

INTRAMOLECULAR POTENTIAL FUNCTION OF POLYATOMIC MOLECULES BY VIBRATION- ROTATION INTERACTIONS

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INTRODUCTION

Vibration-rotation interactions appear in various fields of molecular spectroscopy and their investigation is of considerable interest. The theory of the vibration-rotation energy of molecules was first formulated by Wilson and Howard¹; it has since been brought to perfection by H. H. Nielsen and his co-workers². Amat and others³ have extended Nielsen's second-order theory to the fourth-order and have elucidated many interesting phenomena which have come to light through the recent development of spectroscopic techniques.

High-resolution infrared spectroscopy should be a fertile field for the application of the theory; indeed, the theory has already led to outstanding findings on the molecular structure and potential functions. The study of asymmetric-top molecules by the infrared⁴ is painstaking, because the spectra are very complicated. In this connection the work by Mills⁵, Werner⁶, and Dows⁷ should be mentioned. They have shed fresh light on this field. On the other hand, microwave spectroscopy can treat even asymmetric-top molecules rather easily, because the microwave spectrum involves only simple rotational transitions.

In this situation it must be evident that the cooperation of infrared and microwave spectroscopists promises substantial progress in both fields: the introduction of knowledge about asymmetric-top molecules into the study of the infrared spectrum will give us a basis for the analysis of the complicated pattern of the infrared spectra, while at the same time the introduction of the knowledge of vibrating molecules into the study of microwave spectra will open up a vast new field to the microwave spectroscopists, who have thus far been primarily concerned with the vibrationally-ground states. In each case, the guiding principle is the theory of vibration-rotation interactions, and the results to be obtained concern the properties of vibrating molecules.

Before entering into detail on individual examples, it would be worthwhile to summarize the main sources of the vibration-rotation interactions. The first one is the change in the moments of inertia; the moments of inertia are not constant when atoms vibrate about their equilibrium positions. If we expand the instantaneous moments of inertia in terms of the normal coordinates:

$$I_{\alpha\alpha} = I_{\alpha}^{(e)} + \sum_s a_s^{(\alpha\alpha)} Q_s + \sum_{s,s'} [A_{ss'}^{(\alpha\alpha)} - \sum_{s''} \zeta_{ss''}^{(\alpha)} \zeta_{s''s'}^{(\alpha)}] Q_s Q_{s'} \quad (1)$$

then the second and third terms make so-called harmonic contributions to the interactions.

The second of the main sources is the Fermi resonance. It arises from a term such as $k_{ss's'}q_s q_{s'}^2$ in the anharmonic potential function. It produces a shift of the energy level:

$$\pm [(E_v - E_{v'})^2 + 4k_{ss's'}^2 \langle v | q_s q_{s'}^2 | v' \rangle^2]^{\frac{1}{2}} \quad (2)$$

The $k_{ss's'}/(E_v - E_{v'})$ ratio is a measure of the Fermi resonance, which becomes large when the two vibrating levels come close together. Since the perturbation involves only vibrational coordinates, interaction occurs between the levels with the same K values. By the Fermi resonance, the rotational constants of the two states mix together.

The third source is the Coriolis coupling. The Coriolis force is a virtual force arising from the fact that, if the rotating molecule is observed from the molecule-fixed coordinate system, the molecule appears to be acted upon by a kind of force. It is given by the term:

$$-\frac{\hbar^2}{I_\alpha^{(e)}} \sum_{ss'} \zeta_{ss'}^{(\alpha)} \left(\sqrt{\frac{\omega_{s'}}{\omega_s}} q_s p_{s'} - \sqrt{\frac{\omega_s}{\omega_{s'}}} q_{s'} p_s \right) P_\alpha \quad (3)$$

There is an interaction between the two levels with $\Delta K = 0, \pm 1$ in the two vibrational states, and the effect becomes larger when the two levels come close together. The Coriolis coupling constant between two normal vibrations is given by the sum of the vector products of the atomic displacements in the two vibrations:

$$\zeta_{ss'}^{(\alpha)} = \sum_i (l_{is}(\beta) l_{is'}(\gamma) - l_{is'}(\beta) l_{is}(\gamma)) \quad (4)$$

For instance, for a bent triatomic molecule, $\zeta_{12}^{(c)} = 0$ by the complete cancellation of the two vector products. $\zeta_{13}^{(c)}$ is finite but small, while $\zeta_{23}^{(c)}$ is large, as may be easily understood by referring to *Figure 1*. It may be noted here that, when the molecule has a degenerate vibration, the Coriolis interaction between the two components of the vibration gives a first-order term, $\mp 2\zeta_t^{(z)} A l_t K$.

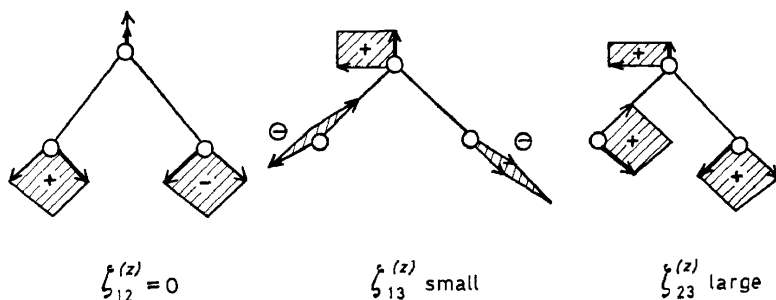


Figure 1. Coriolis coupling in SO_2

CUBIC POTENTIAL CONSTANTS

According to the theory of molecular vibrations², the vibration-rotation interaction constants, α , in the expansion of the rotational constant:

