

## Normal Coordinate Analysis and Infrared Band Intensities of Nitromethane and Nitromethane-D<sub>3</sub>

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**ABSTRACT.** Laser Raman and Infrared (60-3500 cm<sup>-1</sup>) spectra of nitromethane and nitromethane-d<sub>3</sub>, in their standard states are discussed. Complete and unambiguous assignment of all observed vibrational bands of nitromethane are made on the basis of the results of the calculated normal modes, isotope frequency shifts and calculated quantum values of infrared band intensities. Infrared band intensities are calculated using INDO semi-empirical quantum chemical method. The torsion mode of vibration of the CH<sub>3</sub> group was detected at 144 cm<sup>-1</sup>. This indicates the presence of a sort of association between nitromethane molecules in the liquid state. A set of force constants for nitromethane is developed and refined using the least square fit method.

### Introduction

Many vibrational data on nitromethane in gas, liquid or polycrystalline states have been reported<sup>[1-6]</sup>. However, no definite unambiguous assignment of the observed vibrational bands in the infrared and Raman spectra of nitromethane in the standard liquid state has been made. Such unambiguous assignments of vibrational bands should be based on theoretically calculated normal coordinates, vibrational band intensities and the isotope frequency shift expected in the spectra of deuterated derivative. No infrared or Raman frequency value for the torsional mode of vibration of the CH<sub>3</sub> group in liquid state of nitromethane has been mentioned or reported in literature before. This frequency gives directly an indication about the rigidity of internal rotation of this group and consequently the association which may be present between different molecules. However, some microwave studies have been published about the internal rotation of CH<sub>3</sub> group in gaseous state nitromethane molecule<sup>[6,7]</sup>.

In this study, the aim is to report the following main points: 1. Recently measured infrared, Far infrared and Laser Raman spectra for nitromethane and nitromethane- $d_3$  in the liquid standard state. 2. Results obtained from normal coordinate calculations of  $CH_3NO_2$  and  $CD_3NO_2$  and quantum chemical values of infrared band intensities. 3. Assignment of all observed fundamental vibrations to normal modes on the basis of calculated data of previous points. 4. Refined set of force constants representing the force field of the molecule.

## Experimental

Nitromethane and nitromethane- $d_3$  were supplied from Fluka and Scharp & Dohme companies respectively. Their purity was tested by Gas Chromatography and were found to be over 99%.

### 1. Infrared Measurement

IR spectra of the liquid samples and 20% cyclohexane solutions were reported on a Perkin-Elmer 683 spectrophotometer. Standard liquid cells with CsBr windows and 10  $\mu$  spacing for solutions were used. The low frequency range (40-400  $cm^{-1}$ ) was recorded on a PE 180 spectrometer using a liquid cell with 500  $\mu$  spacing and polyethylene windows.

### 2. Raman Measurements

The Raman spectra were recorded in the liquid state on a Coderg PHØ Raman spectrometer equipped with spectra physics Argon-ion laser 171 using 514.5 nm exciting line. The depolarization ratios of different bands were determined.

## Theoretical Treatment

### 1. Normal Coordinate Calculations

The normal modes of vibrations were calculated according to the  $F$  and  $G$  matrix method<sup>[8,9]</sup>. The molecular structural parameters used to construct the  $G$ -matrix were deduced from the reports of Dewar and Setton<sup>[10,11]</sup>. These parameters are:  $r(C-N) = 1.471$ ,  $r(N=O) = 1.22$ ,  $r(C-H) = 1.05$  Å,  $\angle(N-O-N) = 139.0$ ,  $\angle(C-N-O) = 114.3$ ,  $\angle(H-C-N) = 111.0$  and  $\angle(H-C-N) = 109.5$  degrees.

### 2. Infrared Band Intensities

The integrated intensity  $A_k$  of a normal mode of vibration was calculated from the relation :

$$A_k = 8 \pi^3 N_o \nu_k / 3h g_k b_k^2 \left( \frac{\partial \mu}{\partial Q} \right)^2 \quad (1)$$

where  $N_o$  is the avogadro number.

$\nu_k$  is the frequency of the normal mode  $k$  in  $cm^{-1}$ .

$g_k$  is the degeneracy of the normal mode  $k$ .

$b_k$  is the quantum amplitude of the mode  $k$ .

$(d\mu/dQ)_k$  is the derivative of the dipole moment  $\mu$  of the molecule with respect to the normal coordinate  $Q$ .

