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A systematic study of molecular vibrational anharmonicity and vibration–rotation interaction by self-consistent-field higher-derivative methods. Linear polyatomic molecules

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The inclusion of the anharmonicity of molecular vibrations is an important aspect of the goal of making highly accurate theoretical predictions of the spectroscopic properties of molecules. Recently developed analytic third derivative methods for self-consistent-field (SCF) wavefunctions have made it possible to determine the complete cubic and quartic force fields of polyatomic molecules, thus allowing the treatment of anharmonic effects. Here we continue our systematic evaluation of the performance of such theoretical methods by studying several linear molecules which are well characterized experimentally, viz., HCN, DCN, CO_2, N_2O, OCS, C_2H_2, and C_2D_2. A number of anharmonic molecular properties have been determined, including vibration–rotation interaction constants, vibrational anharmonic constants, fundamental vibrational frequencies, sextic centrifugal distortion constants, rotational constants which include zero-point vibrational corrections, and vibrational and rotational *l*-type doubling constants. These anharmonic molecular constants are not as well converged with respect to basis set enlargement as those which were previously determined for asymmetric top molecules, apparently because all the molecules considered here contain multiple bonds. However, the reported anharmonic constants at the SCF level of theory are still in reasonably good agreement with the corresponding experimental constants. Significant improvements in accuracy are achieved by incorporating electron correlation at the configuration interaction singles and doubles (CISD) level of theory. Standard spectroscopic perturbation theory methods are used in this study, which are directly and immediately applicable to larger molecular systems than those studied here.

1. Introduction

The present paper is the continuation of our studies of vibrational anharmonic effects and the feasibility of using computational quantum chemistry to predict the wide variety of constants which characterize the vibration–rotation spectra of semirigid molecules [1]. In the past, most theoretical investigations have been restricted, for very practical reasons, to the harmonic approximation. Numerous ab initio studies [2–8] indicate that for most molecules and normal modes, self-consistent-field (SCF) harmonic vibrational frequencies, which can now be routinely calculated, are higher than experimental frequencies by approximately 10%. It has also been shown that basis set incompleteness, electron correlation effects, and anharmonicity of molecular vibrations all affect this overestimation in an important way. For a more detailed discussion of the relative importance of these factors, see the introductory part of ref. [9], the first paper in the present series (hereafter called

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part I). At this point it suffices to say that recent theoretical developments in analytic derivative methods [10–12] (particularly those which have made possible the calculation of analytic third derivatives of the SCF energy with respect to nuclear displacements [13]) in conjunction with the ever increasing availability of computer resources have made it feasible to reinvestigate the role of these factors, ultimately leading to a better understanding of them, which is one goal of this research. Perhaps an even more important goal is to document the effect of improving the theoretical treatment and thus ascertain a minimum theoretical level that is satisfactory in the prediction of the spectroscopic constants (harmonic and anharmonic) necessary to describe the vibration–rotation spectra of vastly different molecules.

In part I [9] complete quartic force fields were determined at the SCF level of theory for several asymmetric top molecules and compared to appropriate CISD (configuration interaction singles and doubles) force fields (quartic for triatomics and quadratic for larger molecules). Some important results of that study were: (a) for most constants the SCF quartic force fields show rather little variation with basis set extension, and the observed changes may be primarily due to variations in the underlying optimized geometries; (b) for many anharmonic molecular constants and properties, the values predicted via SCF higher (i.e. third and fourth) derivatives seem to have converged with respect to basis set variation at the double-zeta + polarization (DZP) level, although the basis sets considered were certainly not large enough to show this definitively; (c) particularly good agreement between the various theoretical anharmonic constants and experiment was found when the CISD quadratic force field was coupled with the corresponding SCF cubic and/or quartic force constants computed with the same basis set.

In the linear molecules considered in the present paper (HCN, CO_2, N_2O, OCS and C_2H_2) there is substantially more localization of electron density in the form of multiple bonds than in the asymmetric top molecules considered in part I. The proper theoretical description of these multiple bonds and their interaction with other electron pairs is certainly very demanding, and thus the use of extended and flexible basis sets and methods including a substantial portion of the electron correlation might be necessary. While in part I the largest basis set used was of triple-zeta + polarization (TZP) quality, it is feasible to use an even larger basis set here (TZ2P) which contains two sets of polarization functions. Furthermore, for triatomic molecules there is a straightforward and accurate procedure to calculate the complete quartic force field from finite differences of analytic first derivatives (see section 3 below). This allows calculation of pure CISD quartic force fields, and thus an analysis of the utility of the CISD method to predict anharmonic spectroscopic constants is possible. In summary, the present study investigates exhaustively the ability of both the SCF and CISD methods to predict quartic force fields and several of the anharmonic molecular constants of linear molecules, at the same time providing a fundamental perspective on the experimentally observed constants for these well-studied molecules. At this point it is necessary to emphasize that, similarly to part I, spectroscopic constants are calculated from the quartic force fields by formulas obtained using low-order perturbation theory [1]. Thus not only may the calculated force constants contain errors but in certain cases the treatment based on perturbation theory may break down [14,15].

Section 2 serves to review the necessary theory and formulas which have been employed for the determination of the spectroscopic constants of linear molecules. Section 3 describes the theoretical procedures applied in this study and contains a few comments regarding the practical details of obtaining the complete quartic force fields. Section 4 discusses separately the results obtained for each molecule studied. The complete quartic force fields at both levels of theory (SCF and CISD) obtained with the largest basis set (TZ2P in most cases) are also given in section 4 for each molecule.

2. The evaluation of various vibration–rotation constants

Formulas for the various vibration–rotation constants described here and their relationship to molecular geometries and force constants have been determined previously using results of perturbation theory [1,16–23].

Although these formulas have been presented, discussed and reviewed several times, we find it helpful to reiterate formulas and discussions which are useful from our point of view. The method applied in the present study to determine the spectroscopic constants is complementary to the usual spectroscopic practice, in which numerous constants contained in the rovibrational Hamiltonian are fitted to the measured spectra. In contrast, we first determine equilibrium geometries and potential energy derivatives (force constants), which are then used to calculate the spectroscopic constants. In sections 2.1 to 2.8 we present explicitly those formulas which pertain to linear polyatomic molecules.

2.1. Energy expressions

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 [20],

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

The rotational term values $F_v(J)$ of a linear polyatomic molecule are given in the form [21]

$$F_v(J) = B_v[J(J+1) - l^2] - D_J[J(J+1) - l^2]^2 + H_J[J(J+1) - l^2]^3 + \ldots , \tag{2}$$

where l is the quantum number for the total vibrational angular momentum, B_v is the effective rotational constant, D_J is the quartic centrifugal distortion constant, and H_J is the sextic centrifugal distortion constant.

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

$$G(v) = \sum_r \omega_r(v_r + \tfrac{1}{2}d_r) + \sum_{r \geqslant s} \chi_{rs}(v_r + \tfrac{1}{2}d_r)(v_s + \tfrac{1}{2}d_s) + \sum_{t \geqslant t'} \chi_{l_t l_{t'}} l_t l_{t'} + \ldots , \tag{3}$$

where subscripts r and s denote either non-degenerate or degenerate normal modes and t and t' indicate degenerate modes only. In eq. (3), ω_r is the rth harmonic frequency, d_r is the degeneracy of the rth normal mode, and χ_{rs} and $\chi_{l_t l_{t'}}$ are the vibrational anharmonic constants.

Following Nielsen's treatment [17–19] we employ the dimensionless normal coordinate

$$q_r = \gamma_r^{1/2} Q_r , \tag{4}$$

where

$$\gamma_r = \lambda_r^{1/2}/\hbar = 2\pi c \omega_r/\hbar . \tag{5}$$

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

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

where the ϕ_{rst} and ϕ_{rstu} are the cubic and quartic force constants, respectively. It should be noted that the multiple summations in eq. (6) are unrestricted, and thus the ϕs differ from Nielsen's original anharmonic ks by multiplicative factors.

2.2. The vibration–rotation interaction constants

The vibrational dependence of the effective rotational constant for a linear polyatomic molecule is given by

$$B_v = B_e - \sum_r \alpha_r(v_r + \tfrac{1}{2}d_r) + \ldots , \tag{7}$$

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

Perturbation theory gives the formulas for the vibration–rotation interaction constants of a linear molecule as [21]

$$-\alpha_s = \frac{2B_e^2}{\omega_s}\left[\frac{3a_s^2}{4I_e} + \sum_t \zeta_{st}^2 \frac{3\omega_s^2+\omega_t^2}{\omega_s^2-\omega_t^2} + \pi\left(\frac{c}{h}\right)^{1/2} \sum_{s'} \phi_{sss'} a_{s'} \frac{\omega_s}{\omega_{s'}^{3/2}}\right] \tag{8}$$

and

$$-\alpha_t = \frac{2B_e^2}{\omega_t}\left[\frac{1}{2} \sum_s \zeta_{st}^2 \frac{3\omega_t^2+\omega_s^2}{\omega_t^2-\omega_s^2} + \pi\left(\frac{c}{h}\right)^{1/2} \sum_s \phi_{stt} a_s \frac{\omega_t}{\omega_s^{3/2}}\right], \tag{9}$$

where the subscripts s and s' denote non-degenerate modes, and t indicates a degenerate mode. The equilibrium rotational constant B_e in eqs. (7), (8), and (9) is given by

$$B_e = \hbar^2/2hcI_e , \tag{10}$$

and the inertial derivatives over the normal coordinates, a_s, are defined as

$$a_s = (\partial I_{xx}/\partial Q_s)_e = (\partial I_{yy}/\partial Q_s)_e , \tag{11}$$

where I_e $(=I_{xx}=I_{yy})$ is the equilibrium moment of inertia (the molecule is assumed to lie along the z axis). Note that the inertial derivatives in eq. (11) are nonzero only for totally symmetric normal modes.

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

$$\zeta_{st} = \zeta_{st_b}^{x} = -\zeta_{st_a}^{y} , \tag{12}$$

and they are defined by

$$\zeta_{rs}^{(\alpha)} = \sum_i \left[L_{ir}^{(\beta)} L_{is}^{(\gamma)} - L_{ir}^{(\gamma)} L_{is}^{(\beta)}\right] , \tag{13}$$

where α, β, and γ are cyclic permutations of x, y, and z, and L is the matrix which transforms the normal coordinates to mass-weighted Cartesian coordinates. In applying eq. (9), it is useful to note that for a linear polyatomic molecule the nonvanishing cubic force constants involving degenerate coordinates are

$$\phi_{st_at_a} = \phi_{st_bt_b} \tag{14}$$

and

$$\phi_{st_at'_a} = \phi_{st_bt'_b} . \tag{15}$$

2.3. The centrifugal distortion constants

Following Aliev and Watson [22,23], rotational derivatives B_s are defined by

$$B_s = B_s^{xx} = B_s^{yy} = -\frac{\hbar^3}{2h^{3/2}c^{3/2}\omega_s^{1/2}} \frac{a_s}{I_e^2} , \tag{16}$$

where the inertial derivatives a_s are those given in eq. (11). The quartic centrifugal distortion constant, D_J, is expressed in terms of these new parameters as

$$D_J = \frac{1}{2} \sum_s \frac{B_s^2}{\omega_s} , \tag{17}$$

and the sextic centrifugal distortion constant H_J is given by

$$H_J = \frac{4D_J^2}{B_e} - 2B_e^2 \sum_s \frac{B_s^2}{\omega_s^3} - \tfrac{1}{6} \sum_{ss's''} \phi_{ss's''} \frac{B_s B_{s'} B_{s''}}{\omega_s \omega_{s'} \omega_{s''}} . \tag{18}$$

In eqs. (17) and (18), the summations are only over totally symmetric normal modes.

Aliev [24] has investigated lower and upper bounds for quartic centrifugal distortion constants. He obtained an especially simple formula, $D_J^{\max} = 4B_e^3/\omega_{\min}^2$, for the upper bound in the case of linear molecules, where $\omega_{\min}$ is the lowest stretching frequency. Comparing calculated upper bounds with available experimental results, he also showed that experimental D_J constants of linear molecules are typically very close to this upper bound, and thus are insensitive to the complete force field of the molecule. This means that the calculated D_J constants of the present study are not particularly informative about the details of the quadratic force fields. (This situation is in clear contrast to the case of asymmetric top molecules [9,25], where the quartic centrifugal distortion constants are sometimes very sensitive to changes in the quadratic force field.) For the sextic constant H_J, no such simple formula is available which would give similar insight into its sensitivity to the full cubic force field.

2.4. *The rotational l-type doubling constants*

The rotational *l*-type doubling constants q_t associated with a degenerate vibration ω_t of a linear molecule describe, for example, the splitting of the $l = \pm 1$ pair of levels of the $v_t = 1$ fundamental manifold, these levels being separated in energy by an amount $q_t J(J+1)$. These constants have actually been observed to be v, J, and K dependent [21,26], but in the present study only the corrections due to centrifugal distortion are considered using the formulation of Watson [27]

$$q_t \approx q_t^e + q_t^J J(J+1) + q_t^K (K \pm 1)^2 . \tag{19}$$

The q_t^e values are given by

$$q_t^e = -\frac{2B_e^2}{\omega_t} \sum_s \zeta_{st}^2 \frac{3\omega_t^2 + \omega_s^2}{\omega_t^2 - \omega_s^2} , \tag{20}$$

and the formulas for q_t^J and q_t^K are presented in table V of Watson's paper [27] as

$$\begin{aligned} q_t^J = {} & -\frac{4D_J q_t^e}{B_e} + \frac{2B_e^4}{\omega_t^3} + \frac{B_e^2(2\alpha_t - q_t^e)}{\omega_t^2} - 4B_e^2(2\alpha_t + q_t^e) \sum_s \zeta_{st}^2 \frac{\omega_s^2 + \omega_t^2}{(\omega_s^2 - \omega_t^2)^2} - 12B_e\omega_t \left(\sum_s C_s \zeta_{st} \frac{\omega_s^{3/2}}{\omega_s^2 - \omega_t^2} \right)^2 \\ & - 8B_e\omega_t \left(\sum_s C_s \zeta_{st} \frac{\omega_s^{3/2}}{\omega_s^2 - \omega_t^2} \right) \left(\sum_{s'} C_{s'} \zeta_{s't} \frac{1}{\omega_{s'}^{1/2}} \right) - 8B_e^2 \omega_t \sum_{ss's''} C_s \phi_{ss's''} \zeta_{s't} \zeta_{s''t} \frac{(\omega_{s'} \omega_{s''})^{1/2}}{(\omega_{s'}^2 - \omega_t^2)(\omega_{s''}^2 - \omega_t^2)} \\ & - 32B_e^4 \omega_t \sum_{t' \neq t} \left(\frac{3\omega_t^2 + \omega_{t'}^2}{\omega_t^2 - \omega_{t'}^2} \right) \left(\sum_s \zeta_{st} \zeta_{st'} \frac{1}{\omega_s^2 - \omega_t^2} \right)^2 + 16B_e^2 \sum_{t' \neq t} \left(\frac{(\omega_t^3 \omega_{t'})^{1/2}}{\omega_t^2 - \omega_{t'}^2} \right) \left(\sum_s \zeta_{st} \zeta_{st'} \frac{1}{\omega_s^2 - \omega_t^2} \right) \left(\sum_{s'} C_{s'} \phi_{s'tt'} \right) \end{aligned} \tag{21}$$

and

$$q_t^K = -q_t^J - \frac{8B_e^4}{\omega_t} \sum_s \zeta_{st}^2 \frac{\omega_s^4 + 10\omega_s^2 \omega_t^2 + 5\omega_t^4}{(\omega_s^2 - \omega_t^2)^3} , \tag{22}$$

where $C_s = -B_s/\omega_s$, and B_s is given in eq. (16). It should be noted that for a linear polyatomic molecule the q_t^e in eq. (20) is independent of the anharmonic force constants, whereas q_t^J and q_t^K depend on the cubic, but not quartic, force constants.

2.5. The vibrational anharmonic constants

The vibrational anharmonic constants appearing in the vibrational term formula (3) may be determined using the results of perturbation theory [17–21]. For a linear polyatomic molecule, the general formulas are

$$\chi_{ss}=\tfrac{1}{16}\phi_{ssss}-\tfrac{1}{16}\sum_{s'}\phi^2_{sss'}\frac{8\omega_s^2-3\omega_{s'}^2}{\omega_{s'}(4\omega_s^2-\omega_{s'}^2)}\,, \tag{23}$$

$$\chi_{tt}=\tfrac{1}{16}\phi_{tttt}-\tfrac{1}{16}\sum_{s}\phi^2_{stt}\frac{8\omega_t^2-3\omega_s^2}{\omega_s(4\omega_t^2-\omega_s^2)}\,, \tag{24}$$

and

$$\chi_{l_tl_t}=-\tfrac{1}{48}\phi_{tttt}-\tfrac{1}{16}\sum_{s}\phi^2_{stt}\frac{\omega_s}{4\omega_t^2-\omega_s^2}\,, \tag{25}$$

for the diagonal terms, and

$$\chi_{ss'}=\tfrac{1}{4}\phi_{sss's'}-\tfrac{1}{4}\sum_{s''}\phi_{sss''}\phi_{s''s's'}\frac{1}{\omega_{s''}}-\tfrac{1}{2}\sum_{s''}\phi^2_{ss's''}\frac{\omega_{s''}(\omega_{s''}^2-\omega_s^2-\omega_{s'}^2)}{\Delta_{ss's''}}\,, \tag{26}$$

$$\chi_{st}=\tfrac{1}{4}\phi_{sstt}-\tfrac{1}{4}\sum_{s'}\phi_{sss'}\phi_{s'tt}\frac{1}{\omega_{s'}}-\tfrac{1}{2}\sum_{t'}\phi^2_{stt'}\frac{\omega_{t'}(\omega_{t'}^2-\omega_s^2-\omega_t^2)}{\Delta_{stt'}}+B_e\zeta^2_{st}\left(\frac{\omega_s}{\omega_t}+\frac{\omega_t}{\omega_s}\right), \tag{27}$$

$$\chi_{tt'}=\tfrac{1}{8}(\phi_{t_at_at'_at'_a}+\phi_{t_at_at'_bt'_b})-\tfrac{1}{4}\sum_{s}\phi_{stt}\phi_{st't'}\frac{1}{\omega_s}-\tfrac{1}{4}\sum_{s}\phi^2_{stt'}\frac{\omega_s(\omega_s^2-\omega_t^2-\omega_{t'}^2)}{\Delta_{stt'}}\,, \tag{28}$$

and

$$\chi_{l_tl_{t'}}=\tfrac{1}{2}\sum_{s}\phi^2_{stt'}\frac{\omega_s\omega_t\omega_{t'}}{\Delta_{stt'}}\,, \tag{29}$$

for the off-diagonal terms. The denominator $\Delta_{rr'r''}$ in eqs. (26)–(29) is defined by

$$\Delta_{rr'r''}=(\omega_r+\omega_{r'}+\omega_{r''})(\omega_r+\omega_{r'}-\omega_{r''})(\omega_r-\omega_{r'}+\omega_{r''})(\omega_r-\omega_{r'}-\omega_{r''})\,. \tag{30}$$

All of the summations in eqs. (23)–(29) are unrestricted; however, the index s runs only over non-degenerate modes, and the index t runs only over degenerate modes.

2.6. Anharmonic resonance

If either of the following relationships is satisfied accidentally for a linear polyatomic molecule,

$$2\omega_r\approx\omega_{r'}\quad\text{and}\quad\phi_{rrr'}\neq 0\,; \tag{31}$$

$$\omega_r+\omega_{r'}\approx\omega_{r''}\quad\text{and}\quad\phi_{rr'r''}\neq 0 \tag{32}$$

the quantities χ_{rr} and $\chi_{rr'}$ in section 2.5 may become indefinitely large and the perturbation theory method described above will fail. This phenomenon is called vibrational anharmonic resonance [1,19], and the case given in eq. (31) is generally referred to as Fermi–Dennison [28,29] resonance.

