

## Accurate computational prediction of molecular structure and spectra

James E. Boggs

Department of Chemistry, The University of Texas, Austin, Texas 78712, U.S.A.

**Abstract** - Near-equilibrium properties of organic molecules containing up to a few dozen atoms can be obtained with chemical accuracy by procedures involving computation with modest basis sets and complete neglect of electron correlation and vibrational anharmonicity if corrections can be made by comparison with results on known, related molecules. A more difficult problem arises when no known species bearing a sufficiently close relationship to the molecule under study is available. In such a case, the calculation must be made strictly *ab initio* and both the solution of the Schrödinger equation and the treatment of the vibrational dynamics must be at a level high enough that the results are directly of the experiment-equivalent quality that is desirable. For equilibrium structures, this means a large basis set expansion of the molecular wavefunction and a good treatment of electron correlation. For vibrational spectra, at least the same level of solution of the electronic Schrödinger equation is necessary in order to obtain higher-order anharmonic constants, but a still larger part of the problem is computation of the vibrational energy levels from the computed anharmonic potential surface. Recent experience with a CI variational treatment of the vibrational problem is presented.

### INTRODUCTION

The quality of a quantum chemical computation must be assessed in terms of the purpose for which the result is intended. Particularly at a conference on Theoretical Organic Chemistry, it is necessary to keep in mind that quantum chemistry has now reached a stage where it is practiced for specific chemical purposes rather than as an exercise in its own right. Thus, the unqualified characterization of a given procedure as a "good method" or a "poor method" is meaningless without the specification of what it is good for or poor for. An *ab initio* Hartree-Fock calculation may be abysmally poor for determining dissociation pathways but still be excellent for determining equilibrium bond angles. Similarly, the phrase "good agreement with experiment" is often misused, with the adjective "good" understood only by the author. Ideally it should mean that the agreement is within the expected error of the experiment and that there is reason to believe that the agreement is not fortuitous.

The present paper summarizes recent efforts from our laboratory and elsewhere to obtain information on near-equilibrium structures and on molecular vibrational dynamics at a level of accuracy comparable to that obtainable from high-quality experiments. It is not the intent to be able to predict a rotational transition frequency to the one part in 10,000,000 to which it can be easily measured in the microwave spectrum, but rather to achieve the chemically useful goal of computing the relevant molecular property, in this case structure, as accurately as it can be deduced by analysis of the experimental data. Similarly, emphasis is placed on the computation of molecular vibrational potential surfaces as accurately as they can be obtained from spectroscopic sources rather than attempting to reproduce the raw spectroscopic data. Further, attention will be given to recent successes in extending such calculations and accuracy in the direction of progressively larger molecules.

### COMPUTATIONAL DETERMINATION OF MOLECULAR STRUCTURE

As a rough rule, the goal of computing molecular quantities as accurately as they can be deduced from experimental analysis translates into allowable structural inaccuracies on the order of a few thousandths of an Ångstrom in bond lengths and a few tenths of a degree in bond angles. Lesser accuracy may still be useful in some cases, but these figures can be taken as a target level. The significance of this target can be realized by considering that the main interest in molecular structure arises from the utility it has in acting as a probe of the variations in electron distribution that distinguish one molecule from other close relatives, thereby imparting chemical individuality to the properties and reactions of each substance. Structural variations between chemically related molecules, especially in

the organic realm, are typically of the order of, or less than, a few hundredths of an Ångstrom or a few degrees, so chemically useful structural results require accuracy and reliability near the level suggested.

The computational determination of a molecular structure involves minimizing the molecular energy with respect to simultaneous variation of all structural parameters. The resulting equilibrium geometry is not identical with any of the various types of vibrationally averaged geometries obtained by experiment, but conversion among these is well understood, at least in principle (ref. 1). The application of the procedure to complex molecules became practical with introduction of the gradient technique, first given systematic development by Péter Pulay of the Loránd Eötvös University in Budapest (ref. 2). Numerous widely used computer programs now make use of various implementations of the technique.

