Anharmonic Force Field and Isotopic Relations of Ozone

P. Hennig * and G. Strey

Sektion Physik der Universität München, Germany

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The anharmonic force constants of ozone up to fourth order have been determined from recently published spectroscopic data of $^{16}O_3$ and $^{18}O_3$. For the first time all experimental data presently available have been used in a least squares fit. Compared with recent work, the correct formula for the Darling-Dennison resonance parameter γ has been used now. The nonuniqueness of the solution is discussed. In addition, isotopic rules for various spectroscopic parameters are derived.

1. Introduction

Recently, new experimental data and an anharmonic force field calculation for ozone have been published by Barbe, Secroun and Jouve[1, 2]. From an analysis of 18 and 15 band centers of gaseous $^{16}O_3$ and $^{18}O_3$, respectively, these authors have calculated the harmonic vibrational frequencies ω_s and anharmonic corrections x_{rs} including the Darling-Dennison resonance parameter γ for both of these molecules independently. Compared with earlier results published by McCaa and Shaw[3] these new constants clearly are the most accurate and complete ones at the moment.

Besides that, Barbe and coworkers[2] have reported also a set of rotational interaction constants a_r^X for $^{16}O_3$ based on new rotational constants of the ground state[4, 5] and the excited states ν_1, ν_2 and ν_3[6].

The calculation of the potential function up to fourth order has been divided by Barbe and coworkers into a few separated steps. In the first step they used the harmonic vibrational frequencies ω_r of $^{16}O_3$ and in addition the Coriolis constant $\zeta_{13}^C = -0.60 \pm 0.01$ reported by Tanaka and Morino[6] to calculate the harmonic force field. In the next step the cubic potential was calculated using the rotational interaction constants a_r^X (other than a_1^{C*} and a_3^{C*} which are strongly perturbed by a Coriolis-type interaction between the levels ν_1 and ν_3) of $^{16}O_3$, the harmonic force field being fixed. Finally the $x_{rs}-s$ of $^{16}O_3$ served to calculate six of the nine quartic potential constants, holding in turn the harmonic and cubic potential fixed. The force field was then used to calculate the Darling-Dennison resonance parameter γ for $^{16}O_3$ and $^{18}O_3$. It was found that these values were in good agreement with the observed ones. Standard formulae connecting the $a-s$ and $x-s$ with the anharmonic potential as compiled by Kuchitsu and Morino[7] were used in these calculations.

We report here a calculation of the anharmonic potential function of ozone based on the same spectroscopic data but organized as a least squares fit to all the experimental spectroscopic constants a, x and γ known for $^{16}O_3$ and $^{18}O_3$ – that is 23 data in all – and refining to six cubic and six quartic potential constants simultaneously, the harmonic potential being fixed throughout the calculation. Of course, we expected to find our results very close to those of Barbe, Secroun and Jouve. But since we use a least squares procedure, estimates for the dispersions of the force constants are now available, and since we use more input data simultaneously, our results should be more reliable than the previous ones. Besides that we want to show in this paper how the computer program described by Hoy, Mills, and Strey[8] has to be modified in a case of strongly Coriolis-disturbed a-constants as for example in the ozone molecule.

2. Theoretical

The usual formula connecting rotational interaction constants a_r^X (expressed in cm^{-1}) for an asymmetric top with the cubic potential constants Φ_{rst} in dimensionless normal coordinates is obtained by a conventional perturbation calculation up to second order to be

$$a_r^X = -\frac{2X_e^2}{\omega_r}\left[\sum_\xi \frac{3(a_r^{(X\xi)})^2}{4I_\xi} + \sum_s (\zeta_{rs}^X)^2 \frac{3\omega_r^2+\omega_s^2}{\omega_r^2-\omega_s^2} + \pi\left(\frac{c}{h}\right)^{1/2} \sum_s \Phi_{rrs}\, a_s^{(XX)} \frac{\omega_r}{\omega_s^{3/2}}\right], \quad (1)$$

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* Permanent address: Max-Planck-Institut für Physik und Astrophysik, Föhringer Ring 6, *D-8000 München 40*, Germany.
Reprint requests to Dr. G. Strey, Sektion Physik der Universität München, Schellingstr. 4/IV, *D-8000 München 40*, Germany.

