

Polyatomic, Anharmonic, Vibrational–Rotational Analysis. Application to Accurate *Ab Initio* Results for Formaldehyde*

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A computer program SURVIB is described for calculating vibrational anharmonicity constants for polyatomic molecules. The program requires as input a grid of calculated energies in the vicinity of a stationary point. This grid is fit, in a least squares sense, to a polynomial function of the internal coordinates. This analytic representation of the energy surface is employed in a normal mode analysis, and the energy is reexpanded as a polynomial function of the normal mode coordinates (expressed as vectors in the mass-weighted atomic Cartesian coordinate space). The resulting coefficients are used in a second-order perturbation theory analysis to obtain the vibrational anharmonicity constants. Also reported is an application of this program to formaldehyde employing *ab initio*, RHF, MP2, MP3, and RHF-CI calculations. The spectroscopic constants obtained for H₂CO are in good agreement with experimentally derived values recently reported by Reisner.

I. INTRODUCTION

Efficient and accurate procedures have been developed for calculating *ab initio* potential energy surfaces for molecules comprised of three to six or more atoms. These methods include Hartree–Fock theory, several forms of multi-configuration self-consistent-field (MCSCF) theory, configuration interaction (CI) theory, electron pair techniques, and perturbation theory based procedures.¹ One important use of such calculational techniques is in the prediction of spectroscopic properties of molecules at or near their equilibrium geometries. In this article we outline the implementation of a general computer program for extracting from calculated, polyatomic, potential energy surfaces spectroscopic information, including equilibrium geometries, rotational constants, harmonic frequencies, anharmonicity constants, Coriolis couplings, and vibrationally averaged properties.

The development and refinement of analytic methods for calculating first and second

derivatives of potential energy surfaces for certain restricted classes of wave functions has proven to be a major advance in electronic structure theory.² In most cases it has been shown that these techniques are far more efficient than numerical procedures for obtaining derivative information. Unfortunately, these techniques are presently quite limited both in the classes of wave functions for which they are applicable and in the order of differentiation possible. (To our knowledge the implementation of an analytic third-derivative program, for even a Hartree–Fock wave function, has not yet been reported.) Since the procedure used here requires both third and fourth derivatives of the energy we have opted to base the program on a numerical, grid fitting procedure for obtaining the derivatives.

Briefly, the program SURVIB fits a grid of calculated energies in the vicinity of a stationary point to a specified analytic form. This analytic function is then used in a normal mode analysis of the stationary point to determine both the harmonic frequencies and the normal mode eigenvectors. The potential energy is then reexpanded in a Taylor series function of the normal mode

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eigenvectors. This normal mode expansion of the potential energy is then used in a standard perturbation theory analysis of the molecular vibrational-rotational spectroscopic constants employing the formalism of Krohn, Ermler, and Kern.³ Vibrationally averaged values of any property that has been calculated as a function of the geometry can also be computed.

A more detailed discussion of the methods used is given in section II. In section III an application of these methods to a study of the vibrational anharmonicities of formaldehyde is presented using Hartree-Fock, Møller-Plesset perturbation theory, and configuration interaction potential energy surfaces. This last section includes a detailed comparison of the calculated spectroscopic properties to available experimental results.

II. DESCRIPTION OF THE COMPUTER PROGRAM SURVIB

The program SURVIB is comprised of four main parts. The first performs a least-squares fit to a grid of calculated energies. The second part uses the analytic representation of the potential surface in a normal mode analysis. Next the potential energy is reexpanded in a Taylor series polynomial of the normal mode vectors, and finally, perturbation theory is used to determine the spectroscopic constants. Each of these parts is described in some detail in this section.

Two analytic forms have been implemented to provide representations of the potential energy as a function of the internal coordinates (bond lengths, bond angles, and dihedral angles). The first is a standard Taylor series polynomial expansion of arbitrary degree. Alternatively, the Taylor series expansion can be done in terms of Simons-Parr-Finlan⁴ (SPF) coordinates. An SPF coordinate can be expressed in the following form,

$$R_{\text{SPF}} = (R - R_e)/R \quad (1)$$

where R is an internal coordinate (for example, a bond length) and R_e is the equilibrium value of this coordinate. Initially a guess for the equilibrium values of the internal coordinates is used. The expansion is then carried out and a Newton-Rapheson search of the resulting fitted potential energy surface is carried out to determine a new set of equi-

librium coordinates. The SPF expansion is then refit with the new equilibrium coordinates. It has been found that in essentially all cases one cycle through this procedure is sufficient to achieve convergence in the expansion.

It has been found by both Simons, Parr, and Finlan⁴ and Carney, Curtiss, and Langhoff⁵ that Taylor series expansions of this kind in which the bond lengths are replaced by the corresponding SPF coordinates provide superior fits especially in regions significantly removed from the equilibrium geometry. Following the analysis of van Duijneveldt van de Rijdt and van Duijneveldt,⁶ the SPF Taylor series expansion will generally lead to a superior fit if the grid displacements exceed $0.035 R_e$. Conversely, if the grid displacements are less than $0.035 R_e$, then the standard Taylor series form is probably preferable. The SPF form can be particularly useful in geometry searches where the grid fit is being used to estimate the location of a stable point outside the range of the grid.

In either form the expansion can be carried out to arbitrary degree and arbitrary terms can be specifically included or excluded from the expansion. Typically, for anharmonicity analyses, Taylor series expansions of fourth degree are necessary.