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$$B_v = B_e - \alpha_1(v_1 + \frac{1}{2}) - \alpha_2(v_2 + \frac{1}{2}) - \alpha_3(v_3 + \frac{1}{2}), \quad (5)$$

have the following relations to the cubic potential constants⁸:

$$\begin{aligned} \alpha_1^A &= -6 \frac{k_{111}}{\omega_1} \left(2 \frac{A_e^3}{\omega_1}\right)^{\frac{1}{2}} \sin \gamma + 2 \frac{k_{112}}{\omega_2} \left(2 \frac{A_e^3}{\omega_2}\right)^{\frac{1}{2}} \cos \gamma - 6 \frac{A_e^2}{\omega_1} \sin^2 \gamma \\ \alpha_1^B &= -6 \frac{k_{111}}{\omega_1} \left(2 \frac{B_e^3}{\omega_1}\right)^{\frac{1}{2}} \cos \gamma - 2 \frac{k_{112}}{\omega_2} \left(2 \frac{B_e^3}{\omega_2}\right)^{\frac{1}{2}} \sin \gamma - 6 \frac{B_e^2}{\omega_1} \cos^2 \gamma, \\ \alpha_2^A &= +6 \frac{k_{222}}{\omega_2} \left(2 \frac{A_e^3}{\omega_2}\right)^{\frac{1}{2}} \cos \gamma - 2 \frac{k_{122}}{\omega_1} \left(2 \frac{A_e^3}{\omega_1}\right)^{\frac{1}{2}} \sin \gamma - 6 \frac{A_e^2}{\omega_2} \cos^2 \gamma, \end{aligned} \quad (6)$$

$$\begin{aligned} \alpha_2^B &= -6 \frac{k_{222}}{\omega_2} \left(2 \frac{B_e^3}{\omega_2}\right)^{\frac{1}{2}} \sin \gamma - 2 \frac{k_{122}}{\omega_1} \left(2 \frac{B_e^3}{\omega_1}\right)^{\frac{1}{2}} \cos \gamma - 6 \frac{B_e^2}{\omega_2} \sin^2 \gamma, \\ \alpha_3^A &= -2 \frac{k_{133}}{\omega_1} \left(2 \frac{A_e^3}{\omega_1}\right)^{\frac{1}{2}} \sin \gamma + 2 \frac{k_{233}}{\omega_2} \left(2 \frac{A_e^3}{\omega_2}\right)^{\frac{1}{2}} \cos \gamma - 6 \frac{C_e A_e}{\omega_3}, \\ \alpha_3^B &= -2 \frac{k_{133}}{\omega_1} \left(2 \frac{B_e^3}{\omega_1}\right)^{\frac{1}{2}} \cos \gamma - 2 \frac{k_{233}}{\omega_2} \left(2 \frac{B_e^3}{\omega_2}\right)^{\frac{1}{2}} \sin \gamma - 6 \frac{C_e B_e}{\omega_3}, \\ \sin \gamma &= \frac{a_1(aa)}{2\sqrt{Ia(e)}} = \frac{a_2(bb)}{2\sqrt{Ib(e)}}, \quad \cos \gamma = \frac{a_1(bb)}{2\sqrt{Ib(e)}} = -\frac{a_2(aa)}{2\sqrt{Ia(e)}}, \end{aligned} \quad (7)$$

where $k_{ss's''}$ is the coefficient of the expansion of the potential function in terms of the dimensionless normal coordinates:

$$V/hc = \frac{1}{2} \sum_s \omega_s q_s^2 + \sum_{ss'} k_{ss's'} q_s q_{s'} + \sum_{ss's''} k_{ss's''} q_s q_{s'} q_{s''} \quad (8)$$

When we measure the rotational constants in the excited vibrational states, we obtain α ; by then combining α_1^A and α_1^B , we obtain k_{111} and k_{112} . From α_2^A and α_2^B , we obtain k_{122} and k_{222} , and from α_3^A and α_3^B we obtain k_{133} and k_{233} . Thus, from the six α 's we get all of the six cubic constants of the bent triatomic molecule. We have performed the measurement of the microwave spectra in the vibrationally-excited states of SO_2^8 , OF_2^9 , O_3^{10} and SeO_2^{11} . The results are summarized in *Table 1*. A considerable correspondence will be seen among the four molecules: k_{133} is always large, k_{111} is always nearly the same, and k_{222} decreases in magnitude, while k_{133} increases from O_3 to SeO_2 .

With these four molecules we have encountered various cases of vibration-rotation interaction. The SO_2 molecule is a case where neither the Fermi resonance nor the Coriolis coupling gives any serious anomaly⁸. It can be treated with the standard theory of molecular vibrations developed by H. H. Nielsen and his co-workers. We were fortunate that we treated this molecule first, only later extending our study to more difficult cases.

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The OF₂ molecule is a case where the Fermi resonance is remarkable between the ν_1 and ν_{22} states⁹. Figure 2 shows the rotational spectral pattern

Table 1. Cubic potential constants of bent triatomic molecules (cm⁻¹)

	O ₃	OF ₂	SO ₂	SeO ₂
k_{111}	-47.3	-40.0	-44.1	-36.6
k_{222}	-19.1	-16.0	-6.6	-1.4
k_{112}	-29.4	-22.0	-18.9	-2.0
k_{122}	-22.7	-9.8	9.3	-2.4
k_{133}	-216.8	-139.8	-159.7	-100.7
k_{233}	-59.7	-31.8	4.8	11.9

