Ab Initio Calculations of Vibrational Spectra and Their Use in the Identification of Unusual Molecules

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I. Introduction

The synthesis of new compounds and the determination of their structures is one of the main goals in chemistry. In recent decades various kinds of spectroscopy have played a major role in structural determination. Apart from the direct determination of structure by means of X-ray analysis, the most useful among these spectroscopies are electronic (ultraviolet and visible), vibrational (infrared and Raman), nuclear magnetic resonance, and mass spectrometry.

A full use of experimental spectroscopy for the purpose of structure determination requires the availability of a theoretical tool that can provide computed spectral data in a completely independent way and with an accuracy sufficient for a meaningful comparison with the experimental data. An ideal procedure is the following. First record the spectrum of a compound of unknown structure. Assign to it one or more plausible structures, and compute theoretical spectra for all these structures. Compare experimental and theoretical spectra, and accept or reject the assumed structure on the basis of agreement or disagreement between the two.

Historically, quantum chemistry had an impact first in the field of electronic spectroscopy. In the late fifties and early sixties the quantum chemistry of all but the simplest systems was dominated by semiempirical techniques such as the Pariser–Parr–Pople (PPP) method.[1] Calculations of this type were applied mostly in the field of electronic spectroscopy to interpret the electronic spectra of conjugated π-electron systems. An example,[2] the main goal of which was structure determination, concerns the benzenoid hydrocarbon zethrene (I). A hydrocarbon to which the structure of zethrene was originally assigned was actually either a derivative of acepleiadene (II) or the hydrocarbon (III). Com-
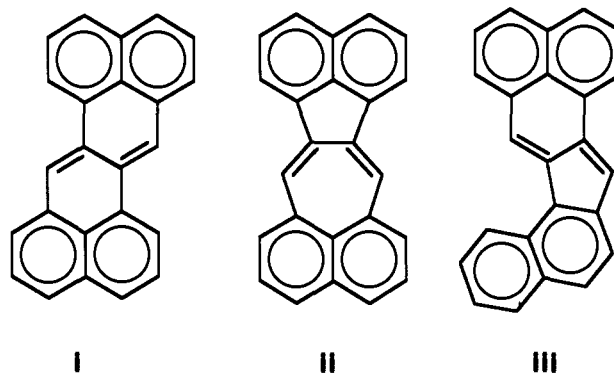
I   II   III

parison of theoretical spectral data for I–III with two available absorption curves showed that the assumed zethrene was actually III and that a newly synthesized hydrocarbon was really zethrene.

Since the 1960s the development of larger and faster computers together with elaborate ab initio programs has allowed the routine computation of theoretical vibrational spectra for molecules of up to, at present, about ten first-row atoms. During the same period the availability of low-temperature matrix isolation has made it possible to isolate highly reactive molecules and to obtain their spectra. This technique coupled with the advent of Fourier-transform IR spectroscopy has provided a powerful new tool to the experimentalist.

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Petr Čársky was born in 1942 in Slovakia and he received his RNDr from Charles University in Prague in 1964. He then joined Dr. Zahradník's group at the Czechoslovak Academy of Sciences and received his C.Sc. (equivalent to Ph.D.) in 1968. He was a postdoctoral fellow at the University of Würzburg (1968) and visiting professor at Vanderbilt University in Nashville (1982) and Pasteur University in Strasbourg (1984). His research interests center on chemical applications of molecular orbital theory and computational chemistry.

Rudolf Zahradník was born 1928 and graduated from the Prague Institute of Technology (1952). In 1956 he received his C.Sc. degree (approximately equivalent to Ph.D.), and in 1968, the D.Sc. degree; he then became Associate Professor of Charles University. At present he is the Head of the Group of Theory of the Chemical Reactivity in J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague. From 1965 to 1984 he spent several periods as visiting professor at universities in Würzburg, Darmstadt, Groningen, Giessen, Basle, Sendai, Osaka, Erlangen, and Leipzig. In 1970 he received a NSF (Washington) senior fellowship. In 1981 he was elected in the International Academy of Quantum Molecular Sciences. He acts as a member of editorial boards of *Journal of Molecular Structure* (*THEOCHEM*), *Reactivity and Structure* (Springer), and *Chemical Reviews*, and is a member of the advisory board of *Theoretica Chemica Acta*. Dr. Zahradník has authored or coauthored about 300 papers, a number of textbooks, and 7 books. These works deal mainly with molecular orbital theory, theory of chemical reactivity, and weak intermolecular interactions in chemistry and biology.

For example the highly reactive thiirene was prepared by the following scheme.[3]
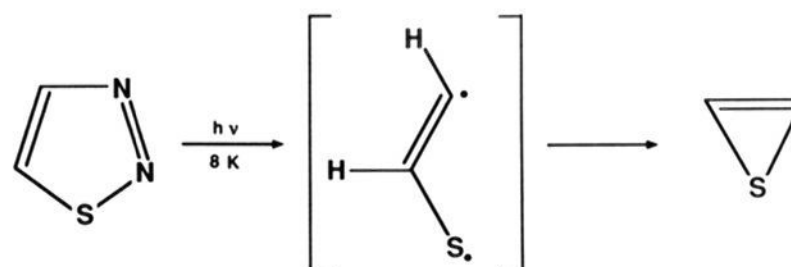
Also present in the product mixture were ethynyl mercaptan and thioketene. IR spectroscopy was the tool by which the presence of thiirene was identified. A spectrum of a reaction mixture obtained by the decomposition of thiadiazol is shown in Figure 1. It is to be expected that the spectra so obtained are of low resolution and that the assignment is uncertain because of side product formation.

The aim of this review is to show the utility of theoretical vibrational spectra in such experiments. It turns out that the accuracy of these spectra is sufficient to give correct overall patterns, but fine details are not yet to be trusted. The next sections outline the theoretical background of vibrational calculations. A practical chemist, whose interest is seeing whether theoretical vibrational spectra can be of use to him, might profitably skip these sections at first reading and turn to the examples of sections IV and V. Such readers should however keep in mind the distinction between two ways of calculating vibrational spectra. In both a force constant matrix is diagonalized to give molecular vibrational frequencies. In the ab initio method of this review, these force constants are derived by as rigorous as possible a solution of the electronic Schrödinger equation of the molecule in the fixed-nucleus approximation. In the other method, which is older and more
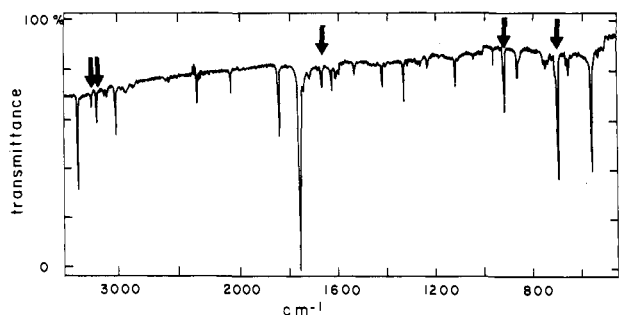
Figure 1. Infrared spectrum of the photolyzed thiadiazole.[3] The arrows mark bands assigned to thiirene.
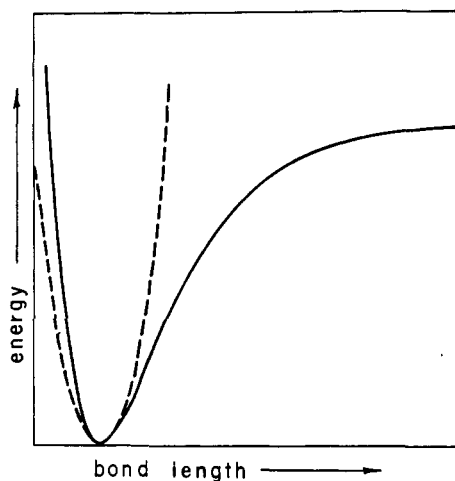

Figure 2. Schematic representation of a potential curve from the fixed nucleus calculation (solid line) and its harmonic approximation (dashed line).

usual among experimental spectroscopists, the force constants are simply guessed. This older method can be useful if the molecule studied is similar enough to others with known force constants, but since there are usually more force constants than vibration frequencies, there are many ways to choose force constants to produce exact agreement with experimental frequencies. It is common to find in the literature a molecule studied by two groups who have produced different, but equally accurate and equally plausible, sets of force constants. One application of ab initio vibrational calculations is in the choice between these sets of experimental force constants. However it is in the case of unusual molecules, such as reactive intermediates, where analogies are poor and guessed force constants particularly doubtful, that we suggest ab initio calculations will be of greatest use.

There are several review articles in the literature with titles similar to ours though their scope is different. As stated by Schutte[4] the purpose of his paper is "to examine the progress which has been made since 1926 in the ab initio calculation of both the vibrational frequencies of molecules as well as the forces acting upon individual atoms when the equilibrium of the molecule has been disturbed". Molecular orbital calculations are dealt with only very briefly, and the paper concerns mostly diatomic molecules. A review by Fredkin, Komornicki, White, and Wilson[5] focuses on treatment of

systems such as liquids, clusters, or floppy molecules, for which normal mode analysis is inappropriate. The subject of the review by Schrader, Bougeard, and Niggemann[6] is most closely related to our paper. It also deals with structure determination by infrared and Raman spectra. Their review is however more general, and the results of only a few ab initio calculations are presented as illustrative examples. Recent reviews by Fogarasi and Pulay[7] summarize the progress made in the last several years in ab initio methods and computational techniques (analytical computation of second and higher derivatives of energy, basis set and correlations effects), and are recommended as an extension of our sections IIC and IIIA.

II. Theoretical Approaches to Vibrational Spectra

A. Harmonic Approximation

Consider the Schrödinger equation for a polyatomic molecule with M nuclei and N electrons

$$\left[\sum_{\alpha=1}^{M} \frac{-\hbar^2}{2m_\alpha} \nabla_\alpha^2 + \sum_{i=1}^{N} \frac{-\hbar^2}{2m_\epsilon} \nabla_i^2 - \sum_{i=1}^{N} \sum_{\alpha=1}^{M} \frac{Z_\alpha \epsilon^2}{r_{i\alpha}} + \sum_{\beta>\alpha}^{M} \sum_{\alpha=1}^{M} \frac{Z_\alpha Z_\beta \epsilon^2}{r_{\alpha\beta}} + \sum_{j>i}^{N} \sum_{i=1}^{N} \frac{\epsilon^2}{r_{ij}} \right] \Psi = E\Psi \quad (1)$$

where m_α and Z_α are the mass and charge (in units of electron charge) of nucleus α, m_ϵ and ϵ are the electronic mass and charge, $r_{i\alpha}$ is the distance between electron i and nucleus α, and r_{ij} and $r_{\alpha\beta}$ are defined analogously. The terms on the left of eq 1 give, in order, the kinetic energy of the nuclei, that of the electrons, the electron–nuclear attraction, the nuclear–nuclear repulsion, and the electron–electron repulsion. The wavefunction Ψ depends upon the $3(M + N)$ coordinates of the electrons and nuclei. Since the nuclei are heavier and move more slowly than the electrons, it is usual to neglect the nuclear kinetic energy term in eq 1 by holding the nuclei stationary. The resulting equation describes the motion of the N electrons in the field of the fixed nuclei, and the energy E of these electrons will depend upon the chosen relative nuclear positions. In the case of a diatomic molecule there is only a single relative position, the bond length R_{12}; and the plot of $E(R_{12})$ vs. R_{12} will be as shown by the solid line in Figure 2. For a polyatomic molecule the electronic energy in this fixed-nuclear approximation will depend on all nuclear positions so that $E = E(R_1...R_M)$, though E is constant for those combinations of nuclear displacements that give translation or rotation of the molecule as a whole.

Born and Oppenheimer[8] showed that if the nuclear kinetic energy is treated as a perturbation on the fixed-nuclear Hamiltonian, the first-order energy correction vanishes at all positions of nuclear equilibrium (i.e., for stable molecules). The second-order energy correction is given by an equation describing the nuclear motion

$$\left[\sum_{\alpha=1}^{M} \frac{-\hbar^2}{2m_\alpha} \nabla_\alpha^2 + V(R_1...R_M) \right] \Psi_{\text{nuc}} = E_{\text{nuc}} \Psi_{\text{nuc}} \quad (2)$$

where the first term in eq 2 is the kinetic energy operator for the nuclei and E_{nuc} is the second-order energy correction and gives the energy of the nuclear motion. The potential $V(R_1...R_M)$ consists of the quadratic terms in a power series expansion of $E(R_1...R_M)$ about the equilibrium position,

$$E = E(X_1^0...X_{3M}^0) + \sum_{i=1}^{3M} \frac{\partial E}{\partial X_i}\bigg|_0 \Delta X_i + \frac{1}{2} \sum_{i,j=1}^{3M} \frac{\partial^2 E}{\partial X_i \partial X_j}\bigg|_0 \Delta X_i \Delta X_j + ... \quad (3)$$

where X_1, $X_2...X_{3M}$ are the Cartesian coordinates of the M nuclei. The first term $E(X_1^0...X_{3M}^0)$ adds only a constant to all allowed E_{nuc} and can be ignored for the purposes of most vibrational calculations. Since E is a minimum at the equilibrium geometry, all

$$\frac{\partial E}{\partial X_i}\bigg|_0 = 0$$

and the second term in eq 3 vanishes. If all terms of order higher than second are neglected, the potential is a quadratic function of the nuclear displacements ΔX_i

$$E(X_1...X_{3M}) \approx \frac{1}{2} \sum_{i,j=1}^{3M} F_{ij} \Delta X_i \Delta X_j \equiv V(R_1...R_M) \quad (4)$$

where the force constants F_{ij} are given by

$$F_{ij} = \frac{\partial^2 E}{\partial X_i \partial X_j}\bigg|_0 \quad (5)$$

Equation 4 is known as the harmonic approximation. In the diatomic case this corresponds to replacing the solid curve of Figure 2 by the parabola shown by the dashed line. As can be seen, this approximation may be satisfactory for small displacements from the equilibrium position R_{12}^0, but it cannot be accurate for large distortions of the molecule.