### Empirical correction of computed geometries: Use of offset values

Inaccuracies in the computational determination of molecular structure arise from the numerous approximations that are commonly made in solving the Schrödinger equation, including use of the Born-Oppenheimer approximation, neglect of relativistic corrections, use of a single-determinant wavefunction, use of a finite basis set in expansion of the molecular wavefunction, and neglect or incomplete treatment of electron correlation. The last two are the most important except in those rather few cases where a multi-configuration wavefunction is necessary, *e.g.*, for proper description of the nitro- group (ref. 3). While such problems are important, they are not considered in the remainder of this paper.

The combined effect of neglect of electron correlation and use of a finite basis set is illustrated in Fig. 1, which has been presented earlier (ref. 4). The figure sketches the error in some one kind of structural parameter, such as a C-H distance or H-C-H bond angle as computed in a variety of molecular environments and with different sized basis sets. With an infinite basis set (the Hartree-Fock limit), the error due to neglect of electron correlation has been found empirically to be remarkably constant for a given parameter. For small basis sets (or semi-empirical calculations), the error varies in different molecular environments. Above a given basis set size, however, the error approaches a fixed value, independent of the molecule in which the bond or angle is found. These observations are not exact, of course, but a great deal of evidence suggests that deviations are usually within the range of uncertainty about the "true" value obtained from experiment. Calculations can be done efficiently at the point marked "X" in Fig. 1, which for many structural parameters corresponds to approximately double zeta basis sets. For some parameters, such as torsional angles around nitrogen or oxygen, it is essential to at least add a set of polarization functions to the basis to reach this point. The constant error for a given molecule parameter with a given, sufficiently large basis set is called the offset value (ref. 4). For example, the offset value for a C-H distance with the 4-21 basis set is +0.005 Å. Most bond angles can be calculated directly with such a basis without convincing deviation from experimental values, so they may be said to have an offset value of zero. Bond distances have non-zero offset values, and for some bond types it is essential to go beyond the double zeta or equivalent split-valence sp basis set size.

The combination of *ab initio* computation at a moderate level with the use of offset values can provide highly accurate structural results in favorable cases, often exceeding the accuracy of experiments available to evaluate the error limit. An indirect test has been made by comparing computed C-H distances in a wide variety of compounds with observed C-H isolated stretching frequencies that are believed to be a sensitive measure of C-H bond length (ref. 5). In this technique, a C-H mode is isolated by substituting all but one of the hydrogen atoms in a molecule with deuterium. The comparison gave evidence for consistency to at least a level of  $\pm 0.00005$  Å. Applications of the technique are now so numerous that any extensive review of them is beyond the scope of this paper.

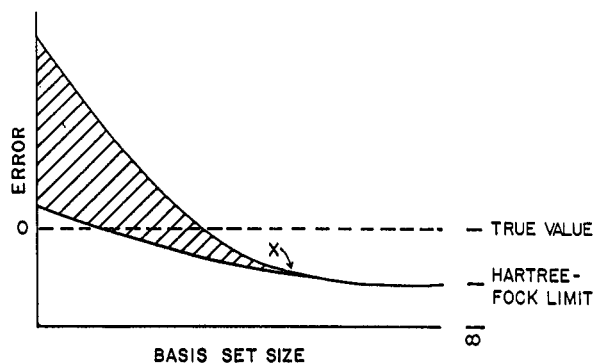


Fig. 1. Schematic representation of the error in calculating some single type of structural parameter in a variety of molecular environments. For wide families of systems, the error is expected to fall within the shaded area.

### Fully *ab initio* evaluation of geometrical parameters

Computation of structure at a modest quantum chemical level coupled with offset value correction essentially solves the problem for a wide range of organic chemistry, but there is an even wider range which cannot be handled by this approach for a variety of reasons. The compounds may be too large for existing computers, they may contain heavy atoms for which non-relativistic calculations with existing basis sets are insufficiently accurate, they may require multiconfiguration wavefunctions, or, most commonly, they may have no close, structurally characterized chemical relatives from which offset values can be obtained. Important examples of the latter difficulty arise with most inorganic molecules and with molecules in reaction transition states or otherwise remote from equilibrium so that the computational error for a given bond type may be expected to be significantly different from that in the equilibrium states where the offset value was determined.