The normal mode frequency  $\nu_k$  is directly produced from the normal coordinate calculations of the molecule as eigenvalue. The theoretical amplitude  $b_k$  is calculated from the produced normalised eigenvector  $L_k$  of the normal coordinates problem according to the relation :

$$b_k = \{ h/[8 \pi^2 c \nu_k \sum_i M_i ((L_k)_{ix} + (L_k)_{iy} + (L_k)_{iz})] \}^{1/2} \quad (2)$$

where:  $(L_k)_{ix}$ ,  $(L_k)_{iy}$  and  $(L_k)_{iz}$  are the components of the eigenvector matrix  $L_k$  for the displacements of atom  $i$  in the directions  $x$ ,  $y$  and  $z$  for the frequency  $\nu_k$ .  $M_i$  is the mass of the  $i$ th atom.

The values for  $(d\mu/dQ)_k$  were calculated using the semi-empirical INDO-MO theory<sup>[12]</sup>. The resulting  $A_k$  values according to this procedure are directly comparable with the experimentally determined quantities for the integrated infrared intensities defined as :

$$A_k = 1/dc \int \ln (I_0/I) d\nu \quad (3)$$

where:  $c$  is the mean concentration of the sample and  $d$  is the sample thickness.

### 3. Refinement of Force Constants

This was performed by the application of the "Least Square Fit" technique<sup>[13]</sup>. All these theoretical calculations were performed on the IBM-PC/XT personal computer (640 kB and equipped with 8087 co-processor). FORTRAN programs were prepared and compiled using a Microsoft Compiler.

## Results and Discussion

The observed fundamental frequencies in the infrared spectra of nitromethane and nitromethane- $d_3$  were found, as expected, coincident with those observed in the Raman spectra. In the spectra of nitromethane there are two bands detected in the infrared spectra which could not be observed in the Raman spectra. The first was the very weak band observed at  $965 \text{ cm}^{-1}$  and the second was that very weak and broad band observed at  $144 \text{ cm}^{-1}$ . In the spectra of nitromethane- $d_3$ , only the first one was detected in the infrared spectrum at  $770 \text{ cm}^{-1}$ . The observed infrared and Raman spectra of nitromethane and nitromethane- $d_3$  in their liquid states are presented in Fig. 1 and Fig. 2 respectively.

The most stable conformation for the nitromethane molecule, defined for normal coordinate calculations was calculated by the INDO-MO method<sup>[1]</sup>. Many conformations are possible for the molecule, mainly depending on the internal rotation of the  $\text{CH}_3$ - (or  $\text{NO}_2$ -) group about the C-N bond. The conformation in which the angle between the  $\text{NO}_2$ - and H-C-N plane is 30 degrees was that found to have minimum total energy ( $-57.688633$  a.u.). This conformation of the molecule belongs to the  $C_s$  point symmetry. The energy difference between this conformer and the highest energy one did not exceed 10 joule/mole. This low total energy difference between conformers indicates the low internal rotational barrier and consequently a very low frequency expected for the ground state torsional transition in the spectra of nitromethane in the free molecular state. Normal coordinate calculations for nit-

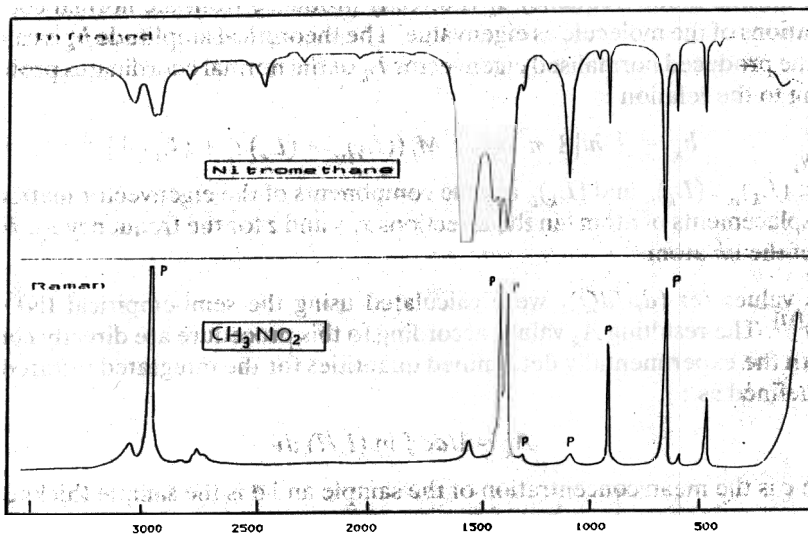


FIG. 1. Infrared and Raman spectra of nitromethane in the liquid state.

