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The Use of Centrifugal Distortion Constants in Force Constant Calculations

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The use of empirically determined ground state quartic distortion constants of a molecule can be instrumental in defining certain constants in the harmonic molecular potential function. However, due to anharmonicity and vibrational averaging effects at the ground state level, it is of the utmost importance that the relative value of each constant is critically assessed before a physically representative set of force constants may be achieved. Five case studies are considered — methyl fluoride, methyl chloride, formaldehyde, ketene and methylene chloride.

INTRODUCTION

Data to which the harmonic force constants of a molecule are sensitive, and which have to date been used in their evaluation, include fundamental vibration frequencies and their displacement on heavy isotopic substitution, Coriolis coupling (ζ) constants, quartic centrifugal distortion constants, infrared and/or Raman fundamental intensities, mean square amplitudes of vibration, inertial defects in planar molecules and *l*-type doubling constants in linear molecules. By far the most common combination of data involves the first three of the above, all being readily available from infrared and/or Raman studies of the fundamental vibration and pure rotation regions of the molecular spectrum under conditions of maximum resolution.

However, the possibility of accumulating an extensive data base does not guarantee the determination of a reliable and physically realistic force field. Even after correction for the effects of known vibrational (Fermi) resonance perturbations, the most careful assessment of the relative value of the individual data is required before a set of force constants of physical and predictive reliability can be assured, particularly when low mass atoms are present in the molecule.

The cases of five molecules are considered here in illustration of the best use of the experimental data, and particularly centrifugal distortion constants, in the determination of empirical force constants. The molecules are methyl fluoride, methyl chloride, formaldehyde, ketene and methylene chloride.

DATA USAGE AND FORCE CONSTANT SETS

a. Methyl Fluoride

For many years the data available for methyl fluoride comprised vibration frequencies (CH_3F, CD_3F), heavy isotopic frequency shifts ($^{13}CH_3F$), Coriolis ζ constants (CH_3F, CD_3F) and D_J°, D_{JK}° distortion constants (CH_3F, CD_3F). Severe Fermi resonance perturbations in the CH stretching region and Coriolis resonance perturbations in the CH and CD deformation regions caused great complications. A number of ζ constants were not very reliable, and the ^{13}C isotopic frequency shift on the ν_1 CH stretching fundamental was subject to a large Fermi resonance correction. The accumulated data seemed to be fairly self-consistent, and yielded the set of force constants in column I of Table I[1], these being in terms of the conventional definition of symmetry coordinates[2], with unscaled angle bending coordinates.

The significant negative value of F_{12} (CH_3 sym. str./CH_3 sym. def.) was determined substantially by the ^{13}C frequency shift $\Delta\omega_1$. Although the Fermi resonance in the CH stretching region was corrected for as accurately as the available spectra permitted, it has been shown subsequently[3] that

TABLE I

Harmonic Force Constants[a] *for Methyl Fluoride (I) in the Absence of* D_K° *Data, (II) Including* D_K° *Data, and (III) From Scaled* ab initio *Calculations*

			I[b]	II[c]	III[d]
A_1	F_{11} (CH_3 str.)		5.214[e]	5.361	5.405
	F_{12}		—0.293	+0.002	+0.089
	F_{13}		+0.465	+0.360	+0.369
	F_{22} (CH_3 def.)		0.766	0.734	0.706
	F_{23}		—0.673	—0.649	—0.558
	F_{33} (CF str.)		5.682	5.656	5.577
E	F_{44} (CH_3 str.)		5.260	5.259	5,231
	F_{45}		—0.127	--0.171	—0.150
	F_{46}		+0.163	+0.082	+0.058
	F_{55} (CH_3 def.)		0.572	0.573	0.576
	F_{56}		—0.063	—0.050	—0.060
	F_{66} (CH_3 rock)		0.904	0.905	0.865
		Obsd.	Calc.	Calc.	Calc.
				CH_3F	
	D_J	60.23[f]	61.4	61.71	62.4
	D_{JK}	439.5	441.0	439.8	442.2
	D_K	2108.4	2528	2088.0	1994
				CD_3F	
	D_J	34.06	34.3	34.80	35.7
	D_{JK}	222.01	218.0	219.3	224.5
	D_K	391.41	506.1	394.3	365.3