A transformation to mass-weighted coordinates, $\rho_i = (m_i)^{1/2}\Delta X_i$, followed by rotation of the coordinates to coincide with the principal axes of the quadratic form in eq 4, gives an expression for V containing only squared terms

$$V = \frac{1}{2} \sum_{i=1}^{3M} \lambda_i Q_i^2 \quad (6)$$

where the Q_i are coordinates relative to the principal axes and are called "normal coordinates". As a result of these transformations eq 2, which depends on $3M$ variables, separates into $3M$ equations, each depending upon a single Q_i. Further, each of these is a harmonic oscillator equation with force constant λ_i.

For a nonlinear polyatomic molecule there turn out to be six of the λ_i with value zero. These correspond to the three translational motions and three rotations of the entire molecule. The six zero-frequency motions can be removed by working in a coordinate system with the origin at the center of mass and rotating with the molecule. The remaining 3M − 6 degrees of freedom are usually specified by internal coordinates such as bond lengths and bond angles. As a result, fewer force constants need be evaluated, and those that are evaluated have chemical interpretation. Minor difficulties arise because the transformation to these coordinates is not linear except in the limit of infinitesimal displacements, and because in particular cases there may

TABLE I. Harmonic and Anharmonic Vibrational Frequencies (cm⁻¹) of the HCOOH Molecule Given by ab Initio SCF 4-31G Calculations[a]

mode	obsd frequency, cm⁻¹	calcd frequency (cm⁻¹)	
		harmonic	anharmonic
OH	3570	3769	3629
CH	2944	3160	3047
C=O	1776	1909	1882
CO	1105	1150	1140
∠HCO	1387	1510	1490
∠OCO	625	659	653
∠COH	1223	1366	1347

[a] Reference 13.

be no nonredundant set of simple internal coordinates. All of this is taken care of in the commonly used GF matrix formulation of the vibrational problem by Wilson.[9]

B. Perturbation Treatment of Anharmonicity

Most of the vibrational calculations discussed in sections IV–VI and listed in Tables IV and V have used the harmonic approximation of eq 4, but in recent years there has been progress in the ab initio calculation of cubic and quartic force constants. These are the third and fourth order terms that were dropped from eq 3, and their availability allows the possibility of including anharmonicity in ab initio treatments of the vibrational problem. Prior to 1980 this was rarely done, but one may anticipate it being done more commonly in the near future. Perturbation theory yields the following formula for the anharmonicity:[10]

$$\chi_{rr} = \frac{1}{16} \phi_{rrrr} - \frac{1}{16} \sum_s \phi_{rrs}^2 [(8 \omega_r^2 - 3 \omega_s^2)/\omega_s(4 \omega_r^2 - \omega_s^2)] \quad (7)$$

Equation 7 contains the quadratic, diagonal and semidiagonal cubic, and diagonal quartic force constants. The ω_k are the harmonic frequencies. The quartic constant ϕ_{rrrr} may be estimated easily[11] (for stretching vibrations) or it may be calculated numerically. Equation 7 does not yield anharmonicities of high accuracy, but it represents the only method suitable for practical application to polyatomic molecules of arbitrary structure. Equation 7 is relatively simple. The only complication met in the calculation of χ_{rr} is that the force constants ϕ_{rrr} and ϕ_{rrs} are derivatives of energy with respect to normal coordinates. They are not therefore force constants obtained by the differentiation of energy with respect to internal coordinates (F_{rrr} and F_{rrs} in the notation of the next sections). The conversion $F \rightarrow \phi$ may be performed by a rather complicated nonlinear transformation.[12] Alternatively, ϕ_{rrs} may be obtained from the changes of the energy gradient along normal coordinates. This way of obtaining ϕ_{rrs} is conceptually simple, but computationally it is not economic.

We have selected two examples of the ab initio calculation of anharmonicity by means of eq 7. The first[13] is for the formic acid molecule. The level of the ab initio calculations was modest, so only a rather approximate potential was obtained. From the results presented in Table I it is seen that the inclusion of anharmonicity by means of eq 7 leads to better agreement between theory and experiment, though the error in the com-

TABLE II. Vibrational Wavenumbers (cm^{-1}) of the Water Molecule Given by ab Initio Calculations

v_1	v_2	v_3	$expt^a$	CI-SDQ,[b] eq 7	CEPA[c] var calcn	MRCI-SD,[d] var calcn
0	1	0	1595	1649 (1670)	1625	1623
0	2	0	3152	3261	3211	
1	0	0	3657	3619 (3869)	3714	3667
0	0	1	3756	3753 (3980)	3814	3752
0	3	0	4667	4835	4759	
1	1	0	5235	5253	5320	
0	1	1	5331	5448	5426	

^{a} For references to experimental data see quoted theoretical papers. ^{b} Potential obtained by CI-SDQ calculations,[14] anharmonicities from eq 7, harmonic frequencies in parenthesis. ^{c} Taken from ref 15; potential obtained by CEPA calculation,[16] vibrational frequencies by a variation method; the frequencies were read from a figure in ref 15, so the fourth digits in the entires may be uncertain. ^{d} Taken from ref 17; potential obtained by MRCI-SD calculations,[17] vibrational frequencies by a variational method.

puted frequencies is still considerable owing to the approximate potential. The second example concerns the water molecule. Table II shows the results of three ab initio studies of this molecule, all using very large basis sets. They differ in the post-Hartree–Fock part of the calculation and in the method used for the calculation of the anharmonic frequencies. Hennig, Kraemer, Diercksen, and Strey[14] carried out a configuration interaction calculation with singly and doubly excited configurations and used Davidson's formula for estimating the contribution of quadruple excitations. The resulting potential was used with eq 7 for the anharmonicity. The computational effort was much greater than in the example of Table I, but the error is still rather large. One might suppose this error to be due to the approximate nature of eq 7. However, Botschwina[15] has performed calculations with a potential[16] of comparable quality and used the more sophisticated method of vibrational configuration interaction for the evaluation of the frequencies. He did not obtain better agreement with experiment. Recent ab initio calculations[17,18] on the water molecule show that it is necessary to go beyond the CI-SD(Q) level of ref 14 if frequencies of high accuracy are to be obtained. Sexton and Handy[17] applied the vibrational variation method to the potential from their multireference configuration interaction calculation with single and double excitations (MRCI-SD). Their calculated fundamental frequencies are in error by only 28 cm^{-1} for the bend and 10 cm^{-1} and 4 cm^{-1} for the two stretches. They also improved the analytic representation of the MRCI-SD surface of Kraemer, Roos, and Siegbahn[18] and arrived at fundamental frequencies that are in error by only 22, -3, and 1 cm^{-1}.

Most of the molecules to be discussed in this review are larger than water, and computations of the accuracy just described are not yet possible for them. Frequency errors of 5–10% will be usual. In spite of these large errors the overall pattern (i.e., relative frequencies and relative intensities) of the computed spectra usually resemble those of the observed spectra sufficiently to be of help to the experimentalist.

C. Classification of ab Initio Calculations

Accumulated experience suggests that the accuracy of calculated vibrational frequencies is affected more by the quality of the calculated potential than by the inclusion of anharmonicity. For this reason we consider it useful to classify ab initio calculations[19–24] as follows: (1) SCF calculations with a small basis set, (2) SCF
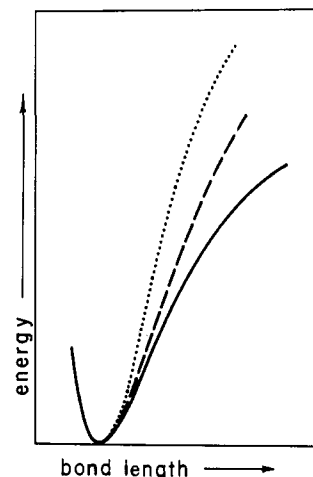
Figure 3. Schematic representation of potential curves given by ab initio calculations for a diatomic molecule at three levels of sophistication: SCF, small basis set (dotted line); SCF, large basis set (dashed line); large basis set with electron correlation (solid line).

calculations with medium and large basis sets, (3) medium and (preferably) large basis set calculations with the inclusion of electron correlation. This rough classification of ab initio calculations, which refers only to the calculated potential, permits us to formulate a general dependence of the accuracy of computed vibrational frequencies on the type of ab initio calculation.

SCF calculations are known to give a good account of the energy hypersurface only in the region close to the equilibrium molecular geometry. At larger deviations from the minimum, the SCF potential curve starts to depart considerably from the "experimental" curve because of the neglect of electron correlation. The simplest case—the case of a diatomic molecule—is schematically presented in Figure 3 for the three levels of calculation above. As this figure shows, the SCF curve is too steep. This implies the force constant at the SCF level will be too high and also the computed vibrational frequency will be too high. The smaller the basis set, the more profound is this effect. Electron correlation will lower the curve toward the exact solid curve of Figure 3. However even the exact curve, if replaced by the harmonic approximation of Figure 2, will give too high frequencies since the approximating parabola rises too steeply at large distances. These arguments concern the potential curves for stretching vibrations, but it has been found empirically that the

Figure 4. The infrared spectrum of cyclobutadiene compared with results of ab initio calculations[25] at three levels of sophistication. Intensities were not computed in the MP2 work.

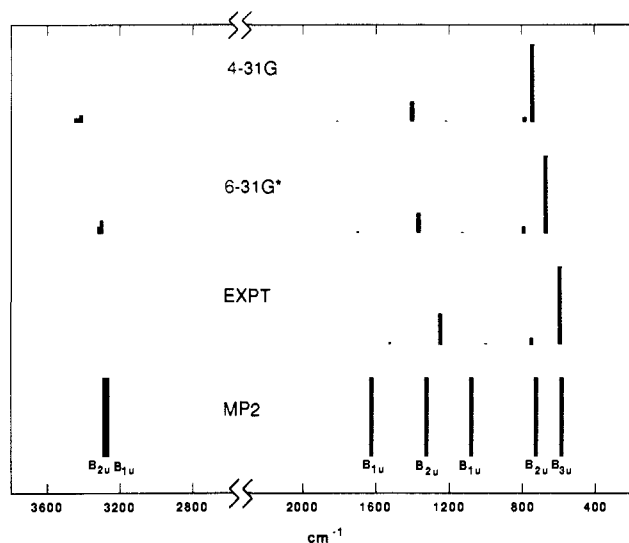same trends hold for bending modes. Figure 4 shows the example of cyclobutadiene,[25] where the three calculations described as 4-31G, 6-31G*, and MP2/6-31G* correspond to the three levels of classification above. If one ignores the two C–H stretches at high frequency which, because of the complexity of the matrix isolation spectrum in the C–H region, have not yet been identified experimentally, all calculated frequencies are too high in the 4-31G calculation. When the basis is improved to 6-31G* all frequencies, except the second lowest, decrease, but are still too high. Inclusion of electron correlation in MP2/6-31G* lowers the frequencies still further.

III. Computation of IR Spectra

This section gives practical details for the ab initio calculation of theoretical infrared spectra. Section IIIA discusses the effective computation of quadratic and cubic force constants. Section IIIB describes the calculation of intensities. The example of the water molecule, noted in section IIB and summarized in Table II, indicates that even the most sophisticated ab initio calculations are not able to compete in accuracy with high-resolution experiments. In practical applications one might wish therefore to adopt a strategy in which one does not insist so strictly on the nonempirical nature of calculations. This will be discussed in section IIIC.

A. Force Constants and Frequencies

Modern programs for ab initio SCF calculations contain packages for the analytical calculation of the energy gradient or, in some programs, for the analytic calculation of the quadratic force constants. If quadratic force constants (eq 5) are not computed analytically by the program, they may be obtained from the energy gradient using the expression[11,26]

$$F_{ij} \approx [f_j(q_i = -\Delta_i) - f_j(q_i = +\Delta_i)]/2\Delta_i$$

$$F_{ij} \approx [f_i(q_j = -\Delta_j) - f_i(q_j = +\Delta_j)]/2\Delta_j \qquad (8)$$

where f_k is a force (the negative of a component of the gradient) acting along the kth coordinate and Δ_k is the deviation from the reference geometry along the kth coordinate. In eq 8 the first differentiation of eq 5 is performed analytically and the second one numerically. Cubic diagonal and semidiagonal force constants

$$F_{iij} = \frac{\partial^3 V}{\partial q_i^2 \partial q_j} = \frac{\partial}{\partial q_j} F_{ii} = -\frac{\partial^2 f_j}{\partial q_i^2} \qquad (9)$$

may be obtained by a single numerical differentiation of analytic quadratic force constants analogous to eq 8 or by a double numerical differentiation of the components of the force[11,26]

$$F_{iij} \approx [2f_j(\text{ref}) - f_j(q_i = +\Delta_i) - f_j(q_i - \Delta_i)]/2\Delta_i^2 \qquad (10)$$

where the first term on the right hand side is the force at the reference geometry. Much of the initial development of this computational method was done by P. Pulay[26] who is the author of the program TEXAS[27] designed especially for this purpose. One may find all information necessary for the effective computation in papers by Pulay (particularly in ref 11 and 26). We restrict ourselves here to noting that the force constants in eq 8 and 10 should be expressed in symmetrized internal coordinates and not in Cartesian coordinates. This reduces the cost considerably. The most efficient use of symmetry coordinates was described by Hehre and co-workers[28] recently, though the method was used a decade earlier by Pulay.[29] Cartesian coordinates are used for example in standard runs in the HONDO5 program. This is convenient from the point of view of preparation of the input data, but the cost is excessive even with relatively small basis sets.