The components of the diagonal terms [eqs. (23)–(25)] which contain $\phi^2_{rrr'}$ may be factored as follows [18]:

$$\phi^2_{rrr'}\frac{8\omega_r^2-3\omega_{r'}^2}{\omega_{r'}(4\omega_r^2-\omega_{r'}^2)}=\tfrac{1}{2}\phi^2_{rrr'}\left(\frac{1}{2\omega_r+\omega_{r'}}-\frac{1}{2\omega_r-\omega_{r'}}+\frac{4}{\omega_{r'}}\right) \tag{33}$$

and

$$\phi^2_{rrr'}\frac{\omega_{r'}}{4\omega_r^2-\omega_{r'}^2}=-\tfrac{1}{2}\phi^2_{rrr'}\left(\frac{1}{2\omega_r+\omega_{r'}}-\frac{1}{2\omega_r-\omega_{r'}}\right), \tag{34}$$

where r and r' denote either non-degenerate or degenerate normal modes. If an anharmonic resonance ($2\omega_r\approx\omega_{r'}$) occurs, the resonating terms are replaced according to

$$\phi^2_{rrr'}\frac{8\omega_r^2-3\omega_{r'}^2}{\omega_{r'}(4\omega_r^2-\omega_{r'}^2)}\rightarrow\tfrac{1}{2}\phi^2_{rrr'}\left(\frac{1}{2\omega_r+\omega_{r'}}+\frac{4}{\omega_{r'}}\right) \tag{35}$$

in eqs. (23) and (24), and

$$\phi^2_{rrr'}\frac{\omega_{r'}}{4\omega_r^2-\omega_{r'}^2}\rightarrow-\tfrac{1}{2}\phi^2_{rrr'}\frac{1}{2\omega_r+\omega_{r'}} \tag{36}$$

in eq. (25).

Similarly, the components of the off-diagonal terms [eqs. (26)–(29)] which have $\phi^2_{rr'r''}$ as a coefficient may be factored according to

$$\phi^2_{rr'r''}\frac{\omega_{r''}(\omega_{r''}^2-\omega_r^2-\omega_{r'}^2)}{\Delta_{rr'r''}}=\tfrac{1}{4}\phi^2_{rr'r''}\left(\frac{1}{\omega_r+\omega_{r'}+\omega_{r''}}-\frac{1}{\omega_r+\omega_{r'}-\omega_{r''}}+\frac{1}{\omega_r-\omega_{r'}+\omega_{r''}}-\frac{1}{\omega_r-\omega_{r'}-\omega_{r''}}\right), \tag{37}$$

and

$$\phi^2_{rr'r''}\frac{\omega_r\omega_{r'}\omega_{r''}}{\Delta_{rr'r''}}=\tfrac{1}{8}\phi^2_{rr'r''}\left(\frac{1}{\omega_r+\omega_{r'}+\omega_{r''}}-\frac{1}{\omega_r+\omega_{r'}-\omega_{r''}}-\frac{1}{\omega_r-\omega_{r'}+\omega_{r''}}+\frac{1}{\omega_r-\omega_{r'}-\omega_{r''}}\right). \tag{38}$$

If the resonance $\omega_r+\omega_{r'}\approx\omega_{r''}$ occurs, the resonating terms are replaced according to

$$\phi^2_{rr'r''}\frac{\omega_{r''}(\omega_{r''}^2-\omega_r^2-\omega_{r'}^2)}{\Delta_{rr'r''}}\rightarrow\tfrac{1}{4}\phi^2_{rr'r''}\left(\frac{1}{\omega_r+\omega_{r'}+\omega_{r''}}+\frac{1}{\omega_r-\omega_{r'}+\omega_{r''}}-\frac{1}{\omega_r-\omega_{r'}-\omega_{r''}}\right) \tag{39}$$

in eqs. (26)–(28) and

$$\phi^2_{rr'r''}\frac{\omega_r\omega_{r'}\omega_{r''}}{\Delta_{rr'r''}}\rightarrow\tfrac{1}{8}\phi^2_{rr'r''}\left(\frac{1}{\omega_r+\omega_{r'}+\omega_{r''}}-\frac{1}{\omega_r-\omega_{r'}+\omega_{r''}}+\frac{1}{\omega_r-\omega_{r'}-\omega_{r''}}\right) \tag{40}$$

in eq. (29).

A complete analysis of the vibration–rotation interaction of resonating levels must involve a first-order rather than a second-order treatment. In many experimental analyses first-order interactions are indeed accounted for independently so that the resulting empirical χ_{rs} constants correspond to deperturbed energy levels. The replacement of terms described in the above equations effectively removes interactions in the second-order treatment which are more properly treated in first order. This provides for a direct comparison between our ab initio constants and empirical constants associated with deperturbed energy levels.

Another type of resonance which may appear in linear molecules is Coriolis resonance, which can occur only if the Coriolis constant ζ_{st} between normal modes s and t is nonzero. Thus, in linear molecules Coriolis resonance always involves a non-degenerate normal mode s and a degenerate normal mode t. No Coriolis resonances are of concern for the molecules studied in this paper.

2.7. *The fundamental frequencies*

The fundamental frequencies [16] of a linear polyatomic molecule are obtained from the harmonic frequencies and the anharmonic constants defined in the preceding sections according to

$$\nu_i=\omega_i+\Delta_i=\omega_i+\chi_{ii}(1+d_i)+\tfrac{1}{2}\sum_{k\neq i}\chi_{ik}d_k+\chi_{l_il_i}, \tag{41}$$

where $\chi_{l_i l_i}$ is non-zero only for degenerate modes. The fundamental frequencies should closely correspond with the frequencies obtained from vibrational–rotational spectra.

2.8. The vibrational l-type doubling constants

Vibrational energy levels of linear polyatomic molecules may also be perturbed by vibrational *l*-type doubling if two or more doubly degenerate vibrational modes are excited [21]. For example, the $(v_4^{l_4}, v_5^{l_5}) = (1^{\pm 1}, 1^{\pm 1})$ manifold of acetylene consists of the following levels: (1) $l=0$, Σ_u^+ symmetry, relative energy $= -r_{45}$; (2) $l=0$, Σ_u^- symmetry, relative energy $= +r_{45}$; and (3) $l = \pm 2$, Δ_u symmetry, relative energy $= 2\chi_{l_4 l_5}$, where $\chi_{l_4 l_5}$ is the vibrational anharmonic constant of eq. (29), and r_{45} is the vibrational *l*-type doubling constant. The general expression for the vibrational *l*-type doubling constant for a linear polyatomic molecule is given by

$$r_{tt'} = -\tfrac{1}{2} \sum_s \phi_{stt'}^2 \frac{\omega_s(\omega_s^2 - \omega_t^2 - \omega_{t'}^2)}{\Delta_{stt'}} + \tfrac{1}{4}(\phi_{t_a t_a t'_a t'_a} - \phi_{t_a t_a t'_b t'_b}) , \tag{42}$$

where $\Delta_{stt'}$ is already defined in eq. (30).

3. Theoretical methods

The test molecules chosen for this portion of our systematic study of anharmonicity are HCN, DCN, CO_2, N_2O, OCS, C_2H_2, and C_2D_2. We have chosen five basis sets, of double-zeta (DZ), triple-zeta (TZ), double-zeta plus polarization (DZP), triple-zeta plus polarization (TZP), and triple-zeta plus double polarization (TZ2P) quality for determination of the quartic force fields and the various harmonic and anharmonic quantities described above. The DZ basis is that of Huzinaga [30] and Dunning [31,32] and consists of a (9s5p/4s2p) set of contracted Gaussian functions for carbon, nitrogen, and oxygen, an (11s7p/6s4p) set for sulfur, and a (4s/2s) set for hydrogen atoms. The TZ basis set is obtained from the same set of primitive Gaussian functions [30] but is more loosely contracted; it may be designated (9s5p/5s3p) for carbon, nitrogen, and oxygen, (11s7p/7s5p) for sulfur, and (4s/3s) for hydrogen atoms. We have employed the primitive functions as they are published by Huzinaga [30], since the more commonly used tabulation of Dunning and Hay [32] contains a minor typographical error; namely, the second most diffuse s exponent of sulfur should be 0.4264 rather than 0.4246. For the DZP and TZP basis sets, a single set of polarization functions, consisting of six Cartesian d-type functions for each heavy atom [$\alpha_d(C)=0.75$, $\alpha_d(N)=0.80$, $\alpha_d(O)=0.85$, $\alpha_d(S)=0.50$] or a set of p-type functions for each hydrogen atom [$\alpha_p(H)=0.75$], was added to the corresponding DZ or TZ bases. For the TZ2P basis set, two sets of polarization functions, consisting of sets of six Cartesian d-type functions for each heavy atom [$\alpha_d(C)=1.50, 0.375$; $\alpha_d(N)=1.60, 0.40$; $\alpha_d(O)=1.70, 0.425$; $\alpha_d(S)=1.00, 0.25$] or sets of p-type functions for each hydrogen atom [$\alpha_p(H)=1.50, 0.375$], were added to the corresponding TZ basis.

Electronic wavefunctions were determined in this study by both the single-configuration, self-consistent-field, restricted Hartree–Fock (SCF) method and the single-reference configuration interaction singles and doubles (CISD) method, the CISD wavefunctions being constructed from the respective SCF orbitals. The numbers of core and virtual orbitals which were frozen in the CI treatments for the different molecules are as follows: 2 core and 2 virtual orbitals for HCN, 3 core and 3 virtual orbitals for CO_2 and N_2O, and 7 core and 1 virtual orbital for OCS.

The equilibrium geometries of the test molecules were obtained by optimization using analytic SCF and CISD gradient methods [2,33–35]. The residual Cartesian gradients were in all cases less than 10^{-7} hartree/bohr.

At the SCF level, quadratic and cubic force constants were determined analytically [10–13,36–38], while quartic force constants were obtained by finite differences of third derivatives. Both positive and negative displacements of the size 0.0001 bohr were applied for the individual atomic Cartesian coordinates.

The complete CISD quartic force fields were determined for the triatomic molecules (HCN, CO_2, N_2O and

OCS) whereas only the quadratic force field was obtained (by finite difference of first derivatives with 0.01 bohr displacements) for C_2H_2. The quartic force fields for the triatomics were obtained from finite differences of analytic CI gradients in the following fashion. Analytic Cartesian first derivatives were computed for 18 different points (11 in the case of CO_2) and transformed to internal coordinates, chosen to be the individual stretches for each molecule and the two equivalent linear bending angles. The single displacements involved perturbations of each symmetry-unique internal coordinate by ±0.01 and ±0.02 Å or ±0.02 and ±0.04 rad. All the symmetry-unique double displacements (i.e. displacements involving a stretch and a bend or the two stretches at the same time) were also made and calculated. These were used in a cost-efficient finite-difference (rather than surface-fitting) procedure to generate all force constants up to fourth order. The quartic force field in internal coordinates was then transformed directly and analytically to Cartesian coordinate derivatives with the program INTDER, written by W.D. Allen. The whole finite-difference procedure using information only from analytic first derivatives was tested at the DZ SCF level for HCN against the procedure using finite differences of analytic third derivatives. The two sets of force constants are compared in table 1, where excellent agreement is seen. For example, the force constants f_{RRR} and f_{RRRR} for the CN stretch are -138.52 aJ $Å^{-3}$ and 723.73 aJ $Å^{-4}$, respectively, using the third derivative method as compared to -138.68 and 724.18 using the first derivative method.

The vibrational anharmonic constants and vibration–rotation interaction constants were then evaluated from the Cartesian quartic force fields by performing a linear transformation into normal coordinates and using the formulas presented in section 2.

No anharmonic resonances involving the lowest vibration–rotation levels occur for HCN, DCN, C_2H_2 or C_2D_2. For CO_2, N_2O and OCS the anharmonic (resonance) interactions between the first overtone of the bending vibration ($2\omega_2$) and one of the stretching vibrations (ω_1 for CO_2 and OCS, and ω_3 for N_2O) have been taken into account experimentally in first-order treatments. A similar experimental analysis has been performed for the interaction between $2\omega_1$ and ω_3 for OCS, levels which involve the two stretching vibrations. Therefore the measured vibrational anharmonic constants (χ_{rs}) correspond to deperturbed energy levels. In the present calculations these resonances have been explicitly removed from the second-order perturbation treatment through the appropriate replacement formulas (see section 2) at all levels of theory, regardless of the values predicted for the harmonic frequencies. This treatment ensures that the calculated anharmonic vibrational constants (cor-

Table 1
Complete quartic force fields of HCN calculated at the DZ SCF level [a]

Constant	Anal. 3rd [b]	Anal. 1st [c]	Constant	Anal. 3rd [b]	Anal. 1st [c]
f_{rr}(CH)	7.169261	7.169259(2)	f_{rrrr}	205.34	205.48(14)
f_{rR}	−0.319451	−0.319451(0)	f_{Rrrr}	−2.7708	−2.7710(2)
f_{RR}(CN)	22.478773	22.478766(7)	f_{RRrr}	−1.9268	−1.9273(5)
$f_{\alpha\alpha}$	0.375665	0.375665(0)	f_{RRRr}	−1.8205	−1.8208(3)
f_{rrr}	−40.510	−40.556(46)	f_{RRRR}	723.73	724.18(45)
f_{Rrr}	0.6680	0.6683(3)	$f_{\alpha\alpha rr}$	0.22816	0.22797(19)
f_{RRr}	0.1766	0.1769(3)	$f_{\alpha\alpha Rr}$	0.27963	0.27971(8)
f_{RRR}	−138.52	−138.68(16)	$f_{\alpha\alpha RR}$	−0.00151	−0.00145(6)
$f_{\alpha\alpha r}$	−0.27539	−0.27541(2)	$f_{\alpha\alpha\alpha\alpha}$	0.36511	0.36131(380)
$f_{\alpha\alpha R}$	−0.72226	−0.72231(5)	$f_{\alpha_x\alpha_x\alpha_y\alpha_y}$	0.71080	0.62132

[a] Units for the force constants are consistent with energy measured in aJ, stretching coordinates in angstroms and bending coordinates in radians.

[b] The force constants were obtained from analytic third derivative procedures; the quartic constants by finite differences.

[c] The force constants were obtained from analytic first derivatives (for details see text); $f_{\alpha_x\alpha_x\alpha_y\alpha_y}$ is calculated from the mathematical identity $f_{\alpha_x\alpha_x\alpha_y\alpha_y}=\frac{1}{3}(f_{\alpha\alpha\alpha\alpha}+4f_{\alpha\alpha})$, where $f_{\alpha\alpha}\equiv f_{\alpha_x\alpha_x}=f_{\alpha_y\alpha_y}$ and $f_{\alpha\alpha\alpha\alpha}\equiv f_{\alpha_x\alpha_x\alpha_x\alpha_x}=f_{\alpha_y\alpha_y\alpha_y\alpha_y}$. The values given in parentheses are the deviations from the analytic cubic force constants.

responding to deperturbed energy levels) can be compared correctly to each other and to experiment. Note also that considerable care should be exercised in comparing the theoretical and experimental vibrational fundamentals in molecules having Fermi resonances, as one should distinguish between the measurable (perturbed) fundamentals (denoted usually as 01^10–00^00, etc.), the so-called ground state vibrational fundamentals (denoted usually as ω_i^0 [16]), and the deperturbed fundamentals (the values which are to be compared with the current theoretical results).

4. Results and discussion

4.1. HCN and DCN

Hydrogen cyanide is one of the few molecules whose vibrational–rotational spectra (and those of its isotopomers) have been studied exhaustively both experimentally and theoretically [39–53]. Results of the present theoretical study are collected in tables 2–5 for HCN and tables 6–9 for DCN, where comparisons are made to the recent experimental data which, according to our analysis, appear to be the most reliable. The TZ2P quartic force fields, calculated at the SCF and CISD levels of theory, are presented in table 10.

One salient trend is that at the CISD level of theory the CH and CN bond lengths decrease with basis set enlargement so that the distances which are too long at the DZ level become too short at the TZ2P level (see table 3). The experimental bond lengths actually lie between the DZP and TZP values. Nevertheless, the TZ2P CISD bond lengths deviate less than 0.01 Å from the experimental distances, and thus the agreement can be considered good. The trend at the SCF level is not as simple (table 2); a similar decrease of the CN distance

Table 2

Theoretical (SCF) and experimental geometries, dipole moments, vibration–rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational *l*-type doubling constants for HCN

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
E (hartree)	−92.83694	−92.84767	−92.88958	−92.89955	−92.90428	-
r_e(CN) (Å)	1.1507	1.1375	1.1366	1.1268	1.1235	1.1532(1) [a]
r_e(CH) (Å)	1.0542	1.0547	1.0638	1.0576	1.0571	1.0655(2) [a]
μ (debye)	3.2963	3.2829	3.2156	3.2439	3.2360	2.985(4) [b]
$\alpha_1 \times 10^3$ (cm^{-1})	8.00	8.30	7.69	7.91	8.00	9.970(20) [c]
$\alpha_2 \times 10^3$	−2.60	−3.08	−3.33	−2.56	−3.28	−3.565(7) [c]
$\alpha_3 \times 10^3$	9.61	9.40	9.59	9.71	9.92	10.441(2) [c]
B_e (cm^{-1})	1.4951	1.5244	1.5223	1.5475	1.5556	1.4847 [d]
B_0	1.4889	1.5186	1.5170	1.5412	1.5499	1.478220(2) [e]
$D_J \times 10^6$ (cm^{-1})	2.4424	2.6159	2.4233	2.5343	2.5777	$D_0=2.906(3)$ [e,f], $D_e=2.853$ [a,f]
$H_J \times 10^{12}$	2.47	2.85	2.64	2.85	2.93	$H_0=2.72(128)$ [g]
$q_2^e \times 10^3$ (cm^{-1})	6.3291	6.5802	6.7139	6.7384	6.9754	7.4869(4) [e,h]
$q_2^J \times 10^8$	−5.019	−5.531	−5.686	−5.234	−5.969	−8.68(8) [e,h]
$q_2^K \times 10^8$	4.342	4.754	4.941	4.429	5.139	-

[a] Ref. [43]. [b] Ref. [52]. [c] Ref. [46]. [d] Ref. [47]. [e] Ref. [45].

[f] D_0 is the quartic centrifugal distortion constant, D_J, in the ground vibrational state. D_e is the equilibrium value of D_J.

[g] Ref. [39]. H_0 is the sextic centrifugal distortion constant, H_J, in the ground vibrational state.

[h] The *l*-type doubling constants were obtained for the fundamental 01^10. The q_2^K term was not included in the experimental fit.

Table 3
Theoretical (CISD) and experimental geometries, dipole moments, vibration–rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational *l*-type doubling constants for HCN

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
E (hartree)	−93.03202	−93.05574	−93.16042	−93.18467	−93.20228	–
r_e(CN) (Å)	1.1832	1.1648	1.1631	1.1497	1.1436	1.1532(1) [a]
r_e(CH) (Å)	1.0720	1.0700	1.0707	1.0625	1.0615	1.0655(2) [a]
μ (debye)	3.1302	3.1379	3.0010	3.0433	3.0469	2.985(4) [b]
$\alpha_1\times10^3$ (cm^{-1})	8.91	9.26	8.54	8.84	8.99	9.970(20) [c]
$\alpha_2\times10^3$	−2.88	−4.01	−3.67	−2.71	−3.61	−3.565(7) [c]
$\alpha_3\times10^3$	9.71	9.65	9.56	9.77	10.21	10.441(2) [c]
B_e (cm^{-1})	1.4189	1.4580	1.4612	1.4937	1.5078	1.4847 [d]
B_0	1.4125	1.4526	1.4558	1.4871	1.5018	1.478220(2) [e]
$D_J\times10^6$ (cm^{-1})	2.5419	2.7581	2.5120	2.6451	2.7031	D_0=2.906(3) [e,f], D_e=2.853 [a,f]
$H_J\times10^{12}$	2.06	2.52	2.30	2.51	2.60	H_0=2.72(128) [g]
$q_2^e\times10^3$ (cm^{-1})	6.3978	6.9272	6.7881	6.7556	7.0968	7.4869(4) [e,h]
$q_2^J\times10^8$	−6.018	−7.622	−6.811	−5.995	−7.066	−8.68(8) [e,h]
$q_2^K\times10^8$	5.348	6.840	6.100	5.219	6.247	–

[a] Ref. [43]. [b] Ref. [52]. [c] Ref. [46]. [d] Ref. [47]. [e] Ref. [45].

