MATRIX AND GAS INFRARED SPECTRA OF NITROETHANE ISOTOPIC SPECIES

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IR and FIR gas phase and Ar matrix isolation spectra of the isotopic species of nitroethane, $CH_3CH_2NO_2$, $CH_3CD_2NO_2$ and $CD_3CD_2NO_2$ are reported. An assignment will be proposed, based mainly on matrix spectra and normal coordinate analysis. An approximate 25 parameter valence force field is given. The analysis of the gas phase spectra is complicated by the fact that only very few band contours comparable to quasirigid model envelopes occur. This phenomenon and unusual band widths and splittings in the matrix spectra are related to the nearly free internal rotation of the nitro group. The Q branch sequence associated with the methyl torsion shows a remarkable splitting into doublets probably also related to the NO₂ rotation. A value of 1080 \pm 20 cm⁻¹ for the methyl torsional barrier is derived.

1. Introduction

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Nitromethane (CH_3NO_2) and nitroethane (CH₃CH₂NO₂) have been found to have extremely low barriers to internal rotation of the nitro group [1,2]. Similarly a very low barrier seems to exist in the mixed isotopic species CH_2DNO_2 and CHD_2NO_2 [3]. Molecules of this sort may approximately be classified as semirigid systems of the C_{2v} frame- C_{3v} top $(C_{2v}F-C_{3v}T)$ and $C_sF-C_{3v}T-C_{2v}T$ and $C_{x}F-C_{2v}T$ type, respectively. For systems of this type the low torsional barrier is expected to lead to characteristic effects in the vibrational spectra. Studies of the gas spectra of nitromethane have been reported by several authors [4,5]. Gas and liquid phase infrared spectra of the 4 lowest nitroalkanes have been published by Smith et al. [6]. By the aid of matrix spectra of nitromethane d_0 and d_3 Verderame et al. [7] were able to improve substantially the assignment of the vibrational modes. Inclusion of vibrational data of N¹⁵ [8] and O¹⁸ [9] isotopic modifications of CH₂NO₂ in a normal coordinate analysis of Trinquecoste et al. [10] lead to a rather complete harmonic force field in which the effects of the internal rotation were disregarded, however. Much less work has been devoted to nitroethane. A fragmentary vibrational analysis has been reported by Popov et al. [11].

Recently, Ekkers et al. [2,12] reported microwave spectra of nitroethane and proposed an assignment based on MW--MW double resonance experiments. From these an upper limit of 3 cm^{-1} for the barrier to internal rotation of the nitro group was derived. Furthermore, Groner et al. [13] reported a study of the complex far infrared absorption between 8 and 60 cm⁻¹ and presented an anlysis of the band contour in terms of a semirigid free internal rotation model.

Though this molecule possesses two finite internal degrees of freedom and as a semirigid system has to be classified as a $C_sF-C_{2v}T-C_{3v}T$ model, sufficient evidence indicates that the methyl group rotational barrier is near 1000 cm⁻¹ and the methyl torsional mode may therefore be considered as a vibrational mode. In this paper infrared spectra of three isotopic species.

$CH_3CH_2NO_2(d_0), CH_3CD_2NO_2(d_2), CD_3CD_2NO_2(d_5)$

in gas phase and isolated in argon matrices will be reported. Furthermore, fragments of the matrix spectra of CH₃CHD NO₂(d_1) and CD₃CH₂NO₂(d_3) were extracted from the spectra of isotopic mixtures.

The matrix spectra will be used as a starting point for an assignment based both on empirical arguments and normal coordinate analysis. By the latter a harmonic force field comprising 25 significant potential constants was derived. Furthermore, it served as an extension of the assignment to the highly complex gas spectra. To support the analysis of the gas spectra extensive computations of model band envelopes within the rigid rotor approximation will be reported. It will be shown that such envelopes approximate experimental band contours only in a few cases. An attempt has also been made to analyze the vibrational spectra within the frame work of the model including the NO₂ internal rotation and harmonic vibrations otherwise.

2. Experimental

2.1. Isotopic species

The light compound has been purchased from Fluka * and purified by preparative gas chromatography (chromosorb 102 column at 170°C).

For preparation of the d_2 species three exchanges of CH₃CH₂NO₂ with D₂O (1:4) and CH₃COONa (3 × 10⁻⁴ molar ratio) at 90°C were used [14]. It was purified by extraction with dried ether, distillation of the solvent and gas chromatography. In order to avoid back exchange of deuterium a three-fold excess of CH₃OD was injected in the GC column prior to the sample. In this manner an isotopic purity of 96% CH₃CD₂NO₂ was achieved. It should be noted that this compound tends to back exchange even by contact with walls of cells, etc.