as described by Mills [9]. Here X and $\xi = A, B, C$ indicate the main axes of inertia of the molecule, X_e is the equilibrium rotational constant expressed in cm^{-1}:

$$X_{\text{e}} = \frac{\hbar^2}{2\,h\,c\,I_X{}^{\text{e}}}\,, \tag{2}$$

ζ_{rs}^{X} is the Coriolis-interaction constant and

$$a_r{}^{(\xi\eta)} = \left(\frac{\partial I_{\xi\eta}}{\partial Q_r}\right)_{\text{e}}, \tag{3}$$

where I_X and $I_{\xi\eta}$ are the moments and products of inertia, respectively.

For the ozone molecule, however, this standard formula cannot be used for $a_1{}^C$ and $a_3{}^C$ because of a strong second order Coriolis interaction between the nearly degenerate vibrational states of the same $v_1 + v_3$ values, so for example between the (100) and (001) states or the (200), (101), and (002) states. This situation is reflected in Eq. (1) where the second term in the square brackets has a resonance denominator $\omega_r{}^2 - \omega_s{}^2$, which causes the perturbation treatment of the corresponding terms in the molecular hamiltonian to be no longer appropriate. By removing these terms Nielsen [10] derived an effective rotational hamiltonian to second order of approximation for such a case of accidental resonance which contains so called unperturbed rotational constants $C_v{}^*$:

$$C_v{}^* = C_{\text{e}} - \sum_r a_r{}^{C*}\,(v_r + 1/2)\,. \tag{4}$$

This hamiltonian was used successfully by Tanaka and Morino [6] in their analysis of rotational spectra of the excited states (100) and (001) of ozone. Tanaka and Morino also gave explicit formulae for the unperturbed rotational interaction constants $a_1{}^{C*}$ and $a_3{}^{C*}$. According to the notation used in Mills' review [9] these formulae take the form

$$a_1{}^{C*} = -\frac{2\,C_{\text{e}}{}^2}{\omega_1}\left[\sum_{\xi}\frac{3\,(a_1{}^{(C\xi)})^2}{4\,I_\xi} - \frac{1}{2}\,(\zeta_{13}^{C})^2\,\frac{(\omega_1-\omega_3)^2}{\omega_3(\omega_1+\omega_3)} + \pi\left(\frac{c}{h}\right)^{1/2}\left\{\Phi_{111}\,a_1{}^{(CC)}\,\frac{\omega_1}{\omega_1{}^{3/2}} + \Phi_{112}\,a_2{}^{(CC)}\,\frac{\omega_1}{\omega_2{}^{3/2}}\right\}\right] \tag{5 a}$$

and

$$a_3{}^{C*} = -\frac{2\,C_{\text{e}}{}^2}{\omega_3}\left[\sum_{\xi}\frac{3\,(a_3{}^{(C\xi)})^2}{4\,I_\xi} - \frac{1}{2}\,(\zeta_{13}^{C})^2\,\frac{(\omega_1-\omega_3)^2}{\omega_1(\omega_1+\omega_3)} + (\zeta_{23}^{C})^2\,\frac{3\,\omega_3{}^2+\omega_2{}^2}{\omega_3{}^2-\omega_2{}^2} + \pi\left(\frac{c}{h}\right)^{1/2}\left\{\Phi_{133}\,a_1{}^{(CC)}\,\frac{\omega_3}{\omega_1{}^{3/2}} + \Phi_{233}\,a_2{}^{(CC)}\,\frac{\omega_3}{\omega_2{}^{3/2}}\right\}\right]. \tag{5 b}$$

As can be seen the resonance terms are removed and replaced by an expression which to a certain degree of approximation could be completely neglected because of the resonance condition $\omega_1 \approx \omega_3$.