[f] D_0 is the quartic centrifugal distortion constant, D_J, in the ground vibrational state. D_e is the equilibrium value of D_J.

[g] Ref. [39]. H_0 is the sextic centrifugal distortion constant, H_J, in the ground vibrational state.

[h] The *l*-type doubling constants were obtained for the fundamental 01^10. The q_2^K term was not included in the experimental fit.

Table 4
Theoretical (SCF) and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies for HCN

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment [a]
ω_1 (cm^{-1})	2326.8	2314.8	2403.2	2409.4	2407.6	2127.2(4)
ω_2	882.7	895.4	856.6	902.6	868.2	726.9(2)
ω_3	3697.0	3626.3	3631.2	3623.2	3603.3	3442.5(1)
χ_{11} (cm^{-1})	−8.19	−7.94	−7.84	−7.86	−7.87	−10.07(19)
χ_{12}	−1.45	0.05	−0.99	−1.49	−0.25	−3.25(20)
χ_{13}	−13.04	−11.96	−13.42	−13.79	−13.58	−13.31(7)
χ_{22}	−0.86	−1.73	−3.30	−6.38	−4.21	−2.55(9)
χ_{23}	−20.74	−18.18	−16.72	−19.04	−16.68	−18.98(6)
χ_{33}	−52.40	−46.00	−47.32	−45.25	−46.15	−52.72(11)
$\chi_{l_2l_2}$	4.81	5.57	5.78	6.62	6.11	5.30(9)
ν_1 (cm^{-1})	2302.4	2293.0	2379.8	2385.3	2384.8	2096.7(2)
ν_2	873.8	886.7	843.7	879.8	853.2	713.5 [b]
ν_3	3564.9	3510.2	3513.2	3506.8	3487.6	3311.5 [b]
Δ_1 (cm^{-1})	−24.3	−21.8	−23.4	−24.1	−22.8	−30.5
Δ_2	−8.9	−8.7	−13.0	−22.8	−15.0	−13.4
Δ_3	−132.1	−116.2	−118.1	−116.4	−115.8	−131.0

[a] Ref. [46]. [b] The experimental precision is considerably higher than indicated here.

Table 5
Theoretical (CISD) and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies for HCN

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment [a]
ω_1 (cm^{-1})	2104.0	2104.3	2213.8	2230.9	2239.0	2127.2(4)
ω_2	761.0	738.6	754.0	814.4	778.9	726.9(2)
ω_3	3492.0	3429.9	3530.9	3530.4	3495.9	3442.5(1)
χ_{11} (cm^{-1})	−9.04	−8.71	−8.74	−8.80	−8.99	−10.07(19)
χ_{12}	−2.99	−1.34	−2.51	−3.28	−1.94	−3.25(20)
χ_{13}	−12.36	−11.34	−12.04	−12.49	−12.64	−13.31(7)
χ_{22}	1.03	5.56	−1.40	−6.23	−4.99	−2.55(9)
χ_{23}	−19.55	−15.03	−16.14	−18.38	−15.24	−18.98(6)
χ_{33}	−56.45	−49.77	−51.38	−48.85	−51.01	−52.72(11)
$\chi_{l_2 l_2}$	3.98	2.98	4.98	6.45	6.35	5.30(9)
ν_1 (cm^{-1})	2076.7	2079.9	2187.8	2203.8	2212.7	2096.7(2)
ν_2	756.8	750.0	745.4	791.3	761.7	713.5 [b]
ν_3	3353.4	3309.7	3406.0	3408.0	3372.4	3311.5 [b]
Δ_1 (cm^{-1})	−27.3	−24.4	−26.0	−27.1	−26.3	−30.5
Δ_2	−4.2	11.5	−8.6	−23.1	−17.2	−13.4
Δ_3	−138.6	−120.2	−124.9	−122.3	−123.6	−131.0

[a] Ref. [46]. [b] The experimental precision is considerably higher than indicated here.

Table 6
Theoretical (SCF) and experimental vibration–rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational *l*-type doubling constants for DCN

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
$\alpha_1 \times 10^3$ (cm^{-1})	5.33	5.37	5.21	5.36	5.43	6.01(11) [a]
$\alpha_2 \times 10^3$	−3.20	−3.56	−3.79	−3.17	−3.77	−4.23(1) [a]
$\alpha_3 \times 10^3$	9.58	9.58	9.42	9.54	9.73	10.84(7) [a]
B_e (cm^{-1})	1.2221	1.2434	1.2397	1.2595	1.2655	1.2120 [b]
B_0	1.2178	1.2395	1.2361	1.2552	1.2617	1.2078 [a]
$D_J \times 10^6$ (cm^{-1})	1.6162	1.7276	1.6119	1.6885	1.7166	$D_0 = 1.929(1)$ [a,c], $D_e = 1.837$ [a,c]
$H_J \times 10^{12}$	1.54	1.81	1.59	1.72	1.77	–
$q_2^e \times 10^3$ (cm^{-1})	5.3043	5.4860	5.5764	5.5901	5.7804	6.211 [d]
$q_2^J \times 10^8$	−3.978	−4.297	−4.547	−4.071	−4.719	−7.362 [d]
$q_2^K \times 10^8$	3.395	3.633	3.904	3.375	4.004	–

[a] Ref. [43]. [b] Approximate value, calculated in the present study from B_0 using only the measured α values.
[c] D_0 is the quartic centrifugal distortion constant, D_J, in the ground vibrational state. D_e is the equilibrium value of D_J.
[d] Ref. [51]. The *l*-type doubling constants were obtained for the fundamental 01^10. The q_2^K term was not included in the experimental fit.

occurs, but the CH bond distance goes through a maximum at the DZP level. It is important to note that the variations in the calculated harmonic wavenumbers ω_1 and ω_3 (tables 4, 5, 8 and 9) do not correlate with the trends in the corresponding bond lengths in any simple manner. Therefore, the trends in the harmonic frequency

Table 7
Theoretical (CISD) and experimental vibration–rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational *l*-type doubling constants for DCN

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
$\alpha_1 \times 10^3$ (cm^{-1})	5.82	5.91	5.56	5.77	5.87	6.01(11) [a]
$\alpha_2 \times 10^3$	−3.57	−4.54	−4.22	−3.44	−4.22	−4.23(1) [a]
$\alpha_3 \times 10^3$	9.87	10.01	9.71	9.89	10.32	10.84(7) [a]
B_e (cm^{-1})	1.1621	1.1912	1.1934	1.2191	1.2296	1.2120 [b]
B_0	1.1578	1.1878	1.1900	1.2147	1.2258	1.2078 [a]
$D_J \times 10^6$ (cm^{-1})	1.6642	1.8022	1.6495	1.7402	1.7814	$D_0 = 1.929(1)$ [a,c], $D_e = 1.837$ [a,c]
$H_J \times 10^{12}$	1.41	1.73	1.50	1.63	1.69	-
$q_2^e \times 10^3$ (cm^{-1})	5.3866	5.7979	5.6774	5.6404	5.9146	6.211 [d]
$q_2^J \times 10^8$	−4.983	−6.316	−5.684	−4.841	−5.810	−7.362 [d]
$q_2^K \times 10^8$	4.411	5.655	5.077	4.180	5.110	-

[a] Ref. [43]. [b] Approximate value, calculated in the present study from B_0 using only the measured α values.
[c] D_0 is the quartic centrifugal distortion constant, D_J, in the ground vibrational state. D_e is the equilibrium value of D_J.
[d] Ref. [51]. The *l*-type doubling constants were obtained for the fundamental 01^10. The q_2^K term was not included in the experimental fit.

Table 8
Theoretical (SCF) and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies for DCN

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment [a]
ω_1 (cm^{-1})	2117.4	2100.0	2155.6	2154.8	2151.6	1952.8
ω_2	703.4	714.2	683.9	720.8	693.5	580.0
ω_3	2926.8	2879.8	2916.5	2918.6	2904.8	2703.9
χ_{11} (cm^{-1})	−5.99	−5.67	−6.07	−6.10	−6.15	−7.03
χ_{12}	3.79	5.17	4.88	4.25	5.38	2.68
χ_{13}	−30.35	−27.94	−31.23	−30.87	−31.46	−32.44
χ_{22}	−1.07	−1.71	−2.67	−4.60	−3.26	−2.08
χ_{23}	−15.77	−14.02	−13.95	−15.22	−13.82	−15.96
χ_{33}	−19.87	−17.38	−16.37	−15.52	−15.61	−20.56
χ_{ll}	2.98	3.54	3.63	4.16	3.86	3.25
ν_1 (cm^{-1})	2094.0	2079.8	2132.8	2131.4	2129.0	1925.3
ν_2	697.2	708.2	675.0	705.7	683.3	570.3
ν_3	2856.1	2817.1	2854.2	2856.9	2844.0	2630.3
Δ_1 (cm^{-1})	−23.4	−20.1	−22.9	−23.4	−22.6	−27.5
Δ_2	−6.2	−6.0	−8.9	−15.1	−10.1	−9.7
Δ_3	−70.7	−62.8	−62.3	−61.7	−60.8	−73.6

[a] Ref. [41].

predictions cannot be attributed primarily to the effect of anharmonicity on the underlying quadratic diagonal stretching constants as the equilibrium distances change [4].

Relatively little sensitivity to basis set is observed for the quartic centrifugal distortion constant, D_J, in ac-

Table 9
Theoretical (CISD) and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies for DCN

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment [a]
ω_1 (cm^{-1})	1940.4	1934.2	2024.9	2033.9	2034.4	1952.8
ω_2	605.8	588.7	601.1	649.4	621.4	580.0
ω_3	2727.9	2688.5	2781.3	2789.7	2772.0	2703.9
χ_{11} (cm^{-1})	−6.36	−5.97	−6.09	−6.14	−6.26	−7.03
χ_{12}	2.76	4.61	3.75	3.00	4.52	2.68
χ_{13}	−28.68	−26.99	−29.50	−29.74	−31.66	−32.44
χ_{22}	0.17	2.96	−1.41	−4.48	−3.73	−2.08
χ_{23}	−15.44	−12.84	−13.85	−15.13	−13.48	−15.96
χ_{33}	−23.17	−20.17	−19.88	−18.50	−18.87	−20.56
$\chi_{l_2 l_2}$	2.40	1.82	3.06	4.00	3.96	3.25
ν_1 (cm^{-1})	1916.1	1913.3	2001.7	2009.8	2010.5	1925.3
ν_2	602.4	595.3	594.9	633.9	609.7	570.3
ν_3	2651.8	2621.8	2712.9	2722.7	2704.9	2630.3
Δ_1 (cm^{-1})	−24.3	−20.8	−23.2	−24.1	−23.8	−27.5
Δ_2	−3.4	6.6	−6.2	−15.5	−11.7	−9.7
Δ_3	−76.1	−66.7	−68.4	−67.0	−67.1	−73.6

[a] Ref. [41].

Table 10
Complete quartic force fields for HCN [a]

In internal coordinates				In normal coordinates			
constant	theory		expt. [b]	constant	theory		expt. [b]
	SCF	CISD			SCF	CISD	
f_{rr}(CH)	6.790	6.433	6.244	ω_1	2407.6	2239.0	2128.7(8)
f_{rR}	−0.169	−0.163	−0.211	ω_2	868.2	778.9	727.1(5)
f_{RR}(CN)	24.129	20.735	18.707	ω_3	3603.3	3495.9	3441.2(4)
$f_{\alpha\alpha}$	0.362	0.295	0.260	ϕ_{111}	−615.6	−625.5	−641.4(30)
f_{rrr}	−37.47	−36.49	−33.76	ϕ_{113}	101.0	110.2	106.6(50)
f_{Rrr}	0.346	0.293	−0.992	ϕ_{122}	226.5	208.5	192.4(28)
f_{RRr}	−0.080	0.067	0.092	ϕ_{133}	−504.3	−452.9	−432.6(92)
f_{RRR}	−149.3	−133.5	−125.1	ϕ_{223}	1035.2	1152.8	1217.8(26)
$f_{\alpha\alpha r}$	−0.159	−0.094	−0.108	ϕ_{333}	−1778.3	−1845.2	−1734.0(47)
$f_{\alpha\alpha R}$	−0.682	−0.664	−0.656	ϕ_{1111}	138.5	148.9	155.3(72)
f_{rrrr}	194.2	190.3	153.1	ϕ_{1113}	−35.5	−38.2	−31.4(48)
f_{Rrrr}	−1.825	−1.906	8.100	ϕ_{1122}	−62.2	−56.3	−57.5(16)
f_{RRrr}	−0.875	−0.466	4.280	ϕ_{1133}	69.3	57.4	56.0(60)
f_{RRRr}	−0.907	−0.996	4.380	ϕ_{1223}	−179.0	−178.3	−178.7(38)
f_{RRRR}	803.7	720.3	650.2	ϕ_{1333}	216.0	200.4	172.4(36)
$f_{\alpha\alpha rr}$	0.140	0.020	−0.440	ϕ_{2222}	1001.6	1231.2	1415(48)
$f_{\alpha\alpha Rr}$	0.062	−0.054	0.276	ϕ_{2233}	−838.6	−950.8	−979(19)
$f_{\alpha\alpha RR}$	0.035	0.191	−0.040	ϕ_{3333}	922.4	979.8	795(36)
$f_{\alpha\alpha\alpha\alpha}$	−0.154	−0.251	0.034				

[a] All the theoretical constants were obtained in the present study using the TZ2P basis set at both the SCF and CISD levels. Units for the force constants in internal coordinates are consistent with energy measured in aJ, stretching coordinates in angstroms and bending coordinates in radians. An additional nonzero quartic constant is fixed by cylindrical symmetry: $f_{\alpha_x\alpha_x\alpha_y\alpha_y} = \frac{1}{3}(f_{\alpha\alpha\alpha\alpha} + 4f_{\alpha\alpha})$, where $f_{\alpha\alpha} \equiv f_{\alpha_x\alpha_x} = f_{\alpha_y\alpha_y}$ and $f_{\alpha\alpha\alpha\alpha} \equiv f_{\alpha_x\alpha_x\alpha_x\alpha_x} = f_{\alpha_y\alpha_y\alpha_y\alpha_y}$. The force constants in normal coordinates are given in cm^{-1}. The normal coordinate force constants refer to $H^{12}C^{14}N$. [b] Ref. [42].

cordance with the discussion in section 2.3. The TZ2P SCF and TZ2P CISD values of HCN (DCN) deviate from the experimental equilibrium values by only 9.6 (6.6)% and 5.3 (3.0)%, respectively. Variations in the sextic constants, H_J, of HCN and DCN are also rather small, especially once the basis set is enlarged past DZ quality. As suggested in table 2, the quality of the predictions for these sextic constants (which are six orders of magnitude smaller than their D_J counterparts) appears to be high, but a detailed analysis is hampered by the lack of precise experimental values.

All theoretical predictions for the vibration–rotation interaction constants for HCN and DCN are qualitatively correct, and the variations with level of theory are generally small. Nevertheless, the inclusion of electron correlation still improves the results significantly. For HCN the errors in the α_1, α_2, and α_3 predictions are 19.8%, 8.0%, and 5.0%, respectively, at the TZ2P SCF level and only 9.8%, 1.3%, and 2.2%, respectively, at the TZ2P CISD level. It is worthwhile to compare the magnitude of the α_i values of HCN with those of DCN. For DCN the experimental α_1 and α_2 constants are smaller and larger, respectively, in absolute value than the corresponding HCN constants [41,43], an occurrence which is reproduced reasonably well by the theoretical values, especially at the CISD level. For α_3 there are two contradictory experimental results. Suzuki et al. [41] measured the DCN constant to be smaller in magnitude than that of HCN, while Winnewisser et al. [43] ascertained the opposite result. The present theoretical predictions are also somewhat inconsistent in addressing this issue; the SCF results (except at the TZ level) support the first experimental analysis while all CISD results support the latter one. Because the overall performance of the calculated CISD quartic force fields is better than that of the SCF force fields, it would seem that for DCN the α_3 value of Winnewisser et al. [43] is to be preferred.

Variations in the theoretical $B_e - B_0$ difference (half the sum of the α_i constants) are remarkably small for HCN. The results scatter around 0.006 cm^{-1} at both the SCF and CISD levels, the experimental result being 0.0065 cm^{-1} [47]. Thus this small correction term (which is, however, rather important in structural determinations) is calculated extremely well at all levels of theory.

The theoretical l-type doubling constants q_2^e for HCN and DCN (tables 2, 3, 6 and 7) range from 5% to 15% in error, the best results being obtained (as one would hope) at the TZ2P CISD level. At all levels of theory the q_2^J constants exhibit considerably larger deviations from experiment than their q_2^e counterparts, the smallest error (12.2%) for HCN occurring fortuitously at the TZ CISD level. However, it should be realized that the q_2^K constant, which is predicted to be of the same magnitude as q_2^J, was not included in the experimental fit. Therefore, the poorer agreement with experiment may not merely be due to subtle cancellations occurring in the large number of terms in eq. (21). In any case the relative changes in the q_2^J l-type doubling constants in going from HCN to DCN are predicted accurately by the present calculations.

There are no strong anharmonic resonances which add to the complexity of the lower vibrational–rotational levels of HCN and DCN, and thus it is not necessary to invoke any of the replacement equations of section 2.6 to facilitate the comparison of theoretical and experimental anharmonic constants χ_{rs}. Four of the seven constants of HCN (χ_{11}, χ_{13}, χ_{23} and χ_{33}) do not vary much with level of theory. For these constants the DZP SCF results are about as good as the TZ2P SCF values, and even the inclusion of electron correlation does not substantially improve the quality of the theoretical predictions. There is a slightly larger scattering of the theoretical results for $\chi_{l_2l_2}$, but again, the DZP SCF prediction is as good as (actually even better than) the TZ2P CISD one. For χ_{12} variation of the theoretical results is clearly larger on a percentage basis, but the wrong sign for this constant is predicted only at the TZ SCF level. The theoretical results appear to be the least dependable for χ_{22}. At the CISD level the predictions extend from -6.2 to 5.6 cm^{-1}, while at the SCF level they extend from -6.4 to -0.9 cm^{-1}. Although the result obtained at the highest level (TZ2P CISD) has the right sign, it is almost twice the magnitude of the measured value. In brief, the scatter of the theoretical values is too large to allow any firm predictions. The reason for this problem is an almost complete cancellation of the two terms determining χ_{22} (see eq. (24)). Although variations in ϕ_{2222}, ϕ_{122} and ϕ_{223} with the theoretical level are reasonably small, the unfortunate cancellation of the two rather large terms makes the theoretical prediction of χ_{22} extremely difficult. Similar problems exist for DCN (see tables 8 and 9), but the calculated constants scatter considerably less.

The agreement between theory and experiment for the vibrational frequencies of HCN and DCN is quite typical of such comparisons for small molecules. The harmonic frequencies ω_1, ω_2, and ω_3 are predicted to be 13.2%, 19.4%, and 4.7% too large, respectively, at the TZ2P SCF level whereas the corresponding TZ2P CISD overestimations are 5.3%, 7.2%, and 1.6%. The theoretical predictions for the total anharmonicities are quite acceptable at the SCF level, but significant improvements for the anharmonic components of the stretching fundamentals are observed if electron correlation is taken into account, as found in our previous study of asymmetric top molecules [9]. Hence the TZ2P CISD ν_1, ν_2, and ν_3 values are 5.5%, 6.8%, and 1.8%, respectively, above their experimental counterparts. In general, the anharmonicities at both the SCF and CISD levels are determined with enough accuracy to make the errors in the theoretical fundamental frequencies ν_i arise almost solely from deficiencies in the harmonic wavenumber predictions.