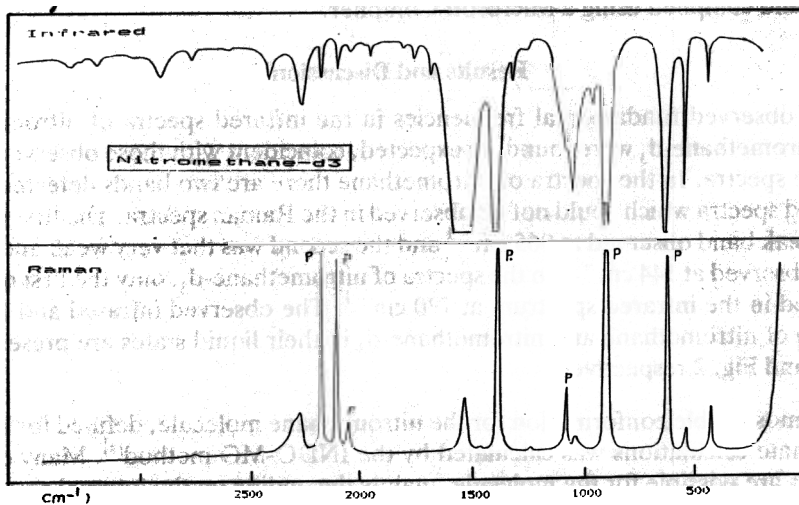


FIG. 2. Infrared and Raman spectra of nitromethane- $\text{d}_3$  in the liquid state.

romethane molecule were done considering the molecules in the lowest energy conformation.

The nitromethane molecule has seven atoms and consequently fifteen fundamental vibrations are expected in its spectra. These are six stretchings, seven angle defor-

mations, one out-of-plane deformation and one torsion. Nine fundamentals belong to the  $A'$  symmetry species and the other six belong to the  $A''$  species of  $C_3$  point group. Both species are infrared as well as Raman active and consequently all vibrational modes, or fundamentals, are expected to be observed in the infrared as well as in the Raman spectra. Analysis of the fundamental modes of vibrations according to their type and symmetry are summarised in Table 1.

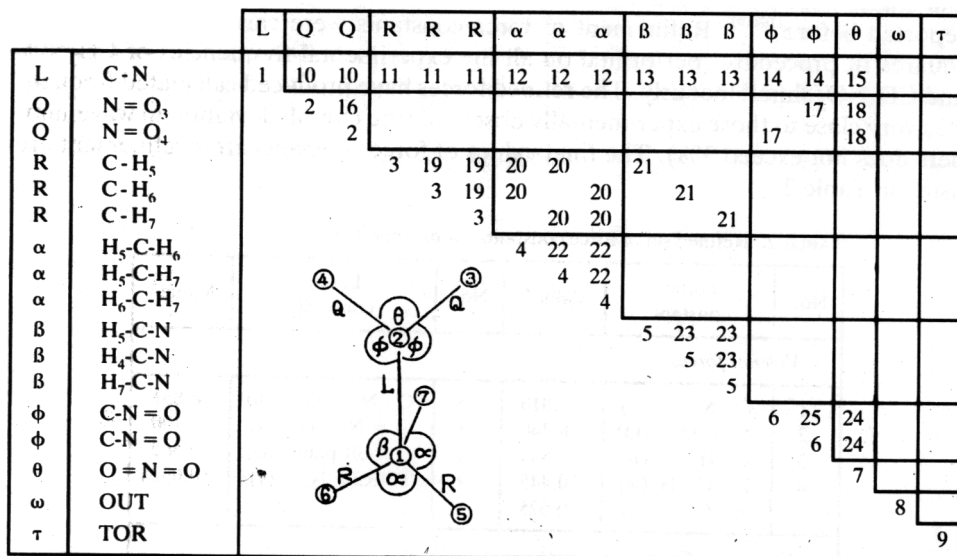


FIG. 3. Force constant matrix and internal coordinates with their symbols for nitromethane (elements of the matrix are force numbers and not their values).

TABLE 1. Types and symmetries of the fundamental vibrations of nitromethane and nitromethane-d<sub>3</sub>.

Type	Mode	C <sub>3</sub> symmetry		No. of modes
		A'	A''	
Stretching	$\nu$ NO <sub>2</sub>	$\nu_1$	$\nu_2$	2
	$\nu$ (CN)	$\nu_3$		1
	$\nu$ (CH)	$\nu_4, \nu_5$	$\nu_6$	3
Deformation	$\delta$ (NO <sub>2</sub> )	$\nu_7$		1
	$\delta$ (CH <sub>3</sub> )	$\nu_8, \nu_9$	$\nu_{10}$	3
Rocking	$\rho$ (NO <sub>2</sub> )		$\nu_{11}$	1
	$\rho$ (CH <sub>3</sub> )	$\nu_{12}$	$\nu_{13}$	2
Out-of-plane	$\omega$ (CNO <sub>2</sub> )	$\nu_{14}$		1
Torsion	$\tau$ (CH <sub>3</sub> )		$\nu_{15}$	1
Total no. of modes		9	6	15