[a] Symmetry coordinates of Ref. (2). Molecular geometry:

$$r\,(CH) = 1.090 \text{ Å}, \quad r\,(CF) = 1.382 \text{ Å}, \quad \alpha\,(HCH) = 110.5^\circ.$$

[b] Ref. (1). [c] This work. [d] Ref. (6). [e] Stretching constants in mdyn Å^{-1} (aJ Å^{-2}), bending constants in mdyn Å (aJ), stretch-bend constants in mdyn (aJ Å^{-1}).

[f] Distortion constants in kHz.

the resonances present in CH_3F are numerous and complex, and that the model originally used was too simple, leading to a poor estimate for $\Delta\omega_1$. The only other spectroscopic datum highly sensitive to F_{12} is the axial distortion constant D_K°, which was unknown at the time. This has since become available, for both CH_3F[4] and CD_3F.[5] Redetermination of the force field including the D_K° values immediately requires the F_{12} constant to take a small positive value, as shown in column II of Table I. This set of force constants is determined by the most recent accumulated data available, including detailed simultaneous analyses of the various strongly interacting rovibrational systems in both CH_3F and CD_3F. The force constants are now in much closer accord with *ab initio* predictions, which are consistent in their prediction of a positive F_{12} value. The most recent set of *ab initio* constants known to us[6] are given in column III of Table I. The discrepancy in the magnitude of F_{12} between empirical and *ab initio* values is ascribed to the fitting of ground state D_K° values rather than equilibrium D_K^e values, (which are not known), and which the harmonic force field calculates. This is supported by the case of methyl chloride considered next.

For methyl fluoride, therefore, the availability of D_K° constants has been crucial to the determination of a realistic set of empirical force constants.

b. *Methyl Chloride*

In this case, the Fermi resonance perturbations in the CH stretching region are much less severe than in methyl fluoride, and may be corrected for simply and effectively[7], according to all subsequent more detailed investigations[8]. The force constants calculated 15 years ago (1) are hardly changed by the inclusion of data determined subsequently, including the axial D_K° distortion constants.[9-11] The most recent empirical force constants are given in Table II, column I. They are in excellent accord with recent *ab initio* predictions[6], given in column III. The small magnitude of the empirical F_{12} constant is due to the inclusion of the D_K° data. If used with their experimental uncertainties of 2% (CH_3Cl) and 10% (CD_3Cl), F_{12} is forced to take a negative value to achieve good reproduction, as shown in column II of Table II. The *ab initio* force constants predict D_K values which are ~10% lower than the observed. Unless a minimum uncertainty on the D_K° data of 5% is allowed, as for the column I force constants, F_{12} takes a negative value. All the evidence points to a positive value for F_{12} in methyl group molecules, and the effect is almost certainly due to use of ground state D_K° values, when numerically different equilibrium D_K^e constants are appropriate.

Allowance for the effects of using ground state distortion constants must be made in force constant calculations if physically realistic results are being sought. This problem arises in ketene in a more extreme form, as discussed in d.

c. *Formaldehyde*

The accumulated spectroscopic data for isotopic species of formaldehyde affords the opportunity of avoiding the above problem. Insufficient data are available to calculate equilibrium distortion constants for any single isotopic

TABLE II

Harmonic Force Constants[a] *for Methyl Chloride, (I) Determined by all Available Data, (II) Weighting* D_K *Constants According to Experimental Errors, and (III) from Scaled ab Initio Calculations*

