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Toward a Better Understanding of Covalent Bonds: The Molecular Mechanics Calculation of C–H Bond Lengths and Stretching Frequencies

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Abstract: Several items which affect the lengths of covalent bonds are enumerated and discussed. A quantitative formulation is derived for C–H bonds so as to permit calculation of the vibrational frequency, stretching force constant, and bond length with the MM3 program if any one of these is known. Illustrations are given for several classes of compounds including alkyl fluorides, ethers, amines, ketones, and sulfones, wherein the C–H stretching frequencies vary over a range of more than 300 cm^{-1} and the calculated values (278 total frequencies) are reproduced with a root mean square error of 24 cm^{-1}.

Introduction

A molecular mechanics force field should properly describe molecules in general, with experimental accuracy. It is an excellent tool for showing us what we do not know about chemistry.[1] When the force field does not correctly calculate molecular properties, it indicates either that we simply have used an inadequate force field or the wrong parameters or that we do not fully understand what is occurring. The original MM3 program[2] (MM3(91)) did not calculate C–H stretching frequencies very well, with a root mean square error of 42 cm^{-1} over 278 frequencies for a broad set of 56 molecules containing 12 different functional groups. The studies reported here were aimed at reducing these errors through a better understanding of the C–H bond.

Covalent bonds hold the living world together and are of great interest in chemistry. We know a great deal about such bonds.[3] Solution of the Schroedinger equation at a high level of accuracy currently offers us fairly good numerical data regarding bond lengths (r_e) of covalent bonds.[4] However, these numbers themselves do not directly convey much understanding. One way of gaining such understanding is in terms of molecular mechanics calculations. If molecular mechanics calculates numbers correctly, then we can understand those numbers in terms of our physical model. If molecular mechanics does not calculate correct numbers, our model is inaccurate, and there may be something fundamental that we do not understand.

The most important thing that determines the length of a covalent bond is the pair of atoms which are attached together.[3] Aside from this obvious fact, there are a number of environmental factors that contribute to the bond length of a given bond. Two factors that have received considerable scrutiny are the steric interactions between groups attached to the bond and electrostatic effects, when charges or dipoles on or near the bond interact with the bond or with each other. There are at least four other factors which can be important under different circumstances and which we will discuss here. They are the electronegativity effect, the anomeric effect, the Bohlmann effect, and the carbonyl effect. (The latter is the only example of the more general hyperconjugative effect so far studied by molecular mechanics.)

C–H Bond. The present work is concerned only with this particular kind of bond. We believe that our conclusions are general in the sense that the principles with apply to all covalent bonds, although the numerical parameters will be different. These principles will be extended in due course to other kinds of bonds, but for now we have limited these studies to the C–H bond.

This particular bond has many unique properties, when compared with covalent bonds in general. The hydrogen atom is relatively difficult to locate in electron diffraction and microwave studies because of the low nuclear charge and light mass of the hydrogen. It is difficult to locate in X-ray crystallographic studies because of its low electron density. The hydrogen lies relatively high up in its vibrational potential well because of the low mass, and therefore its vibrations tend to be quite anharmonic and have large amplitudes. These properties might suggest that this bond is a poor representative for covalent bonds in general, and indeed it is not a typical example. However, there are from the point of view of the present work, nice compensating qualities for the C–H bond. One of these is that quite a lot of previous work has been done in the area of the vibrational spectra of C–H bonds. There have appeared over the years several papers by McKean and co-workers that are especially pertinent here.[5-7] If there is only one hydrogen attached to a carbon, along with various other atoms, the C–H stretching frequency is usually widely separated from the rest of the vibrational spectrum, and that particular vibration can be accurately measured and correctly assigned. This is in marked contrast to the C–C vibration, which is usually coupled to other similar vibrations plus many C–C–H bending motions. For this reason we have chosen the C–H bond for our initial studies, although the C–C bond is of greater intrinsic interest. Unfortunately, C–H stretchings occur at approximately

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(1) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

(2) The MM3 program is available to all users from the Technical Utilization Corporation, Incorporated, 235 Glen Village Court, Powell, OH 43065, and to commercial users only from Tripos Associates, 1699 South Hanley Road, St. Louis, MO 63144, and to academic users only from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405. The current version is available to run on most types of computers, and interested parties could contact one of the distributors directly. The current public version of MM3 (as of 8/93) is called MM3(92). It contains preliminary versions of the calculations of the effects described in the present work. The final version of this work as in this paper will be included in the next release (MM4(94)). The original MM3 contains a preliminary version of the corrections to the bond lengths described herein but not to the stretching constants.

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twice the frequency of CCH bendings, so that the former and the first overtone of the latter frequencies are often coupled through Fermi resonance. This effect will ultimately limit the accuracy obtainable in what we are going to try to do.

McKean et al. have shown that, in general, the stretching frequency of a C–H bond is inversely proportional to the bond length, to high accuracy.[7] This relationship might be useful in molecular mechanics, because we can often determine a C–H stretching frequency experimentally, whereas the corresponding bond length is usually more difficult to accurately determine. We might therefore hope to determine a C–H bond length indirectly by calculating it from the stretching frequency. The force constant for stretching can, of course, be calculated from the stretching frequency, and we will start by developing the details of the nature of these relationships. The goal is to be able to correctly calculate in a general way the bond length, force constant, and stretching frequency from our molecular mechanics model.

At our present level of understanding, a bond length is determined to a first approximation by just the properties of the atoms involved. The next approximation takes into account primary effects that result from the electronegativity difference between those atoms,[1] and steric and electrostatic effects. Bond lengths and angles to this level of approximation were fairly well given by early force fields, such as MM1.[8] The next level of approximation in determining geometries needs to take into account the four effects mentioned above, and three of these (excluding the Bohlmann effect) were included already in different versions of MM2[9] for C–C bonds. These three effects, and a preliminary treatment of the Bohlmann effect, were also included in earlier versions of MM3.[2] We have redone the treatment of the Bohlmann effect in the present work (see below).

In vibrational spectra, one often measures energies with an accuracy of a few wavenumbers (a few small cal/mol), and these energy measurements are an order of magnitude more accurate than those determined via geometries. While "corrections" for these four effects in MM2 and MM3 are adequate for giving good geometries, they do not usually reproduce the potential surface for a molecule as accurately as one might wish, and the errors in the calculated surface are revealed experimentally by spectroscopic measurements.

It has long been known that there is a relationship between bond length and force constant, wherein, other things being equal, a shorter bond is a stronger bond, with a higher stretching force constant.[10] Various ways of putting this relationship on a quantitative basis have previously been proposed, and in the present work we have studied just how this relationship may be best formulated for the case at hand.

A great deal of effort was expended during the early years of infrared and Raman spectroscopy in assigning each band in the vibrational spectra of molecules to a certain chemical moiety or functional group. These early efforts resulted in the compilation of characteristic group frequencies. For example, the 2800–3000-cm^{-1} region is characteristic of the C–H stretching vibration modes in alkanes, while the 3000–3100-cm^{-1} region is indicative of C–H stretching of an unsaturated system. Later investigators assigned certain bands in these regions to methyl C–H stretching, methylene C–H stretching, and methine C–H stretching.[11-13] Deviations of 20 cm^{-1} or more from the tabulated values were noted as rare exceptions.

Within the same context, McKean and co-workers[5-7] have observed a linear relationship between the C–H bond length (r_o) and the vibrational frequency of the same bond for a large number of compounds. Their empirical equation is given by $r_o = 1.3982$ Å $- 0.0001023\nu$, where ν is the observed vibrational frequency of the isolated C–H bond.

Electronegativity Effect. This is the most widespread of the effects to be discussed here and will be taken up first. This is an inductive effect, and it occurs whenever atoms of different electronegativities are bonded together. Since most organic molecules have such substructures, this is a much more general effect than the other three mentioned. Although we have called this the *electronegativity effect* and will discuss it in terms of an electronegative atom, the same situation applies for an electropositive atom, but the frequency and bond length shifts are in directions opposite to those induced by electronegative atoms.