A calculation of the theoretical spectrum of a polyatomic molecule as outlined above requires a rather large amount of computer time and human effort. The analytical calculation of force constants might be expected to lessen this work. The first practical method for the analytical calculation of force constants was developed by Pople and co-workers,[30,31] and now expressions are available for the third[32] and higher derivatives within SCF theory. In spite of this progress, practical application of these higher derivatives is limited by the requirement of enormous amounts of disc space. The situation seems to be similar with correlated wave functions. Pople, Krishnan, Schlegel, and Binkley's second-order Møller-Plesset treatment[30] contained the first practical scheme for the analytical computation of the energy gradient for a correlated wave function. Expressions have been given since[33-36] for up to fourth-order derivatives of energy within the CI[37] and MCSCF[38] framework. Efficient algorithms are however still lacking, so if one wishes to go beyond the Hartree–Fock level, a force field of the form

$$V = V_0 + \sum_{i,j} \frac{1}{2} F_{ij} q_i q_j + \sum_{i,j,k} \frac{1}{6} F_{ijk} q_i q_j q_k + \dots \qquad (11)$$

has to be assumed, and a set of energies fitted to it numerically (by least-squares). In common applications the expansion (11) is truncated at the quadratic term (harmonic approximation).

B. Intensities

Integrated infrared band intensity for the kth fundamental is defined[9] as

$$A_k = \frac{1}{CL} \int \log \frac{I_0}{I} d\nu \tag{12}$$

where C is concentration (mol L^{-1}), L is optical path length (cm), and I_0 and I, respectively, are the intensities of the incident and transmitted light. Assuming electric and mechanical harmonicity, A_k may be approximated[39] by

$$A_k = \frac{\pi N_A g_k}{3000 \, c^2 \times 2.302581} |\partial\mu/\partial Q_k|^2 \tag{13}$$

where N_A is Avogadro's number (mol^{-1}), c is the light velocity (cm s^{-1}), g_k is the degeneracy factor, and $\partial\mu/\partial Q_k$ is the dipole-moment derivative with respect to the kth normal coordinate Q_k. The derivative $\partial\mu/\partial Q_k$ must be expressed in cm$^{3/2}$ s^{-1}, so that A_k be expressed in cm^{-2} L mol^{-1}, as in eq 12. Programs for ab initio calculations yield however the derivatives $\partial\mu/\partial Q_k$ in non-SI units D Å^{-1} U$^{-1/2}$, where U is the unified atomic mass unit $M(^{12}C)/12 = 1.660565 \times 10^{-27}$ kg. Transformation to cm$^{3/2}$ s^{-1} is performed by multiplying[39] the derivatives by 0.7760184×10^2. In actual calculations one first evaluates numerically the derivatives of the dipole moment with respect to symmetry internal coordinates

$$\partial\mu/\partial q_i \approx [\mu(q_i = +\Delta_i) - \mu(q_i = -\Delta_i)]/2\Delta_i \tag{14}$$

Transformation from $\partial\mu/\partial q_i$ to $\partial\mu/\partial Q_k$ is performed by means of the expression

$$\frac{\partial\mu}{\partial Q_k} = \sum_i \frac{\partial q_i}{\partial Q_k} \frac{\partial\mu}{\partial q_i} \equiv \sum_i L_{ik} \frac{\partial\mu}{\partial q_i} \tag{15}$$

where L is the matrix for the transformation of normal coordinates to symmetry coordinates and is obtained from the GF matrix method. For isotopic derivatives of molecules having a nonzero dipole moment, a rotational correction of the dipole moment derivatives must be taken into account.[11]

Komornicki and McIver[40] have shown how the computation of infrared intensities can be carried out in an efficient way that makes use of the energy gradient. The j component of the dipole moment vector of a system of fixed charges is given by

$$\mu_j = \frac{\partial E}{\partial F_j} \tag{16}$$

where E is the energy of the system in a constant electric field F, sufficiently weak that polarization, i.e., rearrangement of the charges in response to the field, can be neglected. Then taking the derivative of eq 16 with respect to the coordinate q_i, and interchanging order of differentiation on the right gives

$$\frac{\partial\mu_j}{\partial q_i} = \frac{\partial}{\partial q_i}\left(\frac{\partial E}{\partial F_j}\right) = \frac{\partial}{\partial F_j}\left(\frac{\partial E}{\partial q_i}\right) \tag{17}$$

The quantities $\partial\mu_j/\partial q_i$ on the left of eq 17 are those needed in eq 15 for the computation of infrared intensities. The quantities $(\partial E/\partial q_i)$ are the components of the energy gradient. These are already available in most programs for the computation of the SCF mo-
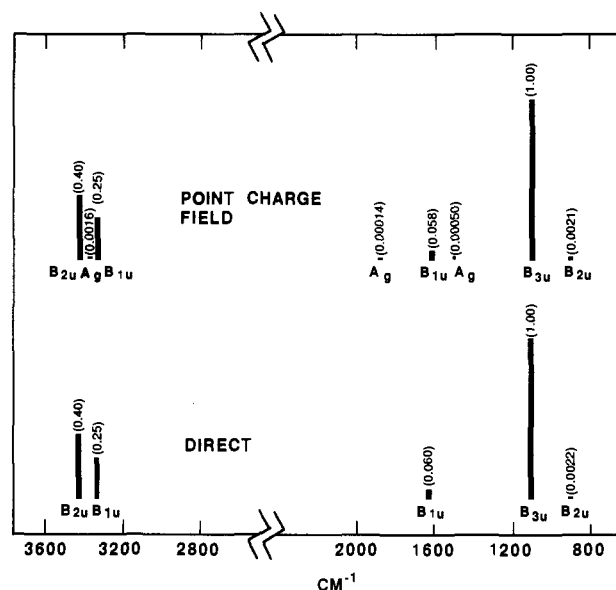
Figure 5. Theoretical infrared spectra of ethylene computed using an 6-31G* basis. Direct calculation of the intensity by eq 13–15 is shown at the bottom. The top shows intensities using eq 17 and an approximately constant field caused by point charges. The A_g intensities are exaggerated.

lecular energy since they are used in the geometry optimization. Therefore instead of (3N-6) computations of the dipole moment to get the $(\partial\mu_j/\partial q_i)$, one need do only three computations of the energy gradient in a constant electric field to compute all $\partial^2 E/\partial F_x \partial q_i$, $\partial^2 E/\partial F_y \partial q_i$ and $\partial^2 E/\partial F_z \partial q_i$.

Bacskay, Saebø, and Taylor[41] describe a program for computing the energy of a molecule in a constant field and for implementing the Komornicki and McIver suggestion. Actually this program revision need not be done in many cases.[42] Many molecular energy programs such as GAUSSIAN 82[43] will allow the use of nuclei of either positive or negative charge, with or without associated orbitals. A constant electric field at a molecule can be approximated by placing two large bare charges of equal magnitude and opposite signs at equally large distances but in opposite directions from the molecule. GAUSSIAN 82 requires no reprogramming to treat this system which it views as an ordinary molecule with no external field. Figure 5 shows the results of such an approximate intensity calculation on ethylene. This method should have no advantage in speed or accuracy over Bacskay's program. It merely avoids reprogramming of the molecular energy calculation.

For correlated wave functions the dipole moment derivatives are usually calculated numerically for eq 14 in which the dipole moments for the two structures at $q_i = +\Delta_i$ and $q_i = -\Delta_i$ are obtained by a finite-field method. Essentially this means the use of eq 16 since the energy of a molecule in an external field is assumed in the form of a power series

$$E(F) = E(0) - \sum_j \mu_j F_j - \frac{1}{2} \sum_{jk} \alpha_{jk} F_j F_k + \dots \tag{18}$$

and μ_j is again obtained numerically[44,45] from $E(F_j)$ and $E(-F_j)$. In the evaluation of $E(F)$ one first carries out the so called coupled Hartree–Fock calculation to get field-dependent SCF molecular orbitals, which are then used[44-47] as input for the calculation of $E(F_j)$ by

standard (field independent) expressions for the correlation energy.

In spite of the fact that intensities are very important for the interpretation of IR spectra and that their calculation at the SCF level requires practically no extra computer time, they have not been commonly computed. Raman intensities are computed still less frequently. These may be computed[48,49] by a direct calculation of polarizabilities from elements of the electronic transition moment. This approach gives however rather poor results, unless a large basis set is used. As for any electric property it is therefore preferable to use special basis sets designed for this purpose.[50,51] In calculations beyond the Hartree–Fock level the derivatives of polarizabilities are obtained as shown above for dipole moment derivatives: polarizabilities by a finite-field method[44,45] and their derivatives by numerical differentiation. Komornicki and McIver's method used with a point charge field should also have application in the calculation of Raman intensities, though problems with numerical accuracy are expected to be more severe here than for infrared intensities.

C. Use of Empirical Parameters

The computation of the vibrational spectrum of a polyatomic molecule of even modest size is lengthy, and one may be forced to work at the SCF level with a small basis set. In such a case, one must count on a large overestimation of calculated vibrational frequencies. Several simple (more or less) empirical ways have been suggested to reduce this error. The first is a proposal by Schwendeman[52] to compute force constants at experimental geometry rather than at the minimum energy geometry of the basis set used. This need not necessarily[26,53] lead to improved values of the force constants, though experience shows that it often does.[54-57] Schwendeman's proposal also shortens the computations since the geometry optimization step is dropped.

Pulay and collaborators as well as Blom and Altona have suggested that even experimental geometries can sometimes lead to difficulties due to errors in these geometries. Blom and Altona have therefore proposed corrections to be applied to various bond distances and angles obtained theoretically with Pople's 4-31G basis set.[58-60] Pulay and collaborators have done the same for Pulay's 4-21G basis set.[11] Corrections for additional bonds have also been proposed.[61]

It has also been found that basis set and electron correlation effects are more important for diagonal force constants than they are for most coupling force constants.[57] A force field given by SCF calculations may therefore be improved considerably if the diagonal of the force constant matrix is replaced by data originating from some other source. There are several possibilities, and the choice depends on the user's taste. One may use experimental data obtained in some independent way for diagonal force constants, or the computed diagonal force constants may be reduced by empirical scaling factors (typical values range from 0.8 to 0.9). To some extent scaling factors also account empirically for anharmonicity. In the simplest instance Pulay and Meyer[62,63] suggested a single scaling of 0.9 for all diagonal stretching force constants and 0.8 for diagonal
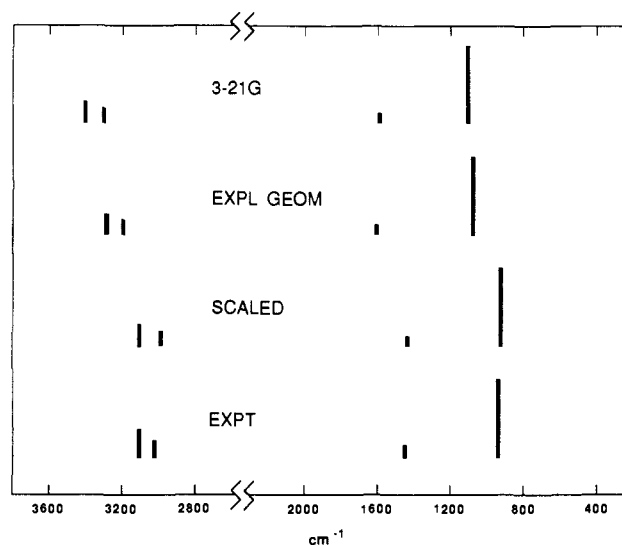
Figure 6. Comparison of 3-21G computed frequencies and intensities (see text) of ethylene with those of experiment.

bending force constants. Blom and Altona[59,60,64,65] have proposed a much more elaborate scheme of scale factors. Based on the experimental spectra of ethane, propane, cyclopropane, ethylene, and dimethyl ether they proposed scale factors (4-31G basis set) for the various types of stretches, bends, torsions, and wags. In addition they suggested a single scale factor to be applied to all off-diagonal force constants. With these scale factors they were able to reproduce experimental spectra with an error of less than 1%. Pulay, Fogarasi, and Boggs[66,67] have proposed a set of standard diagonal force constant scale factors for their 4-21G basis set based on the spectra of glyoxal, acrolein, butadiene, ethylene, formaldehyde, and benzene. Their treatment of the off-diagonal scale factors differed from that of Blom and Altona in that they proposed all off-diagonal force constants (F_{ij}) should be scaled by $(C_iC_j)^{1/2}$ where C_i and C_j are the scale factors for F_{ii} and F_{jj}. Finally Bock, George, and Trachtman have also proposed a set of scale factors for the 4-31G basis set.[68,69] It is noteworthy that useful results may also be obtained by applying scaling factors to semiempirical calculations of the CNDO type.[70,71] This is important with treatments of large molecules for which ab initio calculations are not feasible. If one insists on a strict nonempirical nature of the treatment, the diagonal force constants may be recomputed by means of a more sophisticated approach (using a larger basis set and with the inclusion of electron correlation).