A total of 25 force constants, involving 9 valence and 16 interaction force constants were considered in the normal coordinate calculations. The matrix of force constants used and a definition of internal coordinates of nitromethane and their corresponding symbols used throughout this work are shown in Fig. 3. Other interaction force constants (off-diagonal elements in the matrix) were found to have no significant effect on the vibrational frequencies. Initial values for valence force constants of bonds and angles were transferred from values for bonds and angles of similar compounds reported before<sup>[14,15]</sup>. Refinement of force constants were carried out by at least squares fit procedure, performed on all the experimental frequencies of  $\text{CH}_3\text{NO}_2$  and  $\text{CD}_3\text{NO}_2$  simultaneously. The refined forces have produced calculated frequencies very close to those experimentally observed (the overall deviation in wavenumbers does not exceed 3%). The final values of force constants after refinement are listed in Table 2.

TABLE 2. Refined set of force constants for nitromethane

No.	Force constant	Value*	No.	Force constant	Value*
<i>Valence forces :</i>					
1	C - N (L)	5.010	6	C - N = O ( $\phi$ )	0.831
2	N = O (Q)	8.340	7	O = N = O ( $\theta$ )	1.100
3	C - H (R)	4.844	8	Out-off-plane ( $\omega$ )	0.660
4	H - C - H ( $\alpha$ )	0.445	9	TORSION ( $\tau$ )	0.0324
5	H - C - N ( $\beta$ )	0.625			
<i>Interaction forces :</i>					
10	F(L, Q)	1.110	18	F(Q, O)	- 0.201
11	F(L, R)	0.830	19	F(R, R)	0.081
12	F(L, $\alpha$ )	- 0.101	20	F(R, O)	0.102
13	F(L, $\beta$ )	0.213	21	F(R, $\beta$ )	- 0.052
14	F(L, $\phi$ )	- 0.060	22	F( $\alpha$ , $\alpha$ )	- 0.033
15	F(L, $\theta$ )	0.050	23	F( $\beta$ , $\beta$ )	- 0.054
16	F(Q, Q)	0.055	24	F( $\phi$ , $\theta$ )	- 0.252
17	F(Q, $\phi$ )	0.064	25	F( $\phi$ , $\phi$ )	- 0.021

\*Units are: Newton  $\text{cm}^{-1}$  for stretching; Newton  $\text{cm rad}^{-2}$  for deformation and Newton  $\text{rad}^{-1}$  for interaction force constants.

The main data obtained from the normal coordinate analysis discussed are: (a) The normal coordinates (eigenvectors  $Q_k$ ) in the form of  $L$ -matrix. This  $L$ -matrix describes the relative cartesian displacements of each atom for every normal coordinate. (b) Theoretical values for those expected vibrational frequencies (eigenvalues). (c) The potential energy distribution (PED) values which represent the percent contribution of internal coordinates in the normal coordinate, *i.e.* they are considered a quantitative assignment of the calculated normal coordinate to the normal mode of vibration.

The calculated  $L$ -matrices (the eigenvectors of normal coordinates) were used as input data for the standard INDO-MO quantum mechanical method<sup>[12]</sup> to determine

the  $(d\mu/dQ)_k$  values. The INDO-MO method was used in these calculations because semi-empirical methods were successfully applied to calculate dipole moments and infrared band intensities<sup>[16,17]</sup>. The calculated  $d\mu/dQ$  values are used to calculate theoretically expected integrated intensity values for the infrared bands according to equation (1) in the previous section. The experimental values for intensities are also determined as described before according to equation (3). The area of the absorption band was considered equivalent to the integral quantity  $\ln(I_0/I) dv$  in equation (3). Experimental and theoretical values for infrared intensities are given in Table 3. Correlation between the experimentally and observed frequencies with their integrated band intensities and those theoretically calculated values are given in Fig. 4.

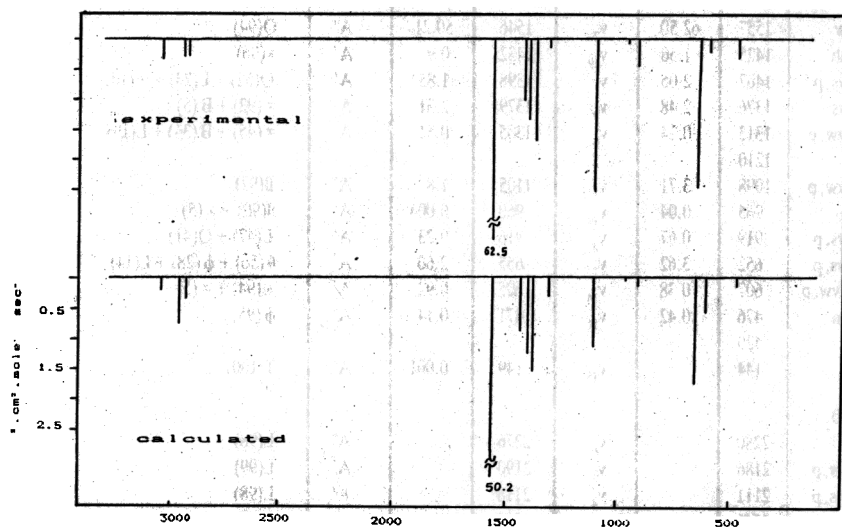


FIG. 4. Correlation between experimentally estimated and theoretically calculated infrared vibrational band intensities of nitromethane molecule.