For the anharmonic correction x_{rs} we use the standard formula which again can be obtained by a perturbation calculation up to second order as reported by Mills [9]

$$x_{rr} = \tfrac{1}{16}\,\Phi_{rrrr} - \tfrac{1}{16}\sum_s \Phi_{rrs}^{2}\,[(8\,\omega_r{}^2 - 3\,\omega_s{}^2)/\omega_s(4\,\omega_r{}^2 - \omega_s{}^2)] \tag{6 a}$$

and

$$x_{rs} = \tfrac{1}{4}\,\Phi_{rrss} - \tfrac{1}{4}\sum_t (\Phi_{rrt}\,\Phi_{tss}/\omega_t) - \tfrac{1}{2}\sum_t [\Phi - \tfrac{1}{2}{}_{rst}^{2}\,\omega_t(\omega_t{}^2 - \omega_r{}^2 - \omega_s{}^2)/\Delta_{rst}] + [A_{\text{e}}(\zeta_{rs}^{A})^2 + B_{\text{e}}(\zeta_{rs}^{B})^2 + C_{\text{e}}(\zeta_{rs}^{C})^2]\left(\frac{\omega_r}{\omega_s} + \frac{\omega_s}{\omega_r}\right), \tag{6 b}$$

where

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

As described by Barbe and coworkers [2] in ozone also Darling-Dennison resonance [11] has to be taken into account which connects vibrational states $(v_1 \geqq 2, v_2, v_3)$ and $(v_1 - 2, v_2, v_3 + 2)$. This resonance is described by an off-diagonal matrix element of the first contact-transformed hamiltonian in an harmonic oscillator representation

$$\langle v_1, v_2, v_3\,|\,\tilde{H}/h\,c\,|\,v_1 - 2, v_2, v_3 + 2)\,\rangle = -\tfrac{1}{2}\gamma\,[(v_1 - 1)\,v_1(v_3 + 1)\,(v_3 + 2)]^{1/2}\,. \tag{7}$$

The formula for the Darling-Dennison resonance parameter γ in this equation can be obtained by a perturbation calculation up to second order as

$$\gamma = \frac{\Phi_{1133}}{8} - \frac{\Phi_{331}^{2}}{4\,\omega_1} + \frac{\Phi_{111}\,\Phi_{331}}{24\,\omega_1} + \frac{\Phi_{112}\,\Phi_{332}}{8} \cdot \frac{\omega_2}{4\,\omega_1{}^2 - \omega_2{}^2} - \frac{C_{\text{e}}}{2}\,(\zeta_{13}^{C})^2\,\frac{(\omega_1+\omega_3)^2}{\omega_1\,\omega_3}\,. \tag{8}$$

This expression differs slightly from that derived by Barbe and coworkers [2] in that their Coriolis term

$$\frac{C_{\text{e}}(\zeta_{13}^{C})^2\,(\omega_1\,\omega_3 - \omega_1{}^2 - \omega_3{}^2)}{2\,\omega_1\,\omega_3} \approx -\frac{C_{\text{e}}(\zeta_{13}^{C})^2}{2}$$

is replaced by

$$-\tfrac{1}{2} C_{\mathrm{e}} (\zeta_{13}^{C})^2 \frac{(\omega_1+\omega_3)^2}{\omega_1 \omega_3} \approx -2\, C_{\mathrm{e}} (\zeta_{13}^{C})^2 .$$

The Coriolis term arises from a first order perturbation calculation and is given by the matrix element

$$\langle v_1, v_2, v_3 \,|\, C_{\mathrm{e}} \pi_C^2 \,|\, v_1-2, v_2, v_3+2 \rangle ,$$

where

$$\pi_C = \sum_{r,s} \zeta_{rs}^{C} q_r p_s (\omega_s/\omega_r)^{1/2}$$

is the vibrational angular momentum operator and q_r and p_s are dimensionless normal coordinate and momentum operators, respectively.

3. Isotopic Relations for Ozone

Since the total isotopic substitution ${}^{16}O_3 \rightarrow {}^{18}O_3$ or ${}^{16}O_3 \rightarrow {}^{17}O_3$ can be regarded merely as the change of a mass-scaling factor in all equations relating observable quantities to the parameters of the molecular hamiltonian, one may expect particularly simple isotopic relations to exist for these molecules. Barbe and coworkers indeed found such relations for the quadratic, cubic, and quartic potential constants in the normal coordinate representation[2]. Using these relations they derived a simple isotopic rule for the rotational interaction constants α_r^{X}, compare[2], Equations (7) – (11).