However, if one computes both frequencies *and* intensities we contend that useful results can be obtained by computing the spectrum at the optimized geometry of the basis set used and without employing scale factors. This is important to note since for unusual and reactive molecules the experimental geometry may be unknown and standard geometry scaling factors would not be applicable. In Figure 6 are plotted (from bottom to top) the experimental IR spectrum of ethylene, its spectrum computed with the 3-21G basis set at the experimental geometry and scaled with the scale factors proposed by Pulay, Fogarasi, and Boggs[67] for the 4-21G basis set, the unscaled spectrum computed at the experimental geometry, and finally the unscaled spectrum

Figure 7. Comparison of frequencies and intensities of ethylene computed with various basis sets with those of experiment.[74]

Figure 8. Comparison of computed IR spectra of cyclopropene with that of experiment. 6-31G** and experimental data are from reference 76.

computed at the 3-21G optimized geometry. The major effect of computing the spectrum at the experimental geometry and using scale factors is to shift the lines to lower frequency and hence into better agreement with experiment. Presumably agreement here could be made even better by developing scale factors specifically for the 3-21G basis set. On the other hand, virtually no effect is seen on compu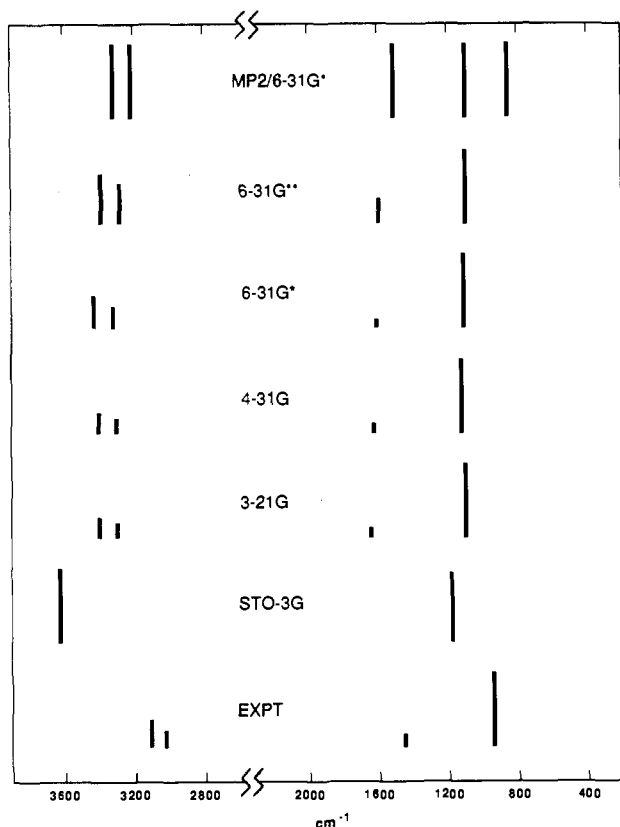ted intensities, and as a consequence the overall pattern seen at the top of the figure compares very favorably with that of the experimental pattern. If one's task were to confirm the structure or to make assignments of the various bands in the experimental spectrum of ethylene, then the spectrum computed at the optimized geometry without scale factors would be sufficient. This point will be given further support by results presented in Section V.

Lowe, Alper, Kawiecki, and Stephens[72] have recently reported frequencies and intensities of ethylene oxide obtained with a 4-31G basis set. These were computed at the experimental geometry of ethylene oxide, and the force field was also scaled. The effect of scaling was to improve significantly the agreement of computed frequencies with experiment; however their computed intensities showed little change from those computed with the similar 6-31G basis set without scaling and at the optimum 6-31G geometry.[73]

IV. A Test of the Method

Since the main purpose here is to show that the computation of IR spectra can provide assistance to experimentalists in confirming the synthesis of unusual systems and/or in making assignments of bands, the reliability of the method must be established by com-

parison of computed spectra with the spectra of a series of well-characterized systems. This has already been done in part for ethylene in section IIIC. In that case it was shown that the experimental pattern could be reproduced without relying on empirical parameters. As a consequence, the vibrational spectra of molecules to be discussed in this section were all computed at the optimized geometry for a given basis set and without employing scale factors.

Figure 7 shows experimental[74] results for ethylene together with computed frequencies and intensities for wavefunctions that range from the minimal basis (STO-3G) to a much larger basis (6-31G**).[75] At the top of the figure the frequencies computed by Pople's group[30] with partial inclusion of electron correlation by the second-order Møller-Plesset (MP2) method are also given (intensities were not computed in this work). It is seen that only the STO-3G basis, which gives a poor estimation of the intensities of the C–H stretches fails to give the observed experimental pattern. In fact at the SCF level, the 3-21G, 4-31G, 6-31G*, and 6-31G** results are all very similar. Inclusion of electron correlation does improve computed frequencies significantly, particularly in the fingerprint region. However, any of the double-zeta SCF results adequately reproduces the experimental pattern of frequencies and intensities.

Wiberg and collaborators[76] have computed the IR frequencies and intensities of cyclopropene with the 6-31G** basis set and have measured the experimental intensities. Frequency assignments had been made earlier by Yum and Eggers.[77] Cyclopropene provides a more demanding test of the method than ethylene because it has thirteen IR active modes and in particular because of the presence of seven bands in the fingerprint region compared to only two for ethylene. The experimental spectrum is plotted in Figure 8 along with Wiberg's 6-31G** computed spectrum.[76] While all computed absorptions are again shifted to higher frequency than experiment, the agreement in pattern is quite good even in the fingerprint region. Lee, Bunge, and Schaefer[78] have also computed the spectrum of cyclopropene with a double zeta plus polarization basis set and obtain results very similar to those of Wiberg and collaborators. The frequencies from our MP2/6-31G*[79] calculation (intensities were not computed) are

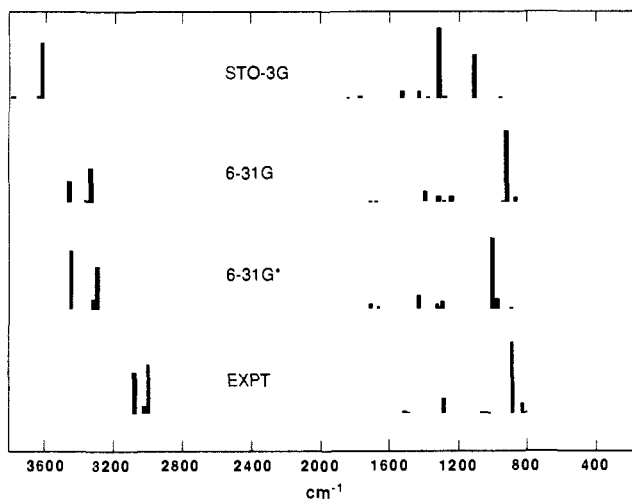**Figure 9.** Comparison of computed IR spectra[73] of ethylene oxide with that of experiment.[80]

Figure 10. Comparison of computed IR spectra[82] of thiirane with that of experiment.

presented at the bottom of this figure and show a somewhat improved agreement with experiment.

The IR spectrum of ethylene oxide has been calculated with the STO-3G, 6-31G and 6-31G* basis sets by Hess, Schaad, and Polavarapu,[73] and these results are compared in Figure 9 with the experimental spectrum by Nakanaga.[80] In all three cases the vibrational spectrum was computed at the optimized geometry for the basis set. Komornicki, Pauzat, and Ellinger[81] have also reported the calculated frequencies of ethylene oxide with the 4-31G and 6-31G** basis sets, and their results compare quite favorably with those of the similar basis sets 6-31G and 6-31G*. It is seen from Figure 9 that again the pattern is well reproduced by the 6-31G* basis set. In the fingerprint region there are three weak bands near 1150 cm⁻¹ that have not been assigned with certainty in the experimental spectrum. The computed spectrum predicts very nicely three weak bands in this region. Although the calculated pattern of the frequencies of the three bands at the lowest frequency is somewhat different from experiment, the relative intensities allowed assignment of these bands with reasonable certainty; and the computed assignments do agree with those assigned from experiment. It is seen that the 6-31G basis is able to reproduce the experimental spectrum reasonably well. However the STO-3G computed spectrum is in very poor agreement with experiment, both in computed frequencies and relative intensities. This was not so much the case for ethylene, and it may be that the disagreement here is because ethylene oxide is a polar molecule while ethylene is not.

A related molecule is thiirane. An interpretation of its experimental spectrum has recently been reported along with the calculation of its spectrum with several basis sets.[82] These results are summarized in Figure 10. In this case the STO-3G spectrum reproduces the experimental pattern surprisingly well. The ordering of the frequencies is correctly predicted, and even the intensities are reasonably good. It is interesting to note that the intermediate basis set (3-21G), while again reproducing the intensities fairly well, does lead to some ambiguity in the frequencies. One band is out of order (C–C stretch), but perhaps more serious is the fact that the intense C–S stretch is predicted to be at lower frequency than observed. In the cases discussed so far,
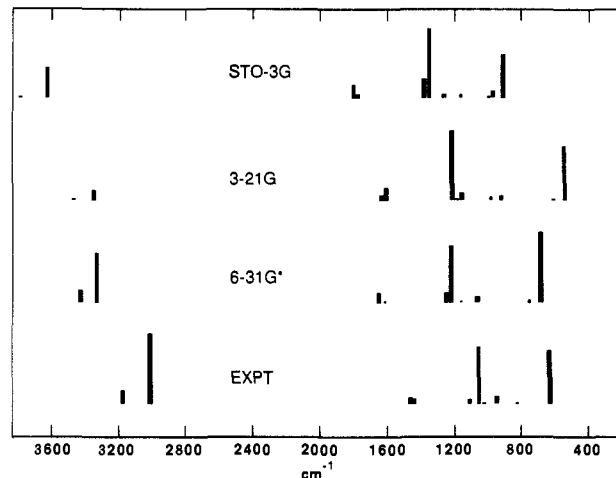
frequencies at the SCF level were all computed to be higher than observed. Hence if the 6-31G* calculation had not been done, one would have predicted the C–S stretch be at a considerably lower frequency than was actually observed. Finally it is seen that the 6-31G* spectrum reproduces the experimental pattern very well. The ordering of frequencies is predicted well, and the relative intensities are in excellent agreement with experiment.

V. Examples of Applications

We have selected from the literature a few examples showing the present possibilities of ab initio calculations of vibrational spectra in their application to the identification of molecular structures. The harmonic approximation was assumed in all cases. We have intentionally selected calculations made with the simpler approaches (SCF, small and medium basis sets) since only such calculations are applicable to larger molecules.

A. HNO

An early example of the use of a computed IR spectrum to confirm the reported observation of a reactive molecule is Botschwina's ab initio calculation[83] on HNO. This molecule was observed in the gas phase as early as 1958 by Dalby,[84] and it was identified primarily by IR spectroscopy. Prior to Botschwina's work there had been controversy over the fundamental frequencies and force field of HNO. Jacox and Milligan[85] reported a matrix IR spectrum of HNO and several isotopic derivatives in 1973 and proposed two possible sets of force constants (see Table III). This is not a unusual situation since, as mentioned in the introduction, there are usually infinitely many sets of force constants that can give the observed frequencies. Not only was Botschwina able to reproduce the frequencies of the parent molecule and five of its isotopic derivatives quite well as seen in Table III, but also to show clearly that the correct force field is B and not A.

TABLE III. Force Constants of the HNO Molecule[a]

force const[b]	assignment A[c]	assignment B[c]	ab initio SCF[d] (7s3p/3s)
F_{rr}	7.15	4.084	4.536 (4.082)
F_{RR}	10.24	11.035	12.594 (11.335)
$F_{\alpha\alpha}$	0.73	1.337	1.585 (1.347)
F_{rR}		0.236	0.813
$F_{r\alpha}$			0.106
$F_{R\alpha}$	−0.11	0.749	0.820

[a] Taken from ref 83. [b] R refers to the NO bond, r to the NH bond; force constants are expressed in 10^2 n m^{-n}, where n is the number of stretching coordinates. [c] Two different solutions of the inverse (for references see the original paper[83]). [d] The entries in parentheses are force constants obtained by applying the scaling factors (0.9 for F_{rr} and F_{RR} and 0.85 for $F_{\alpha\alpha}$).

B. Cyclobutadiene

Cyclobutadiene has attracted the interest of both experimental and theoretical chemists since the last century and provides a nice example of how computed IR spectra can be useful in the identification of unusual species.[86] Although Pettit and co-workers had evidence as early as 1965 for the existence of free cyclobutadiene,[87,88] it was not until 1972 (Krantz)[89] and 1973 (Chapman)[90] that the first IR spectra were reported for this molecule. From the IR spectrum both concluded that cyclobutadiene has a square structure. They reported two strong bands at 570 and 1240 cm^{-1} and a weak one at 650 cm^{-1}. At the time Krantz and Chapman prepared cyclobutadiene, the best ab initio calculation predicted cyclobutadiene to have a rectangular-singlet ground state.[91] More extensive calculations, which supported this prediction by Buenker and Peyerimhoff, were reported in 1977 and 1978 by three groups.[92-94] One of these (Borden, Davidson, and Hart)[94] in fact suggested that the original interpretation of the IR spectrum might not be correct.

In 1978 Kollmar and Staemmler[95] reported the first ab initio calculation of the IR spectrum of cyclobutadiene using a double zeta + polarization basis set. Their results indicated that there should be two strong bands below 2000 cm^{-1}, one at 1377 and the other at 692 cm^{-1}, which they suggested corresponded to the two strong bands observed by Krantz and Chapman in this region (the band at 650 cm^{-1} which had earlier been assigned to cyclobutadiene had been shown subsequently by Masamune to be due instead to CO$_2$[96]). In addition they predicted three relatively weak bands at 790, 1129, and 1697 cm^{-1}.

Later in 1978 Masamune[97] reported a matrix Fourier transform IR spectrum of cyclobutadiene which showed remarkably good agreement with the earlier calculation of Kollmar and Staemmler[95] and with that of Schaad, Hess, and Ewig in which an STO-4G basis set was used.[98] Hence the evidence at this point was strongly in favor of a rectangular structure. Hess, Čársky, and Schaad later reported[25] an improved calculation with the 6-31G* basis set and also with inclusion of electron correlation (MP2), and their results are given in Figure 4. It is seen that there is remarkable agreement between Masamune's observations and the calculated spectra. Similar agreement was found for the tetra-
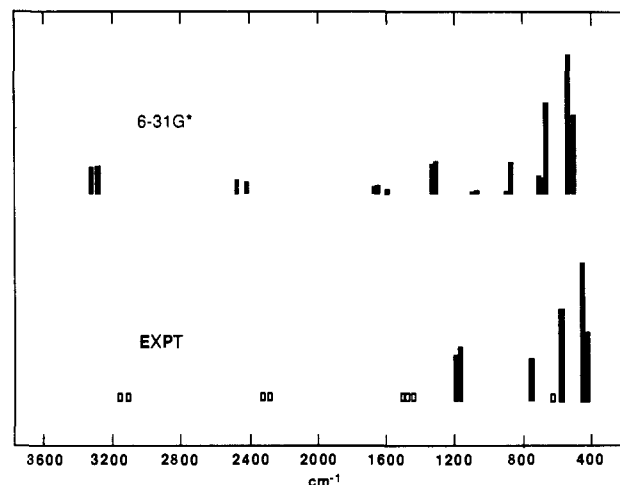
Figure 11. Calculated[25] IR spectra of a 1:1 mixture of [1,2-^{2}H$_2$]- and [1,4-^{2}H$_2$]-cyclobutadiene and the spectra observed by Chapman's group on photolysis of either 2-pyrone-5,6-d_2 or 2-pyrone-3,6-d_2.[98] The open bars show additional weak experimental lines observed for the mixture by Michl.[101a]

deuteriocyclobutadiene.[25,96,98] Hence the conclusion was that cyclobutadiene is indeed rectangular.