In a similar way a sample containing $50\% d_0$, 42% d_1 and 8% d_2 was prepared. This sample was required in order to distinguish isotopic impurity bands from d_2 spectra. Nitroethane- d_5 was prepared by the reaction **

$$CD_3CD_2Br \xrightarrow{Ag NO_2} CD_3CD_2NO_2$$

The reaction was carried out as a solid-gas reaction. This procedure has the following advantages over published preparations [15]: simplicity, lack of solvents, direct operation in the vacuum manifold. Purification by GC was made similar to that of the d_2 species. The degree of deuteration was estimated to be better than 95%, the main impurity being CD_3CHDNO_2 . The latter species was identified by preparation of a sample containing approximately 40% CD_3CHDNO_2 after back exchange.

2.2. Instrumentation

Gas phase spectra in the infrared region were recorded by a Perkin-Elmer Model 225 spectrophotometer equipped with 10 and 70 cm path length gas cells with CsBr windows. For the survey spectra slit widths of $0.6-2.4 \text{ cm}^{-1}$ and for particular spectral regions slit widths of $0.3-1.2 \text{ cm}^{-1}$ were applied, frequency measurements may be considered accurate to 1 cm⁻¹ or better. It proved to be not always possible to compensate completely for atmospheric absorption bands, owing, in part, to minor misalignment of the gas cell.

In order to reduce back exchange of α -deuterons the gas cells had to be impregnated 6 times with gaseous D₂O, even so back exchange remained noticeable. The absorption spectrum of the d_0 species in the 350-150 cm⁻¹ region was determined by means of a Beckmann-RIIC Model FS 720 interferometer, using a gas cell with 14 m path length equipped with TPX windows. A 6.35 μ m Mylar film beam splitter and a black polyethylene lens transparent below 400 cm⁻¹ were used. Interferograms with 8192 points placed symmetrically with respect to $\Delta x = 0$ and $4 \,\mu m$ mechanical mirror displacement were taken, leading to 0.3 cm⁻¹ nominal resolution. Two background and 4 sample spectra were used to derive the transmission spectrum. Reliable determination of the latter was disturbed by pronounced adsorption of nitroethane at and simultaneous desorption of water from the cell walls.

Matrix isolation spectra were taken by means of Perkin-Elmer Model 225 and 325 spectrophotometers and a LHe cryostat of our own design [16]. Argon and the sample were separately injected with flow controlled by calibrated Brooks and Edwards needle valves. Argon was supplied at constant pressure from a LN₂ cooled trap; deposition rates between 3 and 20 μ m/hour, continuously measured by a small laser [17], were applied.

FIR matrix spectra were taken with a Perkin-Elmer Model 301 far infrared spectrophotometer. A home-made LHe cryostat equipped with Rigidex windows and either a CsI plate or a crystal quartz wedge target was used. Weakness of the absorption

^{*} Fluka AG, Buchs, Switzerland.

^{**} CD₃CD₂Br manufactured by C. Roth, Karlsruhe, Germany (98% D).



Fig. 1. Infrared spectra of CH₃CH₂NO₂ in Ar matrix at LHe temperature (a-e) and in gas phase (A-D): a $M/A \approx 1000$, 13 μ m Ar, T + 25%, b $M/A \approx 1000$, 39 μ m, T + 20%, c $M/A \approx 130$, 14 μ m, T + 20%, d $M/A \approx 130$, 14 μ m, T + 30%, e $M/A \approx 190$, 22 μ m, T + 20%, A 70 Torr cm, B 140 Torr cm, C 350 Torr cm, D 840 Torr cm, k atmospheric CO₂, w window absorption.

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Fig. 2. Infrared spectra of CH₃CD₂NO₂ in Ar matrix at LHe temperature (a-c) and in gas phase (A-C): a M/A ~ 600, 14 µm Ar, T + 20%, b M/A = 300, 80 µm, T + 20%, c M/A = 600, 54 µm, T + 20%, A 70 Torr cm, B 350 Torr cm, C 840 Torr cm, w window absorption, v isotopic impurity (CH3CHD NO2). . ~ · · ÷

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Fig. 3. Infrared spectra of CD₃CD₂NO₂ in Ar matrix at LHe temperature (a-c) and in gas phase (A-E): a $M/A \approx 540$, 6 μ m Ar, T+ 20%, b $M/A \approx 540$, 21 μ m, T+ 30%, c $M/A \approx 540$, 21 μ m, T+ 20%, A 70 Torr cm, B 670 Torr cm, C 170 Torr cm, D 700 Torr cm, E 350 Torr cm, w window absorption, v isotopic impurity (CD₃CHD NO₂), k atmospheric CO₂.

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bands in the FIR necessitated deposition of up to 1 mm thick Ar layers with M/A ratios $\approx 10-50$ at a deposition rate of approximately 0.3 mm/hour. For improvement of the signal-to-noise ratio the data were subject to a smoothing process [18].