One important feature of the surface fitting procedure used in SURVIB is the automatic incorporation of certain types of symmetry into the expansion, thus reducing the number of calculated points required to obtain a given expansion. This is accomplished in a simple way without recourse to group theory. First, an arbitrary point of the same symmetry as the stationary point of interest is chosen. Next distortions from this geometry are made for each term in the polynomial expansion. For a given term in the polynomial, the corresponding distortion involves only those variables having a nonzero exponent in that term. The magnitude of the distortion in each variable is proportional to the exponent of that variable. Moments of inertia for each of the distorted geometries are then determined and compared with those of all previous distortions. Whenever two distorted geometries are found to lead to identical moments of inertia it is assumed that the terms in the polynomial corresponding to these distortions must be related by symmetry, and therefore the coefficients of these terms in the expansion

sion are required to be identical. This then reduces the number of unique constants needed to be determined in the fitting procedure.

As an example of the savings that can be obtained with this relatively simple algorithm, for the molecule formaldehyde a full fourth-degree expansion of energy (neglecting symmetry) involves 210 terms. The above analysis reduces this to only 120 unique terms. Of these 120 remaining terms it can be shown that 36 are zero when the expansion is carried out relative to a planar geometry (in this case all terms having an odd power in the out-of-plane coordinate are necessarily zero). By deleting these terms from the expansion a full fourth-degree expansion for formaldehyde can, in principle, be obtained with a grid of just 84 points. In practice it is advisable to use two or three times this many points in order to obtain an accurate statistical analysis of the reliability of the fit.

The second part of the SURVIB program carries out normal mode analyses using the procedure of Gwinn.⁷ This involves diagonalizing a matrix of second derivatives, in which the derivatives are taken with respect to mass-weighted atomic Cartesian coordinates. This second-derivative matrix is derived numerically from the previously obtained polynomial expansion of the energy. This portion of the program was based in part on an earlier program by Schatz.⁸

The third part of SURVIB refits the potential energy (and property surfaces if desired) in a Taylor series, the coordinates of which are the bound normal mode eigenvectors. This is done by making small displacements along the normal mode coordinates and then evaluating the energy using the original internal coordinate expansion. The resulting grid of energies over normal mode coordinates is then fit to a Taylor series polynomial. Since small displacements (0.0002 a.u.) are used, this procedure is equivalent to a numerical differentiation of the internal coordinate force field with respect to the normal coordinates. The accuracy of the results were checked against a quadruple precision calculation employing much smaller displacements.

For the purposes of evaluating vibrational anharmonicities with second-order perturbation theory only a subset of the full fourth-degree expansion is required. In the case of formaldehyde, as noted above, the full fourth-

degree expansion involves 210 terms, while only 84 of these terms actually contribute to the perturbation theory expression. In this case, the above procedure is used to evaluate the energy at approximately 450 points to insure that all important regions of the surface are sampled in the fitting procedure. It should be stressed that the grid of energies used in this fitting are calculated from the internal coordinate polynomial. No additional *ab initio* calculations are required.

The final part of SURVIB computes the anharmonic vibrational energy levels, carries out the Coriolis coupling analysis, evaluates the vibrational expectation values of both properties and internal coordinates. This part of the program employs second-order perturbation theory⁹ using the formalism of Krohn, Ermler, and Kern³ with a generalization of the Coriolis coupling. The results are expressed as coefficients in an expansion of the spectroscopic constants in terms of the vibrational quantum numbers, as follows:

$$G(v_1, v_2, \dots, v_{3N-6}) \quad (2)$$

$$= G_0 + \sum_i \omega_i(v_i + \tfrac{1}{2}) + \sum_{i \leq j} X_{ij}(v_i + \tfrac{1}{2})(v_j + \tfrac{1}{2})$$

The coefficients of eq. (2) are also broken down into contributions arising from third-degree force constants, fourth-degree force constants, and Coriolis coupling effects. The expectation values of properties are expressed in a similar vibrational quantum number expansion of the form

$$P(v_1, v_2, \dots, v_{3N-6}) \quad (3)$$

$$= P_0 + \sum_i A_i(v_i + \tfrac{1}{2}) + \sum_{i \leq j} B_{ij}(v_i + \tfrac{1}{2})(v_j + \tfrac{1}{2})$$

It is important to note that while the formulas of ref. 3 are used for the spectroscopic constants and property expectation values, a proper, nonlinear transformation from internal coordinates to normal coordinates is implicit due to our use of the linear transformation relating mass-weighted cartesian displacement coordinates and normal coordinates. The problems associated with assuming a linear transformation from internal to normal coordinates have been discussed in applications to the water molecule.^{10,11}

At this juncture it is appropriate to provide some justification for the use of the perturbation theory formalism as opposed to the

more accurate variational^{12, 13} and SCF-CI^{12, 14} methods for obtaining the vibrational-rotational energy levels. We chose the perturbation theory approach for three main reasons. First, the methods most often used by experimentalists are based on a parallel formalism in which observed lines are fit to a spectroscopic constant expansion in the vibrational and rotational quantum numbers similar to eq. (2). These spectroscopic constants are then analyzed using a perturbation theory based procedure to derive force constants relative to the normal coordinates and, ultimately, valence force fields relative to the internal coordinates. Thus the final results of an experimental analysis are, in fact, directly analogous to the initial fits obtained in our procedure. The second reason for choosing a perturbation theory approach is that it has been our experience, having examined numerous *ab initio* potential energy surfaces, that the most significant source of errors in the application of any method of vibrational-rotational analysis is the inherent inaccuracies in the analytic fits chosen to represent the *ab initio* surface. Thus, although the vibrational procedures are more accurate, in most cases the differences are not significant relative to the errors in the surfaces. The most important exception here is for high-lying vibrational states for which the variational methods are significantly more reliable due to the convergence properties of the perturbation theory. The final reason for choosing perturbation theory is that the approach, being based on the approximation that the perturbed wave function can be adequately represented by linear combinations of harmonic oscillator wave functions, leads to a relatively small number of analytic expressions for the spectroscopic constants. Thus the procedure is extremely computationally efficient even for relatively large molecules, whereas variational techniques tend to become rather costly for both large expansions and for large molecules. Schlegel, Wolfe, and Bernardi¹⁵ have employed a similar second-order perturbation scheme in analyses of anharmonic effects in Hartree-Fock potential energy surfaces for substituted methanes.

