Title

SYSTEMATIC STUDIES OF MOLECULAR VIBRATIONAL ANHARMONICITY AND VIBRATION-ROTATION INTERACTION BY SELF-CONSISTENT-FIELD HIGHER DERIVATIVE METHODS: APPLICATIONS TO ASYMMETRIC AND SYMMETRIC TOP AND LINEAR POLYATOMIC MOLECULES

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(Ph.D. Thesis)

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Applications to Asymmetric and Symmetric Top and Linear Polyatomic Molecules

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Abstract

Inclusion of the anharmonicity of molecular normal mode vibrations [i.e., the third and fourth (and higher) derivatives of a molecular Born-Oppenheimer potential energy surface] is necessary in order to theoretically reproduce experimental fundamental vibrational frequencies of a molecule. Although *ab initio* determinations of harmonic vibrational frequencies may give errors of only a few percent by the inclusion of electron correlation within a large basis set for small molecules, in general, molecular fundamental vibrational frequencies are more often available from high resolution vibration-rotation spectra. Recently developed analytic third derivatives methods for self-consistent-field (SCF) wavefunctions have made it possible to examine with previously unavailable accuracy and computational efficiency the anharmonic force fields of small molecules. In particular, cubic force constants, and quartic force constants by finite differences of cubic force constants, allow theoretical determination of a number of anharmonic molecular properties, including vibration-rotation interaction constants, vibrational anharmonic constants, fundamental

vibrational frequencies, quartic and sextic centrifugal distortion constants, and rotational constants which include zero-point vibrational and centrifugal distortion corrections, and vibrational and rotational ℓ-type doubling constants and rotational ℓ-type doubling constants.

Application is made here to a variety of asymmetric and symmetric top and linear polyatomic molecules in order to predict their anharmonic properties. Quadratic, cubic, and quartic force constants are evaluated for the molecules H_2O, H_2S, H_2CO, $HCO(^2A')$, $CH_2(^3B_1)$, $CH_2(^1A_1)$, $CH_2(^1B_1)$, C_2H_4, HCN, CO_2, N_2O, COS, C_2H_2, H_3^+, NH_3, and several isotopomers. For most molecules the anharmonic molecular constants which are available from experiments are well reproduced theoretically using DZP or better basis sets, at which level the calculated constants seem to have converged with respect to basis set expansion as well, although execptions have been noted. Particularly good agreement is found for fundamental vibrational frequencies obtained from CISD harmonic frequencies and SCF anharmonic corrections within the same basis set.

To my Parents

and

for Tami

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I. Introduction

It is well known[1-6] that at the *ab initio* self-consistent-field (SCF) level of theory, theoretically determined harmonic vibrational frequencies overestimate experimental fundamental vibrational frequencies by about 8-12% for ordinary (valence bonded) molecules. This deviation is attributed in most cases to (1) basis set incompleteness, (2) electron correlation effects, and (3) anharmonicity.

The recent theoretical development of analytical derivative methods[7-9] makes it possible to examine these errors in more detail. A near Hartree-Fock limit calculation of harmonic vibrational frequencies for H_2O by Amos[10] shows that there still exists about 7% deviation from the experimental harmonic frequencies. Therefore, the errors attributed to basis set incompleteness are, in fact, to a large degree intrinsic to SCF wavefunctions, at least for the wide variety of molecules which have been thoroughly studied.

A systematic study of configuration interaction wavefunctions including all single and double excitations (CISD) for the closed-shell molecules HCN, H_2CO, H_2O and CH_4 was carried out seven years ago.[2] The best agreement between theoretical and experimental harmonic vibrational frequencies is found by using CISD calculations in conjunction with a double-zeta (DZ) basis set. The average error of 2.0% is very satisfactory. One must realize, however, that this good agreement of vibrational frequencies is obtained at the sacrifice of the geometrical parameters. In general, both the bond lengths and bond angles of a molecule are predicted to be a few percent too large at the DZ–CISD level of theory compared to experimental values; this exaggeration of geometrical parameters compensates for the steepness of curvature of the potential energy function to give apparent better agreement of the harmonic vibrational frequencies. With double-zeta plus polarization (DZP) basis sets, CISD calculations produce much better agreement of the geometrical parameters, but, however, overestimate the harmonic vibrational frequencies by somewhat more, with an average error of 3.5%.

These observations suggest the necessity of calculations which include a larger part of the electron correlation. In this regard a study of CI harmonic vibrational frequencies including single, double, triple, and quadruple excitations (CISDTQ) for several small molecules [HF, N_2, CO, H_2O, NH_3, $CH_2(^1A_1)$ and CH_2 $(^3B_1)$] is under way in our laboratory.[12] It has been found so far that 1) the geometries of these molecules agree well with experimental results at the DZP–CISD and TZP–CISD levels of theory, but surprisingly, not as well when higher excitations are included; 2) harmonic vibrational frequencies at the DZP–CISDTQ and TZP–CISDTQ levels of theory are predicted to be 1–2% lower than the corresponding frequencies based on SCF wavefunctions but still 4–8% higher than experimental values[2]; and 3) double polarization functions, even at the CISDTQ level of theory, are necessary to reproduce experimental dipole moments correctly.

Other workers have recently reported studies of harmonic vibrational frequencies which include correlation through the use of second-order Möller-Plesset (many-body) perturbation theory [M(B)P(T)2]. Analytic second derivatives for MP2 wavefunctions have recently been reported.[13-14] Applications have been given to several small molecules using near-Hartree-Fock limit basis sets[15] for which it is found that theoretical harmonic vibrational frequencies are within a mean error of 1.5% of the corresponding experimental vibrational frequency. A comparison of vibrational frequencies for several medium-sized molecules[16] using both MP2 and CISD analytic second derivatives[17,18] has shown that these methods are quite similar in their abilities to predict both molecular structure and harmonic vibrational frequencies within a few percent of experimental values.

Other recent work in this laboratory[19] has involved determination of harmonic vibrational frequencies from finite differences of analytic gradients[20] of coupled cluster wavefunctions including all single and double excitations (CCSD)[21]; preliminary results indicate that CCSD wavefunctions give qualitatively similar results as CISDTQ wavefunctions with, for example, a DZP quality basis set. Thus several methods of including the effects of electron correlation have shown that some improvement may be gained in agreement with experimental vibrational frequencies by inclusion of a substantial fraction of the electronic correlation energy in the molecular wavefunction.[2,12,15,16,19]

The importance of studying anharmonicity in the vibrational-rotational states of polyatomic molecules has become more and more evident by advances in molecular laser spectroscopy of positive[22] and negative[23] molecular ions and clusters[24] and by progress in theoretical and experimental studies of the fine structure of the vibrational-rotational spectra of molecules during the last three decades. A number of *ab initio* studies of anharmonicity have been reported in the literature.[25-37] Most of these papers treat only vibrational anharmonicity, in particular cubic and quartic internal force constants in addition to quadratic force constants. These anharmonic force constants are usually obtained by a least squares fit to a polynomial expansion of the energy and/or lower energy derivatives with respect to internal coordinates.[11] Using recently developed analytic third derivatives of the SCF energy[38-40], anharmonic vibrational constants and vibration-rotation interaction constants have been reported for the H_2O and NH_3 molecules by Gaw and Handy.[36,37] The analytic third derivative method has been extended recently to general open-shell SCF wavefunctions[40] with applications to the vibration-rotation interaction constants (as well as the cubic force constants) of CH_2 ($^3B_1$), CH_2 ($^1B_1$), CH_2 ($^1A_1$), H_2CO ($^3A''$), H_2CO ($^1A''$), and H_2CO ($^3A'$), as well as to both closed- and open-shell two-configuration[41,42] (TC)SCF and pair-excited multi-configuration (PE-MC)SCF wavefunctions.[43]

This thesis represents a systematic study of vibrational anharmonic constants and various vibration-rotation interaction constants for a series of experimentally well-characterized asymmetric and symmetric top and linear polyatomic molecules. This work is the most thorough and systematic evaluation of the performance of analytic third derivatives of SCF wavefunctions for predicting anharmonic properties of small molecules now available. The results presented herein reconfirm the trends indicated by previous workers,[36-40] namely that the SCF cubic force field, as well as the quartic force field obtained from finite differences of the cubic force constants, shows surprisingly little variation with basis set; for most anharmonic molecular constants and properties, the values predicted via analytic SCF higher (i.e., third and fourth) derivatives seem to have converged with repect to basis set variation at the DZP (or better) basis level for most molecules. These results also show that the order of the vibrational anharmonic constants and various vibration-rotation interaction constants is of the order of 10^{-2} of the corresponding harmonic vibrational frequency or equilibrium rotational constant, respectively, as is anticipated by the perturbation theory treatment, and that the anharmonic constants are, in fact, also well reproduced by SCF wavefunctions with DZP or better basis sets. Particularly good agreement with experimental values of the various anharmonic constants is indicated when a CISD harmonic force field, i.e., vibrational and rotational constants, is coupled with and, therefore, corrected by the corresponding SCF cubic and/or quartic force constants computed with the same basis set.

Some limitations are also indicated by the results which are presented. First, one must exercise caution occasionally in the choice of a basis, depite the previously mentioned overall trend of small variation with basis. Second, for some molecules, caution is necessary in the analysis and interpretation of results as, for example, in the case of an asymmetric top which accidentally approximates a symmetric top, a quasi-linear molecule, a molecule exhibiting a strong Coriolis or vibrational anharmonic resonance (vide infra), etc. For these cases, the perturbation theory of non-interacting, well-separated rotational and vibrational energy levels on which these particular calculations are based breaks down.

The next section will serve as a review of the necessary theory and formulas which have been derived from perturbation theory for the calculation of anharmonic quantities in asymmetric and symmetric top and linear polyatomic molecules. The third section will briefly describe the procedures taken in this study, including the molecules chosen of each rotational type, descriptions of the basis sets employed, and a few comments regarding the methods used in practice for determining the quadratic, cubic, and quartic force fields of the molecules which have been examined. Finally, the data are presented, followed by appropriate discussions, including comparisons with the available experimental data.

II. The Evaluation of Various Vibration-Rotation Constants[44-50]

A. Energy expressions[49]

The vibration-rotation term values of a polyatomic molecule may be expressed empirically as the sum of a vibrational term which is independent of the rotational quantum numbers and a rotational term which is largely independent of the vibrational quantum numbers, that is,[49]

$$T(v,J) = G(v) + F_v(J) \quad . \tag{1}$$

The rotational term values $F_v(J)$ are interpreted as the eigenvalues of an effective rotational Hamiltonian which is slightly different for each vibrational state. For a molecule of the asymmetric top rotational type, the form of this Hamiltonian is[51-53]

$$\begin{aligned} H_{rot}/hc = {} & \sum_{\alpha} B_v^{(\alpha)} J_\alpha^2 + 1/4 \sum_{\alpha,\beta} (\tau'_{\alpha\alpha\beta\beta})_v J_\alpha^2 J_\beta^2 \\ & + \sum_{\alpha} \Phi_{\alpha\alpha\alpha} J_\alpha^6 + \sum_{\alpha\neq\beta} \Phi_{\alpha\alpha\beta} (J_\alpha^4 J_\beta^2 + J_\beta^2 J_\alpha^4) \\ & + \sum_{\alpha\neq\beta\neq\gamma} (J_\alpha^2 J_\beta^2 J_\gamma^2 + J_\gamma^2 J_\beta^2 J_\alpha^2) + \cdots \end{aligned} \tag{2}$$

where the summations of α and β go over the principal molecular rotational axes a, b, and c; J_a, J_b, and J_c are then components of the total angular momentum in units of $\hbar$; A_v, B_v, and C_v are the effective rotational constants; the $(\tau'_{\alpha\alpha\beta\beta})_v$ are the quartic centrifugal distortion constants as defined by Kivelson and Wilson[54] and the $\Phi_{\alpha\beta\gamma}$ are effective sextic centrifugal distortion constants[52] in cm^{-1}.

The rotational terms $F_v(J)$ of a symmetric top molecule may be fitted to a formula of the form[49]

$$\begin{aligned} F_v(J) &= B_v[J(J+1) - K^2] + A_v K^2 - \sum_t 2(A\zeta_t)_v k\ell_t \\ &- (D_J)_v [J(J+1)]^2 - (D_{JK})_v J(J+1) K^2 - (D_K)_v K^4 \\ &+ \sum_t (\eta_{tJ})_v J(J+1) k\ell_t + \sum_t (\eta_{tk})_v k^3\ell_t + \cdots \qquad (3) \end{aligned}$$

The first three terms are quadratic in the angular momenta, i.e. in J, the total rotational angular momentum; in k, the component of J along the principal molecular axis (with $K = |k|$); and in ℓ_t the vibrational angular momentum. Thus, the coefficients A_v, B_v, and $(A\zeta_t)_v$ may be thought of as effective rotational constants. The terms in the second and third lines of eq. (3) are quartic in the angular momenta, and the coefficients may be thought of as effective quartic centrifugal distortion constants. The terms which are sextic in the angular momenta are given by Aliev and Watson in eq. (35) of their paper[55] in an alternative form of the rotation-vibration Hamiltonian, namely, in terms of a cylindrical tensor representation of the components of the total angular momentum, $J_\pm = J_x \pm iJ_y$; nonetheless, the coefficients of their eq. (35) are the effective sextic centrifugal distortions of a symmetric top molecule. The first term of eq. (2) is more accurately written as

$$A_v J_z^2 + B_v (J_x^2 + J_y^2) \quad (4)$$

for a rigid rotor prolate symmetric top (A > B = C). For an oblate top (A = B > C), one should replace A by C in (4). One should also recall that, for a rigid rotor symmetric top for which the Hamiltonian (2) is truncated after the first term, namely (4), the first two terms of eq. (3) give exact eigensolutions for the rotational energy levels and that this is simplified from the case of the asymmetric top for which not even approximate solutions for the rotational term values exist in terms of the rotational angular momentum quantum numbers.

A linear polyatomic molecule is only one special case of a symmetric top molecule, for which A = 0 and B = C (note that the rotational constants A is the smallest valued rotational constant in this case). Most of the perturbation formulas which have been derived, therefore, for linear moolecules may be obtained from the corresponding more general relations for a symmetric top molecule by imposing the restrictions implied by symmetry and by the subsequent redefining of the rotational constants. The rotational term values $F_v(J)$ of a linear polyatomic molecule are then given in the form[50]

$$F_v(J) = B_v [J(J + 1) - \ell^2] - D_J [J(J + 1) - \ell^2]^2 + H_J [J(J + 1) - \ell^2]^3 + \cdots , \quad (5)$$

where ℓ is the total vibrational angular momentum ($\ell = \sum_t \ell_t$), B_v is the effective rotational constant, D_J is the effective quartic centrifugal distortion constant, and H_J is the effective sextic centrifugal distortion constant.

The vibrational term values G(v) of an asymmetric molecule are given by[49]

$$G(v) = \sum_r \omega_r(v_r + 1/2) + \sum_{r \geqslant s}\sum \chi_{rs}(v_r + 1/2)(v_s + 1/2) + \cdots , \tag{6}$$

where ω_r is the rth harmonic vibrational frequency and χ_{rs} are the vibrational anharmonic constants.

The vibrational term formula for a symmetric top molecule is[49]

$$G(v) = \sum_r \omega_r(v_s + 1/2\, d_r) + \sum_{r' \neq r} \chi_{rr'}(v_r + 1/2\, d_r)(v_{r'} + 1/2\, d_{r'}) + \sum_{t > t'} g_{tt'}\ell_t\ell_{t'} + \cdots \tag{7}$$

where subscripts r and r' denote either non-degenerate or degenerate normal modes and t and t' indicate degenerate normal modes only. In eq. (7) ω_r and $\omega_{r'}$ are harmonic frequencies, $\chi_{rr'}$ and $g_{tt'}$ are the vibrational anharmonic constants, and d_r is the degeneracy of the rth normal mode.

The vibrational term values G(v) of a linear polyatomic molecule are expressed as

$$G(v) = \sum_{r} \omega_r (v_r + \tfrac{1}{2} d_r) + \sum_{r \geq s} x_{rs} (v_r + \tfrac{1}{2} d_r)(v_s + \tfrac{1}{2} d_s)$$

$$+ \sum_{t \geq t'} x_{\ell_t \ell_{t'}} \ell_t \ell_{t'} + \cdots \qquad (8)$$

where all of the notation is as in eq. (7) for symmetric tops, except that $x_{\ell_t \ell_{t'}}$ labels the vibrational anharmonic constants involving only components of degenerate normal modes.

In order to follow the conventional treatment by Nielsen[45-48] and the previous communications[36-40], the dimensionless normal coordinate is defined as

$$q_r = \gamma_r^{1/2} Q_r \quad , \qquad (9)$$

where

$$\gamma_r = \lambda_r^{1/2} / \hbar = 2\pi c \omega_r / \hbar \quad . \qquad (10)$$

The vibrational energy is then expanded in terms of these dimensionless normal coordinates, q_r, as

$$V/hc = \tfrac{1}{2} \sum_{r} \omega_r q_r^2 + \frac{1}{6} \sum_{rst} \phi_{rst} q_r q_s q_t + \frac{1}{24} \sum_{rstu} \phi_{rstu} q_r q_s q_t q_u$$

$$+ \cdots \quad , \qquad (11)$$

where ϕ_{rst} and ϕ_{rstu} are the cubic and quartic anharmonic force constants, respectively. It should be noticed that the multiple summations in eq. (11) are unrestricted and that the ϕ's differ from Nielsen's original anharmonic k's by multiplicative factors.[49,56]

B. Vibration-rotation interaction constants[49,50,57]

For an asymmetric top the vibrational dependence of the effective rotational constant along the molecular b axis is given by[49]

$$B_v = B_e - \sum_r \alpha_r^B (v_r + 1/2) + \cdots \quad , \qquad (12)$$

where B_e is the equilibrium rotational constant, and the sum runs over all the normal modes. Of course, similar expressions hold for the vibrational dependence of A_v and C_v involving rotation about the molecular a and c axes, repspectively. In general the α_r^B are expected to have a magnitude of the order of 10^{-2} of the corresponding rotational constants.[58-61]

The vibrational dependences of the effective rotational constants for a prolate symmetric top molecule are given by[49]

$$B_v = B_e - \sum_r \alpha_r^B (v_r + 1/2\, d_r) + \cdots \qquad (13)$$

and

$$A_v = A_e - \sum_r \alpha_r^A (v_r + 1/2\, d_r) + \cdots \qquad (14)$$

where B_e and A_e are the two distinct equilibrium rotational constants of a prolate symmetric top molecule; α_r^B and α_r^A are the vibration-rotation interaction constants; and, as before, d_r is the degeneracy of the rth normal mode and the summation runs over all the normal modes. For an oblate top, A in eq. (14) should be replaced by C.

The vibrational dependence of the single degenerate effective rotational constant for a linear polyatomic molecule is given by[50]

$$B_v = B_e - \sum_r \alpha_r (v_r + \tfrac{1}{2} d_r) + \cdots \quad , \qquad (15)$$

where B_e is the equilibrium value of the rotational constant, the α_r are vibration-rotation interaction constants, and, again, the summation runs over all the normal modes.

Perturbation theory provides the formula for α_r^B for asymmetric tops as[49]

$$- \alpha_r^B = \frac{2B^2}{\omega_r} \left\{ \sum_\xi \frac{3[a_r^{(b\xi)}]^2}{4I_\xi} + \sum_{s \neq r} [\zeta_{r,s}^{(b)}]^2 \frac{3\omega_r^2 + \omega_s^2}{\omega_r^2 - \omega_s^2} \right.$$

$$\left. + \pi \left(\frac{c}{h}\right)^{1/2} \sum_s \phi_{rrs} \, a_s^{(bb)} \left(\frac{\omega_r}{\omega_s^{3/2}}\right) \right\} . \qquad (16)$$

In this perturbation formula, as well as in many others to come (*vide infra*), the rotational constants A, B, and C are the experimentally derived values which, of course, contain all of the effects due to zero-point vibrations, centrifugal distortion, etc. At a theoretically determined equilibrium geometry, $\mathbf{R}_e$, the rotational constants which are obtained are the equlibrium rotational constants A_e, B_e, and C_e of the non-vibrating molecule at its equilibrium geometry, $\mathbf{R}_e$ [i.e., the first term of eq. (12)]. Thus, in the calculation of α_r^B from eq. (16), for example, the leading factor in the calculations is, in fact, $2B_e^2/\omega_r$. The reader should bear this in mind throughout the remainder of the presentation of the equations as well as the discussions, since this subtle difference will provide some of the explanation for the small discrepancies between experimental and ab initio rotational constants and related values of vibration-rotation interaction constants.

The equilibrium rotational constants are defined by

$$B_e^{(\alpha)} = \frac{\hbar^2}{2hcI_\alpha} \quad , \tag{17}$$

and the inertial derivatives $a_r^{(\alpha\beta)}$ present in eq. (16) are defined as

$$a_r^{(\alpha\beta)} = \left(\frac{\partial I_{\alpha\beta}}{\partial Q_r}\right)_e \quad , \tag{18}$$

where $I_\alpha = I_{\alpha\alpha}$ and $I_{\alpha\beta}$ are the equilibrium moments and products of inertia. The Coriolis zeta constant $\zeta_{r,s}^{(\alpha)}$, which couples normal coordinates Q_r and Q_s through rotation about the α axis, is defined by

$$\zeta_{r,s}^{(\alpha)} = \sum_i [L_{ir}^{(\beta)} L_{is}^{(\gamma)} - L_{ir}^{(\gamma)} L_{is}^{(\beta)}] \quad , \tag{19}$$

where L is a matrix which transforms the normal coordinates to mass-weighted Cartesian coordinates. In eqs. (17)-(19), α, β, and γ are cyclic permutations of x, y, and z, and for α = z, x, y (i.e., a I^r representation)[51,62], the rotational constants $B_e^{(z)}$, $B_e^{(x)}$, and $B_e^{(y)}$ are those normally associated with the principal rotational axes a, b, and c, respectively, and are those traditionally labeled A, B, and C.

Perturbation calculations give the following formulas for the vibration-rotation interaction constants for a symmetric top[49] (s = non-degenerate mode, t = degenerate mode):

$$-\alpha_s^A = \frac{2A_e^2}{\omega_s}\Big\{\frac{3[a_s^{(zz)}]^2}{4I_A} + \sum_{s'\neq s}[\zeta_{s,s'}^{(z)}]^2\,\frac{3\omega_s^2+\omega_{s'}^2}{\omega_s^2-\omega_{s'}^2} + \pi\left(\frac{c}{h}\right)^{1/2}\sum_{s'}\phi_{sss'}\,a_{s'}^{(zz)}\,\frac{\omega_s}{\omega_{s'}^{3/2}}\Big] \tag{20}$$

$$-\alpha_t^A = \frac{2A_e^2}{\omega_t}\Big\{\frac{3[a_{t_a}^{(xz)}]^2}{4I_B} + \sum_{t'\neq t}[\zeta_{t_a t'_b}^{(z)}]^2\,\frac{3\omega_t^2+\omega_{t'}^2}{\omega_t^2-\omega_{t'}^2} + \pi\left(\frac{c}{h}\right)^{1/2}\sum_{s}\phi_{st_at_a}\,a_{s}^{(zz)}\,\frac{\omega_t}{\omega_{s}^{3/2}}\Big\} \tag{21}$$

$$-\alpha_s^B = \frac{2B_e^2}{\omega_s}\Big\{\frac{3[a_s^{(xx)}]^2+[a_s^{(xy)}]^2}{4I_B} + \sum_{t}\{[\zeta_{s,t_a}^{(y)}]^2+[\zeta_{s,t_a}^{(x)}]^2\}\,\frac{3\omega_s^2+\omega_t^2}{\omega_s^2-\omega_t^2} + \pi\left(\frac{c}{h}\right)^{1/2}\sum_{s'}\phi_{sss'}\,a_{s'}^{(xx)}\,\frac{\omega_s}{\omega_{s'}^{3/2}}\Big\} \tag{22}$$

$$-\alpha_t^B = \frac{2B_e^2}{\omega_t}\Big\{\frac{3[a_{t_a}^{(xz)}]^2}{8I_A} + \frac{3[a_{t_a}^{(xx)}]^2}{4I_B}$$

$$+ \tfrac{1}{2} \sum_{s} \{[\zeta^{(y)}_{s,t_a}]^2 + [\zeta^{(x)}_{s,t_a}]^2\} \frac{3\omega_t^2 + \omega_s^2}{\omega_t^2 - \omega_s^2}$$

$$+ \sum_{t'\neq t} \{[\zeta^{(y)}_{t_a,t'_a}]^2 + [\zeta^{(x)}_{t_a,t'_a}]^2 \} \frac{3\omega_t^2 + \omega_{t'}^2}{\omega_t^2 - \omega_{t'}^2}$$

$$+ \pi \left(\frac{c}{h}\right)^{1/2} \sum_{s} \phi_{st_at_a} a_s^{(xx)} \frac{\omega_t}{\omega_s^{3/2}}] . \qquad (23)$$

These formulas are written in a form that applies to all symmetric top molecules provided that the orientation of the doubly degenerate coordinates has been chosen to make $a^{(xz)}_{t_b} = 0$ and $\zeta^{(z)}_{t_a,t'_a} = 0$ for all t and t'.[49]

Perturbation theory gives the formulas for the vibration-rotation interaction constants α_r of a linear molecule as[50]

$$-\alpha_s = \frac{2B_e^2}{\omega_s} [\frac{3a_s^2}{4I_e} + \sum_{t} \zeta_{st}^2 \frac{3\omega_s^2 + \omega_t^2}{\omega_s^2 - \omega_t^2}$$

$$+ \pi\left(\frac{c}{h}\right)^{1/2} \sum_{s'} \phi_{sss'} a_{s'} \left(\frac{\omega_s}{\omega_{s'}^{3/2}}\right)] \qquad (24)$$

$$-\alpha_t = \frac{2B_e^2}{\omega_t} [\tfrac{1}{2} \sum_{s} \zeta_{st}^2 \frac{3\omega_t^2 + \omega_s^2}{\omega_t^2 - \omega_s^2}$$

$$+ \pi\left(\frac{c}{h}\right)^{1/2} \sum_{s} \phi_{stt} a_s \left(\frac{\omega_t}{\omega_s^{3/2}}\right)] \quad , \qquad (25)$$

where the subscript s and s' denote non-degenerate modes and t indicates a degenerate mode. One should again note the use of A_e and B_e, the equilibrium values of the rotational constants, in eqs. (20)-(25). At the theoretically determined equilibrium geometry, the equilibrium rotational constants are determined and used in the perturbation formulas above. It is most convenient, then, to deal with the various vibration-rotation interactions (vide infra) as corrections to this equilibrium rotational constant [as, for example, in eqs. (13)-(15)]. The parameters a_s are the normal coordinate derivatives of the equilibrium moment of inertia of a linear molecule, in analogy with eq. (18) for asymmetric and symmetric top molecules. For a linear molecule $I_{\alpha\alpha} = I_{\alpha\beta} = I_{\beta\beta}$, and, therefore, the superscripts are suppressed; the inertial derivatives are only evaluated for non-degenerate normal modes.