3. Results

In figs. 1, 2, and 3 matrix and gas IR spectra of the three species d_0 , d_2 and d_5 are reproduced. Expanded sections of the matrix CH stretching region of the three species are shown in fig. 4 and low resolution spectra in the region 4000–2000 cm⁻¹ are given in fig. 5. Finally the FIR spectra (350–20 cm⁻¹) of both gaseous and matrix isolated d_0 -nitroethane are reproduced in fig. 6.

In tables 1, 2 and 3 the observed matrix and gas frequencies, the assignment, the normal coordinate results and the approximate description of the normal vibrations in terms of group modes are given. In table 4 a set of frequencies is listed, which are to be attributed to the species $CD_3CH_2NO_2$ (d_3). These spectral data are derived from matrix spectra of isotopic mixtures containing approx. 10% of the d_3 species. Similarly table 5 gives the matrix frequencies of the d_1 species, which were obtained from isotopic mixtures described in section 2.1.

4. Discussion

The following analysis of the vibrational spectra of nitroethane will be presented as follows:

- (i) normal coordinate analysis and assignment of the matrix spectra,
- (ii) assignment of the gas spectra based on matrix spectra and model envelope calculations,
- (iii) discussion of effects of the internal rotation of the NO₂ rotor in the vibrational spectra.

It should be pointed out that the assignment of the matrix spectra proved to be indispensable for a successful attempt to analyse the gas spectra. The latter are conplicated by effects of the nearly free internal rotation of the nitro group to an extent which leads to pronounced deviations of the band envelopes from rigid rotor harmonic oscillator model envelopes. For most of the absorption bands these



Fig. 4. Infrared spectra from 3050 to 2850 cm⁻¹ of nitroethane- d_0 , -1- d_2 , and $-d_5$ in Ar matrix at LHe temperature. Top: CH₃CH₂NO₂, $M/A \approx 100$, 22 µm, middle: CH₃CD₂NO₂, $M/A \approx 300$, 80 µm, bottom: CD₃CD₂NO₂, $M/A \approx 540$, 21 µm. Spectra of both deuterated species taken with expanded transmission scale.

deviations appear to make the use of model envelopes impossible. The low barrier to internal rotation of the nitro group in principle could lead to torsional transitions in the FIR region even for the isolated molecule.

4.1. Normal coordinate analysis

For the normal coordinate analysis of the vibrational spectrum of nitroethane isolated in solid argon a , quasi-rigid molecular model will be adopted. At the



Fig. 5. Infrared spectra from 3500 to 2000 cm⁻¹ of nitroethane- d_0 , -1,1- d_2 , and - d_5 in Ar matrix at LHe temperature and in gas phase: left: CH₃CH₂NO₂, $M/A \approx 70$, 11 μ m, T + 10%, gas 350 Torr cm, middle: CH₃CD₂NO₂, $M/A \approx 300$, 80 μ m, T + 10%, gas 350 Torr cm, right: CD₃CD₂NO₂, $M/A \approx 540$, 35 μ m, T + 50%, gas 350 Torr cm, w window absorption, c atmospheric or matrix isolated CO₂.

present time no information about the stable conformation of the NO_2 group is available either for the gaseous or for matrix isolated states. Since the coefficients of the kinetic matrix

$$G = (g^{mn}) = BM^{-1}\hat{B}$$

depend on the NO₂ rotation angle τ both vibrational eigenvalues and eigenvectors depend on the nitro group conformation. The following analysis will be based on the assumption of a conformation, in which all heavy nuclei are coplanar, cf. fig. 7 [13]. The following comparison in which symmetry species and number of the normal modes of both the planar and the perpendicular NO₂ conformation are contrasted, should make clear that this assumption is relevant: - planar conformation 15a' \oplus 9a"

- perpendicular conformation $14a' \oplus 10a''$ The internal coordinates used in this work are listed in table 6. Besides the assumptions concerning conformation mentioned above it will be further assumed that the harmonic potential constants of the CH₃-, CH₂and the NO₂- group correspond to local symmetries C₃, C₅ and C₂, respectively. The wagging, twisting and rocking coordinates of the CH₂-group are defined by (cf. fig. 7)

$$\Delta \gamma_{\rm w} = \frac{1}{2} (\Delta \epsilon_1 - \Delta \epsilon_2 + \Delta \epsilon_3 - \Delta \epsilon_4) ,$$

$$\Delta \gamma_{\rm r} = \frac{1}{2} (\Delta \epsilon_1 + \Delta \epsilon_2 - \Delta \epsilon_3 - \Delta \epsilon_4) ,$$

$$\Delta \gamma_{\rm t} = (1/\sqrt{8}) (\Delta \epsilon_1 - \Delta \epsilon_2 - \Delta \epsilon_3 + \Delta \epsilon_4) .$$