This effect has qualitatively been understood for a long time.[14] It can be visualized as follows: If we attach an electronegative atom to a C–C bond, the electronegative atom pulls electrons toward it. Since p electrons are more polarizable, it preferentially pulls them. This puts more p character in the bond toward the electronegative atom, leaving more s character in the remaining bonds. The remaining bonds therefore undergo changes in their lengths (and also bond angles) in accord with their increased s character. That is, they become shorter, and the angles between them become larger. Other changes result from the presence of the electronegative atom. Since the electronegative group takes electron density from the atom to which it is attached, a bond dipole will result. The atom losing electron density has its effective nuclear charge increased, and the occupied orbitals therefore contract. This results in an additional bond shortening, since the bond lengths of the attached bonds will get shorter as the size of the bonding orbitals decreases. The van der Waals radius of the atom is also expected to be decreased.

Since the electronegative atom or group being attached may also simultaneously exert steric and/or electrostatic interactions on the remainder of the molecule, the total net change of any particular bond or angle may be small or large or may in fact be in a direction opposite to that required by the electronegativity effect. In terms of molecular mechanics, what are really being changed by the electronegativity effect are the values of l_0 and θ_0 for the different bonds and angles. But when the rest of the interactions are taken into account, the net overall changes in the bond lengths and angles are not necessarily simply related to the changes in l_0 and θ_0. For example, if we replace the hydrogens by fluorines one at a time in ethane, the first few replacements lead to large but decreasing bond shortenings in accord with the electronegativity effect, but the least two lead to large bond lengthenings. This is because although l_0 continues to shorten monotonically, the van der Waals repulsions (which are larger for fluorine and exponential with distance) finally overwhelm the electronegativity effect. The electronegativity effect as applied to bond lengths was put on a quantitative basis some years ago and has permitted molecular mechanics to calculate much improved geometries for highly functionalized molecules.[15]

As a result of this bond shortening due to the presence of a neighboring electronegative atom, we have introduced an "electronegativity correction" term to l_0 in the parameters used in the MM2[9] and MM3[2] force fields. The equation that describes this effect[15] is

$$l_0(\text{new}) = l_0(\text{old}) + \Delta l_A + (0.62)\Delta l_B + (0.62)^2\Delta l_C + (0.62)^3\Delta l_D + \dots \quad (1)$$

This equation says that there is a shortening from the first

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(9) The original program (MM2(77)) is available from the Quantum Chemistry Program Exchange, Bloomington, IN 47405, Program 395. The latest version of MM2, referred to as MM2(91), is available to academic users from QCPE and to commercial users from Tripos Associates.

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electronegative atom (A) and a second but smaller shortening from a second electronegative atom (B) and so on. The coefficient in eq 1, 0.62, was chosen to reproduce the experimental data for the alkyl fluorides. It should be noted that eq 1 also correctly describes bond lengths in alkyl chlorides, amines, alcohols, and ethers, which have been studied previously.[15]

All of the foregoing applies to what we might call the "primary electronegativity effect", as was worked out originally for MM2. It has been carried over directly to MM3, although some of the parameters have been refined and have slightly different values in MM3 than in MM2. Further study, however, showed that this treatment is incomplete, and we really need to add a "secondary electronegativity effect". For example, when a fluorine atom is attached at carbon 1 in propane, the 1–2 bond shrinks in accord with the primary electronegativity effect. Also, the 2–3 bond shrinks (by a lesser amount) from the secondary electronegativity effect. Presumably this effect continues in diminished intensity down a long chain, but for our present purposes, it essentially vanishes after the secondary effect. We have limited it to the primary effect (when the electronegative atom is attached directly to the bond concerned) and the secondary effect (wherein the bond concerned is one bond removed from the attachment). In the original version of MM3, there is no secondary electronegativity effect.

As the bond length becomes shorter, one would also expect the stretching force constant for the bond to increase. We will now examine the connection between these observed trends to find an "electronegativity correction" to the bond stretching force constant for aliphatic C–H bonds.

There have been several important attempts in the literature to find a correlation between bond length and bond stretching force constants. Badger[10] found a cubic relationship for a handful of diatomic structures in the ground state and in several excited vibrational states. More recently, Herschbach and Laurie[16] compiled a larger data set than was available to Badger and revised the constants in Badger's equation. They also used the same set of data to propose a different empirical equation that is exponential instead of cubic. Other workers have also used an exponential relationship.[17,18]

The relationship based on McKean's equation has an advantage over Badger's and Herschbacher's equations for the case of C–H bonds in that McKean recognized the different ways in which the bond lengths can be described and always used r_o. A relationship between the change in the force constant, Δk_s, and the change in the bond length, Δl_o, can be derived from McKean's empirical equation[6] as given by

$$\nu = \frac{1.3982 - r_o}{0.000\,102\,3} \qquad (2)$$

and the well-known relationship between the force constant (k), vibrational frequency (ν), and C–H reduced mass (μ)

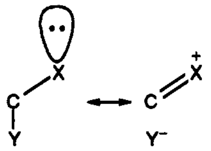
$$k = \nu^2(2\pi c)^2\mu \qquad (3)$$

which strictly holds for a diatomic harmonic oscillator. By substituting eq 2 into eq 3, we obtain a quadratic relationship between bond length and stretching force constant which is different from the cubic and exponential relationships obtained earlier. Taking the partial derivative of the force constant with respect to the bond length, we obtain

$$\Delta k_s = \frac{2\mu(2\pi c)^2}{(-0.000\,102\,3)^2}(l_o - 1.3982)\Delta l_o \qquad (4)$$

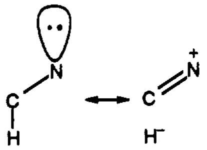
McKean's equation (eq 2) is expected to work well as long as the compounds being considered do not have any great differences in the electrostatic or steric effects being exerted upon the bonds in question. By substituting the molecular mechanics parameter l_o in place of the actual bond length (r_o), eq 4 can be used in a molecular mechanics force field and should be much more general. The rest of the force field will take into account whatever changes arise from steric and electrostatic effects. To this end, one also needs to use eq 4 to determine the force parameter for stretching the bond under examination. And, of course, these principles should apply to covalent bonds in general, not just to C–H bonds.

Anomeric Effect. This effect has long been recognized and is pretty well understood in terms of both quantum mechanics and molecular mechanics.[19] It is observed when two electronegative atoms are attached to a common atom. This effect is only important when there is a lone pair of electrons oriented anti-periplanar to a bond on a vicinal atom which extends to an electronegative atom. The best studied case is when both of these atoms are oxygen, and this case was previously implemented in MM2 and MM3. But the effect occurs when the atoms are various combinations of halogens, oxygen, or nitrogen. The important features of the effect are shown in the diagram. The bond lengths of C–X and C–Y are dependent on the dihedral angle between the lone pair on X and the C–Y bond.



This effect is included here for completeness, but since it does not involve C–H bonds, it will not be discussed further. We want to point out, however, that this is an important example of the more general *trans lone pair effect.*

Bohlmann Effect. It has been known for a long time that amines which have a hydrogen on the carbon attached to nitrogen so that the C–H bond is anti-periplanar to the lone pair axis show abnormally low stretching frequencies for those C–H bonds.[20,21] Such low C–H stretching frequencies in amines are referred to as "Bohlmann Bands". This is another example of the more general phenomenon, in which any vicinal bond anti-periplanar to a lone pair is weakened and has a reduced force constant. The reason for this weakening again can be seen in terms of valence bond pictures:



The structure on the left shows the geometry required. If the C–H bond is rotated so that the dihedral angle with respect to the lone pair is 90°, the effect is minimal. A syn-coplanar arrangement also leads to the effect, although the relative magnitudes of the effect for the syn and anti conformations are quite different. The physical phenomenon involves the delocalization of the lone pair of electrons into the σ^* orbital of the C–H bond, as is illustrated in the resonance form on the right. This structure shows reduced bonding character and hence a longer bond length and a lower force constant for the C–H bond when this geometry is attained, and the analogy to the corresponding structure previously shown for the anomeric effect is emphasized.

