposium on Molecular Structure, Chemical Society of Japan, Sapporo, 1967.

[4] G. A. Segal, J. Chem. Phys. **47**, 1876 (1967); J. A. Pople, D. L. Beveridge, and N. S. Ostlund, Intern. J. Quantum Chem. **1**, 293 (1967); M. S. Gordon and J. A. Pople, J. Chem. Phys. **49**, 4643 (1968).

[5] T. Yonezawa, K. Yamaguchi, and H. Kato, Bull. Chem. Soc. Japan **40**, 536 (1967).

[6] H. Kato, H. Konishi, H. Yamabe, and T. Yonezawa, Bull. Chem. Soc. Japan **40**, 2761 (1967); T. Yonezawa, H. Nakatzuji, T. Kawamura, and H. Kato, *ibid.* **42**, 2437 (1969).

[7] R. Pariser, J. Chem. Phys. **21**, 568 (1953).

[8] For the numerical values, see Ref. 5.

[9] K. Ohno, Theoret. Chim. Acta **2**, 219 (1964).

[10] R. S. Mulliken, J. Chim. Phys. **46**, 497 (1949).

[11] J. Hinze and H. Jaffé, J. Chem. Phys. **38**, 1834 (1963).

[12] M. Wolfsberg and L. Helmholz, J. Chem. Phys. **20**, 837 (1952).

[13] R. G. Parr and R. Pariser, J. Chem. Phys. **23**, 711 (1955).

[14] H. C. Allen, Jr. and E. K. Plyler, J. Am. Chem. Soc. **80**, 2673 (1958).

[15] K. Machida, J. Chem. Phys. **44**, 4186 (1966).

[16] The numbering of symmetry coordinates has been revised to follow that of normal coordinates.

[17] The equilibrium H–C–H angle was calculated to be 117°59′, agreeing practically with the experimental value, 117°22′, by Allen and Plyler.[14]

[18] M. J. S. Dewar and G. Klopman, J. Am. Chem. Soc. **89**, 3089 (1967).

[19] J. Gerratt and I. M. Mills, J. Chem. Phys. **49**, 1719 (1968).

[20] J. Overend and J. R. Scherer, J. Chem. Phys. **33**, 1681 (1960).

[21] R. S. Mulliken and C. C. J. Roothaan, Chem. Rev. **91**, 219 (1947).

[22] R. G. Parr and B. L. Crawford, Jr., J. Chem. Phys. **16**, 526 (1948).

[23] J. W. Moskowitz and M. C. Harrison, J. Chem. Phys. **42**, 1726 (1965).

[24] U. Kaldor and I. Shavitt, J. Chem. Phys. **48**, 191 (1968).

[25] R. J. Buenker, J. Chem. Phys. **48**, 1368 (1968).

[26] J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, J. Chem. Phys. **23**, 315 (1955).

[27] R. McDiarmid and E. Charney, J. Chem. Phys. **47**, 1517 (1967).