The computer time required for standard Hartree-Fock procedures varies as  $n^4$  with molecular size. The recent rapid improvements in computer speed and, at least as important, in memory size and accessibility have greatly expanded the size of molecules for which computational studies are practical. The present record seems to be a calculation on  $C_{150}H_{30}$  employing 1,560 contracted Gaussian basis functions (ref. 6). Such a calculation would involve the evaluation and repeated use of something on the order of  $7 \times 10^{11}$  two-electron integrals, less those saved by use of the hexagonal symmetry of the molecule. Storage and retrieval of such a quantity of information is impossible on any present computer, so the problem was done by recalculating this vast number of integrals and discarding them each time they were used. On very large computers, computation is now less of a problem than storage.

Efforts to solve the Hartree-Fock equations by other methods are continuing. One very promising new approach is the pseudospectral method being developed by Friesner (ref. 7) from which he expects an increase in speed by three orders of magnitude compared with conventional methods. So far, the procedure has been applied to only one triatomic molecule,  $H_2O$ , but development is continuing.

As shown in Fig. 1, however, accurate bond length determination requires incorporation of electron correlation. As an example, Table 1, taken from ref. 8, shows that computed values for geometrical parameters can be obtained that agree with even exceptionally accurate experimental values, although the computational level required is high. The size limitation on such studies comes from the very steep dependence of high-quality correlation treatments on molecular size, a dependence that varies as  $n^6$ . Improvement in computers alone can not make much of a contribution toward extension of such studies to appreciably larger molecules, since an increase by a factor of 1,000 in computer speed and memory would increase the size

TABLE 1. Bond lengths and force constants of hydrogen cyanide<sup>a</sup>

Parameter <sup>b</sup>	Computed <sup>c</sup>		Experimental <sup>d</sup>
	SCF	SCF + CI	
$r_e$	1.0573	1.0656	1.0655 <sup>e</sup>
$R_e$	1.1236	1.1538	1.1532 <sup>e</sup>
$F_{rr}$	6.520	6.301	6.251 (4)
$F_{RR}$	20.201	19.422	18.703 (12)
$F_{\alpha\alpha}$	0.3410	0.2720	0.2596 (4)
$F_{rR}$	-0.185	-0.197	-0.200 (4)
$F_{rrr}$	-35.8	-35.8	-35.4 (24)
$F_{RRR}$	-127.5	-126.1	-126.0 (52)
$F_{rRR}$	-0.05	0.04	0.41 (240)
$F_{rrR}$	0.38	0.36	0.04 (80)
$F_{ra\alpha}$	-0.175	-0.175	-0.19 (50)
$F_{R\alpha\alpha}$	-0.682	-0.682	-0.65 (40)
$F_{rrrr}$	185.	184.	181.
$F_{RRRR}$	676.	685.	580.

<sup>a</sup>Bond lengths in Å. The F's are force constants, defined as  $F_{ijk...} = (\partial E / \partial q_i \partial q_j \partial q_k \dots)$  with E in mdyne and  $q_i$  in Å or radian.

<sup>b</sup> $r$  is the HC bond;  $R$  is the CN bond. <sup>c</sup>6-311G<sup>4\*</sup> basis plus all singles and doubles CI and Davidson correction. <sup>d</sup>G. Strey and I. M. Mills, *Mol. Phys.* 24, 1265 (1979) <sup>e</sup>A. E. Douglas and E. Sharma, *J. Chem. Phys.* 21, 448 (1953).

