

Ab initio study of secondary isotope effects on molecular structure

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An *ab initio* calculation of a secondary isotope effect on a bond length has been carried out for the first time. Single determinant molecular orbital computations indicate that the mean C-C bond length at 0°K is longer in C₂H₆ than in C₂D₆ by 0.0015 Å. A comparison with model calculations supports a steric interpretation in which H atoms act as if they are bulkier than D atoms owing to their larger bending amplitudes of vibration.

INTRODUCTION

Primary isotope effects on structure and kinetics are well understood. The increase in length of a bond when one of the atoms is replaced by a lighter isotope can be attributed to the greater amplitude of vibration of the lighter isotope in a Morse-like anharmonic potential well. The greater ease of rupturing a bond containing the lighter isotope is accounted for by its greater zero-point energy. Secondary isotope effects, in which the length or rate of dissociation of a given bond is altered by isotopic substitution in an adjacent bond, are less well understood. Kinetic isotope effects can arise even if the force fields are perfectly harmonic over the amplitudes of vibrations of the species.¹ In the case of mean (r_e) bond lengths, however, only anharmonic components of the force field can give rise to isotope effects.

Over a decade ago, secondary isotope effects on structure were predicted^{2,3} in the course of an exploration of possible steric isotope effects in kinetics. Estimates of magnitudes in hydrocarbons were made on the basis of crude guesses of nonbonded potential functions⁴ and the deuterium isotope effect on the C...H nonbonded amplitude of vibration.² Measurements by electron diffraction of the difference between the C-C bond length in C₂H₆ and C₂D₆ were consistent with the steric prediction but were of limited precision.⁵ Microwave studies by Schwendeman and Kelley of C-X lengths in CH₃X and CD₃X gave comparable results.⁶ In view of the importance of such information in spectroscopic determinations of molecular structures if structure parameters of known physical significance are desired,⁷ it seemed worthwhile to initiate an *ab initio* molecular orbital computation of the relevant cubic force constants in a prototype case. The present work investigates ethane at the single determinant, 4-31G level,⁸ and compares results with those calculated according to a steric model based on geminal C...H interactions.⁹ The numerical evaluation of the force constants is described elsewhere¹⁰ with a full tabulation of results.

THEORY

From a representation of the ethane force field

$$V = \frac{1}{2} \sum_i \sum_j F_{ij} S_i S_j + \sum_{i \leq j \leq k} \sum_l F_{ijkl} S_i S_j S_k S_l + \dots \quad (1)$$

in terms of symmetry coordinates,¹¹ S_i , the effect of molecular vibrations on the mean displacements $\langle S_i \rangle$, can be derived by setting the generalized forces $\langle -\partial V / \partial S_j \rangle$ equal to zero.¹² The result, through cubic constants, may be written as

$$\mathbf{F} \langle \mathbf{S} \rangle = \mathfrak{F} \quad (2a)$$

or

$$\langle \mathbf{S} \rangle = \mathbf{F}^{-1} \mathfrak{F} \quad (2b)$$

in which the elements of the column matrix $\langle \mathbf{S} \rangle$ are the mean displacements of the totally symmetric symmetry coordinates from the structure of minimum potential energy, \mathbf{F} is the force constant matrix, and the column matrix \mathfrak{F} with elements

$$\mathfrak{F}_i = -3F_{iii} \langle S_i^2 \rangle - 2 \sum_{j \neq i} F_{ijj} \langle S_i S_j \rangle - \sum_{j \neq i} F_{ijj} \langle S_j^2 \rangle \quad (3)$$

may be viewed as representing a vibrational stress due to the mean-square atomic displacements acting in concert with the anharmonic force constants. Equation (2a) is, in a sense, an expression of Hooke's law applied to internal thermal stress. For a particular coordinate, for example, the C-C bond stretch $(r-r_e)_{CC} = S_3$, the isotope effect, $\Delta \langle S_3 \rangle$, can be determined by means of Eq. (3) with the isotopic shifts in the mean-square amplitudes, together with Eq. (2). The result is

$$\Delta \langle S_3 \rangle = \Delta [\mathfrak{F}_3 - F_{13} \langle S_1 \rangle - F_{23} \langle S_2 \rangle] / F_{33} \quad (4a)$$

or

$$\Delta \langle S_3 \rangle = (F^{-1})_{31} \Delta \mathfrak{F}_1 + (F^{-1})_{32} \Delta \mathfrak{F}_2 + (F^{-1})_{33} \Delta \mathfrak{F}_3 \quad (4b)$$

