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Calculation of the Vibrational Frequencies of all Isotopic $WOCl_4$ Molecules

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The vibrational frequencies of the isotopic $WOCl_4$ molecules have been calculated. Their correlations, the isotopic shifts and splittings, respectively, have been presented and the results compared with those of $VOCl_3$.

The isotopic shifts and splittings appearing in vibrational spectra are of great importance in the interpretation of high resolution spectra and the spectra of the matrix-isolated species. It is also an invaluable aid in the determination of an acceptable force-constant matrix for polyatomic molecules. Isotopic effects in the vibrational spectra of $VOCl_3$[1, 2] led to the calculations of the similar $WOCl_4$ molecule, intending to accomplish a theoretical estimation of the magnitude of the shifts and splittings of $WOCl_4$ and to determine whether these effects are observable in vibrational spectra.

The occurrence of two natural chlorine isotopes results in 6 isotopic $WOCl_4$ molecules. Together with their point groups and symmetry operations they are listed in Table 1.

In our calculations we have adopted the structural parameters of *Spiridonov* et al.[3], the symmetry co-ordinates of *Brunvoll* and *Cyvin*[4] and the force constant matrix of *Brockner* et al.[5].

$WO^{35}Cl_4$ and $WO^{37}Cl_4$ belong to the point group C_{4v}. The irreducible representations for the molecular vibrations are[6]

$$\Gamma_{\text{vib}}\ (C_{4v}) = 3\ A_1 + 2\ B_1 + B_2 + 3\ E.$$

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In the other cases the symmetry has been lowered by the introduction of different chlorine isotopes, and it is therefore no longer permissible to use the same block structure of the **F** and **G** matrices as for the molecules with C_{4v}-symmetry. The appropriate correlations[6] are shown in Table 2.

Referring to this correlation table it is easy to write down the irreducible representations of the remaining isomers: For *trans*-$WO^{35}Cl_2{}^{37}Cl_2$ (C_{2v}) σ_v is the only remaining symmetry plane from the C_{4v}-point group. Its representation is therefore:

Table 1. *Point Groups and Symmetry Operations of the Isotopic* $WOCl_4$ *Molecules*

Molecule	Point group	Symmetry operations
$WO^{35}Cl_4$	C_{4v}	E; 2 C_4; C_2; 2 σ_v; 2 σ_d
$WO^{35}Cl_3{}^{37}Cl$	$C_s{}^v$	E; σ_v
trans-$WO^{35}Cl_2{}^{37}Cl_2$	C_{2v}	E; C_2; 2 σ_v
cis-$WO^{35}Cl_2{}^{37}Cl_2$	$C_s{}^d$	E; σ_d
$WO^{35}Cl^{37}Cl_3$	$C_s{}^v$	E; σ_v
$WO^{37}Cl_4$	C_{4v}	E; 2 C_4; C_2; 2 σ_v; 2 σ_d

Table 2. *Correlation Diagram of the Point Groups* C_{4v} — C_{2v} — C_s

C_{4v}	C_{2v}	$C_s{}^v$	$C_s{}^d$
A_1	A_1	A'	A'
A_2	A_2	A''	A''
B_1	A_1	A'	A''
B_2	A_2	A''	A'
E	$B_1 + B_2$	$A' + A''$	$A' + A''$

$$\Gamma_{vib}\,(C_{2v}) = 5\,A_1 + A_2 + B_1 + B_2.$$

The same symmetry plane σ_v has been retained in the case of $WO^{35}Cl_3{}^{37}Cl$ and $WO^{35}Cl^{37}Cl_3$ and their representations are

$$\Gamma_{vib}\,(C_s{}^v) = 8\,A' + 4\,A''.$$

In the case of the isomer *cis*-$WO^{35}Cl_2{}^{37}Cl_2$ the σ_d plane is retained and the irreducible representation is therefore:

$$\Gamma_{vib}\,(C_s{}^d) = 7\,A' + 5\,A''.$$

Table 3. *Calculated Vibrational Frequencies* (cm^{-1}) *of the Isotopic* $WOCl_4$ *Molecules and their Correlations and Assignments*

	$WO^{35}Cl_4$ (C_{4v})	$WO^{35}Cl_2{}^{37}Cl_2$ (C_{2v})	$WO^{35}Cl_3{}^{37}Cl$ ($C_s{}^v$)	$WO^{35}Cl_2{}^{37}Cl_2$* ($C_s{}^d$)	$WO^{35}Cl^{37}Cl_3$ ($C_s{}^v$)	$WO^{37}Cl_4$ (C_{4v})
ν_1	1028.0 (A_1)	1028.0 (A_1)	1028.0 (A')	1028.0 (A')	1028.0 (A')	1028.0 (A_1)
ν_2	407.6 (A_1)	402.6 (A_1)	405.2 (A')	402.6 (A')	399.9 (A')	397.0 (A_1)
ν_3	161.7 (A_1)	160.3 (A_1)	161.0 (A')	160.3 (A')	159.6 (A')	158.9 (A_1)
ν_4	327.2 (B_1)	322.4 (A_1)	324.3 (A')	321.8 (A'')	320.0 (A')	318.2 (B_1)
ν_5	109.7 (B_1)	108.2 (A_1)	109.0 (A')	108.2 (A'')	107.5 (A')	106.8 (B_1)
ν_6	224.5 (B_2)	221.5 (A_2)	223.0 (A'')	221.5 (A')	219.9 (A'')	218.4 (B_2)
ν_7	337.4 (E)	337.4 (B_1) 331.7 (B_2)	335.1 (A') 337.4 (A'')	334.3 (A') 335.5 (A'')	334.8 (A') 331.7 (A'')	331.7 (E)
ν_8	265.4 (E)	265.4 (B_1) 263.8 (B_2)	264.6 (A') 265.4 (A'')	264.6 (A') 264.6 (A'')	264.6 (A') 263.8 (A'')	263.8 (E)
ν_9	149.9 (E)	146.8 (B_1) 149.4 (B_2)	149.6 (A') 148.3 (A'')	148.0 (A') 148.1 (A'')	146.5 (A') 147.8 (A'')	146.2 (E)

The numbering of the frequencies follows that of the C_{4v} model.