One question however still remained. In 1973 Chapman and co-workers[99] reported that photolysis of IV and V yielded products that had identical spectra.
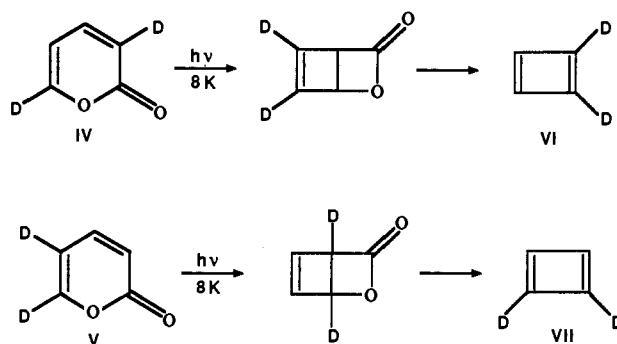
They reasoned therefore that this was evidence for a square structure of cyclobutadiene since IV and V should have given two different d_2-cyclobutadienes (VI and VII) if it were rectangular. However, it has been shown that, while the observed spectrum (Figure 11) does not agree with the computed spectrum of VI or VII, it does correspond to that of a 1:1 ratio of the two isomers.[100] Hence Chapman's group had apparently produced not square cyclobutadiene but rather a 1:1 mixture of the two rectangular isomers VI and VII. In accord with this, Krantz and co-workers had earlier shown[101b] that IV and V are equilibrated with one another during photolysis prior to conversion to cyclobutadiene.

We have learned quite recently that Michl and collaborators have been able to identify additional bands in the IR spectrum of cyclobutadiene and its isotopically labelled derivatives.[101a] They have located the remaining two bands (C–H stretch) in the IR spectrum of cyclobutadiene at 3107 and 3124 cm^{-1}. They have also assigned eight additional bands in the spectrum of the mixture of the two d_2-cyclobutadienes (VI and VII). These correspond very nicely to bands computed earlier for this mixture[25,100] as seen in Figure 11. Finally, Michl et al. have also obtained the spectrum of the corre-

TABLE IV. Vibrational Calculations of Inorganic Systems

formula	structure or name	type of calcn[a]	type[b]	ref	formula	structure or name	type of calcn[a]	type[b]	ref
AlH_2	AlH_2	MRD CI	ν	118	F_2H^-	FHF^-	4-31G	ν	163
BH_2	BH_2	SCF, IEPA/ext	ν	119	F_2Si	SiF_2	TC SCF, DZ+P	ν	164
BH_2	BH_2	STO3G	ν	120	F_2Si	SiF_2	3-21G	ν	165
BH_2	BH_2	CI	ν	121	F_2Mg	MgF_2	DZ+P	ν	166
BHO	HBO	6-31G*, MP2	ν	122	F_2O	F_2O	4-31G	ν	167
BeH_2	BeH_2	CEPA	FC	123	F_2O	F_2O	3-21G	ν	136
C_2Si	SiCC	CI	ν	124	FH_2^+	H_2F^+	DZ+P	ν	168
CClN	ClCN	ext	FC	125	FHN	HNF	MRD CI	ν	169
CClN	ClNC	ext	FC	125	FHO	HOF	DZ	ν	156
CFH	HCF	6-31G*, MP2	ν	122	FHO	HOF	min	FC	170
CFN	FCN	DZ	FC	126	FHO	HOF	6-31G*, MP2	ν	122
CFN	FCN	ext	FC	125	FHSi	HSiF	TC SCF, DZ+P	ν	164
CFN	FCN	4-31G	FC, I	127	FHSi	HSiF	3-21G	ν	165
CFN	FNC	ext	FC	125	FNN^+	N_2F^+	DZ	FC	126
CHN	HCN	4-31G	ν	128	FNO	ONF	DZ	FC	171
CHN	HCN	CI	FC	129	FNS	NSF	6-31G*, MP2	ν, I	172
CHN	HCN	DZ	FC	126	FNS	SNF	6-31G*, MP2	ν, I	172
CHN	HCN	DZ	ν	130	FOS	FSO	4-31G	ν	173
CHN	HCN	DZ+P/CI	FC, I	131	GeH_2	GeH_2	MRD CI	ν	174
CHN	HCN	ext	FC	125	H_3^+	H_3^+	CI	ν	175, 176
CHN	HCN	6-31G**	ν, I	132	H_3^+	H_3^+	CI	ν, I	177
CHN	HCN	6-31G*, MP2	ν	122, 133	H_3^+	H_3^+	CISD	ν	178
CHN	HCN	DZ+P/CEPA	ν	134	H_2F^+	H_2F^+	6-31G*, MP2	ν	138
CHN	HCN	4-31G	FC, I	127	H_2N	H_2N	STO3G	ν	120
CHN	HCN	SCEP	ν	135	H_2N^+	H_2N^+	6-31G*, MP2	ν	138
CHN	HCN	3-21G, 6-31G*	ν	136	H_2O	H_2O	STO3G, 4-31G	FC	54
CHN	HCN	MRD-CI	ν, I	137	H_2O	H_2O	CI	FC, I	179
CHN	HCN	6-31G*	ν	138	H_2O	H_2O	4-31G	ν	180
CHN	HCN	CISD	ν	57, 139	H_2O	H_2O	DZ+P	ν	168, 181, 182
CHN	HCN	CEPA	ν	140					
CHN	HCN	STO-NG, N-31G	I	141	H_2O	H_2O	DZ	ν	156
CHN	HNC	ext	FC	125	H_2O	H_2O	4-21G	FC, I	11
CHN	HNC	6-31G**	ν, I	132	H_2O	H_2O	CI	ν, I	46
CHN	HNC	DZ+P	ν	142	H_2O	H_2O	STO3G, 3-21G, 4-31G, 6-21G	ν	183
CHN	HNC	6-31G*, MP2	ν	122					
CHN	HNC	SCEP, CEPA	ν, I	143	H_2O	H_2O	STO3G	I	95
CHN	HNC	SCEP	ν	135	H_2O	H_2O	CI	FC	184
CHN	HNC	CISD	ν	144	H_2O	H_2O	4-31G	ν	167
CHN	HNC	6-31G*	ν	138	H_2O	H_2O	STO3G, 4-31G	ν	185
CHN	HNC	CEPA	ν	140	H_2O	H_2O	MCSCF/CI	ν	17
CHO^+	HCO^+	6-31G*, MP2	ν	138	H_2O	H_2O	6-31G*, MP2	ν	122
CHO^+	HOC^+	6-31G*, MP2	ν	138	H_2O	H_2O	ext	FC	186
CHP	HCP	DZ+P	ν	142	H_2O	H_2O	CI	FC, ν	14
CHP	HCP	SCEP, CEPA	ν, I	143	H_2O	H_2O	CI	I	46
CHP^+	HCP^+	DZ+P	ν	142, 143	H_2O	H_2O	DZ+P	I	49
CHS^+	HCS^+	6-31G*, MP2	ν	138	H_2O	H_2O	3-21G, 6-31G*	ν	136
CHS^+	HCS^+	CEPA	ν, I	145	H_2O	H_2O	6-31G*	ν	138
CKN	KCN	ext	ν	146	H_2O	H_2O	CISD	ν	139
CKN	KCN	ext	I	147	H_2O	H_2O	MP2, MP3 MBPT-SDQ, CC	FC	187
CLiN	LiCN	ext	I	147					
CLiN	LiCN	ext	FC	125	H_2O^+	H_2O^+	DZ+P	ν	181
CLiN	LiNC	ext	FC	125	H_2O^+	H_2O^+	6-31G*, MP2	ν	138
CO_2	CO_2	DZ	ν	148	H_2O^+	H_2O^+	MCSCF/CI	ν	188
CO_2	CO_2	DZ+P	FC	149	H_2S	H_2S	STO3G, 4-31G	FC	54
CO_2	CO_2	4-31G	ν, I	150	H_2S	H_2S	3-21G, 3-21G*	ν	189
CO_2	CO_2	CI	ν	151	H_2S	H_2S	3-21G, 6-31G*	ν	190
CO_2	CO_2	4-31G	FC, I	127	H_2S	H_2S	STO3G, 3-21G, 4-31G, 6-21G	ν	191
CO_2	CO_2	3-21G	ν	136					
CO_2^+	CO_2^+	4-31G	ν, I	150	H_2S	H_2S	6-31G*, MP2	ν	138
COS	OCS	4-31G	FC, I	127	H_2Si	H_2Si	6-31G*, MP2	ν	138
CS_2	CS_2	4-31G	ν, I	150	H_2Si	H_2Si	TC SCF, DZ+P	ν	164
CS_2^+	CS_2^+	4-31G	ν, I	150	H_2Si	H_2Si	3-21G	ν	165
ClClH⁻	HCl_2^-	min	I	152	H_2Si	H_2Si	3-21G	ν	192
ClClH⁻	HCl_2^-	DZ+P	ν	153	HN_2^+	N_2H^+	CEPA	ν, I	193
ClH_2^+	ClH_2^+	6-31G*, MP2	ν	138	HN_2^+	N_2H^+	6-31G*, MP2	ν	138
ClHH⁻	HClH⁻	4-31G, 4-31G**, DZ + dif.	ν	154	HLiO	LiOH	6-31G*, MP2	ν	122
					HLiO	LiOH	ext/CEPA	FC	194
ClHO	HOCl	4-31G, 6-31G**, DZ+P,TZ+P	ν, I	155	HNO	HNO	DZ	ν	83
					HNO	HNO	DZ	ν	156
ClHO	HOCl	DZ	ν	156	HNO	HNO	CAS SCF	ν	195
ClNO	ONCl	ext	ν	157	HNO	HNO	6-31G*, MP2	ν	122, 138
ClNO	ONCl	DZ	ν	158	HNSi	HNSi	DZ	ν	196
ClNS	NSCl	DZ+P	FC	159	HO_2	HOO	4-31G, 6-31G*, DZ+P, TZ+P	ν, I	155
F_2H^+	HF_2^+	DZ	ν	160					
F_2H^-	FHF^-	DZ	ν	161	HO_2	HOO	DZ+P	ν	197
F_2H^-	FHF^-	4-31G	FC	162	HO_2	HOO^+	ext, CI DZ+P	ν	198

TABLE IV (Continued)