Equation (4b) is more useful for computation, while (4a) is more convenient in interpreting results. All of the quantities in Eq. (4) can be evaluated from the *ab initio* calculations, directly or via a perturbed normal coordinate analysis. In numerical computations we have made the following simplifications. First, the mean-square amplitudes of vibration were calculated from the quadratic force field instead of the full anharmonic force field. The validity of this approximation is discussed in Ref. 12. Secondly, the mean-square amplitudes at 0°K and 298°K were computed from the published experimental \mathbf{L} matrices of Duncan¹¹ instead of from the theoretical \mathbf{F} matrix because the experimental and theoretical force fields are in adequate agreement. Results for the $\Delta \langle S_i^2 \rangle$

TABLE I. Differences in mean-square amplitudes of symmetry coordinates between protiated and deuterated ethane.^a

Symmetry	<i>i, j</i>	$10^3 \times \Delta \langle S_i S_j \rangle$		
		0°K	298°K	
A_{1g}	CH	1.67	1.67	Å ²
	CCH	5.88	5.70	rad ²
	CC	0.06	0.05	Å ²
	...	1,2	-0.28	Å · rad
	...	1,3	0.03	Å ²
	...	2,3	-0.16	Å · rad
A_{1u}	τ	10.0	3.8	rad ²
A_{2u}	CH	1.73	1.73	Å ²
	CCH	5.84	5.70	rad ²
E_u	CH	1.64	1.64	Å ²
	HCH	7.17	7.00	rad ²
	CCH	4.33	3.60	rad ²
E_g	CH	1.66	1.66	Å ²
	HCH	7.36	7.29	rad ²
	CCH	3.55	3.43	rad ²

^aAll values except for $\Delta \langle S_i^2 \rangle$ are computed from the L matrices in Ref. 11. More figures are listed than are significant.

and $\Delta \langle S_i S_j \rangle$ are given in Table I. Except for the mean-square amplitudes in the $\Delta \mathcal{F}_i$ elements in Eq. (4), all quantities were taken from the *ab initio* calculations. The cubic constants are available from no other source.

Values of the A_{1g} elements of the *ab initio* F matrix are presented in Table II and isotopic shifts in the thermal stress elements \mathcal{F}_i are listed in Table III, as resolved into stretch, bend, and torsion components. Force constants were evaluated at the *ab initio* equilibrium structure with $r_{CH} = 1.083$ Å, $r_{CC} = 1.529$ Å, and $\angle HCH = 107.7^\circ$, which agrees with the estimated (but unknown) true equilibrium structure to within 0.01 Å.^{5,7,10}

RESULTS

Deuterium isotope effects on the structure of ethane, derived via Eq. (4) with the quantities listed in Tables I-III, are presented in Tables IV and V. The primary effect on the C-H bond length of 0.0044 Å is of the expected magnitude.^{5,13} It is due mainly to Morse anharmonicity. The change in bond angle is small. Of greatest concern in the present work is the secondary isotope effect on the C-C bond length. *Ab initio* cubic constants

TABLE II. A_{1g} elements of the *ab initio* 4-31G F matrix.^a

	0°K	298°K
5.861	0.150	0.204
	0.754	-0.581
		4.877

^aEnergy, mdyn · Å, S_1, S_3 in Å; S_2 in rad.

TABLE III. Components of the vibrational stress, *ab initio* and geminal steric model.