One final feature was added to the program to give an approximate physical picture of the vibrational motion of each vibrational state.

This involves calculating the expectation values of both the internal displacement coordinates and their squares for each of the vibrational states within the approximation of a linear transformation between normal coordinates and internal coordinates. The procedure is analogous to that outlined in ref. 3 and serves primarily to identify both the kind of motion and the amplitude of motion associated with each vibrational state.

A copy of the program SURVIB will be submitted to the Quantum Chemistry Program Exchange in the near future.

III. APPLICATION TO H₂CO AND SELECTED ISOTOPIC ANALOGUES

Since formaldehyde is the first nonlinear tetra-atomic molecule for which a complete set of experimental anharmonicity constants are available it was chosen as a benchmark molecule with which to gauge the accuracy of anharmonicity constants calculated according to the techniques outlined above. Two basis sets, both of polarized double-zeta quality, were used in these calculations. The first is the 4-31G** basis set of Ditchfield, Hehre, and Pople.¹⁶ With this basis set restricted Hartree-Fock (RHF), and second- and third-order Moller-Plesset perturbation theory (MP2 and MP3) calculations were carried out, for 133 geometries. These calculations were done using the GAUSSIAN-80 computer program¹⁷ on a DEC-System 10 computer. Each point required approximately 2.5 h of computer time. The second set of calculations employed the Dunning-Hay¹⁸ (3s,2p,1d/2s,1p) contraction of the Huzinaga¹⁹ (9s,5p/4s) primitive set. With this basis set RHF and RHF + 1 + 2 configuration interaction calculations were carried out, at 350 geometries. The effect of the Davidson²⁰ unlinked-cluster correction on the calculated spectroscopic constants was also examined. These calculations were carried out with the Argonne electronic structure codes,²¹ BIGGMOLI, GVB164 and UCI, on an FPS-164 attached processor. Each point in the grid required approximately 20 min of computer time.

The quartic internal coordinate force field from the DZP/SDQ-CI calculations is listed in Table I. In general there is good agreement between this *ab initio* force field and an empirical one derived by Tanaka and Machida.²²

Table I. *Ab initio* DZP/SDQ-CI quartic force field. The units are as follows: energy, hartree; distance, atomic units; angle, radians. Only the symmetry unique constants are given.

R_{CO}	Displacement Exponents					Coefficient	Standard Deviation
	R_{CH_1}	R_{CH_2}	θ_{H_1CO}	θ_{H_2CO}	$\theta_{H_1COH_2}$		
2	0	0	0	0	0	0.42720	6.0×10^{-05}
0	0	2	0	0	0	0.16720	3.9×10^{-05}
0	0	0	0	2	0	0.14930	1.5×10^{-05}
0	0	0	0	0	2	0.03093	1.9×10^{-05}
3	0	0	0	0	0	-0.50050	6.4×10^{-04}
0	0	3	0	0	0	-0.17440	3.5×10^{-04}
0	0	0	0	3	0	-0.00877	8.4×10^{-05}
4	0	0	0	0	0	0.39960	5.4×10^{-03}
0	0	4	0	0	0	0.11400	3.2×10^{-03}
0	0	0	0	4	0	0.00641	4.1×10^{-04}
0	0	0	0	0	4	0.00390	1.6×10^{-04}
1	0	1	0	0	0	0.03231	6.3×10^{-05}
1	0	0	0	1	0	0.05598	3.7×10^{-05}
0	1	1	0	0	0	0.00421	6.0×10^{-05}
0	1	0	1	0	0	-0.00691	3.3×10^{-05}
0	0	1	1	0	0	-0.01995	3.3×10^{-05}
0	0	0	1	1	0	0.10450	2.5×10^{-05}
2	0	1	0	0	0	-0.03274	7.9×10^{-04}
2	0	0	0	1	0	-0.03010	4.9×10^{-04}
1	2	0	0	0	0	0.01025	8.1×10^{-04}
0	2	1	0	0	0	0.00052	5.8×10^{-04}
0	2	0	1	0	0	-0.00236	4.1×10^{-04}
0	2	0	0	1	0	-0.00364	4.1×10^{-04}
1	0	0	2	0	0	-0.07952	2.9×10^{-04}
0	1	0	2	0	0	-0.02175	3.0×10^{-04}
0	0	1	2	0	0	-0.01837	3.0×10^{-04}
0	0	0	2	1	0	0.07098	1.6×10^{-04}
1	0	0	0	0	2	-0.00937	1.6×10^{-04}
0	0	1	0	0	2	-0.00865	1.1×10^{-04}
0	0	0	0	1	2	0.01989	6.6×10^{-05}
2	0	2	0	0	0	-0.00305	4.8×10^{-03}
2	0	0	0	2	0	0.02535	1.6×10^{-03}
2	0	0	0	0	2	-0.00595	7.9×10^{-04}
0	2	2	0	0	0	-0.00348	5.3×10^{-03}
0	2	0	2	0	0	-0.01978	1.7×10^{-03}
0	2	0	0	2	0	-0.01771	1.7×10^{-03}
0	2	0	0	0	2	-0.00311	7.1×10^{-04}
0	0	0	2	2	0	0.04711	7.1×10^{-04}
0	0	0	0	2	2	-0.01631	2.6×10^{-04}
3	0	1	0	0	0	0.00780	1.1×10^{-02}
3	0	0	0	1	0	0.00906	6.2×10^{-03}
1	3	0	0	0	0	-0.01361	9.4×10^{-03}
0	3	1	0	0	0	-0.00584	7.1×10^{-03}
0	3	0	1	0	0	0.00115	4.8×10^{-03}
0	3	0	0	1	0	0.00270	5.1×10^{-03}