of molecules that could be treated by a factor of only 3.2. A promising new approach may be the local correlation method (ref. 9) in which localized internal orbitals are used for expansion of the molecular orbitals and the correlation space for each correlating pair of orbitals is restricted to a subset of the atomic orbitals. The method reduces the  $n^6$  time dependence on molecular size for correlation treatments such as MP4 or all singles and doubles CI. The advantage is clearly greatest for larger molecules since the size of the virtual space is independent of molecular size. Even for butadiene, however, it has been shown (ref. 9) that the local orbital approach recovers over 97% of the correlation energy found by the usual method at a reduction of more than an order of magnitude in computer time. Furthermore, there is good reason to believe (ref. 9) that a significant part of the correlation energy not recovered is attributable to basis set superposition artifacts which are eliminated by this method. In fact, a study of the  $H_2 \cdot He$  complex (ref. 10) was led to use the local correlation method primarily to eliminate superposition error rather than because of any concern with the size of the molecule. A still further advantage of this method is that it permits partitioning of the correlation energy into local contributions which may provide more insight into correlation effects (ref. 11). For example, in studies of conformational changes, such partitioning can make possible a distinction between through-space as opposed to through-bond effects (ref. 11).

Recent applications of the local correlation technique include geometry studies on oxetane and difluoroethylene (ref. 12), both of which are molecules which have had serious discrepancies between experiment and previous theoretical studies. Another study on glyoxal provided a resolution to the disagreement in which a very good experiment found the *s-cis*-conformer to lie  $3.2 \pm .6$  kcal/mol above the more stable *s-trans*-structure while a high level SCF calculation found the energy difference to be in the vicinity of 6 kcal/mol (see references and literature survey given in ref. 11). The discrepancy is considerably greater than experience suggests should be reasonable for such a calculation and it was suggested that the experiment was in error. It turns out, however, that when the calculation is done with simultaneous use of a large basis set and a high-level treatment of electron correlation, the computed energy difference becomes only 4.4 kcal/mol (ref. 11). This is still slightly outside the probable error of the experimental result, but not substantially so. The calculation used a triple zeta basis set augmented by two sets of polarization functions and a MP4 (SDQ) treatment of electron correlation with complete geometry optimization at the same level. It was made practical only by use of the local correlation method.

It is difficult to assess the quality of geometrical parameters obtained at this level of theory for larger molecules because there are exceedingly few molecules of this size for which experimental equilibrium geometries are known with sufficient certainty. Tests on smaller molecules work well. For example, for ethylene bond lengths of 1.334 and 1.083 Å have been calculated at the MP4(SDQ)/6-311G\*\* level (ref. 11) compared with experimental values of 1.334 and 1.081 Å (ref. 13). For ethane, the C-C bond length calculated at this level is 1.531 Å compared with the experimental value of 1.526 Å (ref. 14). Krishnan *et al.* have pointed out that bond lengths between second row elements are typically slightly overestimated at this level of calculation, presumably because of neglect of the triple excitations (ref. 15).

## DETERMINATION OF VIBRATIONAL FORCE FIELDS

The calculation of molecular infrared and Raman spectra has become quite common in recent years, often making use of the built-in features of widely available programs that compute transition frequencies automatically. In our opinion, however, it is more useful to consider the vibrational force fields as the primary computational target, even if only a harmonic oscillator treatment of the vibrational motion is planned. In the first place, the force field is the quantity that carries the molecular information. If the purpose is to contribute to chemical understanding, the spectral frequencies must be considered only as convenient observables from which the molecular information can be deduced. Unfortunately for experimentalists, extraction of even the harmonic force field from experimental information alone is possible only for the smallest molecules without extensive approximation, so this area is an open one in which theory can make a very direct and important contribution.

### Empirical correction of computed force fields: Use of scaling factors

Errors due to neglect of electron correlation and use of a finite basis set are consistent and systematic for force constants, just as they are for geometrical parameters. This, of course, might be expected since both are reflections of the deviation of the computed energy hypersurface from the true surface. Unfortunately, the errors are larger for Hartree-Fock computations at the convenient double zeta level, typically 10-20%, while bond length errors from similar calculations are of the order of 1%. Application of systematic corrections, therefore, cannot lead to the same percentage accuracy in vibrational dynamics as in structural calculations. Still, the chemically useful information content comes from data of lower accuracy than in the case of bond lengths, and supplementation of experiment is much more valuable because of the extremely limited information that can be obtained from experiment alone for any but the smallest molecules.