		I[b]	II[b]	III[c]
A_1	F_{11} (CH_3 str.)	5.475[d]	5.421	5.483
	F_{12}	+0.032	—0.025	+0.125
	F_{13}	+0.129	+0.146	+0.140
	F_{22} (CH_3 def.)	0.626	0.627	0.628
	F_{23}	—0.514	—0.509	—0.501
	F_{33} (CCl str.)	3.492	3.490	3.498
E	F_{44} (CH_3 str.)	5.350	5.350	5.368
	F_{45}	—0.138	—0.137	—0.130
	F_{46}	+0.026	+0.027	+0.012
	F_{55} (CH_3 def.)	0.547	0.547	0.539
	F_{56}	—0.022	—0.022	—0.025
	F_{66} (CH_3 rock)	0.710	0.708	0.705

	Obsd.	Calc.	Calc.	Calc.
			CH_3Cl	
D_J[d]	18.093	18.04	18.04	17.96
D_{JK}	198.80	201.1	201.2	196.6
D_K	2576	2468	2565	2330
			CD_3Cl	
D_J	10.714	10.68	10.68	10.66
D_{JK}	102.7	101.4	101.2	100.9
D_K	586	561	585	526

[a] Symmetry coordinates of Ref. (2). Molecular geometry: $r\,(CH) = 1.084$ Å, $r\,(CCl) = 1778$ Å, $\alpha\,(HCH) = 110^\circ\ 50'$.

[b] This work. [c] Ref. (6). [d] Units as in Table I.

species. However, ground state constants of high precision are available over sufficient isotopic species to allow the use of isotopic differences in the quartic distortion constants, rather than the absolute values of the constants. As with heavy isotopic frequency shifts, such data will be very much less subject to anharmonicity and vibrational averaging effects, being small differences in almost equivalent parameters. They should thus be close approximations to the true equilibrium values. This is not the case for the absolute values of the ground state constants, due mainly to the vibrational effects present in each isotopic species.[12]

Force constant refinements over 10 isotopic species ($H_2{}^{12}C^{16}O$, $H_2{}^{13}C^{16}O$, $H_2{}^{12}C^{17}O$, $H_2{}^{12}C^{18}O$, $H_2{}^{13}C^{17}O$, $H_2{}^{13}C^{18}O$, $HD^{12}C^{16}O$, $D_2{}^{12}C^{16}O$, $D_2{}^{13}C^{16}O$, $D_2{}^{12}C^{18}O$) have been made[13]. The use isotopic distortion constant differences from $H_2{}^{12}C^{16}O$ for the five available species and from $D_2{}^{12}C^{16}O$ for the two available species achieves a marked improvement in the precision with which the force constant are determined over the situation when the absolute values are used in each case. The two sets of force constants in terms of the symmetry coordinates of ref.[13], are compared in Table III, and the reproduction of the input data using isotopic differences is given in Table IV. To allow for anharmonicity and vibrational averaging effects at the ground state level,

TABLE III

Harmonic Force Constants[a] *of Formaldehyde, (I) Determined Using Absolute Values of Distortion Constants, and (II) Determined Using Isotopic Distortion Constant Differences From $H_2{}^{12}C^{16}O$ and $D_2{}^{12}C^{16}O$*

		I	II
A_1	F_{11} (CH_2 str.)	4.966(0.023)[b]	4.952(0.022)
	F_{12}	+0.695(0.056)	+0.672(0.029)
	F_{13}	+0.146(0.027)	+0.119(0.015)
	F_{22} (CO str.)	12.874(0.042)	12.824(0.048)
	F_{23}	—0.375(0.011)	—0.377(0.009)
	F_{33} (CH_2 def.)	0.563(0.003)	0.562(0.002)
B_1	F_{44} (CH_2 wag.)	0.402(0.002)	0.402(0.002)
B_2	F_{55} (CH_2 str.)	4.820(0.027)	4.820(0.022)
	F_{56}	+0.109(0.014)	+0.113(0.010)
	F_{66} (CH_2 rock)	0.831(0.004)	0.832(0.003)

[a] Symmetry coordinates of Ref. (13). Molecular geometry: r (CH) = 1.099 Å, r (CO) = 1.203 Å, α (HCH) = 116.5°.

[b] Units as in Table I.