This effect is general in the sense that if one has a lone pair of electrons and an anti-periplanar σ^* orbital, then it will occur. Its importance in any particular case will depend upon ionization

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potentials, overlaps, etc. In practice it is found that the effect is most important in the case of a lone pair on nitrogen, because the nitrogen is not very electronegative, so the electrons in the lone pair are not very tightly held and hence can delocalize readily. In oxygen or fluorine, the electrons are increasingly much more tightly held, and they delocalize to a lesser degree, and the resulting frequency shifts are smaller. With sulfur, the effect is known to be of minor importance. This appears to be due in part to the relatively poor overlap of the lone pair orbital on sulfur with the σ^* orbital. It is noted that the Bohlmann effect occurs together with the electronegativity effect in molecules containing atoms to the right of carbon in the first row of the periodic table. The observed frequency shifts in such molecules must therefore be partitioned between these effects, and this can be done effectively using molecular mechanics.

It will be noted that the anomeric effect and the Bohlmann effect are in fact different manifestations of the same phenomenon, the *trans lone pair effect*. In each case, a lone pair of electrons is donated into a vicinal σ^* bonding orbital, and an anti-periplanar geometry is optimum for such donation. The result is that the presence of electrons in the σ^* orbital causes the corresponding bond to stretch, and the bond becomes weaker and the stretching force constant smaller. While the results of these two effects may seem different from the point of view of the chemist in the laboratory, in fact they are the same effect, as examined via two different observables. Quantitatively, the anomeric effect is larger, resulting in energy changes on the order of 1–2 kcal/mol and bond length changes on the order of 0.020 Å. The Bohlmann effect, on the other hand, usually causes frequency shifts on the order of 100 cm^{-1} (0.4 kcal/mol) and bond length changes on the order of 0.005 Å.

When Henbest, Meakins, and co-workers[11,12] began to examine the infrared spectra of OCH_3-, $N(CH_3)_2$-, and NCH_3-substituted alkanes, they were surprised to find bands around 2815 and 2770 cm^{-1}. They attributed these vibrational bands to the C–H vibrations when the carbon was attached to an oxygen or a nitrogen. These conclusions were later confirmed by Krueger et al.[22]

Independently of Meakins, Bohlmann also noticed these C–H vibrational bands in his study of quinolizidines[20,21] and interpreted them as being dependent on the stereochemistry of the rings containing the nitrogen atom. Krueger et al.[23] clarified when the so-called 'Bohlmann' bands would appear in terms of the orientation of a C–H bond with respect to the N lone pair.

It was not until the early 1970s that a theoretical understanding of the origin of these bands was available. Ernstbrunner and Hudec[24] were the first to show experimentally that the previous theoretical interpretations of the 'Bohlmann' bands were erroneous. They suggested from the unusually strong intensities of these bands that Fermi resonance was a contributing factor.

McKean and Ellis[25] have also shown experimentally that Fermi resonance contributes to the presence of the low-frequency C–H stretching vibrations in amines. The Fermi resonance interaction involves the overtone of a X–C–H (where X = N, O) bending motion and a C–H stretching mode. A qualitative study of a sizable number of compounds has demonstrated that a Fermi resonance coupling which exists between a symmetric methyl stretching mode and a methyl deformation mode is rather common.[26]

Wolfe et al.[27,28] reported a series of *ab initio* studies into the origin of the low-frequency C–H stretching vibrations using a 4-21G basis set. Their conclusions were the same as those of Ernstbrunner and Hudec.[24] They also investigated[28] the presence of low-frequency C–H stretching vibrations in methanol and methanethiol.

An interesting sidelight of the *ab initio* studies[28] was the observation that the C–H bond is longer when it is anti with respect to the X–Lp "bond" than when it is in the gauche position. We note that for methanol and methylamine the C–H bond stretching force constant varies inversely with respect to the C–H bond length. Other *ab initio* studies of methylphosphine[29] and dimethyl ether[30] have found the methyl C–H bond lengths to vary with respect to the lone pair orientation. The presence of the *trans lone pair effect* has also been noticed in halides.[31,32]

There is thus extensive experimental and theoretical evidence that the stretching vibrations of C–H bonds that are trans with respect to a lone pair of electrons on a neighboring nitrogen or oxygen atom appear at lower than normal frequencies.

The parametrization of the original version of MM3 (MM3(91)) for the amines has been previously described.[33] There were several C–H stretching frequencies that were difficult to fit. During the course of the present work, we realized the necessity of taking into account the 'Bohlmann' effect for amines and other heteroatoms. The equation that we now use to calculate the correction, δl_0, is of the form given by eq 5

$$\delta l_0 = V_0 + \frac{V_1}{2}(1 + \cos\omega) + \frac{V_2}{2}(1 - \cos 2\omega) \qquad (5)$$

We have thus constructed a mathematical separation of the electronegativity effect and the trans lone pair effect. The variable V_0 is similar to the electronegativity correction in part, but it also accounts for the Bohlmann effect of fluorine, which has no directional dependence, since the lone pairs are equal in all directions perpendicular to the C–F bond. The constant V_0 differs from the electronegativity constant (Δl_A in eq 1) in an important way. Since V_0 depends on the trans lone pair on the adjacent atom, it shows a primary but no secondary effect, while the electronegativity constant (Δl_A) has an inductive basis and shows both a primary and a secondary effect.

Experimentally it is known that the Bohlmann effect is large when the CH bond in question is antiparallel to the lone pair of electrons on nitrogen, and it is negligibly small when these have a gauche rearrangement. Such a behavior could be modeled by either a 1-fold or 2-fold cosine function, a summation of the two, or otherwise. The available experimental information was not sufficient to delineate the functional form needed here. Consequently, we carried out *ab initio* calculations on ethylamine and determined the relationship between the α-CH bond length and the torsion angle with respect to the amine lone pair. For oxygen, a similar determination was made, which we might think of in terms of two interactions of a given C–H bond with the two lone pairs on oxygen. In practice it was expedient to formulate these functions in terms of the torsion angles of the atoms attached to nitrogen or oxygen rather than in terms of the lone pairs. For fluorine, there are three lone pairs (if we think of sp^3 hybrid orbitals), and because of the cosine relationships, in fact the effect is invariant to torsion angle and hence just a constant. The parameters arrived at are shown in Table 1. Since the electrons are held more tightly when the nuclear charge is higher, the effect is smaller for fluorine, larger for oxygen, and still larger for nitrogen. This is not evident at a glance from the numbers in Table 1 because the dihedral angles are measured differently. In Figures 1 and 2 plots of the C–H bond lengths from the *ab*

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Table 1. Parameters

	V_0	V_1	V_2
F	0.0042	0.0	0.0
O	0.0	0.0040	0.0053
N	0.0	0.0130	0.0035

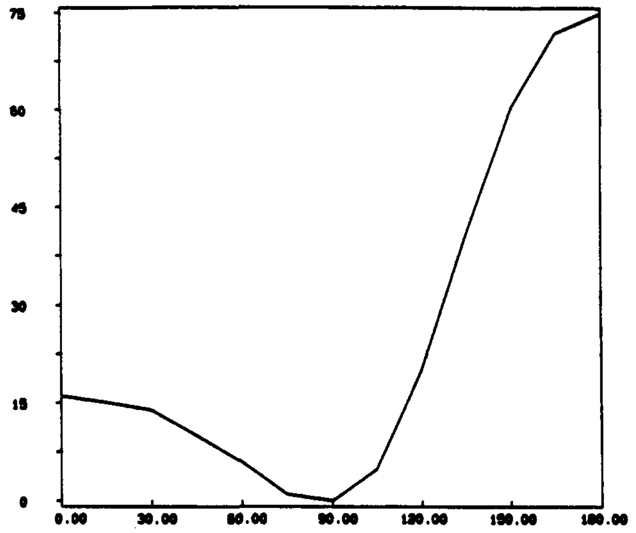


Figure 1. Results of Hartree–Fock (6-31G*) calculations on the bond length of a C–H bond (in units of 10^4 Å) in ethylamine as a function of torsional angle (in degrees) C–C–N–Lp, where the lone pair (Lp) is assumed to lie in the plane that bisects the HNH angle.