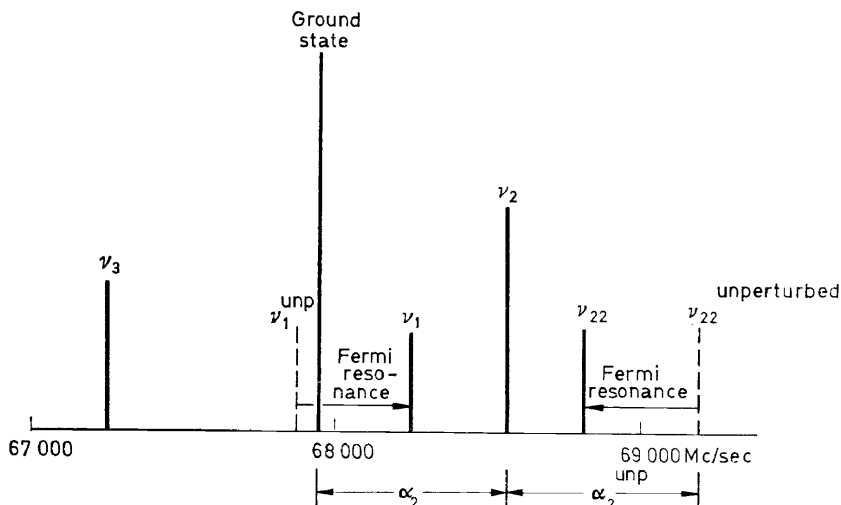


Figure 2. Rotational transition pattern ($1_{11} \leftarrow 0_{00}$) of OF₂
 Mixing ratio $b^2 = 0.325$ ($\Psi_1 = a\Psi_{10} + b\Psi_{22}$)

for the $1 \leftarrow 0$ transitions. The lines for the ν_{22} state show so large a deviation from the expected position that their assignment was very difficult. At any rate, we succeeded in determining the assignment, and as a result we obtained the mixing ratio of the two resonating states: $b^2 = 0.325$ and α for the unperturbed states, and then the cubic potential constants listed in Table 1.

The ozone molecule is a case where the Coriolis coupling is strong between the ν_1 and ν_3 states, as was pointed out by Clough and Kneizys from their study of the infrared spectra¹². Since Coriolis interaction is different for each rotational state, the rigid rotor formula with constant A , B , and C does not hold and we have to solve a secular equation with a cross term between the two vibrational states. The rotational Hamiltonian takes the form of:

$$H_{11} = \nu_1 + A_1 P_a^2 + B_1 P_b^2 + C_1 P_c^2 + \frac{1}{4} \sum \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta, \quad (9)$$

$$H_{33} = \nu_3 + A_3 P_a^2 + B_3 P_b^2 + C_3 P_c^2 + \frac{1}{4} \sum \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta,$$

$$H_{13} = iDP_c + F(P_aP_b + P_bP_a) \quad (10)$$

where

$$D = C_e \left(\sqrt{\frac{\omega_3}{\omega_1}} + \sqrt{\frac{\omega_1}{\omega_3}} \right) \zeta_{13}^{(e)} \quad (11)$$

and

$$F = \frac{A_e}{I_b^{(e)}} \left[\frac{1}{8\pi} \left(\frac{h}{c} \right)^{\frac{3}{2}} \frac{a_3^{(ab)} k_{133}}{\omega_3^{\frac{3}{2}}} \left(\frac{2}{\omega_3} + \frac{1}{\omega_1} + \frac{1}{2\omega_3 - \omega_1} \right) \right. \\ \left. - \frac{h}{8\pi^2 c} \frac{1}{(\omega_1 \omega_3)^{\frac{3}{2}}} \left\{ A_{13}^{(ab)} + A_{13}^{(ba)} - a_3^{(ab)} \left(\frac{a_1^{(aa)}}{I_a^{(e)}} + \frac{a_1^{(bb)}}{I_b^{(e)}} \right) \right\} \right] \quad (12)$$

The last terms in equation (9) designate the centrifugal distortion effect. The matrix elements are calculated on the basis of the rotational wave functions of the Wang type for the asymmetric rotor. The interaction Hamiltonian, H_{13} , couples the (J, K, M) levels of the v_1 state with the $(J, K + 1, M)$ levels of the v_3 state.

By this procedure we obtain the three unperturbed rotational constants A_1 , B_1 , and C_1 , together with $\zeta_{13}^{(e)}$ and two cubic constants, k_{133} and k_{233} . The later two constants, k_{133} and k_{233} , have direct connections with the rotational constants, A_3 , B_3 , and C_3 , as well as with the first term of F . A_1 and B_1 provide k_{111} and k_{112} . The remaining two constants, k_{222} and k_{122} , are obtained from A_2 and B_2 for the v_2 state, where the usual rigid rotor formula holds perfectly. The cubic constants listed in *Table 1* were obtained in this way¹⁰.

Finally, the SeO_2 molecule is a case where we have met with experimental difficulties¹¹. The vapour pressure of selenium dioxide is so low that we have to use a high-temperature cell. On the other hand, SeO_2 easily decomposes at high temperatures, and the selenium metal easily deposits on the inner surface of the waveguide. With regard to the analysis, SeO_2 is a rather simple case, where no special interaction is large and Nielsen's theory can be applied in a straightforward way. One difficulty in the analysis is, however, that the exact frequency of the v_2 vibration is not known. It has been obtained from the inertia defect, as will be described later.