TABLE IV

Reproduction of Distortion Constants and Isotopic Differences in Distortion Constants for Formaldehyde in Terms of Set II Force Constants of Table III All Values in kHz

	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.
Distortion constants:	$H_2{}^{12}C^{16}O$		$HD^{12}C^{16}O$		$D_2{}^{12}C^{16}O$	
Δ_J	75.297	76.010	64.28	63.89	53.1	52.50
Δ_{JK}	1290.3	1289.8	725.7	727.3	623	616.5
Δ_K	19412	18815	10960	10804	4400	4384
δ_J	10.457	9.967	11.704	11.217	11.43	10.99
δ_K	1025.75	893.20	709.9	626.2	520	473.9
Isotopic distortion constant differences:						
	$H_2{}^{13}C^{16}O$		$H_2{}^{12}C^{17}O$		$H_2{}^{12}C^{18}O$	
Δ_J	3.787	3.748	4.227	3.677	6.842	6.868
Δ_{JK}	32.8	32.5	51.3	60.0	112.81	112.63
Δ_K	—	[—36.3]	—	[—63.7]	—	[—119.5]
δ_J	0.826	0.777	0.690	0.698	1.361	1.291
δ_K	36.55	34.84	38.75	38.30	82.35	72.15
			$H_2{}^{13}C^{17}O$		$H_2{}^{13}C^{18}O$	
Δ_J			7.327	7.364	10.467	10.500
Δ_{JK}			87.3	93.1	148.0	146.1
Δ_K			—	[—100.5]	—	[—156.6]
δ_J			1.493	1.444	2.116	2.011
δ_K			78.75	73.34	124.95	107.35
			$D_2{}^{13}C^{16}O$		$D_2{}^{12}C^{18}O$	
Δ_J			1.9	2.27	5.2	5.24
Δ_{JK}			—9	7.7	60	51.3
Δ_K			—	[—3.03]	—	[—56.5]
δ_J			0.93	0.68	1.33	1.47
δ_K			—	[9.68]	—	[35.6]

uncertainties of 2%, 2%, 2.5%, 5% and 10% must be allowed on Δ_J°, Δ_{JK}°, Δ_K°, δ_J° and δ_K° constants. These effects are so reduced on the isotopic differences that the actual experimental errors in the differences can be used. These range from as little as 2% up to 30%.

The results of Table III show that the use of isotopic centrifugal distortion differences, where these are determined to sufficient accuracy, can be expected to give a significant improvement in the precision of determination of the force constants of the molecule concerned.

d. Ketene

For ketene, quartic distortion constants of good precision are available for H_2C_2O, HDC_2O and D_2C_2O from combined infrared and microwave investigations.[14,15] Here it is found that the effects of anharmonicity and vibrational averaging at the ground state level are sufficiently large to give a wide variation in the determined force constants, dependent upon which combination of distortion constants is chosen to be fitted. A simultaneous good fit to all five constants in any single isotopic species cannot be achieved.

This state of affairs affects the A_1 and B_2 species force constants. Attempts to determine accurate ^{13}C isotopic frequency shifts on the A_1 species fundamentals to assist with the problem were confounded in almost every case due to severe resonance perturbations to almost every fundamental of H_2C_2O[16], which rendered the observations of limited value for the determination of force constants.

The situation is depicted in Tables V and VI. Wide variations in both the magnitude and sign of A_1 and B_2 species force constants result from different choices of fits to the distortion constants. No very clear choice between force constant sets can be made on purely empirical grounds, and recourse to the prediction of *ab initio* calculations in this case is necessary before a choice can be made[17]. See column V of Table V.

The molecule ketene thus appears to present a case where effects at the ground state level on the quartic centrifugal distortion constants can be sufficiently large to render them of limited value in the determination of a substantive and physically realistic set of force constants. If distortion constants of comparable accuracy become available for a ^{13}C or ^{18}O isotopic modification of ketene, then it is considered that the use of isotopic differences could result in a much more precise definition of the empirical force constants, as demonstrated in the case of formaldehyde.

e. Methylene Chloride

A large number of data over eight isotopic species exist for methylene chloride from which the general harmonic force field can be determined with apparently good precision, as shown in Table VII column I. The reproduction over all data, including the quartic distortion constants for $^{12}CH_2{}^{35}Cl_2$ and $^{12}CD_2{}^{35}Cl_2$, is excellent[12].

