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AN APPROACH TO DETERMINE THE RELIABLE SET OF FORCE CONSTANTS FOR ISOSTRUCTURAL MOLECULES AND IONS*

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A method has been proposed to determine the reliable set of force constants for isostructural molecules and ions. The approach involves the knowledge of reliable force constants in only one oxidation state of the isostructural systems. The validity of the method is demonstrated in the case of tetrahedral isostructural systems and its application to various isostructural series is suggested.

1. *Introduction*

The reliable molecular force field has attracted considerable interest in recent years. This is on account of the utilization of experimental data such as isotopic shifts, Coriolis coupling constants, centrifugal distortion constants, mean square amplitudes of vibration, and infrared and Raman intensities in the determination of reliable set of force constants for simple molecules in addition to the vibrational frequencies. In case of ions, the isotopic shifts and infrared and Raman intensities are the only source of experimental information besides vibrational frequencies and attempts have been made in literature [1–3] to understand reliable molecular force field for ions, particularly in single oxidation state. Therefore, in the present work, a method has been proposed to study the reliable force fields in case of isostructural ions possessing different oxidation states.

2. *Theoretical considerations*

The molecular vibrations are studied through the secular equation [4]

$$(GF)L = L\Lambda, \tag{1}$$

which is derived using the expressions

$$L^tFL = \Lambda, \tag{2}$$

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and

$$G = LL^t, \tag{3}$$

where the representations used for kinetic energy (G), potential energy (F), eigenvalue (Λ) and eigenvector (L) matrices stand for a member belonging to an isostructural series of the type XY_m^n (e.g. XY_m, XY_m^{1-}, XY_m^{2-}, ...). If the reliable force field is known for this member (using additional experimental data), its L matrix elements can be reasonably determined. For other members of the same isostructural series, Eqs. (2) and (3) take the forms

$$L^t F^{\mathrm{Isos}} L = \Lambda^{\mathrm{Isos}} \tag{4}$$

and

$$G^{\mathrm{Isos}} = LL_t \qquad (\text{as } G = G^{\mathrm{Isos}}). \tag{5}$$

Therefore relations (4) and (5) can be utilized to get reliable set of force constants for other members of the series only with the use of vibrational frequencies.

3. *Results and discussion*

In order to examine the validity of the proposed method to study the reliable force field in isostructural series, we have selected the tetrahedral oxides of the type XO_4^{n-} ($X=$ Ru, Cr or Mo; $n = 0, 1, 2, 3$, or 4). First we have computed the force constants in F_2 species for each representative of the series employing isotopic frequencies as an additional experimental data besides vibrational frequencies [2, 6–8]. The force constants thus determined are compared in Table I with the most reliable values available in literature [2, 9]. The agreement is seen to be quite reasonable. The evaluated force constants, in turn, are used to calculate the eigenvector matrix L. From the knowledge of this matrix and the

TABLE I

The vibrational frequencies (in cm^{-1}) and symmetry force constants (in mdyn/Å) for F_2 species of some isostructural tetrahedral oxyanions*

Molecule ion	ν_1	ν_2	F_{11}	F_{12}	F_{22}	Ref.
$Ru^{16}O_4$	921.0	336.0	6.489 ± 0.026	-0.066 ± 0.090	0.402 ± 0.038	PW
$Ru^{18}O_4$	878.8	320.9	6.49 ± 0.05	0.07 ± 0.05	0.381 ± 0.002	[9]
			6.62 ± 0.09	0.12 ± 0.12	0.378 ± 0.003	[2]
			6.82 ± 0.05	0.07 ± 0.04	0.410 ± 0.015	[2]
$^{50}CrO_4^{2-}$	894.8	384.1	5.211 ± 0.113	0.082 ± 0.063	0.443 ± 0.072	PW
$^{53}CrO_4^{2-}$	886.3	381.6	5.23 ± 0.017	0.08 ± 0.12	0.43 ± 0.02	[2]
$^{92}MoO_4^{2-}$	842.0	317.0	5.166 ± 0.145	-0.198 ± 0.123	0.369 ± 0.100	PW
$^{100}MoO_4^{2-}$	834.0	315.0	5.14 ± 0.21	-0.22 ± 0.21	0.38 ± 0.03	[2]
			5.28 ± 0.12	-0.08 ± 0.13	0.36 ± 0.01	[2]

* PW: Present work.

vibrational frequencies, the force constants are computed for other members of the series. The spectral data and the results are included in Table II. To test the accuracy of the reported force constants, they are further used to reproduce the vibrational frequencies for each member. As is obvious from Table III, the observed and calculated frequencies corresponding to stretching and bending modes differ only by $0.02\ cm^{-1}$ and $0.4\ cm^{-1}$, respectively. This shows that the results reported by us are reliable for tetrahedral isostructural series and the proposed method is valid.

TABLE II

The vibrational frequencies (in cm^{-1}) and symmetry force constants (in mdyn/Å) for F_2 species of some isostructural tetrahedral oxyanions computed using the force fields for the corresponding member (Table I) of the isostructural series

Ion	ν_1	ν_2	F_{11}	F_{12}	F_{22}
RuO_4^-	845.0	312.0	5.464 ± 0.025	-0.052 ± 0.085	0.346 ± 0.036
RuO_4^{2-}	790.0	323.0	4.788 ± 0.023	-0.017 ± 0.064	0.369 ± 0.029
CrO_4^{3-}	860.0	324.0	4.769 ± 0.115	0.012 ± 0.086	0.316 ± 0.084
CrO_4^{4-}	855.0	404.0	4.798 ± 0.104	0.133 ± 0.044	0.487 ± 0.060
MoO_4^{4-}	808.0	373.0	4.804 ± 0.129	-0.098 ± 0.057	0.497 ± 0.072

TABLE III

Comparison of the observed and calculated wavenumbers for the members of the isostructural series included in Table II

Ion	ν_1 (in cm^{-1})			ν_2 (in cm^{-1})		
	obs.	calc.	diff.	obs.	calc.	diff.
RuO_4^-	845.0	845.03	0.03	312.0	311.79	0.21
RuO_4^{2-}	790.0	790.02	0.02	323.0	322.78	0.22
CrO_4^{3-}	860.0	860.0	0.00	324.0	323.56	0.44
CrO_4^{4-}	855.0	855.02	0.02	404.0	403.43	0.57
MoO_4^{4-}	808.0	808.02	0.02	373.0	373.03	0.03

4. *Conclusion*

We therefore conclude that for an isostructural series of molecules and ions (G matrix remaining unchanged) the proposed method is valuable to study reliable force fields for all members with the use of vibrational frequencies alone if the reliable force field is known for one of the members. Furthermore, if the spectral data for a molecule or ion are available in different environments and the reliable force field is known in only single environment, the reasonable set of force constants can be determined in other environments also. The application of this method to various isostructural series is suggested.

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