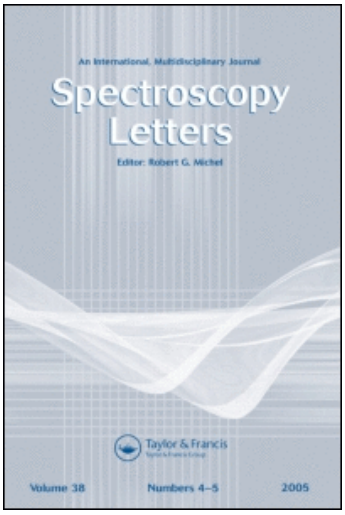

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FT-IR Intensities, Bond Moments and its Derivatives for Nttromethane

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FT-IR INTENSITIES, BOND MOMENTS AND ITS DERIVATIVES FOR NITROMETHANE

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ABSTRACT

Considering the -CH_3 group as a single particle of 15.0 daltons, the infrared absorption intensities of the a_1 fundamentals vibrational bands of CH_3NO_2 in CCl_4 have been measured at different concentrations considering two cases: band intensities with solvent substraction (wss) and without solvent substraction (wtss). In order to obtain the matrix of the normalized amplitudes, **X** , the vibrational problem was solved via compliance constant: $\mathbf{KCX} = \mathbf{X\Phi}$, in this case the use of the minus sign of the $\pm(\partial\mu/\partial Q_i)$'s expressions is justified. The experimental results of the intensities measurements were refined with a variance analysis. From the intensities experimental data, our results are:

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$\partial\mu_{NO}/\partial_{rNO}$ = 6.02 and 6.16 D/Å, μ_{NO} = 1.77 and 1.82D, μ_{NO2} = 1.29 and 1.34D and $\partial\mu_{NC}/\partial_{RNC}$ = -2.62 and -2.68 D/Å for measurements without solvent substraction and with solvent substraction, respectively.

INTRODUCTION

The most representative experimental work on IR intensities was done using grating IR spectrophotometers [1, 2, 3, 4]. For accurate intensity measurements variables such as slit width and grating angle must be considered [5] in the expression of the integrate intensities.

Although studies on IR intensities of nitromethane, CH_3NO_2 in CCl_4 solutions have been adequately reported [6,7] using grating IR spectrophotometers, the purpose of this work was done in order to compare experimental results of infrared intensities measured with the grating Perkin-Elmer 221 IR spectrophotometer using sodium chloride optics, with the experimental results using the Perkin - Elmer FT-IR 2000 spectrophotometer. In this work, we proposed an alternative way to obtain the values of the dipole moments derivatives related to the symmetry coordinates, using compliance constants [8, 9, 10] rather than the conventional way using force constants. In this case the normalized amplitude matrix, **X**, is directly obtained.

EXPERIMENTAL

Nitromethane and carbon tetrachloride were obtained from Merck reagent grade purity. Solutions of nitromethane in CCl_4 were prepared according to the following quantities: 1) 0.923M, 2) 0.830M, 3) 0.728M, 4) 0.646M, 5) 0.554M, 6) 0.461M, 7)0.369M and 8) 0.277M.

The infrared spectra were recorded using an FT-IR 2000 Perkin Elmer spectrophotometer with a deuterated triglycine sulfate (DTGS) detector ; their own software comparing the most characteristic absorptions bands of water vapor carried out the calibration of the instrument. During the measurements, a 0.01 cm path NaCl cell was used. The interference fringe method was used for the calibration of the pathlength of a cell. The gain was 1, and the OPV velocity equal to 0.500 cm/s.The number of scans was in each case 120 with 4 cm^{-1} resolution. For each of the a_1 fundamental modes of the MNO_2 reduced model (M= CH_3): symmetric NC stretching, symmetric ONO bending and symmetric NO stretching, we considered different limits for the measurements of the band area. The values of the absorption band areas and the wavenumbers limits for each absorption band are presented in Table 1. In this table, (wtss) and (wss) means without solvent subtraction and with solvent subtraction, respectively. The total number of band area determination was 20. The obtained values were further refined by statistical method of variance analysis. Band areas corresponding to the N-O and N-C stretching and to the O-N-O bending at different concentrations are illustrated in Figure 1.