	$\Delta \mathcal{F}_1$ (mdyn) × 10 ³		$\Delta \mathcal{F}_2$ (mdyn · Å/rad) × 10 ³		$\Delta \mathcal{F}_3$ (mdyn) × 10 ³	
	0°K	298°K	0°K	298°K	0°K	298°K
From <i>ab initio</i> F_{ijk}						
HCC bend	-4.8	-4.5	9.8	9.0
HCH bend ^b	5.1	5.0	-0.8	-0.8
CH stretch	62.6	62.6	-1.5	-1.5
Torsion	1.7	0.6
Misc. ^c	0.1	0.1	-0.1	-0.1	0.9	0.8
Total	62.7	62.7	0.2 ^d	0.2 ^d	10.1	8.1
From steric model F_{ijk}						
HCC bend	1.6	1.6	-4.5	-4.1	13.6	12.4
HCH bend	2.8	2.8	6.3	6.2	0	0
CH stretch	-0.4	-0.4	5.8	5.9
Torsion	0	0	0	0	0	0
Misc. ^c	0.2	0.2	-0.1	0.0	0.7	0.5
Total	1.4	1.7	20.1	18.8

^aNeglected.

^bVia S_8, S_{11} .

^cCrossterms and CC stretch.

^dNeglects CH stretch.

^eNot embodied in model.

lead to isotopic shifts of 0.0015 Å at 0°K and 0.0011 Å at 298°K which are similar to empirical results reported previously.^{5,6}

Since energies as a function of molecular deformation are the only quantities utilized in the present study, the quantum theoretical results provide no more basis for physical interpretation than would experimental spectra yielding the same potential constants. It is nevertheless worthwhile to consider whether the present calculations support or undermine the basis of the original predictions.² This basis has become the rationale of effects considered to be "steric isotope effects."¹⁴ Fortunately, it is possible to decompose the present results into quite readily interpretable quantities and to compare these with the quantities expected on the basis of a treatment of conventional steric forces. The latter treatment makes use of the nonbonded potential energy functions⁹

$$V_{HH}(r) = 14.72 [\exp(-3.4r)] - 0.3333r^{-6} \quad (5a)$$

and

$$V_{CH}(r) = 135.4 [\exp(-3.75r)] - 1.076r^{-6}, \quad (5b)$$

(energy, mdyn · Å; distance, Å) proposed prior to the present study for an entirely different purpose.⁹ This treatment leads naturally to the values of vibrational stress and strain components identified as steric con-

TABLE IV. Isotope effects on the structure of ethane. Quantities refer to protiated minus deuterated calculated from *ab initio* cubic constants.

Quantity × 10 ³	0°K	298°K	Units
$\Delta \langle S_1 \rangle$	10.1	10.1	Å
$\Delta \langle S_2 \rangle^a$	-0.7	-0.8	rad
$\Delta \langle S_3 \rangle$	1.5	1.1	Å
$\Delta \langle r_{CH} \rangle$	4.4	4.4	Å
$\Delta \langle \Delta \psi_{CCH} \rangle^b$	1.6	0.2	deg

^aNeglects effects of CH stretch and torsion.

^b $\Delta \langle \Delta \psi \rangle \approx (\partial \psi / \partial S_2)_0 \Delta \langle S_2 \rangle + (1/2) (\partial^2 \psi / \partial S_2^2)_0 \Delta \langle S_2^2 \rangle$.

TABLE V. Contributions to secondary isotope effect on C-C bond length in ethane, thousandths of an angstrom unit at 0°K.

Vibration	Component		
	Effective size ^a <i>ab initio</i>	Steric	Effective position ^b <i>ab initio</i>
HCC bend	2, 0	2, 8	-0, 1 ^c
CH stretch	-0, 3	1, 2	-0, 4
Torsion	0, 3	0	...
Misc. ^d	0, 0	0, 1	...

^a $[(\Delta\bar{\nu}_3)_l/F_{33}]$, or effect of mean square amplitudes of type l on thermal stress $\Delta\bar{\nu}_3$.

^b $[-F_{i3}\Delta\langle S_i\rangle/F_{33}]$, or effect of mean isotopic displacement of hydrogen atoms. The steric model, devoid of Morse bond stretching anharmonicity, gives no adequate basis for the effective positions of the hydrogen atoms.

^cNeglects effect of CH stretch and torsion on $\Delta\bar{\nu}_2$.