Table I. (Continued)

R_{CO}	Displacement Exponents					Coefficient	Standard Deviation
	R_{CH_1}	R_{CH_2}	θ_{H_1CO}	θ_{H_2CO}	$\theta_{H_1COH_2}$		
1	0	0	3	0	0	0.02146	1.7×10^{-03}
0	1	0	3	0	0	0.00097	1.7×10^{-03}
0	0	1	3	0	0	0.00003	1.7×10^{-03}
0	0	0	3	1	0	0.01170	8.2×10^{-04}
1	1	1	0	0	0	-0.01150	2.1×10^{-03}
1	1	0	1	0	0	-0.02446	1.2×10^{-03}
1	0	1	1	0	0	0.01103	1.2×10^{-03}
1	0	0	1	1	0	-0.00073	7.1×10^{-04}
0	1	1	0	1	0	0.02176	7.9×10^{-04}
0	0	1	1	1	0	-0.02190	5.2×10^{-04}
2	1	1	0	0	0	0.00295	2.7×10^{-02}
2	1	0	1	0	0	0.03339	1.2×10^{-02}
2	0	1	1	0	0	-0.00812	1.2×10^{-02}
2	0	0	1	1	0	0.00943	8.6×10^{-03}
1	2	1	0	0	0	-0.00743	1.9×10^{-02}
1	2	0	1	0	0	0.00615	1.5×10^{-02}
1	2	0	0	1	0	-0.00254	1.5×10^{-02}
0	2	1	1	0	0	0.00597	1.2×10^{-02}
0	2	1	0	1	0	-0.00389	1.2×10^{-02}
0	2	0	1	1	0	-0.03058	7.7×10^{-03}
1	1	0	2	0	0	0.02081	9.2×10^{-03}
1	0	1	2	0	0	0.01683	9.3×10^{-03}
1	0	0	2	1	0	-0.02607	4.0×10^{-03}
0	1	1	2	0	0	0.02353	8.1×10^{-03}
0	1	0	2	1	0	-0.00207	5.5×10^{-03}
0	0	1	2	1	0	0.00084	5.5×10^{-03}
1	1	0	0	0	2	0.00267	3.3×10^{-03}
1	0	0	1	0	2	-0.00610	2.1×10^{-03}
0	1	1	0	0	2	0.00703	3.2×10^{-03}
0	1	0	1	0	2	-0.00393	1.9×10^{-03}
0	1	0	0	1	2	-0.00691	1.9×10^{-03}
0	0	0	1	1	2	-0.01154	1.4×10^{-03}
1	1	1	1	0	0	-0.00255	3.7×10^{-02}
1	1	0	1	1	0	-0.01533	1.9×10^{-02}
0	1	1	1	1	0	0.03284	2.4×10^{-02}

For example, the *ab initio*, diagonal, cubic and quartic, force constants for the CO stretch are -0.500 and $+0.400$ a.u., respectively, while the corresponding values derived by Tanaka and Machida²² are -0.497 and $+0.518$. The agreement between this *ab initio* force field and the empirical one derived by Gribov, Pavlyuchko, and Lozenko²³ is, however, poor. Gribov, Pavlyuchko, and Lozenko²³ find, for example, diagonal, cubic,

and quartic, CO stretching constants of -0.028 and -0.200 a.u. Maessen and Wolfsberg²⁴ have found reasonable agreement between calculated and observed vibrational energy levels using both of these empirical force fields.

The calculated structural parameters and harmonic frequencies are reported in Table II along with a comparison both with experimental results and with the results of previous

Table II. Geometric parameters and harmonic frequencies for H₂CO.

Source	R _{CO} (Å)	R _{CH} (Å)	θ _{HCO}	ω ₁	ω ₂	ω ₃	ω ₄	ω ₅	ω ₆
4-31G**/RHF	1.181	1.093	122.3	3121	2041	1668	1340	3188	1380
DZP/RHF	1.189	1.094	121.9	3150	2010	1657	1336	3229	1369
DZP/RHF ^a	1.189	1.094	121.8	3149	2006	1656	1335	3226	1367
6-31G*/RHF ^b	1.184	1.092	122.1	3159	2032	1675	1332	3226	1362
TZP/RHF	1.183	1.092	121.9	3111	1998	1659	1373	3185	1341
4-31G**/MP2	1.217	1.100	122.4	3027	1805	1589	1219	3099	1300
6-31G*/MP2 ^b	1.220	1.104	122.2	3019	1786	1567	1194	3064	1249
4-31G**/MP3	1.206	1.098	122.2	3050	1891	1608	1228	3128	1317
DZP/MCSCF-4 ^c	1.188	1.118	122.1	2932	2008	1553	1258	3001	1314
TZP/MCSCF-4 ^c	1.182	1.114	122.1	2890	1996	1571	1273	2958	1329
DZP/SD-CI	1.212	1.100	121.9	3077	1869	1595	1241	3159	1307
DZP/SD-CI ^a	1.212	1.100	121.8	3074	1869	1596	1243	3155	1306
DZP/SDQ-CI	1.221	1.104	121.8	3031	1806	1568	1200	3112	1284
Experiment ^d	1.203	1.099	121.7						
Experiment ^e				2937	1778	1544	1188	3012	1269
Experiment ^f				2944	1764	1563	1191	3009	1288
Experiment ^g				2944	1761	1517	1187	3033	1282
Experiment ^h				2977	1778	1529	1191	2997	1299