RESULTS AND DISCUSSIONS

Absolute Intensity Integrate Absorptions

According to previous assignments of the infrared spectrum of CH_3NO_2 [6], the ν_s(NO), ν_s(NC) and δ_s(ONO) were assigned to the wavenumbers at: 1375.0, 916.0 and at 655.5 cm^{-1}, respectively. These bands do not present significative overlapping with other fundamentals or with overtone and combination bands.

Table 1 - Absorption base line band area values (1a) and frequencies range considered for each absorption band (1b)

(1a)

CL	I-1	I-2	I-3	I-4	I-5	I-6	I-7	I-8	I-9	I-10	I-11	I-12	I-13	I-14	I-15	I-16	I-17	I-18	I-19	I-20
9,23E-3	5,806	6,715	6,353	0,886	0,851	0,754	8,073	8,322	8,401	8,909	5,949	7,000	7,619	0,984	0,978	0,784	10,128	9,803	9,650	6,31
8,30E-3	5,391	6,273	5,867	0,808	0,799	0,708	7,646	7,850	7,881	8,026	5,535	6,558	7,132	0,926	0,926	0,738	9,710	9,331	9,121	5,43
7,38E-3	4,758	5,571	5,085	0,712	0,706	0,633	6,763	6,970	7,025	7,208	4,900	5,812	6,428	0,840	0,842	0,663	9,146	8,738	8,475	4,45
6,46E-3	4,306	4,876	4,147	0,620	0,621	0,581	5,965	6,152	6,196	6,219	4,290	5,117	5,648	0,748	0,756	0,592	8,349	7,920	7,516	3,46
5,54E-3	3,498	4,071	3,348	0,513	0,522	0,476	5,031	5,248	5,288	5,376	3,640	4,312	4,691	0,642	0,658	0,507	7,415	7,016	6,608	2,50
4,61E-3	2,814	3,267	2,439	0,402	0,415	0,389	3,989	4,226	4,277	4,393	2,957	3,508	3,782	0,530	0,551	0,420	6,383	5,994	5,596	1,63
3,69E-3	2,268	2,634	1,713	0,311	0,327	0,318	3,285	3,485	3,523	3,541	2,411	2,876	3,055	0,440	0,463	0,439	5,669	5,253	4,843	0,78
2,77E-3	1,708	1,978	0,971	0,216	0,235	0,244	2,527	2,676	2,723	2,725	1,850	2,220	2,313	0,344	0,371	0,275	4,911	4,444	4,042	-0,03

(1b)

Experiment	Frequencies range (cm^{-1})		Experiment	Frequencies range (cm^{-1})	
I-1	667,0/640,0	(SDS)	I-11	667,0/640,0	(CDS)
I-2	675,0/638,0	(SDS)	I-12	675,0/638,0	(CDS)
I-3	683,0/630,0	(SDS)	I-13	683,0/630,0	(CDS)
I-4	933,0/896,0	(SDS)	I-14	933,0/896,0	(CDS)
I-5	933,0/900,0	(SDS)	I-15	933,0/900,0	(CDS)
I-6	924,0/904,0	(SDS)	I-16	924,0/904,0	(CDS)
I-7	1390,0/1360,0	(SDS)	I-17	1390,0/1360,0	(CDS)
I-8	1386,5/1360,0	(SDS)	I-18	1386,5/1360,0	(CDS)
I-9	1386,5/1358,6	(SDS)	I-19	1386,5/1358,6	(CDS)
I-10	1358,5/1351,0	(SDS)	I-20	1358,5/1351,0	(CDS)