The TZ2P SCF and CISD force fields for HCN are reported in table 10 in two complementary representations: curvilinear internal coordinates and dimensionless normal coordinates, the former being isotopically invariant and allowing maximal physical interpretation and the latter enhancing the comparison with experimental results. In general, the quality of the theoretical predictions is high and the agreement with experiment quite remarkable. However, some of the smaller internal coordinate force constants, like the cubic constant f_{RRr} (R=CN, r=CH) and several quartic constants, are sensitive to the level of theory and are consequently less reliable. For example, f_{RRr} has a value of 0.067 aJ Å^{-3} at the TZ2P CISD level but a value of -0.160 at the TZP CISD level. The range covered in the CISD results for f_{RRrr} extends from -2.05 (DZP) to 0.23 aJ Å^{-4} (TZP). Even more noteworthy is the change in $f_{\alpha\alpha\alpha\alpha}$, the quartic bending constant. Its values at the DZ, TZ, DZP, TZP and TZ2P CISD levels are 0.47, 0.88, 0.15, -0.38 and -0.25 aJ rad^{-4}, respectively. Nevertheless, all these predictions suggest that the bending vibration of HCN is almost harmonic. It appears safe to conclude that the dominant force constants (e.g. the higher-order diagonal stretching constants) are calculated with considerable accuracy even at the SCF level but that accurate predictions of some smaller force constants which have little effect on the observed energy levels may require extremely high levels of theory. In this regard it is worth noting the excellent theoretical work of Dunn et al. [48], in which an anharmonic force field was calculated at the CEPA-2/6-311G(2dp) level of theory for HCN, and the contradictory results for f_{rrR}, f_{RRr}, f_{RRRr}, f_{rrrR}, $f_{RR\alpha\alpha}$ and $f_{rr\alpha\alpha}$ from several careful experimental investigations [41,42,49,50].

In the dimensionless normal coordinate representation, the force constants show considerably less variation than that observed in the case of internal coordinates, specifically, less than 10% for almost all of the constants. The variation with the theoretical level is actually so small that one can confidently assess the merits of the several experimentally derived force fields of HCN [41,42,44,49,50]. From a comparison with the TZ2P CISD results, it seems clear that the widely used force field obtained experimentally by Nakagawa and Morino [42] more than 20 years ago is quite accurate, this being in essential agreement with the more recent, high-quality work of Strey and Mills [49] and Murrell et al. [50]. The average percentage errors of the TZ2P SCF and CISD ϕ_{ijk} and ϕ_{ijkl} constants compared to the values of Nakagawa and Morino [42] are only 13% and 7%, respectively. On the other hand, the recent quartic force field deduced by Quapp [44] differs more substantially from the TZ2P CISD force field; thus we feel that this refinement converged to several constants which are less reasonable on physical grounds.

It is of interest to try to give simple physical interpretations to some selected internal coordinate force constants of HCN. The quadratic stretch–stretch coupling constant, f_{rR}, is calculated to be negative for HCN, in agreement with experiment. Note that this is in contrast to the situation for the other triatomic molecules considered in this study, where f_{rR} (or $f_{rr'}$ in the case of CO_2) is always positive. Indeed, very simple, chemically intuitive arguments would suggest that f_{rR} is positive in general, since in this case elongation of one of the bonds leads to a decrease of the other bond length. But one is able to interpret the difference between f_{rR} of HCN and the other molecules in simple terms as follows. Stretching a bond to the extreme results in a fragmentation of HCN into a diatomic and an atomic radical, and of the two possible products, H+CN is the most stable. The bond length of $\tilde{X}\,^2\Sigma^+$ CN is 1.172 Å [54], and thus differences in electronic structure give a CN bond length which is actually *longer* than that of HCN, viz. 1.153 Å [43]. Thus the negative sign of f_{rR} is explained. This same argument can be used to interpret the positive f_{rR} constants of CO_2, N_2O and OCS, because in these cases the diatomic fragmentation products (CO and N_2) have strong triple bonds as compared to the double bonds of the parent compounds.

Interpretation of the force constants in higher orders seems to be even more challenging. Probably the most straightforward way to visualize them is through derivative relations such as $f_{\alpha\alpha s}=\partial f_{\alpha\alpha}/\partial s$ or $f_{RRs}=\partial f_{RR}/\partial s$ ($s=r$ or R). The higher-order, diagonal stretching force constants for HCN follow the patterns of relative signs and magnitudes which are expected from such relations for simple Morse oscillators, and thus display no unusual features. The off-diagonal, stretch–bend cubic constants $f_{\alpha\alpha r}$ and $f_{\alpha\alpha R}$ are negative for HCN (both theoretically and experimentally), which can be understood by noting that stretching either bond eventually drops $f_{\alpha\alpha}$ to zero. Hence the derivatives $f_{\alpha\alpha r}$ and $f_{\alpha\alpha R}$ are expected to be negative in the equilibrium structure, assuming that over the course of bond formation $f_{\alpha\alpha}$ increases monotonically. The situation is somewhat more complicated with the stretch–stretch cubic interactions f_{RRr} and f_{Rrr}, which are calculated to be positive at the highest level of theory for HCN. (Note, though, that f_{RRr} changes sign at the different theoretical levels and that f_{RRr} and f_{Rrr} have opposite signs experimentally.) Referring again to arguments based on fragmentation products, one notes that the bond lengths in both $\tilde{X}\,^2\Sigma^+$ CN (1.172 Å) and $\tilde{X}\,^2\Pi$ CH (1.120 Å) are substantially longer than those in HCN. Therefore, as predicted by Badger's rule [55], the f_{RR} stretching constant of CN and the f_{rr} stretching constant of CH are smaller than their counterparts in HCN. This, in turn, suggests that the derivatives f_{RRr} and f_{Rrr} should be negative. Consequently there is some disagreement between the values of the cubic stretch–stretch interaction constants in table 10 and those suggested by this simple model. One is lead to the conclusion that f_{RR} and f_{rr} do not change monotonically as the opposite bond is stretched from equilibrium to infinity.

The quartic stretch–bend interaction constants ($f_{\alpha\alpha rr}$, $f_{\alpha\alpha RR}$ and $f_{\alpha\alpha Rr}$) should modulate the first-order effect on $f_{\alpha\alpha}$ represented by the cubic constants $f_{\alpha\alpha r}$ and $f_{\alpha\alpha R}$. Although theory and experiment agree that these quartic constants are not very large, there is substantial disagreement between them concerning signs and magnitudes. The experimental and theoretical signs are different for all three constants while the relative magnitudes are reversed theoretically as compared to experiment. It is important to note that the experimental $f_{\alpha\alpha RR}$ has a larger error than the constant itself [42] and that $f_{\alpha\alpha rr}$ suffers from a similar problem. (Note again the contradictory results obtained for these constants in refs. [49,50].) Therefore, further experimental studies are needed to establish a true physical picture for these quartic interaction constants; it seems, however, that positive values of $f_{\alpha\alpha RR}$ and $f_{\alpha\alpha rr}$ would be more consistent with the theoretical results for the other compounds of this study.

4.2. CO_2

Besides its simple, symmetric structure and ease of experimental handling, carbon dioxide owes a good deal of its spectroscopic recognition to the anharmonic vibrational resonance between ν_1 and $2\nu_2$, identified first by Fermi [28]. Carbon dioxide has been thoroughly studied since then [56–61], and its complete force field through sixth order has been determined experimentally [56,57]. To our best knowledge (and astonishment) not even the complete quartic force field has been previously determined for CO_2 by ab initio methods. The only study aimed at this goal is that of Steele et al. [94], who obtained part of the force field from SCF calculations using the 4-31G basis set (which is somewhat lower than DZ in quality). Thus the present force fields seem to be the first complete theoretical predictions for CO_2. The harmonic and anharmonic molecular constants calculated in this study for CO_2, together with some selected experimental values, are presented in tables 11–14. The TZ2P quartic force fields, obtained at the SCF and CISD levels, are tabulated in table 15.

The theoretical bond distances of carbon dioxide display the same trends which were observed for the CN distance in hydrogen cyanide. In particular, the theoretical CO distance decreases as the basis set is enlarged (both at the SCF and CISD levels), and the experimental bond length is between the DZP and TZP CISD values. The errors in the TZ2P SCF and CISD bond lengths are 0.025 and 0.010 Å, respectively. The B_e-B_0 difference is predicted again with considerable consistency, the TZ2P CISD value being 0.0013 cm^{-1}. Using the measured B_0 value of 0.39022 cm^{-1} and the TZ2P CISD B_e-B_0 difference, one arrives at an r_e(CO) value of 1.1600 Å, which is precisely the value chosen by Suzuki [58] and equivalent to the 1.15999(4) Å result ob-

Table 11
Theoretical (SCF) and experimental geometries, vibration–rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational l-type doubling constants for CO_2

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
E (hartree)	−187.55339	−187.56280	−187.67624	−187.68792	−187.69554	–
r_e(CO) (Å)	1.1652	1.1594	1.1453	1.1387	1.1349	1.1600 [a]
$\alpha_1\times10^3$ (cm^{-1})	1.14	1.12	1.03	1.04	1.07	1.2030 [b]
$\alpha_2\times10^3$	−0.65	−1.18	−0.70	−0.67	−0.74	−0.7325 [b]
$\alpha_3\times10^3$	3.27	3.26	2.96	2.97	3.01	3.1136 [b]
$B_e\times10^1$ (cm^{-1})	3.8817	3.9202	4.0172	4.0639	4.0912	3.9164 [a]
$B_0\times10^1$	3.8661	3.9101	4.0043	4.0505	4.0782	3.9022 [b]
$D_J\times10^7$ (cm^{-1})	1.1932	1.2633	1.1321	1.1701	1.2057	D_0=1.3332(3) [c,d]
$H_J\times10^{14}$	0.88	1.34	1.25	1.39	1.41	H_0=0.898 [b,d], 1.02(25) [c,d]
$q_2^e\times10^4$ (cm^{-1})	5.8751	6.5719	5.8287	5.9622	6.0962	6.154(2) [e], 6.156(2) [e]
$q_2^J\times10^{10}$	−4.837	−11.220	−5.225	−5.028	−5.511	−7.0(4) [e], −8.9(8) [e]
$q_2^K\times10^{10}$	3.686	9.965	4.204	3.921	4.349	–

[a] Ref. [58]. [b] Ref. [56]. [c] Ref. [60].

[d] D_0 and H_0 are the quartic and sextic centrifugal distortion constants, D_J and H_J, respectively, in the ground vibrational state.

[e] Ref. [60]. The different values were obtained from different model assumptions (see the original publication). The q_2^K term was not included in the experimental fit. The constants refer to the fundamental 010.

Table 12
Theoretical (CISD) and experimental geometries, vibration–rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational l-type doubling constants for CO_2

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
E (hartree)	−187.85244	−187.89161	−188.09489	−188.13876	−188.18187	–
r_e(CO) (Å)	1.1925	1.1833	1.1647	1.1567	1.1503	1.1600 [a]
$\alpha_1\times10^3$ (cm^{-1})	1.13	1.12	1.05	1.06	1.10	1.2030 [b]
$\alpha_2\times10^3$	−0.67	−1.27	−0.71	−0.70	−0.78	−0.7325 [b]
$\alpha_3\times10^3$	3.16	3.16	2.93	2.94	3.02	3.1136 [b]
$B_e\times10^1$ (cm^{-1})	3.7059	3.7638	3.8849	3.9387	3.9829	3.9164 [a]
$B_0\times10^1$	3.6912	3.7552	3.8721	3.9257	3.9701	3.9022 [b]
$D_J\times10^7$ (cm^{-1})	1.2250	1.2998	1.1573	1.1983	1.2421	D_0=1.3332(3) [c,d]
$H_J\times10^{14}$	0.91	1.43	1.20	1.34	1.37	H_0=0.898 [b,d], 1.02(25) [c,d]
$q_2^e\times10^4$ (cm^{-1})	5.8014	6.6615	5.7567	5.9263	6.0954	6.154(2) [e], 6.156(2) [e]
$q_2^J\times10^{10}$	−6.470	−15.307	−6.306	−6.317	−6.935	−7.0(4) [e], −8.9(8) [e]
$q_2^K\times10^{10}$	5.373	14.091	5.340	5.258	5.816	–

[a] Ref. [58]. [b] Ref. [56]. [c] Ref. [60].

[d] D_0 and H_0 are the quartic and sextic centrifugal distortion constants, D_J and H_J, respectively, in the ground vibrational state.

[e] Ref. [60]. The different values were obtained from different model assumptions (see the original publication). The q_2^K term was not included in the experimental fit. The constants refer to the fundamental 010.

Table 13
Theoretical (SCF) and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies for CO_2 [a]

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment [b]
ω_1 (cm^{-1})	1400.2	1381.2	1513.4	1514.7	1507.2	1353.8
ω_2	716.6	608.0	766.0	776.5	768.3	672.9
ω_3	2384.5	2301.7	2590.3	2570.7	2550.7	2396.5
χ_{11} (cm^{-1})	−3.05	−2.81	−2.74	−2.74	−2.75	−2.993
χ_{12}	−5.19	−7.31	−5.42	−4.83	−5.35	−5.276
χ_{13}	−25.17	−23.37	−21.34	−21.23	−21.23	−19.140
χ_{22}	1.55	8.17	1.73	1.43	2.52	1.580
χ_{23}	−14.12	−8.52	−12.76	−12.71	−12.27	−12.542
χ_{33}	−15.86	−13.81	−13.17	−12.83	−12.61	−12.503
$\chi_{l_2l_2}$	−0.98	−3.83	−1.12	−0.98	−1.41	−1.014
ν_1 (cm^{-1})	1376.3	1356.6	1491.9	1493.8	1485.8	1332.9
ν_2	710.7	620.8	761.0	771.0	756.6	667.7
ν_3	2326.1	2253.9	2540.5	2521.7	2502.6	2349.1
Δ_1 (cm^{-1})	−23.9	−24.6	−21.6	−20.9	−21.5	−20.9
Δ_2	−6.0	12.8	−5.0	−5.5	−2.7	−5.2
Δ_3	−58.4	−47.8	−49.8	−49.0	−48.1	−47.4

[a] The experimental results given in the table correspond to deperturbed (100)–(020) energy levels. Thus, to correspond to the experimental analysis, the $2\omega_2$–ω_1 interaction has been excluded in second order at all levels of theory shown in the table. [b] Ref. [56].

Table 14
Theoretical (CISD) and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies for CO_2 [a]

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment [b]
ω_1 (cm^{-1})	1289.2	1280.9	1423.5	1428.2	1426.4	1353.8
ω_2	639.0	532.2	705.4	711.6	705.9	672.9
ω_3	2254.0	2188.9	2502.3	2479.1	2468.7	2396.5
χ_{11} (cm^{-1})	−2.76	−2.56	−2.65	−2.65	−2.69	−2.993
χ_{12}	−5.00	−7.67	−5.33	−4.93	−5.32	−5.276
χ_{13}	−20.64	−19.26	−19.16	−19.06	−19.57	−19.140
χ_{22}	1.67	9.22	1.61	1.80	2.89	1.580
χ_{23}	−13.35	−7.97	−12.58	−11.72	−11.81	−12.542
χ_{33}	−13.95	−12.32	−12.65	−11.89	−12.29	−12.503
$\chi_{l_2l_2}$	−1.03	−4.28	−1.07	−1.12	−1.55	−1.014
ν_1 (cm^{-1})	1268.3	1258.5	1403.3	1408.4	1405.9	1332.9
ν_2	633.8	547.8	700.2	707.5	704.4	667.7
ν_3	2202.4	2146.6	2454.8	2434.1	2422.5	2349.1
Δ_1 (cm^{-1})	−20.8	−22.4	−20.2	−19.8	−20.5	−20.9
Δ_2	−5.2	15.6	−5.2	−4.0	−1.4	−5.2
Δ_3	−51.6	−42.2	−47.5	−45.0	−46.2	−47.4

[a] The experimental results given in the table correspond to deperturbed (100)–(020) energy levels. Thus, to correspond to the experimental analysis, the $2\omega_2$–ω_1 interaction has been excluded in second order at all levels of theory. [b] Ref. [56].

Table 15
Complete quartic force fields for CO_2 a)

In internal coordinates				In normal coordinates			
constant	theory		expt. b)	constant	theory		expt.
	SCF	CISD			SCF	CISD	
f_{rr}	19.067	17.421	16.022	ω_1	1507.2	1426.4	1354.3 b), 1353.7 c)
$f_{rr'}$	2.342	1.754	1.2613	ω_2	768.3	705.9	672.9 b), 672.7 c)
$f_{\alpha\alpha}$	0.977	0.847	0.785	ω_3	2550.7	2468.7	2396.3 b), 2396.4 c)
f_{rrr}	−138.6	−124.7	−113.9	ϕ_{111}	−274.3	−267.6	−274.7 b), −273.0 c)
$f_{rrr'}$	−2.917	−2.564	−3.909	ϕ_{122}	165.5	164.3	149.4 b), 150.5 c)
$f_{\alpha\alpha r}$	−1.232	−1.149	−1.218	ϕ_{133}	−547.1	−522.9	−498.3 b), −506.1 c)
f_{rrrr}	750.1	695.3	630.0	ϕ_{1111}	39.2	40.7	46.1 b), 43.1 c)
$f_{rrrr'}$	4.125	6.831	22.06	ϕ_{1122}	−47.0	−47.4	−44.6 b), −48.0 c)
$f_{rrr'r'}$	10.086	6.098	12.090	ϕ_{1133}	78.9	80.2	78.1 b), 82.6 c)
$f_{\alpha\alpha rr}$	0.066	0.692	2.015	ϕ_{2222}	81.2	88.9	58.8 b), 65.4 c)
$f_{\alpha\alpha rr'}$	3.047	2.558	3.740	ϕ_{2233}	−115.1	−113.5	−110.2 b), −112.4 c)
$f_{\alpha\alpha\alpha\alpha}$	2.422	2.594	1.106	ϕ_{3333}	176.5	169.2	151.2 b), 160.4 c)

a) See footnote to table 10. The normal coordinate force constants refer to the $^{12}C^{16}O_2$ isotope. b) Ref. [58].

c) From the 35-parameter potential function of ref. [61]. These results are presently the best available using the direct numerical diagonalization technique.

tained by Lacy [57]. In an interesting electron diffraction study, Gershikov and Spiridonov [59] arrived directly at $r_e = 1.1602(8)$ Å, but upon correction for curvilinearity and centrifugal stretching distortion, they obtained 1.1620 Å, a value too long to be the true r_e(CO) value.

The variations in the quartic centrifugal distortion constant, D_J, are small, as expected, and the CISD results are somewhat better than the SCF values. The peculiar dependence of D_J on basis set can be easily explained as follows. For linear triatomic molecules there is an alternative formula for D_J, which is a simplification of eq. (17):

$$D_J = (4B_e^3/\omega_3^2)[1-(\zeta_{32}^x)^2(\omega_1^2-\omega_3^2)/\omega_1^2] , \tag{43}$$

where ω_1 and ω_3 are the harmonic stretching frequencies, and ζ_{32}^x is the Coriolis coupling constant connecting ω_3 and the linear bending mode. For a symmetric triatomic molecule like CO_2 with a symmetric stretching frequency ω_1, $\zeta_{32}^x = 1$, and eq. (43) reduces to $D_J = 4B_e^3/\omega_1^2$, which is equivalent to the general upper limit formula [24], $D_J^{\max} = 4B_e^3/\omega_{\min}^2$, mentioned in section 2.3. In the present calculations for CO_2, B_e steadily increases with enlargement of the basis set, while ω_1 increases sharply in going from DZ to DZP and remains amazingly constant at the higher levels. Consequently, the DZP SCF and CISD values for D_J are the smallest ones in their respective series. The simple formula mentioned above can also be used to calculate the equilibrium value of D_J using the experimental values of B_e and ω_1. The result is 1.3110×10^{-7} cm^{-1}; thus, the vibrational effect on D_J is rather small, about 2.2×10^{-9} cm^{-1}. The TZ2P SCF and CISD D_J equilibrium constants lie 8.0 and 5.3%, respectively, below this calculated experimental equilibrium value.