For the nitro group, the in-plane rocking coordinate was defined as

$$\Delta \Omega = \frac{1}{2} (\Delta \omega_2 - \Delta \omega_1)$$

and the out-of-plane coordinate $\Delta\Gamma$ as the first-order differential of the angle between the normal to NO₂plane and the N-C₁ unit vector [19]. Torsional coordinates of the CH₃ and the NO₂ group are given respectively by

$$\Delta \zeta = \frac{1}{3} (\Delta \tau_{3128} + \Delta \tau_{3129} + \Delta \tau_{31210}),$$

$$\Delta \tau = \frac{1}{2} (\Delta \tau_{2134} + \Delta \tau_{2135}),$$

where the $\Delta \tau$'s were chosen according to Wilson et al. [19]. All other coordinates listed in table 6 were chosen as conventional stretching and bending coordinates; symmetry coordinates were adapted to the local symmetry of the CH₃, CH₂ and NO₂ group. The methyl group bending coordinates are involved in the redundancy

$$(1/\sqrt{6})(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3) = 0.$$

For numerical computation of the vibrational frequencies and the potential energy distribution (PED) a

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Assignment ²⁾	Mode description a,b)	Frequency (cm ⁻¹)					
·		Calculated	Ar matrix c)	Gas			
2¥4(A')		· ·		3220 v			
v1(a')	ν _a (CH ₃) (99)	3012	3024* w	min? 3019			
				(R 3010)			
u16(2")	ν _a (CH ₃) (98)	3012	2999* w	Q 3001 π			
				(P 2991)			
v ₁₇ (a")	ν ₂ (CH ₂) (98)	2977	2972* vw				
ν4 ⁺ ν7(Α')		-	2961 w	(R 2966)			
v2(a')	ν _s (CH ₃) (97)	2953	2954* w	Q 2957 m			
			2948 w	(P 2947)			
v3(a')	v _s (CH ₂) (96)	2936	2925* w	Q? 2926 m			
2=5(A')							
2 ^µ 18(A')			2919 w				
ν5 ⁺ ν18(A"))				1			
(A') קע ²				R 2/60			
				(P 2/40			
				(p 2450			
₽4+₽ ₁₂ (Å')			2434 vw	D 2430			
Hatun(A')				(r 2430 2260 m			
			1571	/P 1585 \			
wa(s')	$w_{1}(NO_{2})(45) \sim (NO_{2})(19) \delta(CH_{2})(13)$	1584	1569+	min 1576			
		1504	1566 5	D 1569			
		-	1563.5	(F 15087			
			1303.3	. D 1480 .			
We(8')	8-(CH2) (91)	(1462	1463 5** m	0 1471			
· 3 · - / .	δ ₂ (CH ₂) (95)	1462	1400.5	(D 1450)			
-1		.(D 1460			
w.(n')	5(CH_)(64) ··· (N(1_)(11) ~ (CH_)(11)	1447	14418				
-0(* /	0(CH2)(04), 02(HO2)(11), 74(CH2)(11)	1447	1441 10				
		-	1200 5 1	P 1439			
·	(0, 0, 0, 0, 1/21) = (0, 0, 1/26) = 0, 0, 0, 1/20	1308	1399.5				
7(2)	3(102)(31), 7W(CH2)(20), 78(102)(14)	1330	1397~ 8	Q 1390 8			
			1371	P 1360			
	δg(CH3) (38), νg(NO2) (28), δ(NO2) (16),		1370	(K 1360)			
· · · · · · · · · · · · · · · · · · ·	δ(CC) (15), μ(CN) (13)	13/2	1366*	Q 1367 8			
				P 1938			
			en and a second				