^aReference 27.^bR. F. Hont, B. A. Levi and W. J. Hehre, *J. Comput. Chem.*, **3**, 234 (1982); D. J. DeFrees, B. A. Levi, S. K. Pollack, W. J. Hehre, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, **101**, 4085 (1979).^cM. Dupuis, W. A. Lester, Jr., B. H. Lengsfeld III, and B. Liu, *J. Chem. Phys.*, **79**, 6167 (1983).^dK. Yamada, T. Nakagawa, K. Kuchitsu, and Y. Morino, *J. Mol. Spectrosc.*, **38**, 70 (1971).^eThis work (see text).^fReference 25.^gReference 22.^hReference 26.

calculations. Focusing on the frequencies, note first that here and elsewhere in this article the modes are ordered in the standard spectroscopic ordering. So in what follows, for H₂CO, mode 1 corresponds to the symmetric CH stretch, mode 2 to the CO stretch, mode 3 to the CH₂ scissors, mode 4 to the out-of-plane bend, mode 5 to the CH antisymmetric stretch, and mode 6 to the CH₂ rock.

Before comparing the calculated harmonic frequencies with those derived experimentally it is relevant to note that there have been at least three attempts to derive harmonic frequencies for formaldehyde from experimental information. Duncan and

Mallinson²⁵ derived harmonized frequencies by fitting a general harmonic force field to observed isotope shifts, rotational constants, and centrifugal distortion constants. Tanaka and Machida²³ performed a similar analysis, including a small set of overtone and combination bands in their fitting procedure (one of these overtone assignments, 1₂, has since been shown to be incorrect²⁶). Finally, Reisner and co-workers²⁶ have derived harmonized frequencies by fitting a large number of overtone and combination bands of H₂CO to a vibrational quantum number expansion, eq. (3), thereby obtaining both the anharmonicity constants and a set of harmonized frequen-

cies. The harmonized frequencies from these three studies are listed in Table II. Care should be taken to distinguish these experimentally derived, harmonized frequencies from the theoretically derived harmonic frequencies. Since the observed frequencies of H_2CO are significantly affected by Fermi resonances, the harmonized frequencies derived from these frequencies reflect these perturbations. This effect is probably most significant in the harmonized frequencies derived by Reisner and co-workers²⁶ who include in their fitting procedure a number of very strongly perturbed states.

In light of this ambiguity in the experimentally derived harmonized frequencies we have derived a new set of harmonic frequencies by making small adjustments ($<10\%$) to the quadratic part of the SDQ-CI force field to fit the observed fundamental frequencies of D_2CO . The assumption here is that while the SDQ-CI cubic and quartic force constants are not exact, they are sufficiently accurate to allow the extraction of the harmonic frequencies. D_2CO was chosen both because its fundamental frequencies should be more strongly dominated by the harmonic part of the potential and because there appear to be no significant Fermi resonances involving the fundamentals of D_2CO , while the fundamentals of both H_2CO and HDCO are thought to be perturbed by Fermi resonances. The results of this procedure are also given in Table II and will be used here as the basis of comparison with the calculated results. The errors in the RHF harmonic frequencies relative to these experimentally derived values range from 100 to 264 cm^{-1} , with the largest errors being in the CO stretching frequency (mode 2). Correlation is found to substantially improve the agreement with experiment. Considering the MP results first, the largest error in the MP2 frequencies is 90 cm^{-1} for the symmetric stretch, while the largest error in the MP3 frequencies is slightly larger, 117 cm^{-1} . In general the MP3 frequencies are found to lie between the corresponding RHF and MP2 frequencies with the MP2 results being in the best agreement with experiment.

Considering now the CI results, note first the excellent agreement between the DZP/SD-CI results reported here and those reported previously by Yamaguchi and Schaefer.²⁷ The

errors in the CI harmonic frequencies range from 38 to 148 cm^{-1} with the largest error being in the antisymmetric CH stretching frequency. Addition of the Davidson correction for quadruple excitations leads to a significant improvement in the agreement, the largest error being 101 cm^{-1} (3.4%), again, for the antisymmetric CH stretch.

In all but one case the calculated frequencies are higher than those observed. The exception is the MP2/6-31G* which can probably be attributed to the usual tendency of second order perturbation theory to overshoot. Indeed, as noted above, MP3 calculations lead, in all cases, to higher frequencies than MP2 calculations.

Table III summarizes the calculated and experimentally derived energy level expansion coefficients for H_2CO . Before comparing these results in detail it is important to note several points concerning the experimentally and theoretically derived values. The vibrational states of H_2CO are strongly perturbed by a Fermi resonance involving modes 3, 5, and 6 ($\omega_5 \approx \omega_3 + \omega_6$). The experimentally derived spectroscopic constants involving these modes reflect this perturbation. However, the theoretical derived constants do not. For this reason the experimentally derived constants for modes 3, 5, and 6 should not be directly compared with the theoretical values. Some of the theoretical results are affected by a different kind of accidental degeneracy, one involving the harmonic frequencies for modes 2, 5, and 6. This near degeneracy results in a near singularity in one of the terms of the perturbation theory expression for the spectroscopic constants X_{25} , X_{26} , and X_{56} . Following the method of Mills,⁹ the near singular term is simply deleted from the expression. The spectroscopic constants resulting from this procedure yield deperturbed vibrational energy levels. Schlegel, Wolfe, and Bernardi¹⁵ have shown that these deperturbed energy levels can, to a first approximation, be corrected by solving the appropriate 2×2 eigenvalue problem. The effect, however, cannot be directly incorporated into the spectroscopic constants themselves.