Values calculated for the sextic centrifugal distortion constant, H_J, are extremely small, about two orders of magnitude smaller than for HCN. Consequently, the contribution of the term involving H_J to a rotational–vibrational line is of the order of 10^{-5} cm^{-1} (for J values lower than about 30), i.e. of the order of the usual experimental precision. Therefore it is not surprising that somewhat different experimental values have been determined for H_J, the range of the effective H_0 constants being from 0.898×10^{-14} [56] to $1.02(25)\times10^{-14}$ cm^{-1} [60]. Although one should keep in mind that the measured values are effective constants while theory predicts equilibrium constants, the relatively large deviation between the best theoretical prediction (1.37×10^{-14}

cm^{-1}, TZ2P CISD) and experiment suggests that the H_0 might actually be closer to the upper limit of the value reported by Bailly et al. [60].

The theoretical vibration–rotation interaction constants for CO_2 exhibit little sensitivity to level of theory (except in the case of the TZ predictions for α_2), and the general agreement with experiment is quite remarkable. The errors in the α_1, α_2, and α_3 predictions are only 11.1%, 1.0%, and 3.3%, respectively, at the TZ2P SCF level and only 8.6%, 6.5%, and 3.0% at the TZ2P CISD level.

For XY_2 molecules the *l*-type doubling constant q_2^e takes an especially simple form (cf. eq. (20)):

$$q_2^e = (2B_e^2/\omega_2)[(\omega_3^2+3\omega_2^2)/(\omega_3^2-\omega_2^2)] . \tag{44}$$

Because ω_2 (the linear bending frequency) and ω_3 (the antisymmetric stretching frequency) do not vary much in all the polarized basis set calculations (at the respective SCF or CISD levels), the increase of B_e in going from DZP to TZ2P is responsible for the corresponding increase of q_2^e. Eq. (44) can be used to determine the equilibrium value of q_2^e from the experimental B_e, ω_2 and ω_3 values. The result is 6.12×10^{-4} cm^{-1}, just slightly smaller than the measured value. This shows that the vibrational effects are small for this constant as well. Note also that the TZ2P SCF and CISD values deviate from the thus determined value of q_2^e by only 0.4%!

As shown by Watson (eq. (28) of ref. [27]), the general formula for q_2^J also simplifies considerably for symmetric XY_2 molecules. In this case the dependence of q_2^J on the anharmonic force field arises only from two terms which contain α_2 and α_3 as multiplicative factors. Except in the TZ case, the α_i constants in tables 11 and 12 show little variation, and consequently neither does q_2^J (or even q_2^K). The TZ2P CISD result of -6.93×10^{-10} cm^{-1} for q_2^J agrees excellently with the experimental value extrapolated to $v_3=-1/2$, which is -7.0×10^{-10} cm^{-1} [27,60].

Most of the anharmonic vibrational constants, χ_{rs}, are in excellent agreement with the experimental values. Especially gratifying is the agreement at the TZ2P CISD level. Note that the measured χ_{rs} constants correspond to deperturbed energy levels, i.e. the effects of the ω_1–$2\omega_2$ anharmonic resonance have been removed. Thus, in the theoretical calculation of these constants it was necessary to invoke the replacement equations of section 2.6. This affects three constants: χ_{12}, χ_{22} and $\chi_{l_2l_2}$. To demonstrate the dramatic effect of the resonance term on the anharmonic vibrational constants, the theoretical values calculated at the TZ2P CISD level excluding (including) the ω_1–$2\omega_2$ interaction as compared to the experimental values [56] are as follows (all data in cm^{-1}): $\chi_{12}=-5.32$ (224.7) versus -5.28, $\chi_{22}=2.89$ (-54.6) versus 1.58, and $\chi_{l_2l_2}=-1.55$ (56.0) versus -1.01.

It is clear from tables 13 and 14 that the theoretical total anharmonicities are not as substantially improved by the inclusion of electron correlation as the harmonic frequencies are. The ω_1, ω_2 and ω_3 values for CO_2 are predicted to be 11.3 (5.4)%, 14.2 (4.9)% and 6.4 (3.0)% too large, respectively, at the TZ2P SCF (CISD) levels. On the other hand, the TZ2P SCF (CISD) *differences* between the calculated and measured values for the total anharmonicities ($\Delta_1=\nu_1-\omega_1$, $\Delta_2=\nu_2-\omega_2$ and $\Delta_3=\nu_3-\omega_3$) are only -0.6 (0.4), 2.5 (3.8) and -0.7 (1.2) cm^{-1}, respectively. The excellent agreement for Δ_1 between experiment and theory is especially impressive, because this level is not measured explicitly but rather obtained from the measured values of 1286 and 1388 cm^{-1} by considering the effect of Fermi resonance on the ν_1 and $2\nu_2$ levels.

As seen from table 15, the TZ2P CISD cubic and quartic internal-coordinate force constants agree with experiment better than the SCF values in only four of the nine cases, but in those four cases the improvement is substantial. The representations of the TZ2P force fields in normal coordinates are in almost complete agreement with the best experimental results [56–58,61], which also show considerable consistency among themselves, despite the fact that they were obtained using different techniques. Specifically, the average percentage errors of the TZ2P SCF and CISD ϕ_{ijk} and ϕ_{ijkl} constants compared to the values of Wattson and Rothman [61] are only 5.8% and 3.8%, respectively (neglecting in both cases the large discrepancies for ϕ_{2222}). However, even at the highest level of theory applied in the present study (TZ2P CISD), the description of the bending motion, similarly to HCN, appears to still be deficient, ϕ_{2222} being in error by 36%. Finally, for reasons detailed in section 4.1, one finds $f_{rr'}>0$ and $f_{\alpha\alpha r}<0$ for CO_2. Unlike the case for HCN, $f_{rrr'}$ is unambiguously negative and of significant magnitude, but it is not in accord with qualitative arguments which suggest that $f_{rrr'}$ should be positive because upon fragmentation to O+CO, the quadratic force constant for CO stretching increases. The difficulty of qualitatively predicting the signs of small interaction constants is apparent once again in the case of $f_{rrrr'}$ and $f_{rrr'r'}$, which in the theoretical results have signs opposite those of their HCN counterparts.

4.3. N_2O

Nitrous oxide, N_2O, has been the subject of a number of theoretical and experimental studies [62–70], and particular attention has been paid experimentally to rotational l-type doubling and the Fermi resonance between the ν_3 and $2\nu_2$ vibrational states. Since these two states are separated by more than 100 cm^{-1}, the Fermi resonance is substantially weaker than in the analogous case of CO_2. Nevertheless, proper comparison between the theoretical and experimental results is ensured only if they refer to the same handling of data; thus this resonance has been taken into account in the theoretical calculations. Experimental force fields up to sixth order are available for N_2O. It should be realized that these force fields were obtained by three rather different approaches: (a) numerical, algebraic contact transformation [68]; (b) second-order perturbation theory [69]; and (c) direct numerical diagonalization [63,64]. To the best of our knowledge, no ab initio study of the quartic force field of N_2O exists in the literature besides the work of Steele et al. [94]; thus the present theoretical results have an additional significance. These results, together with some selected experimental values, are compiled into tables 16–19. The TZ2P quartic force fields, calculated at the SCF and CISD levels of theory, are presented in table 20.

Similarly to HCN and CO_2, the bond lengths of N_2O decrease as the basis set increases, and they do not appear to be converged even at the highest level (the difference between the NO bond lengths at the TZP and TZ2P CISD levels is still 0.01 Å). It is also noteworthy that the addition of polarization functions to the basis set causes a very large change in the bond lengths, the difference in the NO distances at the SCF/CISD DZ and

Table 16
Theoretical (SCF) and experimental geometries, dipole moments, vibration–rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational l-type doubling constants for N_2O

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
E (hartree)	−183.59541	−183.60967	−183.71576	−183.72672	−183.73825	–
r_e(NN) (Å)	1.1069	1.0963	1.0955	1.0866	1.0815	1.1273 [a]
r_e(NO) (Å)	1.2557	1.2496	1.1872	1.1796	1.1723	1.1851 [a]
μ (debye)	1.5395	1.5610	0.8244	0.7950	0.6586	0.1609 [b]
$\alpha_1 \times 10^3$ (cm^{-1})	1.78	2.03	2.55	2.65	2.68	3.444 [a]
$\alpha_2 \times 10^4$	−0.046	−4.30	−4.80	−3.02	−3.86	−5.697 [a]
$\alpha_3 \times 10^3$	6.03	5.37	2.85	2.86	2.92	1.925 [a]
$B_e \times 10^1$ (cm^{-1})	4.0234	4.0802	4.3171	4.3801	4.4286	4.2112 [a]
$B_0 \times 10^1$	3.9843	4.0474	4.2949	4.3556	4.4045	4.1901 [a]
$D_J \times 10^7$ (cm^{-1})	2.3815	2.3811	1.6098	1.6947	1.7447	$D_0=1.7610(1)$ [c]
$H_J \times 10^{14}$	−64.98	−51.98	−7.77	−8.02	−8.38	$H_0=-1.555(130)$ [c]
$q_2^e \times 10^4$ (cm^{-1})	8.9537	9.0842	7.7623	7.8300	8.0278	7.920 [d,e]
$q_2^J \times 10^{10}$	26.936	8.603	−3.617	−1.497	−1.619	−10.13(7) [d]
$q_2^K \times 10^{10}$	−39.688	−17.511	0.405	−2.245	−2.346	–

[a] Ref. [68]. [b] Ref. [65]. [c] Ref. [62]. D_0 and H_0 are the ground vibrational state D_J and H_J constants, respectively.
[d] Ref. [62]. The l-type doubling constants were obtained for the fundamental 01^10. The q_2^K term was not included in the experimental fit. [e] The experimental precision is considerably higher than indicated.

Table 17
Theoretical (CISD) and experimental geometries, dipole moments, vibration–rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational *l*-type doubling constants for N_2O

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
E (hartree)	−183.91871	−183.96041	−184.16117	−184.20324	−184.24327	–
r_e(NN) (Å)	1.1494	1.1337	1.1285	1.1162	1.1073	1.1273 [a]
r_e(NO) (Å)	1.2577	1.2492	1.1990	1.1900	1.1809	1.1851 [a]
μ (debye)	0.9643	0.9928	0.4692	0.4544	0.3428	0.1609 [b]
$\alpha_1 \times 10^3$ (cm^{-1})	2.70	2.80	2.93	3.01	3.08	3.444 [a]
$\alpha_2 \times 10^4$	−5.30	−9.18	−6.28	−4.59	−5.41	−5.697 [a]
$\alpha_3 \times 10^3$	2.73	2.63	1.93	2.00	2.11	1.925 [a]
$B_e \times 10^1$ (cm^{-1})	3.8813	3.9592	4.1556	4.2320	4.2988	4.2112 [a]
$B_0 \times 10^1$	3.8594	3.9413	4.1376	4.2116	4.2782	4.1901 [a]
$D_J \times 10^7$ (cm^{-1})	1.7424	1.8471	1.5055	1.6010	1.6743	$D_0 = 1.7610(1)$ [c]
$H_J \times 10^{14}$	−9.61	−8.49	−2.07	−2.28	−2.78	$H_0 = -1.555(130)$ [c]
$q_2^e \times 10^4$ (cm^{-1})	7.8729	8.5487	7.4968	7.5507	7.8160	7.920 [d,e]
$q_2^J \times 10^{10}$	−7.920	−17.434	−8.875	−6.898	−7.218	−10.13(7) [d]
$q_2^K \times 10^{10}$	4.474	14.223	6.769	4.496	4.551	–

[a] Ref. [68]. [b] Ref. [65]. [c] Ref. [62]. D_0 and H_0 are the ground vibrational state D_J and H_J constants, respectively.
[d] Ref. [62]. The *l*-type doubling constants were obtained for the fundamental 01^10. The q_2^K term was not included in the experimental fit. [e] The experimental precision is considerably higher than indicated.

Table 18
Theoretical (SCF) and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies for N_2O

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
ω_1 (cm^{-1})	2430.9	2404.1	2589.0	2595.8	2588.7	2281.7 [a], 2282.1 [b]
ω_2	554.9	519.1	668.4	707.0	706.9	596.5 [a], 596.3 [b]
ω_3	964.0	991.1	1358.0	1354.2	1355.6	1298.5 [a], 1298.3 [b]
χ_{11} (cm^{-1})	−15.46	−13.67	−14.07	−14.15	−14.26	−15.138 [b]
χ_{12}	−7.92	−7.40	−11.64	−12.73	−11.80	−14.328 [b]
χ_{13}	27.01	23.09	−73.68	−79.72	−74.77	−27.207 [b]
χ_{22}	0.20	5.30	0.52	−1.01	−0.011	1.112 [b]
χ_{23}	−17.20	−13.80	−8.79	−8.87	−8.74	−5.374 [b]
χ_{33}	−39.40	−34.55	−0.12	1.93	0.57	−4.319 [b]
χ_{ll}	0.30	−1.46	−0.12	0.48	0.12	−0.575 [b]
ν_1 (cm^{-1})	2405.6	2380.9	2512.4	2514.9	2511.0	2223.8 [c,d]
ν_2	543.2	523.0	659.6	693.6	696.7	588.8 [c,d]
ν_3	881.5	919.7	1312.1	1309.3	1310.6	1271.4 [b]
Δ_1 (cm^{-1})	−25.3	−23.2	−76.6	−80.9	−77.7	−58.3 [b]
Δ_2	−11.7	3.8	−8.8	−13.3	−10.2	−7.6 [b]
Δ_3	−82.5	−71.4	−45.9	−44.9	−45.0	−26.9 [b]

[a] Ref. [64]. [b] Ref. [68]. [c] Refs. [62,67]. [d] The experimental precision is considerably higher than indicated here.

Table 19
Theoretical (CISD) and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies for N_2O

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
ω_1 (cm^{-1})	2164.1	2160.0	2402.4	2418.8	2419.5	2281.7 [a], 2282.1 [b]
ω_2	507.2	461.8	606.4	644.5	645.5	596.5 [a], 596.3 [b]
ω_3	1109.4	1113.4	1352.3	1347.3	1345.9	1298.5 [a], 1298.3 [b]
χ_{11} (cm^{-1})	−14.37	−13.08	−13.67	−13.77	−14.14	−15.138 [b]
χ_{12}	−11.39	−9.96	−12.78	−13.88	−12.88	−14.328 [b]
χ_{13}	−4.08 [e]	−6.43 [e]	−30.16	−31.17	−32.57	−27.207 [b]
χ_{22}	2.79	9.51	1.64	0.10	1.30	1.112 [b]
χ_{23}	−7.32	−7.18	−6.15	−6.00	−6.10	−5.374 [b]
χ_{33}	−12.61 [e]	−11.57 [e]	−4.31	−3.93	−4.05	−4.319 [b]
$\chi_{l_2l_2}$	−0.91	−3.35	−0.78	−0.11	−0.54	−0.575 [b]
ν_1 (cm^{-1})	2121.9 [e]	2120.7 [e]	2347.2	2361.8	2362.1	2223.8 [c,d]
ν_2	505.3	478.4	601.1	634.7	639.4	588.8 [c,d]
ν_3	1074.8	1079.9	1322.4	1317.9	1315.4	1271.4 [b]
Δ_1 (cm^{-1})	−42.2 [e]	−39.3 [e]	−55.2	−57.0	−57.4	−58.3 [b]
Δ_2	−1.9	16.6	−5.3	−9.8	−6.1	−7.6 [b]
Δ_3	−34.6	−33.5	−29.8	−29.4	−30.5	−26.9 [b]

[a] Ref. [64]. [b] Ref. [68]. [c] Refs. [62,67]. [d] The experimental precision is considerably larger than indicated here.

[e] Due to the accidental $2\omega_3$–ω_1 near-degeneracy at this level of theory, these constants were obtained by excluding both the $2\omega_2$–ω_3 and the $2\omega_3$–ω_1 resonances in second order. Therefore these constants cannot be properly compared with the other respective theoretical and experimental values.

Table 20
Complete quartic force fields for N_2O [a]

In internal coordinates				In normal coordinates			
constant	theory		expt. [b]	constant	theory		expt. [b]
	SCF	CISD			SCF	CISD	
f_{rr}(NN)	26.533	21.914	18.251	ω_1	2588.7	2419.5	2282.1
f_{rR}	2.257	1.635	1.028	ω_2	706.9	645.5	596.3
f_{RR}(NO)	11.678	12.096	11.960	ω_3	1355.6	1345.9	1298.3
$f_{\alpha\alpha}$	0.886	0.763	0.666	ϕ_{111}	−660.4	−519.8	−308.8
f_{rrr}	−191.2	−161.1	−133.6	ϕ_{113}	−316.4	−401.6	−463.7
f_{Rrr}	0.660	−1.069	−6.872	ϕ_{122}	189.6	142.4	106.4
f_{RRr}	−3.976	−0.928	1.498	ϕ_{133}	257.4	204.7	142.4
f_{RRR}	−113.9	−104.3	−98.83	ϕ_{223}	75.0	103.7	111.1
$f_{\alpha\alpha r}$	−1.837	−1.722	−1.580	ϕ_{333}	−519.1	−402.0	−346.8
$f_{\alpha\alpha R}$	−2.051	−1.655	−1.537	ϕ_{1111}	194.8	189.5	142.0
f_{rrrr}	1074.1	931.3	691.4	ϕ_{1113}	9.1	18.6	5.7
f_{Rrrr}	8.754	5.699	46.45	ϕ_{1122}	−130.1	−125.8	−122.9
f_{RRrr}	10.653	5.077	−3.485	ϕ_{1133}	53.7	62.9	81.4
f_{RRRr}	5.356	12.17	−7.691	ϕ_{1223}	14.1	6.1	2.5
f_{RRRR}	642.6	614.0	634.9	ϕ_{1333}	−72.1	−60.4	−52.1
$f_{\alpha\alpha rr}$	−1.157	0.237	1.808	ϕ_{2222}	56.7	67.3	56.4
$f_{\alpha\alpha Rr}$	4.881	4.117	5.105	ϕ_{2233}	−44.3	−41.6	−42.4
$f_{\alpha\alpha RR}$	2.098	2.491	1.491	ϕ_{3333}	127.5	97.0	79.4
$f_{\alpha\alpha\alpha\alpha}$	1.797	2.414	1.897				

[a] See footnote to table 10. The normal coordinate force constants refer to $^{14}N_2{}^{16}O$. [b] Ref. [68].

DZP levels being 0.07/0.06 Å. Consequently, the calculations with unpolarized basis sets result in very poor predictions for the bond lengths of N_2O. Note that the experimental NN bond length lies between the DZP and TZP CISD values. The errors in the TZ2P CISD predictions for r_e(NN) and r_e(NO) are 0.020 and 0.004 Å, respectively.

The sign of the electric dipole moment of N_2O has been the subject of some controversy [66]. Jalink et al. [66] finally gave experimental verification that the sign of the dipole is $^+$NNO$^-$. This is in accord with the present (and previous [70]) theoretical results. The magnitude of the dipole moment obtained from Stark measurements is $|\mu_{el}| = 0.16$ D [65]. Although the calculated dipole moments decrease with increasing level of theory, at the highest level (TZ2P CISD) the dipole moment is still about twice the measured value, yet in an absolute sense the error is small, only 0.18 D. Note, however, that the basis sets employed are much too small to expect the calculated dipole moment to be fully converged.

It is clear in tables 16–19 that the theoretical description of N_2O provided by unpolarized basis sets (DZ and TZ) is poor in general. This is true not only for the geometry and the dipole moment but also for the harmonic vibrational frequencies and the anharmonic potential. For example, at both the SCF and CISD levels, ω_2 and ω_3 are significantly *below* experiment, and the predictions for α_2, H_J, χ_{13} and χ_{33} show blatant errors. Therefore, in the following discussion results obtained with the DZ or TZ basis sets are not mentioned further.

The predictive power of the SCF and CISD methods for the vibration–rotation interaction constants, α_i, of N_2O is not as impressive as was observed for HCN or CO_2. To wit, the TZ2P SCF errors for α_1, α_2, and α_3 are 22.2%, 32.2%, and 51.7%, respectively. However, the respective TZ2P CISD errors are reduced to 10.6%, 5.0%, and 9.6%, which are quite respectable. As usual, the α_2 constant is the least stable against variation in the basis set.