formula	structure or name	type of calcn[a]	type[b]	ref	formula	structure or name	type of calcn[a]	type[b]	ref
HOSi	HSiO	6-31G*	ν	199	H_3P^+	PH_3^+	DZ+P	ν	234
HOSi+	HSiO+	6-31G*, MP2	ν	138	H_3S^+	SH_3^+	6-31G*, MP2	ν	138
HOSi+	HSiO+	CEPA	ν, I	200	H_3Si	SiH_3	3-21G	ν	165
HOP	HPO	6-31G*	ν	201	H_3Si	SiH_3	MRD CI	ν	235
N_2O	N_2O	4-31G	FC,I	127	H_2CN^+	$HCNH^+$	6-31G*, MP2	ν	138
N_2O	N_2O	3-21G	ν	136	H_2LiO^+	$H_2O...Li^+$	ext	ν	236
O_2P	PO_2	6-31G*	ν	201	H_2N_2	HNNH	CI	ν	237
O_2P^-	PO_2^-	6-31G*	ν	201	H_2N_2	HNNH	STO3G, 4-31G	ν, I	238
O_2S	SO_2	3-21G, 3-21G*, 6-31G*	ν	189	H_2N_2	HNNH	6-31G*, MP2	ν	122, 138
O_2S	SO_2	STO-4G	I	202	H_2O_2	H_2O_2	4-31G	ν, I	239
O_2Si	SiO_2	TZ+P	ν	203	H_2O_2	H_2O_2	6-31G*, MP2	ν	122, 138
B_2H_4	BH_2H_2B	DZ+P	ν	204	H_2O_2	H_2O_2	DZ	FC	240
BH_3	BH_3	DZ	ν	205	H_2OSi	H_2OSi	CI, CEPA	ν	241
BH_3	BH_3	4-21G	FC, I	11	H_2OSi	H_2SiO	6-31G*	ν	199
BH_3	BH_3	6-31G*, MP2	ν	122, 138	H_2OSi	HSiOH	6-31G*	ν	199
BH_2N	HBNH	6-31G*, MP2	ν	122	H_2S_2	H_2S_2	3-21G*, 6-31G*	ν	189
C_3O	C_3O	3-21G	ν	206	$HCLiN^+$	$HCN...Li^+$	DZ,EFV	ν, I	242
C_2N_2	NCCN	DZ	FC	126	HCO_2	HCO_2	6-31G*, MP2	ν	138
C_2N_2	NCCN	DZ+P/CEPA	ν, I	207	HNO_2	HONO	ext	ν	243
C_2N_2	NCCN	SCEP, CEPA	ν, I	143	HNOS	HNSO	STO3G*, 3-21G*, 6-31G*, MP2, MP3	ν	244
C_2N_2	NCCN	STO-NG, N-31G	I	141					
CHNO	HNCO	DZ	FC	208	Li_2O_2	Li_2O_2	DZ+P	ν	245
$CLiO_2$	$LiCO_2$	3-21G, 6-31G*	ν	209	N_2O_2	$(NO)_2$	DZ	ν	246
$CNaO_2$	$NaCO_2$	3-21G, 6-31G*	ν	209	N_2O_2	$(NO)_2$	4-31G	ν	247
CNNO	ONCN	DZ	ν	210	N_2OS	ONNS	4-31G	ν	247
CO_3	CO_3	3-21G, 3-21G* 6-31G, 6-31G*	ν, I	211	N_2S_2	S_2N_2	CEPA	ν	248
Cl_2H_2	$(HCl)_2$	ext	ν, I	212	O_3S	SO_3	3-21G, 3-21G*, 6-31G*	ν	189
ClF_3	ClF_3	3-21G, 3-21G*	ν	189	Al_2CH_2	Al_2CH_2	DZ, DZ+P	ν	249
F_3N	NF_3	STO3G, DZ	I	213	$AlBr_3H_3N$	$H_3N:AlBr_3$	STO3G	ν	250
F_3N	NF_3	DZ	FC	171	$AlCl_3H_3N$	$H_3N:AlCl_3$	STO3G	ν	250
F_3N	NF_3	3-21G	ν	136	AlF_3H_3N	$H_3N:AlF_3$	STO3G	ν	250
F_3P	PF_3	STO3G, DZ	I	213	B_2H_6	$H_2BH_2BH_2$	4-31G	FC	251
F_3Si	SiF_3	3-21G	ν	165	B_2H_6	$H_2BH_2BH_2$	4-31G	ν	252
F_2H_2	$(HF)_2$	ext/CEPA	ν	214	B_2H_6	$H_2BH_2BH_2$	6-31G*, MP2	ν	122, 138
F_2H_2	$(HF)_2$	DZ+P	ν	215	B_2O_3	OBOBO	DZ+P	ν, I	253
F_2H_2	$(HF)_2$	DZ+P, CI	ν	216	BH_4^-	BH_4^-	DZ	ν	254
F_2HN	HNF_2	DZ	FC	217	BeF_3Li	$LiBeF_3$	DZ	ν, I	255
F_2HSi	$HSiF_2$	3-21G	ν	165	C_3O_2	C_3O_2	6-31G*	ν	256
F_2Li_2	$(LIF)_2$	DZ	ν	218	$C_2Li_2O_4$	$Li_2C_2O_4$	3-21G	ν	209
FH_2N	H_2NF	DZ	FC	217	CCl_3N	$ClNCCl_2$	DZ	ν	257
FH_2O^-	$H_2O...F^-$	4-31G, EFV	I	219	CFH_2N	$HCN...HF$	4-31G	ν	128
FH_2Si	H_2SiF	3-21G	ν	165	CH_3NO_2	$CO_2...NH_3$	DZ	ν	258
FNO_2	NO_2F	DZ	ν	220	CH_2N_2	H_2NCN	4-31G, 4-31G*	ν, I	259
FNO_2	NO_2F	min	ν	221	CH_2N_2	H_2NNC	4-31G, 4-31G*	ν, I	259
H_3N	NH_3	ext	FC	222	CH_2CO_3	H_2CO_3	4-31G	ν	260
H_3N	NH_3	STO3G, 4-31G	FC	54	CLi_2O_2	Li_2CO_2	3-21G	ν	209
H_3N	NH_3	4-21G	FC, I	11	CNa_2O_2	Na_2CO_2	3-21G	ν	209
H_3N	NH_3	STO3G	I	223	CHO_3^-	HCO_3^-	4-31G	ν	260
H_3N	NH_3	HF limit	FC	224	F_5P	PF_5	3-21G, 3-21G*	ν	189
H_3N	NH_3	4-31G*	ν	225	F_5P	PF_5	DZ	ν	261
H_3N	NH_3	DZ	I	226	F_4Si	SiF_4	3-21G	ν	165
H_3N	NH_3	STO3G, 3-21G, 4-21G, 6-21G	ν	183	F_3H_3	$(HF)_3$	DZ+P, CI	ν	216
H_3N	NH_3	STO3G, DZ	I	213	F_3HSi	$HSiF_3$	3-21G	ν	165
H_3N	NH_3	6-31G*, MP2	ν	122, 138	F_2H_2Si	H_2SiF_2	3-21G	ν	165
H_3N	NH_3	3-21G, 6-31G*	ν	136	FH_3O	$H_2O...HF$	6-31G	ν	262
H_3N	NH_3	DZ+P	I	49	FH_3O	$H_2O...HF$	TZ+P	ν	263
H_3N^+	NH_3^+	6-31G**	ν	227	FH_3O	$H_2O...HF$	CSID	ν	264
H_3N	NH_3	CISD	ν	57, 228	FH_3Si	SiH_3F	3-21G	ν	192
H_3O^+	H_3O^+	CI	ν	229	FH_3Si	SiH_3F	3-21G	ν	165
H_3O^+	H_3O^+	SCEP,CEPA	ν, I	230	H_9^+	H_9^+	CISD	ν	178
H_3O^+	H_3O^+	ext	ν, I	231	H_7^+	H_7^+	CISD	ν	178
H_3O^+	H_3O^+	CISD	ν	232	H_5^+	H_5^+	CISD	ν	178
H_3O^+	H_3O^+	DZ+P	ν	168	H_5P	PH_5	CEPA	FC	233
H_3O^+	H_3O^+	6-31G*, MP2	ν	138	H_4N^+	NH_4^+	6-31G**	ν, I	75
H_3P	PH_3	STO3G, 4-31G	FC	54	H_4N^+	NH_4^+	6-31G*, MP2	ν	138
H_3P	PH_3	STO3G, 3-21G, 4-31G, 6-21G	ν	191	H_4N^+	NH_4^+	CISD	ν	139
H_3P	PH_3	3-21G, 3-21G*	ν	189	H_4N_2	H_2NNH_2	STO3G, 4-31G, 4-31G*, 6-31G*, CI	ν	265
H_3P	PH_3	CEPA	FC	233	H_4O_2	H_2NNH_2	6-31G*, MP2	ν	122, 138
H_3P	PH_3	STO3G, DZ	I	213	H_4O_2	$(H_2O)_2$	4-31G, 6-31G*	ν	266
H_3P	PH_3	DZ+P	ν	234	H_4O_2	$(H_2O)_2$	CI	ν	267
H_3P	PH_3	6-31G*, MP2	ν	138	H_4O_2	$(H_2O)_2$	4-31G	FC, I	268
H_3P	PH_3	3-21G, 6-31G*	ν	190	H_4O_2	$(H_2O)_2$	4-31G	I	269
					H_4O_2	$(H_2O)_2$	DZ+P	ν, I	270
					H_4O_2	$(H_2O)_2$	4-31G	ν, I	271
					H_4O_2	$(H_2O)_2$	4-31G	ν	272

TABLE IV (Continued)

formula	structure or name	type of calcn[a]	type[b]	ref	formula	structure or name	type of calcn[a]	type[b]	ref
$H_4O_2Li^+$	$(H_2O)_2Li^+$	4-31G	FC, I	268	H_4Si_2	disilene	DZ, DZ+P	ν	275
$H_4O_2Si_2$	$(H_2SiO)_2$	3-21G	ν	273	H_3N_3	triaziridine	6-31G*, MP2	ν, I	276
H_4P^+	H_4P^+	6-31G*, MP2	ν	138	H_3N_3	triazine	6-31G*, MP2	ν, I	276
$H_4S_2Si_2$	$(H_2SiS)_2$	3-21G	ν	273	H_3NO	$HONH_2$	4-31G	ν, I	277
H_4Si	SiH_4	STO3G, 4-31G	FC	54	H_3NO	$HONH_2$	6-31G*, MP2	ν	122, 138
H_4Si	SiH_4	6-31G*, MP2	ν	138	H_3NO	$HONH_2$	DZ	FC	240
H_4Si	SiH_4	3-21G, 3-21G*	ν	189	H_3NO	$HONH_2$	STO3G, 4-31G	ν, I	278
H_4Si	SiH_4	3-21G, 6-31G*	ν	190			4-31G		
H_4Si	SiH_4	DZ, DZ+P	ν	274	H_2N_2O	$H_2N=NO$	4-31G	ν, I	279
H_4Si	SiH_4	6-31G**	ν, I	75	H_2N_2O	$HN=NOH$	4-31G	ν, I	279
H_4Si	SiH_4	3-21G	ν	165	H_2O_4	$(HO_2)_2$	DZ+P	ν	197

[a] DZ means generally a true double-zeta basis set. It may also mean a valence-shell DZ set or a medium-sized basis set of a quality somewhat better than DZ. [b] ν:frequencies computed. FC: force constants reported only. I: intensities computed (IR and/or Raman).
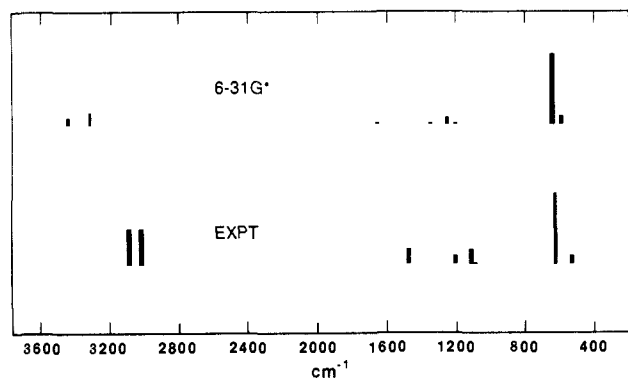

Figure 12. Comparison of computed IR spectra[103] of [1.1.1]-propellane with that of experiment.[102]

Figure 13. Comparison of computed IR spectra[106] of methylenecyclopropene with that of experiment.[104]

sponding $^{13}C_2$-cyclobutadiene mixture. The observed and computed spectra are in good agreement. In the computed spectrum[25] there are six bands below 1700 cm^{-1} of relative intensity greater than 0.01. Michl et al. observed six bands in this region which correspond well with those computed. At high frequency a broad band is observed at 3049 cm^{-1}. Calculations[25] predict five weak C–H stretches within an 18-cm^{-1} region and a sixth of very weak intensity at somewhat higher frequency.

C. [1.1.1]Propellane

Wiberg and Walker reported in 1982 the synthesis and IR spectrum of the highly strained but remarkably stable hydrocarbon [1.1.1]propellane (VIII).[102] An

VIII

unusual aspect of the IR spectra of VIII is a very intense band at 612 cm^{-1} which appears to be characteristic of highly strained cyclopropanes.[102] Wiberg, Dailey, and Walker carried out a vibrational calculation[103] (6-31G*) of frequencies and IR intensities. It is seen from Figure 12 that not only is there predicted a very intense band at low frequency but the overall experimental pattern is reasonably well reproduced by the calculated spectrum. With the aid of the computed spectrum Wiberg
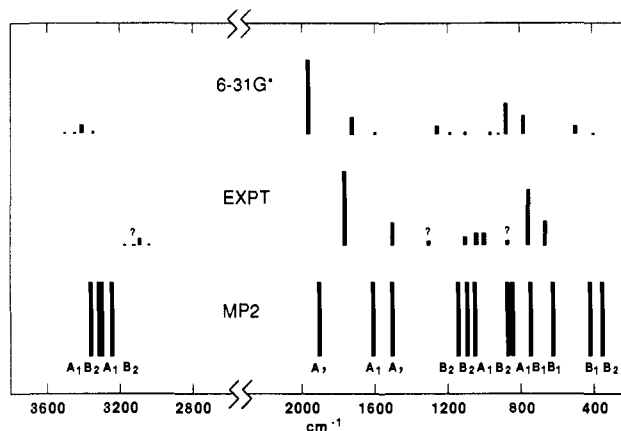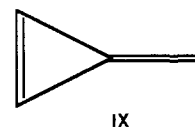
and co-workers were able to assign the fundamentals in the IR and Raman spectra.

D. Methylenecyclopropene

The recent synthesis of methylenecyclopropene (IX)[104,105] was confirmed in part by its IR spectrum.[104] Billups reported five bands which he assigned to the spectrum of IX. However, while the computed spec-

IX

trum (6-31G*)[106] agreed very well with four of the bands reported (Figure 13), the relatively intense band at 904 cm^{-1} (not shown in the figure) did not appear to correlate with any of the computed frequencies. While several bands were computed to lie in this region (taking into account the fact that computed bands usually appear at higher frequency than experiment), all were computed to be of quite low intensity. Billups subsequently informed us that the band at 904 cm^{-1} is in fact not due to IX. This was further confirmed by Maier and collaborators[107] in an independent synthesis of IX in which they found no absorption in the 900 cm^{-1} region due to IX. Billups[108] has since located additional bands in the experimental spectrum and these along with 6-31G*/MP2 computed frequencies[79] are also given in Figure 13.
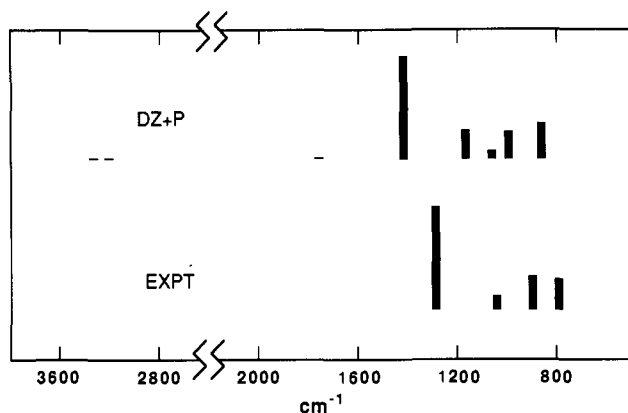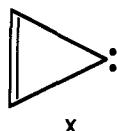
Figure 14. Comparison of computed[78] IR spectra of cyclopropenylidene with that of experiment.[109]

Figure 15. Comparison of computed IR spectra of thiirene with that of experiment.[111] Open bars give estimated uncertainty of experimental intensities, i.e., experimental intensity is estimated to lie somewhere within the open bar.