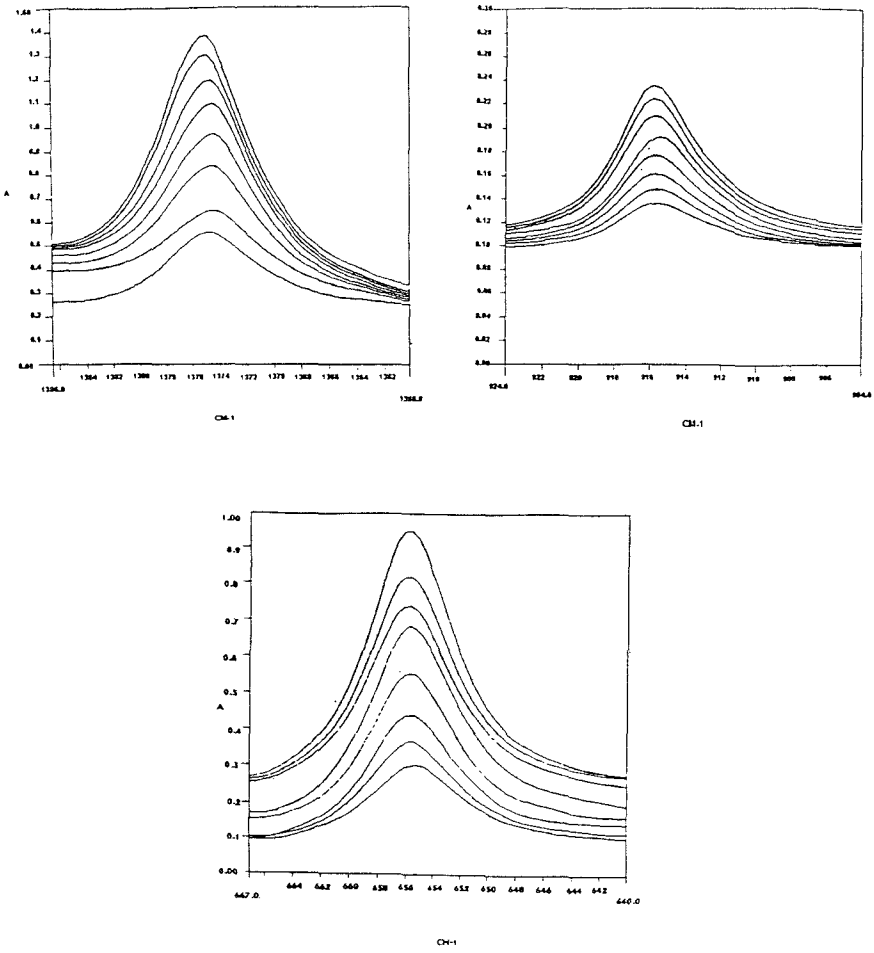


Figure 1. Band areas corresponding to the N-O and N-C stretching and to the O-N-O bending at different concentrations.

The band area representing absorbance is given by the expression:

$$A = 2.303 \int_{\nu_0}^{\nu} log\frac{I_0}{I} d\nu \qquad (1)$$

Where I_0 and I are intensities of the incident and transmitted light, ν is the wavenumber in cm^{-1} units. Denoting by c, the concentration of the solution in mol L^{-1} units, and by l, the path length of the cell,according to Ramsay[2], the integrated intensity B, is defined by the expression:

$$B = \frac{2.303}{cl} \int_{\nu_0}^{\nu} log\frac{I_0}{I} d\nu \qquad (2)$$

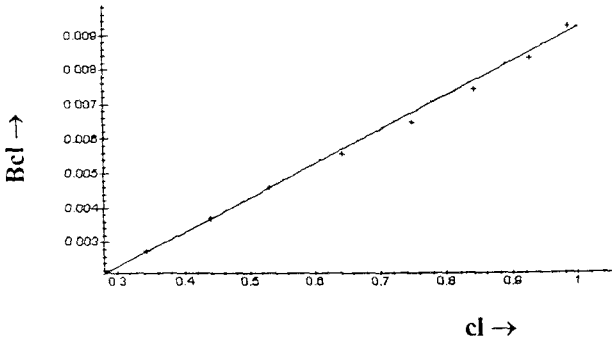
The dipole moment derivatives were calculated from the experimental intensities by means of the equation:

$$A = \frac{N\pi\theta d}{3c^2}\left(\frac{\partial\mu}{\partial Q_i}\right)^2 \qquad (3)$$

Where A is the absolutes integrate intensity, N is the Avogadro number, c is the light velocity in cms^{-1} units, d is the degeneracy and θ is a constant depending on refractive index. $\partial\mu/\partial Q_i$ represent the derivative of the dipole moment with relation to the normal Q_i coordinate.

A values were obtained plotting Bcl vs. cl.The plots of Bcl vs. optical concentration cl for N-O symmetric stretching, N-C symmetric stretching and for O-N-O symmetrical bending are given in figure 2.