The predictions for the $B_0 - B_e$ difference are surprisingly accurate once again. The TZ2P CISD prediction is in almost perfect agreement with the measured value of 0.0021 cm^{-1}, and even the TZ2P SCF result of 0.0024 cm^{-1} is quite reasonable. This fact, observed repeatedly in this study, suggests that the $B_0 - B_e$ difference is not particularly sensitive to the force field and that the errors in the theoretical vibration–rotation interaction constants (α_i) more or less cancel one another.

The theoretical values for the quartic centrifugal distortion constant, D_J, approach the measured value with the extension of the basis. The TZ2P SCF result, which is in error by only 1%, is actually more accurate than the TZ2P CISD value. This is a consequence of fortuitous cancellation of errors arising when the overestimation of ω_3, which is nearly the same at the SCF and CISD levels, is balanced by an overestimation of B_e, which is 3% larger at the SCF level. Prediction of the small sextic centrifugal distortion constant, H_J, is quite poor at most theoretical levels. Both extension of the basis set and inclusion of electron correlation are necessary to obtain reasonable agreement with the measured value, but even at the TZ2P CISD level the predicted value is 78% too large in magnitude.

The theoretical predictions of the *l*-type doubling constant q_2^e are quite successful, and the calculated results show little variation with the extension of the one-particle basis. The predicted values of q_2^J deviate substantially (about 30% even at the CISD level) from the measured value, the best result being obtained at the DZP CISD level.

Although the vibrational anharmonic constants χ_{rs} are somewhat inaccurate at the SCF level (note χ_{13} in particular), the TZ2P CISD results agree very nicely with the experimental values [68]. This excellent agreement can be obtained only if the replacement equations of section 2.6 are used in the evaluation of these constants, i.e. terms corresponding to the ω_3–$2\omega_2$ interaction are removed even though the separation between these zeroth-order levels is over 100 cm^{-1}. In particular, the TZ2P CISD values excluding (including) this interaction as compared to the experimental values [68] are as follows (all data in cm^{-1}): $\chi_{22} = 1.30$ (-4.83) versus 1.11, $\chi_{23} = -6.10$ (18.41) versus -5.37, and $\chi_{l_2 l_2} = -0.54$ (5.59) versus -0.58.

The overall agreement between the theoretical and experimental harmonic vibrational frequencies of N_2O must be considered good. The ω_1, ω_2 and ω_3 values are predicted to be 13.4 (6.0)%, 18.5 (8.2)% and 4.4 (3.6)% too large, respectively, at the TZ2P SCF (CISD) levels. This type of agreement is typical for such levels of theory.

The vibrational fundamentals of N_2O were measured with exceptionally high precision by Maki and co-workers [62]: 10^00–$00^00 = 2223.8$ cm^{-1}, 01^10–$00^00 = 588.8$ cm^{-1}, and 00^01–$00^00 = 1284.9$ cm^{-1}. The existence of a first-order anharmonic interaction (Fermi resonance) between the levels $2\nu_2$ and ν_3 of $^{14}N_2{}^{16}O$ was already noted by Herzberg [16] and was investigated in detail by Plíva [67]. This interaction causes the unperturbed value of ν_3 (which should be compared with our calculated values) to be different from the measured one. Plíva's [67] analysis placed the unperturbed ν_3 at 1276.9 cm^{-1}, but his χ_{22} and χ_{23} constants are substantially different from the more recent ones obtained by Teffo and Chédin [68], these new values being supported by our theoretical data (see tables 18 and 19). Consequently, Teffo and Chédin arrive at a somewhat different value for ν_3, namely, 1271.4 cm^{-1}, which is accepted here as giving the experimental anharmonicity of this mode.

The agreement between the TZ2P SCF results and the measured values for the total anharmonicities is quite poor for Δ_1 and Δ_3 but respectable for Δ_2. In contrast, the TZ2P CISD values are excellent for all three constants, Δ_1, Δ_2, and Δ_3 exhibiting errors of only 0.9, 1.5 and 3.6 cm^{-1}, respectively. Note that the anharmonicity of the bending fundamental is quite small. Although this fact is reproduced at all levels of theory, quantitatively correct results are obtained only with the polarized basis sets. Since the Fermi resonance in the case of N_2O is rather weak, it is of interest to see whether, by retaining the resonance term, second-order perturbation theory can be used to correctly predict the difference ($d_3 = -13.4$ cm^{-1}) between the measured (perturbed) frequency 00^01–00^00 (1284.9 cm^{-1}) and the harmonic frequency ω_3 (1298.3 cm^{-1}). The TZ2P CISD anharmonic constants obtained in this manner (and listed above) yield $d_3 = -6.0$ cm^{-1}, whose accuracy is quite reasonable. Nevertheless, the corresponding Δ_3 value in table 19 displays more impressive agreement with experiment (when compared to the deperturbed value of ν_3) than that observed for d_3.

A critical evaluation of the theoretical force constants obtained in this study for N_2O (see table 20) is complicated by the fact that the experimental quartic force field of N_2O is considerably less accurately determined than those of HCN and CO_2. Deviations of 5–10% are typical among the normal coordinate force constants obtained by Lacy and Whiffen [63], Kobayashi and Suzuki [64], and Teffo and Chédin [68], who, as mentioned above, used different techniques to derive their potentials. Possibly as a consequence of this, some of the force constants are substantially different in these studies: the range for ϕ_{111} is from -271.8 [64] to -477.7 cm^{-1} [63]; for ϕ_{122} it is from 38.7 [63] to 106.4 cm^{-1} [68]; for ϕ_{1113} from -82.6 [63] to 5.7 cm^{-1} [68], for ϕ_{1223} from -4.1 [63] to 21.7 cm^{-1} [64], and for ϕ_{3333} from 73.7 [64] to 103.9 cm^{-1} [63]. If the experimentally uncertain force constants (ϕ_{111}, ϕ_{122}, ϕ_{1113}, ϕ_{1223}, and ϕ_{3333}) are left out of the comparison, the average percentage errors of the TZ2P SCF and CISD ϕ_{ijk} and ϕ_{ijkl} force constants compared to the values of Teffo and Chédin [68] are 32% and 18%, respectively. Therefore, by any account it is clear that the agreement between theory and experiment is worse for N_2O than for HCN and CO_2.

One of the problems appears to be in the prediction of the diagonal cubic NN stretching constant ϕ_{111} as well as the other constants involving NN stretching. The value of ϕ_{111} is -660.4 cm^{-1} at the TZ2P SCF level and -519.8 cm^{-1} in the TZ2P CISD case, while the experimental value is probably around -300 cm^{-1}. The ϕ_{113} value at the TZ2P SCF level is -316.4 cm^{-1}, which improves to -401.6 cm^{-1} in the TZ2P CISD case, but the best result is still considerably smaller in magnitude than the well established experimental value of -463.7 cm^{-1} [68]. Similar problems are seen for ϕ_{133}, for which the TZ2P CISD prediction is 44% in error. Finally, the TZ2P CISD value for ϕ_{2222}, the diagonal quartic constant for linear bending, is 19% too large and thus of about the same accuracy as the analogous value for HCN. In summary, for N_2O there are problems not only with the theoretical description of the bending vibration (as for HCN and CO_2) but also with the stretching vibrations, especially with the NN stretch. The current results should encourage further theoretical studies on this molecule and on other similarly multiply-bonded species, using larger basis sets (including f and even g functions) and methods which include a larger portion of the correlation energy (for example, MR CI, CCSD(T) or MR (A)CPF methods).

4.4. OCS

Although the vibration–rotation spectrum of carbonyl sulfide, OCS, is about as thoroughly studied [71–78] as those of the other triatomics considered in this investigation, only its quartic force field has been determined experimentally [73,74]. The only theoretical investigation known to us to obtain even a partial ab initio quartic force field for OCS is that of Steele et al. [94], who studied the system at the SCF level using the 4-31G basis set. Thus, for OCS (as well as for CO_2 and N_2O) the present study is the first theoretical work in which the complete quartic force field is obtained. Because calculating the complete quartic force field of OCS at the TZ2P CISD level proved not to be cost effective, no TZ2P basis calculations were performed for this molecule. The various theoretical vibration–rotation constants of OCS, along with some recent experimental data (mostly the equilibrium molecular parameters determined by Lahaye et al. [78]), are presented in tables 21–24. The TZP quartic force fields of OCS, obtained at the SCF and CISD levels, are compiled into table 25.

The trends in the SCF and CISD predictions for the geometrical parameters of OCS are that the length of the CO bond decreases continually with basis set enlargement while the length of the CS bond goes through a maximum at the TZ level. The unpolarized basis sets, as expected, are clearly unsatisfactory for predicting the length of the CS bond. The errors in the TZP SCF (CISD) results for $r_e(\mathrm{CO})$ and $r_e(\mathrm{CS})$ are −0.029 (−0.006) and 0.012 (0.009) Å, respectively. The fact that the CS bond lengths are overestimated in these cases clearly indicates that the TZP basis is farther from saturation for sulfur than for the H, C, N, and O atoms. Accordingly, the agreement of the TZP CISD dipole moment with experiment (0.16 D error) must be considered good.

The theoretical results for the vibration–rotation interaction constants display an agreement with experiment which is worse than for HCN and CO_2 but better than for N_2O. In particular, the errors in the TZP SCF (CISD) α_1, α_2, and α_3 values are 20.1% (1.1%), 19.2% (11.3%), and 19.7% (9.0%), respectively. Even though the individual vibration–rotation interaction constants have noticeable errors, the small correction term (half the

Table 21
Theoretical (SCF) and experimental geometries, dipole moments, vibration–rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational *l*-type doubling constants for OCS

Basis set	DZ	TZ	DZP	TZP	Experiment
E (hartree)	−510.17603	−510.18752	−510.27995	−510.28684	–
$r_e(\mathrm{CO})$ (Å)	1.1511	1.1411	1.1352	1.1273	1.15617(14) [a]
$r_e(\mathrm{CS})$ (Å)	1.6085	1.6151	1.5736	1.5739	1.56140(14) [a]
μ (debye)	0.1610	0.0569	0.3376	0.3247	0.7150(15) [a]
$\alpha_1 \times 10^4$ (cm^{-1})	9.70	9.10	7.86	8.04	6.6950(5) [a]
$\alpha_2 \times 10^4$	−2.61	−3.15	−3.07	−2.90	−3.5870(3) [a]
$\alpha_3 \times 10^4$	10.83	10.32	10.11	10.03	12.496(1) [a]
$B_e \times 10^1$ (cm^{-1})	1.9663	1.9684	2.0423	2.0522	2.0346 [a]
$B_0 \times 10^1$	1.9587	1.9618	2.0364	2.0461	2.0286 [a,c]
$D_J \times 10^8$ (cm^{-1})	4.5429	4.5035	4.0917	4.1884	$D_0=4.3405(3)$ [b,c], $D_e=4.272$ [a,b]
$H_J \times 10^{14}$	−1.48	−1.25	−0.69	−0.74	$H_0=-0.344(35)$ [c,d]
$q_2^e \times 10^4$ (cm^{-1})	2.0769	2.0733	2.0448	2.0646	2.122 [c,e]
$q_2^J \times 10^{11}$	0.854	−1.341	−5.179	−3.732	−14.33(9) [c,e]
$q_2^K \times 10^{11}$	−9.878	−7.227	−0.763	−3.033	–

[a] Ref. [78]. [b] D_0 is the quartic centrifugal distortion constant, D_J, in the ground vibrational state. D_e is the equilibrium value of D_J.
[c] Ref. [71]. [d] H_0 is the sextic centrifugal distortion constant, H_J, in the ground vibrational state. H_e is the equilibrium value of H_J.
[e] The *l*-type doubling constants were obtained for the fundamental 01^10. The q_2^K term was not included in the experimental fit.

Table 22

Theoretical (CISD) and experimental geometries, dipole moments, vibration–rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational *l*-type doubling constants for OCS

Basis set	DZ	TZ	DZP	TZP	Experiment
E (hartree)	−510.43023	−510.45810	−510.66945	−510.69510	–
r_e(CO) (Å)	1.1845	1.1710	1.1595	1.1501	1.15617(14) [a]
r_e(CS) (Å)	1.6164	1.6198	1.5732	1.5707	1.56140(14) [a]
μ (debye)	0.4420	0.3697	0.5243	0.5510	0.7150(15) [a]
$\alpha_1 \times 10^4$ (cm^{-1})	7.54	7.21	6.62	6.77	6.6950(5) [a]
$\alpha_2 \times 10^4$	−3.12	−3.85	−3.41	−3.18	−3.5870(3) [a]
$\alpha_3 \times 10^4$	12.01	11.52	11.32	11.37	12.496(1) [a]
$B_e \times 10^1$ (cm^{-1})	1.9132	1.9245	2.0112	2.0275	2.0346 [a]
$B_0 \times 10^1$	1.9066	1.9190	2.0057	2.0216	2.0286 [a,c]
$D_J \times 10^8$ (cm^{-1})	4.2563	4.2651	3.9511	4.0422	$D_0=4.3405(3)$ [b,c], $D_e=4.272$ [a,b]
$H_J \times 10^{14}$	−0.70	−0.58	−0.34	−0.37	$H_0=-0.344(35)$ [c,d]
$q_2^e \times 10^4$ (cm^{-1})	2.0195	2.0444	2.0182	2.0297	2.122 [c,e]
$q_2^J \times 10^{11}$	−10.67	−13.16	−11.63	−10.14	−14.33(9) [c,e]
$q_2^K \times 10^{11}$	6.279	8.937	8.104	6.173	–

[a] Ref. [78]. [b] D_0 is the quartic centrifugal distortion constant, D_J, in the ground vibrational state. D_e is the equilibrium value of D_J.
[c] Ref. [71]. [d] H_0 is the sextic centrifugal distortion constant, H_J, in the ground vibrational state. H_e is the equilibrium value of H_J.
[e] The *l*-type doubling constants were obtained for the fundamental 01^10. The q_2^K term was not included in the experimental fit.

Table 23

Theoretical (SCF) and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies for OCS

Basis set	DZ	TZ	DZP	TZP	Experiment [a]
ω_1 (cm^{-1})	797.0	802.3	891.0	886.8	875.291(8)
ω_2	534.9	536.4	574.8	583.1	524.3587(7)
ω_3	2170.1	2155.9	2298.5	2297.3	2093.723(6)
χ_{11} (cm^{-1})	−5.86	−5.36	−4.63	−4.65	−2.736(32)
χ_{12}	−4.00	−4.26	−3.61	−3.60	−3.214(2)
χ_{13}	−1.43	−1.25	−1.44	−1.19	−6.458(127)
χ_{22}	0.41	0.63	0.48	0.27	0.6084
χ_{23}	−6.36	−5.69	−5.88	−5.85	−7.547(1)
χ_{33}	−13.61	−12.56	−12.57	−12.42	−11.457(2)
χ_{hh}	0.16	0.039	0.072	0.17	−0.1714(4)
ν_1 (cm^{-1})	780.6	786.7	877.4	873.3	863.3
ν_2	531.1	533.3	571.5	579.4	520.6
ν_3	2135.8	2124.5	2266.7	2266.1	2060.0
Δ_1 (cm^{-1})	−16.4	−15.6	−13.6	−13.5	−12.0
Δ_2	−3.8	−3.1	−3.2	−3.8	−3.8
Δ_3	−34.3	−31.4	−31.7	−31.3	−33.7

[a] Ref. [78].

Table 24
Theoretical (CISD) and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies for OCS

Basis set	DZ	TZ	DZP	TZP	Experiment [a]
ω_1 (cm^{-1})	796.1	802.5	891.7	892.2	875.291(8)
ω_2	487.3	485.0	536.3	550.7	524.3587(7)
ω_3	2008.2	2002.6	2192.7	2195.6	2093.723(6)
χ_{11} (cm^{-1})	−3.81	−3.59	−3.40	−3.42	−2.736(32)
χ_{12}	−3.15	−3.59	−3.25	−3.17	−3.214(2)
χ_{13}	−4.17	−3.78	−4.06	−3.97	−6.458(127)
χ_{22}	0.97	1.46	0.84	0.47	0.6084(4)
χ_{23}	−7.36	−6.53	−6.84	−7.05	−7.547(1)
χ_{33}	−12.13	−11.23	−11.60	−11.55	−11.457(2)
$\chi_{l_2 l_2}$	−0.20	−0.44	−0.19	−0.039	−0.1714(4)
ν_1 (cm^{-1})	783.3	789.9	879.6	880.2	863.3
ν_2	484.8	483.9	533.6	547.0	520.6
ν_3	1974.5	1971.8	2160.7	2163.5	2060.0
Δ_1 (cm^{-1})	−12.9	−12.7	−12.1	−12.0	−12.0
Δ_2	−2.5	−1.1	−2.7	−3.7	−3.8
Δ_3	−33.7	−30.9	−32.1	−32.1	−33.7

[a] Ref. [78].

Table 25
Complete quartic force fields for OCS [a]

In internal coordinates				In normal coordinates			
constant	theory		expt. [b]	constant	theory		expt. [b]
	SCF	CISD			SCF	CISD	
f_{rr}(CS)	7.26	7.61	7.51	ω_1	886.8	892.2	875.7
f_{rR}	1.65	1.23	0.99	ω_2	583.1	550.7	523.6
f_{RR}(CO)	20.68	18.12	16.01	ω_3	2297.3	2195.6	2092.5
$f_{\alpha\alpha}$	0.79	0.72	0.65	ϕ_{111}	−235.1	−208.7	−201.5
f_{rrr}	−45.7	−45.3	−46.5	ϕ_{113}	117.8	103.7	107.0
f_{Rrr}	−1.95	−0.98	0.64	ϕ_{122}	66.1	76.3	85.9
f_{RRr}	−1.41	−2.02	−3.47	ϕ_{133}	−193.8	−234.4	−250.5
f_{RRR}	−145.7	−126.4	−95.2	ϕ_{223}	258.8	226.5	102.6
$f_{\alpha\alpha r}$	−1.20	−1.12	−0.31	ϕ_{333}	−657.5	−574.9	−402.1
$f_{\alpha\alpha R}$	−0.82	−0.92	−3.09	ϕ_{1111}	43.3	37.8	37.2
f_{rrrr}	187.9	190.9	205.2	ϕ_{1113}	−26.5	−23.8	−26.4
f_{Rrrr}	−2.44	0.38	0.0*	ϕ_{1122}	−17.7	−18.4	−19.8
f_{RRrr}	7.58	4.38	0.0*	ϕ_{1133}	23.1	26.2	25.6
f_{RRRr}	−3.01	2.03	0.0*	ϕ_{1223}	−6.12	−10.8	−4.8
f_{RRRR}	814.6	722.7	317.1	ϕ_{1333}	12.9	22.5	5.0
$f_{\alpha\alpha rr}$	0.84	1.00	0.89	ϕ_{2222}	112.7	99.9	42.5
$f_{\alpha\alpha Rr}$	1.97	1.89	0.0*	ϕ_{2233}	−135.1	−126.5	−77.1
$f_{\alpha\alpha RR}$	−0.16	0.25	11.1	ϕ_{3333}	198.0	186.6	95.5
$f_{\alpha\alpha\alpha\alpha}$	1.28	1.22	2.16				

[a] TZP results. The normal coordinate force constants refer to $^{16}O^{12}C^{32}S$. See footnote to table 10.

[b] Ref. [74]. The numbers indicated with an asterisk were constrained to zero.

sum of the α_i constants) leading from B_e to B_0 is calculated with high accuracy. Note that the best theoretical result of 0.00059 cm^{-1}, obtained at the TZP CISD level, is in excellent agreement with the measured value of 0.0006 cm^{-1} [78]. This remarkable fact has been observed repeatedly in this study and perhaps warrants further investigation.

The theoretical D_J values for OCS exhibit the type of consistency and accuracy which was found for the other molecules in this study. For example, the TZP SCF and CISD equilibrium values deviate from experiment by only 2% and 5%, respectively. In contrast, the calculated values for H_J are more sensitive to the underlying (cubic) force fields and show considerable variation with the level of theory. Nevertheless, it is gratifying that the higher levels of theory are in the best agreement with experiment, and the TZP CISD prediction of -0.37×10^{-14} cm^{-1} is in accord with the experimental result, $H_0=-0.344(35)\times10^{-14}$ cm^{-1} [71].