E. Cyclopropenylidene

Computed spectra are not only of use in identifying unstable molecules but also in aiding in the characterization of reactive intermediates. The recent synthesis of the singlet carbene cyclopropenylidene (X)[109]

X

and the confirmation of this synthesis by comparison of experimental and computed IR spectra provides a nice example of this. Lee, Bunge, and Schaefer[78] have carried out an SCF computation of the IR spectrum with a double zeta plus polarization basis. The result compared very favorably with the matrix spectrum observed by Maier's group (Figure 14).[109] Schaefer and collaborators have also calculated the spectrum of the lowest triplet state ($^3B_1$) of X. This does not compare as well as with the experimental spectrum of X as does the calculated spectrum of the lower energy singlet ($^1A_1$) ground state. Hence the synthesis of X was confirmed by ab initio results, and its electronic state is identified as $^1A_1$.

F. Thiirene

Thiirene (XI), like cyclobutadiene, is a Hückel $4n$ system and is potentially antiaromatic.[110] Its synthesis

XI

in a matrix was reported independently by two groups in 1977[3] and 1978.[111] Both obtained the thiirene spectrum which was found to agree reasonably well with a computed 4-31G spectrum.[112] However, Strausz assigned a band of medium intensity at 657 cm^{-1} to the A_1 symmetric ring deformation. This is at a higher frequency than the corresponding 4-31G computed band (509 cm^{-1}). Normally frequencies computed with a double zeta or larger basis set are computed to be of too high frequency. Hence it was suggested that the original assignment by Strausz was incorrect and that
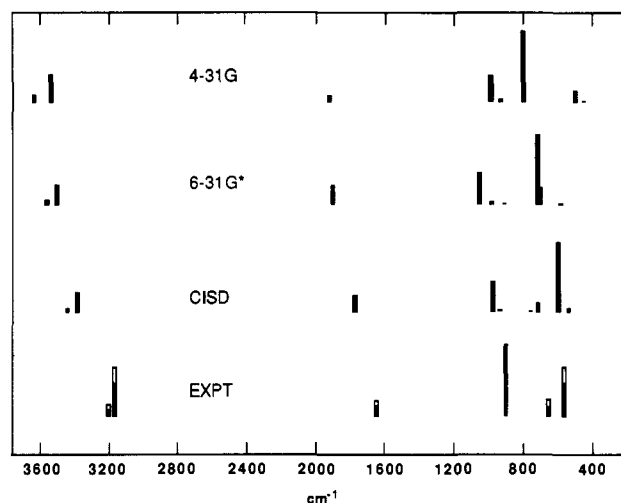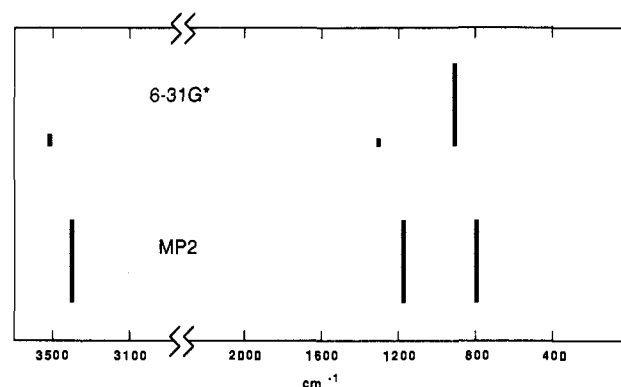

Figure 16. Calculated ab initio spectra of tetrahedrane.[114]

this ring deformation should occur most likely below 400 cm^{-1}.[113] However, it was subsequently shown that this prediction is likely to be wrong since when the spectrum was calculated with a better basis set (6-31G*)[82] the A_1 ring deformation is computed to be at a significantly higher frequency than with the 4-31G basis set. In fact with the 6-31G* basis set it is calculated to be at slightly higher frequency than found by Strausz (see Figure 15), but still at slightly lower frequency (711 cm^{-1}) than the more intense C–H bend at 717 cm^{-1}. Subsequently the vibrational spectrum was recomputed with inclusion of correlation (DZP-CISD),[82] and these results are also shown in Figure 15. It is apparent that the original assignment of the C–S stretch by Strausz is correct since this best calculation places it at 723 cm^{-1} which is 123 cm^{-1} higher in frequency than the more intense C–H bend, and in agreement with Strausz's original assignment. This unexpected shift in computed frequencies serves as a useful warning against implicit trust in the theoretical results.

VI. Some Predictions of IR Spectra of Unknown Molecules

The IR spectra of two interesting but unknown molecules on the C_4H_4 potential surface have recently

TABLE V. Vibrational Calculations of Organic Systems

formula	structure or name	type of calcn[a]	type[b]	ref
CF_2	CF_2	6-31G*	ν	280
CF_2^+	CF_2^+	6-31G*	ν	280
CF_2^{++}	CF_2^{++}	6-31G*	ν	280
CF_4	CF_4	3-21G	ν	136
CF_3O	CF_3O	3-21G	ν, I	281
CF_3O^-	CF_3O^-	3-21G	ν, I	281
CF_3O_2	CF_3OO	3-21G	ν, I	282
$CHCl_3$	$CHCl_3$	STO4G	I	283
CHF_3	CHF_3	4-31G	ν	284
CHF_3	CHF_3	3-21G	ν	136
CHO	HCO	min	ν	285
CHO	HCO	CI, STO3G, DZ+P	FC	286
CHO^+	HCO^+	6-31G**	ν, I	132
CHO^+	HOC^+	6-31G**	ν, I	132
CHO^+	HCO^+	CI	ν	287
CHO_2^-	HCO_2^-	STO3G, 4-31G	ν	288
CH_2	CH_2	CISD	ν	33
CH_2	CH_2	CI	FC	184
CH_2^+	CH_2^+	6-31G*, MP2	ν	138
CH_2^+	CH_2^+	STO3G	ν	120
CH_2F_2	CH_2F_2	4-31G	ν	284
CH_2F_2	CH_2F_2	6-31G*, MP2	ν	133
CH_2N	H_2CN	GVB-CI	ν	289
CH_2N	HCNH	GVB-CI	ν	289
CH_2N_2	$CH_2{=}N_2$	STO3G	FC	290
CH_2N_2	H_2NCN	6-31G*	ν	291
CH_2NO_2	CH_2NO_2	3-21G, 6-31G*	ν	292
CH_2O	$H_2C{=}O$	DZ, CI	ν	293
CH_2O	$H_2C{=}O$	4-31G	ν, I	66
CH_2O	$H_2C{=}O$	DZ+P	ν	294
CH_2O	$H_2C{=}O$	ext	ν, I	41, 63
CH_2O	$H_2C{=}O$	MCSCF, CI	ν	295
CH_2O	$H_2C{=}O$	DZ	ν, I	296
CH_2O	$H_2C{=}O$	6-31G*, MP2	ν, I	122, 133
CH_2O	$H_2C{=}O$	6-31G*	ν	138
CH_2O	$H_2C{=}O$	CI, CEPA	ν	241
CH_2O	$H_2C{=}O$	STO3G	ν	297
CH_2O	$H_2C{=}O$	3-21G, 6-31G*	ν	136
CH_2O	$H_2C{=}O$	DZ, DZ+P, CI	ν	298
CH_2O	$H_2C{=}O$	STO3G, 4-31G	ν	185
CH_2O	HOCH	DZ+P	ν	294
CH_2O	HOCH	STO3G	ν	297
CH_2O^+	HC_2O^+	6-31G*, MP2	ν	138
CH_2O_2	HCOOH	6-31G	FC	299
CH_2O_2	HCOOH	3-21G	ν	136
CH_2O_2	HCOOH	DZ, 4-31G	ν	300
CH_2O_2	HCOOH	STO3G, DZ	ν	301
CH_2O_2	HCOOH	6-31G*, MP2	ν	133
CH_2O_3	HCOOOH	4-31G	ν	13
CH_2OS	HCOSH	4-31G	ν	302
CH_2S	$H_2C{=}S$	CI, CEPA	ν	241
CH_2S	$H_2C{=}S$	3-21G*, 6-31G*	ν	189
CH_2S	$H_2C{=}S$	DZ+P	ν	303
CH_3	CH_3	CI	ν	304
CH_3	CH_3	DZ+P, CEPA	ν, I	305
CH_3^+	CH_3^+	6-31G*, MP2	ν	138
CH_3Br	CH_3Br	DZ+P	FC, I	306
CH_3Cl	CH_3Cl	4-31G	ν	307
CH_3Cl	CH_3Cl	6-31G*, MP2	ν	133
CH_3Cl	CH_3Cl	3-21G*, 6-31G*	ν	190
CH_3Cl	CH_3Cl	4-31G, 6-31G*	FC, I	308
CH_3Cl	CH_3Cl	3-21G, 6-31G*	ν	309
CH_3Cl	CH_3Cl	DZ+P	FC, I	306
CH_3Cl	CH_3Cl	DZ+P, 6-311G**, MP2	ν	310
CH_3ClMg	CH_3MgCl	3-21G, 6-31G*	ν	309
CH_3F	CH_3F	4-31G	ν	284, 307
CH_3F	CH_3F	DZ+P	FC, I	306
CH_3F	CH_3F	4-31G, 6-31G*	FC, I	308
CH_3F	CH_3F	DZ+P	FC, I	311
CH_3F	CH_3F	3-21G, 6-31G*	ν	136
CH_3F	CH_3F	6-31G*, MP2	ν	122, 133
CH_3F	CH_3F	6-31G*	ν	138
CH_3F	CH_3F	DZ+P, 6-311G**, MP2	ν	310
CH_3F	CH_3F	DZ+P	FC	312
CH_3F_2OP	CH_3POF_2	3-21G	ν, I	313
CH_3I	CH_3I	DZ+P	FC, I	306
CH_3N	$H_2C{=}NH$	ext	ν	314
CH_3N	$H_2C{=}NH$	6-31G*	ν	138
CH_3N	$H_2C{=}NH$	6-31G*, MP2	ν	122, 133
CH_3NO	$HCONH_2$	4-31G	ν, I	315
CH_3NO	$HCONH_2$	4-31G*	ν	316
CH_3NO	$HCONH_2$	4-31G	ν, I	317
CH_3NO	CH_3NO	4-31G	ν, I	318
CH_3NO	$H_2C{=}NOH$	STO3G, 4-31G	ν	319, 320
CH_3NO_2	CH_3NO_2	3-21G, 6-31G*	ν	291
CH_3NS	$HCSNH_2$	4-31G	ν	316
CH_3O^+	H_2COH^+	6-31G*, MP2	ν	138
CH_3O	CH_3O	3-21G, 6-31G*	ν	321
CH_3O	CH_3O	DZ, CASSCF	ν	322
CH_3O	CH_3O	DZ	ν	323
CH_3O	CH_2OH	3-21G, 6-31G*	ν	321
CH_3O	CH_2OH	DZ, CASSCF	ν	322
CH_3S^+	CH_3S^+	3-21G	ν	324
CH_3S^+	CH_2SH^+	3-21G	ν	324
CH_4	CH_4	DZ+P	FC, I	325
CH_4	CH_4	DZ+P	I	46, 49
CH_4	CH_4	6-31G**	ν, I	75
CH_4	CH_4	6-31G*, MP2	ν	122, 133, 138
CH_4	CH_4	STO3G, 4-31G	FC	54
CH_4	CH_4	CEPA	FC	326
CH_4	CH_4	4-31G	ν	58
CH_4	CH_4	4-21G	ν, I	11
CH_4	CH_4	CISD	ν	139
CH_4	CH_4	CI	ν	304
CH_4	CH_4	3-21G, 6-31G*	ν	136
CH_4	CH_4	4-31G	I	327
CH_4F^+	H_3CFH^+	6-31G*, MP2	ν	138
CH_4N^+	$H_2CNH_2^+$	6-31G*, MP2	ν	138
CH_4O	CH_3OH	min	FC	328
CH_4O	CH_3OH	4-31G	ν	180, 329
CH_4O	CH_3OH	3-21G, 6-31G*	ν	136, 321
CH_4O	CH_3OH	DZ	FC	240
CH_4O	CH_3OH	6-31G*, MP2	ν	122, 133
CH_4O	CH_3OH	6-31G*	ν	138
CH_4O_2	$CH_2(OH)_2$	STO3G, 4-31G	ν	185
CH_4S	CH_3SH	4-31G	ν	329
CH_4S	CH_3SH	3-21G*, 6-31G*	ν	189
CH_4S^+	$CH_2SH_2^+$	3-21G	ν	324
CH_4Si	$H_2Si{=}CH_2$	4-31G	ν	330
CH_5^+	CH_5^+	6-31G*, MP2	ν	138
CH_5N	CH_3NH_2	4-31G	ν	329
CH_5N	CH_3NH_2	6-31G*	ν	138
CH_5N	CH_3NH_2	3-21G, 6-31G*	ν	136
CH_5N	CH_3NH_2	6-31G*, MP2	ν	122, 133
CH_5N	CH_3NH_2	STO3G, 4-31G, 4-31G*	ν, I	331
CH_5O^+	$H_3COH_2^+$	6-31G*, MP2	ν	138
CH_6N^+	$H_3CNH_3^+$	6-31G*, MP2	ν	138
CH_6Si	CH_3SiH_3	DZ, DZ+P	ν	274
CH_8B_2	methyldiborane	4-21G	ν	332
C_2H	HCC	CISD, 6-31G**	ν	333
C_2H^+	C_2H^+	6-31G*, MP2	ν	138
C_2H^-	HCC^-	CEPA, ext	ν	194
C_2HCl^+	$HCCCl^+$	DZ+P	ν	334
C_2HCl	HCCCl	DZ+P	ν	335
C_2HCl	HCCCl	DZ+P, CEPA	ν	134
C_2HF	FCCH	DZ+P	ν	335
C_2HF	FCCH	3-21G	ν	136
C_2HF	FCCH	DZ+P, CEPA	ν	134
C_2HN	HCCN	6-31G, 6-31G*, MP2	ν	336
C_2H_2	HCCH	DZ	ν	63
C_2H_2	HCCH	6-31G*, MP2	ν	122, 133
C_2H_2	HCCH	6-31G*	ν	138
C_2H_2	HCCH	4-31G	I	327
C_2H_2	HCCH	6-31G**	ν, I	75
C_2H_2	HCCH	DZ+P, CI	FC	337
C_2H_2	HCCH	TZ+P, CI	ν	338
C_2H_2	HCCH	DZ+P	ν	335
C_2H_2	HCCH	ext	ν, I	339