In this study, we considered the calculation of the areas of the absorption bands under two conditions: i) experiments without subtraction of the solvent effect, and ii) experiments with subtraction of the solvent effect. For each area calculation under these



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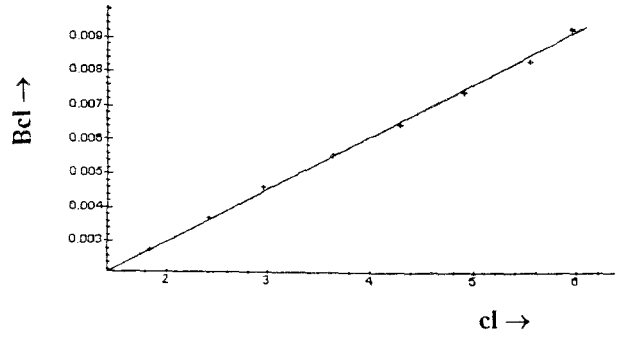

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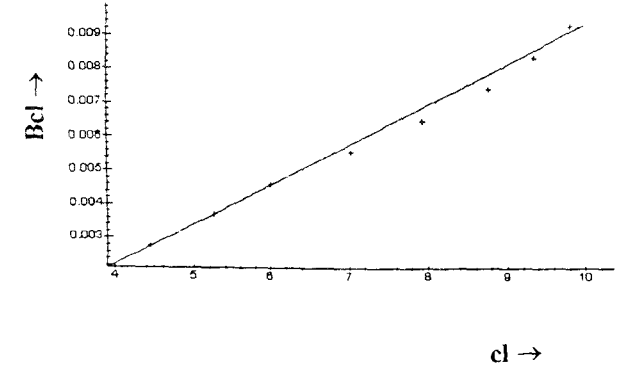

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Figure 2. Plots of Bcl vs. cl for NO_2 symmetric stretching, NO_2 symmetric bending and N-C stretching bands.

two conditions we chose three frequency limits for each symmetrical normal mode. The final results are related to the mean value of the considered frequencies limits and are presented in Table 2.

Dipole Moment Derivatives

The equation used for the determination of the dipole moment derivatives was:

$$\left(\frac{\partial \mu}{\partial Q_i}\right) = \pm\left(\frac{3c^2 A_i}{N\pi\theta d}\right)^{1/2} \quad (4)$$

Introducing the constant values in the above equation we obtained:

$$\left(\frac{\partial \mu}{\partial Q_i}\right) = \pm 3.7704 \times 10^{-2} A_i^{1/2} \quad (5)$$

From the experimental band area measurements of solutions (wtss), the mean values of $\pm(\partial\mu/\partial Q_i)$'s were: ±1.0133, ±0.3642 and ±1.1518 correlated with the 655.5, 916.0 and 1375 cm^{-1} wavenumbers. For experiments (wss), the $\pm(\partial\mu/\partial Q_i)$'s were: ±1.0424, ±0.3752 and ±1.1749 for the same set of wavenumbers, respectively.

The normalized amplitude **X** matrix is directly related to $(\partial\mu/\partial_{Sj})$ through the expression:

$$\left(\frac{\partial \mu}{\partial S_j}\right) = \sum (\mathbf{X}^t)_{ij}\left(\frac{\partial \mu}{\partial Q_i}\right) \quad (6)$$

where **X** relates the normal coordinates to the symmetry coordinates according to:

$$Q_i = \Sigma(\mathbf{X}^t)_{ij} S_j \quad (7)$$

Considering the geometry of the molecule and the expression $(\partial\mu/\partial S_j)=\Sigma(\partial\mu/\partial Q_i)(\partial Q_i/\partial S_j)$, we obtain different relations between $\partial\mu/\partial S_j$ and polar properties, dipole moment and effective charge:

$$\frac{\partial \mu}{\partial S_1} = \frac{\partial \mu_{NC}}{\partial R_{NC}} \quad (8), \qquad \frac{\partial \mu}{\partial S_2} = \sqrt{2}\cos\frac{\alpha}{2}\frac{\partial \mu_{NO}}{\partial r_{NO}} \quad (9) \text{ and}$$

$$\frac{\partial \mu}{\partial S_3} = \sqrt{\frac{3}{2}}\,sen\frac{\alpha}{2}\frac{\partial \mu_{NO}}{\partial r_{NO}} \quad (10)$$