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* The symmetry co-ordinates of *cis*-$WO^{35}Cl_2{}^{37}Cl_2$ ($C_s{}^d$; ν_7–ν_9) cannot be directly compared with those of the other molecules.

Each of the degenerate symmetry co-ordinates of the C_{4v} model can be used as a basis for a block diagonal secular equation for the C_{2v} or C_s^v model. A symmetry analysis of the co-ordinates belonging to the degenerate species E of the C_{4v} point group shows that a direct transfer of the co-ordinates to the C_s^d point group is not allowed because they do not belong to either the A′ or the A″ species. This separation into the two species is accomplished by taking the sum and the difference of two degenerate co-ordinates, the sum belonging to the A′ species and the difference to the A″ species.

Table 4. *Calculated Vibrational Frequencies* (cm^{-1}) *of the Isotopic* $VOCl_3$ *Molecules and their Correlations and Assignments*

	$VO\,^{35}Cl_3$	$VO\,^{35}Cl_2{}^{37}Cl$	$VO\,^{35}Cl^{37}Cl_2$	$VO\,^{37}Cl_3$
ν_1	1037.5 (A_1)	1037.5 (A′)	1037.5 (A′)	1037.5 (A_1)
ν_4	505.0 (E)	505.0 (A″) 501.0 (A′)	503.1 (A′) 498.8 (A″)	498.8 (E)
ν_2	410.7 (A_1)	407.4 (A′)	404.2 (A′)	401.1 (A_1)
ν_5	247.0 (E)	247.0 (A″) 245.9 (A′)	246.4 (A′) 245.3 (A″)	245.3 (E)
ν_3	163.5 (A_1)	162.7 (A′)	161.9 (A′)	161.1 (A_1)
ν_6	128.5 (E)	128.0 (A′) 127.0 (A″)	127.0 (A″) 126.9 (A′)	125.4 (E)

The numbering of the frequencies follows that of the C_{3v} model.

By rearranging the co-ordinates of the $WOCl_4$ molecule with C_{4v} symmetry according to the scheme outlined above and rearranging the blocks of the **F** matrix correspondingly a secular equation may be set up and solved for each of the isomers. Using this approach we have abandoned the method of standard symmetry co-ordinates and gained the advantage of transferring the blocks of the force constant matrix[5] directly to the molecules with lower symmetry.

The calculated frequencies of the isotopic $WOCl_4$ species are summarized in Table 3 and for sake of comparison the vibrational frequencies of the isotopic $VOCl_3$ molecules[2] are listed in Table 4.

Comparing our $WOCl_4$ results (Table 3) with those of the isotopic $VOCl_3$ molecules[2] (Table 4) there is the same order and magnitude of the isotopic effects:

The most prominent shift in the spectrum of the $WOCl_4$ molecule will be found for the symmetric W—Cl-stretching frequencies ν_2 ($WO^{35}Cl_4$: 407.6 cm^{-1}; $WO^{37}Cl_4$: 397.0 cm^{-1}). A relatively large isotopic shift has been determined for the asymmetric stretching frequencies ν_4 (9 cm^{-1}), but this fundamental appears as a weak and broad band[7, 8] making a resolution into the different frequencies impossible. Also the other frequencies show minor shifts and splittings respectively (except ν_1) and according to the intensities of the fundamentals and the statistical distribution of the isotopic species it will be expected that an experimental detection is very difficult or impossible.

For the crystalline $WOCl_4$[9–11] consisting of an infinite oxygen bridged chain isotopic effects may also be expected particularly for the symmetric W—Cl-stretching frequency, because the WCl_4 part can be regarded as a separate unit.

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References

[1] *R. J. H. Clark* and *P. D. Mitchell*, J. Chem. Soc. Dalton **1972**, 2429.
[2] *H. Hovdan*, *S. J. Cyvin*, and *W. Brockner*, Z. Naturforsch. **a**, in press.
[3] *V. P. Spiridonov*, *E. Z. Zasorin*, *I. M. Zharskii*, and *G. I. Novikov*, J. Strukt. Khim. **13**, 511 (1972).
[4] *J. Brunvoll* and *S. J. Cyvin*, J. Mol. Structure **6**, 289 (1970).
[5] *W. Brockner*, *H. Hovdan*, and *S. J. Cyvin*, Z. Naturforsch. **29 a**, 620 (1974).
[6] *E. B. Wilson*, *J. C. Decius*, and *P. C. Cross*, Molecular Vibrations. New York-London-Toronto: McGraw-Hill. 1955.
[7] *W. Bues*, *W. Brockner*, and *F. Demiray*, Spectrochim. Acta **30 A**, 579 (1974).
[8] *W. Bues*, *W. Brockner*, and *F. Demiray*, Raman Newsletter **57**, 13 (1973).
[9] *H. Hess* and *L. Dorn*, Angew. Chem. **76**, 587 (1964).
[10] *H. Hartung*, Z. Chem. **4**, 232 (1964).
[11] *H. Hess* and *H. Hartung*, Z. allg. anorg. Chem. **344**, 157 (1966).

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