The above treatment assumes that the higher terms, γ_{ss}' can be neglected in the expansion of the rotational constants:

$$B_v = B_e - \sum_s \alpha_s (v_s + \frac{1}{2}) + \sum_{ss'} \gamma_{ss}' (v_s + \frac{1}{2}) (v_{s'} + \frac{1}{2}). \quad (13)$$

Thus, one may wonder whether the cubic constants obtained above do not involve uncertainties arising from this neglect. The good correspondence among the cubic constants of the four molecules may be an indication of the reliability of the results; however, in order to test this point further, we have measured the microwave spectra of the SO_2 molecule in highly excited states, i.e., in the first-overtone and combination states of the three normal vibrations. The measurement was difficult because of the small Boltzmann factor, $\exp(-\Delta E/kT)$, at higher excited states; really, the intensity of the

microwave absorption in the ν_{33} state decreases to 0.01 per cent of the ground-state line. It was found that the $\gamma_{ss'}$ constants were only a few per cent or less of the corresponding α_s , as is shown in *Table 2*. Accordingly, the uncertainties of the cubic constants may be of this order. This confirmation has

Table 2. Rotational constants of SO_2 (MHz)

s	α_s^A	α_s^B	α_s^C
1	-33.60	50.14	42.75
2	-1127.41	-2.40	15.98
3	612.44	34.24	32.03
s s'	$\gamma_{ss'}^A$	$\gamma_{ss'}^B$	$\gamma_{ss'}^C$
1 1	0.46	0.13	0.21
2 2	27.31	-0.12	-0.03
3 3	3.01	-0.25	-0.03
1 2	7.00	0.30	0.65
2 3	-19.25	-0.26	-0.58
3 1	-7.94	-0.04	0.99

$$A_0 = 60502.05 \quad B_0 = 10359.24 \quad C_0 = 8845.57$$

been obtained only for SO_2 , not for other molecules, but this finding at least gives us some evidence regarding the magnitude of the γ constants.

QUARTIC POTENTIAL CONSTANTS

The anharmonic factors in the vibrational frequencies, usually called $x_{ss'}$:

$$E_{v_1 v_2 v_3} / hc = \omega_1(v_1 + \frac{1}{2}) + \omega_2(v_2 + \frac{1}{2}) + \omega_3(v_3 + \frac{1}{2}) + \sum_{ss'} x_{ss'}(v_s + \frac{1}{2})(v_{s'} + \frac{1}{2})$$
(14)

are functions of quadratic, cubic, and quartic potential constants⁸:

$$\begin{aligned}
 x_{11} &= \frac{3}{2}k_{11111} - \frac{15}{4} \frac{1}{\omega_1} k_{111}^2 - \frac{8\omega_1^2 - 3\omega_2^2}{4\omega_2(4\omega_1^2 - \omega_2^2)} k_{112}^2 \\
 x_{22} &= \frac{3}{2}k_{22222} - \frac{15}{4} \frac{1}{\omega_2} k_{222}^2 - \frac{8\omega_2^2 - 3\omega_1^2}{4\omega_1(4\omega_2^2 - \omega_1^2)} k_{122}^2 \\
 x_{33} &= \frac{3}{2}k_{33333} - \frac{8\omega_3^2 - 3\omega_1^2}{4\omega_1(4\omega_3^2 - \omega_1^2)} k_{133}^2 - \frac{8\omega_3^2 - 3\omega_2^2}{4\omega_2(4\omega_3^2 - \omega_2^2)} k_{233}^2 \\
 x_{12} &= k_{11222} - \frac{3}{\omega_1} k_{111} k_{112} - \frac{3}{\omega_2} k_{112} k_{222} - \frac{2\omega_1}{4\omega_1^2 - \omega_2^2} k_{112}^2 \\
 &\quad - \frac{2\omega_2}{4\omega_2^2 - \omega_1^2} k_{122}^2
 \end{aligned}
 \tag{15}$$

$$x_{13} = k_{1133} - \frac{3}{\omega_1} k_{111} k_{133} - \frac{3}{\omega_2} k_{112} k_{233} - \frac{2\omega_3}{4\omega_3^2 - \omega_1^2} k_{133}^2 + C_e \left(\frac{\omega_3}{\omega_1} + \frac{\omega_1}{\omega_3} \right) \left(\zeta_{13}^{(c)} \right)^2$$

$$x_{23} = k_{2233} - \frac{3}{\omega_2} k_{222} k_{233} - \frac{1}{\omega_1} k_{122} k_{133} - \frac{2\omega_3}{4\omega_3^2 - \omega_2^2} k_{233}^2 + C_e \left(\frac{\omega_3}{\omega_2} + \frac{\omega_2}{\omega_3} \right) \left(\zeta_{23}^{(c)} \right)^2$$

Now that we have obtained all the cubic constants, the observed values of $x_{ss'}$ immediately yield the quartic potential constants. We have made the calculations on SO_2 , using the results of the vibrational analysis carried out by Shelton, Nielsen, and Fletcher¹³. The results are shown in *Table 3*. Recently Nebgen obtained the $x_{ss'}$ of OF_2 from an analysis of the infrared band maxima¹⁴, taking into account the results of the microwave study of the Fermi resonance. For exact treatment, we should use the band-origins, not the band maxima, but the calculated values without the corrections have shown nice correspondence with those for SO_2 , as is shown in *Table 3*.

Table 3. Quartic potential constants of SO_2 and OF_2 (cm^{-1})

	SO_2	OF_2
k_{1111}	1.7	1.8
k_{2222}	-1.7	1.1
k_{3333}	3.1	1.8
k_{1122}	-2.6	-0.6
k_{1133}	15.4	17.0
k_{2233}	-6.1	-5.8

NATURE OF POTENTIAL FUNCTION

The potential functions obtained above were expressed in terms of the normal coordinates. Other expressions of the potential functions may be introduced either by expansion using the internal coordinates, i.e., small displacements in bond lengths and bond angles, or by expansion in terms of the localized Cartesian coordinates¹⁵. Mathematically speaking, they are all equivalent; any one can be transformed into any other, using a transformation of the coordinate system. The problem is, which of them is the most convenient for discussing the nature of the potential function. It has been current opinion in vibrational spectroscopy, where only the harmonic force field is important, that the transferability of the potential function from molecule to molecule may be a guiding principle for the selection of the potential function expression¹⁶. However, if we treat the potential function involving higher-order terms, we may have another kind of criterion:

a potential function expression is preferable when it converges more rapidly than the others.