The Coriolis zeta constants ζ_{st}, which couple normal coordinates Q_s and Q_t through rotation about the x and y axes, have the following relationship for linear molecules:

$$\zeta_{st} = \zeta^{x}_{st_b} = -\zeta^{y}_{st_a} \quad . \tag{26}$$

It is useful to note that for a linear molecule the nonvanishing cubic force constants involving degenerate coordinates t are[57]

$$\phi_{st_at_a} = \phi_{st_bt_b} \tag{27}$$

$$\phi_{st_at'_a} = \phi_{st_bt'_b} \quad . \tag{28}$$

C. Coriolis resonance[46,47,50,63]

When two vibrational states of an asymmetric top molecule are accidentally degenerate, i.e., $\omega_r \simeq \omega_s$, the second term in eq. (16) due to Coriolis interactions is no longer valid since the treatment of such terms by perturbation theory is no longer adequate. This situation is known as Coriolis resonance, and in such a case the second term for resonating states in eq. (16) should be replaced[47] according to

$$[\zeta_{r,s}^{(b)}]^2 \frac{3\omega_r^2 + \omega_s^2}{\omega_r^2 - \omega_s^2} \rightarrow -\tfrac{1}{2}[\zeta_{r,s}^{(b)}]^2 \frac{(\omega_r - \omega_s)^2}{\omega_s(\omega_r + \omega_s)} \quad . \qquad (29)$$

One should notice that the Coriolis resonance can be observed between modes only when the corresponding ζ value does not vanish from symmetry conditions. This replacing of terms, or, rather, removal of offending terms, is not a solution to the problem of accidental near-degeneracy. A proper treatment would involve diagonalization of the 2x2 Hamiltonian matrix which couples the normal modes involved to give the exact vibrational energy eigenvalues.

For an accidental degeneracy of two different normal modes r and r' in a symmetric top molecule ($\omega_r \simeq \omega_{r'}$, where r and r' are either non-degenerate or degenerate normal modes and r ≠ r'), then the term (or terms) in eqs. (20)-(23) which contain $\omega_r - \omega_{r'}$ in their denominators are no longer valid for the description of the so-called Coriolis contribution to the vibration-rotation interaction constants. In this case, the modes r and r' are said to have a Coriolis resonance, and the offending terms are replaced accordingly. Thus, for the Coriolis interaction of two non-degenerate normal modes s and s' caused by rotation about the z axis, the second term of eq. (20) must be replaced in the case of resonance according to

$$[\zeta^{(z)}_{s,s'}]^2 \frac{3\omega_s^2 + \omega_{s'}^2}{\omega_s^2 - \omega_{s'}^2} \rightarrow -\tfrac{1}{2}\,[\zeta^{(z)}_{s,s'}]^2 \frac{(\omega_s - \omega_{s'})^2}{\omega_{s'}(\omega_s + \omega_{s'})} \qquad (30)$$

For two different degenerate normal modes coupled by a Coriolis interaction by rotation about the z axis, the second term of eq. (21) is replaced in the case of a resonance by[50]

$$[\zeta^{(z)}_{t_a,t'_b}]^2 \frac{3\omega_t^2 + \omega_{t'}^2}{\omega_t^2 - \omega_{t'}^2} \rightarrow -\tfrac{1}{2}\,[\zeta^{(z)}_{t_a,t'_b}]^2 \frac{(\omega_t - \omega_{t'})^2}{\omega_{t'}(\omega_t + \omega_{t'})} \qquad (31)$$

For the Coriolis interaction between a non-degenerate normal mode s and a degenerate normal mode t induced by rotation about the x or y axis, the second term of eq. (22) is replaced in the case of resonance by[50]

$$\{[\zeta^{(y)}_{s,t_a}]^2 + [\zeta^{(x)}_{s,t_a}]^2\} \frac{3\omega_s^2 + \omega_t^2}{\omega_s^2 - \omega_t^2}$$

$$\rightarrow \{[\zeta^{(y)}_{s,t_a}]^2 + [\zeta^{(x)}_{s,t_a}]^2\} \frac{(\omega_s - \omega_t)^2}{\omega_t(\omega_s + \omega_t)} \qquad (32)$$

and the third term in eq. (23) is replaced[50] by

$$\{[\zeta^{(y)}_{s,t_a}]^2 + [\zeta^{(x)}_{s,t_a}]^2\} \frac{3\omega_t^2 + \omega_s^2}{\omega_t^2 - \omega_s^2}$$

$$\rightarrow -\tfrac{1}{2}\,\{[\zeta^{(y)}_{s,t_a}]^2 + [\zeta^{(x)}_{s,t_a}]^2\} \frac{(\omega_t - \omega_s)^2}{\omega_s(\omega_t + \omega_s)} \qquad (33)$$

Lastly, for the Coriolis interaction between two different degenerate normal modes t and t' via rotation about the x or y axis, the fourth term of eq. (23) is replaced in the case of a Coriolis resonance by

$$\{[\zeta^{(y)}_{t_a,t'_a}]^2 + [\zeta^{(x)}_{t_a,t'_a}]^2\} \frac{3\omega_t^2 + \omega_{t'}^2}{\omega_t^2 - \omega_{t'}^2}$$

$$\rightarrow -\tfrac{1}{2}\{[\zeta_{t_a,t'_a}]^2 + [\zeta_{t_a,t'_a}]^2\} \frac{(\omega_t - \omega_{t'})^2}{\omega_{t'}(\omega_t + \omega_{t'})} \quad (34)$$

If the vibrational frequencies of two distinct normal modes s and t of a linear polyatomic molecule are accidentally degenerate ($\omega_s \simeq \omega_t$), then the second terms of eqs. (24) and (25) are no longer valid for describing the Coriolis contribution to vibration-rotation interaction. That is, the perturbation theory treatment of two such accidentally interacting states is no longer adequate. In this situation, the normal modes s and t are said to have a Coriolis resonance, and the offending terms are replaced[47] according to

$$\zeta_{st}^2 \frac{3\omega_s^2 + \omega_t}{\omega_s^2 - \omega_t^2} \rightarrow -\tfrac{1}{2}\zeta_{st}^2 \frac{(\omega_s - \omega_t)^2}{\omega_t(\omega_s + \omega_t)} \quad (35)$$

in eq. (24) and

$$\zeta_{st}^2 \frac{3\omega_t^2 + \omega_s^2}{\omega_t^2 - \omega_s^2} \rightarrow -\tfrac{1}{2}\zeta_{st}^2 \frac{(\omega_t - \omega_s)^2}{\omega_s(\omega_t + \omega_s)} \quad (36)$$

in eq. (25). Of course, a Coriolis resonance will only be observed between normal modes s and t if the corresponding value of the Coriolis constant ζ_{st} is non-vanishing from symmetry considerations. Note that in linear molecules s is always a non-degenerate normal mode and t is always a degenerate normal mode.

D. Centrifugal distortion constants[49-51,55]

The centrifugal distortion tensor of Wilson and Howard[64] is a term in the transformed Hamiltonian of the form

$$\sum_{\alpha\beta\gamma\delta} \tfrac{1}{4}\, \tau_{\alpha\beta\gamma\delta}\, J_\alpha J_\beta J_\gamma J_\delta \tag{37}$$

and is expressed as

$$\tau_{\alpha\beta\gamma\delta} = - \frac{\hbar^4}{2hcI_\alpha I_\beta I_\gamma I_\delta} \sum_k \frac{a_k^{(\alpha\beta)} a_k^{(\gamma\delta)}}{\lambda_k} \quad . \tag{38}$$

One should note that the quartic centrifugal distortion constants of eq. (38) depend only upon the quadratic (harmonic) part of the vibrational potential [see eqs. (10) and (11)][58] and are expected to be of the order of 10^{-4} of the corresponding rotational constants.[49,61] Kivelson and Wilson[54] and Watson[65,66] have shown that the only terms in the summation (37) which influence the rotational Hamiltonian to first order can be written in the form of the quartic centrifugal distortion constants $\tau'_{\alpha\alpha\beta\beta}$ in eq. (2), where

$$\tau'_{\alpha\alpha\beta\beta} = \tau_{\alpha\alpha\beta\beta} + 2\tau_{\alpha\beta\alpha\beta}(1-\delta_{\alpha\beta}) \quad . \tag{39}$$

In eqs. (37)-(39) the formulas are written in a form such that τ and τ' have units of cm^{-1}.

Following Aliev and Watson,[50,51,55] the rotational derivatives are defined as

$$B_k^{\alpha\beta} = - \frac{\hbar^3}{2h^{3/2}c^{3/2}\omega_k^{1/2}} \left[\frac{a_k^{(\alpha\beta)}}{I_\alpha I_\beta}\right] . \tag{40}$$

Watson[51] has proposed the use of the dimensionless parameter $C_k^{\alpha\beta}$ which is related to $B_k^{\alpha\beta}$ by[55,67]

$$C_k^{\alpha\beta} = - \frac{B_k^{\alpha\beta}}{\omega_k} , \tag{41}$$

in order to simplify the form of many relations involving vibration-rotation interaction.[51] Eq. (38) may then be rewritten in the following alternative forms using these newly defined parameters:

$$\tau_{\alpha\beta\gamma\delta} = - 2 \sum_k \frac{B_k^{\alpha\beta} B_k^{\gamma\delta}}{\omega_k} \tag{42}$$

$$\tau_{\alpha\beta\gamma\delta} = - 2 \sum_k \omega_k C_k^{\alpha\beta} C_k^{\gamma\delta} . \tag{43}$$

The rotational constants are then expressed with quartic centrifugal distortion corrections as

$$A' = A + 1/4\,(3\tau_{bcbc} - 2\tau_{caca} - 2\tau_{abab}) \tag{44}$$

$$B' = B + 1/4\,(3\tau_{caca} - 2\tau_{abab} - 2\tau_{bcbc}) \tag{45}$$

$$C' = C + 1/4\,(3\tau_{abab} - 2\tau_{bcbc} - 2\tau_{caca}) , \tag{46}$$

and the asymmetry parameter σ is defined as

$$\sigma = \frac{2A' - B' - C'}{B' - C'} \quad . \tag{47}$$

One should note that the convention used here is that in which the rotational constants corrected for quartic centrifugal distortion are labeled by primes (i.e., A', B', C') and that this is the opposite of the labeling used by Kivelson and Wilson[54]. The formulas given in eqs. (44)-(46) are general for the correction due to centrifugal distortion for any rotational constant; that is, one may equally well obtain A_e' from A_e, A_v' from A_v, etc. (and similarly for B and C) from these equations. In particular, the values of A_0', B_0', and C_0' (and the corresponding value for σ), that is, equilibrium rotational constants (vide supra) which are corrected for both zero-point vibration-rotation interaction (eq. (12), v=0) and quartic centrifugal distortion [eqs. (44)-(46)] are reported in the results and accompanying discussion which follow below; this is the result which is suggested by Kivelson and Wilson's treatment.[54]

The quartic centrifugal distortion constants appearing in the Kivelson-Wilson formalism[54] for an asymmetric top molecule are

$$D_J = -\frac{1}{32}\left[3\tau_{bbbb} + 3\tau_{cccc} + 2(\tau_{bbcc} + 2\tau_{bcbc})\right] \tag{48}$$

$$D_K = D_J - {}^1\!/_4\left[\tau_{aaaa} - (\tau_{aabb} + 2\tau_{abab}) - (\tau_{ccaa} + 2\tau_{caca})\right] \tag{49}$$

$$D_{JK} = - D_J - D_K - 1/4\,\tau_{aaaa} \tag{50}$$

$$R_5 = -\frac{1}{32}[\tau_{bbbb} - \tau_{cccc} - 2(\tau_{aabb} + 2\tau_{abab}) + 2(\tau_{ccaa} + 2\tau_{caca})] \tag{51}$$

$$R_6 = \frac{1}{64}[\tau_{bbbb} + \tau_{cccc} - 2(\tau_{bbcc} + 2\tau_{bcbc})] \tag{52}$$

$$\delta_J = -\frac{1}{16}(\tau_{bbbb} - \tau_{cccc}) \, . \tag{53}$$

In these formulas, $\tau_{\alpha\alpha\beta\beta}$ and $\tau_{\alpha\beta\alpha\beta}$ appear only in the form of $\tau_{\alpha\alpha\beta\beta} + 2\tau_{\alpha\beta\alpha\beta}(1-\delta_{\alpha\beta})$ as already described in eq. (39).

Watson[65,66] has shown that only five linear combinations of the six τ' constants can be determined from spectra. In his reduced form the five independent centrifugal distortion constants are related to the quantities defined above by

$$\Delta_J = D_J - 2R_6 \tag{54}$$

$$\Delta_{JK} = D_{JK} + 12R_6 \tag{55}$$

$$\Delta_K = D_K - 10R_6 \tag{56}$$

$$\delta_J = \delta_J \tag{57}$$

$$\delta_K = -2R_5 - \frac{4(2A - B - C)}{B - C} R_6 \quad . \tag{58}$$

In eq. (58) the rotational constants which are employed in the present implementation are the effective (i.e., zero-point corrected) constants which have also been corrected for quartic centrifugal distortion, namely A_0', B_0', and C_0', as is implied by Kivelson and Wilson[54] and as has been discussed previously (vide supra).

Using the centrifugal distortion tensor of eqs. (42)-(43), the quartic centrifugal distortion constants for a symmetric molecule are given by

$$D_J = -\frac{1}{32}(3\tau_{xxxx} + 3\tau_{yyyy} + 2\tau_{xxyy} + 4\tau_{xyxy}) \quad , \tag{59}$$

$$D_K = D_J - 1/4(\tau_{zzzz} - \tau_{zzxx} - \tau_{yyzz} - 2\tau_{xzxz} - 2\tau_{yzyz}) \quad , \tag{60}$$

and

$$D_{JK} = -D_J - D_K - 1/4\,\tau_{zzzz} \quad . \tag{61}$$

For a linear molecule, the inertial derivatives a_s defined by eq. (18) and following eq. (25) are used to redefine the rotational derivatives of eq. (35) for a linear molecule following Aliev and Watson[51,55] by

$$B_s = B_s^{xx} = B_s^{yy} = -\frac{\hbar^3}{2h^{3/2}c^{3/2}\omega_s^{1/2}}\left(\frac{a_s}{I_e^2}\right) \quad . \tag{62}$$

The quartic centrifugal distortion constant D_J is then expressed in terms of B_s and ω_s as

$$D_J = \tfrac{1}{2} \sum_s \frac{B_s^2}{\omega_s} , \qquad (63)$$

and the sextic centrifugal distortion constant H_J is given by

$$H_J = \frac{4D_J^2}{B_e} - 2B_e^2 \sum_s \frac{B_s^2}{\omega_s^3} - \frac{1}{6} \sum_{ss's''} \phi_{ss's''} \frac{B_s B_{s'} B_{s''}}{\omega_s \omega_{s'} \omega_{s''}} . \qquad (64)$$

In eqs. (63) and (64), the summations are only over totally symmetric normal modes.

In order to calculate the sextic centrifugal distortion constants of asymmetric and symmetric top molecules, additional parameters must be introduced. The parameters $b_k^{\alpha\beta\gamma}$ of Aliev and Watson[50,55] are defined as follows:

$$b_k^{\alpha\alpha\alpha} = \sum_\ell (\omega_\ell^{-2} + 2\omega_k^{-2})\, \omega_\ell^{1/2} B_\ell^{\alpha\alpha} B_\alpha \zeta_{\ell,k}^{(\alpha)} \qquad (65)$$

$$b_k^{\alpha\alpha\beta} = \sum_\ell (\omega_\ell^{-2} + 2\omega_k^{-2})\, \omega_\ell^{1/2} [B_\ell^{\alpha\alpha} B_\beta \zeta_{\ell,k}^{(\beta)} + 2B_1^{\alpha\beta} B_\alpha \zeta_{\ell,k}^{(\alpha)}] \qquad (66)$$

$$b_k^{xyz} = \sum_\ell (\omega_\ell^{-2} + 2\omega_k^{-2})\, \omega_\ell^{1/2} [B_\ell^{yz} B_x \zeta_{\ell,k}^{(x)} + B_\ell^{zx} B_y \zeta_{\ell,k}^{(y)}$$

$$+ B_{\ell}^{xy} B_z \zeta_{\ell,k}^{(z)}] \quad , \tag{67}$$

in which, in eqs. (65) and (66), α and β range over x, y, and z[37], and, in eq. (66), $\alpha \neq \beta$. Watson[51] has also defined a dimensionless higher-order Coriolis tensor $c_k^{\alpha\beta\gamma}$ related to $b_k^{\alpha\beta\gamma}$ according to

$$c_k^{\alpha\beta\gamma} = - \frac{b_k^{\alpha\beta\gamma}}{\omega_k^{1/2}} \quad . \tag{68}$$

The components of $c_k^{\alpha\beta\lambda}$ are given explicitly by Watson in eq. (124) of his review article[51] in terms of the harmonic vibrational frequencies (ω_k), rotational constants [$B_e^{(\alpha)}$], Coriolis coupling coefficients [$\zeta_{\ell,k}^{(\alpha)}$], and the coupling parameters $C_k^{\alpha\beta}$ [eq. (41)]; recall that α and β range over the principal rotational axes a, b, c.

The empirical expressions for the sextic centrifugal distortion constants of an asymmetric top molecule are[55]

$$H_J = \Phi_{600} + 2\Phi_{204} \tag{69}$$

$$H_{JK} = \Phi_{420} - 12\Phi_{204} + 2\Phi_{024} + 16\sigma\,\Phi_{006}$$

$$- 16\,(R_5 - 2\sigma R_6)\, s_{111} + 8(2A - B - C)\, s_{111}^2 \tag{70}$$

$$H_{KJ} = \Phi_{240} + \frac{10}{3}\Phi_{420} - 30\Phi_{204} - \frac{10}{3} H_{JK} \tag{71}$$

$$H_K = \Phi_{060} - \frac{7}{3}\Phi_{420} + 28\Phi_{204} + \frac{7}{3}H_{JK} \qquad (72)$$

$$h_J = \Phi_{402} + \Phi_{006} \qquad (73)$$

$$h_{JK} = \Phi_{222} - 10\Phi_{006} + 4\sigma\,\Phi_{204} + 2(D_{JK} - 2\sigma\,\delta_J - 4R_6)\,s_{111}$$

$$- 4(B - C)\,s_{111}^2 \qquad (74)$$

$$h_K = \Phi_{042} + \frac{4\sigma}{3}\Phi_{024} + (9 + \frac{32\sigma^2}{3})\,\Phi_{006}$$

$$+ 4[D_K - \frac{2\sigma}{3}R_5 + 2(1 + \frac{8\sigma^2}{3})\,R_6]\,s_{111}$$

$$+ (6 + \frac{10\sigma^2}{3})\,(B - C)\,s_{111}^2 \quad . \qquad (75)$$

The constants defined by eqs. (69)-(75) are the seven determinable combinations of the ten sextic centrifugal distortion constants.[52,55,58,66] To determine these constants, the equilibrium values of the rotational constants are used in eqs. (70), (74), and (75), and the parameter σ of eqs. (70), (74), and (75) is as defined by eq. (47) and is used as is discussed above.

The formulas for the Φ's as they appear in the orthorhombic

Hamiltonian (2) are presented in Table IV of Aliev and Watson's paper[55] and in Table 7 of Watson's paper.[51] The formulas given above are those obtained by Aliev and Watson[55] from the cylindrical tensor representation of the rotation-vibration Hamiltonian; their paper defines these parameters $\Phi_{2\ell,2m,2n}$ in terms of the $\Phi_{\alpha\beta\lambda}$ of the orthorhombic Hamiltonian (2) (see Table VII of ref. 55). The formulas above are derived from the particular treatment in which the parameter s_{111} of the first rotational contact transformation has been left free $[s_{111} = -4R_6/(B - C)]$.[66]

The sextic distortion constants for the particular case of a symmetric top molecule with C_{3v} symmetry are obtained similarly[55] by

$$H_J = \tfrac{1}{2}(\Phi_{xxx} + \Phi_{yyy}) \tag{76}$$

$$H_{JK} = 2\Phi_{zxx} - 3H_J \tag{77}$$

$$H_{KJ} = 2\Phi_{zzx} - 2H_{JK} - 3H_J \tag{78}$$

$$H_K = \Phi_{zzz} - H_{KJ} - H_{JK} - H_J \tag{79}$$

$$\Delta_3 = \tfrac{1}{2}(\Phi_{xxx} - \Phi_{yyy}) \quad , \tag{80}$$

where, for a symmetric top molecule, the formulas for the Φ's are also presented in Table IV of Aliev and Watson's paper[55] and in Table 7 of Watson's paper.[51]

At this point it would be appropriate to correct the rotational constants further to account for the effects of sextic centrifugal distortion. However, no formulas which define this correction (by, for example,the addition of terms to eqs. (44)-(46) which would involve the $\Phi_{\alpha\beta\lambda}$ coefficients) in terms of the available (i.e., previously determined) molecular constants have been given or are presently available.

E. Vibrational anharmonic constants[45-50]

The vibrational anharmonic constants appearing in the vibrational term formula (3) may be determined using the results of perturbation theory. For an asymmetric top molecule the general formulas are[49]

$$\chi_{rr} = \frac{1}{16}\,\phi_{rrrr} - \frac{1}{16}\sum_{s}\phi_{rrs}^{2}\,\frac{8\omega_r^2 - 3\omega_s^2}{\omega_s(4\omega_r^2 - \omega_s^2)} \qquad (81)$$

for the diagonal terms and

$$\begin{aligned}\chi_{rs} = {} & 1/4\,\phi_{rrss} - 1/4\sum_{t}\frac{\phi_{rrt}\phi_{tss}}{\omega_t} \\ & - 1/2\sum_{t}\phi_{rst}^{2}\,\frac{\omega_t(\omega_t^2 - \omega_r^2 - \omega_s^2)}{\Delta_{rst}} \\ & + \{A[\zeta_{r,s}^{(a)}]^2 + B[\zeta_{r,s}^{(b)}]^2 + C[\zeta_{r,s}^{(c)}]^2\}\left(\frac{\omega_r}{\omega_s} + \frac{\omega_s}{\omega_r}\right)\end{aligned} \qquad (82)$$

for the off-diagonal terms, where

$$\Delta_{rst} = (\omega_r + \omega_s + \omega_t)(\omega_r + \omega_s - \omega_t)$$

$$\times\ (\omega_r - \omega_s + \omega_t)(\omega_r - \omega_s - \omega_t) \quad . \qquad (83)$$

All of the summations in eqs. (81) and (82) are unrestricted.

For a symmetric top molecule the general formulas are[49]

$$\chi_{ss} = \frac{1}{16}\,\phi_{ssss} - \frac{1}{16}\sum_{s'} \phi^2_{sss'}\,\frac{8\omega_s^2 - 3\omega_{s'}^2}{\omega_{s'}(4\omega_s^2 - \omega_{s'}^2)} \qquad (84)$$

$$\chi_{tt} = \frac{1}{16}\,\phi_{tttt} - \frac{1}{16}\sum_{s} \phi^2_{stt}\,\frac{8\omega_t^2 - 3\omega_s^2}{\omega_s(4\omega_t^2 - \omega_s^2)}$$

$$- \frac{1}{16}\sum_{t'} \phi^2_{ttt'}\,\frac{8\omega_t^2 - 3\omega_{t'}^2}{\omega_{t'}(4\omega_t^2 - \omega_{t'}^2)} \qquad (85)$$

$$g_{tt} = -\frac{1}{48}\,\phi_{tttt} - \frac{1}{16}\sum_{s} \phi^2_{stt}\,\frac{\omega_s}{4\omega_t^2 - \omega_s^2}$$

$$+ \frac{1}{16}\sum_{t'} \phi^2_{ttt'}\,\frac{8\omega_t^2 - \omega_{t'}^2}{\omega_{t'}(4\omega_t^2 - \omega_{t'}^2)}$$

$$+ A[\zeta^{(z)}_{t_a,t_b}]^2 \ , \qquad (86)$$

for the diagonal terms and

$$\chi_{ss'} = 1/4\,\phi_{sss's'} - 1/4 \sum_{s''} \frac{\phi_{sss''}\phi_{s''s's'}}{\omega_{s''}} - 1/2 \sum_{s''} \phi_{ss's''} \frac{\omega_{s''}(\omega_{s''}^2 - \omega_s^2 - \omega_{s'}^2)}{\Delta_{ss's''}} + A\,[\zeta_{s,s'}^{(z)}]^2 \left(\frac{\omega_s}{\omega_{s'}} + \frac{\omega_{s'}}{\omega_s}\right) \tag{87}$$

$$\chi_{st} = 1/4\,\phi_{sstt} - 1/4 \sum_{s'} \frac{\phi_{sss'}\,\phi_{s'tt}}{\omega_{s'}} - 1/2 \sum_{t'} \phi_{stt'}^2 \frac{\omega_{t'}(\omega_{t'}^2 - \omega_s^2 - \omega_t^2)}{\Delta_{stt'}} + B\,\{[\zeta_{s,t_a}^{(x)}]^2 + [\zeta_{s,t_a}^{(y)}]^2\} \left(\frac{\omega_s}{\omega_t} + \frac{\omega_t}{\omega_s}\right) \tag{88}$$

$$\chi_{tt'} = \frac{1}{8}\,(\phi_{t_a t_a t'_a t'_a} + \phi_{t_a t_a t'_b t'_b}) - 1/4 \sum_{s} \frac{\phi_{stt}\phi_{st't'}}{\omega_s} - 1/4 \sum_{s} \phi_{stt'}^2 \frac{\omega_s(\omega_s^2 - \omega_t^2 - \omega_{t'}^2)}{\Delta_{stt'}} - 1/2 \sum_{t''} \phi_{tt't''}^2 \frac{\omega_{t''}(\omega_{t''}^2 - \omega_t^2 - \omega_{t'}^2)}{\Delta_{tt't''}} + \{1/2\,A[\zeta_{t_a,t'_b}^{(z)}]^2 + B[\zeta_{t_a,t'_a}^{(y)}]^2\} \left(\frac{\omega_t}{\omega_{t'}} + \frac{\omega_{t'}}{\omega_t}\right) \tag{89}$$

$$g_{tt'} = \tfrac{1}{2} \sum_{s} \phi^{2}_{stt'} \frac{\omega_s \omega_t \omega_{t'}}{\Delta_{stt'}} - \sum_{t''} \phi^{2}_{tt't''} \frac{\omega_s \omega_{t'} \omega_{t''}}{\Delta_{tt't''}}$$

$$- 2B \, [\zeta^{(y)}_{t_a, t'_a}]^{2} + A \, [\zeta^{(z)}_{t_a, t'_b}]^{2} + 2A \, \zeta^{(z)}_{t_a, t_b} \, \zeta^{(z)}_{t'_a, t'_b} \qquad (90)$$

for the off-diagonal terms. All of the summations in eqs. (84)-(90) are unrestricted, however, as previously, the index s runs only over non-degenerate normal modes and the index t runs only over degenerate normal modes.