^dCrossterms and $\Delta\langle S_i^2\rangle$ for $i=3, 8, 11$.

tributions in Tables III and V. That is, the necessary cubic coupling constants for Eq. (3) can be evaluated for the steric model by differentiating the potential energy if it is assumed that the entire energy consists of the pairwise repulsions (5) acting between nonbonded interaction centers (with C-H bonds foreshortened by 0.117 Å). For simplicity, in this work only geminal (1...3) interactions are considered.

DISCUSSION

In the original treatment of steric isotope effects on molecular structure it was considered that the nonbonded forces of repulsion between carbon and hydrogen atoms in ethane, averaged over molecular vibrations, could be written as

$$\langle f(r_{C\dots H}) \rangle = f(r_e) + (\partial f / \partial r_{C\dots H})_e \langle \Delta r_{C\dots H} \rangle + 1/2 (\partial^2 f / \partial r_{C\dots H}^2)_e \langle \Delta r_{C\dots H}^2 \rangle + \dots \quad (6)$$

The second term on the rhs expresses the attenuation of forces with increasing distance and corresponds to the quantities $F_{ij}\langle S_i \rangle$ in Eq. (2a) and (4a), and to the "effective position" contributions in Table V. The last term on the rhs of Eq. (6) expresses the fact that the mean repulsive force, averaged over molecular vibrations, is greater the greater the amplitude of vibration owing to the positive curvature of the force function. This term (or its *ab initio* representation) is broken down into various physical components in Eq. (3). It is responsible for the vibrational stress in the first place and leads to the entries designated in Table V as components of the "effective size" of hydrogen atoms.

The fact that the vibrational stress components listed in Table III for *ab initio* theory and for the geminal steric model are in semiquantitative agreement for the bending modes suggests that the steric model has a substantial element of truth in it. The steric model, however, fails to work for the vibrational stress due to C-H stretching, giving an incorrect sign for $\Delta\bar{\nu}_3$. That is, the steric cubic constants F_{i3} , with i a C-H stretch, differ in sign from the corresponding *ab initio* constants. This may be related to a similar observation in the case

of F_{ij} constants for hydrides where stretch-bend interactions were found to be correlated with steric forces but where stretch-stretch interactions were dominated by an opposing factor whose origin has been speculated upon elsewhere.^{10,15} In any event, the purely stretching F_{i3} are less important than the bend-bend-stretch interactions in the secondary isotope effect.

The zero-point C_2D_6 to C_2H_6 shift of $\Delta\langle r_{CC} \rangle = 0.0015$ Å based on *ab initio* cubic constants can be compared with the original crude steric prediction² of 0.003 Å, with the experimental electron diffraction value⁵ ($\pm \sigma$) of $\Delta\langle r_{CC} \rangle = 0.0016 \pm 0.0007$ Å, and with the methyl halide values of Schwendeman and Kelley⁶ of $2\Delta r_{CCl} = 0.0016$ Å and $2\Delta r_{CBr} = 0.0020$ Å. Factors of 2 are included in the latter two values to compensate, approximately, for the fact that there are only half as many hydrogen interactions in the methyl halides as in ethane.

While it is interesting and probably significant to find that the above experimental and theoretical values are in substantial agreement with each other, none of the values are unequivocally reliable. The microwave distances are from r_s structures, the precise physical meaning of which is obscure. Sometimes r_s lengths are considered to be "close to" equilibrium lengths r_e , but true equilibrium lengths would show no isotope effect in the Born-Oppenheimer potential surface. The *ab initio* cubic constants, while probably close to the true SCF values, may be somewhat in error because of the distortion of the potential surface associated with the fact that SCF wavefunctions lead to incorrect dissociation products.¹⁶ The calculated steric contributions to the cubic constants seem of reasonable magnitude for the bending modes but not for the C-H stretching modes.

CONCLUSION

The above caveats notwithstanding, it is reasonable to conclude that we have established the magnitude of the secondary deuterium isotope effect upon bond lengths in ethane and related molecules. The new *ab initio* calculations support the interpretation that a significant component of the effect arises from steric interactions contributed by bending modes. That is, the lighter isotope, vibrating with a larger amplitude, behaves in repulsive interactions as if it is larger than the heavier isotope.

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