A likely hint is given by the potential maps of CO_2 and HCN obtained by Pariseau, Suzuki, and Overend with the least-squares calculations^{17, 18}. They found that the potential valley has a curvature very close to a circle, with its centre at the carbon atom (see *Figure 3*). This fact clearly indicates

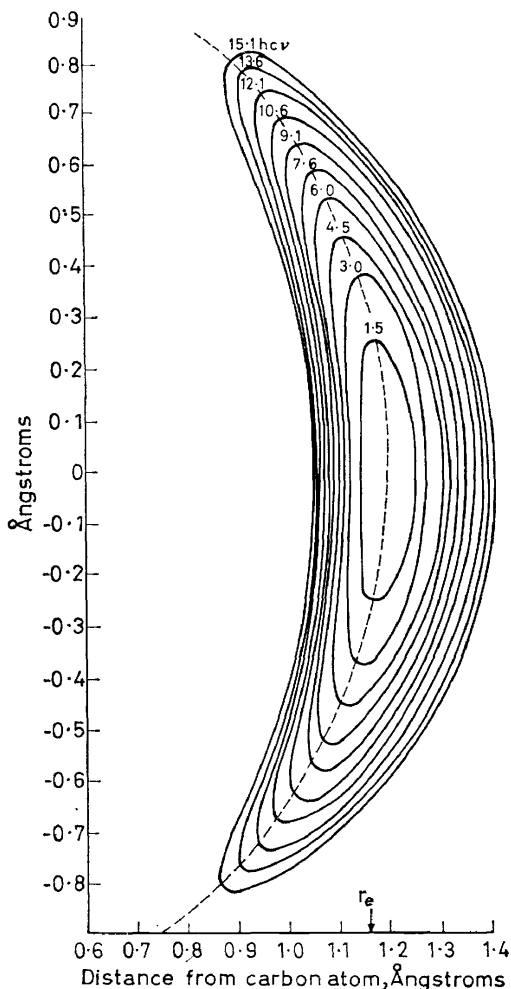


Figure 3. Potential map for CO_2 by Pariseau, Suzuki and Overend

that the internal coordinate system is preferable if the bond-angle deviation is taken as one of the coordinates.

Table 4 illustrates the third-order constants of the potential function which is transformed into the internal coordinate system. The table reveals several interesting facts. First, almost all the constants have negative values, if we take the plus directions of the variables as the increase in the bond lengths

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and bond angles. The other fact is that f_{rrr} is large compared with the other five. Even more interesting is that, as has already been pointed out also by Overend and others^{17, 18}, the observed values of f_{rrr} and even f_{rrrr} are close to those of the diatomic molecule or radical consisting of the corresponding

Table 4. Third-order potential constants in internal coordinates

		O ₃	OF ₂	SO ₂	SeO ₂
f_{rrr}	md/Å ²	-8.43	-4.53	-11.85	-6.86
f_{rrr}'	md/Å ²	-1.28	-0.82	-0.57	-0.93
f_{rra}	md/Å	-1.37	-0.67	-0.68	0.68
$f_{rr'a}$	md/Å	-1.06	-0.41	-0.76	-1.03
f_{raa}	md	-1.81	-1.31	-0.90	-1.44
f_{aaa}	mdÅ	-0.63	-0.55	-0.41	-0.08

two atoms. Thus, we have a simple but convenient model for the potential function: that is, in addition to the harmonic potentials, anharmonic terms are assumed only for the bonded atom pairs, which are transferred from the corresponding diatomic molecule or radical¹⁹. We will call this model the *Valence Force Model*. The assumption is very simple, but it reproduces fairly well the largest term of the anharmonic potential function, as is shown in Figure 4. Yet, of course, this model gives only the f_{rrr} and f_{rrrr} terms; all the

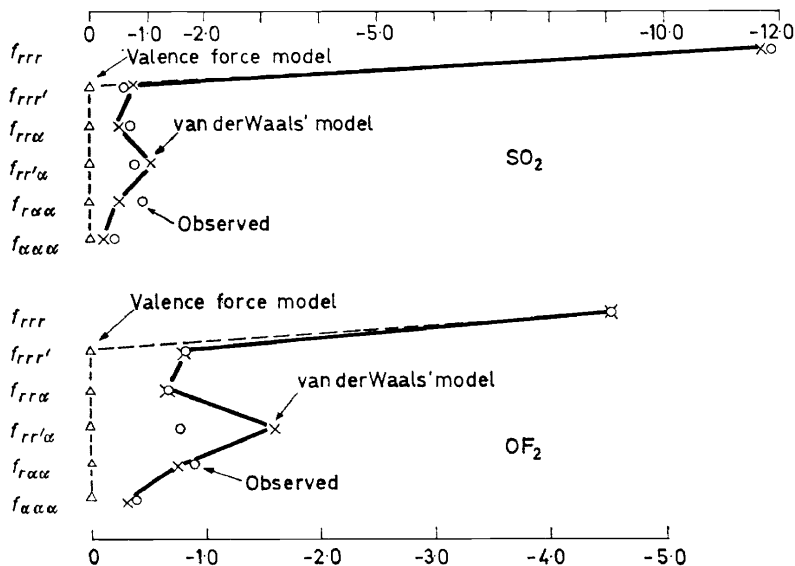


Figure 4. Approximate estimate of potential function

other terms are zero according to this assumption. Their actual values are in fact finite, although they are small. The important point is that they were almost all found to be negative. For the refinement of the simple Valence Force Model on this point, the van der Waals' interaction between the

nonbonded atoms seems to be attractive²⁰. A Lennard-Jones-type or Buckingham-type potential with suitable parameter values offers an improved model. *Figure 4* shows that the *van der Waals' Model* brings the calculated values towards the observed values, although there are still a few minor deviations.