For a linear polyatomic molecule the general formulas are[50]

$$\chi_{ss} = \frac{1}{16} \phi_{ssss} - \frac{1}{16} \sum_{s'} \phi^{2}_{sss'} \frac{8\omega_s^{2} - 3\omega_{s'}^{2}}{\omega_{s'}(4\omega_s^{2} - \omega_{s'}^{2})} \qquad (91)$$

$$\chi_{tt} = \frac{1}{16} \phi_{tttt} - \frac{1}{16} \sum_{s} \phi^{2}_{stt} \frac{8\omega_t^{2} - 3\omega_s^{2}}{\omega_s \, (4\omega_t^{2} - \omega_s^{2})} \qquad (92)$$

$$\chi_{\ell_t \ell_t} = - \frac{1}{48} \phi_{tttt} - \frac{1}{16} \sum_{s} \phi^{2}_{stt} \frac{\omega_s}{(4\omega_t^{2} - \omega_s^{2})} \qquad (93)$$

for the diagonal terms and

$$\chi_{ss'} = \frac{1}{4} \phi_{sss's'} - \frac{1}{4} \sum_{s''} \phi_{sss''} \phi_{s''s's'} \frac{1}{\omega_{s''}}$$

$$- \tfrac{1}{2} \sum_{s''} \phi^{2}_{ss's''} \frac{\omega_{s''} \, (\omega_{s''}^{2} - \omega_s^{2} - \omega_{s'}^{2})}{\Delta_{ss's''}} \qquad (94)$$

$$\chi_{st} = 1/4\phi_{sstt} - 1/4 \sum_{s'} \phi_{sss'} \phi_{s'tt} \frac{1}{\omega_{s'}} - 1/2 \sum_{t'} \phi^2_{stt'} \frac{\omega_{t'} (\omega^2_{t'} - \omega^2_s - \omega^2_t)}{\Delta_{stt'}} + B_e \zeta^2_{st} [\frac{\omega_s}{\omega_t} + \frac{\omega_t}{\omega_s}] \qquad (95)$$

$$\chi_{tt'} = \frac{1}{8} (\phi_{t_a t_a t'_a t'_a} + \phi_{t_a t_a t'_b t'_b}) - 1/4 \sum_s \phi_{stt} \phi_{st't'} \frac{1}{\omega_s} - 1/4 \sum_s \phi^2_{stt'} \frac{\omega_s (\omega^2_s - \omega^2_t - \omega^2_{t'})}{\Delta_{stt'}} \qquad (96)$$

$$\chi_{\ell_t \ell_{t'}} = 1/2 \sum_s \phi^2_{stt'} \frac{\omega_s \omega_t \omega_{t'}}{\Delta_{stt'}} \qquad (97)$$

for the off-diagonal terms. The denominator $\Delta_{rr'r''}$ in eqs. (87), (90), and (94)-(96) is that defined in general by eq. (83).

F. Anharmonic resonance[46,47]

If either of the relationships (98) or (99) is satisfied accidentally for an asymmetric top molecule,

$$2\omega_r \approx \omega_s \text{ and } \phi_{rrs} \neq 0 \qquad (98)$$

$$\omega_r + \omega_s \approx \omega_t \quad \text{and} \quad \phi_{rst} \neq 0 \qquad (99)$$

the quantities χ_{rr} and χ_{rs} described in the preceding section may become indefinitely large and, thus, the method described above, which is based on perturbation theory, will fail. This phenomenon is known as vibrational anharmonic resonance[47], and the case given in eq. (98) is generally referred to as Fermi-Dennison[68,69] resonance.

The component of the diagonal terms [eq. (81)] which contains ϕ^2_{rrs} as a coefficient may be factored as[46,47]

$$\phi^2_{rrs} \frac{8\omega_r^2 - 3\omega_s^2}{\omega_s(4\omega_r^2 - \omega_s^2)} = \tfrac{1}{2}\,\phi^2_{rrs} \left[\frac{1}{2\omega_r + \omega_s} - \frac{1}{2\omega_r - \omega_s} + \frac{4}{\omega_s}\right] . \qquad (100)$$

When the anharmonic resonance $2\omega_r \approx \omega_s$ occurs, the resonating terms are replaced[47] according to

$$\phi^2_{rrs} \frac{8\omega_r^2 - 3\omega_s^2}{\omega_s(4\omega_r^2 - \omega_s^2)} \rightarrow \tfrac{1}{2}\,\phi^2_{rrs} \left[\frac{1}{2\omega_r + \omega_s} + \frac{4}{\omega_s}\right] \quad . \ (101)$$

Similarly the component of the off-diagonal terms [eq. (82)] which has ϕ^2_{rst} as a coefficient may be factored into

$$\phi^2_{rst} \frac{\omega_t(\omega_t^2 - \omega_r^2 - \omega_s^2)}{(\omega_r + \omega_s + \omega_t)\,(\omega_r + \omega_s - \omega_t)\,(\omega_r - \omega_s + \omega_t)\,(\omega_r - \omega_s - \omega_t)}$$

$$= \tfrac{1}{4}\,\phi^2_{rst} \left[\frac{1}{\omega_r + \omega_s + \omega_t} - \frac{1}{\omega_r + \omega_s - \omega_t} + \frac{1}{\omega_r - \omega_s + \omega_t}\right.$$

$$- \frac{1}{\omega_r - \omega_s - \omega_t}] \qquad (102)$$

Thus, if $\omega_r + \omega_s \simeq \omega_t$, the resonating terms should be replaced[47] according to

$$\phi^2_{rst} \frac{\omega_t(\omega^2_t - \omega^2_r - \omega^2_s)}{\Delta_{rst}} \rightarrow {}^1\!/_4\, \phi^2_{rst} [\frac{1}{\omega_r + \omega_s + \omega_t} + \frac{1}{\omega_r - \omega_s + \omega_t} - \frac{1}{\omega_r - \omega_s - \omega_t}] \quad . \qquad (103)$$

The components of the diagonal vibrational anharmonic terms for a symmetric top molecule [eqs. (84)-(86)] and for a linear molecule [eqs. (91)-(93)] which have $\phi^2_{rrr'}$ as a coefficient may be factored just as eq. (100) for asymmetric top molecules into

$$\phi^2_{rrr'} \frac{8\omega^2_r - 3\omega^2_{r'}}{\omega_{r'}(4\omega^2_r - \omega^2_{r'})} = {}^1\!/_2\, \phi^2_{rrr'} [\frac{1}{2\omega_r + \omega_{r'}} - \frac{1}{2\omega_r - \omega_{r'}} + \frac{4}{\omega_{r'}}] \qquad (104)$$

where r and r', denoting either non-degenerate or degenerate normal modes, replace r and s in eq. (100);

$$\phi^2_{rrr'} \frac{\omega_{r'}}{4\omega^2_r - \omega^2_{r'}} = - {}^1\!/_2\, \phi^2_{rrr'} [\frac{1}{2\omega_r + \omega_{r'}} - \frac{1}{2\omega_r - \omega_{r'}}] \quad ; \qquad (105)$$

and

$$\phi^2_{ttt'} \frac{8\omega_t^2 - \omega_{t'}^2}{\omega_{t'}(4\omega_t^2 - \omega_{t'}^2)} = -\tfrac{1}{2}\,\phi^2_{ttt'}\left(\frac{1}{2\omega_t + \omega_{t'}} - \frac{1}{2\omega_t - \omega_{t'}} - \frac{4}{\omega_{t'}}\right) \quad (106)$$

If an anharmonic resonance ($2\omega_r \approx \omega_{r'}$) occurs, the resonating terms should be replaced according to

$$\phi^2_{rrr'} \frac{8\omega_r^2 - 3\omega_{r'}^2}{\omega_{r'}(4\omega_r^2 - \omega_{r'}^2)} \rightarrow \tfrac{1}{2}\,\phi^2_{rrr'}\left[\frac{1}{2\omega_r + \omega_{r'}} + \frac{4}{\omega_{r'}}\right] \quad (107)$$

in eqs. (84)-(86), (91), and (92);

$$\phi^2_{rrr'} \frac{\omega_{r'}}{4\omega_r^2 - \omega_{r'}^2} \rightarrow -\tfrac{1}{2}\,\phi^2_{rrr'}\left[\frac{1}{2\omega_r + \omega_{r'}}\right] \quad , (108)$$

in eqs. (86) and (93); and

$$\phi^2_{ttt'} \frac{8\omega_r^2 - \omega_{r'}^2}{\omega_{t'}(4\omega_t^2 - \omega_{r'}^2)} \rightarrow -\tfrac{1}{2}\,\phi^2_{ttt'}\left(\frac{1}{2\omega_r + \omega_{r'}} + \frac{4}{\omega_{r'}}\right) \quad (109)$$

in eq. (86).

Similarly, the components of the off-diagonal terms [eqs. (87)-(90) and (94)-(97)] which have $\phi^2_{rr'r''}$ as a coefficient may be factored into

$$\phi^2_{rr'r''} \frac{\omega_{r''}\,(\omega^2_{r''} - \omega^2_r - \omega^2_{r'})}{(\omega_r + \omega_{r'} + \omega_{r''})\,(\omega_r + \omega_{r'} - \omega_{r''})\,(\omega_r - \omega_{r'} + \omega_{r''})\,(\omega_r - \omega_{r'} - \omega_{r''})}$$

$$= 1/4\, \phi^2_{rr'r''} \left[\frac{1}{\omega_r + \omega_{r'} + \omega_{r''}} - \frac{1}{\omega_r + \omega_{r'} - \omega_{r''}} + \frac{1}{\omega_r - \omega_{r'} + \omega_{r''}} - \frac{1}{\omega_r - \omega_{r'} - \omega_{r''}}\right] \tag{110}$$

and

$$\phi^2_{rr'r''} \frac{\omega_r \omega_{r'} \omega_{r''}}{(\omega_r + \omega_{r'} + \omega_{r''})\,(\omega_r + \omega_{r'} - \omega_{r''})\,(\omega_r - \omega_{r'} + \omega_{r''})\,(\omega_r - \omega_{r'} - \omega_{r''})}$$

$$= \frac{1}{8}\, \phi^2_{rr'r''} \left[\frac{1}{\omega_r + \omega_{r'} + \omega_{r''}} - \frac{1}{\omega_r + \omega_{r'} - \omega_{r''}} - \frac{1}{\omega_r - \omega_{r'} + \omega_{r''}} + \frac{1}{\omega_r - \omega_{r'} - \omega_{r''}}\right]. \tag{111}$$

If the resonance $\omega_r + \omega_{r'} \simeq \omega_{r''}$ occurs, the resonating terms should be replaced according to

$$\phi^2_{rr'r''} \frac{\omega_{r''}(\omega^2_{r''} - \omega^2_r - \omega^2_{r'})}{\Delta_{rr'r''}} \to 1/4\, \phi^2_{rr'r''} \left[\frac{1}{\omega_r + \omega_{r'} + \omega_{r''}} + \frac{1}{\omega_r - \omega_{r'} + \omega_{r''}} - \frac{1}{\omega_r - \omega_{r'} - \omega_{r''}}\right] \tag{112}$$

in eqs. (87)-(89) and (94)-(96) and

$$\phi^2_{rr'r''} \frac{\omega_r \omega_{r'} \omega_{r''}}{\Delta_{rr'r''}} \rightarrow \frac{1}{8} \phi^2_{rr'r''} \left[\frac{1}{\omega_r + \omega_{r'} + \omega_{r''}} - \frac{1}{\omega_r - \omega_{r'} + \omega_{r''}} + \frac{1}{\omega_r - \omega_{r'} - \omega_{r''}} \right] \qquad (113)$$

respectively. One should recall that $\Delta_{rr'r''}$ in eqs. (103), (112), and (113) has been defined previously by eq. (83).

G. Fundamental vibrational frequencies[44]

The fundamental vibrational frequencies ν_r of an asymmetric top molecule are obtained from harmonic frequencies ω_r and anharmonic constants χ_{rs} defined in the preceding sections by

$$\nu_r = \omega_r + 2\chi_{rs} + \tfrac{1}{2} \sum_{s \neq r} \chi_{rs} \quad . \qquad (114)$$

The fundamental frequencies are those which correspond most closely with those obtained from high-resolution (infra-red, Raman, microwave, etc.) vibration-rotation spectra.

The fundamental frequencies of a symmetric top molecule are obtained similarly from the harmonic frequencies and the anharmonic vibrational constants using a more general formula of the form of eq. (114) which takes explicit account of the degeneracies within normal modes which exist in symmetric top molecules as follows:

$$\nu_r = \omega_r + x_{rr} (1 + d_r) + \tfrac{1}{2} \sum_{r' \neq r} \chi_{rr'} d_{r'} + g_{rr} \quad , \qquad (115)$$

where d_r is the degeneracy of normal mode r and g_{rr} is zero for non-degenerate modes.

The fundamental frequencies of a linear molecule are obtained from the harmonic frequencies and the anharmonic constants in exactly the same way as for the more general symmetric top, with the exception of the anharmonic vibrational constants involving only degenerate modes, which are labelled as $\chi_{\ell_r \ell_r}$ as indicated previously, so that

$$\nu_r = \omega_r + \chi_{rr} (1 + d_r) + {}^1\!/_2 \sum_{r' \neq r} \chi_{rr'} d_{r'} + \chi_{\ell_r \ell_r} \quad , \quad (116)$$

where $\chi_{\ell_r \ell_r}$ is also zero for non-degenerate modes.

H. Vibrational ℓ-type doubling constants.[50,61,70-72]

Vibrational ℓ-doubling is an effective interaction between two otherwise degenerate vibrational wavefunctions differing only in the ℓ-quantum numbers such that $\Delta \ell_t = +1$, $\Delta \ell_{t'} = -1$. The expression for the vibrational ℓ-doubling constant in a symmetric top molecule is obtained as

$$r_{tt'} = - \sum_s \phi^2_{stt'} \frac{\omega_s (\omega_s^2 - \omega_t^2 - \omega_{t'}^2)}{2\Lambda_{stt'}}$$

$$- \sum_{t''} \frac{\phi_{ttt''} \phi_{t't't''}}{2\omega_{t''}} + {}^1\!/_4 (\phi_{t_a t_a t'_a t'_a} - \phi_{t_a t_a t'_b t'_b})$$

$$- A\,[\zeta_{tt'}^{(z)}]^2 \; \frac{\omega_t^2 + \omega_{t'}^2}{\omega_t \omega_{t'}} \qquad (117)$$

where $\Delta_{stt'}$ is already defined in eq. (83).

The vibrational energy levels of a linear polyatomic molecule may also be perturbed by vibrational ℓ-type doubling if two or more doubly degenerate vibrational modes are excited. The expression for the vibrational ℓ-doubling constant for a linear molecule is given by

$$r_{tt'} = - \sum_s \phi_{stt'}^2 \frac{\omega_s(\omega_s^2 - \omega_t^2 - \omega_{t'}^2)}{2\Delta_{stt'}}$$

$$+ \tfrac{1}{4}(\phi_{t_a t_a t'_a t'_a} - \phi_{t_a t_a t'_b t'_b}) \quad , \qquad (118)$$

where $\Delta_{stt'}$ is as defined by eq. (83).

I. Rotational ℓ-type doubling constants.[49,50,61,73,74]

For any symmetric-top molecule the k=ℓ= ± 1 levels in a degenerate vibrational state are split by a second-order vibration-rotation interaction into a doublet which is referred to as the rotational ℓ-type doubling. Perturbation calculations have been described by both Grenier-Besson[74] and Oka.[61] Their results give the following formula for the ℓ-type doubling constant q_t for C_{3v} molecules:

$$q_t = \frac{2B^2}{\omega_t} \{ - \frac{3[a_{t_a}^{(xz)}]^2}{4I_A} + \sum_s \{[\zeta_{s,t_a}^{(y)}]^2 - [\zeta_{s,t_a}^{(x)}]^2\} \frac{3\omega_t^2 + \omega_s^2}{\omega_t^2 - \omega_s^2}$$

$$+ 2\pi \left(\frac{c}{h}\right)^{1/2} \sum_{t'} \phi_{t_a t_a t'_a} a^{(yy)}_{t'_a} \frac{\omega_t}{\omega_{t'}^{3/2}} \} \qquad (119)$$

This equation may be applied to a molecule belonging to any symmetric-top point goup of which C_{3v} is a subgroup. Molecules with fourfold axes require a different formula.

It should be realized that rotational ℓ-type doubling constants must be expected to show both a dependence on the vibrational quantum numbers v_r and the rotational quantum numbers J and K of the form

$$q_t \rightarrow q_t^{(e)} + q_t^{(J)} J(J + 1) + q_t^{(K)} (K - \ell_t^2)$$

$$+ \sum_r q_t^{(v)} (v_r + \frac{d_r}{2}) + \cdot \cdot \cdot \qquad (120)$$

In the present study only the leading term $q_t^{(e)}$ is considered, although there have occasionally been observations of the vibrational and rotational dependences. In fact, eq. (119) only applies strictly to $q_t^{(e)}$.

The rotational ℓ-type doubling constant q_t associated with a degenerate normal mode vibration ω_t of a linear molecule has also been observed to have v, J, and K dependence, but in the present study only the contributions due to the centrifugal distortion are considered using the formulation by Watson[73]

$$q_t \rightarrow q_t^{(e)} + q_t^{(J)} J(J + 1) + q_t^{(K)} (K \pm 1)^2 \ . \qquad (121)$$

The $q_t^{(e)}$ values are given by

$$q_t^{(e)} = -\left(\frac{2B_e^2}{\omega_t}\right) \sum_s \zeta_{st}^2 \frac{3\omega_t^2 + \omega_s^2}{\omega_t^2 - \omega_s^2} \quad , \qquad (122)$$

and the formulas for $q_t^{(J)}$ and $q_t^{(K)}$ are presented in Table V of Watson's paper.[73]

III. Test Molecules and Basis Sets

In order to study the anharmonic properties of asymmetric top molecules, we have chosen the molecules H_2O, H_2S, H_2CO, HCO, $CH_2(^3B_1)$, $CH_2(^1A_1)$, $CH_2(^1B_1)$, C_2H_4, and their isotopic variants. For most of these molecules, the anharmonic rotational and vibrational behaviour has been well-described experimentally (*vide infra*). In order to determine the effects on the calculated anharmonicity of a change in basis set, we have chosen four basis sets, of double-zeta (DZ), triple-zeta (TZ), double-zeta plus polarization (DZP), and triple-zeta plus polarization (TZP) quality. The DZ basis is derived from the primitive gaussian set of Huzinaga[75] which is contracted to form a (9s5p/4s2p) set of functions for carbon, nitrogen, and oxygen, an (11s7p/6s4p) set on sulfur, and a (4s/2s) set on hydrogen, as suggested by Dunning.[76,77] The TZ basis consists of the same primitive functions[75] which are more loosely contracted to give a (9s5p/5s3p) basis for carbon and oxygen, an (11s7p/7s5p) basis for sulfur and a (4s/3s) basis for hydrogen. For the DZP and TZP bases, a single set of polarization functions, consisting of six cartesian d-type gaussian functions for each heavy atom, with exponents $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, $\alpha_d(O) = 0.85$, $\alpha_d(S) = 0.75$, or a set of p-type functions for hydrogen, $\alpha_p(H) = 0.75$, was added to the DZ and TZ bases, respectively.

The geometries of all of the test molecules were completely optimized with each of the four basis sets at both the SCF and CISD levels of theory using analytic gradient methods[1,5], in conjunction with a Newton-Raphson optimization scheme, such that residual gradients were less than 10^{-7} hartree/bohr (or radian). Harmonic vibrational frequencies were determined analytically for SCF wavefunctions[78-80] and by finite differences of analytic gradients for CISD wavefunctions.[81] Cubic force constants were determined analytically[38-40] and quartic force constants by finite differences of third derivatives for SCF wavefunctions. The rotational and vibrational anharmonic constants were then evaluated using the various formulas presented in the previous section.

As test molecules of symmetric-top type, H_3^+, D_3^+, NH_3, and ND_3 were chosen. The equlibrium geometries and harmonic vibrational frequencies of the parent molecules were determined as above in conjunction with the analytic SCF first and second and CISD first derivative methods, within each of the four basis sets already designated.

The linear polyatomic molecules chosen for inclusion in the systematic study of anharmonicity are HCN, DCN, CO_2, N_2O, COS, and C_2H_2. In this case, the primitive functions as they are published by Huzinaga[75] were employed, since the more commonly used tabulation of Dunning and Hay[77] contains a minor typographical error; namely, the second most diffuse s exponent of sulfur should be 0.4264[75]. Otherwise, the basis sets and optimization methods were unchanged for this set of molecules as well.

Finite difference calculations were performed to obtain SCF fourth and CISD second derivatives. Calculations of SCF third and CISD first derivatives were performed after taking both positive and negative displacements of the individual atomic Cartesian coordinates; the displacements used were 0.0001 bohr for the determination of SCF fourth derivatives and 0.001 bohr for CISD second derivatives. These small displacements were chosen to insure that the potential energy surface near the theoretical equilibrium geometry was being properly described. Descriptions of properties of potential energy surfaces which depend on the magnitude of the coordinate displacement have been noted previously when rather large displacements were used.[11]

IV. Results and Discussion

A. H_2O[82-84]

The vibrational and rotational spectra of the H_2O molecule have been for many years among the most frequently and intensely studied molecular spectra, both experimentally and theoretically. Thus, it is not surprising that the full quartic force field of the H_2O molecule has been known quite accurately for some time experimentally and that numerous workers have attempted to reproduce this quartic force field theoretically. One should note, however, that until very recently[85,86] molecular spectroscopists were unable to determine the full quartic force field of molecules larger than triatomics and that the number of such triatomics was itself relatively small. The recent development of third derivative methods for SCF potential energy surfaces has made it possible to examine theoretically the anharmonic properties of small molecules with greater accuracy and more efficiently than was previously possible by using, for example, surface fitting procedures or other similar methods. Thus, not surprisingly, the H_2O molecule was among the first examined by Gaw *et al.*[36,37,39] using analytic SCF third derivative techniques. The vibration-rotation interaction constants determined from the analytic SCF cubic force field which were reported were, indeed, in excellent agreement with the experimentally determined values, somewhat more accurate than previous theoretical estimates, and at a cost considerably less than for a surface fitting procedure, for example. The vibration-rotation constants α_r^B are presented in Table 1, along with the energy, geometrical parameters, dipole moment, and rotational constants for the H_2O molecule. One should notice that the vibration-rotation constants in Table 1 agree exactly with those presented by Gaw[39] and are in excellent agreement with the best available experimentally derived values of these molecular constants.

The harmonic and fundamental vibrational frequencies and vibrational anharmonic constants of H_2O are presented in Table 2. The harmonic frequencies are seen to converge smoothly toward the experimental values, so that there remains only about 50 cm^{-1} difference at the largest basis set correlated level of theory (TZP CISD). The DZP CISD and TZP CISD levels of theory are expected, based on past experience, to give between them the best overall agreement in both geometry and vibrational frequencies for small molecules. The fundamental frequencies appear to be in slightly poorer agreement, up to approximately 75 cm^{-1} higher than the experimental fundamental frequencies. The numbers given in parentheses in Table 2 are the CISD harmonic frequencies which have been adjusted according to the SCF quartic force field with the same basis. The quantities labeled Δ_r are the differences $\nu_r - \omega_r$ between the fundamental and harmonic vibrational frequencies. For the CISD values of Δ_r, the SCF values have been transcribed and placed in parentheses for clarity. It appears then that the SCF quartic force field underestimates the anharmonicity measured experimentally by a few percent. The bend and asymmetric stretch normal mode differences are underestimated by only 3-4%, but the symmetric stretch anharmonicity is lower by almost 10% compared to experiment.

The quartic and sextic centrifugal distortion constants of H_2O are given in Table 3. It is impossible to state what level of certainty may be associated with these constants. Experimental values of these constants have not been located. Thus, although both the harmonic force field on which the quartic constants are based and the cubic force field for the sextic constants have been seen to be rather reliable for determination of harmonic frequencies and vibration-rotation constants, for example, one must use caution since the theoretical prediction of these constants from <u>ab initio</u> molecular wavefunctions is presently unprecedented. The leading quartic terms, Δ_K and Δ_{JK}, appear to be much too large, since, in principal, these distortion constants should be of the order of 10^{-4} of the equilibrium rotational constants. The origin of the order of magnitude discrepancy for these constants is presently unclear.

The vibration-rotation interaction constants for D_2O are given in Table 4. Similar good to fair agreement is seen for these constants as for the corresponding constants for H_2O. The rotational constants in Table 4 are similarly well-behaved and convergent with repect to basis set expansion, as has been seen previously for H_2O.

The vibrational frequencies and anharmonic constants of D_2O are presented in Table 5. The excellent convergence toward the experimental harmonic frequencies is again noted for this isotopomer. The only notable features are that the CISD harmonic frequencies consistently underestimate the values of the harmonic frequencies and that the fundamental frequencies are in slightly better agreement with experiment than was noted for H_2O.