Table 2. Mean values of absolute intensities (A) ($mol^{-1}.L.cm^{-2}$)

wavenumber (cm^{-1})	A(wtss)	A(wss)	Deviation (%)
655.5	0.07193×10^4	0.07609×10^4	5.8
916.0	0.00929×10^4	0.00986×10^4	6.0
1375.0	0.09293×10^4	0.09690×10^4	4.0
		Mean deviation	5.3

The KCX = XΦ Vibrational Problem.

According to Decius [8], the principal obstacle to a wide option of the compliance matrix **C** in place of **F**, the force constant matrix, is the established custom to solve the vibrational problem via force constants. Compliance constants are related with vibrational amplitudes. They also appear directly and linearly in the centrifugal distortion parameters, and as we can see now, they are connected to the bond moments and its derivatives. The compliance matrix **C** can be defined in terms of the normalized amplitudes and with the frequencies through the expression: $\mathbf{C} = (\mathbf{X}^t)^{-1}\Phi\mathbf{X}^{-1}$. Φ is the eigenvalues matrix with elements $\phi_k = 1/0.589141.10^{-6}\omega_k^2$ (ω in cm^{-1}).

Compliance constants matrix **C** for the a_1 symmetry type species for $(CH_3)NO_2$ has been determined on the basis of the experimental frequencies using the iterative consistency method [11]. The following system of symmetry coordinates has been used: $S_1(a_1) = \Delta R$, $S_2(a_1) = 1/\sqrt{2}\,\Delta(r_1 + r_2)$ and $S_3(a_1) = 1/\sqrt{6}\,\Delta(\alpha + \beta_1 + \beta_2)$. Δr_i (i=1,2) and ΔR are the stretching internal coordinates defined along the N-O and N-CH_3 bonds, respectively. $\Delta\beta_i$ and $\Delta\alpha$ are the valence bond bending internal coordinates defined through the M-N-O (M=CH_3) and O-N-O angles, respectively.

The diagonal matrix $C_{ii}^{0} = \phi_i/K_{ii}$, $\phi = \lambda^{-1}$ was selected as the matrix of zero approximation. K_{ii} represent the diagonal elements of kinetic energy matrix. **K**, **C** matrix and the normalized amplitudes matrix **X** are given below:

K matrix			C matrix			X matrix		
11.3309	2.4811	-2.8811	0.2193	-0.0070	0.1222	2.3379	2.2389	-0.9244
	14.3294	1.9341		0.0934	-0.0809	-0.4699	2.6843	2.6274
		3.0948			1.3263	-1.6958	0.4661	-0.0433

Polarity Parameters

The polarity parameters were obtained using the expression (6) considering the minus sign of the $\pm(\partial\mu/\partial Q_i)$ values. The same set of derivatives of dipole moment with respect to symmetry coordinates can be obtained using the $\mathbf{L}^{-1}$ matrix solving the vibrational problem via force constants and considering the plus sign of the $\pm(\partial\mu/\partial Q_i)$ expression.We can conclude that there is not ambiguity in the sign of the expression (4) and the use of the minus sign is justified.

Considering that the number of sign configurations is equal to $2^n = 8$ (n = number of normal modes) , we can obtain the eight sets of derivatives of dipole moments related to symmetry coordinates. These values are given in Table 3.

The choice of one of the eight sign combinations as the best solution for the electro optical parameters is highly controversial. CNDO calculations including all the atoms in nitromethane indicate the combination - - + and + - + as the most probable [7]. Singh [6] based on a reduced model of CH_3NO_2 indicates the + - - sign combination as required to give an acceptable solution. Following the same procedure as is given in reference [6], the $\mathbf{L}^{-1}$ matrix obtained by inversion of the **L** matrix resulting from the **GFL=LΛ** secular equation, we obtained the - + - sign combination as a more reasonable