ANHARMONIC POTENTIAL FUNCTION FOR HIGHER POLYATOMIC MOLECULES

So far the vibration-rotation interactions have been considered for bent triatomic molecules. The same method of attack may be extended to higher polyatomic molecules. As a matter of fact, a number of attempts have already been made in the studies of, for instance, NF_3 ²¹, formaldehyde²², methyl halide²³, malononitrile²⁴, and acetonitrile²⁵. As one can easily imagine, with the increase in the number of atoms in the molecule, the complexity of the potential function increases rapidly and the standard method such as that used for triatomic molecules must be modified somewhat. The most reasonable approach for these complex molecules must start with finding an approximate potential function on the basis of some drastic assumptions, and then refine it further by the measurement of other molecular properties. Let us consider ammonia as an example²⁶.

The third-order potential of this molecule is described by the 14 parameters listed in *Table 5*. This molecule has four normal frequencies and two different values of the moments of inertia, so that we have 8 α 's for NH_3 and another

Table 5. Third-order potential constants of NH_3 and ND_3

f_{rrr}	Δr_1^3	-7.01 md/Å ²	f_{raa}	$\Delta r_1 \Delta \alpha_1^2$	} -0.17 md
f_{rrr}'	$\Delta r_1^2 \Delta r_2$	-0.55 md/Å ²	$f_{r'aa}$	$\Delta r_1 \Delta \alpha_2^2$	
f_{rrr}''	$\Delta r_1 \Delta r_2 \Delta r_3$	-0.54 md/Å ²	f_{raa}'	$\Delta r_1 \Delta \alpha_1 \Delta \alpha_2$	} -0.13 md
f_{rrr}'''	$\Delta r_1^2 \Delta \alpha_1$	} (a) -0.27 md/Å	f_{raa}''	$\Delta r_1 \Delta \alpha_2 \Delta \alpha_3$	
f_{rra}	$\Delta r_1^2 \Delta \alpha_2$		f_{aaa}	$\Delta \alpha_1^3$	-0.17 mdÅ
$f_{rr'a}$	$\Delta r_1 \Delta r_2 \Delta \alpha_1$	} -0.40 md/Å	f_{aaa}'	$\Delta \alpha_1^2 \Delta \alpha_2$	} (0.00) assumed
$f_{rr'a}''$	$\Delta r_1 \Delta r_2 \Delta \alpha_3$		f_{aaa}''	$\Delta \alpha_1 \Delta \alpha_2 \Delta \alpha_3$	

(a) Terms linked by braces area assumed to be equal in magnitude.

8 α 's for ND_3 . Thus, 16 observed quantities are available for the 14 parameters to be determined. It turns out, however, that the 8 α 's of ND_3 are related to the corresponding NH_3 constants so closely that the isotope data supply little independent information on the cubic constants. After several attempts, we concluded that the most reasonable way was to get only 8 parameters by the use of the assumptions shown in *Table 5*. These assumptions are not at all free of arguable points, and they must be refined further with other kinds of observations. At any rate, it is interesting to see that the f constants are all of a reasonable magnitude and that they are all negative, just as was found with the triatomic molecules.

HARMONIC FORCE CONSTANTS

For the general quadratic potential function of a bent triatomic molecule, four force constants are necessary:

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$$V = \frac{1}{2}f_r[(\Delta r_1)^2 + (\Delta r_2)^2] + \frac{1}{2}f_\alpha(\Delta\alpha)^2 + f_{rr'}\Delta r_1\Delta r_2 + f_{r\alpha}(\Delta r_1 + \Delta r_2)\Delta\alpha \quad (16)$$

However, we have only three vibrational frequencies. The Coriolis coupling constant is the most convenient to fill the gap; we obtained it from the inertia defect of the rotational constant. The inertia defect is defined as the difference between the moments of inertia, I_c , perpendicular to the molecular plane, minus the sum of $I_a + I_b$. It is zero for the equilibrium configuration of a planar molecule, but it is not zero when the atoms vibrate about their equilibrium positions. The inertia defect involves a number of additional terms, such as the electronic contribution or the centrifugal distortion correction²⁷, but if we take the difference between the inertia defect in a vibrationally-excited state and that in the ground state, the difference is directly connected only with the Coriolis coupling constant:

$$\begin{aligned} \Delta(v_1 = 1) - \Delta_0 &= \frac{h}{\pi^2c} \frac{\omega_3^2}{\omega_1(\omega_3^2 - \omega_1^2)} (\zeta_{13}^{(c)})^2 \\ \Delta(v_2 = 1) - \Delta_0 &= \frac{h}{\pi^2c} \frac{\omega_3^2}{\omega_2(\omega_3^2 - \omega_2^2)} [1 - (\zeta_{13}^{(c)})^2], \\ \Delta(v_3 = 1) - \Delta_0 &= \frac{h}{\pi^2c} \frac{1}{\omega_3} \left[\frac{\omega_2^2}{\omega_2^2 - \omega_3^2} + \left(\frac{\omega_1^2}{\omega_1^2 - \omega_3^2} + \frac{\omega_2^2}{\omega_2^2 - \omega_3^2} \right) \right. \\ &\quad \left. (\zeta_{13}^{(c)})^2 \right] \end{aligned} \quad (17)$$

By combining the Coriolis coupling constant thus obtained with the three vibrational frequencies, the quadratic force constants listed in *Table 6* were

Table 6. Harmonic potential constants for bent triatomic molecules

	O ₃	OF ₂	SO ₂	SeO ₂
$(\zeta_{13}^{(c)})^2$	0.371	0.426	0.094	0.031
f_r md/Å	5.74	3.97	10.33	6.92
$f_{rr'}$ md/Å	1.57	0.83	0.08	0.04
f_α md/Å	2.05	1.42	1.68	1.38
$f_{r\alpha}$ md	0.50	0.21	0.33	0.04