B. $CH_2(^3B_1)$[87-91]

Methylene, CH_2, has become a paradigm for computational quantum chemistry,[92] by serving as a principal indicator of the cooperative role that computation can play with experiments. The controversies regarding the bent structure of methylene and the singlet-triplet (S-T) energy gap between the ground state ($^3B_1$) and the first excited singlet state ($^1A_1$), have now been clearly resolved with the aid of theory.[93] However, as with many other small molecules, there still exists some discrepancy regarding the exact bond lengths and vibrational frequencies of CH_2, indicating that the anharmonic nature of the potential energy surface must play a key role, as is known to be the case for many small molecules. In particular, CH_2 is known to be a quasi-linear molecule,[93] that is, the bending mode involves large amplitude displacements from the molecular equilibrium structure (giving rise to the term "quasi-linear") so that the molecular normal mode vibrations are not well described within the harmonic approximation.

The theoretically determined geometrical parameters of CH_2 at the various levels of theory and of basis set are given in Table 6, along with the vibration-rotation interaction constants and rotational constants. As has been noted for many molecules, the geometry is somewhat underestimated at the DZ and TZ SCF levels of calculation. However, in contrast to the expected improvement upon going to a polarized basis, neither the DZP nor TZP SCF results appear to approach the experimental structural values; most surprising is that, for the HCH bond angle, the DZ CISD value, which for most molecules would be severely overestimated, is in the best agreement with the experiment. Even the inclusion of correlation with the largest basis set used here (TZP CISD) leads to underestimation of both the bond length and angle, by 0.004 Å and 1.2°, respectively. This somewhat unusual behaviour involving the geometry of this molecule hints at what has been indicated above, that is, that anharmonicity is important for the description of the potential energy surface on which CH_2 resides.

The rotation-vibration interaction constants α_r^B of CH_2 have been previously reported; the values reported in Table 6 agree exactly with those of Gaw, et al.[40] These values support the contention of CH_2 being a quasi-linear molecule, specifically that there exists a strong coupling between the ν_2 bending mode and rotation about the molecular a axis (the symmetry z axis). The values obtained for α_2^A are unrealistically large, and are, therefore, not reported in Table 6. Based on perturbation theory, the α constants should be of the order of 10^{-2} of the corresponding rotational constant; otherwise, one must conclude that the vibrational normal mode is not, in fact, merely a perturbation of the rotational motion, as is the case here. It is seen also that the interaction between ν_3, the asymmetric CH stretch, and rotation about the a axis is also quite large; although the values of α_3^A are, in fact, approximately 28% of A_e, it is nonetheless seen that the total effect due to zero-point vibration is only about 2%, or, of the expected order of magnitude. It is for this reason that α_3^A is reported in Table 6. The vibration-rotation interaction between the other vibration-rotation pairs is seen to be at least a factor of 10 smaller than those through which ν_2 and ν_3 interact with molecular a axis rotation. Because the experimental values of the geometry and the rotational constants are interdependent, some small differences in the geometry determined theoretically, as noted above, would be expected to lead to small differences in calculated (equilibrium) rotational constants; the extremely large difference between the reported and calculated values in Table 6 is certainly related to the magnitude of the vibration-rotation interactions. If, for example, the experimental determination did not take into account a large vibration-rotation interaction, the (indirectly) measured A_e could be erroneous; on the other hand, if, in fact, the reported experimental value includes vibration-rotation interaction, the large discrepancy indicates the magnitude of such an interaction, i.e., ~50% of the theoretical A_e, and confirms the previous contention that this interaction is indeed not a simple perturbation. The remaining rotational constants are seen to agree acceptably well, i.e., within 2% when using the highest level of calculation available in this work.

The harmonic and fundamental vibrational frequencies and the vibrational anharmonic constants of CH_2 are given in Table 7. It is seen that, at the SCF level of theory, there remains somewhat more than 10% difference between the theoretical harmonic and experimental fundamental frequencies (somewhat more still for the bending mode ν_2). The large discrepancy still remaining at the CISD level is again unusual for a small molecule. The theoretical fundamental frequencies are predicted to lie closer to the experimental frequencies, as they must, but, however, there is still a much larger difference between the experimental and theoretical frequencies than one would expect. The frequency differences Δ_r show that the anharmonicity in $^3B_1$ CH_2 is quite considerably underestimated by the SCF quartic force field described here. Evidently, there are large contributions to the vibrational potential due to higher-order force constamts.

The quartic and sextic centrifugal distortion constants of methylene are given in Table 8. As with H_2O, the leading quartic terms are much larger than would be expected from the perturbation theory treatment which defines these constants. The quartic distortion term Δ_K is not reported in Table 8 because its magnitude is nearly that of a rotational constant based on the perturbation formulas. In addition, the leading sextic term, H_K, is approximately an order of magnitude larger than would have been anticipated from expected order of magnitude considerations. Again, there is no indication of the origin of the evident breakdown of the perturbation theory for the description of the centrifugal distortions of this molecule. For a quasi-linear molecule such as CH_2, the molecular distortions caused by the large amplitude bending mode coupled to molecular rotations could contribute significantly to higher-order (i.e., quartic, sextic, etc.) distortions. Without the benefit of experimental insight, little else may be said.

The rotational constants and vibration-rotation constants of CD_2 are given in Table 9. As for the protiated isotopomer, the strong vibration-rotation interaction between molecular a axis rotation and vibrational normal mode ν_2 precludes accurate prediction of rotational constant A. Thus, this constant is predicted significantly lower theoretically than the experimental data indicate.

The harmonic and fundamental vibrational frequencies and vibrational anharmonic constants of CD_2 are reported in Table 10. The lack of available experimental data precludes much comment on the data there. The fundamental frequency ν_2 is seen to be predicted quite a bit too large compared to experiment. Evidently, as with CH_2, the anharmonicity of vibration is significantly underestimated and higher-order force constants are important.

Other theoretical methods which are not based on perturbation theory have been developed for treating molecules like $^3B_1$ CH_2 which have large amplitude stretching or bending motions or other large deviations from the rigid rotor and/or harmonic oscillator approximations of molecular spectroscopy. One of the most successful methods is based on the semi-rigid bender or non-rigid bender Hamiltonians[94] which have been developed and applied to a number of non-rigid (e.g., quasi-linear) molecules, including CH_2.[95]

C. CH_2 ($^1A_1$)[89,96]

In contrast to triplet methylene, singlet methylene is much more strongly bent at its equilibrium geometry, and, therefore, provides much better agreement between theoretical and experimental descriptions of the potential energy surface of the molecule near its minimum energy conformation. As a consequence of the smaller bond angle, singlet methylene does not have the same large amplitude bending motion which caused a poor description of vibrational anharmonicity and vibration-rotation interaction in triplet methylene. The geometry, vibration-rotation interaction constants, and rotational constants of $^1A_1$ CH_2 are presented in Table 11. A comparison with the corresponding data for $^3B_1$ CH_2 in Table 6 shows that the bond lengths of the singlet are somewhat longer, by 0.025 Å at the TZP SCF level of theory and by 0.033 Å at the TZP CISD level of theory. More striking, however, is the difference in bond angles between the two electronic states of this molecule; the bond angle for singlet methylene is predicted theoretically to be 25-31° less than for the triplet. Another way to view this effect is to realize that the singlet bond angle is slightly smaller than that expected for an sp^3 hybridized atom, whereas the triplet has an angle which is much larger than even that expected for an sp^2 hybridized center. This decrease in bending angle is seen to result in a much larger dipole moment, as might be expected from the localization of the non-bonding electron pair into a single molecular orbital, as opposed to the separation into different carbon 2p-like orbitals in the triplet. Another consequence of the increased bending of the molecule away from linearity is that correspondingly more vibrational quanta are required to reach a linear nuclear configuration; thus, the bending potential of singlet methylene is deeper than that for triplet methylene. This further leads to an expectation that the vibration-rotation interaction in the singlet molecule will be somewhat less than in the triplet, particularly the interaction with rotation about the molecular a axis. This is, in fact, what is observed in the data of Table 11, in which all of the vibration-rotation interaction constants appear to be well-behaved, that is, of the proper order of magnitude relative to the equilibrium values of the rotational constants. Even the largest interaction constants, those involving, not surprisingly, the bend ν_2 and rotation about the molecular a axis, are less than 10 % of the affected rotational constant, A, and the overall zero-point correction is approximately 1%.

The frequencies and anharmonic constants associated with the normal mode vibrations of CH_2 ($^1A_1$) are presented in Table 12. The agreement between theoretical and experimental fundamental frequencies is seen to be excellent. The more strongly bent singlet methylene is not only free from large vibration-rotation perturbations, but, evidently, also from large vibrational anharmonic coupling between normal modes. The anharmonicity as determined theoretically, although predicted to be of about the same magnitude for singlet as for triplet methylene, seems to reproduce the experimental anharmonicity much better in the case of singlet methylene.

The quartic and sextic distortion constants of $^1A_1$ CH_2 are given in Table 13. Once more, in the absence of experimental verification or contradiction, little can be added to the simple presentation of the theoretical data. The leading quartic term Δ_K is once again larger than one might expect, and there is no indication in the geometry, rotational constants, etc. that might suggest an explanation for the persistent (evident) breakdown of the perturbation theory for this term.

The vibration-rotation interaction constants and rotational constants of CD_2 are given in Table 14. The rotational constants an interaction terms are well-behaved theoretically and converge with both basis expansion and inclusion of correlation. These data for this experimentally easily accesible small molecule should encourage further spectroscopic investigation of the vibration-rotation spectra in order to help to confirm (or refute) the reliability of ab initio cubic (and quartic) force fields.

The harmonic and fundamental frequencies of singlet CD_2 are given in Table 15 along with the vibrational anharmonic constants and are presented with only one comment. Singlet methylene has proven theoretically to provide data related to its ab initio cubic and quartic force fields which is both well-converged theoretically and in excellent agreement with the available experimental data. One would hope for more experimental data to test the conclusions made as well as to shed light on the ambiguous portions of the anharmonic force field, for example, the centrifugal distortion constants.

D. CH_2 $(^1B_1)$[96]

The open-shell singlet electronic state $(^1B_1)$ of methylene (CH_2) is structurally similar to the ground (triplet) state. That is, the CH bond lengths are shorter and the HCH bond angle quite a bit larger than those of the lower singlet $(^1A_1)$ state. In this respect, it also has many of the same difficulties associated, from a theoretical point of view, with a quasi-linear molecule. The geometrical parameters, vibration-rotation interaction constants, and rotational constants for CH_2 $(^1B_1)$ are given in Table 16. As can be seen there, the interbond angle is, in fact, approximately 10° larger than even for the triplet state discussed above. One might expect, then, an even greater coupling between vibration and rotation, particularly rotation about the molecular a axis causing significant centrifugal distortion of (or being significantly affected by) the ν_2 HCH bending mode. This is strikingly evident in that the interaction constants α involving all three normal mode vibrations and the rotational constant A are quite large; in fact, each has been judged meaningless in the context of a perturbation theory approach to vibration-rotation interaction and are, hence, not presented in Table 16. The values of α_1^A are given at the DZP and TZP SCF levels of theory, since these values seem to be much more reasonable (3-4% of A_e at the same level of theory), and, in fact show little variation upon going to the larger of the two bases. The interaction constants involving the other rotational constants B and C are, however, well behaved, indicating that these (much smaller) rotational constants have less interaction with the normal mode vibrations, including the highly anharmonic quasi-linear mode ν_2.

Table 17 contains the harmonic and fundamental vibrational frequencies of CH_2 ($^1B_1$), as well as the vibrational anharmonic constants. Although this particular electronic state of this molecule is somewhat more poorly characterized than the two previously discussed lower lying states, one has a sense from Table 17 that many of the difficulties seen for the vibrational frequencies of the triplet may occur here as well and, most likely for similar reasons. The normal mode frequencies change by only about 100 cm^{-1} from the harmonic to fundamental values (e.g., TZP SCF) and only by a similar amount upon inclusion of electron correlation in the harmonic values (e.g., TZP CISD). This is what was seen previously (for the triplet) and, in that case, was seen to severely underestimate the effects of anharmonicity in the vibrational normal modes (or, at least, the experimental and theoretical fundamental frequencies were still somewhat in disagreement). The large positive values of the anharmonic vibrational constants χ_{12} and χ_{23} which show the effect of normal mode frequency ν_2 on the frequencies ν_1 and ν_3 (that is, the anharmonic coupling between the normal modes) are unusual in sign (most anharmonic constants are expected to be negative, and a fundamental frequency is almost always smaller than the corresponding harmonic frequency), but show two other important points as well. First, the effect of addition of polarization functions is seen to be very important, changing the value of the constants by a factor of 2-3 (DZ vs. DZP, for example). Next, the constants seem to vary very little with improvement of the basis after the addition of polarization functions (DZP vs. TZP), and, therefore, appear to have almost converged with respect to basis set expansion at the TZP SCF level of theory in this case. The necessity of polarization functions is also seen clearly in a comparison of the values of ω_2, ν_2, and Δ_2; the harmonic frequency changes by over 30% with the addition of higher angular momentum functions to the basis, with the corresponding change in the fundamental of almost 100%. This is clearly due, not only to the poor description of the geometry and harmonic potential using an unpolarized basis, but, in addition, a poor description of the cubic and quartic potentials, as evidenced especially in the values of χ_{12}, χ_{22}, and χ_{23}.

Quartic and sextic centrifugal distortion constants of CH_2 ($^1B_1$) are given in Table 18. As was the case for the triplet (ground state) methylene, the quasi-linear $^1B_1$ state must certainly have large higher-order centrifugal distortion effects which cannot be properly treated by perturbation theory. Thus, the leading quartic distortion terms Δ_K and Δ_{JK} are not surprisingly predicted to be very large. The values of Δ_{JK} which are given in Table 18 are almost certainly not meaningful in the context of a perturbation treatment of vibration-rotation interaction, but are reported nonetheless for information or for potential future reference. In addition to the leading sextic term H_K also being too large, the true importance of these higher-order centrifugal distortion effects is seen in the magnitude of two other distortion constants, the quartic constant ϕ_K and the sextic constant H_{KJ}. Of course, in a case like this, proper rotational energy levels, including the effects of higher-order distortion explicitly, could be obtained by rigorous diagonalization of a rotational Hamiltonian which included all of the higher-order term values. For this molecule, it seems likely that a much better description of the features of the vibration-rotation specrum could be obtained theoretically <u>via</u> a different formulation of the vibration-rotation Hamiltonian, for example, by using the semi-rigid (or non-rigid) bender Hamiltonian of Jensen and Bunker.[94,95]

Table 19 includes the vibration-rotation interaction constants and rotational constants of CD_2 $(^1B_1)$. Of course, the interaction constants involving rotational constant A have been ommitted because in general they are too large to be properly considered based on perturbation formulas. The dramatic change of the values of the rotational constant A_e and of the interaction constant α_2^B upon going to a polarized basis at the SCF level of theory again emphasizes the importance of using polarization functions in order to properly describe a molecular potential energy surface. The fact that the only values of α_1^A which have reasonable values are those obtained from polarized bases also speaks to the necessity of using a balanced basis set which includes higher angular momentum functions, particularly for molecules in which a bending (internal or normal) coordinate must be properly described.

The anharmonic constants reported in Table 20 also show dramatic evidence of the effect of polarization functions on molecular constants. The values of all of the constants in Table 20 which involve the bending normal coordinate (ω_2, χ_{12}, χ_{22}, χ_{23}, ν_2, and Δ_2) change markedly upon introduction of polarization functions into the basis (from DZ or TZ to DZP or TZP). The harmonic frequency increases by 200 cm^{-1}; the anharmonic constants change by over 50%; the fundamental frequency increases by almost 300 cm^{-1}; and the frequency difference (anharmonicity) is reduced by over half when polarization functions are included in the basis set. This is a very dramatic demonstration of the role of higher angular momentum functions in the proper description of properties of the anharmonic force field as well as of the harmonic force field.

E. HCO ($^2A'$)[97-101]

The formyl radical, HCO ($^2A'$), has been found to play an important role in the chemistry of flames, and, after an earlier surge of work on its vibration-rotation spectra,[97-100] has recently been the object of renewed interest and investigation.[101,157-162] This molecule falls unfortunately into the category of quasi-linear molecules which have already been discussed and shows the same breakdowns in the perturbation treatment of its vibration-rotation spectra as do CH_2 ($^3B_1$) and CH_2

($^1B_1$).[94,95] The molecular structure, vibration-rotation interaction constants, and rotational constants are presented in Table 21. The equlibrium CH bond length is slightly longer here than, for example, in CH_4 since the central carbon atom is effectively sp^2 hybridized, with the equlibrium bond angle being 125-128°, or, only a few degrees larger than the idealized value of 120°; the equilibrium value of the CO bond length is, however, also longer than a typical CO double bond, as, for example, in H_2CO (vide infra). The theoretical methods are seen to reproduce the experimentally determined CO bond length extremely well; the slight underestimation of the CH bond, even at the polarized (DZP or TZP) CISD level of theory is symptomatic of the inherent difficulty often encountered theoretically with molecules which are weakly bound, even with respect to linearization, for example. Of course this discrepancy may also be due to the increased difficulty in fitting experimental spectral data for such a non-rigid molecule; in any case, the geometrical parameters are less well determined than one would expect for a typical small molecule, with the resultant expectation, as above, that the experimental rotational constants (particularly A) may be considerably larger than those theoretically determined and presented in Table 21. The vibration-rotation interaction constant α_r^3 is not given in Table 21 since it describes the interaction between rotation about the molecular a axis and bending mode ν_3. This large vibration-rotation interaction is that which is not well (or properly) described by the perturbation theory treatment. The remaining vibration-rotation constants are seen to be much smaller, often several orders of magnitude smaller than would be required by the magnitude ordering of the various vibration-rotation terms in eq. (2) or eq. (12).

Both the harmonic and anharmonic vibrational frequencies and the vibrational anharmonic constants of HCO are given in Table 22. The most striking feature of this table is the difference between the theoretical and experimental values of the anharmonic constants χ_{rs}. The theoretical values seem to be failing to reproduce even the relative magnitudes of these constants. However, examination of the paper by Dixon[97] from which the experimental values of the anharmonic constants and harmonic frequencies are taken reveals that the spectral data which were available were fitted after fixing the values of the anharmonic constants χ_{22}, χ_{23}, and χ_{33} to be identically zero. Thus, the "experimental" values may well be grossly in error, particularly since the theoretical values of Dixon's[97] ignored constants are clearly non-negligible, i.e. ~-2 to -11 cm^{-1}. The only fact which remains clear from Dixon's analysis,[97] in light of this theoretical determination, is that χ_{11} has a much larger value than any of the other anharmonic constants. This should be taken as a first indication that theory is now capable of providing spectroscopic data which are difficult (or impossible) to obtain directly from molecular spectra; in addition, it may now be seen that comparisons between theoretical and experimental values derived from anharmonic molecular force fields may, in fact, only be valid in cases where the experiments are based only on assumptions which are well-defined and justified from previous experience. In fact, almost any assumptions about the values of anharmonic molecular constants which are made in an experimental treatment of spectral data might now be made more accurately based on relatively easily available theoretical anharmonic force fields. In this regard, one would hope that molecular spectroscopists might re-examine HCO (for example) with the *a priori* expectation of finding a richer, more informative rotation-vibration spectrum based upon having an improved (*ab initio*) quartic force field in hand.

The centrifugal distortion constants of HCO are presented in Table 23. With the exception of the largest quartic term, the various coefficients are very small. This suggests that the equilibrium rotational constants may be more accurate than usual in this case for describing molecular rotational behaviour and the associated rotation-vibration fine structure. The rotational constants would be particularly well-defined, it would seem, by inclusion of only the terms involving Δ_K (and possibly H_K) into a rotational Hamiltonian to be diagonalized.

The vibration-rotation interaction constants and rotational constants of DCO are given in Table 24. Just as for HCO (Table 21), the theoretical rotational constants are expected to underestimate the value of the experimental value(s), particularly A, because of the fact that the large vibration-rotation terms are neglected in the present treatment.

The harmonic and fundamental frequencies and vibrational anharmonic constants of DCO are given in Table 25. Just as for HCO the agreement between the theoretical and "experimental" harmonic frequencies is rather poor due to the neglect of some of the anharmonic constants in the fitting of the observed fundamental bands.[97] As with HCO, the present availability of a complete quartic force field should encourage re-examination of the anharmonic constants and harmonic frequencies of DCO.

F. H_2CO[35,85,102-105]

Formaldehyde, H_2CO, ranks along with acetylene (C_2H_2) among the most studied tetra-atomic molecules. These two molecules are, in fact, the only two molecules of greater than three atoms for which a complete quartic force field has been determined experimentally. In addition, formaldehyde is a theoretically well-behaved molecule and, as such, provides one of the best comparisons of molecular constants obtained from theoretical and experimental quartic force fields. In Table 26, it should be noted that the geometrical parameters are in much better agreement, both at the SCF and CISD levels of theory and with all four basis sets, than any of the previously discussed molecules. At the TZP CISD level of theory, the agreement is exact; this is very satisfying and provides high expectations regarding the theoretical prediction of the anharmonic force field of formaldehyde. The lower levels of theory and of basis are seen to perform satisfactorily as well for this strongly bound molecule which is subject only to small perturbations via rotation-vibration interaction.

The theoretical harmonic and fundamental frequencies of H_2CO are given in Table 27 along with those found experimentally in the landmark work of Reisner, et al.,[85] as well as previously by Duncan and Mallinson.[104] The theoretical harmonic frequencies are seen to be in much better agreement (even compared to the experimental fundamentals) than for most of the previously considered molecules. In addition, one may see that the frequency differences Δ are, in general, smaller than observed previously for molecules having large amplitude, highly anharmonic normal mode vibrations. Thus, the improvement gained upon increasing the basis set, inclusion of electron corelation, and consideration of the anharmonic force constants results in even better agreement between the experimental and theoretical (anharmonic) vibrational frequencies. The anharmonicities associated with normal modes ν_1 and ν_6 are the most severely underestimated theoretically; this is somewhat surprising for the CH stretching mode ν_1, but considerably less so for the out-of-plane bending mode ν_6 which could be expected to be rather more anharmonic.

The vibrational anharmonic constants χ_{rs} are given in Table 28. These constants are seen to agree quite well with the corresponding experimentally derived values.[85] The exceptions appear to be χ_{12}, χ_{33}, χ_{34}, χ_{35}, and χ_{46}, all of which disagree in sign with the experimental constants; note, however, that all of these disagreements in sign are among constants of small absolute value, and, in fact, the absolute values of each of these constants is in agreement between the theoretical and experimental values (at least as much as the other anharmonic constants are in agreement). Additionally, the constants χ_{15} and χ_{16} appear to significantly underestimate the experimental values (perhaps these are the major contributions to the underestimated anharmonic contribution to ν_1); χ_{14} and χ_{55} appear to be somewhat more in disagreement than the majority of the reported constants; and χ_{56} amazingly is underestimated at the highest level of theory, after being in good agreement with the smaller bases.

The singular anomaly associated with the vibration-rotation spectrum of formaldehyde is indicated in Table 29, along with the centrifugal distortion constants. The asymmetry parameter σ is much larger than the rotational constants; this is indicative of an approximate symmetric top molecule. That is, the rotational constants B and C of H_2CO are accidentally nearly degenerate; thus, many of the centrifugal distortion constants may not be well-defined since they may have denominators containing the quantity (B-C). In addition, H_2CO is the first molecule which has been examined here for which the quartic and sextic distortion constants are well-behaved. That is, there is no (apparent) breakdown of the perturbation formulas as has been seen previously when treating the formaldehyde molecule. This provides reassurance that the present implementation of the perturbation theory based formulas for centrifugal distortion constants is not flawed.

Table 30 provides the vibrational frequencies of D_2CO. Both the harmonic and fundamental frequencies are in good agreement theoretically with the experimental values. Although the agreement is not quite as good as for H_2CO, the average deviation is only approximately 50 cm^{-1} in the harmonic frequencies and approximately 40 cm^{-1} in the fundamental frequencies. The frequency differences show that the anharmonicity associated with a number of the normal mode frequencies is somewhat underestimated theoretically, in particular, Δ_1, Δ_3, and Δ_6.

The vibrational anharmonic constants of D_2CO are presented in Table 31. In light of the previously mentioned underestimation of the anharmonicities of some normal modes, one might expect that the corresponding anharmonic constants might also be underestimated theoretically by similar amounts. Otherwise, the excellent agreement seen for the anharmonic constants of H_2CO should carry over to D_2CO as well.

G. $H_2S^{106-117}$

The hydrogen sulfide molecule, although closely related in the periodic table to water, has been much less studied than its more common periodic neighbor (vide supra). In fact, one of the earliest papers which discussed the anharmonic force field of H_2S appears to have been challenged very little by more recent experiments, despite the fact that the assumed structure is far from the currently accepted picture of the geometry of H_2S. Thus, it appears that the most definitive work concerning the anharmonic force field of H_2S is the theoretical surface fitting reported by Botschwina, et al. last year.[107] Therefore, although the interbond (HSH) angle is in excellent agreement with the most accurate previous experimental determination, the small discrepancy in the bond length cannot be too surprising since the experimental result is not the result of a high-resolution (or high accuracy) experiment. The vibration-rotation interaction constants in Table 32 are theoretically among the most well-behaved such constants which are presented in this work; the rotational constants are well separated and reasonably small, and the interaction constants are proportionately smaller, as they should be for the present perturbation treatment to apply (and as has been discussed previously). Thus, the present accumulation of data concerning the rotational constants and the interaction with the molecular normal mode vibrations should serve as a highly reliable source of information for future investigation of the hydrogen sulfide molecule and its rotation-vibration spectra.

The theoretical harmonic and anharmonic vibrational frequencies are compared with the available experimental data in Table 33. Even for a molecule which contains a third-row atom, H_2S shows the same trends as seen previously with regard to expansion of the basis and inclusion of correlation. The overestimation of the experimental fundamental frequencies by the theoretical harmonic values is reduced somewhat at the CISD level of theory, and, by the inclusion of the effects of anharmonicity, both the harmonic and fundamental frequencies agree within a few cm^{-1} at the highest level of theory employed here.