The theoretical values of the l-type doubling constant q_2^e, as we repeatedly observe, are quite accurate at all levels of theory. This constant depends on the calculated values of the harmonic vibrational fundamentals (ω_i, $i=1, 3$), the equilibrium rotational constant (B_e) and on ζ_{23}^x, a Coriolis interaction constant (only one of the two Coriolis constants for linear triatomics is independent). If the fundamental vibrational frequencies of $O^{12}CS$ and $O^{13}CS$ are used to obtain this constant, its value is $\zeta^2=0.0421$ [75]. If it is calculated from the measurements of the rotational l-type doubling constant q_2^e, one arrives at the value of $\zeta^2=0.0266$ [76]. Our calculated value at the TZP CISD level is $\zeta^2=0.0416$, in almost perfect agreement with the former value. The q_2^J constants in table 21 show extreme sensitivity to the quality of the basis set at the SCF level, and concomitantly the agreement with experiment is poor. The sensitivity to basis set is reduced with the CISD method, and, in fact, the TZP CISD prediction of -10.14×10^{-11} cm^{-1} is in reasonable agreement with the $q_2^J=-14.33(9)$ $\times10^{-11}$ cm^{-1} experimental result [71].

Two anharmonic (resonance) interactions have been included in first order (rather than second order) in the experimental analysis used to obtain the vibrational anharmonic constants for OCS: $\nu_1-2\nu_2$ and $2\nu_1-\nu_3$ [78]. Although the theoretical predictions for the differences between these levels are several hundred cm^{-1} in some cases, the exclusion of their interactions in second order is necessary to obtain data directly comparable to the experimental results. As seen in tables 23 and 24, the agreement between the theoretical χ_{rs} constants calculated in this manner and the experimental values is remarkable, especially at the TZP CISD level. Exclusion of the two anharmonic resonance interactions affects all but two constants. The theoretical values obtained at the TZP CISD level excluding (including) the two interactions as compared to the experimental values [78] are as follows (all data in cm^{-1}): $\chi_{11}=-3.42$ (-4.24) versus -2.74, $\chi_{12}=-3.17$ (-6.65) versus -3.21, $\chi_{13}=-3.97$ (-0.69) versus -6.46, $\chi_{22}=0.47$ (1.34) versus 0.61, and $\chi_{l_2l_2}=-0.04$ (-0.91) versus -0.17.

At the TZP SCF (CISD) level, the harmonic vibrational frequencies ω_1, ω_2 and ω_3 are in error by 1.3% (1.9%), 11.2% (5.0%), and 9.7% (4.9%), respectively. The errors for ω_1, the CS stretch, are unusually and fortuitously small due to basis set deficiencies, but the deviations for ω_2 and ω_3 are of the expected size. The anharmonic corrections to the harmonic frequencies are predicted with great accuracy at all levels of theory. For example, the TZP CISD errors are only 0.0, 0.1, and 1.6 cm^{-1}, respectively, for Δ_1, Δ_2, and Δ_3. Finally, the experimental differences (d_1 and d_3) between the deperturbed fundamentals, $\nu_1=863.3$ cm^{-1} and $\nu_3=2060.0$ cm^{-1} [78], and the perturbed, measurable frequencies, $\nu_1=859.0$ cm^{-1} and $\nu_3=2062.2$ cm^{-1} [78], are of interest. By including the ν_1-$2\nu_2$ and $2\nu_1$-ν_3 interactions in determining the TZP CISD χ_{rs} constants (listed above), one arrives at theoretical predictions of $d_1=3.5$ cm^{-1} and $d_3=-1.6$ cm^{-1}, which are in accord with the experimental values $d_1=4.4$ cm^{-1} and $d_3=-2.2$ cm^{-1}.

The agreement between the TZP force constants calculated in internal coordinates (see table 25) and those of Foord, Smith and Whiffen [74] (hereafter FSW) is generally good, especially considering the decision of FSW to constrain f_{Rrrr}, f_{RRrr}, f_{RRRr}, and $f_{\alpha\alpha Rr}$ to zero in their refinement. However, there is a substantial disparity between the TZP CISD prediction for f_{RRRR}, 723 aJ Å^{-4}, and the somewhat uncertain value of FSW, 317(76) aJ Å^{-4}. The qualitative principles pertaining to the signs and magnitudes of the internal coordinate force constants of OCS are the same as those discussed in detail for HCN and the other compounds studied here.

The overall agreement between the calculated ϕ_{ijk} and ϕ_{ijkl} force constants with those of FSW is good. The noteworthy deviations concern the cubic constant ϕ_{223} and the quartic constants ϕ_{1223}, ϕ_{1333}, ϕ_{2222}, ϕ_{2233}, and ϕ_{3333}. For ϕ_{223}, FSW obtained 102.6 cm^{-1}, while Morino and Nakagawa [73] (hereafter MN) obtained 240.8 cm^{-1}, the latter value being in nice agreement with our theoretical values. Note also that for ϕ_{333}, MN obtained $-961.2(246)$ cm^{-1}, while FSW ascertained -402.1 cm^{-1}. Our theoretical values lie in between the two results, the TZP CISD value being -575 cm^{-1}. Among the quartic constants, FSW and MN agree only in the constants ϕ_{1111}, ϕ_{1113}, ϕ_{1122} and ϕ_{1133}. For these constants the average deviation between the TZP CISD and FSW values is only 5.2%. For the other quartic constants, for which the two experimental studies disagree substantially, the present values generally lie in between the two sets of experimental results. Leaving out six constants (ϕ_{223}, ϕ_{1223}, ϕ_{1333}, ϕ_{2222}, ϕ_{2233} and ϕ_{3333}) from the comparison, the average deviations between the experimental force constants of FSW [74] and the TZP SCF and CISD results are 16.3% and 8.3%, respectively. Finally, note that ϕ_{2222}, the diagonal quartic constant for linear bending, is rather poorly predicted even at the highest level of theory, as is the case for all the other molecules studied here.

4.5. C_2H_2 and C_2D_2

Acetylene, C_2H_2 [79–91], is one of those few molecules having more than three atoms whose quartic force field has been determined experimentally [80,81] with some degree of completeness. Results of the present study for C_2H_2 and C_2D_2 are collected into tables 26–29 and tables 30–33, respectively. Only the harmonic force fields have been determined for acetylene at the CISD level, and thus none of the molecular constants depending on the cubic or quartic force fields have been calculated. The TZ2P SCF harmonic and anharmonic force con-

Table 26
Theoretical (SCF) and experimental geometries, vibration–rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational *l*-type doubling constants for C_2H_2

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
E (hartree)	−76.79923	−76.81113	−76.83190	−76.84305	−76.84505	–
r_e(CC) (Å)	1.2010	1.1875	1.1912	1.1811	1.1793	1.2033 [a]
r_e(CH) (Å)	1.0538	1.0536	1.0616	1.0554	1.0539	1.0605 [a]
$\alpha_1 \times 10^3$ (cm^{-1})	6.38	6.25	6.25	6.40	6.55	6.86 [a], 6.89 [b]
$\alpha_2 \times 10^3$	4.73	5.02	4.74	4.93	5.01	6.21 [a], 6.22 [b]
$\alpha_3 \times 10^3$	5.52	5.25	5.36	5.42	5.57	5.60 [a], 6.00 [b]
$\alpha_4 \times 10^3$	−0.61	−0.68	−1.46	−1.12	−1.13	−1.29 [a], −1.30 [b]
$\alpha_5 \times 10^3$	−1.68	−1.93	−2.12	−2.02	−2.14	−2.15 [a], −2.11 [b]
B_e (cm^{-1})	1.1897	1.2101	1.1999	1.2189	1.2225	1.1824 [c]
B_0	1.1836	1.2045	1.1953	1.2137	1.2172	1.1766 [a]
$D_J \times 10^6$ (cm^{-1})	1.3931	1.4508	1.3839	1.4322	1.4542	$D_0 = 1.627(6)$ [b,d]
$H_J \times 10^{12}$	1.29	1.31	1.27	1.30	1.33	–
$q_4^e \times 10^3$ (cm^{-1})	4.1517	4.1400	4.4991	4.4477	4.6305	5.232(1) [e]
$q_4^J \times 10^8$	−2.029	−1.983	−2.618	−2.394	−2.609	−4.1(1) [e]
$q_4^K \times 10^8$	1.722	1.632	2.300	2.055	2.266	–
$q_5^e \times 10^3$ (cm^{-1})	4.0053	4.1418	4.1779	4.2637	4.3402	4.6996(5) [e]
$q_5^J \times 10^8$	−2.275	−2.432	−2.524	−2.538	−2.680	−3.94(4) [e]
$q_5^K \times 10^8$	2.007	2.127	2.235	2.226	2.364	–

[a] Ref. [81]. [b] Ref. [89]. [c] Ref. [85].

[d] D_0 is the quartic centrifugal distortion constant, D_J, in the ground vibrational state. [e] Refs. [84,87].

Table 27

Theoretical (CISD) and experimental geometries, rotational constants, centrifugal distortion constants, and rotational *l*-type doubling constants for C_2H_2

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
E (hartree)	−76.97729	−77.00072	−77.08231	−77.10696	−77.12005	−
r_e(CC) (Å)	1.2299	1.2101	1.2131	1.1979	1.1950	1.2033 [a]
r_e(CH) (Å)	1.0707	1.0686	1.0691	1.0601	1.0578	1.0605 [a]
B_e (cm^{-1})	1.1388	1.1680	1.1635	1.1907	1.1963	1.1824 [b]
$D_J \times 10^6$ (cm^{-1})	1.4207	1.5053	1.4180	1.4808	1.5157	D_0=1.627(6) [c,d]
$q_4^e \times 10^3$ (cm^{-1})	4.4749	4.7380	5.0250	4.9350	5.3497	5.232(1) [e]
$q_5^e \times 10^3$ (cm^{-1})	4.1532	4.4285	4.2749	4.3613	4.4875	4.6996(5) [e]

[a] Ref. [81]. [b] Ref. [85]. [c] Ref. [89].

[d] D_0 is the quartic centrifugal distortion constant, D_J, in the ground vibrational state. [e] Refs. [84,87].

Table 28

Theoretical (SCF) and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies for C_2H_2

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
ω_1 (cm^{-1})	3732.3	3681.6	3676.7	3673.4	3665.8	3495.1 [a]
ω_2	2167.6	2179.0	2203.4	2219.2	2211.3	2007.6 [a]
ω_3	3622.2	3557.4	3571.3	3558.6	3554.7	3415.2 [a]
ω_4	842.7	909.2	766.7	820.0	777.3	624.0 [a]
ω_5	887.1	901.1	858.2	877.4	859.9	746.7 [a]
χ_{11} (cm^{-1})	−25.51	−22.95	−23.40	−23.09	−24.02	−18.57 [a], −26.20 [b]
χ_{12}	−9.87	−9.60	−9.38	−9.33	−9.74	−13.09 [a], −12.61 [b]
χ_{13}	−104.76	−93.11	−96.91	−94.30	−99.11	−102.39 [a], −104.8 [b]
χ_{14}	−13.02	−13.36	−10.25	−10.79	−11.40	−16.54 [a], −15.67 [b]
χ_{15}	−9.46	−10.90	−8.22	−10.04	−10.03	−10.85 [a], −10.85 [b]
χ_{22}	−5.25	−5.56	−5.43	−5.67	−5.67	−5.77 [a], −7.87 [b]
χ_{23}	−4.97	−5.07	−4.62	−5.20	−5.55	−2.82 [a], −6.11 [b]
χ_{24}	−9.35	−8.77	−10.30	−9.67	−9.66	−12.70 [a], −12.48 [b]
χ_{25}	1.73	2.26	1.96	1.71	1.91	−1.38 [a], −1.574 [b]
χ_{33}	−27.06	−23.17	−25.13	−24.26	−25.31	−30.95 [a], −26.20 [b]
χ_{34}	−8.12	−7.67	−5.00	−5.96	−5.10	−8.22 [a], −11.00 [b]
χ_{35}	−9.69	−8.46	−8.02	−8.31	−8.72	−8.68 [a], −10.88 [b]
χ_{44}	0.47	−8.07	2.48	1.50	15.60	3.072 [a], 3.082(15) [c]
χ_{45}	−4.22	−10.44	−6.11	−7.48	−3.04	−2.406 [a], −2.406(14) [c]
χ_{55}	−1.29	−3.44	−2.15	−2.50	−1.79	−2.334 [a], −2.335(6) [c]
$\chi_{l_4l_4}$	1.65	4.69	1.16	1.41	−3.36	0.756 [a], 0.759(21) [c]
$\chi_{l_4l_5}$	6.57	6.91	6.77	6.55	6.66	6.539 [a], 6.541(14) [c]
$\chi_{l_5l_5}$	3.34	4.29	3.71	3.81	3.57	3.492 [a], 3.490(8) [c]
r_{45}	−6.02	−13.12	−7.31	−9.96	−3.63	−6.239 [a], −6.238(5) [c]
ν_1 (cm^{-1})	3601.5	3560.1	3558.3	3554.6	3541.9	3372.9 [b]
ν_2	2142.1	2154.0	2177.2	2192.6	2184.6	1974.3 [b]
ν_3	3495.4	3445.8	3457.3	3446.0	3437.9	3288.4 [b]
ν_4	826.3	864.4	756.4	805.2	804.6	612.9 [b]
ν_5	873.6	876.1	842.3	857.9	846.6	730.3 [b]
Δ_1 (cm^{-1})	−130.8	−121.5	−118.4	−118.8	−123.9	−122.2 [d]
Δ_2	−25.5	−25.0	−26.2	−26.6	−26.7	−33.3 [d]
Δ_3	−126.8	−111.5	−114.0	−112.5	−116.8	−126.8 [d]
Δ_4	−16.4	−44.8	−10.3	−14.8	27.3	−11.1 [d]
Δ_5	−13.5	−25.0	−16.0	−19.5	−13.3	−16.4 [d]

[a] Ref. [81]. [b] Ref. [89]. [c] Ref. [83].

[d] Calculated using the harmonic frequencies of ref. [81] and the fundamental frequencies of ref. [89].

Table 29
Theoretical (CISD) and experimental harmonic vibrational frequencies for C_2H_2

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment [a]
ω_1 (cm^{-1})	3531.3	3485.3	3572.9	3588.8	3566.6	3495.1
ω_2	2005.9	2023.8	2072.1	2101.5	2091.4	2007.6
ω_3	3431.7	3373.2	3478.1	3477.5	3466.7	3415.2
ω_4	678.6	675.6	610.7	664.5	604.8	624.0
ω_5	749.7	741.1	760.5	792.7	770.3	746.7

[a] Ref. [81].

Table 30
Theoretical (SCF) and experimental vibration–rotation interaction constants, rotational constants, centrifugal distortion constants, and rotational l-type doubling constants for C_2D_2

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
$\alpha_1 \times 10^3$ (cm^{-1})	5.53	5.47	5.45	5.52	5.63	5.53 [a]
$\alpha_2 \times 10^3$	2.43	2.55	2.39	2.53	2.58	3.03 [a]
$\alpha_3 \times 10^3$	4.29	4.11	4.20	4.24	4.35	4.51 [a]
$\alpha_4 \times 10^3$	−1.25	−1.24	−1.90	−1.61	−1.69	−2.01 [a]
$\alpha_5 \times 10^3$	−1.66	−1.77	−1.93	−1.85	−1.95	−2.05 [a]
B_e (cm^{-1})	0.8567	0.8693	0.8612	0.8743	0.8768	0.8507 [b]
B_0	0.8535	0.8663	0.8590	0.8716	0.8742	0.8479 [c]
$D_J \times 10^7$ (cm^{-1})	6.8612	7.1293	6.8048	7.0597	7.1593	D_0=8.0(7) [c,d]
$H_J \times 10^{13}$	5.20	5.39	5.14	5.26	5.34	–
$q_4^e \times 10^3$ (cm^{-1})	2.5782	2.5539	2.7722	2.7360	2.8489	3.2 [c]
$q_4^J \times 10^8$	−1.028	−0.949	−1.379	−1.214	−1.364	–
$q_4^K \times 10^8$	0.900	0.807	1.245	1.072	1.220	–
$q_5^e \times 10^3$ (cm^{-1})	2.8288	2.9110	2.9307	2.9874	3.0409	5.0 [c], 3.17 [e]
$q_5^J \times 10^8$	−1.275	−1.333	−1.425	−1.414	−1.506	–
$q_5^K \times 10^8$	1.093	1.128	1.232	1.205	1.295	–

[a] Ref. [81]. [b] Ref. [85]. [c] Ref. [90]. [d] D_0 is the ground vibrational state quartic centrifugal distortion constant, D_J.
[e] Calculated from an experimental force field in ref. [81].

Table 31
Theoretical (CISD) and experimental rotational constants, centrifugal distortion constants, and rotational l-type doubling constants for C_2D_2

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
B_e (cm^{-1})	0.8215	0.8399	0.8370	0.8558	0.8598	0.8507 [a]
$D_J \times 10^7$ (cm^{-1})	6.9512	7.3406	6.9107	7.2365	7.4028	D_0=8.0(7) [b,c]
$q_4^e \times 10^3$ (cm^{-1})	2.9433	3.1190	3.1166	3.0534	3.3101	3.2 [b]
$q_5^e \times 10^3$ (cm^{-1})	2.7926	2.9341	3.0134	3.0688	3.1572	5.0 [b], 3.17 [d]

[a] Ref. [85]. [b] Ref. [90]. [c] D_0 is the ground vibrational state quartic centrifugal distortion constant, D_J.
[d] Calculated from an experimental force field in ref. [81].

Table 32
Theoretical (SCF) and experimental harmonic vibrational frequencies, vibrational anharmonic constants, and fundamental vibrational frequencies for C_2D_2

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment
ω_1 (cm^{-1})	2989.2	2955.7	2957.8	2963.9	2954.9	2781.6 a)
ω_2	1914.5	1919.9	1937.4	1945.6	1940.5	1793.1 a)
ω_3	2659.5	2611.9	2622.2	2612.8	2609.9	2507.9 a)
ω_4	702.5	758.9	640.2	684.9	649.3	528.5 a)
ω_5	651.3	661.6	630.1	644.2	631.3	558.0 a)
χ_{11} (cm^{-1})	−11.87	−10.67	−10.65	−10.43	−10.77	−10.87 a)
χ_{12}	−15.09	−15.04	−15.18	−15.64	−16.10	−20.20 a)
χ_{13}	−45.63	−41.52	−42.65	−41.09	−43.04	−47.26 a)
χ_{14}	−13.36	−13.17	−12.48	−12.67	−13.29	−15.92 a)
χ_{15}	−7.42	−7.64	−6.69	−7.28	−7.15	−8.22 a)
χ_{22}	−3.34	−3.38	−3.33	−3.38	−3.43	−4.61 a)
χ_{23}	−12.59	−12.35	−12.93	−13.45	−14.23	−13.60 a)
χ_{24}	−1.34	0.06	−1.05	−0.64	−0.93	−3.89 a)
χ_{25}	3.65	3.48	3.93	3.38	3.47	1.64 a)
χ_{33}	−14.30	−12.22	−13.28	−12.81	−13.37	−14.51 a)
χ_{34}	−4.39	−4.06	−2.53	−3.09	−2.59	−4.93 a)
χ_{35}	−5.25	−4.48	−4.28	−4.50	−4.71	−5.25 a)
χ_{44}	−0.28	−6.50	1.10	0.40	10.33	1.48 a)
χ_{45}	−2.89	−6.68	−4.04	−4.88	−2.17	−8.55 a)
χ_{55}	−0.92	−2.07	−1.39	−1.58	−1.20	−1.70 a)
$\chi_{l_4l_4}$	1.36	3.76	1.03	1.25	−2.18	0.76 a)
$\chi_{l_4l_5}$	3.36	3.58	3.48	3.35	3.41	3.32 a,b)
$\chi_{l_5l_5}$	2.03	2.52	2.24	2.29	2.16	−0.10 a)
r_{45}	−3.39	−7.76	−4.23	−5.81	−1.95	−3.03 a,b)
ν_1 (cm^{-1})	2913.3	2885.3	2888.4	2894.7	2883.4	2703.6 c)
ν_2	1896.3	1903.0	1919.6	1927.1	1921.0	1764.7 c)
ν_3	2591.1	2552.0	2561.0	2552.3	2547.3	2439.1 c)
ν_4	690.6	727.9	632.5	674.2	667.5	511.4 c)
ν_5	643.2	646.9	620.6	632.7	623.5	538.7 c)
Δ_1 (cm^{-1})	−75.9	−70.4	−69.4	−69.2	−71.5	−78.0 d)
Δ_2	−18.2	−16.9	−17.8	−18.6	−19.5	−28.4 d)
Δ_3	−68.3	−59.9	−61.2	−60.5	−62.7	−68.8 d)
Δ_4	−11.9	−31.0	−7.7	−10.6	18.2	−17.1 d)
Δ_5	−8.1	−14.7	−9.5	−11.5	−7.8	−19.3 d)

a) Ref. [81]. b) Calculated from the experimental force field in ref. [81]. c) Ref. [86].
d) Calculated using the harmonic frequencies of ref. [81] and the fundamental frequencies of ref. [86].