On the basis of results of normal coordinate calculations (frequencies, modes and PED values), and the expected isotope frequency shift of observed frequencies to lower wavenumbers in the spectra of deuterated nitromethane, an unambiguous assignment of the different observed bands in the spectra of nitromethane was made. The experimentally observed frequencies from infrared and Raman spectra with the observed infrared band intensities as well as the calculated results of normal coordinate analysis with the calculated infrared band intensities are correlated in Table 3. The calculated eigenvectors (the  $L$ -matrices) of the different modes of vibrations are represented graphically in Fig. 5 and their data are collected in separate tables available for any request.

As seen from PED values in Table 3, there are strong couplings between the different modes of vibrations. The  $\nu$  (C-N) stretching mode  $\nu_3$  is strongly coupled with the  $\nu$  ( $\text{NO}_2$ ) stretching mode  $\nu_1$  and  $\delta$  ( $\text{NO}_2$ ) angle deformation mode  $\nu_7$ . This is indi-

TABLE 3. Experimental and calculated vibrational frequencies with their assignments and the infrared band intensities for nitromethane and nitromethane-d<sub>3</sub>.

Obs. freq. cm <sup>-1</sup>		Obs. IR int.	Mode	Calc. freq.	Calc. int. <sup>+</sup>	Symm. species	% Pot. energy** distribution	Assign
Raman*	IR							
CH <sub>3</sub> NO <sub>2</sub> :								
3046 w	3046	0.45	v <sub>6</sub>	3050	0.35	A''	L(99)	ν <sub>as</sub> CH <sub>3</sub>
2970 vs, p	2968	0.41	v <sub>4</sub>	2961	1.1	A'	L(96)	ν <sub>s</sub> CH <sub>3</sub>
2949 sh	2950	0.41	v <sub>5</sub>	2950	0.54	A'	L(99)	ν <sub>s</sub> CH <sub>3</sub>
-	2800							combin.
2770 vw, p	2770							combin.
2745 vw, p	2743							combin.
1557 w	1557	62.50	v <sub>2</sub>	1546	50.21	A''	Q(94)	ν <sub>as</sub> NO <sub>2</sub>
1425 sh	1425	1.50	v <sub>10</sub>	1432	0.9	A''	α(96)	δ <sub>as</sub> CH <sub>3</sub>
1403 vs, p	1402	2.05	v <sub>1</sub>	1398	1.85	A'	Q(52) + L(24) + α(10)	ν <sub>s</sub> NO <sub>2</sub>
1375 vs	1376	2.48	v <sub>9</sub>	1379	2.31	A'	α(92) + B(5)	δ <sub>s</sub> CH <sub>3</sub>
1311 vw, p	1313	0.24	v <sub>8</sub>	1305	0.51	A'	α(45) + B(34) + L(19)	δ <sub>s</sub> CH <sub>3</sub>
-	1210							combin.
1100 vw, p	1098	3.71	v <sub>13</sub>	1105	1.8	A''	B(92)	ρ <sub>as</sub> CH <sub>3</sub>
-	965	0.04	v <sub>12</sub>	960	0.004	A'	B(90) + α(5)	ρ <sub>s</sub> CH <sub>3</sub>
920 vs, p	919	0.67	v <sub>3</sub>	916	0.23	A'	L(47) + Q(41)	vC-N
654 vs, p	652	3.62	v <sub>7</sub>	655	2.60	A'	θ(56) + φ(28) + L(14)	δ NO <sub>2</sub> in
605, vw, p	607	0.38	v <sub>14</sub>	605	0.92	A'	ω(94) + α(5)	ω NO <sub>2</sub> out
478 m	476	0.42	v <sub>11</sub>	471	0.14	A''	φ(95)	ρ NO <sub>2</sub> in
-	420							comb.
-	144		v <sub>15</sub>	149	0.001	A''	T(100)	torsion
CD <sub>3</sub> NO <sub>2</sub> :								
2282	2280		v <sub>6</sub>	2276		A''	L(98)	ν <sub>as</sub> CD <sub>3</sub>
2184 vs, p	2186		v <sub>5</sub>	2190		A'	L(99)	ν <sub>as</sub> CH <sub>3</sub>
2112 vs, p	2111		v <sub>4</sub>	2118		A'	L(98)	ν <sub>s</sub> CD <sub>3</sub>
1540 m	1540		v <sub>2</sub>	1537		A''	Q(96)	ν <sub>as</sub> NO <sub>2</sub>
1388 vs, p	1388		v <sub>1</sub>	1390		A'	Q(46) + L(18) + α(14)	ν <sub>s</sub> NO <sub>2</sub>
1068 m, p	1069		v <sub>8</sub>	1063		A'	α(97)	δν <sub>as</sub> CD <sub>3</sub>
1038 vw	1040		v <sub>10</sub>	1044		A''	α(97)	δ <sub>as</sub> CD <sub>3</sub>
-	942		v <sub>9</sub>	939		A'	α(30) + B(30) + Q(21)	δ <sub>s</sub> CD <sub>3</sub>
894 vs, p	895		v <sub>3</sub>	899		A'	L(40) + Q(26) + B(13)	v(C-N)
877 vw	876		v <sub>13</sub>	873		A''	B(94)	ρ <sub>as</sub> CD <sub>3</sub>
-	770		v <sub>12</sub>	774		A'	B(94) + α(19)	ρ CD <sub>3</sub>
625 vs, p	625		v <sub>7</sub>	628		A''	θ(52) + φ(26) + L(17)	δ NO <sub>2</sub>
544 w, p	546		v <sub>14</sub>	540		A'	OUT(81) + B(18)	ω NO <sub>2</sub>
434 m	435		v <sub>11</sub>	430		A''	φ(92)	ρ NO <sub>2</sub>
-	-		v <sub>15</sub>	136		A''	τ(100)	torsion