We want to point out here that there exist a few more of such relations and that in fact all observable quantities of ${}^{17}O_3$ and ${}^{18}O_3$ can be calculated if the corresponding quantity of the parent molecule ${}^{16}O_3$ is known experimentally. This of course is true only within the Born-Oppenheimer approximation which leads to the conclusion that the equilibrium geometry and the molecular potential function is the same for all isotopic variants of a given molecule. Just recently Parker[12] has given an analysis of isotopic relations in nonlinear triatomic molecules. But his approach is too general to be applied conveniently to the total isotopic substitution of ozone and so instead we shall use a more direct method.

Since for ozone all normal coordinates and vibrational frequencies depend only on one single mass parameter m, the mass of the oxygen atom, this dependence clearly must be of the form

$$Q_r \equiv \sum_{i\alpha} l_{\alpha i,r}\, m_i^{1/2} (r_{\alpha i} - r_{\alpha i}^{\mathrm{e}}) = m^{1/2} \sum_{i\alpha} l_{\alpha i,r} (r_{\alpha i} - r_{\alpha i}^{\mathrm{e}}) = m^{1/2} Q_r^{(0)} \qquad (9)$$

and

$$\omega_r = m^{-1/2} \omega_r^{(0)} ,$$

where $r_{\alpha i} - r_{\alpha i}^{\mathrm{e}}$, $(\alpha = x, y, z;\ i = 1, 2, \ldots, N)$ denotes the cartesian displacement components of the i-th atom in molecular fixed axes, see[13]. $Q_r^{(0)}$ and $\omega^{(0)}$ are thus invariant under changes of m.

Now passing over to dimensionless normal coordinates

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

with

$$\gamma_r = 2 \pi c\, \omega_r / \hbar$$

one gets

$$q_r = m^{1/4} q_r^{(0)} .$$

This leads to the isotopic relation

$$q_r' = q_r (m'/m)^{1/4} . \qquad (10)$$

The expansion coefficients Φ of the vibrational potential function into normal coordinates q_r

$$V/h c = \tfrac{1}{2} \sum_r \omega_r q_r^2 + \tfrac{1}{6} \Phi^{rst} q_r q_s q_t + \tfrac{1}{24} \Phi^{rstu} q_r q_s q_t q_u + \ldots$$

are therefore seen to be proportional to

$$\omega_r \sim m^{-1/2} ,$$
$$\Phi^{rst} \sim m^{-3/4} ,$$
$$\Phi^{rstu} \sim m^{-1} ,$$

and so we get the isotopic relations

$$\omega'_r = \omega_r (m/m')^{1/2} , \qquad (11)$$

$$\Phi'_{rst} = \Phi_{rst} (m/m')^{3/4} , \qquad (12)$$

$$\Phi'_{rstu} = \Phi_{rstu} (m/m') . \qquad (13)$$

According to their definition in Eq. (2) the rotational constants X_{e} ($X_{\mathrm{e}} = A_{\mathrm{e}}$, B_{e} and C_{e}) satisfy the isotopic relation

$$X_{\mathrm{e}}' = X_{\mathrm{e}} (m/m') . \qquad (14)$$

Using these equations it is now easy to derive isotopic relations also for the centrifugal distortion constants $\tau_{\alpha\beta\gamma\delta}$ and Coriolis constants ζ_{rs}^{α}, defined by

$$\tau_{\alpha\beta\gamma\delta} = -\tfrac{1}{2} \sum_r a_r^{(\alpha\beta)} a_r^{(\gamma\delta)} / (\lambda_r I_\alpha I_\beta I_\gamma I_\delta)$$

with

$$\alpha, \beta, \gamma, \delta = x, y, z ,$$
$$\lambda_r = (2 \pi c\, \omega_r)^2 ,$$

and

$$\zeta_{rs}^{\alpha} = e_{\alpha\beta\gamma} \sum_i l_{\beta i,r}\, l_{\gamma i,s}$$

with $l_{\beta i,r}$ from Eq. (9) and $e_{\alpha\beta\gamma}$ being the unit antisymmetric tensor, see[13]. The isotopic relations for these quantities are

$$\tau'_{\alpha\beta\gamma\delta} = \tau_{\alpha\beta\gamma\delta} (m/m')^2 \qquad (15)$$

and
$$(\zeta^{\alpha}_{rs})' = \zeta^{\alpha}_{rs} \,. \tag{16}$$

With the help of the equations given so far we are now in a position to derive isotopic relations also for α_r^X, x_{rs} and γ. From their definitions in Eqs. (1), (6) and (8) follows

$$(\alpha_r^X)' = \alpha_r^X (m/m')^{3/2} \,, \tag{17}$$

$$x'_{rs} = x_{rs} (m/m') \tag{18}$$

and

$$\gamma' = \gamma (m/m') \,. \tag{19}$$

The relations (9 – 19) are not confined to the special case of the total substitution of the ozone molecule but are true quite generally whenever a parent molecule consists of only one type of atoms and is totally substituted by an isotope of this atom.