The same questionable certainty associated with almost all of the centrifugal distortion constants tabulated for molecules here so far must also be applied to the quartic and sextic distortion constants of H_2S in Table 34. Although the molecule is well-behaved theoretically in every other way, the leading quartic distortion terms of the H_2S molecule are once again larger than those in which one would be able to place any measure of confidence.

H. C_2H_4[118-121]

A recent paper by Lee, Allen, and Schaefer[122] which reports the harmonic vibrational frequencies of ozone (O_3) and ethylene (C_2H_4) using multi-reference (MR) CISD wavefunctions also gives an excellent discussion of the experimental state of affairs with respect to the vibrational (infra-red and Raman) spectrum of ethylene, and their key points are reviewed here. Although the ethylene molecule has a great deal of symmetry (D_{2h}), it has not been the object of high-resolution infra-red or Raman spectroscopic investigation until very recently. In fact, the observation and identification of the features in the infrared and Raman spectra of C_2H_4 and their assignment to ethylene's normal modes was a matter of some controversy until relatively recently. Now, however, with the assistance of large scale ab initio calculations, the vibrational spectrum appears to be somewhat more clearly understood.

The theoretically determined geometry of C_2H_4 at the DZP SCF and DZP CISD levels of theory are given in Table 35. Because of the number of atoms (and, therefore, the number of degrees of freedom) in ethylene, it was determined to perform only these levels of calculation with this molecule. In addition, the displacements required for the finite differences of third derivatives were performed with respect to symmetrized internal coordinates of C_2H_4 in order to minimize the number of third derivative calculations required. This technique, which substantially reduces the amount of computation time required relative to that for displacements of all the Cartesian coordinates (as was done for all of the other molecules herein), is certainly one which will become of greater use as both the number and size of molecules for which full quartic (and higher) force fields are being determined by ab initio methods grows.

The harmonic and fundamental vibrational frequencies at the SCF and CISD levels of theory are compared with experiment in Table 36. In all cases the frequencies are in remarkable agreement. For the SCF values, the error in theoretical fundamental frequencies is between 5 and 14% higher than the corresponding experimental fundamental frequency. At the CISD level of theory, the errors are reduced to within only 1 to 8% of the experimental values. The DZP SCF quartic force field is also seen to provide excellent agreement with the experimentally derived frequency differences; the underestimation is no more than 30 cm^{-1} in any case. Lee, Allen, and Schaefer deal with the vibrational spectrum of C_2H_4 in much more detail, and for further discussion, the reader is referred to their paper.[122]

I. HCN[29,123,124]

The HCN molecule is another of the molecules whose vibration-rotation spectra have been well studied both experimentally and theoretically for many years. It is therefore somewhat surprising that the geometrical parameters presented in Table 37 for this molecule are not in better agreement. This is not to say that extensive study should necessarily lead to better agreement; however, since HCN is well-behaved and easily studied both experimentally and theoretically, and since both the experimental and theoretical techniques have been seen often to produce excellent agreement, it is in this way surprising that there is some discrepancy (although certainly not of a magnitude to demand great concern) in the geometrical parameters. Table 37 also provides the first available comparison in this work of two experimentally available sets of values for the vibration-rotation interaction constants with those determined from the *ab initio* cubic force field. It is seen that reasonable agreement is, in fact, achieved, with the theoretical values in all cases being slightly smaller in absolute value. The quartic centrifugal distortion constant is seen, likewise, to be in excellent agreement with the experimentally derived constant; this is an encouraging indication of the quality of many of the other quartic (and sextic) distortion constants which have been presented, but for which there do not exist experimental data with which to compare.

The harmonic and anharmonic vibrational frequencies and anharmonic vibrational constants of HCN are given in Table 38. As with most molecules here, there is convergence of the molecular constants with basis set expansion, and improved agreement with experimental data upon the inclusion of electron correlation and anharmonic force field effects. Thus, the HCN molecule adds confirmation to the accuracy and reliability of *ab initio* determined anharmonic force fields and molecular constants.

The vibration-rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational ℓ-type doubling constants of DCN are reported in Table 39. The same excellent agreement with the available experimental values is seen as was seen for HCN.

The harmonic and anharmonic vibrational frequencies and the vibrational anharmonic constants of the DCN molecule are presented in Table 40. Considering the consistent agreement of all of the anharmonic molecular constants discussed so far of HCN/DCN, it is not surprising that the vibrational frequencies and anharmonic constants are in excellent agreement with the available experimentally derived data for these constants as well.

J. CO_2[68,69,127-129]

The carbon dioxide molecule, CO_2, owes much of its recognition spectroscopically to the identification by Fermi[68] of the anharmonic resonance between normal mode vibrations ν_1 and $2\nu_2$. Because of this, CO_2 has been thoroughly studied spectroscopically and is the only molecule for which a force field complete through sixth order has been determined experimentally. The molecular constants of CO_2 are presented in Table 41. The best agreement for the CO bond length is at the DZP CISD level of theory; the increase in basis set to TZP at the correlated level of calculation leads to a striking change in the predicted bond length, giving very poor agreement for the structure of this molecule. The amount of fluctuation in the predicted bond lengths across Table 41 with increasing basis set and with inclusion of correlation is quite unusual as well; there does not appear to be any obvious convergence of the molecular structure within the levels of theory considered here. The other molecular constants in Table 41 show good agreement with the extensive available spectroscopic data, however, the parameters show slower convergence with basis set than has been observed previously. (The poorer agreement with the experiments at the largest basis set levels compared to smaller bases, both here and for HCN considered above, may lead one to speculate that the potential energy surface of molecules having a substantial (fractional) portion of their bonding as multiple bonds may be less well described theoretically than those for molecules with mostly single bonds. The excellent agreement in, for example, vibrational frequencies for the molecules H_2O, NH_3, CH_4, NH_4^+, HF, etc. which are often used as theoretical test cases may tend to overshadow the less spectacular, although nonetheless still good, results for such molecules as HCCH, HCN, H_2CO, which themselves are often used as small test molecules.)

The vibrational frequencies and anharmonic constants of carbon dioxide are given in Table 42. As for most molecules, it is clear in the Table that the SCF harmonic frequencies overestimate the experimental fundamental frequencies by somewhat more than 10% on average; the frequencies are corrected, becoming closer to both the harmonic and fundamental experimental frequencies by the inclusion of correlation and effects due anharmonicity. The values of the anharmonic constants $\chi_{rr'}$ are also in agreement with the experimentally well-determined values of these constants. One may note in Table 42, however, the very poor agreement indicated by the use of the TZ basis; in particular, several of the constants predicted at this level of basis are in disagreement with the other theoretical determinations (as well as with experiment) in regard to either the sign or the magnitude of the constants (note, for example χ_{12}, χ_{22}, and $\chi_{\ell_2\ell_2}$, as well as the prediction of a positive frequency shift on going from the harmonic to the fundamental frequencies of normal modes ν_1 and ν_2). The further saturation of the sp basis without inclusion of polarization functions in the basis is clearly disfavored.

K. $N_2O^{130-132}$

Nitrous oxide, N_2O, has been the object of a number of studies which have been concerned particularly with ℓ-type doubling as a result of the anharmonic force field of a molecule. Thus, a large number of the molecular constants associated with the cubic and quartic force field of this molecule have been reported experimentally. The molecular structure and other constants are given in Table 43 for the N_2O molecule. As with CO_2 (vide supra) the bond lengths of N_2O show rather poor convergence with basis set, with the TZP CISD result again showing a substantial deterioration of agreement with experiment relative to the corresponding DZP result (for the NN bond). The other values in Table 43 show similar trends, i.e., not approaching the experimental values in a consistent way, either with expansion of the basis or, where applicable, with inclusion of electron correlation. This seemingly unfortunate result should rather encourage further studies on this molecule (and other multiply bonded molecules) both with respect to further basis set enlargement as well as to inclusion of a larger portion of the correlation energy, by, for example, CISD(T)(Q) or CCSD(T) methods, in order to better model both the harmonic and anharmonic force fields associated with N_2O.

The vibrational frequencies and anharmonic constants of nitrous oxide are given in Table 44. The agreement between theoretical and experimental values is rather good, especially considering the rather poor and erractic behaviour already noted in regard to the molecular structure. The most unique feature of the values of the constants given in the Table is the remarkably small difference Δ_2 between the harmonic and anharmonic values of the molecular bending frequency (ω_2 and ν_2, respectively). The unpolarized bases (DZ and TZ) again show severe discrepancies with the experimental data, indicative once more of the necessity of using a polarized basis for a proper description of the anharmonic potential energy surface of a molecule, even near its equilibrium where, in many cases, the geometry and frequencies, for example, may be in sufficiently good agreement with experimental evidence for many purposes (see, for example, the values χ_{13} and χ_{33}).

L. COS[133-138]

The carbonyl sulfide molecule, COS, although not as well-known as some of the other molecules investigated here, has a long spectroscopic history and, consequently, has been remarkably well characterized. The geometry and various vibration-rotation constants are compared with the experimental data in Table 45. A similar trend is seen as has been seen previously with respect to the bond lengths in this molecule. That is, there appears to be very slow convergence of the structural parameters with basis set enlargement, at least up to the levels of basis investigated here. This slow convergence is particularly noticeable once more for the CO bond length, for which the DZP CISD result is again in the best agreement with the experiment, and the TZP CISD result, although typically expected to give some small improvement, shows a large change away from the experimental value. The CS bond length shows somewhat better convergence with respect to basis set expansion on inclusion of electron correlation, with fair agreement with experiment at the TZP SCF level of theory, but much better agreement at the TZP CISD level of theory. The quartic centrifugal distortion constant D_J is in excellent accord with the experimental value, as is the equilibrium ℓ-type doubling constant q_2^e, with the differences being only approximately 2%.

The harmonic and fundamental vibrational frequencies and the vibrational anharmonic constants of COS are compared with experiment in

Table 46. The harmonic frequencies show remarkable agreement with the experimental values, with deviations of only a few wavenumbers in ω_1 and ω_2. The CO stretch ω_3 seems to be somewhat larger than the experimental value, particularly with the DZP or TZP bases at either the SCF or CISD levels of theory.

M. C_2H_2[6,71,86,139-141]

The acetylene molecule, C_2H_2, as mentioned previously, is one of only two molecules of more than three atoms for which there exists a completely determined experimental quartic force field. Thus, C_2H_2 provides another opportunity (with H_2CO) for thorough examination of the performance of ab initio higher derivative methods in the prediction of properties associated with the cubic and quartic anharmonic force constants of a molecule. The geometry, vibration-rotation interaction constants, rotational constants, centrifugal distortion constants, and ℓ-type doubling constants of the C_2H_2 molecule are given in Table 49. The geometry suffers from the same distressing deterioration in quality of results (as compared to the experimental values) at the TZP CISD level of theory (relative to the DZP CISD results, for example) as has been seen repeatedly here for linear multiply bonded molecules. The theoretical vibration-rotation interaction constants appear to underestimate the corresponding experimental values by 2% or more, with strikingly less agreement between theory and experiment for the value of α_2. The quartic centrifugal distortion constant shows the same remarkable agreement between theoretical and experimental values at the highest levels of theory examined here as has been seen for each of the preceding molecules for which there has been a reliable spectroscopic determination of this constant. This is encouraging once again in that many of the molecular constants which have never before been predicted by an ab initio theoretical approach appear to be in excellent accord with experimentally derived values, and, therefore, these constants (and others) should be of substantial value to molecular spectroscopists desiring to measure the fine structure associated with molecular vibration-rotation spectra.

The vibrational frequencies and anharmonic constants of C_2H_2 are given in Table 48. The harmonic frequencies, for the most part show excellent convergence with size of basis; the exceptions, particularly ν_4 and ν_5, are much better represented by the CISD level of theory. The inclusion of the anharmonic force field effects, therefore, leads to excellent agreement as well with the experimental fundamental frequencies; normal mode vibrations ν_4 and ν_5 are then in better agreement with the experiments after correction of the CISD harmonic frequencies via the SCF cubic and quartic force constants. In general, the vibrational anharmonic constants are in very good agreement with those determined from experiment; the major exception appears to be the value of χ_{45}. In this case, one might argue that, based on the previously mentioned severe overestimation of the harmonic frequencies ω_4 and ω_5, it is not surprising that this anharmonic interaction term is poorly described; on the other hand, this difference of both order of magnitude and sign for this constant might suggest an experimental re-examination of the vibrational spectrum of acetylene (even in light of the poorly converged theoretical value). A few other of the anharmonic constants have a somewhat larger than average (fractional) deviation from the experiment; however, these are in all cases small valued constants which could very well be in error either experimentally or theoretically (for example, χ_{25}, χ_{44}, and $\chi_{\ell_4 \ell_4}$).

N. H_3^+ 142-145

The H_3^+ molecular ion is the only example of a symmetric top molecule for which data are given here. The geometry, vibration-rotation interaction constants, rotational constants, and centrifugal distortion constants are presented in Table 49. It will be noticed that only calculations at the SCF level of theory are given. It is also seen that the basis sets were extended further in this case to see the effect of approaching a saturated sp basis on the cubic and quartic anharmonic properties. The most notable feature of Table 49 is that although the (4s2p) extended basis gives almost identical results to the TZP basis, the further extension of the sp basis leads to quite substantial deterioration of the quality of the predicted molecular constants. Thus, even for a molecule of only hydrogen atoms, one must employ a basis which is well balanced (in addition to having polarization functions) in order to maintain the quality of results (even those which haved appeared to have converged with respect to basis set enlargement).

The vibrational constants of H_3^+ are given in Table 50. In much the sane way as the vibration-rotation constants, for example, in Table 49, the data of Table 50 converge well up to the (4s2p) basis set level; however, the results with the (evidently) unbalanced (oversaturated) basis of (6s3p) composition are somewhat erratic and not always in line with the other theoretical values of the molecular constants. It would be worthwhile, it seems, to investigate a basis of (4s2p1d) character, for example, in order to see the effect of a more balanced basis expansion (i.e., inclusion of yet higher angular momentum functions rather than further saturation of the sp space) on the anharmonic force field of this molecule.

The vibrational anharmonic constants were checked independently by the use of Watson's formulation[146] for the special case of an X_3 molecule. Exact agreement was found for all of the anharmonic constants by comparison with the results obtained from the general perturbation formulas for symmetric top molecules presented in section II. These independent calculations give reassurance once again that the present implementation of the general formulations of Mills, Watson, et al. is not in error.

O. NH_3[29,147-149]

Preliminary results on the anharmonic force field of the ammonia molecule, NH_3, have been obtained. These early results indicate that the major points which have been noted repeatedly apply to NH_3 as well. In particular, the geometry is in good agreement with experimental values at the DZP and TZP CISD levels of theory. The harmonic force field (i.e., the vibrational frequencies) show a convergence toward the experimental values with increase of the size of the basis as well as with the inclusion of electron correlation. The inversion motion of the NH_3 molecule is found to be highly anharmonic (as it is known to be from experimental data), and the use of unpolarized basis sets gives an unreasonably large correction to the harmonic frequency ν_2 due to the effects of anharmonicity. It will be of interest to see the performance of the larger basis sets and the effects of correlation on the description of this normal mode in particular.

V. Concluding Remarks

This thesis has described a portion of the research which has been undertaken to investigate the feasibility of using ab initio SCF cubic and quartic force constants, determined from the new methods of analytic SCF third derivatives, for determining anharmonic molecular constants of a wide variety of molecules.[163-165] The research presented here has added immensely to the knowledge previously available (either experimentally or theoretically) concerning many vibration-rotation interaction constants (i.e., constants determined from higher potential energy derivatives). For a number of the molecules, the information given here should provide motivation for experimental re-examination of the molecular vibration-rotation spectra with the expectation of being able to derive much more insight due to the now available ab initio molecular cubic and quartic (anharmonic) force fields. In addition, some of the results presented raise additional questions. Specifically, how is one to deal with the apparent breakdown of the perturbation formulas for centrifugal distortion for many molecules and what level of basis set or correlation is necessary to properly converge the anharmonic constants of molecules containing multiple bonding?[166] Other more subtle points may also be further investigated. For example, the vibrational and rotational ℓ-type doubling constants have not been examined in detail with respect to the relative contributions from the harmonic, cubic and quartic terms; that is, one might find a way to approximate some of the molecular constants which depend on the higher order force constants (and which are, therefore, not reported in standard *ab initio* calculations) using lower order force constants.

With the full quartic force field of many molecules in hand, it should be possible to extend immensely the range of anharmonic molecular constants which are determined by *ab initio* methods. There are many spectroscopic constants which depend on the (cubic and) quartic force field of a molecule[150]; all that is required is the formulation of these spectroscopic constants in terms of the potential energy derivatives (i.e., the cubic and quartic force constants). One particular set of constants which depends on the quartic force field is the set of octic centrifugal distortion constants. These constants are rarely measured, but often invoked as important for detailed description of molecular rotational fine structure. The ten independent octic centrifugal distortion constants (that is, the measurable combinations of the fifteen pure distortion constants of this order) have been discussed and described recently.[153,154] However, these octic centrifugal distortion constants have not been defined or formulated explicitly in terms of the quartic force field on which they depend; if this were to occur, the octic distortion constants of all the molecules discussed here (as well as many others[162-164]) would be immediately available. It is hoped, therefore, that *ab initio* determinations of cubic and quartic force fields will continue, not only to give additional comment regarding the reliability of the anharmonic molecular constants determined in this way, but also to provide motivation for further development and study in both experimental and theoretical molecular spectroscopy.

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164. Linear Polyatomic Molecules: D. A. Clabo, Jr., R. B. Remington, W. D. Allen, Y. Yamaguchi, and H. F. Schaefer III, manuscript in preparation.

165. Symmetric and Spherical Top Molecules: D. A. Clabo, Jr., R. B. Remington, W. D. Allen, Y. Yamaguchi, and H. F. Schaefer III, research in progress.

166. Prof. W. Maier is thanked for pointing out that, in addition to multiple bonding, each of the molecules which shows poor convergence of anharmonic properties with basis set has a number of lone-pair/lone-pair (or similar) interactions which are also almost certainly poorly described theoretically without the use of an extensive and flexible basis.

Table 1. Theoretical and experimental geometries, dipole moments, vibration-rotation interaction constants and rotational constants of H_2O.

	SCF				CISD				Experiment[a]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Energy in hartree	-76.01100	-76.01429	-76.04681	-76.04828	-76.13712	-76.15527	-76.24379	-76.26066	
r_e(OH) in Å	0.9514	0.9527	0.9457	0.9453	0.9759	0.9744	0.9623	0.9624	0.9572
θ_e(HOH) in deg.	112.52	111.82	106.16	106.12	110.54	110.22	104.13	104.36	104.52
μ in D	2.530	2.512	2.133	2.129	2.495	2.470	2.093	2.090	
α_1^A in cm^{-1}	0.9442	0.7703	0.5854	0.5445	-	-	-	-	0.750
α_2^A	- 4.4795	- 4.2390	- 2.8426	- 2.8377	-	-	-	-	-2.941
α_3^A	1.5746	1.4551	1.1003	1.0656	-	-	-	-	1.253
α_1^B	0.1795	0.1743	0.2170	0.2103	-	-	-	-	0.238
α_2^B	- 0.0470	- 0.0502	- 0.1527	- 0.1520	-	-	-	-	-0.160
α_3^B	0.1021	0.0826	0.1019	0.0947	-	-	-	-	0.078

Table 1 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
α_1^C	0.1688	0.1534	0.1616	0.1541	-	-	-	-	0.202
α_2^C	0.1283	0.1312	0.1372	0.1408	-	-	-	-	0.139
α_3^C	0.1440	0.1262	0.1319	0.1238	-	-	-	-	0.145
A_e in cm^{-1}	33.7248	33.0245	29.1829	29.1792	30.4693	30.3179	26.9091	27.0440	
B_e	13.3635	13.4364	14.6301	14.6506	13.0017	13.0929	14.5169	14.4714	
C_e	9.5710	9.5506	9.7448	9.7535	9.1130	9.1440	9.4297	9.4270	
A_0	34.7051	34.0313	29.7613	29.7930	-	-	-	-	
B_0	13.2462	13.3331	14.5470	14.5742	-	-	-	-	
C_0	9.3504	9.3452	9.5295	9.5441	-	-	-	-	
A_0'	34.7071	34.0333	29.7631	29.7949					
B_0'	13.2482	13.3351	14.5488	14.5760					
C_0'	9.3475	9.3423	9.5267	9.5413					

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[a] Ref. 56.

Table 2. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies of H_2O.

	SCF				CISD				Experiments[a]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	4028.3	3990.3	4151.5	4114.5	3704.4	3683.0	3935.4	3885.7	3832.0, 3825.3
ω_2	1710.6	1723.2	1749.8	1748.1	1648.2	1663.6	1686.3	1660.8	1648.9, 1653.9
ω_3	4204.2	4156.2	4267.1	4226.2	3875.3	3845.8	4048.4	3997.7	3942.5, 3935.6
χ_{11} in cm^{-1}	- 42.466	- 38.215	- 40.084	- 38.395	-	-	-	-	- 42.6
χ_{12}	- 11.157	- 8.118	- 15.628	- 14.653	-	-	-	-	- 15.9
χ_{13}	-163.077	-149.321	-157.208	-150.864	-	-	-	-	-165.8
χ_{22}	- 28.719	- 29.910	- 19.9897	- 20.702	-	-	-	-	- 16.8
χ_{23}	- 12.255	- 9.226	- 17.921	- 17.117	-	-	-	-	- 20.3
χ_{33}	- 49.836	- 46.408	- 45.355	- 43.838	-	-	-	-	- 47.6
ν_1 in cm^{-1}	3865.3	3835.1	3984.9	3954.9	(3532.4)	(3527.9)	(3768.8)	(3726.2)	3651.7
ν_2	1641.5	1654.7	1693.1	1690.8	(1579.1)	(1595.1)	(1629.6)	(1603.5)	1595.0
ν_3	4016.8	3984.2	4088.8	4054.5	(3688.0)	(3673.7)	(3870.1)	(3826.0)	3755.8

Table 2 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	-172.0	-155.1	-166.6	-159.5	(-172.0)	(-155.1)	(-166.6)	(-159.5)	-173.6
Δ_2	- 69.1	- 68.5	- 56.7	- 57.3	(- 69.1)	(- 68.5)	(- 56.7)	(- 57.3)	-58.9
Δ_3	-187.3	-172.1	-178.3	-171.7	(-187.3)	(-172.1)	(-178.3)	(-171.7)	-179.8

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[a] Ref. 56.

Table 3. Theoretical and experimental values of quartic and sextic centrifugal distortion constants and asymmetry parameter for H_2O.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
$\Delta_J \times 10^6$ in cm^{-1}	760.45	774.81	1050.20	769.70	784.60	1179.57	1124.68		
$\Delta_{JK} \times 10^6$	-3928.65	-3762.78	-4791.29	-3253.53	-3167.82	-4876.84			
$\Delta_K \times 10^6$	44088.77	40798.61	27270.75	35430.12	34212.68	24443.88			
$\Phi_J \times 10^6$	272.01	277.79	415.48	273.73	278.78	411.52	451.34		
$\Phi_K \times 10^6$	680.06	674.94	442.67	611.95	633.08	335.63			
$H_J \times 10^6$ in cm^{-1}	0.1913	0.1965			0.3704				
$H_{JK} \times 10^6$	-1.7632	-1.7196			-2.9064				
$H_{KJ} \times 10^6$	-11.1880	-9.6691			-3.8411				
$H_K \times 10^6$	190.2246	165.7759			73.2317				
$h_J \times 10^6$	0.0938	0.0960			0.1830				
$h_{JK} \times 10^6$	-0.0837	-0.0788			-0.3775				
$h_K \times 10^6$	-4.5646	-3.7454			-0.6053				
σ in cm^{-1}	12.0026	11.3678			7.0456				

Table 4. Theoretical and experimental vibration-rotation interaction constants and rotational constants of D_2O.

	SCF				CISD				Experiment[a]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
α_1^A in cm^{-1}	0.3033	0.2363	0.1743	0.1583	-	-	-	-	0.246
α_2^A	- 1.7990	- 1.7009	- 1.1316	- 1.1297	-	-	-	-	-1.161
α_3^A	0.7001	0.6479	0.4918	0.4774	-	-	-	-	0.593
α_1^B	0.0752	0.0733	0.0918	0.0893	-	-	-	-	0.096
α_2^B	- 0.0219	- 0.0232	- 0.0617	- 0.0615	-	-	-	-	-0.082
α_3^B	0.0342	0.0271	0.0316	0.0290	-	-	-	-	0.042
α_1^C	0.0627	0.0571	0.0639	0.0611	-	-	-	-	0.077
α_2^C	0.0489	0.0501	0.0516	0.0529	-	-	-	-	0.050
α_3^C	0.0538	0.0472	0.0464	0.0435	-	-	-	-	0.054
A_e in cm^{-1}	18.7618	18.3722	16.2351	16.2330	16.9507	16.8665	14.9701	15.0451	
B_e	6.6872	6.7237	7.3210	7.3313	6.5062	6.5518	7.2644	7.2416	
C_e	4.9330	4.9223	5.0457	5.0504	4.7016	4.7188	4.8910	4.8886	

Table 4 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
A_0	19.1596	18.7806	16.4678	16.4800	-	-	-	-	
B_0	6.6435	6.6851	7.2902	7.3029	-	-	-	-	
C_0	4.8473	4.8451	4.9648	4.9716	-	-	-	-	
A'_0	19.1601	18.7811	16.4683	16.4805	-	-	-	-	
B'_0	6.6440	6.6856	7.2907	7.3034	-	-	-	-	
C'_0	4.8466	4.8443	4.9640	4.9709	-	-	-	-	

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[a] Ref. 56.

Table 5. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants and fundamental vibrational frequencies of D_2O.