For the remaining terms excellent agreement is found between the calculated results and those derived from the experimental spectra. Considering the SDQ-CI results, the

Table III. Calculated and observed energy level expansion constants (cm^{-1}) for H_2CO .

Spectroscopic Constant	4-31G**/ RHF	DZP/ RHF	4-31G*/ MP2	4-31G*/ MP3	DZP/ SD-CI	DZP/ SDQ-CI	Exp ^a τ^a
X_{11}	-30	-28	-30	-31	-30	-33	-29.0
X_{22}	-8	-9	-10	-9	-8	-8	-9.9
X_{33}	0	-2	0	1	2	1	-0.2
X_{44}	-1	-4	-2	-1	-3	-3	-3.2
X_{55}	-31	-30	-34	-39	-32	-36	-18.0
X_{66}	-1	-2	-5	2	-1	-1	-1.6
X_{12}	3	-5	-5	0	-4	-5	1.2
X_{13}	-31	-36	-28	-35	-37	-34	-23.0
X_{14}	-8	-5	-6	-3	-8	-9	-10.1
X_{15}	-111	-111	-126	-125	-122	-133	-193.3
X_{16}	0	-3	-8	-8	-5	-6	-49.8
X_{23}	-5	-5	-9	-6	-5	-6	-8.3
X_{24}	-1	-4	-7	-8	-5	-6	-7.2
X_{25}	-9	-17	-1 ^b	-4	-1 ^b	-3 ^b	-17.2
X_{26}	5	10	-4 ^b	-3	-3 ^b	-3 ^b	6.6
X_{34}	3	-2	0	5	-3	-4	-1.8
X_{35}	1	-10	-9	-3	-15	-16	6.0
X_{36}	-29	-21	-17	-20	-16	-15	-29.9
X_{45}	1	-17	-18	-16	-18	-19	-13.4
X_{46}	5	10	7	7	10	10	-2.9
X_{56}	-9	-16	-12 ^b	-4	-10 ^b	-12 ^b	-17.6
G_0	2	5	5	4	5	5	-

^aReference 26.^bThese constants are affected by an accidental, near degeneracy in the harmonic frequencies for modes 2, 5, and 6. Following the method of ref. 9, the near singular terms in the perturbation theory expression for these constants were deleted.

only one of these remaining terms for which there is a significant disagreement is X_{12} . The SDQ-CI calculations here predict a value of -5 cm^{-1} while the result derived from the experimental spectra is $+1.2 \text{ cm}^{-1}$. Expansion coefficients for HDCO and D_2CO are summarized in Tables IV and V (no experimental results are available yet for comparison).

Table VI summarizes the calculated and observed fundamental frequencies (the energy difference between the $v = 0$ and $v = 1$ levels for each of the modes) for H_2CO , HDCO, and D_2CO . There is in general good

agreement between the calculated and observed results with the correlated calculations again leading to significantly better agreement than the RHF calculations. In the SDQ-CI calculations, for H_2CO , the error in each of the calculated fundamental frequencies is within 10 cm^{-1} of the error in the corresponding harmonic frequency. Thus, for example, the theory predicts a difference of 175 cm^{-1} between the harmonic and fundamental frequencies for the CH antisymmetric stretch, while the difference derived from the observed spectra is 169 cm^{-1} .

Table IV. Calculated harmonic frequencies and energy level expansion constants (cm^{-1}) for HDCO.

Spectroscopic Constant	4-31G**/ RHF	DZP/ RHF	4-31G*/ MP2	4-31G*/ MP3	DZP/ SD-CI	DZP/ SDQ-CI
ω_1 (CH str)	3157	3192	3065	3092	3121	3075
ω_2 (CD str)	2335	2359	2255	2277	2299	2263
ω_3 (CO str)	2006	1975	1773	1863	1839	1776
ω_4 (HCO bend)	1547	1537	1476	1490	1479	1456
ω_5 (DCO bend)	1135	1125	1071	1084	1076	1057
ω_6 (HDCO wag)	1216	1211	1105	1113	1124	1087
x_{11}	-60	-57	-65	-66	-63	-68
x_{22}	-28	-29	-34	-34	-32	-36
x_{33}	-7	-8	-10	-9	-8	-8
x_{44}	-27	-15	-14	-14	-10	-10
x_{55}	-8	-6	-7	-4	-4	-4
x_{66}	3	1	-7	-5	-7	-5
x_{12}	0	3	2	-1	1	-1
x_{13}	0 ^a	-1	-3	-1	-3	-5
x_{14}	60	13	2	10	-9	-15
x_{15}	-4 ^a	1	-3	-1	-2	-2
x_{16}	-5	-13	-13	-11	-14	-15
x_{23}	-5	-8	-1	-3	-3	-2
x_{24}	-5	-7	-6	-5	-7	-7
x_{25}	16	4	0	1	-4	-5
x_{26}	-16	-26	16	16	11	2
x_{34}	-3	-3	-2	-2	-1	0
x_{35}	-5 ^a	-8	-8	-7	-7	-7
x_{36}	0	-3	-6	-8	-4	-5
x_{45}	0	0	-2	2	0	0
x_{46}	4	3	3	6	2	1
x_{56}	1	3	2	3	3	3
G_0	-27	-17	-22	-23	-19	-17

^aThese constants are affected by an accidental, near degeneracy in the harmonic frequencies for modes 1, 3, and 6. Following the method of ref. 9, the near singular terms in the perturbation theory expression for these constants were deleted.