Table 33
Theoretical (CISD) and experimental harmonic vibrational frequencies for C_2D_2

Basis set	DZ	TZ	DZP	TZP	TZ2P	Experiment a)
ω_1 (cm^{-1})	2806.5	2777.4	2843.4	2866.2	2847.5	2781.6
ω_2	1785.3	1796.5	1841.8	1861.3	1853.0	1793.1
ω_3	2519.7	2476.7	2553.7	2553.3	2545.3	2507.9
ω_4	550.5	544.1	509.3	554.4	504.6	528.5
ω_5	565.2	563.5	558.4	582.0	565.6	558.0

a) Ref. [81].

Table 34
Complete quartic force fields for C_2H_2 [a]

In internal coordinates						In normal coordinates			
constant	theory	expt. [b]	constant	theory	expt. [b]	constant	theory	constant	theory
f_{rr}(CH)	6.926	6.370(10)	f_{rrrr}	196.0	161.5(352)	ω_1	3665.8	ϕ_{1111}	456.8
$f_{rr'}$	0.004	−0.019(5)	$f_{rrrr'}$	−0.191	[0]	ω_2	2211.3	ϕ_{1112}	102.8
f_{rR}	−0.082	−0.095(10)	$f_{rrr'r'}$	0.242	[0]	ω_3	3554.7	ϕ_{1122}	42.5
f_{RR}(CC)	19.907	16.341(50)	f_{rrrR}	−2.663	[0]	ω_4	777.3	ϕ_{1133}	482.8
$f_{\alpha\alpha}$	0.345	0.2510(5)	$f_{rrr'R}$	0.004	[0]	ω_5	859.9	ϕ_{1144}	−454.3
$f_{\alpha\alpha'}$	0.104	0.0925(5)	f_{rrRR}	−1.287	3.4(71)	ϕ_{111}	−1253.0	ϕ_{1155}	−470.2
f_{rrr}	−38.35	−34.82(190)	$f_{rr'RR}$	−0.079	[0]	ϕ_{112}	−384.8	ϕ_{1222}	−38.6
$f_{rrr'}$	−0.011	0.60(21)	f_{rRRR}	−0.675	[0]	ϕ_{122}	121.0	ϕ_{1233}	115.4
f_{rrR}	0.397	−0.36(47)	f_{RRRR}	536.2	436(136)	ϕ_{133}	−1363.4	ϕ_{1244}	−77.7
$f_{rr'R}$	−0.012	−0.60(84)	$f_{rr\alpha\alpha}$	0.242	5.19(66)	ϕ_{144}	804.2	ϕ_{1255}	−108.7
f_{rRR}	−0.193	0.71(129)	$f_{rr\alpha\alpha'}$	−0.159	[0]	ϕ_{155}	839.8	ϕ_{1345}	473.6
f_{RRR}	−109.23	−97.77(643)	$f_{rr\alpha'\alpha'}$	0.095	[0]	ϕ_{222}	−517.4	ϕ_{2222}	110.2
$f_{r\alpha\alpha}$	−0.202	−0.67(4)	$f_{rr'\alpha\alpha}$	−0.042	[0]	ϕ_{233}	−327.3	ϕ_{2233}	26.1
$f_{r\alpha\alpha'}$	0.007	−0.02(1)	$f_{rr'\alpha\alpha'}$	0.072	[0]	ϕ_{244}	112.3	ϕ_{2244}	−46.9
$f_{r\alpha'\alpha'}$	−0.038	−0.52(4)	$f_{rR\alpha\alpha}$	−0.025	1.07(49)	ϕ_{255}	156.9	ϕ_{2255}	−23.3
$f_{R\alpha\alpha}$	−0.802	−0.34(3)	$f_{rR\alpha'\alpha'}$	−0.054	[0]	ϕ_{345}	−839.6	ϕ_{2345}	100.6
$f_{R\alpha\alpha'}$	0.346	0.27(1)	$f_{rR\alpha\alpha'}$	0.009	[0]			ϕ_{3333}	517.4
			$f_{RR\alpha\alpha}$	0.137	−3.36(81)			ϕ_{3344}	−456.7
			$f_{RR\alpha\alpha'}$	0.436	[0]			ϕ_{3355}	−503.2
			$f_{\alpha\alpha\alpha\alpha}$	1.752	1.418(43)			ϕ_{4444}	840.2
			$f_{\alpha\alpha\alpha\alpha'}$	−0.389	[0]			$\phi_{4455}^{(+)}$	217.8
			$f_{\alpha\alpha\alpha'\alpha'}^{(+)}$	0.227	0.160(17)			$\phi_{4455}^{(-)}$	216.3
			$f_{\alpha\alpha\alpha'\alpha'}^{(-)}$	0.13	[0]			ϕ_{5555}	653.3

[a] The theoretical constants were obtained at the SCF level using the TZ2P basis set. The normal coordinate force constants refer to $^{12}C_2H_2$. For units see footnote to table 10. The internal coordinates were chosen to be exactly the same as those in ref. [81], i.e. the magnitude of the bending coordinate is defined as $\alpha = \sin(\delta\Theta)$, where $\delta\Theta$ is the true C–C–H linear bending angle. Note that this choice differs from the $\alpha = \delta\Theta$ relation used for the other molecules in this study. Only two constants in this table are affected by this change of definition: $f_{\alpha\alpha\alpha\alpha} = f_{\Theta\Theta\Theta\Theta} + 4f_{\Theta\Theta}$ and $f_{\alpha\alpha\alpha\alpha'} = f_{\Theta\Theta\Theta\Theta'} + f_{\Theta\Theta'}$. Finally, cylindrical symmetry relationships for the quartic bending constants (eqs. (4c)–(4f) of ref. [81]) have been imposed to reduce the number of independent constants listed in the table.

[b] Ref. [81].

stants for C_2H_2 are listed in table 34. We are not aware of any previous theoretical determination of the complete quartic force field of acetylene, and thus the current results are of particular significance.

The theoretical bond lengths of acetylene show characteristics similar to those observed for the triatomic molecules, specifically, a general trend for bond length contraction upon basis set enlargement. This trend is most evident at the CISD level and most important for the CC bond. Fortuitously, at the SCF level the length of the CC bond is best approximated at the DZ level. At the CISD level, as repeatedly observed in this study, the DZP and TZP values bracket the experimental results. At the TZ2P CISD level, the CC and CH lengths are predicted to be only 0.008 and 0.003 Å too short, respectively.

Values obtained for D_J, the quartic centrifugal distortion constant, show a steady improvement with extension of the polarized basis sets (from DZP to TZ2P). The TZ2P SCF and CISD results for C_2H_2 (C_2D_2) deviate from the experimental D_0 value by 10.6 (10.5)% and 6.8 (7.5)%, respectively. The sextic centrifugal distortion constants, H_J, of C_2H_2 and C_2D_2 are predicted with remarkable internal consistency at the SCF level. Unfortunately, to the best of our knowledge, no experimental data are available for comparison.

Most of the theoretical vibration–rotation interaction constants (α_i, $i = 1, 5$) appear to underestimate the magnitude of the corresponding experimental values, but only by a few percent. The average errors at the TZ2P SCF level are only 7.4% and 8.2%, respectively, for C_2H_2 and C_2D_2. The least satisfactory agreement is found for.the constant involving the CC stretch, α_2, for which the TZ2P SCF results for C_2H_2 and C_2D_2 lie 19.3% and 14.9%, respectively, below experiment. As observed for all the triatomic molecules, the small correction term based on the α_i constants, $B_e - B_0$, is predicted with high accuracy; the TZ2P SCF results for C_2H_2 and C_2D_2, 0.0053 and 0.0026 cm^{-1}, respectively, compare favorably with the measured values of 0.0058 and 0.0028 cm^{-1}.

The general trend in the rotational *l*-type doubling constants of C_2H_2 and C_2D_2 is that the theoretical constants improve with basis set enlargement. The TZ2P SCF results for q_4^e and q_5^e of C_2H_2 are 11.5% and 7.7% below experiment [84,87,90], respectively. However, the corresponding CISD values are considerably closer to the experimental results. At the TZ2P CISD level the average deviation for q_4^e and q_5^e is only 3.4% for C_2H_2. The analogous error for q_4^e of C_2D_2 is also 3.4%. For q_5^e of C_2D_2, there is a large deviation between the TZ2P CISD prediction and the measured [90] value (table 31), suggesting that the true equilibrium value of this constant is probably around 3.2×10^{-3} cm^{-1}, the value calculated from the experimental force field of Strey and Mills [81]. The predicted values for q_4^J and q_5^J of C_2H_2 deviate considerably from the measured values, as observed for some of the triatomic molecules, but these constants do not show large variations with level of theory.

In general, the harmonic vibrational frequencies of C_2H_2 (C_2D_2) are reproduced with the expected accuracy both by the SCF and CISD methods. Excluding ω_4, the trans bending frequency, the TZ2P SCF and CISD predictions for C_2H_2 (C_2D_2) are on average 8.6 (7.9)% and 2.7 (2.1)%, respectively, above experiment. In the DZ CISD case this average is only 0.5 (0.8)%, revealing a particularly striking cancellation of errors. On the other hand, the TZ2P SCF value for ω_4 of C_2H_2 (C_2D_2) is 24.6 (22.9)% too large while the analogous TZ2P CISD result is 3.1 (4.5)% too *small*. Thus, peculiar difficulties are encountered in the theoretical description of the trans bending frequency, a fact which has been documented previously [91]. In particular, the curvature of the potential surface along this mode is very sensitive to basis set.

The vibrational anharmonic constants for C_2H_2 and C_2D_2 obtained at the SCF level are for the most part in very good agreement with the experimentally observed values. For example, the $\chi_{l_4l_5}$ and $\chi_{l_5l_5}$ values for C_2H_2 do not change much as the basis set is varied, and the TZ2P SCF results are in almost perfect agreement with experiment. Other examples include χ_{13} for C_2H_2, and χ_{11} and χ_{23} for C_2D_2. Nevertheless, difficulties are apparent in both the C_2H_2 and C_2D_2 cases for the following constants: χ_{25}, χ_{44}, χ_{45}, and $\chi_{l_4l_4}$. Note that χ_{25} of C_2H_2 has a different sign than experiment at all levels of theory, while the disparity for C_2D_2 is not one of sign but rather magnitude. The χ_{44} constant for C_2H_2 has a value of -8.1 cm^{-1} at the TZ level but 15.6 cm^{-1} with the TZ2P basis. The strikingly inaccurate TZ2P SCF values of χ_{44} for both C_2H_2 and C_2D_2 even give rise to an erroneous predicted sign of the total vibrational anharmonicity Δ_4 at this level of theory. Thus, it appears that the peculiarities encountered previously [91] in the prediction of the harmonic frequency ω_4 also carry over to the theoretical determination of the anharmonic constants for this trans bending mode. For $\chi_{l_4l_4}$ of C_2H_2, the theoretical values range from -3.4 (TZ2P) to 4.7 cm^{-1} (TZ), and for χ_{45} the range is from -3.0 (TZ2P) to -10.4 cm^{-1} (TZ). Hence, in neither case is there satisfactory convergence with level of theory, and only in the latter case is the best theoretical prediction in accord with experiment.

By appending the TZ2P SCF total anharmonicities to the TZ2P CISD harmonic frequencies, one arrives at the following fundamental frequency predictions (in cm^{-1}) for C_2H_2 (C_2D_2): $\nu_1=3443$ (2776), $\nu_2=2065$ (1834), $\nu_3=3350$ (2483), $\nu_4=632$ (523), and $\nu_5=757$ (558). These results for C_2H_2 (C_2D_2) overestimate the experimental values for ν_1, ν_2, ν_3, ν_4, and ν_5 by 2.1 (2.7)%, 4.6 (3.9)%, 1.9 (1.8)%, 3.1 (2.2)%, and 3.7 (3.6)%, respectively. The good agreement for ν_4 is fortuitous because of the underestimation of ω_4 and the incorrect sign of Δ_4 in the theoretical results, but the excellent agreement for the other modes must be considered a success of theory in predicting fundamental frequencies ab initio.

The values obtained for the vibrational *l*-type doubling constant, r_{45}, are seen to scatter considerably for both C_2H_2 and C_2D_2, and concomitantly they exhibit only modest agreement with experiment. This behavior is similar to that observed for some of the χ_{rs} constants which involve the trans bending mode, and the reliability of analogous theoretical predictions for vibrational *l*-type doubling constants of this type is thereby vitiated.

5. Conclusions

This paper describes a continuation of research on the use of ab initio derivative methods (in particular analytic SCF third derivatives) for predicting anharmonic constants of polyatomic molecules [9]. The procedure involves the determination of the full quartic force field of the molecule using its respective equilibrium geometry as the reference, followed by an application of standard perturbation theory to obtain the various spectroscopic constants from the unadjusted force field. Many of the known vibration–rotation and anharmonic vibrational constants have been included in the present study, but some remain for possible ab initio studies in the future. Among the latter are some constants for which explicit formulas have already been derived, such as those describing the vibrational dependence of Fermi resonance (denoted as $d_{stt'}$ and $d'_{stt'}$ [92] for triatomic molecules) or the vibrational dependence of the quartic centrifugal distortion constant (denoted as β_i, $i=1, 3$ [93] for triatomic molecules). For other constants, detailed formulas are not yet available [1,23].

Although the representation of the anharmonic force fields in dimensionless normal coordinates is generally not preferred over representation in curvilinear internal coordinates (only the latter representation is isotopically invariant and allows useful physical interpretation), the present study indicates that the comparison of theoretical and experimental force fields is enhanced using normal coordinates, because both sets of force constants tend to be more uniform in this representation. The agreement between the present theoretical results and the previously determined experimental normal coordinate force fields of the molecules studied is very satisfactory, with the possible exception of N_2O. The average deviation between the theoretical and experimental constants is less than 10% at the highest level of theory (TZ2P CISD). Although the SCF errors are somewhat higher than their CISD counterparts, at the TZ2P SCF level the average deviation between theory and experiment is still only about 15%.

As shown in the respective data tables, the different vibration–rotation interaction constants (α_i) may have different signs. In all cases the constants associated with stretching motions (α_1 and α_3 for triatomic molecules, and α_1, α_2 and α_3 for C_2H_2) are positive, while the constants corresponding to the degenerate bending modes (α_2 for the triatomic molecules, and α_4 and α_5 for C_2H_2) are negative. The overall agreement of the theoretical α_i constants with the experimentally determined ones is quite satisfactory. In most cases the CISD results agree substantially better with experiment than the SCF results, as indicated by the fact that the median TZ2P SCF and CISD errors for all the molecules studied here are 10.9% and 5.0%, respectively.

One of the most successfully predicted quantities of the present study is the small correction term leading from B_e to B_0. At all levels of theory, this correction term is calculated with considerable consistency. Although the TZ2P CISD values are somewhat better than the TZ2P SCF values, the predictive power of this latter theoretical level is nonetheless very impressive (TZ2P SCF versus experimental values, all data in cm^{-1}): 0.0057 versus 0.0065 for HCN, 0.0038 versus 0.0042 for DCN, 0.0013 versus 0.0014 for CO_2, 0.0024 versus 0.0021 for N_2O, 0.0053 versus 0.0058 for C_2H_2, and 0.0026 versus 0.0028 for C_2D_2.

For the quartic centrifugal distortion constant, D_J, of a linear molecule there is a simple upper limit formula, $D_J^{\max} = 4B_e^3/\omega_{\min}^2$, where $\omega_{\min}$ is the lowest stretching frequency, and B_e is the equilibrium rotational constant. The experimental results are typically very close to this upper bound. Consequently, the theoretical D_J constants of the present study are not particularly informative about the details of the underlying quadratic force fields. Since the present ab initio calculations usually overestimate the harmonic frequencies, the predicted values of D_J are usually somewhat low, the typical error being less than 10%. Naturally, this underestimation is less pronounced at the CISD level. The sextic centrifugal distortion constants, H_J, are predicted somewhat less accurately, although it should also be noted that in some cases the experimental determinations of these extremely small constants involve substantial errors, thus hindering the comparison between the theoretical and experimental results.

The otherwise degenerate bending vibrational levels $l_t = \pm 1$ become split upon excitation, a separation of $q_t J(J+1)$ occurring in the $v_t = 1$ vibrational state. Some of the l-type doubling constants q_t (e.g., q_2^e for triatomic molecules, and q_4^e and q_5^e for C_2H_2 and C_2D_2) are of the same order of magnitude as the vibration–rotation interaction constants α_i. These q^e values, which depend only on the quadratic part of the force field, are predicted with high accuracy by the present ab initio calculations. The TZ2P CISD calculations underestimate the experimental values usually by less than 5%. Although the errors at the SCF level are somewhat larger, they are still acceptable (usually 7–8% at the TZ2P SCF level). The accuracy in predicting the higher-order q_2^J constants is substantially smaller, the errors remaining around 20% even at the highest levels of theory. Since the anharmonic force fields determined in this study are generally of high quality, this problem might not be solely a consequence of deficiencies in the theory. Differences in the experimental analysis of the *l*-type doubling interaction (e.g., neglect of the term including the q_2^K constant and inclusion of another term in the experimental fit) as compared to that used in this study might be responsible for at least part of the disparity. This question is left open for future investigations.

In most cases the vibrational anharmonic constants, χ_{rs}, are predicted with considerable accuracy (the average deviation between the TZ2P CISD and the experimental results is less than 10%). On the other hand it should be emphasized that this agreement can be obtained only if the effects of possible Fermi resonances are treated in a fashion similar to the experimental analyses used for comparison. Recognizing the high quality of the predicted vibrational anharmonic constants, it is perhaps not surprising that the differences between the harmonic and ground-state vibrational fundamentals are predicted reliably, even at the SCF level. The average error of these differences is 20% at the TZ2P SCF level, and 14% at the TZ2P CISD level. Thus the two methods have comparable accuracy. In general, the anharmonicities at both the SCF and CISD levels are determined with enough accuracy to make the errors in the theoretical fundamental frequencies ν_i arise almost solely from the deficiencies in the harmonic wavenumber predictions.

The results of the present research should further increase confidence in the quality of anharmonic force fields determined by ab initio methods, despite some cases such as N_2O which are not very amenable to facile and reliable predictions. As demonstrated repeatedly in this study, the vibration–rotation constants determined at the SCF level of theory can be of considerable quality, if large enough basis sets (including polarization functions) are used. The highest theoretical level applied in this study, TZ2P CISD, provides in most cases firm, quantitative predictions, which is very encouraging since these (and even higher level) theoretical calculations are becoming more routine. Therefore, it is hoped that the increasing availability of full ab initio quartic force fields will continue not only to allow assessment of the reliability of experimental molecular constants and to provide trustworthy predictions for unknown quantities, but also to provide motivation for further development of the theory of high-resolution molecular spectroscopy.

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