	SCF				CISD				Experiment[a]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	2892.7	2865.9	2992.6	2965.8	2659.1	2644.2	2837.9	2801.4	2855.6
ω_2	1256.9	1265.9	1280.8	1279.6	1211.5	1222.6	1233.8	1215.5	1233.5
ω_3	3090.7	3054.6	3128.8	3098.8	2846.7	2824.6	2965.9	2929.1	2990.1
χ_{11} in cm^{-1}	- 21.698	- 19.590	- 20.786	- 19.914	-	-	-	-	- 22.6
χ_{12}	- 4.367	- 2.238	- 7.889	- 7.299	-	-	-	-	- 7.6
χ_{13}	- 84.659	- 77.281	- 81.542	- 78.196	-	-	-	-	- 87.2
χ_{22}	- 15.873	- 16.617	- 10.792	- 11.192	-	-	-	-	- 9.2
χ_{23}	- 5.953	- 4.390	- 9.250	- 8.839	-	-	-	-	- 10.6
χ_{33}	- 28.424	- 26.470	- 25.655	- 24.792	-	-	-	-	- 26.2
ν_1 in cm^{-1}	2804.8	2787.0	2906.3	2965.8	(2571.2)	(2565.3)	(2751.6)	(2718.8)	2763.8
ν_2	1220.0	1229.4	1250.6	1279.6	(1174.6)	(1186.1)	(1203.6)	(1185.0)	1206.4
ν_3	2988.6	2960.9	3032.1	3098.8	(2744.5)	(2730.8)	(2869.2)	(2836.0)	2888.8

Table 5 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	- 87.9	- 78.9	- 86.3	- 82.6	(- 87.9)	(- 78.9)	(- 86.3)	(- 82.6)	-92.6
Δ_2	- 36.9	- 36.5	- 30.2	- 30.5	(- 36.9)	(- 36.5)	(- 30.2)	(- 30.5)	-27.5
Δ_3	-102.2	- 93.8	- 96.7	- 93.1	(-102.2)	(- 93.8)	(- 96.7)	(- 93.1)	-101.3

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[a] Ref. 56.

Table 6. Theoretical and experimental geometries, dipole moments, vibration-rotation interaction constants, and rotational constants of CH_2 ($^3B_1$).

	SCF				CISD				Experiments[a,b]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Energy in hartree	-38.91369	-38.91454	-38.92764	-38.92893	-38.98226	-38.98986	-39.04947		
r_e(CH) in Å	1.0743	1.0724	1.0756	1.0724	1.0951	1.0879	1.0853	1.0789	1.0748
θ_e(HCH) in deg.	130.26	130.32	129.36	129.61	133.12	132.99	132.68	133.84	
μ in D	0.681	0.673	0.614	0.588	0.689	0.674			
α_1^A in cm^{-1}	0.8209	0.8128	0.7205	0.7362	-	-	-	-	
α_2^A	-	-	-	-	-	-	-	-	
α_3^A	2.3024	2.2822	2.0085	2.1255	-	-	-	-	
α_1^B	0.1241	0.1166	0.1218	0.1189	-	-	-	-	
α_2^B	- 0.0084	- 0.0056	- 0.0217	- 0.0233	-	-	-	-	
α_3^B	0.0941	0.0868	0.0932	0.0885	-	-	-	-	

Table 6 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
α_1^C	0.1091	0.1035	0.1055	0.1035	-	-	-	-	
α_2^C	0.0772	0.0809	0.0785	0.0788	-	-	-	-	
α_3^C	0.1029	0.0960	0.0965	0.0951	-	-	-	-	
A_e in cm^{-1}	47.8557	48.1416	46.1705	46.8784	51.4721	51.8798	49.7190		73.810575
B_e	8.8036	8.8306	8.8472	8.8818	8.2856	8.4027	8.5218		8.45042
C_e	7.4357	7.4619	7.4245	7.4671	7.1368	7.2315	7.2749		7.18431
A_0	-	-	-	-	-	-	-	-	
B_0	8.6987	8.7317	8.7505	8.7898	-	-	-	-	
C_0	7.2911	7.3217	7.2843	7.3284	-	-	-	-	
A_0'									
B_0'	8.7008	8.7339	8.7525	8.7918					
C_0'	7.2881	7.3185	7.2813	7.3252					

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[a] Ref. 85.

[b] Ref. 91.

Table 7. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental frequencies of CH_2 ($^3B_1$).

	SCF				CISD				Experiments[a]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	3292.3	3238.3	3287.4	3266.3	3093.1	3059.2	3192.6	3178.8	3090
ω_2	1277.9	1269.4	1299.7	1298.2	1097.3	1104.5	1166.8	1147.5	1080
ω_3	3514.0	3453.6	3494.4	3478.1	3310.9	3274.1	3407.5	3404.6	3220
χ_{11} in cm^{-1}	- 29.122	- 26.032	- 27.014	- 26.090	-	-	-	-	
χ_{12}	- 1.063	2.117	1.122	2.027	-	-	-	-	
χ_{13}	-113.536	-100.686	-105.682	-102.025	-	-	-	-	
χ_{22}	- 25.092	- 24.483	- 23.815	- 23.931	-	-	-	-	
χ_{23}	- 3.023	- 2.329	- 4.117	- 3.095	-	-	-	-	
χ_{33}	- 35.585	- 32.180	-32.432	- 32.286	-	-	-	-	
ν_1 in cm^{-1}	3176.7	3136.9	3181.0	3164.2	(2977.6)	(2957.9)	(3086.3)	(3076.6)	2950
ν_2	1225.6	1220.3	1250.6	1249.8	(1045.1)	(1055.4)	(1117.7)	(1099.1)	963.0995[b]
ν_3	3384.6	3337.7	3374.6	3361.0	(3181.4)	(3158.2)	(3287.7)	(3287.5)	3080

Table 7 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	-115.5	-101.3	-106.3	-102.2	(-115.5)	(-101.3)	(-106.3)	(-102.2)	-140
Δ_2	- 52.2	- 49.1	- 49.1	- 48.4	(- 52.2)	(- 49.1)	(- 49.1)	(- 48.4)	-117
Δ_3	-129.5	-115.9	-119.8	-117.1	(-129.5)	(-115.9)	(-119.8)	(-117.1)	-140

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[a] Ref. 85, unless otherwise noted.

[b] Ref. 91; see also ref. 89.

Table 8. Theoretical and experimental values of quartic and sextic centrifugal distortion constants and asymmetry parameter for CH_2 ($^3B_1$).

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
$\Delta_J \times 10^6$ in cm^{-1}	325.68	337.07	331.03	334.57	320.81	340.78	327.02		
$\Delta_{JK} \times 10^6$	-4925.70	-4991.00	-4591.49	-4573.59	-7008.63	-7225.46	-6274.74		
$\Delta_K \times 10^6$	-	-	-	-	-	-	-	-	
$\Phi_J \times 10^6$	86.71	88.99	89.41	88.97	84.22	89.24	87.65		
$\Phi_K \times 10^6$	1092.57	1148.93	1074.90	1105.42	1187.27	1276.39	1146.65		
$H_J \times 10^6$ in cm^{-1}	0.0470	0.0497	0.0494	0.0500					
$H_{JK} \times 10^6$	-1.0129	-1.0285	-1.0685	-1.1286					
$H_{KJ} \times 10^6$	-84.8645	-89.5647	-68.7874	-71.1565					
$H_K \times 10^6$	3954.731	4189.528	3023.409	3299.503					
$h_J \times 10^6$	0.0220	0.0231	0.0232	0.0233					
$h_{JK} \times 10^6$	0.1406	0.4620	0.1368	0.1497					
$h_K \times 10^6$	-52.3126	-54.6888	-40.3055	-43.1414					
σ in cm^{-1}	63.4715	63.9287	57.8923	59.1526					

Table 9. Theoretical and experimental vibration-rotation interaction constants, and rotational constants of $CD_2(^3B_1)$.

	SCF				CISD				Experiment[a]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
α_1^A in cm^{-1}	0.1102	0.1042	0.0802	0.0823	-	-	-	-	
α_2^A	-	-	-	-	-	-	-	-	
α_3^A	-	-	0.9940	1.0473	-	-	-	-	
α_1^B	0.0513	0.0486	0.0507	0.0496	-	-	-	-	
α_2^B	- 0.0059	- 0.0049	- 0.0110	- 0.0116	-	-	-	-	
α_3^B	0.0352	0.0325	0.0348	0.0332	-	-	-	-	
α_1^C	0.0419	0.0400	0.0410	0.0401	-	-	-	-	
α_2^C	0.0281	0.0295	0.0281	0.0282	-	-	-	-	
α_3^C	0.0400	0.0374	0.0375	0.0370	-	-	-	-	
A_e in cm^{-1}	27.3858	27.5494	26.4214	26.8266	29.4553	29.6886	28.4521		37.786863
B_e	4.4054	4.4189	4.4272	4.4446	4.1462	4.2048	4.2644		
C_e	3.7949	3.8081	3.7919	3.8129	3.6346	3.6831	3.7086		

Table 9 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
A_0 in cm^{-1}	-	-	-	-	-	-	-	-	
B_0	4.3651	4.3808	4.3900	4.4090	-	-	-	-	
C_0	3.7399	3.7545	3.7386	3.7602	-	-	-	-	
A_0' in cm^{-1}	-	-	-	-	-	-	-	-	
B_0'	4.3657	4.3813	4.3905	4.4095	-	-	-	-	
C_0'	3.7391	3.7539	3.7378	3.7594	-	-	-	-	

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[a] Ref. 92.

Table 10. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies of CD_2 ($^3B_1$).

	SCF				CISD				Experiment[a]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	2358.5	2319.3	2356.5	2340.7	2212.2	2188.8	2285.5	2273.9	
ω_2	954.6	948.2	970.3	969.5	821.0	826.1	872.2	858.4	
ω_3	2632.2	2587.0	2616.6	2604.7	2482.7	2455.0	2553.9	2552.6	
x_{11} in cm^{-1}	- 15.043	- 13.429	- 13.989	- 13.467	-	-	-	-	
x_{12}	1.950	3.774	3.627	4.518	-	-	-	-	
x_{13}	- 58.792	- 52.008	- 54.647	- 52.660	-	-	-	-	
x_{22}	- 14.495	- 14.189	- 13.877	- 14.044	-	-	-	-	
x_{23}	- 1.511	- 1.109	- 2.267	- 1.725	-	-	-	-	
x_{33}	- 21.335	- 19.368	- 19.460	- 19.397	-	-	-	-	
ν_1 in cm^{-1}	2300.0	2268.9	2303.0	2340.7	(2153.7)	(2137.8)	(2232.0)	(2222.9)	
ν_2	925.8	921.1	943.2	969.5	(792.2)	(799.1)	(845.1)	(831.7)	752.3748
ν_3	2559.4	2521.7	2549.2	2604.7	(2409.9)	(2389.7)	(2486.5)	(2486.6)	

Table 10 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	- 58.5	- 51.0	- 53.5	- 51.0	(- 58.5)	(- 51.0)	(- 53.5)	(- 51.0)	
Δ_2	- 28.8	- 27.0	- 27.1	- 26.7	(- 28.8)	(- 27.0)	(- 27.1)	(- 26.7)	
Δ_3	- 72.8	- 65.3	- 67.4	- 66.0	(- 72.8)	(- 65.3)	(- 67.4)	(- 66.0)	

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[a] Ref. 92.

Table II. Theoretical and experimental geometries, dipole moments, vibration-rotation interaction constants, and rotational constants of CH_2 ($^1A_1$).

	SCF				CISD				Experiment^a
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Energy in hartree	- 38.86201	- 38.86354	- 38.88559	- 38.88698	- 38.94463	- 38.95287	- 39.01760	- 39.02513	
r_e(CH) in Å	1.1034	1.1020	1.1005	1.0979	1.1338	1.1256	1.1167	1.1113	
θ_e(HCH) in deg.	106.65	106.23	103.74	103.71	104.41	104.53	101.29	101.54	
μ in D	2.411	2.377	2.103	2.065	2.186	2.171	1.884	1.867	
α_1^A in cm^{-1}	0.5691	0.4982	0.4325	0.4144	-	-	-	-	
α_2^A	- 2.0905	- 2.0306	- 1.6597	- 1.6865	-	-	-	-	
α_3^A	0.9717	0.9327	0.7935	0.7893	-	-	-	-	
α_1^B	0.1291	0.1259	0.1408	0.1391	-	-	-	-	
α_2^B	- 0.0683	- 0.0649	- 0.1215	- 0.1237	-	-	-	-	
α_3^B	0.0598	0.0457	0.0581	0.0521	-	-	-	-	

Table II continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
α_1^C	0.1184	0.1101	0.1119	0.1091	-	-	-	-	
α_2^C	0.1137	0.1231	0.1163	0.1179	-	-	-	-	
α_3^C	0.0913	0.0780	0.0823	0.0781	-	-	-	-	
A_e in cm^{-1}	22.4901	22.3264	21.1572	21.2427	20.2312	20.5863	19.4805	19.7780	
B_e	10.6793	10.7645	11.1610	11.2175	10.4192	10.5548	11.2166	11.2862	
C_e	7.2410	7.2628	7.3066	7.3410	6.8773	6.9774	7.1181	7.1857	
A_0	22.7650	22.6262	21.3741	21.4841	-	-	-	-	
B_0	10.6190	10.7112	11.1223	11.1837	-	-	-	-	
C_0	7.0793	7.1072	7.1513	7.1884	-	-	-	-	
A_0'	22.7664	22.6277	21.3755	21.4855					20.1182
B_0'	10.6203	10.7126	11.1237	11.1851					11.2050
C_0'	7.0772	7.1051	7.1493	7.1863					7.0686

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[a] Ref. 89.

Table 12. Theoretical and experimental harmonic frequencies, anharmonic constants, and fundamental frequencies of CH_2 ($^1A_1$).

	SCF				CISD				Experiment[a]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	3086.9	3031.9	3120.1	3097.6	2804.2	2783.6	2969.3	2954.5	
ω_2	1483.3	1498.0	1490.3	1485.0	1396.3	1418.6	1428.6	1420.0	
ω_3	3172.8	3098.3	3193.4	3164.8	2891.5	2856.7	3047.2	3022.4	
x_{11} in cm^{-1}	- 31.267	- 27.155	- 27.971	- 26.653	-	-	-	-	
x_{12}	21.624	- 24.268	17.747	24.948	-	-	-	-	
x_{13}	-124.916	-108.567	-112.579	-107.959	-	-	-	-	
x_{22}	- 25.015	- 14.833	- 19.940	- 20.749	-	-	-	-	
x_{23}	- 8.649	- 7.895	- 12.486	- 10.214	-	-	-	-	
x_{33}	- 37.494	- 33.406	- 33.132	- 32.183	-	-	-	-	
ν_1 in cm^{-1}	2972.8	2911.2	3016.7	3002.8	(2690.0)	(2662.7)	(2865.9)	(2859.7)	2805.9
ν_2	1439.8	1452.2	1453.0	1450.9	(1352.8)	(1372.9)	(1391.3)	(1385.9)	
ν_3	3031.0	2973.3	3064.6	3041.3	(2749.7)	(2731.7)	(2918.4)	(2898.9)	2864.5

Table 12 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	-114.2	-120.7	-103.4	- 94.8	(-114.2)	(-120.7)	(-103.4)	(- 94.8)	
Δ_2	- 43.5	- 45.7	- 37.3	- 34.1	(- 43.5)	(- 45.7)	(- 37.3)	(- 34.1)	
Δ_3	-141.8	-125.0	-128.8	-123.5	(-141.8)	(-125.0)	(-128.8)	(-123.5)	

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[a] Ref. 95.

Table 13. Theoretical and experimental values of quartic and sextic centrifugal distortion constants and asymmetry parameter for CH_2 ($^1A_1$).

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
$\Delta_J \times 10^6$ in cm^{-1}	596.19	614.08	701.36	719.45	638.11	653.10	785.49	806.93	
$\Delta_{JK} \times 10^6$	-2043.51	-1914.46	-2446.40	-2482.54	-1909.65	-1791.34	-2641.28	-2712.33	
$\Delta_K \times 10^6$	17255.38	16512.34	14230.06	14494.57	14344.57	14598.59	12327.13	13028.54	
$\Phi_J \times 10^6$	218.34	223.60	270.54	277.26	236.00	238.47	310.93	318.45	
$\Phi_K \times 10^6$	461.40	497.97	384.01	399.99	415.74	469.98	297.64	322.17	
$H_J \times 10^6$ in cm^{-1}	0.1482	0.1522	0.2103	0.2206					
$H_{JK} \times 10^6$	-1.1187	-1.0607	-1.5177	-1.5658					
$H_{KJ} \times 10^6$	-2.3278	-2.1866	-1.0030	-1.0328					
$H_K \times 10^6$	41.8808	38.9166	27.5613	28.6164					
$h_J \times 10^6$	0.0726	0.0743	0.1036	0.1085					
$h_{JK} \times 10^6$	-0.0657	-0.0469	-0.1603	-0.1601					
$h_K \times 10^6$	-0.2568	-0.0688	0.2945	0.3241					
σ in cm^{-1}	7.8561	7.6055	6.1589	6.1518					

Table 14. Theoretical and experimental vibration-rotation interaction constants, and rotational constants of $CD_2(^1A_1)$.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
α_1^A in cm^{-1}	0.1809	0.1528	0.1284	0.1193	-	-	-	-	
α_2^A	-0.8583	-0.8327	-0.6759	-0.6864	-	-	-	-	
α_3^A	0.4464	0.4279	0.3665	0.3649	-	-	-	-	
α_1^B	0.0579	0.0566	0.0636	0.0633	-	-	-	-	
α_2^B	-0.0308	-0.0296	-0.0509	-0.0519	-	-	-	-	
α_3^B	0.0195	0.0146	0.0178	0.0156	-	-	-	-	
α_1^C	0.0467	0.0440	0.0428	0.0418	-	-	-	-	
α_2^C	0.0431	0.0467	0.0435	0.0441	-	-	-	-	
α_3^C	0.0328	0.0274	0.0316	0.0300	-	-	-	-	
A_e in cm^{-1}	12.8702	12.7764	12.1074	12.1563	11.5775	11.7807	11.1479	11.3181	
B_e	5.3440	5.3867	5.5851	5.6133	5.2139	5.2817	5.6129	5.6477	
C_e	3.7761	3.7891	3.8220	3.8401	3.5949	3.6468	3.7332	3.7677	

Table 14 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
A_0	12.9857	12.9024	12.1979	12.2574	-	-	11.4827	11.6656	
B_0	5.3207	5.3659	5.5699	5.5999	-	-	5.7036	5.7401	
C_0	3.7148	3.7300	3.7631	3.7822	-	-	3.7502	3.7851	
A'_0	12.9861	12.9028	12.1983	12.2577	-	-	-	-	
B'_0	5.3211	5.3663	5.5702	5.6002	-	-	-	-	
C'_0	3.7142	3.7295	3.7625	3.7816	-	-	-	-	

Table 15. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies of $CD_2(^1A_1)$.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	2232.6	2193.2	2262.9	2246.7	2028.2	2012.7	2155.6	2144.4	
ω_2	1097.6	1108.2	1099.6	1095.6	1033.1	1049.9	1053.0	1046.9	
ω_3	2351.1	2295.5	2362.8	2341.6	2140.2	2114.5	2251.6	2233.6	
χ_{11} in cm^{-1}	- 16.220	- 14.083	- 14.626	- 13.961	-	-	-	-	
χ_{12}	- 15.778	- 15.406	- 15.834	- 15.575	-	-	-	-	
χ_{13}	- 65.696	- 56.824	- 59.043	- 56.489	-	-	-	-	
χ_{22}	- 6.715	- 7.499	- 4.427	- 3.944	-	-	-	-	
χ_{23}	- 4.294	- 3.941	- 6.636	- 5.424	-	-	-	-	
χ_{33}	- 21.980	- 19.668	- 19.368	- 18.836	-	-	-	-	
ν_1 in cm^{-1}	2159.4	2193.2	2196.2	2182.7	(1955.0)	(1948.4)	(2088.9)	(2080.4)	
ν_2	1074.1	1108.2	1079.5	1077.3	(1009.6)	(1025.2)	(1032.9)	(1028.5)	
ν_3	2272.2	2295.5	2291.2	2273.0	(2061.2)	(2044.8)	(2180.0)	(2165.0)	

Table 15 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	- 73.2	- 64.3	- 66.7	- 64.0	(- 73.2)	(- 64.3)	(- 66.7)	(- 64.0)	
Δ_2	- 23.5	- 24.7	- 20.1	- 18.4	(- 23.5)	(- 24.7)	(- 20.1)	(- 18.4)	
Δ_3	- 79.0	- 69.7	- 71.6	- 68.6	(- 79.0)	(- 69.7)	(- 71.6)	(- 68.6)	

Table 16. Theoretical and experimental geometries, dipole moments, vibration-rotation interaction constants, and rotational constants of CH_2 ($^1B_1$).

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Energy in hartree	-38.84520	-38.84588	-38.86191	-38.86330	-38.91129	-38.91891	-38.98014	-38.98880	
r_e(CH) in Å	1.0670	1.0653	1.0701	1.0664	1.0915	1.0861	1.0817	1.0748	
θ_e(HCH) in deg.	150.41	150.88	142.65	143.03	143.87	143.19	141.36	142.49	
μ in D					0.965	0.958	0.804	0.762	
α_1^A in cm^{-1}	-	-	3.1395	3.2889	-	-	-	-	
α_2^A	-	-	-	-	-	-	-	-	
α_3^A	-	-	-	-	-	-	-	-	
α_1^B	0.0837	0.0717	0.0948	0.0936	-	-	-	-	
α_2^B	0.1927	0.1980	0.0741	0.0722	-	-	-	-	
α_3^B	0.0669	0.0607	0.0801	0.0776	-	-	-	-	

Table 16 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
α_1^C	0.1059	0.1015	0.1036	0.1030	-	-	-	-	
α_2^C	0.0227	0.0259	0.0493	0.0492	-	-	-	-	
α_3^C	0.1205	0.1146	0.1089	0.1087	-	-	-	-	
A_e in cm^{-1}	131.5393	136.1817	83.1981	85.4619	85.2786	83.0596	76.2584	81.7995	
B_e	7.8586	7.8672	8.1381	8.1754	7.7663	7.8748	8.0262	8.0746	
C_e	7.4156	7.4375	7.4130	7.4616	7.1181	7.1929	7.2619	7.3491	
A_0	-	-	-	-	-	-	-	-	
B_0	7.6869	7.7020	8.0136	8.0537	-	-	-	-	
C_0	7.2910	7.3165	7.2821	7.3311	-	-	-	-	
A_0'	-	-	-	-					
B_0'	7.6915	7.7069	8.0167	8.0569					
C_0'	7.2841	7.3092	7.2774	7.3262					

Table 17. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies of CH_2 ($^1B_1$).

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	3334.9	3281.8	3321.9	3299.0	3092.7	3045.9	3198.9	3188.6	
ω_2	785.9	768.7	1034.3	1033.3	922.1	942.8	1011.4	992.4	
ω_3	3664.0	3601.9	3602.7	3589.2	3394.1	3338.3	3477.6	3478.2	
x_{11} in cm^{-1}	- 30.406	- 28.351	- 28.503	- 27.517	-	-	-	-	
x_{12}	23.385	32.609	11.355	11.124	-	-	-	-	
x_{13}	-114.270	-103.547	-107.756	-104.439	-	-	-	-	
x_{22}	-166.839	-169.198	- 71.863	- 72.331	-	-	-	-	
x_{23}	49.441	49.156	17.807	18.344	-	-	-	-	
x_{33}	- 40.396	- 36.745	- 35.280	- 35.317	-	-	-	-	
ν_1 in cm^{-1}	3228.6	3189.6	3216.6	3197.3	(2986.4)	(2953.7)	(3093.7)	(3086.7)	
ν_2	488.7	471.2	905.1	903.3	(624.8)	(645.3)	(882.3)	(862.5)	
ν_3	3550.8	3501.2	3487.1	3475.6	(3280.9)	(3237.6)	(3361.5)	(3364.5)	

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Table 17 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	-106.3	- 92.2	-105.2	-101.9	(-106.3)	(- 92.2)	(-105.2)	(-101.9)	
Δ_2	-297.3	-297.5	-129.1	-129.9	(-297.3)	(-297.5)	(-129.1)	(-129.9)	
Δ_3	-113.2	-100.7	-115.5	-113.7	(-113.2)	(-100.7)	(-115.5)	(-113.7)	

Table 18. Theoretical and experimental values of quartic and sextic centrifugal distortion constants and asymmetry parameter for CH_2 ($^1B_1$).

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
$\Delta_J \times 10^6$ in cm^{-1}	239.53	247.85	255.42	257.97	247.66	266.27	260.81	263.83	
$\Delta_{JK} \times 10^6$	-	-	-13323.43	-13357.01	-13490.19	-13441.66	-11464.63	-12601.64	
$\Delta_K \times 10^6$	-	-	-	-	-	-	-	-	
$\phi_J \times 10^6$	46.37	47.48	53.86	52.64	48.17	52.84	55.55	53.78	
$\phi_K \times 10^6$	2265.15	2452.00	1629.61	1687.12	1595.82	1701.69	1507.80	1621.79	
$H_J \times 10^6$ in cm^{-1}	0.0249	0.0270	0.0292	0.0290					
$H_{JK} \times 10^6$	-0.2010	-0.2262	-0.4028	-0.5834					
$H_{KJ} \times 10^6$	-	-	-1219.41	-1298.70					
$H_K \times 10^6$	-	-	-	-					
$h_J \times 10^6$	0.0111	0.0120	0.0132	0.0130					
$h_{JK} \times 10^6$	-	-	0.3264	0.3742					
$h_K \times 10^6$	-	-	-	-					
σ in cm^{-1}	-	-	-	-					

Table 19. Theoretical and experimental vibration-rotation interaction constants and rotational constants of $CD_2(^1B_1)$.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
α_1^A in cm^{-1}	-	-	0.7058	0.7607	-	-	-	-	
α_2^A	-	-	-	-	-	-	-	-	
α_3^A	-	-	-	-	-	-	-	-	
α_1^B	0.0340	0.0298	0.0387	0.0381	-	-	-	-	
α_2^B	0.0716	0.0736	0.0262	0.0256	-	-	-	-	
α_3^B	0.0259	0.0236	0.0309	0.0301	-	-	-	-	
α_1^C	0.0373	0.0355	0.0377	0.0373	-	-	-	-	
α_2^C	0.0171	0.0184	0.0210	0.0209	-	-	-	-	
α_3^C	0.0467	0.0445	0.0428	0.0428	-	-	-	-	
A_e in cm^{-1}	75.2744	77.9310	47.6108	48.9063	43.8013	47.5315	43.6395	46.8104	
B_e	3.9325	3.9368	4.0724	4.0910	3.8863	3.9406	4.0164	4.0406	
C_e	3.7373	3.7475	3.7515	3.7752	3.5997	3.6389	3.6779	3.7195	

Table 19 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
A_0	-	-	-	-	-	-	-	-	
B_0	3.8668	3.8733	4.0245	4.0442	-	-	-	-	
C_0	3.6867	3.6983	3.7007	3.7247	-	-	-	-	
A_0'	-	-	-	-	-	-	-	-	
B_0'	3.8679	3.8746	4.0252	4.0450	-	-	-	-	
C_0'	3.6850	3.6964	3.6995	3.7234	-	-	-	-	

Table 20. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies of CD_2 ($^1B_1$).