The most common approach in vibrational studies is to compute the fundamental transition frequencies (band centers) at some modest quantum chemical level and then multiply them all by a single scaling factor, perhaps 0.9. Highly useful results have been obtained by this procedure, but we find it preferable to use a more extensive analysis, based on the computed force field rather than the transition frequencies. This approach is useful because it is observed that force constants for different types of vibrations are consistently computed with different magnitudes of error. As with offset values for geometrical parameters, a small set of scaling factors can be developed, each referring to a certain type of vibration expressed in internal coordinates. These factors are chosen to best reproduce the known vibrational spectrum of one or more reference molecules and are then transferred to correct the computed harmonic force fields of related species (ref. 16). Dozens of test cases have now been run (representative examples are listed as ref. 17) and it is found that spectra can be reproduced with average deviations on the order of  $10\text{ cm}^{-1}$  without using any input data from the molecule in question. As by-products, these studies have clarified a number of uncertain or incorrect assignments in the experimental spectra. The procedure transfers corrections for vibrational anharmonicity to the extent that it is similar in related molecules as well as corrections for computational errors. In some cases, for example a C-H stretching vibration, it is reasonable to suppose that the anharmonicity correction would be quite similar in related molecules. The largest molecules for which such calculations have been reported contain about a dozen second- or third- period atoms and a corresponding number of hydrogens.

It is also a simple matter to obtain approximate infrared absorption intensities from the computed dipole moment derivatives with respect to displacement. Extremely accurate wavefunctions are needed to obtain high accuracy, but even modest-sized basis sets without any correlation treatment can give values that compare with the strong, medium, weak classifications that are commonly reported from experiment. It is a bit less routine to obtain Raman intensities, but these can also be computed.

One recent example that illustrates the usefulness of the information that can be obtained in this manner as well as the accuracy that is achievable has been presented in a related pair of papers on rotational isomerism in acrylic acid (ref. 18). A monomeric form of acrylic acid,  $\text{H}_2\text{C}=\text{CHCOOH}$ , was obtained in Ar, Kr, or  $\text{N}_2$  matrices and an infrared spectrum was observed. After several hours irradiation in the ultraviolet, significant changes in band intensities were noted. The obvious interpretation was to attribute them to *s-cis*- and *s-trans*- conformers with respect to rotation around the C-C linkage, but there was no evidence to indicate which spectrum corresponded to which conformation. Force fields were calculated at the Hartree-Fock 4-21 level, corrected with scaling factors previously obtained from related molecules, and the two spectra were predicted. The spectral changes between the two conformations were small, but an unequivocal assignment of the two forms could be made as shown in Table 2, which lists only the bands for which spectral data were available from the experiment. This example shows the very fine level of discrimination which is possible using transfer of sets of scaling factors when closely related molecules are available for comparison. Regrettably, this is not always the case.

TABLE 2. Frequency differences between *s-trans*- and *s-cis*- acrylic acids,  $\text{H}_2\text{C}=\text{CHCOOH}^a$

Approximate description	Calculated <i>trans</i> - <i>cis</i>	Observed Set 1 - Set 2
C=O deformation	+ 39	+ 30
C-C-O bend	- 45	- 53
C-C stretch	- 4	- 4
CH <sub>2</sub> rock	- 48	- 40
C-O stretch	+ 9	+ 5
CH <sub>2</sub> scissors	0	0
C=C stretch	- 10	- 12
C=O stretch	+ 12	+ 12
C-C torsion	- 4	- 10
C=O wag	+ 1	0
C-O torsion	- 35	- 41
C-H & C-O wag	+ 3	- 7
CH <sub>2</sub> twist	+ 2	0
CH <sub>2</sub> wag	0	- 6

<sup>a</sup>Frequency differences in  $\text{cm}^{-1}$ . Set 1 increased intensity on ultraviolet radiation relative to Set 2.