Close examination of the determined force constants gives cause for concern, however. In terms of the symmetry coordinates used[18], the negative value of F_{13} (CH_2 sym.str./CH_2 def., and counterpart of F_{12} in methyl group molecules) is not expected. For all other CH_3 and CH_2 group molecules, now

TABLE V

Harmonic Force Constant Sets[a] for Ketene Determined From Different Fits to Spectroscopic Distortion Constants for H_2C_2O, HDC_2O and D_2C_2O and all Other Available Data

		I	II	III	IV	V
		Fit to all constants	Fit to Δ_J°, Δ_{JK}°	Fit to Δ_{JK}°, Δ_K°	Fit to Δ_J°, δ_J°, δ_K°	*ab initio* prediction[b]
A_1	F_{11} (CH_2 str.)	5.925[c]	5.884	5.829	5.827	5.857
	F_{12}	+0.732	+0.202	+0.409	+0.897	+0.131
	F_{13}	0[d]	0	0	0	—0.077
	F_{14}	—0.225	+0.041	—0.211	—0.442	+0.039
	F_{22} (CC str.)	8.994	9.234	9.323	9.054	9.323
	F_{23}	+0.618	+0.535	+0.679	+0.714	+1.089[e]
	F_{24}	—0.243	—0.276	—0.279	—0.262	—0.302
	F_{33} (CO str.)	15.564	15.438	15.545	15.676	15.58
	F_{34}	0[d]	0	0	0	—0.002
	F_{44} (CH_2 def.)	0.611	0.602	0.614	0.640	0.594
B_1	F_{55} (CCO bend)	0.670	0.670	0.670	0.670	0.666
	F_{56}	+0.0962	+0.0962	+0.0962	+0.0962	+0.075
	F_{66} (CH_2 wag.)	0.0885	0.0885	0.0885	0.0885	0.087
B_2	F_{77} (CH_2 str.)	5.712	5.785	5.688	5.724	5.800
	F_{78}	—0.007	—0.220	+0.092	—0.047	—0.254
	F_{79}	0[d]	0	0	0	+0.011
	F_{88} (CH_2 rock)			ETAOIN	SHRDLU	CMFWđP UN
	F_{89}	—0.261	—0.189	—0.189	—0.201	—0.194
	F_{99} (CCO bend)	0.667	[illegible]	0.646	0.669	0.650

[a] Symmetry coordinates of Ref. (17). Molecular geometry: r (CH) = 1.079, r (CC) = = 1.314, r (CO) = 1.161 Å, α (HCH) = 122.3°.

[b] Scaled force constants from 6-31G** basis (17).

[c] Units as in Table 1.

[d] Constrained to zero.

[e] Over-estimated by a factor of ca. 2 without allowance for electron correlation.

including methyl fluoride, this constant is determined to be positive. Equally, the rather large negative value for F_{14} (CH_2 sym.str./CCl_2 def.) is unexpected, a much smaller value being anticipated between a CH_2 stretch and a CCl_2 deformation in opposite halves of the molecule. In this refinement, all distortion constants carry uncertainties of 3%. The poorest fitted values are those of δ_J° and δ_K° for both CH_2Cl_2 and CD_2Cl_2. Indeed, the fit to δ_K° barely falls within the 3% uncertainty allowed. Increasing the uncertainties on δ_J° to 5% and δ_K° to 10% immediately produces a dramatic effect in the determined force constants[19], as shown in Table VII column II, and particularly in the previously suspect values of F_{13} and F_{14}. F_{13} now takes a small positive value, and the magnitude of F_{14} is dramatically reduced. This seems to be a much more physically acceptable set of empirical force constants for methylene chloride. The overall fit to the accumulated data is hardly changed.