4. Calculation of Force Constants

The computer program used in our calculation was described by Hoy, Mills, and Strey[8] and applied previously to molecules such as HCN[16], H_2O, H_2S, H_2Se, SO_2[17] and C_2H_2[18]. We use an unscaled potential expansion with no summation restrictions as defined in[8], Eq. (6), so that our potential constants in natural internal coordinates as well as in normal coordinates differ from those of Barbe and coworkers by some simple numerical factors given in appendix 1 of[8]. The equilibrium geometry used for ozone was $r_e = 1.2717 (\pm 2)$ Å and $\alpha_e = 116° 47'$ $(\pm 2')$ as reported in[2]. The atomic masses were taken from Rao's tabulation in[19].

The results of our force constant calculation for ozone are summarized in Tables 1 – 5.

Table 1 gives the input data used in the least squares refinement, along with the estimated uncertainties σ_i used to determine weights according to the usual equation $w_i = 1/\sigma_i^2$ and the error vector ε = obs-calc obtained from the refined force field up to fourth order.

The harmonic force field was calculated by a separate least squares procedure refining to the harmonic wavenumbers ω_i of $^{16}O_3$ and $^{18}O_3$ of Barbe and coworkers[2] and to the Coriolis constant ζ^C_{13} of Tanaka and Morino[6], see Table 1, column 2, that is seven data to determine four force constants. The result was found practically identical with that of Barbe and coworkers and is shown in Table 2.

In refining the cubic and quartic force field simultaneously to the $\alpha - s$, $x - s$, and the Darling-Dennison resonance parameters γ given in Table 1 we constrained the quadratic force field to the values in Table 2. Furthermore, as was done by Barbe and coworkers, we constrained three of the quartic potential constants – namely $f_{rrr\alpha}$, $f_{rrr'\alpha}$, and $f_{r\alpha\alpha\alpha}$ – to zero, since the experimental $x - s$ and $\gamma - s$ do not depend on these constants sensitively enough so that these constants have large uncertainties in an unconstrained calculation. Compare a similar discussion for HCN[16] and H_2O[17]. Table 2 gives the best estimates of the force constants up to fourth order with their standard errors compared with the corresponding results obtained by Barbe and coworkers[2].

Although our standard errors are quite small, we feel that they should be multiplied by at least 5 to obtain a realistic assessment of the uncertainties of the force constants due to experimental errors in the spectroscopic parameters.

All cubic constants turn out to be negative. This can roughly be understood through relations such as $f_{rrr} = \partial f_{rr}/\partial r$, $f_{rr\alpha} = \partial f_{r\alpha}/\partial r$, $f_{rrr'} = \partial f_{rr'}/\partial r$, $f_{r\alpha\alpha} = \partial f_{\alpha\alpha}/\partial r$ etc. As was discussed by Strey and Mills[18], one would expect f_{rr}, $f_{rr'}$, $f_{r\alpha}$ and $f_{\alpha\alpha}$ to drop to zero as the OO bonds are stretched symmetrically and hence the cubic constants f_{rrr}, $f_{rrr'}$, $f_{rr\alpha}$, $f_{rr'\alpha}$ and $f_{r\alpha\alpha}$ to be negative. On the other hand arguments of this kind seem not to be conclusive in all cases: in H_2O, for example, the cubic constant $f_{rr\alpha} = 0.404$ ± 0.2 mdyn Å^{-1} is positive in spite of the fact that $f_{r\alpha} = 0.219$ mdyn is also positive.

Table 3 gives the normal coordinate force constants Φ in cm^{-1} for $^{16}O_3$ and $^{18}O_3$.