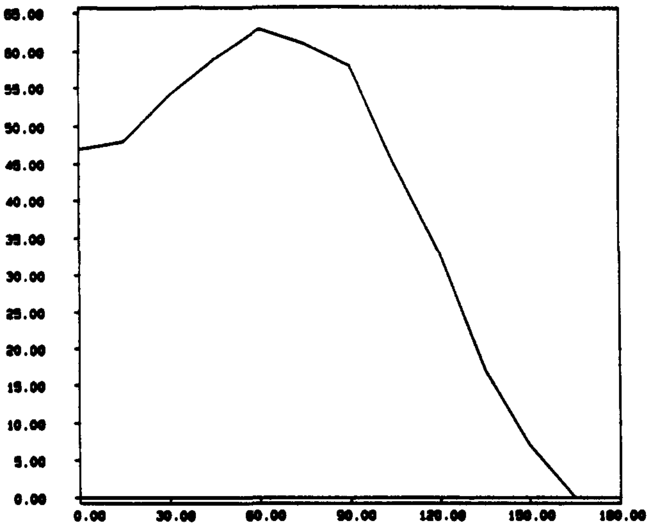
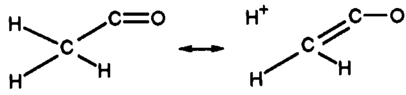


Figure 2. Results of Hartree–Fock (6-31G*) calculations of the bond length of a C–H bond (in units of 10^4Å) in methanol as a function of torsional angle (in degrees) H–C–O–H.

initio calculations (6-31G*) as functions of torsion angle are shown, where ω is the dihedral angle between the C–H bond and the O–H bond of an alcohol. For an amine the lone pair was specified to have a torsion angle which was 180° away from the bisector of the torsion angle of the other two substituents on nitrogen, and ω refers to the torsion angle of the lone pair. The MM3 curves were fit to the *ab initio* curves and then adjusted to improve the fit of the vibrational frequencies to experiment.

Carbonyl Effect (Hyperconjugation). This effect applies to a relatively limited class of compounds which contain either a carbonyl group or something approximating that in an electronic sense (aldehydes, ketones, esters, imines, etc., and also alkenes). If we think of a methyl ketone, for example, the effect can be illustrated in the following way. A C–H bond of the methyl group which lies in the plane of the carbonyl has some length, determined by various factors. If another hydrogen on the methyl group is out of the plane, the bond length to that hydrogen will in general be longer than that of the one which is in the plane. *Ab initio* calculations[34] show that the bond length is approximated by a cos 2ω type function, where the minima are at 0° and 180° and the maxima are at ±90°. The lengthening of the bond can be understood in terms of valence bond structures.



The structure on the left is the principal resonance form, and the structure on the right a hyperconjugated form. The latter contributes to the overall structure to the extent that electrons are donated from the C–H σ bonding orbital into the π^* orbital of the carbonyl group. This effect is maximal when these two orbitals overlap maximally, i.e. when the O–C–C–H dihedral angle is 90°. As suggested by the hyperconjugated resonance form, the bond is more broken, that is the bond order is lower, and the bond is longer, the farther from the C=O plane the bond lies. The C=C and C=O bonds do not change in length from this effect as the methyl rotates, because the changes brought about by one C–H bond are compensated by changes from the other C–H bonds. The bond lengthening effect here can be substantial, so this is an important contributor to overall bond lengths, but in only a restricted class of compounds. If one draws valence bond structures analogous to the structures shown but for an alkene in which the carbonyl oxygen is replaced by carbon, one has the more general hyperconjugative effect. The shifts here are similar to those found in the carbonyl case but smaller. We have also studied this effect in detail and will report on it separately.

One would also expect an electronegativity correction to be required for the C–H bond on a carbon attached to a carbonyl group. Previously, MM3 did not make electronegativity corrections for stretching constants. However, it does adjust the bond length parameter, l_0 on the basis of the dihedral angle of H—C—C=O. The values used earlier in MM3 were based upon the results of *ab initio* calculations (4-21G).[34] The variation of the α C–H and C–C bond lengths in acetaldehyde and propanal were examined. There was a substantial change in the methyl C—C bond length in propanal (0.016 Å) as the C—C—C=O dihedral angle went from 0° to 90°. The α C—H bond length changed by a maximum of 0.007 Å. Wiberg[35–38] has reported the same trend in bond lengths for a number of aldehydes and ketones (6-31G* basis set).

We have chosen to reproduce the change in the bond length with a cosine function as given by

$$l_0(\text{new}) = l_0(\text{old}) + \text{SCO}[1 - \cos(2\omega)] \qquad (6)$$

where ω is the O=C—X—Y dihedral angle. In MM2[34] we used SCO = +0.0080 Å for C—C bonds and +0.0035 Å for C—H bonds. The changes in the respective bond lengths are twice these values or 0.016 and 0.007 Å for C—C and C—H bonds, respectively. These parameters were used for esters and carboxylic acids[39] as well as for aldehydes and ketones.[40] We will discuss only the change in the C—H bond length here and have reduced the value of SCO for it to +0.0025 Å in MM3(94) to better fit additional data now available.

Discussion of Results

Electronegativity Effect. The overall procedure for implementing these effects in MM3 was the following. Since it is

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(40) Allinger, N. L.; Chen, K.; Rahman, M.; Pathiaseril, A. *J. Am. Chem. Soc.* **1991**, *113*, 4505.

Table 2. Hydrocarbon C–H Stretching (cm^{-1})

		exp	MM3[a]	MM3(92)[b]	assignment
methane[c]	A1	2916	2823/–93	2871/–45	sym CH_4 str
	T	3019	2984/–35	3034/15	asym CH_4 str
ethane[d]	A1g	2915	2882/–33	2885/–30	sym CH_3 str
	A2u	2915	2864/–51	2867/–48	sym CH_3 str
	Eu	2974	2968/–6	2971/–3	asym CH_3 str
	Eg	2950	2963/13	2967/17	asym CH_3 str
propane[d]	A1	2965	2966/1	2969/4	asym CH_3 str
		2875	2890/15	2884/9	sym CH_2 str
			2875	2865	sym CH_3 str
	A2		2968	2970	asym CH_3 str
	B1	2965	2964/–1	2968/3	asym CH_3 str
		2875	2974/–1	2877/2	sym CH_3 str
	B2	2965	2968/3	2970/5	asym CH_3 str
		2915	2943/28	2924/9	asym CH_2 str
isobutane[d]	A1	2962	2969/7	2972/10	asym CH_3 str
		2904	2890/–14	2910/6	CH str
		2880	2871/–9	2876/–4	sym CH_3 str
	A2	2958	2965/7	2968/10	asym CH_3 str
	E	2962	2968/6	2971/9	asym CH_3 str
		2962	2967/5	2970/8	asym CH_3 str
		2894	2875/–19	2878/–16	sym CH_3 str
			signed av/RMS	signed av/RMS	
		overall:	–9.5/26.8	+0.2/17.3	

[a] MM3: C–H stretching constant is 4.74 mdyn/(Å·mol). [b] MM3(92): C–H stretching constant is 4.90 mdyn/(Å·mol) for CH4 group; 4.75 mdyn/(Å·mol) for CR-H3 group; 4.68 mdyn/(Å·mol) for CR2-H2 group; 4.81 mdyn/(Å·mol) for CR3-H group. The C–H l_0 is always 1.1120 Å. [c] Poussigue, G.; Pascand, E.; Champion, J. P.; Pierre, G. *J. Mol. Spectrosc.* **1982**, *93*, 351. [d] Schachtschneider, J. H.; Snyder, R. G. *Spectrochim. Acta* **1963**, *117*, 19.