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	2368.1	2330.3	2365.6	2348.6	2199.5	2167.4	2278.3	2269.6	
ω_2	592.3	579.3	777.2	776.7	693.9	709.0	760.0	746.1	
ω_3	2761.9	2715.4	2710.1	2700.3	2554.1	2511.6	2615.0	2616.3	
x_{11} in cm^{-1}	- 15.063	- 13.909	- 14.333	- 13.802	-	-	-	-	
x_{12}	10.198	15.076	6.379	6.437	-	-	-	-	
x_{13}	- 59.071	- 53.559	- 55.742	- 53.983	-	-	-	-	
x_{22}	- 94.474	- 95.831	- 40.643	- 40.964	-	-	-	-	
x_{23}	31.567	31.396	11.392	11.664	-	-	-	-	
ν_1 in cm^{-1}	2313.6	2283.2	2312.2	2297.2	(2144.9)	(2120.3)	(2225.0)	(2218.2)	
ν_2	424.2	410.9	704.8	703.8	(525.8)	(540.6)	(687.6)	(673.2)	
ν_3	2698.4	2658.8	2644.8	2636.0	(2490.6)	(2455.0)	(2549.8)	(2552.0)	

Table 20 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	- 54.6	- 47.1	- 53.3	- 51.4	(- 54.6)	(- 47.1)	(- 53.3)	(- 51.4)	
Δ_2	-168.1	-168.4	- 72.4	- 72.9	(-168.1)	(-168.4)	(- 72.4)	(- 72.9)	
Δ_3	- 63.5	- 56.6	- 65.2	- 64.3	(- 63.5)	(- 56.6)	(- 65.2)	(- 64.3)	

Table 21. Theoretical and experimental geometries, dipole moments, vibration-rotation interaction constants, and rotational constants of HCO ($^2A'$).

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Energy in hartree	-113.20457	-113.21217	-113.26955	-113.27586	-113.40109	-113.42746	-113.55127	-113.57694	
r_e(CH) in Å	1.0921	1.0920	1.1064	1.1049	1.1178	1.1122	1.1190	1.1144	1.125[a], 1.16[b]
r_e(CO)	1.1873	1.1766	1.1619	1.1543	1.2182	1.2028	1.1843	1.1752	1.175 , 1.17
θ_e(HCO) in deg.	129.39	128.82	127.49	127.70	127.15	126.61	125.18	125.56	124.95 ,123.8
μ in D	2.678	2.620	2.1891	2.191	2.169	2.141	1.779	1.807	
α_1^A in cm^{-1}	1.4555	1.3964	1.2614	1.3317	-	-	-	-	
α_2^A	-0.0680	-0.0880	-0.0601	-0.0653	-	-	-	-	
α_3^A	-	-	-	-	-	-	-	-	
α_1^B	0.0016	0.0010	0.0013	0.0009	-	-	-	-	
α_2^B	0.0114	0.0115	0.0109	0.0111	-	-	-	-	
α_3^B	- 0.0028	- 0.0023	- 0.0047	- 0.0050	-	-	-	-	

Table 21 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
α_1^C	0.0038	0.0032	0.0035	0.0032	-	-	-	-	
α_2^C	0.0104	0.0105	0.0100	0.0101	-	-	-	-	
α_3^C	0.0049	0.0058	0.0047	0.0048	-	-	-	-	
A_e in cm^{-1}	29.2204	28.7594	27.0190	27.2869	26.0172	25.0026	24.3790	25.1419	
B_e	1.4520	1.4787	1.5159	1.5333	1.3900	1.4263	1.4727	1.4928	
C_e	1.3833	1.4064	1.4353	1.4517	1.3195	1.3510	1.3888	1.4091	
A_0	30.0640	29.5654	27.5813	27.8492	-	-	-	-	
B_0	1.4469	1.4736	1.5121	1.5298	-	-	-	-	
C_0	1.3737	1.3967	1.4262	1.4427	-	-	-	-	
A_0'	30.0641	29.5656	27.5814	27.8493					
B_0'	1.4470	1.4738	1.5122	1.5300					
C_0	1.3735	1.3965	1.4260	1.4424					

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[a] Ref. 97.

[b] Ref. 98.

Table 22. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies of HCO ($^2A'$).

	SCF				CISD				Experiments[a,b]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	3150.5	3063.3	3006.6	2962.7	2868.0	2812.9	2853.4	2824.5	2768.2
ω_2	1983.0	1976.4	2135.3	2135.5	1794.9	1807.7	1991.8	1992.0	1862.2
ω_3	1240.6	1252.3	1254.2	1251.0	1140.4	1165.9	1159.9	1159.3	1092.6
x_{11} in cm^{-1}	- 86.033	- 80.361	- 86.191	- 86.427	-	-	-	-	-140.1
x_{12}	0.018	- 7.580	0.446	1.239	-	-	-	-	- 0.3
x_{13}	- 19.425	- 30.021	- 23.249	- 20.837	-	-	-	-	- 0.2
x_{22}	- 10.683	- 10.406	- 10.466	- 10.590	-	-	-	-	0.0
x_{23}	- 5.129	2.547	- 1.692	- 2.028	-	-	-	-	0.0
x_{33}	- 10.272	- 11.294	- 10.622	- 10.717	-	-	-	-	0.0
ν_1 in cm^{-1}	2968.8	2883.8	2822.8	2780.0	(2686.2)	(2633.4)	(2669.6)	(2641.8)	2488, 2442
ν_2	1959.1	1953.1	2113.7	2114.0	(1771.0)	(1784.4)	(1970.2)	(1975.4)	1861, 1868.1704
ν_3	1207.8	1216.0	1220.5	1218.2	(1107.6)	(1129.6)	(1126.2)	(1126.4)	1090, 1080.7618

Table 22 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	-181.8	-179.5	-183.8	-182.7	(-181.8)	(-179.5)	(-183.8)	(-182.7)	-280.2, -326.2
Δ_2	- 23.9	- 23.3	- 21.6	- 21.6	(- 23.9)	(- 23.3)	(-21.6)	(- 21.6)	-1.2, 5.97
Δ_3	- 32.8	- 36.3	- 33.7	- 32.9	(- 32.8)	(- 36.3)	(- 33.7)	(- 32.9)	-2.6, -11.84

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[a] Harmonic frequencies and anharmonic constants from Ref. 97.

[b] Fundamental frequencies from Refs. 99, 100.

Table 23. Theoretical and experimental values of quartic and sextic centrifugal distortion constants and asymmetry parameter for HCO ($^2A'$).

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
$\Delta_J \times 10^6$ in cm^{-1}	3.25	3.48	3.28	3.39	3.41	3.65	3.40	3.53	
$\Delta_{JK} \times 10^6$	-	-	-14.02	-15.98	-1.04	-1.03	6.18	2.18	
$\Delta_K \times 10^6$	39514.31	36794.90	29596.78	31161.92	31715.59	28911.68	24086.12	27029.30	
$\phi_J \times 10^6$	0.25	0.27	0.29	0.30	0.27	0.30	0.31	0.32	
$\phi_K \times 10^6$	78.05	79.81	80.79	83.06	80.16	80.39	83.80	87.97	
$H_J \times 10^6$ in cm^{-1}	0.0000	0.0000	0.0000	0.0000					
$H_{JK} \times 10^6$	0.0034	0.0036	0.0040	0.0041					
$H_{KJ} \times 10^6$	-0.6181	-0.5976	-0.4824	-0.5126					
$H_K \times 10^6$	191.5518	167.2178	113.8156	123.9871					
$h_J \times 10^6$	0.0000	0.0000	0.0000	0.0000					
$h_{JK} \times 10^6$	0.0014	0.0014	0.0016	0.0018					
$h_K \times 10^6$	0.7332	0.7248	0.6496	0.6736					
σ in cm^{-1}	-	-	-	-					

Table 24. Theoretical and experimental vibration-rotation interaction constants and rotational constants of DCO.

	SCF				CISD				Experiment[a]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
α_1^A in cm^{-1}	-	-	-	-	-	-	-	-	
α_2^A	-	-	-	-	-	-	-	-	
α_3^A	-	-	-	-	-	-	-	-	
α_1^B	0.0042	0.0039	0.0050	0.0051	-	-	-	-	
α_2^B	0.0092	0.0093	0.0084	0.0082	-	-	-	-	
α_3^B	-0.0032	-0.0027	-0.0050	-0.0052	-	-	-	-	
α_1^C	0.0053	0.0049	0.0051	0.0051	-	-	-	-	
α_2^C	0.0084	0.0086	0.0084	0.0084	-	-	-	-	
α_3^C	0.0034	0.0041	0.0032	0.0033	-	-	-	-	
A_e in cm^{-1}	17.7017	17.4282	16.3976	16.5811	15.6876	14.712	15.1881		
B_e	1.2410	1.2634	1.2932	1.3065	1.1936	1.2636	1.2795		
C_e	1.1597	1.1780	1.1987	1.2111	1.1092	1.1636	1.1801		

Table 24 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
A_0	-	-	-	-	-	-	-	-	
B_0	1.2359	1.2582	1.2890	1.3024	-	-	-	-	
C_0	1.1511	1.1692	1.1903	1.2027	-	-	-	-	
A'_0	-	-	-	-	-	-	-	-	14.6920
B'_0	1.2360	1.2583	1.2891	1.3025	-	-	-	-	1.281408
C'_0	1.1510	1.1691	1.1902	1.2025	-	-	-	-	1.171439

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[a] Ref. 98.

Table 25. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies of DCO.

	SCF				CISD				Experiments^{a,b}
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	2359.8	2295.8	2287.3	2264.3	2132.2	2092.0	2143.9	2129.4	2068.3
ω_2	1926.0	1918.5	2044.2	2034.2	1757.1	1768.8	1931.7	1929.0	1820.3
ω_3	964.4	973.9	975.7	974.1	884.9	905.0	900.2	900.7	848.8
x_{11} in cm^{-1}	- 42.414	- 39.308	- 29.221	-26.417	-	-	-	-	- 58.1
x_{12}	- 14.572	- 14.456	- 39.228	-43.880	-	-	-	-	- 32.4
x_{13}	- 10.751	- 11.797	- 11.446	-10.564	-	-	-	-	- 0.5
x_{22}	- 8.419	- 8.000	- 7.818	- 8.408	-	-	-	-	- 1.1
x_{23}	- 7.659	- 8.258	- 12.474	-14.016	-	-	-	-	0.0
x_{33}	- 4.966	- 5.583	- 3.805	- 3.388	-	-	-	-	0.0
ν_1 in cm^{-1}	2262.3	2204.0	2203.5	2184.3	(2034.7)	(2000.3)	(2060.1)	(2049.3)	1937, 1909.7738
ν_2	1898.0	1891.1	2002.7	1988.4	(1729.1)	(1741.4)	(1890.3)	(1883.2)	1800, 1794.857
ν_3	945.2	952.7	956.1	955.1	(865.8)	(883.8)	(880.6)	(881.6)	852, 846.5

Table 25 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	-97.5	-91.7	-83.8	-80.1	(-97.5)	(-91.7)	(-83.8)	(-80.1)	-31.3, -158.53
Δ_2	-28.0	-27.4	-41.5	-45.8	(-28.0)	(-27.4)	(-41.4)	(-45.8)	-20.3, -25.44
Δ_3	-19.1	-21.2	-19.6	-19.1	(-19.1)	(-21.2)	(-19.6)	(-19.1)	3.2, -2.3

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[a] Harmonic frequencies and anharmonic constants from Ref. 97.

[b] Fundamental frequencies from Refs. 99, 100.

Table 26. Theoretical and experimental geometries, dipole moments, vibration-rotation interaction constants, and rotational constants of H_2CO.

	SCF				CISD				Experiment[a]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Energy in hartree	-113.83071	-113.83755	-113.89476	-113.90005	-114.03746	-114.06478	-114.19558	-114.22102	
r_e(CO) in Å	1.2170	1.2080	1.1885	1.1823	1.2501	1.2363	1.2019	1.2036	1.203
r_e(CH) in Å	1.0843	1.0828	1.0960	1.0943	1.1046	1.0963	1.1038	1.0994	1.099
θ_e(HCO) in deg.	121.60	121.68	121.91	121.98					116.5
μ in D	3.1904	3.1051	2.7753	2.8440	2.7785	2.4878	2.4779		
A_e in cm^{-1}	9.7989	9.8306	9.6605	9.7086	9.4485	9.6091	9.5247	9.6173	
B_e	1.2815	1.2989	1.3315	1.3436	1.2165	1.2519	1.2959	1.3106	
C_e	1.1333	1.1473	1.1702	1.1803	1.0777	1.1076	1.1407	1.1534	
A_0		9.7443	9.5763	9.6258					
B_0		1.2934	1.3272	1.3394					
C_0		1.1377	1.1613	1.1714					

Table 26 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
A_0'		9.7444	9.5764	9.6258					
B_0'		1.2934	1.3272	1.3395					
C_0'		1.1376	1.1612	1.1713					

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[a] Ref. 127.

Table 27. Theoretical and experimental harmonic and fundamental vibrational frequencies of H_2CO.

	SCF				CISD				Experiments[a,b]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 (A_1) in cm^{-1}	3223.5	3158.0	3136.2	3099.2	3022.0	2988.6	3052.5	3021.7	2977.91,2944.3
ω_2 (A_1)	1878.2	1876.5	2005.9	2000.8	1697.3	1726.4	1868.4	1866.2	1778.26,1763.7
ω_3 (A_1)	1651.4	1649.8	1651.9	1654.8	1540.2	1557.9	1586.8	1592.1	1528.95,1562.6
ω_4 (B_1)	1324.5	1330.3	1331.9	1341.5	1189.8	1206.3	1234.7	1245.2	1191.02,1191.0
ω_5 (B_2)	3315.3	3242.8	3213.7	3173.7	3106.2	3077.1	3131.1	3096.9	2997.04,3008.7
ω_6 (B_2)	1350.2	1371.3	1364.5	1369.6	1261.2	1302.3	1299.1	1306.9	1298.91,1287.7
ν_1 in cm^{-1}	3075.2	3023.9	3001.6	2969.9	(2873.7)	(2854.5)	(2917.9)	(2892.4)	2811.42,2782.4
ν_2	1850.6	1847.1	1980.8	1976.0	(1669.7)	(1697.1)	(1843.4)	(1841.4)	1755.86,1746.0
ν_3	1624.1	1621.5	1621.0	1625.3	(1512.8)	(1529.7)	(1556.0)	(1562.6)	1500.32,1500.1
ν_4	1305.3	1310.8	1313.5	1322.2	(1170.5)	(1186.9)	(1216.4)	(1225.9)	1170.22,1167.2
ν_5	3155.1	3095.1	3065.0	3036.1	(2946.0)	(2929.4)	(2982.5)	(2959.3)	2861.30,2843.2
ν_6	1331.6	1348.9	1345.3	1350.9	(1242.6)	(1279.9)	(1279.8)	(1288.2)	1250.56,1249.1

Table 27 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	-148.3	-134.1	-134.6	-129.3	(-148.3)	(-134.1)	(-134.6)	(-129.3)	-195.44,-161.9
Δ_2	- 27.6	- 29.3	- 25.0	- 24.8	(- 27.6)	(- 29.3)	(- 25.0)	(- 24.8)	- 32.33,- 17.7
Δ_3	- 27.4	- 28.2	- 30.8	- 29.5	(- 27.4)	(- 28.2)	(- 30.8)	(- 29.5)	- 28.79,- 62.5
Δ_4	- 19.3	- 19.4	- 18.3	- 19.3	(- 19.3)	(- 19.4)	(- 18.3)	(- 19.3)	- 23.95,- 23.8
Δ_5	-160.2	-147.7	-148.6	-137.6	(-160.2)	(-147.7)	(-148.6)	(-137.6)	-153.71,-165.5
Δ_6	- 18.6	- 22.4	- 19.3	- 18.7	(- 18.6)	(- 22.4)	(- 19.3)	(- 18.7)	- 49.91,- 38.6

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[a] First entry from Ref. 85.

[b] Second entry from Ref. 104.

Table 28. Vibrational anharmonic constants of H_2CO.

	SCF				Experiment
	DZ	TZ	DZ+P	TZ+P	
x_{11} in cm^{-1}	- 30.404	- 27.459	- 27.699	- 26.951	- 28.95
x_{12}	- 9.503	- 8.771	- 1.086	- 0.955	1.115
x_{13}	- 25.988	- 24.448	- 33.912	- 31.890	- 23.03
x_{14}	- 7.243	- 5.258	- 3.866	- 2.832	- 10.099
x_{15}	-124.194	-111.353	-113.265	-110.334	-193.32
x_{16}	- 8.144	- 8.584	- 6.199	- 4.775	- 49.78
x_{22}	- 6.186	- 5.984	- 8.190	- 8.286	- 9.926
x_{23}	- 5.163	- 7.307	- 5.034	- 4.731	- 8.26
x_{24}	- 3.461	- 3.267	- 4.064	- 3.928	- 7.199
x_{25}	- 7.873	- 10.210	- 15.426	- 12.178	- 17.23
x_{26}	- 4.534	- 5.206	8.308	5.324	6.581
x_{33}	0.150	0.270	1.722	1.598	- 0.164
x_{34}	1.471	1.462	0.510	0.633	- 1.769
x_{35}	- 15.252	- 13.968	- 8.549	- 2.029	6.00
x_{36}	- 10.379	- 13.308	- 21.599	- 27.363	- 29.861

Table 28 continued.

	SCF				Experiment
	DZ	TZ	DZ+P	TZ+P	
χ_{44}	- 4.161	- 4.738	- 4.578	- 5.193	- 3.157
χ_{45}	- 19.757	- 19.613	- 17.779	- 18.376	-13.35
χ_{46}	7.047	6.769	6.825	6.770	- 2.860
χ_{55}	- 34.504	- 31.242	- 31.183	- 30.977	-17.97
χ_{56}	- 15.324	- 15.288	- 17.534	- 8.424	-17.63
χ_{66}	- 1.471	- 2.300	- 2.080	- 2.225	- 1.567

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[a] Ref. 85.

Table 29. Theoretical and experimental values of quartic and sextic centrifugal distortion constants and asymmetry parameter of H_2CO.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
$\Delta_J \times 10^6$ in cm^{-1}		2.29	2.14	2.20	2.28	2.46	2.26	2.33	
$\Delta_{JK} \times 10^6$		38.97	39.52	40.12	39.46	39.64	40.66	41.53	
$\Delta_K \times 10^6$		594.57	572.95	586.55	585.15	607.56	538.72	604.25	
$\Phi_J \times 10^6$		0.29	0.29	0.30	0.28	0.30	0.30	0.31	
$\Phi_K \times 10^6$		27.14	27.78	28.20	27.03	27.57	28.67	29.22	
$H_J \times 10^6$ in cm^{-1}		0.0000	0.0000	0.0000					
$H_{JK} \times 10^6$		0.0009	0.0010	0.0010					
$H_{KJ} \times 10^6$		-0.0014	-0.0021	-0.0020					
$H_K \times 10^6$		0.1114	0.1087	0.1129					
$h_J \times 10^6$		0.0000	0.0000	0.0000					
$h_{JK} \times 10^6$		0.0004	0.0004	0.0004					
$h_K \times 10^6$		0.0296	0.0294	0.0299					
σ in cm^{-1}		109.4490	100.3625	99.5349					

Table 30. Theoretical and experimental harmonic and fundamental vibrational frequencies of D_2CO.

	SCF				CISD				Experiment[a]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
$\omega_1(A_1)$ in cm^{-1}	2360.5	2311.2	2308.2	2280.0	2199.9	2176.7	2232.3	2208.6	2143.5
$\omega_2(A_1)$	1809.4	1802.4	1935.1	1931.2	1629.3	1642.6	1810.0	1809.5	1716.7
$\omega_3(A_1)$	1210.1	1213.2	1202.6	1204.7	1139.3	1162.1	1157.9	1161.2	1139.6
$\omega_4(B_1)$	1059.8	1064.8	1068.4	1076.5	951.6	965.1	989.8	998.5	955.0
$\omega_5(B_2)$	2471.6	2419.1	2399.2	2368.9	2316.3	2296.2	2337.7	2311.5	2254.5
$\omega_6(B_2)$	1063.9	1080.5	1077.8	1082.4	992.7	1024.8	1024.7	1031.5	1014.3
ν_1 in cm^{-1}	2286.2	2243.5	2245.7	2218.9	(2125.6)	(2109.0)	(2169.8)	(2147.5)	2056.4
ν_2	1785.0	1778.2	1908.2	1904.4	(1604.9)	(1618.4)	(1783.1)	(1782.8)	1700.0
ν_3	1194.0	1195.9	1185.1	1190.7	(1123.2)	(1144.8)	(1140.4)	(1147.3)	1106.0
ν_4	1047.1	1052.0	1056.3	1063.8	(938.8)	(952.3)	(977.7)	(985.8)	938.0
ν_5	2383.5	2340.1	2325.0	2283.4	(2228.2)	(2217.2)	(2263.5)	(2226.1)	2160.0
ν_6	1052.7	1067.1	1066.3	1074.0	(981.5)	(1011.3)	(1013.2)	(1023.1)	990.2

Table 30 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	- 74.3	- 67.7	- 62.5	- 61.1	(- 74.3)	(- 67.7)	(- 62.5)	(- 61.1)	-87.1
Δ_2	- 24.4	- 24.2	- 26.9	- 26.7	(- 24.4)	(- 24.2)	(- 26.9)	(- 26.7)	-16.7
Δ_3	- 16.1	- 17.3	- 17.5	- 13.9	(- 16.1)	(- 17.3)	(- 17.5)	(- 13.9)	-33.6
Δ_4	- 12.8	- 12.8	- 12.1	- 12.7	(- 12.8)	(- 12.8)	(- 12.1)	(- 12.7)	-17.0
Δ_5	- 88.1	- 79.0	- 74.2	- 85.4	(- 88.1)	(- 79.0)	(- 74.2)	(- 85.4)	-94.5
Δ_6	- 11.2	- 13.5	- 11.5	- 8.4	(- 11.2)	(- 13.5)	(- 11.5)	(- 8.4)	-24.1

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[a] Ref. 104.

Table 31. Vibrational anharmonic constants of D_2CO.

	SCF				Experiment
	DZ	TZ	DZ+P	TZ+P	
x_{11} in cm^{-1}	- 15.269	- 13.805	- 12.388	- 12.045	
x_{12}	- 5.523	- 5.135	- 8.274	- 8.318	
x_{13}	- 17.295	- 21.152	- 16.029	- 22.180	
x_{14}	1.726	5.403	4.815	8.801	
x_{15}	- 62.790	- 56.151	- 53.372	- 51.792	
x_{16}	- 3.630	- 3.081	- 2.559	- 0.506	
x_{22}	- 6.927	- 6.713	- 6.390	- 6.364	
x_{23}	- 2.655	- 3.284	- 2.252	- 2.277	
x_{24}	- 4.595	- 4.644	- 7.456	- 7.065	
x_{25}	- 4.345	- 3.920	- 5.617	- 5.386	
x_{26}	- 3.909	- 4.654	- 4.634	- 4.903	
x_{33}	0.728	1.722	0.079	1.890	
x_{34}	1.763	1.859	0.804	0.900	
x_{35}	- 9.650	- 8.167	- 4.804	- 16.866	
x_{36}	- 7.262	- 10.675	- 13.019	5.025	

Table 31 continued.

	SCF				Experiment
	DZ	TZ	DZ+P	TZ+P	
χ_{44}	- 3.973	- 4.911	- 3.758	- 5.058	
χ_{45}	- 11.576	- 11.617	- 10.313	- 10.633	
χ_{46}	3.064	2.963	2.902	2.884	
χ_{55}	- 20.321	- 18.477	- 18.503	- 18.405	
χ_{56}	- 6.594	- 4.328	- 0.262	- 12.588	
χ_{66}	- 1.025	- 1.786	- 1.366	- 1.692	

Table 32. Theoretical and experimental geometries, dipole moments, vibration-rotation interaction constants, and rotational constants of H_2S.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Energy in hartree	-398.62451		-398.67165	-398.67211		-398.70550	-398.83505	-398.83689	
r_e(SH) in Å	1.3505	1.3471	1.3347	1.3349	1.3762	1.3723	1.3405	1.3401	1.334
θ_e(HSH) in deg.		96.08	94.00	94.06	94.71	94.71	92.57	92.58	92.27
μ in D	1.824	1.834	1.297	1.306	1.692	1.710	1.216	1.226	
α_1^A in cm^{-1}	0.1874	0.1873	0.1370	0.1357	-	-	-	-	
α_2^A	-0.4004	-0.3996	-0.3488	-0.3481	-	-	-	-	
α_3^A	0.2524	0.2514	0.1921	0.1911	-	-	-	-	
α_1^B	0.1138	0.1148	0.1147	0.1138	-	-	-	-	
α_2^B	-0.1095	-0.1076	-0.1069	-0.1632	-	-	-	-	
α_3^B	0.0762	0.0773	0.0775	0.0767	-	-	-	-	

Table 32 continued.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
α_1^C	0.0717	0.0720	0.0624	0.0619	-	-	-	-	
α_2^C	0.0669	0.0676	0.0597	0.0592	-	-	-	-	
α_3^C	0.0511	0.0512	0.0449	0.0446	-	-	-	-	
A_e in cm^{-1}	10.9000	10.9584	10.7301	10.7393	10.2880				
B_e	8.2947	8.3343	8.7766	8.7660	8.2079				
C_e	4.7103	4.7339	4.8278	4.8264	4.5655				

Table 33. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies of H_2S.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	2677.7	2708.3	2860.3	2861.4	2455.0	2485.3	2785.3	2784.2	2721
ω_2	1317.0	1331.9	1321.5	1318.5	1208.3	1219.4	1250.7	1249.0	1201
ω_3	2695.3	2724.0	2871.6	2872.9	2478.3	2505.3	2801.3	2799.9	2734
χ_{11} in cm^{-1}	- 24.378	- 25.263	-21.216	-20.992	-	-	-	-	
χ_{12}	- 22.849	- 23.295	- 11.774	- 11.315	-	-	-	-	
χ_{13}	- 95.316	- 98.967	- 84.705	- 83.922	-	-	-	-	
χ_{22}	- 4.767	- 5.762	- 6.124	- 6.141	-	-	-	-	
χ_{23}	- 20.774	- 21.880	- 18.587	- 18.305	-	-	-	-	
χ_{33}	- 24.556	- 25.246	- 21.542	- 21.341	-	-	-	-	
ν_1 in cm^{-1}	2569.9	2596.7	2769.6	2771.8	(2347.2)	(2373.7)	(2694.6)	(2694.6)	2615
ν_2	1285.6	1297.8	1294.1	1291.4	(1177.0)	(1185.3)	(1223.3)	(1221.9)	1183
ν_3	2588.1	2613.1	2776.9	2779.1	(2371.1)	(2397.4)	(2706.6)	(2706.1)	2626

Table 33 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	-107.8	-111.6	- 90.7	- 89.6	(-107.8)	(-111.6)	(- 90.7)	(- 89.6)	-106
Δ_2	- 31.3	- 34.1	- 27.4	- 27.1	(- 31.3)	(- 34.1)	(- 27.4)	(- 27.1)	- 18
Δ_3	-107.2	-110.9	- 94.7	- 93.8	(-107.2)	(-110.9)	(- 94.7)	(- 93.8)	-108

Table 34. Theoretical values of some quartic centrifugal distortion constants of H_2S.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
$\Delta_J \times 10^6$ in cm^{-1}		246.16	471.62	471.58			447.22		
$\Delta_{JK} \times 10^6$		-1213.81	-1573.07	-1578.57			-1379.44		
$\Delta_K \times 10^6$		2844.62	2912.07	2928.95			2926.88		
$\phi_J \times 10^6$		168.11	208.30	208.32			192.74		
$\phi_K \times 10^6$							-46.10		

Table 35. Theoretical and experimental geometries and rotational constants of C_2H_4.