TABLE V (Continued)

formula	structure or name	type of calcn[a]	type[b]	ref
C₂H₂	HCCH	3-21G, 6-31G*	ν	136
C₂H₂	HCCH	DZ+P	ν, I	340
C₂H₂	HCCH	DZ+P, CEPA	ν	134
C₂H₂	H₂C=C	CISD	ν	341
C₂H₂	H₂C=C	CI, TZ+P	ν	338
C₂H₂F₂	HFC=CFH	DZ	ν	342
C₂H₂F₂	HFC=CFH	3-21G	ν	136
C₂H₂N₂	H₂NCN	6-31G*	ν	291
C₂H₂O	CH₂=C=O	STO3G	FC	290
C₂H₂O	oxirene	3-21G	ν, I	113
C₂H₂O₂	glyoxal	DZ	ν	68
C₂H₂O₂	glyoxal	4-31G	ν, I	66
C₂H₂S	thiirene	4-31G	ν, I	112
C₂H₂S	thiirene	3-21G	ν, I	113
C₂H₃	vinyl	6-31G**, GVB	ν, I	343
C₂H₃⁺	CH₂=CH⁺	6-31G*, MP2	ν	138
C₂H₃F	H₂C=CHF	3-21G	ν	345
C₂H₃N	H₂NCCH	6-31G*	ν	291
C₂H₃N	CH₃CN	3-21G	ν	136
C₂H₃N	CH₃CN	4-31G*	ν, I	346
C₂H₃N	CH₃CN	6-31G*	ν	291
C₂H₃N	CH₃NC	3-21G	ν	136
C₂H₃N	azirene	3-21G	ν, I	113
C₂H₄	H₂C=CH₂	3-21G, 6-31G*	ν	136
C₂H₄	H₂C=CH₂	DZ	ν	63, 342
C₂H₄	H₂C=CH₂	6-31G*, MP2	ν	30, 122, 133
C₂H₄	H₂C=CH₂	6-31G*	ν	138
C₂H₄	H₂C=CH₂	4-31G	I	327
C₂H₄	H₂C=CH₂	6-31G**	ν, I	75
C₂H₄	H₂C=CH₂	DZ+P	ν	194
C₂H₄	H₂C=CH₂	ext	ν, I	339
C₂H₄	H₂C=CH₂	4-31G	ν, I	64, 66
C₂H₄	H₂C=CH₂	STO4G	ν, I	98
C₂H₄	H₂C=CH₂	DZ+P	I	40
C₂H₄	H₂C=CH₂	STO3G, 6-31G*	ν, I	106
C₂H₄	H₂C=CH₂	3-21G	ν	345
C₂H₄B₂	2,4-diboramethyl-enecyclopropane	DZ	ν, I	347
C₂H₄F	CH₃CHF	3-21G	ν	345
C₂H₄O	oxirane	STO3G, 4-31G, 6-31G**	ν	81
C₂H₄O	oxirane	6-31G*	ν, I	73
C₂H₄O	oxirane	4-31G	ν, I	72
C₂H₄O	oxirane	3-21G	ν	136
C₂H₄O	CH₃CHO	4-31G, 6-31G**	ν, I	348
C₂H₄O	CH₃CHO	3-21G	ν, I	136
C₂H₄O₂	HCOOCH₃	3-21G	ν	136
C₂H₄O₂	CH₃COOH	3-21G	ν	136
C₂H₄O₂	(H₂CO)₂	3-21G	ν	273
C₂H₄O₄	(HCOOH)₂	STO3G, DZ	ν	301
C₂H₄S	H₂C=CHSH	4-31G	ν	349
C₂H₄S	thiirane	6-31G*	ν, I	82
C₂H₅	CH₃CH₂	3-21G	ν	345
C₂H₅	CH₃CH₂	4-21G	ν	350
C₂H₅⁺	CH₃CH₂⁺	6-31G*, MP2	ν	138
C₂H₅F	CH₃CH₂F	3-21G	ν	136
C₂H₅N	aziridine	STO3G, 4-31G, 6-31G*	ν	81
C₂H₅N	aziridine	3-21G, 6-31G**	ν	136
C₂H₅N	CH₃CH=NH	DZ	ν	351
C₂H₅N	CH₃CN=CH₂	DZ	ν	351
C₂H₅NO	HCONHCH₃	4-31G, 4-31G*	ν, I	352
C₂H₆	CH₃CH₃	DZ	ν	63
C₂H₆	CH₃CH₃	4-31G	FC	353
C₂H₆	CH₃CH₃	4-31G	ν	58, 59, 354
C₂H₆	CH₃CH₃	3-21G	ν	59
C₂H₆	CH₃CH₃	6-31G*, MP2	ν	122
C₂H₆	CH₃CH₃	6-31G*	ν	138
C₂H₆	CH₃CH₃	4-31G	I	327
C₂H₆	CH₃CH₃	6-31G**	ν, I	75
C₂H₆N₂O₂	(H₂C=NOH)₂	STO3G	ν	320
C₂H₆O	CH₃OCH₃	4-31G	ν, I	65
C₂H₆O	CH₃OCH₃	3-21G	ν	136
C₂H₆O	CH₃OCH₃	6-31G*, MP2	ν	133

formula	structure or name	type of calcn[a]	type[b]	ref
C₂H₆O₂	HOCH₂CH₂OH	DZ	ν	355
C₂H₆S⁺	CH₂SHCH₃⁺	3-21G	ν	324
C₂H₆S⁺	CH₃SCH₃⁺	3-21G	ν	324
C₃HO⁺	HCCCO⁺	3-21G, 6-31G*	ν	356
C₃HN	HCCCN	DZ+P, CEPA	ν	134
C₃HN	HCCCN	DZ+P	ν	142
C₃HP	HCCCP	DZ+P	ν	142
C₃H₂	cyclopropenylidene	DZ, DZ+P TCSCF/DZ, DZ+P	ν	78
C₃H₂O	HCCCHO	CI/DZ+P	ν	357
C₃H₃	cyclopropenyl rad.	MCSCF/3-21G	ν	358
C₃H₄	cyclopropene	4-31G	ν	58
C₃H₄	cyclopropene	6-31G**	ν, I	76
C₃H₄	cyclopropene	6-31G*, MP2	ν, I	79
C₃H₄	cyclopropene	DZ+P	ν, I	78
C₃H₄	CH₂CCH₂	3-21G	ν	136
C₃H₄	CH₂CCH₂	6-31G*	ν	291
C₃H₄	CH₃CCH	3-21G	ν	136
C₃H₄	CH₃CCH	6-31G*	ν	291
C₃H₄N	HCCCH₂NH₂	4-31G(N*)	ν, I	359, 360
C₃H₄O	CH₂=CHCHO	DZ, 4-31G	ν	69
C₃H₄O	CH₂=CHCHO	3-21G	ν	136
C₃H₄O	CH₂=CHCHO	4-31G	ν, I	66
C₃H₄O₂	malonaldehyde	DZ+P	ν	361
C₃H₅	CH₂=CHCH₂	3-21G/MCHF	ν	362
C₃H₅	cyclopropyl radical	4-31G	ν	363
C₃H₅N	CH₃CH₂CN	3-21G	ν	136
C₃H₆	CH₃CH=CH₂	4-31G	ν	60
C₃H₆	CH₃CH=CH₂	3-21G, MCHF	ν	362
C₃H₆	cyclopropane	4-31G	ν	58, 59, 363
C₃H₆	cyclopropane	3-21G	ν	136
C₃H₆	cyclopropane	STO3G, 4-31G, 6-31G**	ν	81
C₃H₆	CH₂CH₂CH₂	MCSCF/DZ	ν	364
C₃H₆	CH₂CH₂CH₂	DZ	ν	365
C₃H₆O	CH₃CH₂CHO	4-21G	ν, I	366
C₃H₆O	oxetane	4-21G	ν, I	367
C₃H₆O	acetone	3-21G	ν	136
C₃H₆O	epoxypropane	6-31G*	ν, I	368
C₃H₆O	epoxypropane	4-31G	ν, I	72
C₃H₆S	methylthirane	6-31G	ν, I	369
C₃H₇NO	CH₃CONHCH₃	4-31G	ν	370
C₃H₇NO	CH₃CONHCH₃	STO3G, 3-21G	I	371
C₃H₈	CH₃CH₂CH₃	4-31G	ν	58, 59
C₃H₈	CH₃CH₂CH₃	6-31G*, MP2	ν	133
C₃H₈Si	CH₂=Si(CH₃)₂	4-31G	ν, I	372
C₃H₉N₂O₂	(H₂C=NOH)₃	STO3G	ν	320
C₄Li₄	tetralithio-tetrahedrane	STO3G, 4-31G/5-21G(Li)	ν	373
C₄H₂	HCCCCH	DZ+P	ν, I	374
C₄H₂	HCCCCH	3-21G	ν	136
C₄H₄	cyclobutadiene	STO4G	ν, I	98, 100
C₄H₄	cyclobutadiene	6-31G*, MP2	ν, I	25
C₄H₄	cyclobutadiene	DZ+P	ν, I	95
C₄H₄	tetrahedrane	6-31G*, MP2	ν, I	114
C₄H₄	bicyclobutene	6-31G*, MP2	ν, I	115
C₄H₄	methylenecyclopropene	6-31G*	ν, I	106
C₄H₄	methylenecyclopropene	6-31G*, MP2	ν	79
C₄H₄	cyclobutyne	DZ, DZ+P	ν	375
C₄H₄N₂O₂	uracil	STO3G	ν	376
C₄H₄N₂O₂	uracil	4-31G	ν, I	377
C₄H₄O	CH₃CCCHO	DZ	ν	357
C₄H₆	1,3-butadiene	4-31G	ν	378
C₄H₆	1,3-butadiene	DZ+P	ν	379
C₄H₆	1,3-butadiene	4-31G	ν, I	66
C₄H₆	1,3-butadiene	3-21G	ν	136
C₄H₆	CH₃CCCH₃	3-21G	ν	136
C₄H₈	cyclobutane	4-21G	ν, I	380
C₄H₁₀	butane	6-31G	ν	381
C₅H₅Li	lithium cyclopentadienide	DZ, DZ+P	FC	382
C₅H₅N	pyridine	4-31G	ν, I	383

TABLE V (Continued)

formula	structure or name	type of calcn[a]	type[b]	ref	formula	structure or name	type of calcn[a]	type[b]	ref
C_5H_5N	pyridine	4-21G	ν, I	384	C_6H_6	benzene	4-21G	ν, I	67
$C_5H_5N_5O$	guanine	STO3G	ν	385	C_6H_6	triprismane	4-21G	ν, I	388
C_5H_6	[1.1.1]propellane	6-31G*	ν, I	103	C_8H_8	cubane	DZ	ν	389
C_5H_6O	CH_2=CHCOCH=CH_2	4-31G	FC	386	C_8H_8	cubane	DZ	ν, I	390
$C_5N_3O^-$	$(NC)_2C$=C(CN)O$^-$	STO3G	ν	387	$C_{10}H_8$	naphthalene	4-21G	ν, I	391
C_6N_4	$(NC)_2C$=C(CN)$_2$	STO3G	ν	387	C_nH_n	polyacetylene	STO3G, 4-31G	ν	392

[a] DZ means generally a true double-zeta basis set. It may also mean a valence-shell DZ set or a medium-sized basis set of a quality somewhat better than DZ. [b] ν: frequencies computed. FC: force constants reported only. I: intensities computed (IR and/or Raman).
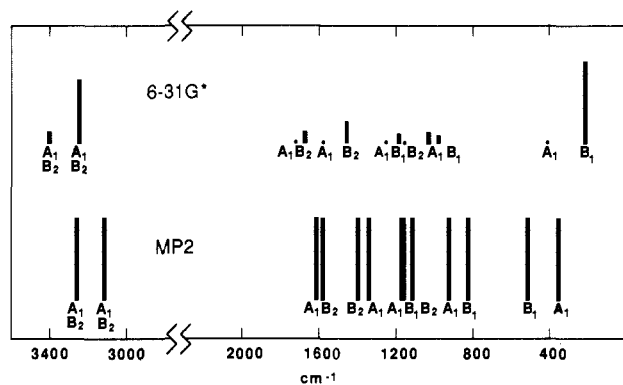
Figure 17. Calculated ab initio spectra of bicyclobutene.[115]

been calculated.[114,115] Tetrahedrane (XII) and bicyclobutene (XIII) are both of synthetic interest; the

XII   XIII

former because of its unique structure and the latter because of its unusual predicted geometry. Hehre and Pople[116] found that XIII is computed (STO-3G) to have a puckered structure rather than the expected planar one. This was given further support when the same result was obtained for XIII with the larger 4-31G basis set.[117] It is hoped that these computed spectra (Figures 16 and 17) will be of eventual use in the identification of XII and XIII.

VII. Compilation of ab Initio Vibrational Calculations

A compilation of ab initio vibrational calculations of molecules containing three or more atoms is given in Tables IV (inorganic) and V (organic). Only those molecules have been included for which the complete force constant matrix has been computed for at least one set of the vibrational symmetries (i.e., papers that report only computed diagonal force constants have been excluded). The order of molecules in the tables is that suggested by *Chemical Abstracts*.

VIII. Summary

It has been seen that ab initio quantum chemical calculations yield vibrational frequencies with the accuracy of 20–200 cm^{-1}, depending on the level of so-

phistication of the calculation. This accuracy, of course, can hardly compete with high-resolution experiments. Finer details of a theoretical spectrum must not be trusted, but the overall pattern is usually remarkably accurate and can aid in the identification of new species and in the interpretation of their experimental spectra.

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