Table 1 Matrix and gas infrared frequencies of nitroethane- d_0

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Table	1	(continued)
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Assignment a)	Mode description a,b)	Frequency	(cm ⁻¹)		
		Calculated	Ar matrix C)	Gas	
(a')	δ ₃ (CH ₃) (43), _{7w} (CH ₂) (27)	1330	1329.5° m	R min P	1333 1328
v19(a")	γ _t (CH ₂) (95)	1267	1271• 1268.5	•	1264
v20(a")	γ _r (CH ₃) (62), γ _r (CH ₂) (18)	1145	1133.5° m	$\begin{cases} R \\ Q? \\ P \end{cases}$	$\left. \begin{array}{c} 1142\\ 1136\\ 1130 \end{array} \right\}$
v ₁₀ (a')	γ _[(CH ₃) (61), ν(CC) (12)	1087	1106.5 · } 1104* } m	{ Q	1115 · 1102 [}]
v ₁₁ (a')	ν(CC) (40), γ _w (CH ₂) (18), γ _r (CH ₃) (16)	1010	996* m		1004 995 986
u12(a')	ν _S (NO ₂) (31), δ(NO ₂) (31), ν(CN) (16)	902	873.5• 871	R Q sh P	884 876 874 866
v21(a")	γ _f (CH ₂) (65), γ _f (CH ₃) (29), γ _W (NO ₂) (15)	802	808 805* } m	Q	805
v ₁₃ (a')	ν(CN) (22), δ(NO ₂) (22), δ(CCN) (22), γ _I (NO ₂) (13)	648	668 644* 624 vw	min?	670
v22(a")	γ _w (NO ₂) (81), γ ₁ (CH ₂) (17)	566	582* ₩ 526 v₩ 508 \₩	Q?	616 583
v14(a')	γ _I (NO ₂) (42), μ(CN) (28), δ (NO ₂) (11), ν(CC) (10)	505	503 500* w 494 w	. {R P	504 489
۳ ¹⁵ (\$')	δ(CCN) (62), γ ₁ (NO ₂) (21), ν(CN) (13)	300	474 vw 303 297* w 289 ?		285
P ₂₃ (8") P ₂₄ (8")	т (ССН ₂) (98) т (СNO ₂) (100)	222 0.4	221 vw		

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a) Based on quasirigid model with planar skeletal conformation.
b) Numbers in brackets indicate percentage potential energy distribution.
c) An asterisk denotes frequencies used for the force constant refinement.

Assignment a)	Mode description 2,b)	Frequency ((cm ⁻¹)			
		Calculated	Ar matrix c)	Gas		
2#4(A')?					3210	v
Y1(a')	ν _a (CH ₃) (99)	.3012	3022* w	min?	3025	
····(")	(CH-) (80)	2011	20024	. ∫ R	3009	1
16(a)	•2(-13)(>>)	2011	3002* W) Q P	2990	} "
4+26(A')			2959 w	(R	2966	}
2(a')	ν _s (CH ₃) (100)	2953	2952* w	Q	2957	1
				` P	2946	,
ν ₅ (A')			2923 w		001 5	
*18(A)		1	2916 W 2892 VW		2915	រា
2 - 10/11 / /			2882 vw	sh	2885	
			2846 vw			
¥6(A')			2750 vw		2750	W
4+P11(A')			2439 vw		2445	
17(2")	ν _a (CD ₂) (98)	2223	2285 VW 2230* VW		2280	W
3(2')	ν _s (CD ₂) (95)	2160	2174* vw		2180	W
			2138 vw	sh?	2150	
			2125 vw			
4(1')	$v_{\rm g}({ m NO}_2)$ (62), $\gamma_{\rm f}({ m NO}_2)$ (20)	1551	1563*	∫ R	1579	}
			1560) P	1561)]
			1529 vw			
		이지 이 것 수많은 이기가 들었다. 같은 무엇이 안 물로 한 것 같은 것		R	1478	1
5(2')	8 ₂ (CH ₃) (96)	1461	1461.5* m	{ Q	1469	} m
(a'')	δ ₂ (CH ₃)(96)	1460	1448.5° m	СР /в	1455	J V
6(2 ')	ν.(NO2) (69), δ(NO2) (31), ν(CN) (13)	1376	1394* s		1394	
				· · · · · ·	1382	J
			1272#)	ſR.	1382	Ì
2(a')	δ ₄ (CH ₃) (75), ν(CC) (25)	1371	1367.5 m	. (Q)	1370	•
				LP.	1360	
	7 ₉ (CD2)(39), γ ₁ (CD3)(18), ν(CN)(17), ν(C δ.(CK-)(10)	J(IV), 1239				
	~2(~13) (14)					