Clearly the most careful assessment of the derived force constants of a molecule must be made, both in relation to the reproduction of the employed data and in comparison with results for similar molecules, before the most physically realistic set consistent with the available data can be presented.

TABLE VI

Reproduction of Quartic Distortion Constants of Isotopic Ketenes for Force Constants sets I—IV of Table V. All Values in kHz

		Obsd.	Calc.				
			I Fit to all constants	II Fit to Δ_J°, Δ_{JK}°	III Fit to Δ_{JK}°, Δ_K°	IV Fit to Δ_J°, δ_J°, δ_K°	V *ab initio*
	Δ_J	3.394	3.418	3.402	3.324	3.390	3.245
	Δ_{JK}	476.0	480.6	478.5	475.7	475.7	466.9
H_2CCO	Δ_K	23535	22790	20060	22740	24380	20343
	δ_J	0.145	0.1446	0.1354	0.1354	0.1455	0.1281
	δ_K	329.6	284.2	269.5	272.3	284.7	260.6
	Δ_J	3.164	3.180	3.168	3.095	3.155	3.033
	Δ_{JK}	327.0	331.6	327.0	328.0	327.6	317.7
HDCCO	Δ_K	15000	15840	14600	15540	16650	14645
	δ_J	0.225	0.2236	0.2117	0.2109	0.2250	0.2026
	δ_K	239.0	234.6	222.4	225.0	234.9	215.2
	Δ_{JK}	2.719	2.679	2.692	2.612	2.654	2.584
	Δ_J	321.7	329.3	320.8	321.8	326.8	310.8
D_2CCO	Δ_K	5391	5495	4821	5490	5895	4897.8
	δ_J	0.218	0.2171	0.2057	0.2052	0.2185	0.1973
	δ_K	212.7	198.4	187.6	190.2	198.6	181.4

TABLE VII

Harmonic Force Constants[a] for Methylene Chloride Determined From all Available Data, (I) with Equal Weighting on all Distortion Constants, and (II) with $\delta_J°$ and $\delta_K°$ Given Lower Weighting

		I[b]	II[c]			I[b]	II[c]
A_1	F_{11} CH$_2$ str.)	5.507[d]	5.512	A_2	F_{55} (torsion)	0.633	0.633
	F_{12}	+0.074	+0.052				
	F_{13}	—0.047	+0.055		F_{66} (CH$_2$ str.)	5.435	5.435
	F_{14}	—0.297	—0.070	B_1	F_{67}	—0.136	—0.136
	F_{22} (CCl$_2$ str.)	3.941	3.911		F_{77} (CH$_2$ rock)	0.858	0.858
	F_{23}	—0.333	—0.292				
	F_{24}	+0.303	+0.266		F_{88} (CCl$_2$ str.)	3.039	3.038
	F_{33} (CH$_2$ def.)	0.640	0.617	B_2	F_{89}	—0.600	—0.600
	F_{34}	—0.275	—0.214		F_{99} (CH$_2$ wag)	0.711	0.711
	F_{44} (CCl$_2$ def.)	1.073	1.051				

	Obsd.	Calc. I	Calc. II
		CH_2Cl_2	
Δ_J	1.392[e]	1.3810	1.3819
Δ_{JK}	—26.176	—26.200	—26.173
Δ_K	473.16	468.90	466.01
δ_J	0.17699	0.17782	0.17549
δ_K	5.365	5.212	5.082
		CD_2Cl_2	
Δ_J	1.2977	1.2855	1.2845
Δ_{JK}	—15.884	—15.828	—15.861
Δ_K	204.05	200.87	200.33
δ_J	0.19014	0.19239	0.18819
δ_K	4.079	3.992	3.816

[a] Symmetry coordinates of Ref. (18). Molecular geometry: r (CH) = 1.0895, r (CCl) = = 1.7708 Å, α (HCH) = 111.60°, β (ClCCl) = 112.03°.

[b] This work. [c] Ref. (19). [d] Units as in Table I.

[e] Distortion constants in kHz.