Table 3. Compound Classes and Effects Present (+) in Each

class	electronegativity	Bohlmann	carbonyl
alkanes	–	–	–
nitroalkanes	+	–	–
sulfones	+	–	–
sulfoxides	+	–	–
alkynes and nitriles	+	–	–
silanes	–	–	–
alkyl fluorides	+	+	–
amines	+	+	–
alcohols and ethers	+	+	–
carbonyl compounds	+	–	+

known that methane, primary, secondary, and tertiary hydrogens all have slightly different stretching constants,[41] k_s was at the outset initialized at the appropriate value (Table 2) while l_0 was taken as constant throughout this series. The program then identifies any heteroatoms in the molecule. For each of these, it then calculates primary and secondary electronegativity effects, a carbonyl effect, and a Bohlmann effect, depending on the structural features present. Having taken these effects into account, the total change in l_0 for each C–H bond in the molecule is known, and these values are adjusted. Having established the value for each l_0 for each C–H bond in the molecule, the corresponding stretching constant for each bond is then calculated using eq 4. During the geometry optimization, the changes in bond length and force constant introduced by these effects (other than the electronegativity effect) may change. The bond lengths and stretching constants are accordingly updated during each iteraction of the geometry optimization. When the energy minimization is complete, we have the optimum values for l_0 and k_s for each C–H bond.

The above is a description of how MM3(93) actually works. A more efficient way of including these effects would be with off-diagonal terms in the force constant matrix. This has not been done yet, because it was easier to extend the existing program than to reformulate these things, but it will be done at some time in the future.

Since C–H stretching frequencies are usually known much more accurately than the corresponding bond lengths, it was necessary to find the optimum values for Δl_0 that would adjust k_s so as to best fit the C–H frequencies. The results are presented in a series of tables which follow. We wished to study a broad selection of compounds to sketch an outline of what happens when these various effects are taken into account, so we have chosen the saturated hydrocarbons as a basis, followed by 11 classes of functionalized molecules. As listed in Table 3, these different classes of compounds show the different effects in various combinations. The original version took all C–H stretching constants to have the same value (4.74 mdyn/Å·mol), while the constants actually have values which vary over a range of about 5%. For MM3(92), slightly different values were assigned for 1°, 2°, and 3°, as shown. The root mean square error in the group of frequencies shown was 27 cm^{-1} with MM3 and was reduced to 17 cm^{-1} in MM3(92). If a very large data set of hydrocarbon frequencies was used, these errors would be expected to be somewhat larger, about 35 and 25 cm^{-1}, respectively. While the latter value could probably be reduced somewhat with the aid of interaction constants, we have not examined that improvement yet. The hydrocarbon force field accuracy will therefore limit the accuracy of what follows to about 25 cm^{-1} (root mean square).[42] In Table 4 are given the electronegativity parameters finally arrived at. The corrections given are the shortening of a C–H bond when the group shown is attached to the same (α) carbon in Å, and these are seen to range from 0.000 in silanes to –0.0081 for the fluorine. Other groups studied are between these limits, more or less in order according to their electronegativities. The effect on bond length is thus pretty small, less than 0.02 Å for trinitromethane, an extreme value, and usually more in the range of 0.002–0.005 Å. The effect at the β carbon is 0.40 times the effect at the α carbon. The changes in the C–H stretching frequencies brought about by these substituents are, however, more dramatic. We might look next at Table 5, for nitroalkanes. This group shows only an inductive effect as formulated. (The nitro group is not axially symmetrical, so resonance effects might be expected. It is almost a free rotor, however, so that such

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(41) Snyder, R. G.; Schachtschneider, J. H. *Spectrochim. Acta* **1965**, *21*, 169; **1963**, *19*, 117.

(42) A referee has noted that "the rms error in frequencies in the present work is overall 24 cm^{-1}, which is still far from what can be obtained using spectroscopic force fields". He further states that "in a recent paper (Derreumaux, P.; Dauchez, M.; Vergoten, G. *J. Mol. Struct.* **1993**, *295*, 203–221.) the so called Urey–Bradley term was included in the AMBER force field. Its effect on all bond stretching (not only CH bonds) frequencies is evident. The agreement achieved is spectacular (13 wavenumbers). Introducing a Urey–Bradley term is equivalent to adding cross terms to the potential energy function. A discussion on the possible relation between the Urey–Bradley term and the effects described in the present paper would be appreciated before publication." Since many misunderstandings may arise with respect to the above, the following comments are added. First, Snyder and Schactschneider (ref 41) showed long ago that if one uses the same number of parameters, a Urey–Bradley force field and a valence force field give equivalent accuracy in the results. Molecular mechanics force fields have been divided between the two types, but there is no compelling reason to choose one over the other. That paper cited concerns a force field for strainless saturated hydrocarbons only and uses the AMBER program as a mechanical device for the calculations but does not use the AMBER force field *per se*. Snyder and Schactschneider and later Ermer (Ermer, O. In *Structure and Bonding*; Simonetta, G., Warren, K. D., Eds.; Springer Verlag: New York, 1976; Vol. 27.) also showed that it was possible to obtain such excellent results between calculation and experiments for saturated hydrocarbons. The lower accuracy here is presumably in part due to the omission of some interaction terms (fewer parameters), but it also suffers from the fact that when one looks specifically at CH stretching vibrations, there is a shifting about of the frequencies because of Fermi resonance, and this ultimately limits the accuracy possible. The Urey–Bradley term is a way for taking into account certain kinds of nonbonded interactions, which are taken into account in a different way in a valence force field by interaction terms. The present formulation is that of a valence force field. This could also be done within the Urey–Bradley formulation, but there is no reason to think that there would be any difference in the accuracy of the results from the Urey–Bradley scheme, and the physical interpretation would probably be less straightforward. Also, note that the present work examines not just hydrocarbons but molecules containing eleven different functional groups as well, certainly a much more complicated set of compounds to deal with.

Table 4. C–H Bond Length Electronegativity (Primary) Correction Parameters (Å)

atom type	group	correction
11	F	−0.0081
46	O—N—O	−0.0058
10	≡N	−0.0055
3(7)	C═O	−0.0050
75	O—(C═O)	−0.0035
18	O—S—O	−0.0030
6	O—	−0.0028
17	S—O	−0.0025
4	C≡	−0.0015
8	N—	−0.0011
19	Si	0.0000

Table 5. Nitroalkane's C–H Stretching (cm^{-1})

		exp	MM3	MM3(94)
nitromethane[a]	A′	3065	2970/−95	3032/−33
		2967	2872/−95	2931/−36
	A″	3045	2970/−75	3031/−14
dinitromethane[b]	A	2940	2873/−67	2967/27
	B	2970	2925/−45	3021/51
trinitromethane[c]	A	3066	2900/−166	3017/−49
nitroethane[d]	A′	3001	2964/−37	2992/−9
		2957	2869/−88	2896/−61
		2926	2897/−29	2935/9
	A″	3019	2962/−57	2989/−30
		2972	2946/−26	2986/14
2-nitropropane[e]	A′	3007	2899/−108	2977/−30
		2954	2968/14	2995/41
		2936	2966/30	2992/56
		2882	2872/−10	2899/17
	A″	2997	2967/−30	2994/−3
		2984	2964/−20	2991/7
		2916	2874/−42	2900/−16
			signed av/RMS	signed av/RMS
		α:	−78.4/88.8	−6.8/32.5
		β:	−26.7/43.0	0.2/33.5
		overall:	−52.6/69.7	−3.3/33.0