Assignment 2)	Mode description a,b)	Frequency		
		Calculated	Ar matrix ^{c)}	Gas
v9(a)	δ(CD ₂) (34), ν(CC) (16), γ _I (CH ₃) (13), ν ₈ (NO ₂) (12), δ _S (CH ₃) (11)	1185	1166* m	1152 m
v19(a")	γ _Γ (CH ₃) (77)	1118	1119 1115* } w	
			1042.5	(R 1041)
			1033 m	Q 1031 w
v ₁₀ (a')	γ _I (CH ₃) (56), δ(CD ₂) (29)	י 1007	1021.5*)	(P 1020)
v20(a")	γ _t (CD ₂) (91)	918		
			· · ·	(R 895)
v11(a')	$\delta(CD_2)$ (25), $\delta(NO_2)$ (24), $\nu(CC)$ (19), $\nu_3(NO_2)$ (15)	884	884* m	Q 886 m
		· · · ·		P 875
· · · · ·			865 vw	(sh 864
v12(a')	$\gamma_{W}(CD_{2})$ (50), $\nu_{s}(NO_{2})$ (17), $\delta(NO_{2})$ (14), $\nu(CC)$ (11)	829	852* m	sh 854
				sh 848
			696sh	700
v21(a")	$\gamma_{\rm I}({\rm CD}_2)$ (48), $\gamma_{\rm W}({\rm NO}_2)$ (35), $\gamma_{\rm I}({\rm CH}_3)$ (15)	709	693* m	Q 694
ν13(a')	δ(CCN) (21), γ ₁ (NO ₂) (20), ν(CN) (17), δ(NO ₂) (13),	617	629* w	sh 640
	₽ ₄ (NO ₂)(11)		600 vw	596 ^m
			537	
v22(a")	$\gamma_{\rm W}({\rm NO}_2)$ (56), $\gamma_{\rm r}({\rm CD}_2)$ (42)	505	528*	Q 526 vw
v14(2')	γ ₅ (NO ₂) (35), ν(CN) (34), δ(NO ₂) (13)	488	497* vw	490 ?
			303.5 ?	
v15(a')	δ(CCN) (62), γ ₁ (NO ₂) (20), ν(CN) (13)	299	296.5* w	284 w
v23(a")	7 (CCH ₃) (98)	219	-	
v24(2")	r(CNO ₂) (100)	0.3	a 🚣 👘 🖓 👘	

a) Based on quasirigid model with planar skeletal conformation. b) Numbers in brackets indicate percentage potential energy distribution.

c) An asterisk denotes frequencies used for the force constant refinement.

Table 3

Table 2 (continued)

Matrix and gas infrared frequencies of nitroethane-ds

Assignment 2) Mode description 2,b)	Frequency (cm ⁻¹)
	Calculated Ar matrix ⁽²⁾ Gas
204(A')? 24+V5(A')	3140 vw (R 2941) 2924 w (min 2933) w
	(P 2924 J

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Assignment a)	Mode description a,b)	Frequency (cm ⁻¹)						
		Calculated	Ar matrix c)	Gas				
2v5(A')					2750	V¥		
v4+v10(A')					2435	VW		
			2269 vw					
V16(2")	va(CD3) (87), va(CD2) (10)	2253	2261 vw		2255	. w		
v1(2')	v _a (CD ₃) (96)	2252	2246 vw			-		
v17(2")	va(CD2) (88), va(CD3) (11)	2219	2189 vw	e state				
v2(2')	ν _ε (CD ₂) (84)	2162		(R?	2158)		
			2147 vw	Q?	2149	} vw		
		a station		(p?	2140	J .		
	·· (CD-) (89)	2126	2112 vw					
n3(a)	N((CD3) (07)	2120	2112 **	(p	2002	`		
			2022		2095	۱ <u> </u>		
			2077 VW		2005	1		
				VP	2076			
v4(2')	$\nu_{a}(NO_{2})$ (64), $\gamma_{I}(NO_{2})$ (20)	1550	1561.5*		1577	12		
			1559 vs	{ min	1568	VS		
			1556	(P.	1559)		
			1527 vw			- 1		
			1381	(R	1388	1		
v5(a')	ν ₅ (NO ₂) (69), δ(NO ₂) (31), ν(CN) (13)	1376	1378.5*	Q	1379	s		
in the second				(P	1372)		
				R	1308]		
			1305 w	{Q	1301	5		
v6(2')	ν(CC) (52), γ _W (CD ₂) (20), ν ₂ (NO ₂) (13), δ ₅ (CD ₃) (12)	1275	1302*	(P	1295	1		
			1203 ?					
			1199)					
¥7(2')	δ(CD2) (36), γw(CD2) (16), ν(CN) (14)	1175	1195* m		1188	w		
			1192					
					1100	Va		
6- R N		1049	1077*	ഹ	1080	570		
P18(#)-	0 ⁸ (CD3)(22)	1020		X ·	1000			
				K r	1009)		
				{. sh	1063) m		
ν ₈ (2')	8 ₂ (CD ₃)(96)	1057	1060.5* w	0	1060			
			1052 ?	∖ P	1051	1		
Þ9(&')	δ ₃ (CD ₃) (56), δ(CD ₂) (23), γ _W (CD ₂) (12)	1037	1048* m			-		
			931.5	Q?	935	W		
¥19(a")	7r(CD3) (49), 7t(CD2) (23), 7r(CD2) (17)	930	929.5*					
¥20(8")	γ _t (CD ₂) (67), γ _t (CD ₂) (11), γ _t (NO ₂) (10)	912	907• vw		918	< W		

