A Method for the Solution of the Inverse Eigenvalue Problem

II. Application to Methyl Mercuric Bromide

A. Ažman and Z. Bohte

Department of Chemistry, University of Ljubljana, Ljubljana, Yugoslavia

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Some time ago [1] we proposed a method for the solution of the inverse eigenvalue problem. The method was tested by the determination of the force field of several molecules. The method can be used when the following inequality is satisfied

$$m \leqq \tfrac{1}{2}\, n(n+1)$$

where m is number of parameters to be determined and n the number of measured frequencies. The number of equations is $\frac{1}{2}\, n(n+1)$ with m unknown parameters. The least square method is used if $m < n$ or $m > n$. If $m < n$ the calculated force field can not reproduce the frequencies exactly. When $m > n$ this is possible though the values of force constants can be unphysical. In order to prevent this, to every force constant a range is imposed. When this procedure is used the calculated frequencies can differ from the measured ones. This procedure is not necessary if the initial values of force constants are chosen from an acceptable basis. If $m > n$, any set of force constants can reproduce the frequencies and the above described procedures intend to select an aceptable force field.

In this note we give a specific example of the method. Meić and Randić [2] have found, using Mills [3] method that the force constant F_{23} (connected with symmetry A vibrations with four frequencies) changes sign from the initial negative value ($-0{,}15$) to a positive one ($0{,}13$) during the refinement of the force field calculation. This value is in contradiction to many examples [4], and they attributed this to facts such as anharmonicity, a need for more precise refinement etc. In Table 1 we have listed results for $m = \frac{1}{2}\, n(n+1)$ ($m = 10$, $n = 4$). The initial values were as in Ref. [2].

	initial values [2]	final values [2]		this work
F_{11}	4,95	4,95		4,91
F_{12}	0,05	0,05		0,05
F_{22}	0,35	0,412		0,38
F_{23}	−0,15	0,13		−0,12
F_{33}	2,50	2,48		2,68
F_{44}	1,50	1,41		1,41
			F_{13}	0,01
			F_{34}	0,02

Table 1. Force constants (mdyn Å^{-1}).

F_{ij} elements not listed in column three are calculated to be zero. The parameters in column three reproduce the measured frequencies exactly, and almost exactly the frequencies of the deuterated species. The same results were obtained with the set F_{11}, F_{12}, F_{22}, F_{23}, F_{33}, F_{13} and F_{34}. When the following set was used F_{11}, F_{12}, F_{22}, F_{23}, F_{33}, F_{44} unreasonable values were obtained though the calculated frequencies were equal to the measured ones. If the boundaries are imposed on the force field constante e. g. $-0{,}15 < F_{23} < 0{,}15$ the calculated force field constants and the frequencies (different from the measured ones) are almost the same as in Ref. [2].

There are two possible explanations why the value of F_{23} is positive in the calculation by Meić and Randić: inadequacy of the experimental data and F_{13} and F_{34} are zero or the influence of F_{13} and F_{34} is important.

The force field of symmetry $E(n=4)$ was calculated with $m = 7$. The calculated set is almost identical with that of Meić and Randić. The largest difference is in the value of F_{55} for which they obtained 4,92 and we 4,89. Accidentaly this set reproduces exactly the frequencies of the deuterated species.

The calculation was done on a IBM computer 11-30 with the program written in Fortran IV. The convergence of the method was found to be extremely good. The second iteration gives the values of the parameters identical to five decimals with the values from the third iteration.

Reprints request to Dr. A. Ažman, Oddelek za Kemijo Univerze v Ljubljani, Murnikova 6 — P. O. B. 537, *Ljubljana*, Yugoslavia.

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