### Fully *ab initio* evaluation of vibrational potential surfaces

There is little point in going beyond modest basis set Hartree-Fock computations, corrected when possible with sets of scaling factors, unless anharmonicity is considered. Table 1 illustrates the level of accuracy in harmonic and low-order anharmonic force constants which can be obtained using a reasonably high level of computation including a good treatment of electron correlation. Compared with experiment, from which unusually reliable results are available in this example, the largest computational error remains in the diagonal quadratic constants, while the off-diagonal quadratic and the anharmonic constants have better relative accuracy. In fact, we believe that there are very few cases in which anharmonic constants calculated at this level are not more accurate than those obtained from the very difficult and extensive experiments needed to obtain the same information. For much larger molecules or higher-order force and coupling constants, it is difficult to see how similar information could be obtained by any experiment. Consequently, the strictest test of computed anharmonic contributions to the potential surface can not come from direct comparison with values of the corresponding elements deduced from experimental analysis, but rather from comparison of transition frequencies obtained from the computed surface with those observed experimentally, a matter discussed more fully below.

As can be seen from the example in Table 1, absolute computation of potential energy surfaces requires a very high level of calculation, which restricts the procedure to relatively small molecules. Force constants through sixth order have been calculated for molecules the size of  $\text{CH}_3\text{F}$ ,  $\text{C}_3\text{H}_3^+$ , and  $\text{C}_3\text{F}_3^+$  (refs. 19, 20) and the work could be extended without difficulty to somewhat larger systems. Use of the local correlation procedure described above makes the computational job more efficient without loss of accuracy, or possibly with an increase in accuracy if the elimination of superposition errors outweighs the remaining small losses. The difficulty arises not from limitations on the calculations, large as these are, but from the tremendous number of constants resulting from full evaluation of the coefficients in the higher order expansion of the energy, and from lack of ability to do much useful with the results.

If less complete information is sufficient, it is worthy of note that evaluation of the quadratic force field from numerical derivation of the energy gradient, rather than by direct computation of the second derivatives, yields the diagonal and first off-diagonal cubic constants without additional computational cost (ref. 16).

### VIBRATIONAL ANHARMONICITY

While it is relatively straightforward to compute a vibrational potential surface with reasonable accuracy, it is not at all a trivial matter to obtain the energy levels from that surface for polyatomic molecules. Most recent progress has been made using variational methods, which are very close analogs of the common variational SCF and CI techniques for electronic energy levels. Such studies in the past were largely limited to triatomic molecules, but a recent paper published the first full variational CI anharmonic calculation on all nine modes of a pentatomic molecule,  $\text{CH}_3\text{F}$  (ref. 16). Work on hexatomic ions,  $\text{C}_3\text{H}_3^+$  and  $\text{C}_3\text{F}_3^+$ , is essentially completed (ref. 20). These calculations are based on further development of a vibrational direct CI program first described in 1981 (ref. 21).

Since force constant matrices are normally available in curvilinear coordinates while the kinetic energy terms are most easily expressed in rectilinear coordinates, the first step is to convert these two contributions to the Hamiltonian to a common form. We have chosen to convert the potential energy to a rectilinear representation by a somewhat complex least-squares fitting procedure with careful tests to ensure no loss of accuracy over the region of the potential surface of interest (ref. 22). Next the vibrational wavefunction is expanded in a series of harmonic oscillator basis functions and the Schrödinger equation is solved by a correlation interaction method (ref. 22). Use of anharmonic oscillator basis functions was investigated, but they did not seem to be worth the additional complexity.

In studies of HCN (ref. 23) and of  $\text{CH}_3\text{F}$  and  $\text{CHD}_2\text{F}$  (ref. 19), it was thought that the quality of the available *ab initio* potential surface was such that diagonal force constants that could be obtained from it would be less accurate than those that could be obtained from experiment, while all coupling and anharmonic constants were thought to be more reliable from the computation. Consequently, the diagonal quadratic constants were taken as variables to be fitted to the observed fundamental frequencies, all other potential terms coming from the computed surface. For HCN, 69 anharmonic energy levels were calculated for states involving up to four quanta of excitation distributed among the four modes. Where comparison with experiment was possible, agreement was within a maximum error of  $10\text{ cm}^{-1}$  for transitions up to  $10,000\text{ cm}^{-1}$ .