In Table VII a comparison is made of the SDQ-CI and experimental vibrational energy levels for states with two and three quanta of vibrational excitation. The errors in the calculated frequencies closely track those found in the calculated harmonic frequencies, with the largest errors being in states with either the CH antisymmetric or symmetric stretch

excited. There is an unusually large error in the calculated energy of the combination band involving the antisymmetric and symmetric CH stretches. It is likely that the observed state is strongly perturbed by a Fermi resonance interaction with the state having one quantum of excitation each in modes 1, 3, and 6 (see below). This kind of effect is, of

Table V. Calculated harmonic frequencies and energy level expansion constants (cm^{-1}) for D_2CO .

Spectroscopic Constant	4-31G**/ RHF	DZP/ RHF	4-31G*/ MP2	4-31G*/ MP3	DZP/ SD-CI	DZP/ SDQ-CI
ω_1 (CD_2 sym str)	2299	2318	2204	2228	2248	2210
ω_2 (CO str)	1968	1939	1746	1835	1810	1749
ω_3 (CD_2 scissors)	1214	1207	1166	1172	1165	1148
ω_4 (D_2CO wag)	1076	1072	978	985	994	961
ω_5 (CD_2 asym str)	2379	2410	2314	2334	2358	2324
ω_6 (CD_2 rock)	1091	1081	1025	1039	1030	1012
X_{11}	-13	-12	-15	-14	-14	-16
X_{22}	-5	-7	-10	-7	-8	-8
X_{33}	1	3	1	1	3	2
X_{44}	-2	-4	-3	-1	-3	-3
X_{55}	-18	-17	-20	-22	-20	-22
X_{66}	-1	-2	-3	1	-1	-1
X_{12}	-9	-11	-5	-6	-6	-4
X_{13}	-21	-27	-22	-25	-28	-26
X_{14}	1	4	2	6	0	-1
X_{15}	-50	-52	-63	-62	-60	-67
X_{16}	4	-1	-3	-2	-2	-3
X_{23}	-2	-3	-4	-2	-3	-3
X_{24}	-3	-7	-6	-11	-6	-6
X_{25}	-6	-6	1	-4	-3	-2
X_{26}	-5	-3	-6	-4	-4	-5
X_{34}	2	-1	1	3	-1	-2
X_{35}	4	-6	-4	-2	-9	-10
X_{36}	-20	-13	-13	-13	-10	-10
X_{45}	1	-10	-10	-9	-11	-11
X_{46}	2	5	2	3	5	4
X_{56}	4	1	-3	0	-4	-5
G_0	0	1	1	3	3	2

course, neglected in the energy level expansion used here.

Also shown in Table VII are the energy levels calculated with the adjusted SDQ-CI force field. (The quadratic part of this force field was adjusted to reproduce the observed fundamentals of D_2CO .) The largest errors in the energy levels from this adjusted force field again occur in states that are expected to be significantly perturbed by Fermi resonances.

For example, in the state mentioned above, the combination band involving the anti-symmetric and symmetric CH stretches, the error is 46 cm^{-1} . However, the adjusted force field predicts that a second state, one having one quantum each in modes 1, 3, and 6, lies only 6 cm^{-1} below this combination band. Since these two states are of the same symmetry it is probable that there will be significant mixing of the two states.

Table VI. Calculated and observed fundamental (cm^{-1}) for H_2CO , HDCO , and D_2CO .

Molecule	Method	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
H_2CO	4-31G**/RHF	2939	2022	1638	1339	3064	1363
	DZP/RHF	3014	1982	1624	1319	3084	1355
	4-31G**/MP2	2879	1773	1558	1203	2948	1273
	4-31G**/MP3	2903	1863	1580	1219	2974	1307
	DZP/SD-CI	2927	1841	1561	1222	2997	1295
	DZP/SDQ-CI	2871	1778	1533	1180	2937	1273
	Experiment ^a	2782	1746	1500	1167	2843	1249
	4-31G**/RHF	2272	1986	1523	1123	3066	1213
	DZP/RHF	2285	1948	1510	1114	3079	1196
	4-31G**/MP2	2193	1742	1447	1052	2930	1091
HDCO	4-31G**/MP3	2214	1836	1466	1076	2957	1105
	DZP/SD-CI	2233	1813	1450	1063	2981	1109
	DZP/SDQ-CI	2185	1749	1426	1044	2919	1070
	Experiment ^a	2121	1724	1400	1028	2844	1058
	4-31G**/RHF	2236	1944	1198	1074	2320	1081
	DZP/RHF	2251	1910	1188	1060	2340	1073
	4-31G**/MP2	2130	1717	1147	966	2234	1007
	4-31G**/MP3	2155	1807	1156	979	2252	1032
	DZP/SD-CI	2172	1784	1145	982	2275	1020
	DZP/SDQ-CI	2127	1723	1127	948	2233	1001
D_2CO	Experiment ^a	2056	1702	1106	938	2160	989

^aD. J. Clouthier and D. A. Ramsay, *Ann. Rev. Phys. Chem.*, **34**, (1983).

Calculated vibrationally averaged displacements and root-mean-square displacements of the internal coordinates for the ground vibrational state and each of the fundamentals are given in Table VIII. It is found, for example, that the average value of the CO distance in the ground vibrational state is 0.004 Å longer than the equilibrium value. Putting one quantum into the CO stretch increases the average displacement to 0.012 Å.