74 P. Groner et al./Matrix and gas infrared spectra of nitroethane isotopic species Table 3 (continued)

Assignment a)	Mode description 2,b)	Frequency (cm ⁻¹)					
		Calculated	Calculated Ar matrix C				
				• 23	(R	890	1
v10(a')	$\delta(NO_2)$ (25), $\nu_s(NO_2)$ (21), $\delta(CD_2)$ (19)	865	880.5*	m	10	880	{ m
			879	sh	(p	872	J
v11(a')	$\gamma_{\rm f}({\rm CD}_3)$ (41), $\delta({\rm NO}_2)$ (14), $\delta({\rm CD}_2)$ (11), $\nu_{\rm s}({\rm NO}_2)$ (11)	839	860*	w		851	
			846	?	Q?	845	5 VW
					R	793	1
v12(a')	$\gamma_{\rm W}({\rm CD}_2)$ (32), $\gamma_{\rm I}({\rm CD}_3)$ (29), $\nu({\rm CC})$ (14), $\delta_{\rm S}({\rm CD}_3)$ (14)	762	772*	m	{Q	784	} m
					P sh	776	J.
						644	۱
v21(a")	$\gamma_{W}(NO_{2})$ (41), $\gamma_{f}(CD_{3})$ (35), $\gamma_{f}(CD_{2})$ (23)	653	627*	w	Q?	629) «
v ₁₃ (a')	ν (CN) (21), $\gamma_{\rm r}$ (NO ₂) (20), $\gamma_{\rm r}$ (CD ₃) (13), δ (NO ₂) (13),	585	587*	w		581	m
	δ(CCN) (13)						
v22(a")	$\gamma_{I}(CD_{2})$ (48), $\gamma_{W}(NO_{2})$ (46), $\gamma_{I}(CD_{3})$ (10)	494	510*	vw			
v ₁₄ (a')	$\gamma_{\rm I}({\rm NO}_2)$ (35), $\nu({\rm CN})$ (33), $\delta({\rm NO}_2)$ (12)	478	478*	vw	Q?	476	?
			462	vw			
v15(a')	$δ$ (CCN) (64), $γ_{r}$ (NO ₂) (18), $ν$ (CN) (11)	276	269	w		260	W
v23(2")	τ(CCD ₃) (98)	161	-				
v24(a")	τ(CNO ₂) (100)	0.3					

Table 3 (continued)

a) Based on quasirigid model with planar skeletal conformation.
 b) Numbers in brackets indicate percentage potential energy distribution.
 c) An asterisk denotes frequencies used for the force constant refinement.

Table 4

Matrix infrared frequencies of nitroethane-(2,2,2)- d_3

Assignment a)	Mode description a,b)	Frequency (cm ⁻¹)			
		Calculated	Ar matrix C)		
v16(a")	v _a (CH ₂) (99)	2977			
v1(a')	v ₅ (CH ₂) (99)	2936			
v2(a')	ν _a (CD ₃) (97)	2251			
v17(a")	v _a (CD ₃) (98)	2250			
¥3(a')	ν <mark>s</mark> (CD ₃) (98)	2130	an a		
¥4(8')	ν ₂ (NO ₂) (46), γ _Γ (NO ₂) (19), δ(CH ₂) (13)	1582	1568.5* vs		
V5(8')	δ(CH ₂)(73), μ ₂ (NO ₂)(11)	1444	1442* m		
v6(a')	ν ₅ (NO ₂) (44), γ _W (CH ₂) (22), δ(NO ₂) (15), ν ₂ (NO ₂) (11)	1395	1379* s		
v7(2')	γ _w (CH ₂) (34), ν _s (NO ₂) (23), ν(CN) (20), δ(NO ₂) (17), ν(CC) (13)	1350	1328* m		
v18(a")	γ ₁ (CH ₂) (98)	1266			

4	25	P .	Grone	ret al	/Matrix	and go	is inf	rared :	pectra	of ni	troeth	ne isot	opic s	Deci	è
1.10															. 2

Table 4 (continued)

Assignment a)	Mode description a,b)	Frequency (c	m ⁻¹)
		Calculated	Ar matrix ()
v _B (a')	ν(CC) (41), δ ₁ (CD ₃) (39), γ _W (CH ₂) (11)	1161	1142* w
vg(2')	δ ₂ (CD ₃)(97)	1057	1054* w
¥19(8")	δ ₄ (CD ₃) (97)	1052	1044* w
v20(a")	γ _f (CH ₂)(48), γ _f (CD ₃)(34)	1002	
v10(1)	γ ₂ (CD ₃) (20), ν ₃ (NO ₂) (16), ν(CN) (13), δ(NO ₂) (10)	937	
F'11(a')	δ _g (CD ₃) (39), ν ₅ (NO ₂) (11)	898	
112(8)	$\gamma_{r}(CD_{3})(51), \delta(NO_{2})(19)$	818	811* m
¥21(8")	$\gamma_{r}(CD_{3})$ (62), $\gamma_{r}(CH_{2})$ (30), $\gamma_{W}(NO_{2})$ (17)	697	683* m
V13(a')	ν (CN) (25), $\gamma_{\rm f}$ (CD ₃) (20), δ (NO ₂) (17), $\gamma_{\rm f}$ (NO ₂) (14), δ (CCN) (12)	605	
P22(2")	γw(NO ₂) (75), γ _f (CH ₂) (21)	562	
¥14(2')	7r(NO2) (41), v(CN) (26), v(CC) (12), 8(NO2) (10)	490	
v15(a')	δ(CCN) (64), γ ₁ (NO ₂) (18), μ(CN) (11)	277	
ν23(a") +24(a")	τ(CCD ₃) (98) τ(CNO ₂) (100)	164 0.3	