The HCN study, as well as others of a similar type, permits an investigation of the extent to which the local mode concept of overtone bands of the C-H stretching mode is valid. Table 3 lists the contributions greater than 0.1 to the eigenvectors of the C-H stretching fundamental

and overtones. An interesting feature of these states is that the eigenvectors contain significant contributions from basis functions with two quanta in the bend. In  $\text{CD}_3\text{H}$ , such contributions have been attributed to Fermi resonance stemming from the bending fundamental being approximately half of the C-H stretching fundamental (ref. 24). Such is not the case in HCN. The large contributions here stem not from near resonance but from large matrix elements  $\langle 0,0,0, \nu_{\text{CH}} | \mathbf{H} | 0,2,0, \nu_{\text{CH}} - 1 \rangle$ . These large matrix elements are a consequence of the curvature of the potential surface. Stretch-bend interactions of this type should therefore be general rather than being restricted to special cases in which the stretch fundamental is a multiple of the bend fundamental (ref. 22).

TABLE 3. Dominant contributions to C-H overtone states in  $\text{HCN}^a$ 

$$\begin{aligned}
 |00^0_1\rangle &= 0.958|0001\rangle + 0.147|0200\rangle + 0.147|0020\rangle + 0.114|1001\rangle \\
 |00^0_2\rangle &= 0.879|0002\rangle + 0.241|0003\rangle + 0.195|0201\rangle + 0.195|0021\rangle + 0.183|1002\rangle \\
 |00^0_3\rangle &= 0.716|0003\rangle + 0.376|0004\rangle - 0.247|0002\rangle + 0.205|0202\rangle + 0.205|0022\rangle + 0.170|1003\rangle \\
 &\quad + 0.164|0005\rangle + 0.138|0006\rangle - 0.126|1002\rangle + 0.108|0402\rangle + 0.108|0042\rangle \\
 |00^0_4\rangle &= 0.523|0004\rangle + 0.440|0005\rangle - 0.389|0003\rangle + 0.233|0006\rangle + 0.192|0203\rangle + 0.192|0023\rangle \\
 &\quad + 0.191|0007\rangle - 0.191|1003\rangle + 0.121|1004\rangle + 0.121|0008\rangle + 0.119|0204\rangle + 0.119|0024\rangle \\
 &\quad + 0.102|1005\rangle
 \end{aligned}$$

<sup>a</sup> $|\nu_{\text{CN}}\nu_{\text{bend}}^m\nu_{\text{CH}}\rangle$  represents an eigenvector with vibrational angular quantum number  $m$ .  
 $|\nu_{\text{CN}}\nu_{\text{bend}}i\nu_{\text{bend}}2\nu_{\text{CH}}\rangle$  represents a harmonic oscillator product function.

The cyclopropenyl cation,  $\text{C}_3\text{H}_3^+$ , along with its deuterated forms and the fluorinated analog,  $\text{C}_3\text{F}_3^+$ , have been studied in a similar manner (ref. 20) except that the treatment has been completely theoretical with no fitting to any sort of experimental data. At the present time, only powder or solution data are available, so the observed frequencies may be somewhat perturbed by interaction with solvent molecules and with the counterion. Varying the latter had little effect, however, so the error may be small. As an illustration of the results, Table 4 shows the fundamental bands of  $\text{C}_3\text{H}_3^+$  as calculated using the harmonic oscillator approximation, as computed from the full anharmonic treatment, and as observed in the Raman spectrum (ref. 20). We are very pleased with the result, considering that this is an absolute calculation with no use of experimental data and also that the experimental values are from solution rather than from gas-phase experiments. It is interesting to note the magnitude of the contributions of anharmonicity, ranging up to  $129\text{ cm}^{-1}$  for the C-H stretching fundamental band.

TABLE 4. Fundamental vibrational frequencies of  $\text{C}_3\text{H}_3^+$ 

Description	Theoretical calculation		Experimental Raman <sup>a</sup>
	Harmonic	Anharmonic	
C-H stretch	3331	3202	3183
C-C stretch	1665	1624	1626
C-H bend	1074	1016	
C-H stretch	3281	3156	3138
C-C stretch	1335	1299	1290
C-H bend	961	917	927
C-H wag	772	758	
C-H wag	1016	1002	

<sup>a</sup>Ref. 25.

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