\* Units are 10<sup>15</sup> · cm<sup>2</sup> · mole<sup>-1</sup> · sec<sup>-1</sup>.

\* Symbols: vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; p: polarised.

\*\* Values lower than 5% are not reported.

cated from its calculated PED values (see Table 3), it contains 47%, 41% and about 10% contributions from C-N (L), N = O (Q) and O = N = O (θ) internal coordinates respectively. This mode was observed at 919 cm<sup>-1</sup> as a strong band in the infrared and as expected, as strong polarized band in the Raman spectra. The wavenumber of this band, as expected, was not considerably shifted to lower value in the nit-



spectrum. All  $\text{C-H}_3$  stretching modes  $\nu_4$ ,  $\nu_5$  and  $\nu_6$ , are approximately pure C-H stretchings. The C-H (L) internal coordinate contribution in PED values of all these modes is over 97%. The stretching modes of vibration of the nitromethane molecule are represented graphically according to their calculated eigenvectors ( $L$ -matrices) in Fig. 5-a.

The  $\delta(\text{NO}_2)$  angle deformation mode  $\nu_7$  was observed as a very strong band in the infrared as well as in the Raman spectra at  $652\text{ cm}^{-1}$ . This mode of vibration has only 56% of its contribution from the  $\text{O}=\text{N}=\text{O}$  ( $\theta$ ) internal coordinate and the rest from out-of-plane ( $\omega$ ) and C-N (L) internal coordinates, (28%) and (14%) respectively. The  $\delta_s(\text{CH}_3)$  the symmetric angle deformation mode of the  $\text{CH}_3$  group  $\nu_8$  was detected at  $1311\text{ cm}^{-1}$ . This mode is highly coupled with the  $\text{CH}_3$  rocking mode  $\nu_{12}$  and the  $\nu(\text{C-N})$  stretching mode  $\nu_3$  (PED values are 45%  $\alpha$ , 34%  $\beta$  and 19%  $L$ ). This attributes its detection at a lower wavenumber than the usual value expected for the symmetric deformation of the  $\text{CH}_3$  group. The  $\delta_{as}(\text{CH}_3)$  asymmetric deformation modes  $\nu_9$  and  $\nu_{10}$ , are not coupled and both have their main contributions (over 92%) from H-C-H internal coordinate ( $\alpha$ ). The mode  $\nu_9$  was detected at  $1376\text{ cm}^{-1}$  as very strong infrared as well as Raman band, whereas the mode  $\nu_{10}$  was observed at  $1425\text{ cm}^{-1}$  as a strong infrared and weak Raman band. The different deformation modes of vibrations are presented graphically according to their calculated atomic displacements in the  $L$ -matrices in Fig. 5-b.

