

SHORT COMMUNICATIONS

FORCE FIELD CALCULATIONS FROM RAMAN AND INFRARED INTENSITIES

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GENERALLY force constants are evaluated by solving the secular determinant $|GF - E \lambda| = 0$. But the number of force constants to be evaluated is always greater than the eigenvalues. Another way of solving for L elements is by using relations $L'FL = \lambda$, where $LL' = G$. While L is nonsymmetric, G is symmetric. In this method also, even for 2×2 system, one equation is less to get all the L elements. Such a problem is solved usually by two ways (i) using isotopic masses (ii) using coriolis interaction or centrifugal distortion constants and obtaining an additional equation for L elements. On the other hand we present in this note a method of getting F elements using Raman and infrared intensities along with the relation $LL' = G$.

L element from intensities

Raman or infrared intensities are given by a formula

like

$$I = L'A \quad (1)$$

I is $\delta P\sigma/\delta Q$ or $\delta\alpha_{ij}/\delta Q$ depending on infrared or Raman intensities and should not be confused with intensity which is proportional to I^2 . A is a column matrix of electro-optical parameters. I being a square root of I^2 has sign ambiguity. But, this problem was earlier solved and that it was shown how elements of A can be obtained^{1,2}.

Though, this problem is of real importance to crystals we shall demonstrate the method in a simple case taking F_2 species of CH_4 , CD_4 and CT_4 . The Raman intensities³ and infrared intensities⁴ are analyzed to obtain A elements. They can also be calculated from the data reported earlier^{1,2} and these are given in table 1. I 's in this table are again derivatives P_σ and α_{ij} and not intensities. Adding

$$LL' = G \quad (2)$$

and
$$L'FL = \lambda \quad (3)$$

In the Raman spectra a 2×2 matrix generally contains a stretching and a bending frequency, the intensity of the latter being almost negligible compared to the former. Then the expressions for F elements

Table 1 Experimental data and the electrooptical constants of CH_4 , CD_4 and CT_4

Molecule	F_2 Species		Raman*		Infrared	
	λ_1	λ_2	I_1	I_2	I_1	I_2
CH_4	3.530898	0.65361	2.470	0.110	0.6163	0.4080
CD_4	1.93193	0.37437	1.832	0.0	0.4137	0.3203
CT_4	1.331745	0.261290	—	—	0.32157	0.2781
		Experimental value		γ'^2 Value	$\gamma' = I$ Value as given above	
CH_4	λ_1	128		6.0952	2.470	
	λ_2	0.24		0.0114	0.11	
CD_4	λ_1	70.5		3.3571	1.832	
	λ_2	0.2		0.0	0.0	

* Raman intensities of Abbet *et al*³ for F_2 modes (For this species the degeneracy factor is 3 and $\alpha^{-2} = 0$)
The values of electro-optical constants were: (1) Raman intensities: $A_1 = 3.106$, $A_2 = 0.404$; (2) Infrared intensities: $A_1 = -0.73612$, $A_2 = -0.46638$

Table 2 Force constant contributions from $G^{-1} \lambda$ and intensities

Force Constant	Molecule	CH ₄ F ₂ Species	CD ₄ F ₂ Species	CT ₄ F ₂ Species
F_{11}	$G_{11}^{-1} \lambda_1$	5.373	5.559	6.466
	$F'_{11} (R)$	-0.01	-0.009	-
	$F'_{11} (IR)$	-0.004	-0.018	-0.139
F_{22}	$G_{22}^{-1} \lambda_2$	0.540	0.544	0.528
	$F'_{22} (R)$	0.191	0.078	-
	$F'_{22} (IR)$	0.072	0.063	0.188
F_{12}	$G_{12}^{-1} \lambda_1$	-0.099	0.063	-0.277
	$F'_{12} (R)$	0.580	0.582	-
	$F'_{12} (IR)$	0.165	0.034	0.156

become very simple.

$$F_{11} = G_{11}^{-1} \lambda_1 + \frac{(\lambda_2 - \lambda_1)}{I_1^2} (G_{11}^{-1} I_1^2 - A_1^2),$$

$$F_{22} = G_{22}^{-1} \lambda_2 + \frac{(\lambda_1 - \lambda_2)}{I_1^2} A_2^2,$$

$$F_{12} = G_{12}^{-1} \lambda_1 + \frac{(\lambda_2 - \lambda_1)}{I_1^2} (G_{12}^{-1} I_1^2 - A_1 A_2).$$

F elements evaluated are given in table 2.

There are two striking features. (i) The contribution of the first term is very large compared to the intensity term. Though we do not have the Raman intensity for CT₄ one can perhaps say it is of the same order of magnitude as CH₄ and CD₄. It is really interesting to see that $G_{11}^{-1} \lambda_1$, $G_{22}^{-1} \lambda_2$ and $G_{12}^{-1} \lambda_1$ are so different for CT₄ compared to CH₄ and CD₄; one wonders whether F_{11} , F_{22} and F_{12} are really the same for these molecules. Perhaps the A elements are also not the same for isotopic molecules, but the intensity contribution is so small that the small variations of A are not important. It is also not possible to explain the difference in the value of $G_{11}^{-1} \lambda_1$ as due to error in the determination of anharmonicity correction. (ii) The other point of interest is that F_{11} is a function of A_1^2 . The polarizability derivative of stretching, F_{22} the bending force constant is proportional to A_2^2 the polarizability change due to bending and in the same token F_{12} is proportional to $A_1 A_2$.

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ANISALDEHYDE-4-PHENYL-3-THIOSEMICARBAZONE AS A NEW ANALYTICAL REAGENT FOR THE EXTRACTION SPECTROPHOTOMETRIC DETERMINATION OF COPPER

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ONLY a few phenylthiosemicarbazones are synthesized and used as chromogenic reagents for the spectrophotometric determination of metal ions. The renewed interest in synthesizing phenylthiosemicarbazones¹⁻⁷ is due to their sensitive reactions with metal ions and (easy) extractability of metal-phenylthio-semicarbazone complexes into organic solvents. Hence we describe the synthesis of anisaldehyde-4-phenyl-3-thiosemicarbazone and its use as analytical reagent for the determination of copper. A survey of the literature for the spectrophotometric determination of copper showed that relatively few reagents show high sensitivity for the metal ion. In some of these methods, tolerance limit of associated ions is less⁹⁻¹¹ and some others involve heating of the reaction mixture¹². The proposed method besides being sensitive, is simple, rapid, requires no heating and has the advantage of virtual freedom from interference from many associated foreign ions. The high tolerance limit of zinc makes the method useful for the determination of copper in brass. The method is also extended for the determination of copper in steel samples.

Synthesis of reagent:

A solution prepared by dissolving 0.835 g of 4-phenyl-3-thiosemicarbazide in 2 ml of glacial acetic acid was added dropwise to a solution of anisaldehyde (0.68 g) in 50 ml methanol while stirring. A white product quickly separated and was recrystallized in methanol or carbon tetrachloride (m.p. 182-184°C, yield 75%). The reagent (0.285 g) was dissolved in 50 ml of DMF (2×10^{-2} M). Solutions of lower concentrations were obtained by dilution with DMF. Stock solution of Cu(II) containing 6.35 mg/ml was prepared from copper sulphate pentahydrate (BDH AR) and standardized titrimetrically⁸.

All chemicals used were of BDH AR grade.

Recommended procedure

To an aliquot containing 0.11 to 1.7 μ g/ml of copper in a 25 ml separating funnel, add 5 ml buffer (sodium