[a] Trinquecoate, C.; Rey-Leon, N.; Forel, M. T. *Spectrochim. Acta* **1974**, *30A*, 813. [b] Singh, K. *Spectrochim. Acta* **1967**, *23A*, 1089. [c] Brookes, M. J.; Jonathan, N. *J. Chem. Soc. A* **1968**, 2266. [d] Groner, P.; Myer, R.; Gunthard, H. H. *Chem. Phys.* **1975**, *11*, 63. [e] Durig, J. R.; Smith, J. A.; Li, Y. S.; Wasacz, F. M. *J. Mol. Struct.* **1983**, *99*, 45.

effects should be pretty well averaged out.) The nitro group is strongly electron withdrawing, and hence the effect causes the C–H bonds to shorten, quite a lot if they are in the α position to the nitro group and to a lesser amount if they are in the β position. Without this correction, the stretching frequencies were calculated by MM3 to be much too low (negative errors). With trinitromethane, the error was most severe (−166 cm^{-1}). When the electronegativity correction was made, the frequencies were increased, and they now agree with experiment. It is shown in the table that, for the five reference compounds, the α hydrogens showed frequencies that were too negative by 78 cm^{-1} on the average, while the β frequencies were 27 cm^{-1} too negative. When the appropriate corrections are made, these numbers become 7 and 0 cm^{-1}, respectively. The root mean square error over all of these frequencies, initially 70 cm^{-1}, was reduced to 33 cm^{-1}. Since the hydrocarbon part of the force field itself has a root mean square error of about 25 cm^{-1}, the systematic error has been almost completely removed, and the accuracy is down to close to the hydrocarbon limit.

Tables 10–12 in the supplementary material show the results for sulfones, sulfoxides, acetylenes, and nitriles, where only an electronegativity effect is present; we notice qualitatively the same situation. The sulfones had their C–H frequencies calculated too negative by 38 cm^{-1} for the α hydrogens and by 16 cm^{-1} for the β hydrogens. The sulfoxide frequencies were similarly calculated 29 cm^{-1} too low for the α hydrogens. For the alkynes and nitriles, the overall C–H frequencies are too low by 13 cm^{-1}. These systematic errors were largely corrected, as shown in the tables.

Trans Lone Pair Effect. The next groups of compounds that we would like to consider are those that show both the electronegativity effect and the Bohlmann effect, starting with the alkyl fluorides. The electronegativity effect of fluorine is quite strong, and since the fluorine holds tightly to its electron pairs, that leads to a relatively weak Bohlmann effect. If we look at Table 13 in the supplementary material, we see (first and second columns) that the average frequencies were calculated too low, by quite a large amount (39 cm^{-1} for the α hydrogens and 61 cm^{-1} for the β). In ethers and amines these same two effects are present. However, whereas the electronegativity effect is quite strong with fluorides, intermediate with ethers, and weak for the amines, the Bohlmann effect is the other way around, being strong for amines and weak for fluorides. Hence while we calculate without any correction the fluoride frequencies too low, those for the amines are too high, and those for the ethers are about right on average. When these effects are correctly apportioned, the results improve markedly. (Note that in MM3 the Bohlmann effect was already taken into account approximately, and so the change from MM3 to MM3(94) is relatively small.)

In Table 13 in the supplementary material are given the experimental and MM3 results; then the next column shows the effect of adding only the electronegativity corrections to the MM3 (plus hydrocarbon corrections) results. The β hydrogen frequencies are now well calculated, but the α hydrogen frequencies are much over corrected and are now too positive. The α hydrogen average errors have gone from −39 to +60 cm^{-1}, a shift of 99 cm^{-1}. The β hydrogen errors have shifted less, from −61 to 0 cm^{-1}, and are now negligible.

The next column shows the result of adding only the Bohlmann correction to the MM3 results. The average α hydrogen errors shift from −39 to −92, a shift of −53 cm^{-1}. The β hydrogen errors shift from −61 to −69 cm^{-1}. The rightmost column shows the result of adding both corrections to the original MM3 values. In this case the average errors are all less than 6 cm^{-1}, and the overall root mean square error has been reduced from 51 to 20 cm^{-1}, down to the hydrocarbon limit.

Table 6 shows the analogous information for alcohols and ethers. Here the electronegativity and Bohlmann effects are not very large, and they mostly cancel, so the improvements in the averages in MM3(94) are from 21 to −3 cm^{-1} for the α hydrogen errors and from −5 to 2 for the β hydrogens. The root mean square error overall does go down somewhat from 39 to 27 cm^{-1}.

The best values found for the coefficients in eq 5 for the amines are listed in Table 1. These numbers show that a C–H bond on an adjacent carbon oriented trans to the nitrogen lone pair will be elongated by up to 0.0126 Å by the Bohlmann effect. The columns labeled as MM3 are the calculated results[33] that do not include the electronegativity correction to the bond stretching force constants as described in this paper. An examination of Table 7 shows that eq 5 does a good job at improving the fit to the vibrational frequencies of the amines. The electronegativity effect causes small increases in the already positive α hydrogen errors (+37 to +49) and in the β hydrogen errors (+12 to +18). The larger Bohlmann effect causes the frequencies all to be reduced, and the final averages are 0 and +4 cm^{-1}, respectively. The overall root mean square error has gone down from 47 to 17 cm^{-1}.

Carbonyl Effect. In an earlier section we discussed the change of C—H bond length as a function of the dihedral angle O═C—C—H. Coupled with the electronegativity effect, there are these two influences upon the bond length for a C—H bond attached to a carbonyl moiety. We have taken both factors into account, and the results are given in Table 8. Equation 6 is used