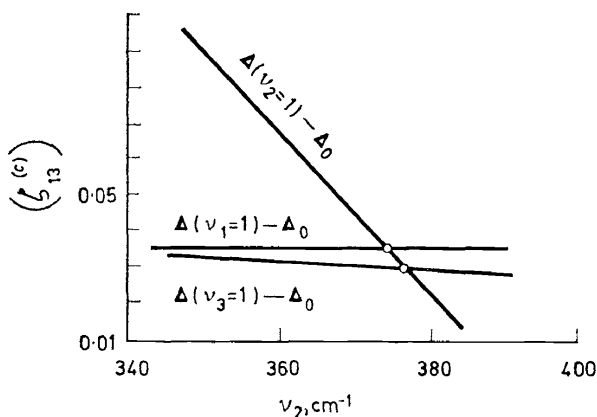
obtained in a straightforward way. Their values are in good agreement with those obtained by means of the centrifugal distortion constants or by means of the frequency shifts in isotopic species. An example is shown for SO₂ in *Table 7*^{28, 29}.

As has already been mentioned, the exact frequency, ν_2 , of SeO₂ is not known. Considering the fact that the inertia defect differences are functions of vibrational frequencies and the Coriolis coupling constant [see equations (17)], ν_2 and $\zeta_{13}^{(c)}$ can easily be obtained by combining the inertia defect

Table 7. Comparison of harmonic potential constants of SO₂ obtained by various methods

	From inertia defect Morino <i>et al.</i>	From isotopic shifts Polo, Wilson ²⁹	From D Kivelson ²⁸
f_r md/Å	10.33	10.02	10.006
f_{rr} md/Å	0.08	0.03	0.0236
f_a mdÅ	1.668	1.624	1.623
f_{ra} md	0.33	0.29	0.270

differences for three vibrationally-excited states¹¹. The intercepts of the three lines in Figure 5 give $\nu_2 = 376 \pm 10$ cm⁻¹ and $(\zeta_{13}^{(e)})^2 = 0.031 \pm 0.015$. The force constants shown in Table 5 were obtained by the use of these constants.

Figure 5. Inertia defect differences of SeO₂

$$\Delta(v_1 = 1) - \Delta_0 = \frac{h}{\pi^2 c} \frac{\omega_3^2}{\omega_1(\omega_3^2 - \omega_1^2)} (\zeta_{13}^{(e)})^2,$$

$$\Delta(v_2 = 1) - \Delta_0 = \frac{h}{\pi^2 c} \frac{\omega_3^2}{\omega_2(\omega_3^2 - \omega_2^2)} [1 - (\zeta_{13}^{(e)})^2]$$

$$\Delta(v_3 = 1) - \Delta_0 = \frac{h}{\pi^2 c} \frac{1}{\omega_3} \left[\frac{\omega_2^2}{\omega_2^2 - \omega_3^2} + \left(\frac{\omega_1^2}{\omega_1^2 - \omega_3^2} - \frac{\omega_2^2}{\omega_2^2 - \omega_3^2} \right) (\zeta_{13}^{(e)})^2 \right]$$

$$\nu_1 = 910 \text{ cm}^{-1}; \quad \nu_3 = 967 \text{ cm}^{-1}; \quad \nu_2 = 376 \pm 10 \text{ cm}^{-1}; \quad (\zeta_{13}^{(e)})^2 = 0.031 \pm 0.015$$

LEAST-SQUARES DETERMINATION

We have learned that many phenomena which arise from the vibration-rotation interactions can be used in determining the potential function. When the phenomena appear separately, we can obtain information rather easily from each of them, just as has been described above. Sometimes, however, it happens that various effects mix together to produce complicated features in the vibrational and rotational spectra. The OCS molecule is a

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typical example of this³¹. It is known that there exists a strong Fermi resonance between ν_1 and ν_{22} , but the possibility of another Fermi resonance between ν_3 and ν_{22} must also be taken into account³¹, while at the same time the possibility of an appreciable contribution of the higher-order terms, γ_{ss}' cannot be neglected. The trouble is that these effects cannot be separated in this molecule. Thus, we have to treat the problem as a whole by least-squares calculations, along the same lines as the treatment carried out by Pariseau, Suzuki, and Overend for CO₂ and HCN^{17, 18} and by Pliva for N₂O³³. The vibrational frequencies and the rotational constants in various excited states—135 in total—were used as the observables in the least-squares. The calculated values to be compared with the observed values were obtained by the use of a molecular model with a potential function involving 19 parameters up to the fourth-order anharmonic terms, which are treated with the second-order perturbation theory.

There is yet another complication in this molecule; the existence of a higher-order perturbation between ν_3 and $4\nu_2$ states has been pointed out by Triaille and Courtoy³⁴. They attributed the resonance to the coupling between two states, (2⁰1) and (24²⁰), that is, between the Σ^+ state and the Δ state. However, it seems more reasonable to assign the resonance to the coupling between the (2⁰1) and (24⁰⁰) state, both with the same symmetry, Σ^+ . We corrected this effect also for all other possible sets of energy states, and the corrected values of ν and B were used in the least-squares calculations. By this correction the linearity of B against the vibrational quantum numbers was greatly improved, and the residuals of ν and B in the least squares decreased by half. The final values of the parameters are listed in Table 8. It must be emphasized that in these calculations the Fermi resonances were treated as a natural consequence of the anharmonic potential function, just the same as the α constants in the rotational constants.