The  $\text{NO}_2$  in-plane rocking mode  $\nu_{11}$  was observed at  $476\text{ cm}^{-1}$  as a medium band in both the infrared and Raman spectra. It is not coupled with other modes. The symmetric rocking mode  $\rho_s \text{OH}_3\text{-CH}_3$ ,  $\nu_{12}$  was observed at  $965\text{ cm}^{-1}$  as a very weak band, whereas the asymmetric rocking  $\rho_{as} \text{CH}_3$ ,  $\nu_{13}$ , was observed at  $1098\text{ cm}^{-1}$  as a very strong band. The mode  $\nu_{12}$  could not be detected in a Raman spectrum and  $\nu_{13}$  is detected as a weak band. Both  $\nu_{12}$  and  $\nu_{13}$  are not effectively coupled with other modes (more than 90% contribution from the H-C-N internal coordinate). The different angle deformation and rocking modes of vibration for nitromethane are represented according to their calculated atomic displacements (in  $L$ -matrices) in Fig. 5-b.

The out-of-plane mode of vibration  $\omega(\text{CNO}_2)$   $\nu_{14}$ , was detected at  $607\text{ cm}^{-1}$  as a medium band in the infrared and a weak polarised band in the Raman spectra. The calculated PED values showed that it is an independent mode (94% contribution from  $\text{CNO}_2$  ( $\omega$ ) internal coordinate).

The observed infrared spectrum of nitromethane in its liquid state showed a very weak and broad absorption band at  $144\text{ cm}^{-1}$ . This band could not be observed in the infrared or in the Raman spectra for solution in cyclohexane. This band was assigned to the  $\text{CH}_3$  torsion mode of vibration. This band has not been reported for liquid nitromethane before. However, in the infrared spectrum of nitromethane in the polycrystalline state a similar absorption band at  $149$  was reported<sup>[18]</sup>. Infrared spectra in this low frequency region for substances in the polycrystalline state, are usually crowded with absorption bands which are attributed mainly to the crystal lattice vibrations of the substance. In the liquid state nitromethane the only expected band to appear in this region is the torsion mode of vibration for the  $\text{CH}_3$  group. Torsional

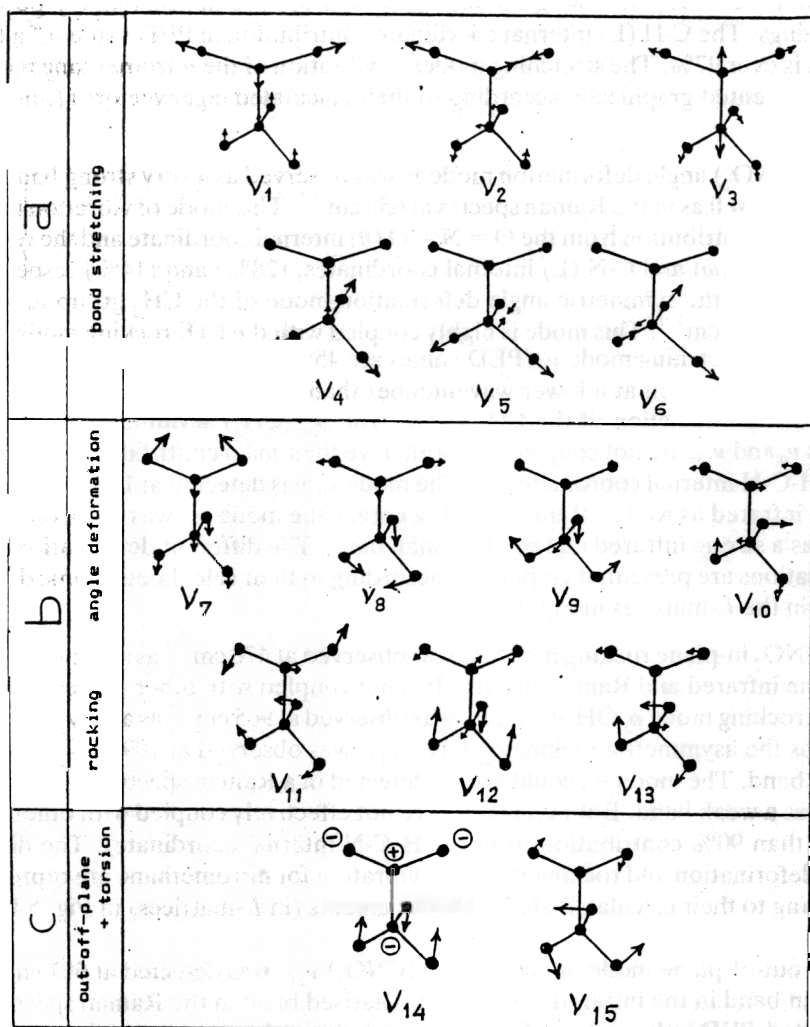


FIG. 5. Calculated atomic displacements (eigenvectors) for the different normal vibrations of nitromethane.