Values of the vibration-rotation coupling constants are given in Table IX. Since only those constants corresponding to rotation about the CO axis (A axis) have values exceeding 0.02 cm^{-1} , only these values are reported. The contact transformation given by Papoušek and Aliiev²⁸ has been employed to account for Coriolis resonances between modes 4 and 6 in H_2CO and D_2CO and between modes 5 and 6 in HDCO . Agreement with the experimentally derived values is generally good except for modes 4 and 6 of H_2CO (for the corresponding modes of D_2CO

there is good agreement). The cause of this disagreement is unclear.

It is concluded then that the approach outlined above leads to reliable anharmonicity constants for polyatomic molecules, except in those cases where the energy levels are significantly perturbed by Fermi resonances. A more extensive comparison of theoretical and experimentally derived anharmonicity constants will have to await the reporting of experimentally derived constants for a polyatomic molecule not significantly perturbed by low-energy Fermi resonances. In this regard D_2CO would seem to be an ideal candidate.

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Table VII. Comparison of *ab initio* DZP/SDQ-CI, adjusted SDQ-CI, and observed vibrational overtone and combination energy levels (cm^{-1}) for H_2CO .

Vibrational State	Calculated (error)		Observed ^a
	SDQ-CI	Adjusted	
Overtones (two quanta each)			
1 ₂	5678 (171)	5480 (-27)	5507
2 ₂	3543 (72)	3477 (6)	3471
3 ₂	3071 (71)	3011 (11)	3000
4 ₂	2357 (30)	2326 (-1)	2327
5 ₂	5823 (172)	5607 (-44)	5651
6 ₂	2534	2498	--
Overtones (three quanta each)			
1 ₃	8419	8118	--
2 ₃	5291 (114)	5189 (12)	5177
3 ₃	4611	4518	--
4 ₃	3528	3479	--
5 ₃	8626	8293	--
6 ₃	3798	3742	--
Combinations (one quantum each)			
1 ₁ 2 ₁	4646 (118)	4519 (-9)	4528
1 ₁ 3 ₁	4372 (112)	4247 (-13)	4260
1 ₁ 4 ₁	4044	3931	--
1 ₁ 5 ₁	5688 (255)	5479 (46)	5433
1 ₁ 6 ₁	4134	4019	--
2 ₁ 3 ₁	3307 (69)	3247 (9)	3238
2 ₁ 4 ₁	2954 (49)	2907 (2)	2905
2 ₁ 5 ₁	4724	4590	--
2 ₁ 6 ₁	3044 (44)	2994 (-6)	3000
3 ₁ 4 ₁	2712 (57)	2667 (12)	2655
3 ₁ 5 ₁	4467 (117)	4333 (-13)	4350
3 ₁ 6 ₁	2788 (69)	2737 (18)	2719
4 ₁ 5 ₁	4111	3990	--
4 ₁ 6 ₁	2459	2427	--
5 ₁ 6 ₁	4205 (112)	4085 (-8)	4093

^aReference 26.

Table VIII. Average values and RMS amplitudes of the internal displacement coordinates for various vibrational states of H_2CO obtained using the SDQ-CI/DZP force field. Bond length displacements are in angstroms and bond angle displacements are in degrees.

Vibrational State	Average Displacement			RMS Displacement			
	R_{CO}	R_{CH}	θ_{HCO}	R_{CO}	R_{CH}	θ_{HCO}	$\theta_{\text{H}_1\text{COH}_2}$
ground state	0.004	0.013	0.026	0.037	0.077	6.36	12.05
1_1 (CH sym str)	0.003	0.030	0.068	0.038	0.108	6.36	12.05
2_1 (CO str)	0.012	0.011	-0.171	0.061	0.077	6.98	12.05
3_1 (CH_2 scissors)	0.006	0.011	-0.083	0.041	0.077	7.94	12.05
4_1 (H_2CO wag)	0.005	0.008	-0.099	0.037	0.077	6.36	20.86
5_1 (CH antisym str)	0.002	0.031	0.322	0.037	0.109	6.41	12.05
6_1 (CH_2 rock)	0.005	0.010	0.172	0.037	0.077	9.48	12.05

Table IX. Vibration-rotation coupling constants (α_i^A) (cm^{-1}).

Molecule	Mode	SDQ-CI	Empirical ^a	Expt.
H_2CO	1	0.159	0.183	0.161 ^b
	2	-0.003	0.006	0.008 ^c
	3	-0.060	-0.064	-0.060 ^c
	4	0.134	0.028	0.028 ^d
	5	0.093	0.150	0.190 ^b
	6	-0.119	0.018	0.017 ^d
D_2CO	1	0.068	0.078	-
	2	-0.002	-0.002	-0.001 ^a
	3	-0.027	-0.026	-0.023 ^a
	4	0.047	-0.001	0.068 ^a
	5	0.033	0.057	-
	6	-0.042	0.006	-0.057 ^a
HDCO	1	0.065	0.088	-
	2	0.084	0.109	-
	3	-0.004	-0.001	-
	4	-0.050	-0.014	-
	5	-0.088	-0.014	-
	6	0.108	0.036	-

^aReference 22.

^bK. Yamada, T. Nakagawa, K. Kuchitsu, and Y. Morino, *J. Mol. Spectrosc.*, **38**, 70 (1971).

^cT. Nakagawa, H. Kashiwagi, H. Kurihara, and Y. Morino, *J. Mol. Spectrosc.*, **31**, 436 (1969).

^dT. Nakagawa and Y. Morino, *J. Mol. Spectrosc.*, **38**, 84 (1971).

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