Table 8. Parameters of fourth-order potential function of OCS

$f_R(\text{CS})$	7.44	± 0.04	md/Å	$f_{RRRR}(\text{CS})$	8.2	± 5.2	md/Å ³
f_{Rr}	1.04	± 0.07	md/Å	f_{RRRr}	4.2	± 4.7	md/Å ³
$f_r(\text{CO})$	16.14	± 0.11	md/Å	f_{RRrr}	-14.0	± 26.0	md/Å ³
f_a	0.6513	± 0.0004	md/Å	f_{Rrrr}	-53.4	± 33.0	md/Å ³
$f_{RRR}(\text{CS})$	-6.67	± 0.56	md/Å ²	$f_{rrrr}(\text{CO})$	74.2	± 40.0	md/Å ³
f_{RRr}	-2.9	± 1.9	md/Å ²	f_{RRraa}	-0.21	± 0.59	md/Å
f_{Rrr}	5.2	± 3.6	md/Å ²	f_{Rraa}	3.2	± 2.0	md/Å
$f_{rrr}(\text{CO})$	-26.1	± 4.5	md/Å ²	f_{rraa}	0.0	± 1.7	md/Å
f_{Raa}	-0.61	± 0.06	md	f_{aaaa}	0.05	± 0.01	md/Å
f_{aaa}	-0.09	± 0.17	md				

The treatment stated above may be refined more, with the revised experimental values, and with the consideration of other interactions such as the Fermi resonance due to the term k_{113} . However, it is interesting to note that the third- and the fourth-order constants for the CS and CO atom pairs in OCS thus obtained are of the same order of magnitude as those of the CS and CO radicals, as is shown in Table 9.

The potential constants obtained above have been checked by the use of other phenomena which were not employed in the least-squares calculations. *Table 10* compares the calculated values of the *l*-type doubling constant and the centrifugal distortion constant with the observed values. In these

Table 9. Diatomic approximation for OCS

	OCS <i>obs</i>	CS and CO <i>diatomic</i>
$f_{RRR}(\text{CS})$ $f_{rrr}(\text{CO})$	-6.7 ± 0.6 -26.1 ± 4.5	-10.1 md/\AA^2 -22.7 md/\AA^2
$f_{RRRR}(\text{CS})$ $f_{rrrr}(\text{CO})$	8.1 ± 5.2 74.0 ± 40.0	12.9 md/\AA^3 33.6 md/\AA^3

Table 10. Test of the potential function of OCS

<i>l</i> -Type doubling			Centrifugal distortion		
q_e	calc.	$0.2110 \times 10^{-3} \text{ cm}^{-1}$	D_e	calc.	$4.280 \times 10^{-8} \text{ cm}^{-1}$
$q(01^{10})$	calc.	0.2130 ± 0.0005	D_o	calc.	4.332 ± 0.010
$q(01^{10})$	obs. ³⁵	0.212190	D_0	obs. ³⁶	4.37 ± 0.03

calculations we add the corrections due to the fourth-order perturbation, which has been formulated by Amat³. The agreement is satisfactory and the higher-order corrections make the agreement better. The agreement gives a support for the above potential function.

The *l*-type doubling constant, q_e , is related to the Coriolis coupling constant as follows:

$$q_e = \frac{2B_e^2}{\omega_2} \left[1 + 4 \frac{\omega_2^2}{\omega_3^2 - \omega_2^2} + 4(\zeta_{12}^{(c)})^2 \frac{\omega_2^2(\omega_3^2 - \omega_1^2)}{(\omega_1^2 - \omega_2^2)(\omega_3^2 - \omega_2^2)} \right] \quad (18)$$

Since the separation of the doublet in the excited state of the ν_2 degenerate vibration is given by $(\frac{1}{2})q_e(\nu_2 + 1)\mathcal{J}(\mathcal{J} + 1)$, it seems likely that the measurement of the doublet separation would give the Coriolis coupling constant, $\zeta_{12}^{(c)}$, immediately and that the quadratic force constants would be easily derived. However, the Coriolis coupling constant of this molecule is small—only 4% of the total q_v —and is of the same order of magnitude as the higher-order correction, $(\frac{1}{2})(q_{v1} + 4q_{v2} + q_{v3})$, which amounts to roughly 1 or 2% in q :

$$q_e = q(01^{10}) - \frac{1}{2}(q_{v1} + 4q_{v2} + q_{v3}). \quad (19)$$

Therefore, we must eliminate the latter in order to get the exact value of the Coriolis coupling constant. Thus, we have measured the *l*-type doublings in various higher excited states, as is shown in *Table 11*³². For a direct comparison, the vibrational changes have been calculated using the potential function

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determined by the least-squares calculations. The calculated value of q_v for each state is in fairly good agreement with the observed value, though the former is slightly smaller³⁷. The calculated values of $q(01^10)$ and D_0 shown in *Table 11* were thus corrected for the fourth-order perturbation.

Table 11. l -Type doubling constant of OCS

v_1	v_2^l	v_3	q_v	$q_v - q(01^10)$	
				<i>obs.</i>	<i>calc.</i>
0	1 ¹	0	0.2118	—	—
1	1 ¹	0	0.2287	0.0169	0.0100
0	3 ¹	0	0.2062	-0.0055	-0.0042
0	1 ¹	1	0.2151	0.0033	0.0026
1	1 ¹	0	0.2430	0.0312	0.0209
1	3 ¹	0	0.217	0.005	0.0030
0	5 ¹	0	0.2020	-0.0098	-0.0070

$$\frac{1}{2}(q_{v1} + 4q_{v2} + q_{v3}) \text{ calc.} = 0.0020 \times 10^{-3} \text{ cm}^{-1}$$

$$\text{obs.} = 0.0037 \times 10^{-3}$$

The observed values of q or D are very often used for the determination of the potential function. In that case it seems natural and inevitable to ignore the difference between q_e and $q(01^10)$ or that between D_e and D_0 . In the above example, we have learned that the higher-order corrections are 1 or 2% of the total q or D , and yet the uncertainties of the final force constants come to several times more than the standard deviations of the least-squares calculations. We should carefully consider the uncertainties of the final results due to such a neglect, and, if possible, make corrections, or extend the approximation, in order to arrive at more trustworthy results.

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