CONCLUSIONS

To allow for differences between empirical ground state quartic distortion constants and their calculated harmonic equivalents in force constant calculations, uncertainties of some 2—5% of the individual values have normally been advocated, even when the precision of their determination is much greater. However, this can lead to the calculation of physically unreasonable force constant sets, particularly for those constants sensitive to axial distortion constants in molecules containing light atoms. In such cases, careful appraisal of the relative value of each distortion constant is essential before a physically representative harmonic potential function can be claimed. Differences between accurately determined ground state and calculated harmonic (i. e. equilibrium) distortion constants *can* be as large a 10%[17,20] in molecules for which a harmonic model would be expected to apply.

Wherever the experimental accuracy is sufficiently high, the use of isotopic ground state centrifugal distortion constant differences is recommended as a means of maximising the value of such data towards realistic force constant calculations.

REFERENCES

1. J. L. Duncan, D. C. McKean, and G. K. Speirs, *Mol. Phys.* **24** (1972) 553.
2. J. Aldous and I. M. Mills, *Spectrochim. Acta* **18** (1962) 1073.
3. J. P. Champion, A. G. Robiette, I. M. Mills, and G. Graner, *J. Mol. Spectrosc.* **96** (1982) 422.
4. G. Graner, *Mol. Phys.* **31** (1976) 1833.
5. L. Halonen, J. Kauppinen and G. L. Caldow, *J. Chem. Phys.* **81** (1984) 2257.
6. W. Schneider and W. Thiel, *J. Chem. Phys.* **86** (1987) 923.
7. J. L. Duncan, A. Allan, and D. C. McKean, *Mol. Phys.* **18** (1970) 289.
8. N. Bensari-Zizi and C. Alamichel, *Mol Phys.* **43** (1981) 1255.
9. P. Jensen, S. Brodersen, and G. Guelachvili, *J. Mol. Spectrosc.* **88** (1981) 393.
10. S. Brodersen, *J. Mol. Spectrosc.* **71** (1978) 312.
11. A. Mito, J. Sakai, and M. Katayama, *J. Mol. Spectrosc.* **112** (1985) 252.
12. J. L. Duncan, D. A. Lawie, G. D. Nivellini, F. Tullini, A. M. Ferguson, J. Harper, and K. H. Tonge, *J. Mol. Spectrosc.* **121** (1987) 294.
13. J. L. Duncan and H. Merson, *Chem. Phys. Lett.* **138** (1987) 55.
14. L. Nemes and M. Winnewisser, *Z. Naturforsch.* **31A** (1976) 272.
15. F. Hegelund, J. Kauppinen and F. Winther, *Mol. Phys.* **61** (1987) 261.
16. J. L. Duncan, A. M. Ferguson, J. Harper, K. H. Tonge, and F. Hegelund, *J. Mol. Spectrosc.* **122** (1987) 72.
17. J. L. Duncan, A. M. Ferguson, J. Harper, and K. H. Tonge, *J. Mol. Spectrosc.* **125** (1987) 196.
18. R. W. Davis, A. G. Robiette, and M. C. L. Gerry, *J. Mol. Spectrosc.* **85** (1981) 399.
19. J. L. Duncan, A. M. Ferguson, J. Harper, and K. H. Tonge, *Mol. Phys.* **63** (1988) 647.
20. J. L. Duncan and D. C. McKean, *J. Mol. Spectrosc.* **107** (1984) 301.

SAŽETAK

Upotreba centrifugalnih distorzijskih konstanti u proračunu konstanti sila

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Upotreba empirijski određenih kvartnih distorzijskih konstanti osnovnoga stanja može biti sredstvo za određivanje stanovitih konstanti u harmoničkoj molekulskoj potencijalnoj funkciji. Međutim, zbog neharmoničnosti i efekata uprosječivanja vibracija na razini osnovnog stanja, neobično je važno kritički procijeniti relativnu vrijednost svake konstante, da bi se postigao fizički reprezentativan niz konstanti sila. Razmotreno je pet slučajeva: metil-fluorid, metil-klorid, formaldehid, keten i metilen-klorid.