Table 6. C–H Stretching (cm^{-1}) of Alcohols and Ethers

		exp	MM3	electro.	Bohlmann	MM3(94)
methanol[a]	A′	2977	2976/−1	3001/24	2970/−7	2993/16
		2844	2873/29	2897/53	2847/3	2847/3
	A″		2970	2996	2934	2930
ethanol[b]	A′	2989	2964/−25	2977/−12	2968/−21	2979/−10
		2900	2898/−2	2901/1	2876/−24	2834/−66
			2870	2881	2834	2887
	A″	2989	2965/−24	2977/−12	2968/−21	2979/−10
			2949	2953	2887	2887
dimethyl ether[c]	A1	2991	2978/−13	3004/13	2973/−18	2995/4
		2820	2876/56	2900/80	2853/23	2851/31
	A2		2974	3000	2941	2933
	B1	2991	2976/−15	3001/10	2970/−21	2993/3
		2820	2876/56	2900/80	2853/33	2850/35
	B2		2975	3001	2942	2935
isopropyl alcohol[d]	A		2966	2979	2969	2981
			2966	2978	2969	2980
			2965	2978	2969	2980
			2963	2976	2967	2978
			2900	2943	2879	2893
			2873	2885	2876	2887
		2875	2871/−4	2884/9	2842/−33	2880/5
ethylene glycol[e]	A	2968	2956/−12	2969/1	2933/−35	2960/−7
		2940	2950/10	2963/23	2888/−52	2899/−41
		2891	2905/14	2918/27	2878/−13	2864/−27
		2885	2893/8	2905/20	2835/−50	2845/−40
diethyl ether[f]	A1	2948	2964/18	2976/28	2967/19	2979/31
			2901	2905	2876	2887
		2869	2870/1	2881/12	2840/−29	2837/−32
	A2	2985	2964/−21	2977/−8	2967/−18	2979/−6
			2952	2956	2876	2890
	B1	2948	2964/18	2976/28	2967/19	2979/31
			2899	2903	2876	2887
		2869	2870/1	2881/12	2838/−32	2835/−34
	B2	2990	2965/−25	2977/−13	2967/−23	2979/−11
			2954	2957	2894	2891
methyl *tert*-butyl ether[g]	A′	2986	2982/−4	3008/22	2978/−8	2996/10
		2977	2974/−3	2986/9	2975/−2	2989/12
			2967	2980	2970	2982
			2966	2978	2969	2981
		2917	2890/−27	2914/−3	2881/−36	2892/−25
			2873	2885	2876	2887
		2828	2878/50	2890/62	2872/−44	2868/40
	A″	2986	2996/10	3021/35	2977/−9	2988/2
		2977	2973/−4	2985/8	2969/−8	2980/3
			2965	2978	2967	2979
			2964	2976	2967	2955
		2917	2878/−39	2890/−27	2881/−36	2892/−25
tetrahydropyran[h]	A′	2969	2950/−19	2962/−7	2930/−39	2939/−30
		2946	2949/3	2935/−11	2926/−20	2951/5
		2932	2945/13	2929/−3	2925/−7	2929/−3
		2860	2908/48	2910/50	2884/24	2981/31
		2849	2900/51	2889/50	2869/20	2872/23
		2842	2885/43	2871/29	2858/16	2860/18
	A″	2969	2956/−13	2960/−9	2926/−43	2949/−20
		2924	2944/20	2937/13	2924/0	2937/13
		2860	2907/47	2909/49	2876/16	2886/26
		2849	2891/42	2882/33	2858/9	2859/10
1,4-dioxane[i]	Ag	2968	2957/−11	2970/2	2929/−39	2964/−4
		2856	2910/54	2922/66	2869/13	2872/16
	Au	2970	2955/−15	2967/3	2927/−43	2962/−8
		2863	2909/46	2922/59	2868/5	2871/18
	Bg	2968	2957/−11	2970/2	2926/−42	2959/−9
		2856	2898/42	2911/55	2860/4	2864/8
	Bu	2970	2959/−11	2972/2	2929/−42	2961/−9
		2863	2898/35	2911/48	2859/−4	2866/3
1,3,5-trioxane[j]	A1	3025	2971/−54	2987/38	2935/−90	2976/−49
		2850	2912/62	2928/78	2844/−6	2811/−39
	E	3025	2966/−59	2982/−37	2932/−93	2973/−52
		2850	2912/62	2927/77	2842/−8	2809/−41
1,3,5,7-tetraoxocane[k]	A1	2990	2967/−23	2981/−9	2912/−78	2937/−53
		2780	2911/131	2926/146	2748/−32	2847/67
	B1		2959	2974	2910	2934
			2910	2925	2741	2842
	E	2920	2963/43	2978/58	2911/−9	2935/18
		2850	2911/61	2926/76	2744/−106	2845/−5

Table 6 (Continued)

exp	MM3	electro.	Bohlmann	MM3(94)
	signed av/RMS	signed av/RMS	signed av/RMS	signed av/RMS
α:	20.7/47.6	38.0/55.1	−24.4/47.1	−5.6/32.1
β:	−4.9/27.0	5.8/23.9	−12.1/25.8	2.4/22.6
overall:	12.9/39.1	26.6/44.3	−19.7/39.2	−4.3/27.1

[a] Serrallach, A.; Meyer, R.; Gunthard, H. H. *J. Mol. Spectrosc.* **1974**, *52*, 94. [b] (a) Perchard, J. P.; Josien, M. L.; *J. Chem. Phys.* **1956**, *65*, 1834 and 1856. (b) Barnes, A. J.; Hallam, H. E. *Trans. Faraday Soc.* **1970**, *66*, 1932. [c] (a) Kanazawa, Y.; Nukada, K. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 612. (b) Fateley, W. G.; Miller, F. A. *Spectrochim. Acta* **1962**, *18*, 977. (c) Snyder, R. G.; Zerbi, G. *Spectrochim. Acta* **1967**, *23A*, 391. (d) Crawford, B. L., Jr.; Joyce, L. *J. Chem. Phys.* **1939**, *7*, 307. [d] Green, J. H. S. *Trans. Faraday Soc.* **1963**, *59*, 1559. [e] Frei, H.; Ha, T. K.; Meyer, R.; Gunthard, H. H. *Chem. Phys.* **1977**, *25*, 271. [f] Weiser, H.; Laidlaw, W. G.; Krueger, P. J.; Fuher, H. *Spectrochim. Acta* **1968**, *24A*, 1055. [g] Suwa, A.; Ohta, H.; Konaka, S. *J. Mol. Struct.* **1988**, *172*, 275. [h] Vedal, D.; Ellestad, O. H.; Klaboe, P.; Hagen, G. *Spectrochim. Acta* **1975**, *31A*, 339. [i] Ellestad, O. H.; Klaboe, P.; Hagen, G. *Spectrochim. Acta* **1971**, *27A*, 1025. [j] Pickett, H. M.; Strauss, H. L. *J. Chem. Phys.* **1970**, *53*, 376. [k] Kobayashi, M.; Kawabata, S. *Spectrochim. Acta* **1977**, *33A*, 549.

Table 7. C–H Stretching (cm^{-1}) of Amines

		exp	MM3	electro.	Bohlmann	MM3(94)
methylamine[a]	A′	2961	2969/8	2987/26	2927/−34	2937/−24
		2820	2872/52	2889/79	2790/−30	2801/−19
	A″	2985	2970/−15	2989/4	2973/−8	2984/−1
dimethylamine[b]	A′	2986	2972/−14	2990/4	2975/−11	2985/1
		2960	2970/10	2988/28	2928/−32	2938/−22
		2795	2873/78	2890/95	2792/−3	2802/7
	A″	2986	2970/−16	2989/3	2973/−13	2983/−3
		2955	2968/13	2987/32	2927/−28	2938/−17
		2795	2873/78	2891/96	2792/−3	2802/7
trimethylamine[c]	A1	2950	2972/22	2990/40	2930/−20	2940/−10
		2774	2874/100	2892/118	2792/18	2804/30
	A2		2970	2988	2973	2984
	E	2978	2974/−4	2977/−3	2992/14	2987/9
			2970	2988	2929	2939
			2874	2892	2973	2803
isopropylamine[d]	A′	2968	2966/−2	2975/7	2969/1	2974/6
		2945	2966/21	2975/30	2969/24	2973/28
		2878	2896/18	2932/54	2879/1	2881/3
		2807	2871/64	2881/74	2786/−21	2797/−10
	A″	2965	2966/1	2975/10	2969/4	2973/8
		2950	2964/14	2973/23	2967/17	2971/21
		2860	2873/13	2882/22	2876/16	2881/21
piperidine[e]	A′	2944	2945/1	2942/−2	2929/−15	2932/−12
		2930	2945/15	2933/3	2925/−5	2927/−3
		2916	2944/28	2927/11	2906/−10	2916/0
		2887	2903/16	2892/5	2882/−5	2885/−2
		2854	2892/38	2883/29	2866/12	2868/14
		2736	2883/147	2869/133	2763/27	2774/38
	A″	2944	2945/1	2940/−4	2925/−19	2930/−14
		2904	2943/39	2931/27	2905/1	2915/11
		2854	2898/34	2891/37	2874/20	2878/24
		2805	2886/81	2877/72	2762/−43	2773/−32
			signed av/RMS	signed av/RMS	signed av/RMS	signed av/RMS
		α:	37.1/58.2	46.1/62.5	−12.0/21.2	−1.5/17.6
		β:	12.0/16.0	18.2/25.3	0.7/15.3	8.3/16.4
		overall:	28.0/46.6	34.8/50.8	−6.7/18.8	2.2/16.8

[a] Gray, A. P.; Lord, R. C. *J. Chem. Phys.* **1957**, *26*, 690. [b] Muldagaliev, K. K.; Pesterev, V. I.; Agashkin, O. V. *Russian J. Phys. Chem.* **1984**, *58*, 1757. [c] Dellepiane, G.; Zerbi, G. *J. Chem. Phys.* **1968**, *48*, 3573. [d] Durig, J. R.; Guirgis, G. A.; Compton, D. A. C. *J. Phys. Chem.* **1979**, *83*, 1313. [e] Vedal, D.; Ellestad, O. H.; Klaboe, P. *Spectrochim. Acta* **1976**, *32A*, 877.

to make a correction to the l_0 parameter. The column labeled as MM3(94) also uses eq 4 to make a correction for the k_s parameter on the basis of the electronegativity effect. The column labeled as "carbonyl" uses that correction for the l_0 parameter and for the Δl_0 parameter in eq 6 to correct the k_s parameter. The column labeled as "electro." uses the correction to the l_0 parameter from the electronegativity effect from eq 1 and to the k_s parameter as given by eq 4. Both of these corrections are used to yield the results shown in the column MM3(94).