It is interesting to note that also in ozone the stretching constants f_{rr}, f_{rrr} and f_{rrrr} dominate the whole rest of comparable interaction constants as was already found for many other triatomics studied so far, compare for instance[7, 16, 17] and also the recent review by Mills[20].

But, on the other hand, this domination in ozone is by far not as distinctive (note for example the large positive value of $f_{rr'}$) as for example in H_2O or HCN, where in fact many of the interaction constants might as well be taken to be zero without losing much of the agreement between calculated and observed spectroscopic parameters. More precisely this situation can be illustrated by analyzing the normal coordinate force constants Φ into their contributions from various internal coordinate force constants according to Eqs. (11) in[8]. This analysis[21] shows that the contributions of many of the inter-

Table 1. Observed data (obs), uncertainties (σ) used to determine weights, and observed-calculated (ε) values obtained from the final force field in Table 2, column 1. Numbers in parentheses give the calculated values where there are no observed ones.

	$^{16}O_3$			$^{18}O_3$		
	obs	σ	ε	obs	σ	ε
ω_1/cm^{-1}	1134.9	0.2	−0.1	1070.0	0.2	0.0
ω_2/cm^{-1}	716.0	0.2	0.1	674.75	0.2	−0.1
ω_3/cm^{-1}	1089.2	0.2	0.1	1026.5	0.2	−0.2
$\zeta^C{}_{13}$	0.60	0.02	0.0			
$\alpha_1{}^A/10^{-3}\ cm^{-1}$	−2.981	0.01	0.00			(−2.50)
$\alpha_2{}^A/10^{-3}\ cm^{-1}$	−53.415	0.01	−0.01			(−44.75)
$\alpha_3{}^A/10^{-3}\ cm^{-1}$	53.118	0.01	0.00			(44.50)
$\alpha_1{}^B/10^{-3}\ cm^{-1}$	2.554	0.01	0.01			(2.13)
$\alpha_2{}^B/10^{-3}\ cm^{-1}$	1.269	0.01	0.00			(1.06)
$\alpha_3{}^B/10^{-3}\ cm^{-1}$	3.992	0.01	−0.01			(3.35)
$\alpha_1{}^{C*}/10^{-3}\ cm^{-1}$	2.319	0.10	0.05			(1.90)
$\alpha_2{}^C\ /10^{-3}\ cm^{-1}$	2.307	0.01	−0.03			(1.95)
$\alpha_3{}^{C*}/10^{-3}\ cm^{-1}$	3.613	0.10	−0.04			(2.99)
x_{11}/cm^{-1}	−4.9	0.2	−0.03	−4.3	0.2	0.03
x_{12}/cm^{-1}	−9.1	0.2	−0.2	−7.7	0.2	0.2
x_{13}/cm^{-1}	−34.8	0.2	0.5	−31.4	0.2	0.00
x_{22}/cm^{-1}	−1.0	0.2	0.01	−0.9	0.2	−0.01
x_{23}/cm^{-1}	−17.0	0.2	−0.2	−14.8	0.2	0.2
x_{33}/cm^{-1}	−10.6	0.2	−0.01	−9.4	0.2	0.01
$\gamma\ /cm^{-1}$	−27.05	0.2	−0.5	−24.2	0.2	−0.6

Table 2. Force field for ozone derived in this work, compared with that of Barbe and coworkers. Numbers in parentheses are standard errors of the least squares refinement. The values $\pm\Delta$ are estimated uncertainties as given in [2]. Constrained force constants are marked with an *.