	DZP SCF	DZP CISD	Experiment[118]
Energy in hartree	-78.049308	-78.328495	
r_e(CC) in Å	1.3245	1.3390	1.339
r_e(CH)	1.0788	1.0855	1.085
θ_e(HCH) in deg.	116.83	116.99	117.83
A_e in cm^{-1}	4.9514		
B_e	1.0157		
C_e	0.8428		
A_0 in cm^{-1}	4.9082		
B_0	1.0095		
C_0	0.8351		

Table 36. Theoretical and experimental harmonic and fundamental vibrational frequencies of C_2H_4.

	DZP SCF	DZP CISD	Experiments[a,b]
ω_1 (a_g) in cm^{-1}	3322	3252	3153
ω_2 (a_g)	1817	1737	1655
ω_3 (a_g)	1471	1410	1370
ω_4 (a_g)	1132	1070	1044
ω_5 (b_{1g})	3385	3321	3232
ω_6 (b_{1g})	1336	1273	1245
ω_7 (b_{1u})	1078	983	969
ω_8 (b_{2g})	1085	885	959
ω_9 (b_{2u})	3411	3349	3234
ω_{10} (b_{2u})	887	842	843
ω_{11} (b_{3u})	3300	3226	3147
ω_{12} (b_{3u})	1582	1518	1473
ν_1 in cm^{-1}	3199	3129	3026
ν_2	1784	1704	1623
ν_3	1449	1388	1342

Table 36 continued.

	DZP SCF	DZP CISD	Experiments^{a,b}
ν_4	1111	1049	1023
ν_5	3260	3196	3086
ν_6	1316	1253	1222
ν_7	1063	968	949
ν_8	1068	868	940
ν_9	3280	3218	3105
ν_{10}	887	842	826
ν_{11}	3159	3085	2989
ν_{12}	1550	1486	1444
Δ_1 in cm^{-1}	-123	(-123)	-127
Δ_2	-33	(-33)	-32
Δ_3	-22	(-22)	-28
Δ_4	-21	(-21)	-21
Δ_5	-125	(-125)	-146
Δ_6	-20	(-20)	-23

Table 36 continued.

	DZP SCF	DZP CISD	Experiments[a,b]
Δ_7	-15	(-15)	-15
Δ_8	-17	(-17)	-19
Δ_9	-131	(-131)	-129
Δ_{10}	0	(0)	-17
Δ_{11}	-141	(-141)	-158
Δ_{12}	-32	(-32)	-29

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[a] Harmonic frequencies from Ref. 119.

[b] Fundamental frequencies as found in Ref. 120.

Table 37. Theoretical and experimental geometries, dipole moments, vibration-rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational ℓ-type doubling constants of HCN.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Energy in hartree	-92.83694	-92.84767	-92.87520	-92.89955	-93.03202	-93.05574	-93.16042	-93.18467	
r_e(CH) in Å	1.0542	1.0547	1.0638	1.0576	1.0720	1.0700	1.0707	1.0625	1.0657,1.0655[a]
r_e(CN)	1.1507	1.1375	1.1366	1.1268	1.1832	1.1648	1.1631	1.1497	1.1530,1.1532[a]
μ in D	3.296	3.283	3.216	3.244	3.130	3.138	3.001	3.043	
α_1 $\times 10^3$ in cm^{-1}	8.002	8.296	7.690	7.913	--	--	--	--	9.309,10.0
α_2 $\times 10^3$	-2.602	-3.079	-3.327	-2.556	--	--	--	--	-3.750,-3.6
α_3 $\times 10^3$	9.605	9.403	9.590	9.707	--	--	--	--	10.776,10.4
B_e in cm^{-1}	1.4951	1.5244	1.5223	1.5475	1.4189	1.4580	1.4612		
B_0	1.4889	1.5186	1.5170	1.5412	-	-	-	-	1.47822162

Table 37 continued.

	SCF				CISD				Experiment[a]
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
D_J x10^6 in cm^{-1}	2.442	2.616	2.432	2.534	2.542	2.758	2.512	2.9093	
H_J x10^{12}	2.474	2.852	2.639	2.847	--	--	--	--	
q_2^e x10^3 in cm^{-1}	6.329	6.580	6.714	6.738	6.398	6.927	6.789	--	7.483
q_2^J x10^8	-5.019	-5.531	-5.686	-5.234	--	--	--	--	-8.9
q_2^K x10^8	4.342	4.754	4.941	4.429	--	--	--	--	

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[a] Ref. 114.

Table 38. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants and fundamental vibrational frequencies of HCN.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	2326.8	2314.8	2403.2	2409.4	2104.0	2104.3	2213.9		2131.82,2128.9[a]
ω_2	882.7	895.4	856.6	902.6	761.0	738.6	753.9		726.61, 727.0[a]
ω_3	3697.0	3626.3	3631.2	3623.2	34921	3430.0	3531.0		3438.34,3442.0[a]
x_{11}	- 8.188			- 7.861	--	--	--	--	-11.25
x_{12}	- 1.446			- 1.488	--	--	--	--	- 3.06
x_{13}	-13.036			-13.793	--	--	--	--	-16.78
x_{22}	- 0.734			- 6.286	--	--	--	--	- 2.43
x_{23}	-20.744			-19.038	--	--	--	--	-19.06
x_{33}	-52.399			-45.250	--	--	--	--	-50.25
$x_{\ell_2\ell_2}$	4.767			6.583	--	--	--	--	5.27

Table 38 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ν_1	2302.4			2385.3	(2079.7)				2096.68
ν_2	874.2			880.1	(752.5)				713.74
ν_3	3564.9			3506.8	(3360.0)				3311.47
Δ_1 in cm^{-1}				-24.1				(-24.1)	
Δ_2	- 8.5			-22.5	(-8.5)			(-22.5)	- 12.87
Δ_3	-132.1			-116.4	(-132.1)			(-116.4)	-126.87

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[a] Ref. 126.

Table 39. Theoretical and experimental vibration-rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational ℓ-type doubling constants of DCN.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
α_1 x10^3 in cm^{-1}	5.328	5.369	5.210	5.356					6.690
α_2 x10^3	-3.200	-3.562	-3.793	-3.167					-4.290
α_3 x10^3	9.577	9.580	9.423	9.544					10.170
B_e in cm^{-1}	1.2221	1.2434	1.2397	1.2595	1.1621	1.1912	1.1934		
B_0	1.2178	1.2395	1.2362	1.2552					
D_J x10^6 in cm^{-1}	1.616	1.728	1.612	1.689	1.664	1.802	1.649		
H_J x10^{12}	1.538	1.807	1.592	1.721					
q_2^e x10^3 in cm^{-1}	5.304	5.486	5.577	5.590	5.387	5.798	5.678		
q_2^J x10^8	-3.978	-4.297	-4.547	-4.071					
q_2^K x10^8	3.395	3.633	3.904	3.375					

Table 40. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants and fundamental vibrational frequencies of DCN.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	2117.4	2100.0	2155.7	2154.9	1940.4	1934.2	2024.9		1952.81
ω_2	703.4	714.2	683.9	720.8	605.8	588.7	601.0		580.03
ω_3	2926.8	2879.8	2916.5	2918.7	2728.0	2688.5	2781.3		2703.85
x_{11}	- 5.988			- 6.103					-7.03
x_{12}	3.790			4.247					2.68
x_{13}	-30.351			-30.872					-32.44
x_{22}	- 0.997			- 4.560					-2.08
x_{23}	-15.765			-15.224					-15.96
x_{33}	-19.869			-15.524					-20.56
$x_{\ell_2\ell_2}$	2.952			4.149					3.25
ν_1	2094.1			2131.5	(1917.0)				1925.27
ν_2	697.4			705.8	(599.8)				570.34
ν_3	2856.2			2857.0	(2657.3)				2630.33

Table 40 continued

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1	-23.4			-23.4	(-23.4)			(-23.4)	-27.54
Δ_2	- 6.0			-15.0	(- 6.0)			(-15.0)	- 9.69
Δ_3	-70.7			-61.7	(-70.7)			(-61.7)	-73.52

Table 41. Theoretical and experimental geometries, vibration-rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational ℓ-type doubling constants of CO_2.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Energy in hartree	-187.55339	-187.56279	-187.67624	-187.68791	-187.85244	-187.89160	-188.09488	-188.13506	
r_e(CO) in Å	1.1651	1.1594	1.1453	1.1387	1.1925	1.1833	1.1647	1.1287	1.1621
α_1 x10^3 in cm^{-1}	1.137	1.1155	1.0296	1.04	-	-	-	-	1.21
α_2 x10^3	-0.648	-1.1800	-0.7025	-0.67	-	-	-	-	-0.72
α_3 x10^3	3.268	3.2642	2.9603	2.97	-	-	-	-	3.09
B_e in cm^{-1}	0.3882	0.3920	0.4017	0.4064	0.3706	-	-	-	0.3939
B_0	0.3866	0.3910	0.4044	0.4051	-	-	-	-	0.39021
D_J x10^6 in cm^{-1}	0.119	0.1263	0.1132	0.1170	0.1225	-	-	-	0.135
H_J x10^{12}	0.009	0.0134	0.0125	0.014	-	-	-	-	

Table 41 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
$q_2^e \times 10^3$ in cm^{-1}	0.587	0.6571	0.5829	-	-	-	-	-	
$q_2^J \times 10^8$	-0.048	-0.1122	-0.0522	-	-	-	-	-	
$q_2^K \times 10^8$	0.037	0.0996	0.0420	-	-	-	-	-	

Table 42. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies of CO_2.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	1400.2	1381.2	1513.4	1514.7	1289.3			1428.3	
ω_2	717.4	608.0	766.0	776.5	639.0			711.6	
ω_3	2383.7	2301.7	2590.3	2570.7	2254.2			2479.3	
x_{11}	-3.053	-2.805	-2.739		-	-	-	-	
x_{12}	-5.172	30.352	-5.417		-	-	-	-	
x_{13}	-25.206	-23.365	-21.336		-	-	-	-	
x_{22}	1.546	-1.246	1.729		-	-	-	-	
x_{23}	-14.099	-8.518	-12.760		-	-	-	-	
x_{33}	-15.874	-13.812	-13.170		-	-	-	-	
$x_{\ell_2\ell_2}$	-0.982	5.592	-1.123		-	-	-	-	

Table 42 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ν_1	1376.3	1394.2	1491.9		(1265.4)				1388.17
ν_2	711.5	620.8	761.0		(633.0)				667.40
ν_3	2325.3	2253.9	2540.5		(2195.8)				2349.16
Δ_1 in cm^{-1}	-23.9	13.1	-21.6		(-23.9)	(13.1)	(-21.6)		
Δ_2	-6.0	12.8	-5.0		(-6.0)	(12.8)	(-5.8)		
Δ_3	-58.4	-47.8	-49.8		(-58.4)	(-47.8)	(-49.8)		

Table 43. Theoretical and experimental geometries, dipole moments, vibration-rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational ℓ-type doubling constants of N_2O.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Energy in hartree	-183.595411	-183.609675	-183.715760	-183.726722	-183.918705	-183.960408	-184.161173	-184.203237	
r_e(NN) in Å	1.1069	1.0963	1.0955	1.0866	1.1494	1.1337	1.1285	1.1162	1.128
r_e(NO)	1.2557	1.2496	1.1872	1.1796	1.2577	1.2492	1.1990	1.1900	1.184
μ in D	1.5395	1.5610	0.8244	0.7950					0.4543
α_1 x10^3 in cm^{-1}	1.7785	2.03	2.55						3.45
α_2 x10^3	-0.0046	-0.43	-0.48						-0.56
α_3 x10^3	6.0340	5.37	2.85						1.79
B_e in cm^{-1}	0.4023	0.4080	0.4317	0.4380	0.3881	0.3959	0.4156	0.4232	0.419011
B_0	0.3984	0.4047	0.4295						

Table 43 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
$D_J \times 10^6$ in cm^{-1}	0.238	0.2381	0.1610						0.176
$H_J \times 10^{12}$	-0.650	-0.520	-0.078						
$q_2^e \times 10^3$ in cm^{-1}	0.8954								0.792
$q_2^J \times 10^8$	0.2694								
$q_2^K \times 10^8$	-0.3969								

Table 44. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies of N_2O.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	2430.9	2404.1	2589.0	2595.8	2164.4	2160.2	2402.6	2419.1	
ω_2	554.9	519.1	668.4	707.0	507.2	461.8	606.4	644.5	
ω_3	964.0	991.1	1358.0	1354.2	1109.6	1113.6	1352.4	1347.5	
x_{11}	-15.457		-14.073		-	-	-	-	
x_{12}	-7.923		-11.637		-	-	-	-	
x_{13}	27.013		-73.678		-	-	-	-	
x_{22}	0.219		0.529		-	-	-	-	
x_{23}	-17.261		-6.621		-	-	-	-	
x_{33}	-39.404		-0.123		-	-	-	-	
$x_{\ell_2\ell_2}$	0.282		-0.215		-	-	-	-	

Table 44 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ν_1	2405.6		2512.4		(2139.1)		(2326.0)		2223.76
ν_2	543.2		661.7		(495.5)		(599.7)		588.78
ν_3	881.4		1314.3		(1027.0)		(1308.7)		1284.9
Δ_1 in cm^{-1}	-25.3		-76.6		(-25.3)		(-76.6)		
Δ_2	-11.7		-6.7		(-11.7)		(-6.7)		
Δ_3	-82.6		-43.7		(-82.6)		(-43.7)		

Table 45. Theoretical and experimental geometries, dipole moments, vibration-rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational ℓ-type doubling constants of COS.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Energy in hartree	-510.176021	-510.187518	-510.279955	-510.286839	-510.430225	-510.458104	-510.669445		
r_e(CO) in Å	1.1511	1.1411	1.1352	1.1273	1.1845	1.1710	1.1595	1.1494	1.1545,1.1554
r_e(CS)	1.6085	1.6151	1.5736	1.5739	1.6164	1.6251	1.5732	1.5688	1.5630,1.5620
μ in D	0.1612	0.0569	0.3376	0.3247	0.4419	0.3696	0.5241	0.5566	
α_1 x10^3 in cm^{-1}	1.0827	1.0320	1.01						0.6298
α_2 x10^3	-0.2609	-0.3150	-0.31						-0.3524
α_3 x10^3	0.9698	0.9098	0.79						1.2262
B_e in cm^{-1}	0.1966	0.1968	0.2042	0.2052	0.1905	0.1917	0.1966		0.2034282
B_0	0.1959	0.1962	0.2036						0.2028563

Table 45 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
D_J x10^6 in cm^{-1}	0.0454	0.0450	0.0409						0.04280
H_J x10^{12}	-0.0148	-0.0125	-0.007						
q_2^e x10^3 in cm^{-1}	0.2077	0.2073							0.2110
q_2^J x10^8	0.0008	-0.0013							
q_2^K x10^8	-0.0098	-0.0072							

Table 46. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies of COS.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	797.1	802.3	891.0	886.8	796.2	802.6	891.6		874.27
ω_2	534.9	536.4	574.8	583.1	-	485.0	536.3		524.20
ω_3	2170.1	2155.9	2298.5	2297.3	2008.4	2002.8	2193.0		2094.15
x_{11}	-6.717	-6.155			-	-	-	-	-3.25
x_{12}	-3.460	-6.205			-	-	-	-	-3.14
x_{13}	2.004	1.928			-	-	-	-	-2.53
x_{22}	0.743	1.406			-	-	-	-	2.35
x_{23}	-3.773	-5.692			-	-	-	-	-14.56
x_{33}	-13.607	-12.564			-	-	-	-	-11.59
$x_{\ell_2\ell_2}$			-0.545		-	-	-	-	-1.79

Table 46 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ν_1	780.3	784.8			(779.4)	(785.0)			858.95
ν_2		534.8				(483.4)			
ν_3	2138.8	2126.1			(1977.1)	(1972.9)			2062.22
Δ_1 in cm^{-1}	-16.8	-17.6			(-16.8)	(-17.6)			
Δ_2		-1.6				(-1.6)			
Δ_3	-31.3	-29.9			(-31.3)	(-29.9)			

Table 47. Theoretical and experimental geometries, vibration-rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational ℓ-type doubling constants of C_2H_2.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Energy in hartree	-76.799232	-76.811127	-76.831903	-76.843052	-76.977294	-77.000722	-77.082305	-77.106963	
r_e(CC) in Å	1.2010	1.1875	1.1912	1.1811	1.2299	1.2101	1.2131	1.1979	
r_e(CH)	1.0538	1.0536	1.0616	1.0554	1.0707	1.0686	1.0691	1.0601	
α_1 x10^3 in cm^{-1}	6.3808	6.2490	6.25	6.3954					6.86
α_2 x10^3	4.7264	5.0156	4.74	4.9314					6.21
α_3 x10^3	5.5233	5.2544	5.36	5.4236					5.60
α_4 x10^3	-0.6090	-1.9262	-1.46	-1.1190					-1.29
α_5 x10^3	-1.6821	-0.6804	-2.12	-2.0195					-2.15
B_e in cm^{-1}	1.1897	1.2101	1.1999	1.2189	1.1388	1.1680			
B_0	1.1836	1.2045	1.1953	1.2137					

Table 47 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
$D_J \times 10^6$ in cm^{-1}	1.3930	1.4508	1.3839	1.4322	1.4207	1.5053			1.580
$H_J \times 10^{12}$	1.2883	1.3088	1.2695	1.3010					
$q_4^e \times 10^3$ in cm^{-1}	4.1517	4.1418	4.4991	4.4477					
$q_4^J \times 10^8$									
$q_4^K \times 10^8$									
$q_5^e \times 10^3$ in cm^{-1}	4.0053	4.1400	4.1779	4.2637					
$q_5^J \times 10^8$									
$q_5^K \times 10^8$									

Table 48. Theoretical and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies of C_2H_2.

	SCF				CISD				Experiment
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
ω_1 in cm^{-1}	3732.3	3681.6	3676.7	3673.4	3531.3	3485.3			3495.1
ω_2	2167.6	2179.0	2203.4	2219.2	2005.9	2023.8			2007.6
ω_3	3622.2	3557.4	3571.3	3558.6	3431.7	3373.2			3415.2
ω_4	842.7	909.2	766.7	820.0	678.6	675.6			624.0
ω_5	887.1	901.1	858.2	877.4	749.7	741.1			746.7
χ_{11}	-25.510	-22.950	-23.398	-23.093	-	-	-	-	-18.57
χ_{12}	-9.870	-9.598	-9.380	-9.332	-	-	-	-	-13.09
χ_{13}	-104.761	-93.111	-96.905	-94.302	-	-	-	-	-102.39
χ_{14}	-13.018	-13.359	-10.251	-10.792	-	-	-	-	-16.54
χ_{15}	-9.462	-10.904	-8.219	-10.037	-	-	-	-	-10.85
χ_{22}	-5.251	-5.560	-5.432	-5.669	-	-	-	-	-5.77
χ_{23}	-4.969	-5.069	-4.616	-5.198	-	-	-	-	-2.82
χ_{24}	-9.349	-8.771	-10.295	-9.667	-	-	-	-	-12.70
χ_{25}	1.733	2.263	1.960	1.705	-	-	-	-	-1.38

Table 48 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
x_{33}	-27.056	-23.165	-25.133	-24.264					-30.95
x_{34}	-8.122	-7.667	-5.000	-5.956					-8.22
x_{35}	-9.688	-8.460	-8.016	-8.313					-8.68
x_{44}	0.470	-8.067	2.479	1.506					3.072
x_{45}	47.336	36.150	52.664	43.753					-2.406
x_{55}	-1.290	-3.438	-2.146	-2.501					-2.334
$x_{\ell_4\ell_4}$	1.650	4.691	1.158	1.413					0.756
$x_{\ell_4\ell_5}$	-	-	-	-	-	-	-	-	6.539
$x_{\ell_5\ell_5}$	3.338	4.288	3.714	3.815	-	-	-	-	3.492
ν_1	3601.5	3560.1	3558.3	3554.6	(3400.5)	(3363.8)			
ν_2	2142.1	2154.0	2177.2	2192.6	(1980.4)	(1998.8)			
ν_3	3495.4	3445.8	3457.3	3446.0	(3304.9)	(3261.7)			
ν_4	877.9	922.7	815.2	856.4	(713.8)	(697.2)			
ν_5	925.2	911.0	901.0	909.1	(787.8)	(742.8)			

Table 48 continued.

	SCF				CISD				Experiments
	DZ	TZ	DZ+P	TZ+P	DZ	TZ	DZ+P	TZ+P	
Δ_1 in cm^{-1}	-130.8	-121.5	-118.4	-118.8	(-130.8)	(-121.5)	(-118.4)	(-118.8)	
Δ_2	-25.5	-25.0	-26.2	-26.6	(-25.5)	(-25.0)	(-26.2)	(-26.6)	
Δ_3	-126.8	-111.5	-114.0	-112.5	(-126.8)	(-111.5)	(-114.0)	(-112.5)	
Δ_4	35.2	21.6	48.5	36.5	(35.2)	(21.6)	(48.5)	(36.5)	
Δ_5	38.1	1.7	42.8	31.7	(38.1)	(1.7)	(42.8)	(31.7)	

Table 49. Theoretical geometries, vibration-rotation interaction constants, rotational constants, and centrifugal distortion constants of H_3^+.

	SCF					
	DZ	TZ	DZP	TZP	(4s2p)	(6s3p)
Energy in hartree	-1.27582	-1.27978	-1.29575	-1.29675	-1.29935	-1.29972
r_e in Å	0.8497	0.8611	0.8613	0.8657	0.8692	0.8683
α_1^B in cm^{-1}	1.6103	1.1538	1.3273	1.2172	1.1841	1.1729
α_2^B	-0.1541	-0.2374	-0.1416	-0.1324	-0.1354	-0.1194
α_1^C	0.8052	0.5769	0.6637	0.6086	0.5920	0.5028
α_2^C	1.0328	0.9274	0.9791	0.9657	0.9603	0.4863
B_e in cm^{-1}	46.3355	45.1216	45.0949	44.6389	44.2833	44.3693
C_e	23.1677	22.5608	22.5475	22.3194	22.1417	22.1846
B_0	45.6844	44.7821	44.5729	44.1627	43.8267	43.1281
C_0	21.7323	21.3449	21.2365	21.0495	20.8853	21.7050

Table 49 continued.

	SCF					
	DZ	TZ	DZ+P	TZ+P	(4s2p)	(6s3p)
D_J in cm^{-1}	0.03793	0.03479	0.03585	0.03511	0.03511	0.04145
D_K	0.02721	0.02487	0.02526	0.02468	0.02469	0.02777
D_{JK}	-0.06156	-0.05635	-0.05758	-0.05631	-0.05632	-0.06071
H_J x10^3 in cm^{-1}	0.0510	0.0465	0.0483	0.0471	0.0476	0.1068
H_{JK}	-0.1951	-0.1729	-0.1782	-0.1726	-0.1743	-0.2830
H_{KJ}	0.2407	0.2102	0.2156	0.2081	0.2101	0.2349
H_K	-0.0960	-0.0831	-0.0850	-0.0819	-0.0827	-0.0589
Δ_3	-0.0151	-0.0125	-0.0118	-0.0114	-0.0115	0.0470

Table 50. Theoretical harmonic vibrational frequencies, vibrational anharmonic constants and fundamental vibrational frequencies of H_3^+.

	SCF					
	DZ	TZ	DZP	TZP	(4s2p)	(6s3p)
ω_1 in cm^{-1}	3729.8	3727.0	3604.4	3576.6	3535.4	3521.7
ω_2	2901.7	2919.3	2905.2	2896.6	2861.3	2860.8
x_{11}	-77.370	-63.030	-52.639	-52.574	-49.278	-48.308
x_{12}	-233.817	-188.826	-171.104	-167.201	-162.789	-160.394
x_{22}	-96.459	-93.987	-81.043	-81.363	-81.145	-81.862
g_{22}	86.101	840118	70.256	70.034	69.902	47.832
ν_1	3351.2	3412.1	3328.1	3304.2	3274.1	3264.7
ν_2	2586.5	2627.0	2646.8	2639.0	2606.4	2582.8
Δ_1 in cm^{-1}	-378.6	-314.9	-276.4	-272.3	-261.3	-257.0
Δ_2	-315.2	-292.3	-258.4	-257.7	-254.9	-278.0