romethane- $d_3$  spectra. The  $\nu_s$  ( $\text{NO}_2$ ) stretching mode  $\nu_1$  is coupled with  $\nu_3$  and  $\nu_{12}$  modes, where the contribution from  $\text{N} = \text{O}$  (Q) internal coordinate in this mode does not exceed 52%. This mode was observed at  $1403 \text{ cm}^{-1}$  in both infrared and Raman spectra as a strong band. It was highly polarised in the Raman spectrum. On the other hand, the  $\nu_{as}$  ( $\text{NO}_2$ ) stretching mode  $\nu_2$ , is not effectively coupled with other modes and has its main contribution from the  $\text{N} = \text{O}$  (Q) internal coordinate (about 94%). This band was detected at  $1557 \text{ cm}^{-1}$  as a very strong band in the infrared, stronger than the  $\nu_1$  mode, and as a medium strong unpolarised band in the Raman

frequency of  $\text{CH}_3$  for similar molecular species such as acetaldehyde and methylvinylketone were reported at 150 and  $101 \text{ cm}^{-1}$  respectively<sup>[19,20]</sup>. Detection of this band in the spectrum of its liquid state and not in solution state may be attributed to the presence of a sort of association between oxygen atom of one molecule with the hydrogen atoms of other molecules in the liquid state. Such association is more effective in the case of the solid state and consequently more rigid  $\text{CH}_3$  torsion and higher frequency values for this mode are expected. This torsion mode is completely independent one, its calculated PED is 100% contribution from the torsion internal coordinate ( $\tau$ ). This torsion mode is not detectable in the gaseous or in position states of nitromethane because the association between molecules are extremely small so that it does not play any role in the three fold barrier of rotation of the methyl group. The barrier in these states is a six-fold rotational barrier and has a very small magnitude and the methyl group is approximately free to rotate about the C-N bond. The calculated force constant for the  $\text{CH}_3$  torsion was  $0.0324 \text{ N cm}^{-1}$ . This value indicates that a very low frequency value is expected for the torsion mode of vibration of nitromethane in the gaseous state.

The calculated infrared band intensities with the standard INDO method produced values which satisfactorily agreed with the experimentally observed values. However, there are discrepancies between some values especially located for the  $\text{CH}_3$  modes. These discrepancies may be due to the strong polarisation which exists in the molecule and accordingly the values of orbital exponents of the valence shell atomic orbitals of different atoms used in the INDO calculations should be refined to represent this polarisation. Lower values for the orbital exponents of the H-atoms seems to 'release' the electrons and facilitate their donation, whereas higher values for orbital exponents on the oxygen atoms lead to 'fixed' electrons on these atoms.

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## التقدير الكمي للاهتزازات الجزيئية وشدة امتصاص عصابات الاهتزاز في طيف الأشعة تحت الحمراء لجزيء نيتروميثان وثلاثي ديترونيتروميثان

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المستخلص . في هذا البحث تم تسجيل دقيق لطيف الاهتزاز الجزيئي لجزيئات النيتروميثان وثلاثي ديترونيتروميثان في حالتها السائلة القياسية وذلك بقياس طيف الرامان باستخدام أشعة الليزر كمصدر للضوء (أحادي الطول الموجي) وكذلك طيف الأشعة تحت الحمراء في المجالين القريب والبعيد (بين ٦٠-٣٥٠٠ سم<sup>-1</sup>).

كما تم إجراء حسابات ميكانيكا الكم وتقدير طاقات الاهتزازات الجزيئية المختلفة وكيفية حركة الذرات في كل واحد من هذه الاهتزازات المختلفة . كما تم إجراء الحسابات الكمية أيضاً لتقدير شدة الامتصاص المتوقع لكل اهتزاز جزيئي وبالتالي لكل عصابة امتصاص تظهر في طيف الأشعة تحت الحمراء . وعلى ضوء نتائج هذه الحسابات الكمية النظرية للاهتزازات الجزيئية من حيث طاقتها وشدة امتصاصها وكذلك الانحراف المتوقع لهذه الاهتزازات في طيف الاهتزاز لمشتق ثلاثي ديترونيتروميثان ، تم تفسير جميع عصابات الامتصاص التي ظهرت في طيف الاهتزاز الجزيئي في طيف الرامان وطيف الأشعة تحت الحمراء وتحصيص محدد (لاشك فيه) لكل عصابة امتصاص لأحد الاهتزازات الجزيئية .

ولقد أمكن تسجيل الاهتزاز الجزيئي لالتواء مجموعة الميثيل في الجزيء عند الطول الموجي ١٤٤ م<sup>-1</sup> . وهذا يدل على وجود نوع من الترابط بين جزيئات النيتروميثان في الحالة السائلة . كذلك تم تقدير مجموعة متكاملة لثوابت القوى الجزيئية وتحديد بدقة باستخدام الطرق الاحصائية وهي تمثل قوى الروابط بين الذرات وقوى الزوايا بين هذه الروابط وقوى التأثير المتبادل بينها .