Table 3. Derivatives of dipole moment related to symmetry coordinates

	(wtss)			(wss)		
$(\partial\mu/\partial Q)$ sign configuration	$(\partial\mu/\partial S_1)$	$(\partial\mu/\partial S_2)$	$(\partial\mu/\partial S_3)$	$(\partial\mu/\partial S_1)$	$(\partial\mu/\partial S_2)$	$(\partial\mu/\partial S_3)$
+ + +	-2.119	-3.528	1.599	-2.191	-3.604	1.644
- - -	2.119	3.528	-1.599	2.191	3.604	-1.644
+ + -	4.249	5.525	1.499	4.363	2.570	1.542
- - +	-4.249	-2.525	-1.499	-4.363	-2.570	-1.542
+ - +	0.489	1.572	-1.938	0.511	1.590	-1.994
- + -	-0.489	-1.572	1.938	-0.511	-1.590	1.994
+ - -	2.619	-4.480	-1.838	2.683	-4.584	-1.892
- + +	-2.619	4.480	1.838	-2.683	4.584	1.892

solution. Here, the sign combination is highly dependent on the best solution of the indeterminated problem $\mathbf{GFL = L\Lambda}$, as in the case of the solution of the equation $\mathbf{KCX=X\Phi}$, where the best sign combination was - + +. Dividing the values given in Table 3, by the constants values of the expressions (8), (9) and (10) we could obtain the polarity parameters which are presented in Table 4 Using the polarity parameters with the appropriate choice sign configuration, we obtained the following results:

a) Vibronic contribution: $\mathbf{M}=(\partial\mu_{NO}/\partial r_{NO}) - \mu_{NO}/r_{NO}$. M = 4.26 D/Å(wtss), 4.34/Å(wss).

b) μ_{NO} = 1.45 D (wtss), 1.50 D(wss). c) μ_{NO2} = 1.29 D (wtss), 1.34 D(wss).

d) $(\partial\mu_{NO}/\partial r_{NO})$ = 6.02 (wtss), 6.16 (wss). e) μ_{NO}/r_{NO} = 1.77 (wtss), 1.82 (wss).

f) $(\partial\mu_{NC}/\partial R_{NC})$ = -2.62 (wtss) and -2.68 (wss).

Table 4. Polarity parameters

Sign configuration	$\partial\mu_{NC}/\partial R_{NC}$	$\partial\mu/\partial r_{NO}$	μ_{NC}/r_{NO}	$\partial\mu_{NC}/\partial R_{NC}$	$\partial\mu_{NC}/\partial R_{nO}$	μ_{NO}/r_{NO}
+ + +	-2.119	-4.740	1.535	-2.191	-4.843	1.578
- - -	2.119	4.740	-1 535	2.191	4 843	-1.578
+ + -	4.249	3.393	1.439	4.363	3 453	1.480
- - +	-4.249	-3.393	-1.439	-4.363	-3.453	-1.480
+ - +	0.489	2.113	-1.861	0.511	2.137	-1.914
- + -	-0.489	-2.113	1.861	-0.511	-2.137	1.914
+ - -	2.619	-6.020	-1.765	2.683	-6.159	-1.816
- + +	-2.619	6.020	1.765	-2.683	6.159	1.816

Conclusions

Using the same approximations as in [6] concerning the factor θ and to the degeneracy d,(in equation 3), our results agreed well with the Singh's previous reports [6]. Advantages of the FT-IR bands intensities determinations are: calculated band areas can be computed using the software of the spectrophotometer, meaning that band area calculations by graphical count, planimeter or others, are not necessary. Slit correction is also out of consideration in FT-IR spectrophotometers. In FT-IR band intensity measurements, the spectrum of the solvent can be substracted directly in each measurement of the mixture substance plus solvent. The solvent effect has an incidence around the 5% on the experimental results. As the **X** matrix of the normalized amplitudes is directly related to the $(\partial\mu/\partial Q_i)$'s derivatives, their matrix elements can be directly obtained solving the equation $\mathbf{KCX=X\Phi}$. Using the $\mathbf{X}^t$ matrix and selecting the minus sign of $\pm\ (\partial\mu/\partial Q_i)$, the polarity parameters can be obtained. The solutions are equivalent to

those obtained using the $\mathbf{L}^{-1}$ matrix (via force constants) and the plus sign of the polarity derivatives. There are not sign ambiguities in equation (4).

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