force constant	units	this work		Barbe and coworkers [2]	$\pm\Delta$
f_{rr}	mdynÅ^{-1}	6.164	(3)	6.163	0.002
$f_{rr'}$	mdynÅ^{-1}	1.603	(3)	1.602	0.002
$f_{r\alpha}$	mdyn	0.511	(3)	0.511	0.003
$f_{\alpha\alpha}$	mdynÅ	2.102	(1)	2.102	0.001
f_{rrr}	mdynÅ^{-2}	−54.924	(85)	−54.92	1.89
$f_{rrr'}$	mdynÅ^{-2}	−2.586	(56)	−2.64	0.63
$f_{rr\alpha}$	mdynÅ^{-1}	−3.174	(30)	−3.16	1.00
$f_{rr'\alpha}$	mdynÅ^{-1}	−1.290	(30)	−1.30	0.30
$f_{r\alpha\alpha}$	mdyn	−3.937	(24)	−3.92	0.51
$f_{\alpha\alpha\alpha}$	mdynÅ	−3.794	(3)	−3.78	1.62
f_{rrrr}	mdynÅ^{-3}	397.0	(6.1)	394.7	22.3
$f_{rrrr'}$	mdynÅ^{-3}	77.5	(5.7)	70.1	11.1
$f_{rrr\alpha}$	mdynÅ^{-2}	zero *	—	zero *	—
$f_{rrr'r'}$	mdynÅ^{-3}	74.0	(5.7)	64.6	7.4
$f_{rrr'\alpha}$	mdynÅ^{-2}	zero *	—	zero *	—
$f_{rr\alpha\alpha}$	mdynÅ^{-1}	−32.4	(2.5)	−32.8	12.0
$f_{rr'\alpha\alpha}$	mdynÅ^{-1}	−31.9	(2.5)	−31.6	6.0
$f_{r\alpha\alpha\alpha}$	mdyn	zero *	—	zero *	—
$f_{\alpha\alpha\alpha\alpha}$	mdynÅ	33.8	(2.4)	34.9	7.8

Table 3. Cubic and quartic normal coordinate force constants Φ in cm^{-1} for $^{16}O_3$ and $^{18}O_3$.

	$^{16}O_3$	$^{18}O_3$
Φ_{111}	−288.44	−264.00
Φ_{112}	−59.02	−54.02
Φ_{122}	−50.96	−46.64
Φ_{133}	−452.27	−413.95
Φ_{222}	−114.96	−105.22
Φ_{233}	−119.04	−108.95
Φ_{1111}	53.39	47.44
Φ_{1122}	−6.62	−5.89
Φ_{1133}	111.15	98.78
Φ_{2222}	15.38	13.67
Φ_{2233}	−22.90	−20.35
Φ_{3333}	161.01	143.08

Table 4. L-tensor transposed for $^{16}O_3$. Units are such that $Q_r \sim u^{1/2}$ Å for $r=$ 1, 2, 3; S_1 and $S_3 \sim$ Å, and $S_2 \sim$ radians.

$r\ s\ t$	S_1	S_2	S_3
1	0.30687	−0.26117	—
2	0.05192	0.34823	—
3	—	—	0.39142
1 1	0.03067	0.08913	—
1 2	−0.04089	−0.05188	—
1 3	—	—	−0.01862
2 2	0.05452	−0.02011	—
2 3	—	—	0.02483
3 3	0.01130	−0.06902	—
1 1 1	−0.01570	−0.03672	—
1 1 2	0.01307	0.00326	—
1 1 3	—	—	−0.00032
1 2 2	−0.00696	0.02226	—
1 2 3	—	—	0.00520
1 3 3	0.00618	0.00210	—
2 2 2	−0.00472	−0.01937	—
2 2 3	—	—	−0.01330
2 3 3	−0.01113	0.03260	—
3 3 3	—	—	−0.00738

Table 5. Parameters a_3 and a_4 for O_2 and O_3 molecules.

	O_2 (from [20])	O_3
a_3/Å^{-1}	2.48	2.97
a_4/Å^{-1}	2.75	3.03

action constants are not negligible any more. Bearing in mind that we were forced to constrain three of the interaction force constants of fourth order to zero because of lack of additional experimental data, one should be even more careful in judging the accuracy of the calculated force constants given in Table 2. If one would include these remaining interaction force constants this could perhaps affect considerably the values of some of the others.

Table 4 gives the expansion coefficients of the internal symmetry coordinates $S_1 = (\delta r_1 + \delta r_2)/\sqrt{2}$, $S_2 = \delta\alpha$ and $S_3 = (\delta r_1 - \delta r_2)/\sqrt{2}$ into normal coordinates Q_r, that is, the L-tensor elements for $^{16}O_3$. The units of the L-tensor elements are obtained by dividing the units of the symmetry coordinates (Å for stretches, or dimensionless for bends) by the appropriate powers of units of the normal coordinates (which are $u^{1/2}$ Å; $u = \mathrm{kg}/6.022169 \times 10^{26}$).

As can be seen, the higher derivatives are much smaller than for other molecules as for example H_2O.