With carbonyl compounds, the electronegativity effect tends to raise the C–H stretching frequencies as usual, while the carbonyl effect tends to lower them. The latter, however, is geometry dependent, but generally speaking the electronegativity effect is stronger, and the frequencies initially were calculated too low on the average, by 27 cm^{-1} for the α hydrogens and by 11 cm^{-1} for the β. When the electronegativity and carbonyl effects are added, the result is that the α hydrogens are too low by 5 cm^{-1} and the β hydrogens too high by 11 cm^{-1}. The overall root mean square error is reduced from 41 down to 20 cm^{-1}.

For the esters, the carbonyl group is given its usual effect on the α and β positions (in both directions). Additionally, the alkyl oxygen of the ester is also allowed to exert an interaction. This oxygen is somewhat more electronegative than the ordinary (type 6) oxygen, as shown by the shifts in Table 8. This is as anticipated, since the electrons on this oxygen are to some extent withdrawn into the carbonyl group, leaving the oxygen as a more electronegative moiety.

The attachment of a silicon atom (in the form of a silane) to a C–C bond causes that bond to stretch out, due to the electropositive nature of silicon. One might expect the same thing to happen with C–H bonds, but in fact the frequency change brought about by the introduction of the silyl group was negligibly

Table 8. Carbonyl Compounds C–H Stretching (cm^{-1})

		exp	MM3	electro.	carbonyl	MM3(94)
acetaldehyde[a]	A′	3014	2973/–41	3027/13	2966/–48	3017/3
		2923	2877/–46	2928/5	2853/–70	2901/–22
	A″	2966	2973/7	3027/61	2938/–28	2988/22
acetone[b]	A1	3020	2976/–44	3029/9	2969/–51	3019/–1
		2926	2877/–49	2928/2	2853/–73	2901/–25
	A2	2973	2974/1	3027/54	2983/10	2989/16
	B1	3020	2972/–48	3026/6	2965/–55	3016/–4
		2926	2877/–49	2929/3	2853/–73	2902/–24
	B2	2973	2971/2	3026/53	2939/–34	2990/17
propanal[c]	A′	2991	2964/–27	2987/–4	2967/–24	2987/–4
		2940	2898/–42	2928/–12	2876/–64	2899/–41
		2905	2870/–35	2892/–13	2840/–65	2885/–20
	A″	2991	2965/–26	2988/–3	2968/–23	2988/–3
		2951	2946/–5	2978/27	2890/–61	2941/–10
diethylketone[d]	A1	2950	2963/13	2987/37	2967/17	2987/37
		2915	2899/–16	2930/15	2876/–39	2900/–15
		2890	2870/–20	2893/3	2841/–49	2886/–4
	A2	2984	2965/–19	2988/4	2968/–16	2988/4
			2946	2978	2890	2941
	B1	2950	2963/13	2987/37	2967/17	2987/37
		2915	2897/–18	2928/13	2876/–39	2899/–16
		2890	2870/–20	2893/3	2839/–51	2885/–5
	B2	2984	2965/–19	2988/4	2968/–16	2988/4
			2947	2979	2891	2942
isopropyl methyl ketone[e]	A	3010	2977/–33	3031/21	2974/–36	3016/6
		3010	2974/–36	3028/18	2970/–40	2995/–15
		2980	2971/–9	2994/14	2969/–11	2993/13
			2967	2990	2967	2990
			2965	2989	2966	2989
		2946	2964/18	2987/41	2943/–3	2987/41
		2918	2893/–25	2963/45	2886/–32	2927/9
		2895	2879/–16	2931/36	2878/–17	2904/9
		2886	2876/–10	2901/15	2870/–16	2899/13
		2872	2871/–1	2895/23	2855/–17	2894/22
acetic acid[f]	A′	3051	2971/–80	3041/–10	2967/–84	3031/–20
		2944	2875/–69	2940/–4	2851/–93	2913/–31
	A″	2996	2970/–26	3037/41	2935/–61	2999/3
methyl acetate[g]	A′	3040	2974/–66	3041/1	2978/–62	3034/–6
		3028	2971/–57	3034/6	2967/–61	3031/3
		2955	2875/–80	2940/–15	2876/–79	2930/–25
		2940	2873/–67	2930/–10	2851/–89	2913/–27
	A″	3002	2971/–31	3037/35	2974/–28	3030/28
		3002	2970/–32	3030/28	2934/–68	2999/–3
methyl formate[h]	A′	3045	2974/–71	3033/–12	2978/–67	3033/–12
		2969	2873/–96	2929/–40	2976/–93	2929/–40
	A″	3012	2970/–42	3029/17	2974/–38	3029/17
			signed av/RMS	signed av/RMS	signed av/RMS	signed av/RMS
		α:	–27.0/33.0	21.7/29.8	–44.1/48.9	–5.3/17.9
		β:	–10.9/19.6	12.4/20.8	–21.2/31.7	10.5/21.1
		overall:[i]	–31.4/41.4	13.5/25.3	–43.6/52.1	–1.3/19.8

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small, so the silicon was assigned an electronegativity effect of zero (Table 14 in the supplementary material).

Table 9. Summary of Frequency Errors (cm^{-1}) from Calculations[a]

	MM3 signed av/RMS	MM3(94) signed av/RMS
nitroalkanes	–52.6/69.7	–3.3/33.0
sulfones	–33.9/38.0	–3.9/17.5
sulfoxides	–28.5/30.2	0.2/13.6
alkynes and nitriles	–13.1/30.0	0.1/25.9
fluorides	–50.9/56.8	–0.4/19.7
alcohols and ethers	12.9/39.1	–4.3/27.1
amines	28.0/46.6	2.2/16.8
carbonyl compounds	–31.4/41.4	1.3/19.8
silanes	–0.3/26.4	–1.7/25.8
overall	–12.4/42.0	–1.3/23.9

[a] No. of bonds = 278.

Conclusions

As an initial study directed at a better understanding of covalent bonds, the C–H bond has been examined. The stretching frequency, stretching constant, and bond length for this bond are all closely related, and for several classes of functionalized molecules, all can be calculated if any one is known. These quantities are influenced by several different effects, of which the electronegativity effect, the Bohlmann effect, and the carbonyl effect have been explicitly studied. The results of these three effects can be clearly demonstrated from both *ab initio* calculations and experimental data on appropriate classes of compounds. When these effects are all combined in the molecular mechanics program MM3 and parameters are chosen to optimize the results, the C–H bond lengths can all be calculated to approximately within experimental error, and the stretching frequencies within a 24

cm^{-1} root mean square error for 278 frequencies in 56 compounds containing 12 different functional groups (Table 9). The overall accuracy of the calculation is comparable to the accuracy that can be obtained for hydrocarbon with the force field used, and approaches the limitations thus imposed.[42]

In Table 15 in the supplementary material are shown the signed errors and the root mean square errors for the different classes of molecules, separately for the α and β hydrogens. It is possible that small systematic errors remain which could be reduced by further study, but if so, it appears that they are pretty small.

It is believed that the principles here are general and, with appropriate parameters, can be applied to most or all covalent bonds.

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Supplementary Material Available: Tables of stretching frequencies and frequency errors (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.