Another difference between ozone and other molecules studied so far is found by comparing the stretching constants f_{rr}, f_{rrr} and f_{rrrr} with the corresponding constants of oxygen O_2 and analyzing them in terms of a Morse curve model potential $V = D\,(1 - e^{-a(r - r_e)})^2$, as was first proposed by Kuchitsu and Morino [7, 22]. Expanding this function around $r = r_e$ allows to compare the coefficients a and D with our (unscaled) potential constants.

One gets

$$\begin{aligned} f_{rr} &= 2\,a^2 D\,, \\ f_{rrr} &= -6\,a^3 D = -3\,a\,f_{rr}\,, \\ f_{rrrr} &= 14\,a^4 D = 7\,a^2 f_{rr}\,. \end{aligned}$$

Even diatomic molecules of course do not fit these formulae accurately. Therefore it is advantageous to write

$$\begin{aligned} f_{rrr} &= -3\,a_3 f_{rr}\,, \\ f_{rrrr} &= 7\,a_4^2 f_{rr} \end{aligned} \tag{20}$$

taking a_3 and a_4 as independent parameters which in practice appear to be nearly equal and in many cases are close to 2 Å^{-1}, compare also Mills [20]. As shown in Table 5, for ozone there is a considerable increase of these parameters compared with the values for oxygen O_2 taken from Mills' tabulation [20].

We have also investigated the problem of multiple solutions for the potential constants which has been discussed extensively in two recent papers by Spirko and Speirs [23, 24].

Excluding the two Coriolis disturbed rotational interaction constants α_1^{C*} and α_3^{C*} from our input data and starting the iteration process with a few randomly chosen trial sets of force constants we found two different, mathematically equivalent solutions which reproduce the anharmonic corrections x_{rs} equally well but which predict nonequivalent sets of the rotational interaction constants α_r^X (the constant α_3^B has opposite signs in the two calculations, and also α_1^B, α_1^{C*} and α_3^{C*} are rather different).

Only solution I given in Table 2, however, has been found to be physically acceptable, because for solution II the quartic stretching constant is negative ($f_{rrrr} = -198$ mdyn/Å^3) and the interaction force constant $f_{rrr'r'}$ is very large – even larger than $|f_{rrrr}|$.

When we included the two remaining experimental data α_1^{C*} and α_3^{C*} the final solution I became unambiguously determined and independent of the input trial force field.

There exists another force field calculation up to fourth order for ozone published by Smith [25] in 1973. However, it is difficult to compare his results

Table 6. Vibrational band centers in cm^{-1} for non totally isotopic substituted ozone molecules. Observed (obs) from Barbe and coworkers [2], calculated (calc) from the force constants in Table 2, column 1, observed-calculated (obs-calc). Levels disturbed by Darling-Dennison resonance are connected by a bracket.

molecule	level	obs	calc	obs-calc
$^{16}O^{18}O^{16}O$	001	1008.5	1008.2	0.3
	101	2049.3	2049.5	−0.2
	111	2718.1	2714.9	3.2
$^{18}O^{16}O^{18}O$	001	1019.1	1019.2	−0.1
	011	1671.2	1672.1	−0.9
	101	2060.1	2057.8	2.3
	111	2703.4	2705.2	−1.8
	003 }	2980.3	2990.5	−10.2
	201 }	—	3090.3	—
$^{16}O^{16}O^{18}O$	001	1028.0	1028.2	−0.2
	011	1695.4	1697.9	−2.5
	101	2090.0	2097.9	−7.9
	111	2748.5	2759.4	−10.9
	003 }	2998.8	3005.6	−6.8
	201 }	—	3148.4	—
$^{16}O^{18}O^{18}O$	001	994.0	994.0	0.0
	011	1656.8	1656.5	0.3
	101	2027.5	2034.5	−7.0
	111	2680.5	2686.8	−6.3
	003 }	2903.0	2910.7	−7.7
	201 }	—	3059.5	—

with ours since Smith used the vibrational levels of liquid ozone as input data which were the only available at that time.

For testing the quality of our force field we have finally calculated the band centers of some mixed substituted ozone molecules not used in the refinement. In Table 6 some of these calculated band centers are compared with experimental values, as listed by Barbe, Secroun, and Jouve [2], Table XIII.

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