a) Based on quasirigid model with planar skeletal conformation.
 b) Numbers in brackets indicate percentage potential energy distribution.
 c) An asterisk denotes frequencies used for the force constant refinement.

Table 5

• Matrix infrared frequencies of nitroethane-(1)- d_1

Assignment 2)	Mode description a,b,c)	Frequency (cm ⁻¹)		
	에는 여행 전에 가지 않는 것은 것이 있는 것이 있는 것이 있는 것이 있다. 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이 이	Calculated Ar matrix		
P1	ν _a (CH ₃) (94)	3012		
¥2	ν ₁ (CH ₃) (94)	3011		
¥3	vg(CHD) (46), vs(CHD) (40), vs(CH3) (13)	2958		
V4	ν ₃ (CH ₃) (87)	2952		
¥5	ν _s (CHD) (51), ν _a (CHD) (45)	2192		
V6	ν ₃ (NO ₂) (56), ₇₁ (NO ₂) (20)	1564 1567.5		
		1564 🛛 💘		
	성상이 가지도 있는 것이다. 이 것이 가지도 가지도 가지도 가지도 않는 것이 있는 것을 알았다. 이 것은 것은 것은 것은 것은 것은 것이 있는 것을 많은 것이 같다. 것은 것은 것은 것은 것은 것을 못했는 것은 것을 못했다.	1559 J		
17	δ ₂ (CH ₃) (79), δ ₁ (CH ₃) (17)	14621463.5 m		
P8	δ ₁ (CH ₃) (79), δ ₂ (CH ₃) (17)	1461 1449.5 m		
29	μ _g (NO ₂) (45), δ(NO ₂) (16), δ _g (CH ₃) (10), γ _W (CHD) (10)	1386 1395 s		
P10	δ ₃ (CH ₃) (52), ν(CC) (19), ν ₃ (NO ₂) (18)	- 1374 1374 :		
PII	γw(CHD) (31), 6(CHD) (25), s(CN) (15), γt(CHD) (11)	1345 1309 w		
<u></u>		1293 1292 🗰		
		STATISTICS AND		

Table 5 (continued)

Assignment a)	Mode description a,b,c)	Frequency (cm ⁻¹)		
		Calculated	Ar matrix	
ν ₁₃	γ ₁ (CH ₃) (52), γ _t (CHD) (13)	1141	1140 w	
v ₁₄	γ _t (CHD) (35), γ _I (CH ₃) (33)	1104	1080 w	
V15	γ _f (CH ₃) (34), ν(CC) (16), δ(CHD) (15), γ ₁ (CH ₃) (13)	1054	1049 w	
v16	ν (CC) (17), δ (NO ₂) (15), $\gamma_{\rm f}$ (CH ₃) (13), $\nu_{\rm S}$ (NO ₂) (10)	924		
V17	$\gamma_{\rm W}$ (CHD) (32), $\nu_{\rm S}$ (NO ₂) (22), δ (NO ₂) (20), $\gamma_{\rm t}$ (CHD) (14)	854	871 m	
ν ₁₈	$\gamma_{I}(CHD)$ (51), $\gamma_{W}(NO_{2})$ (26), $\gamma_{\perp}(CH_{3})$ (17)	735	723 w	
V19	$\delta(\text{CCN})$ (21), $\nu(\text{CN})$ (20), $\delta(\text{NO}_2)$ (17), $\gamma_{\text{I}}(\text{NO}_2)$ (15)	636	634 w	
² 20	$\gamma_{\rm W}({\rm NO}_2)$ (59), $\gamma_{\rm I}$ (CHD) (30)	530		
² 21	$\gamma_{r}(NO_{2})$ (35), $\nu(CN)$ (31), $\delta(NO_{2})$ (12)	495		
¥22	$\delta(CCN)$ (62), $\gamma_1(NO_2)$ (21), $\nu(CN)$ (13)	300		
² 23	τ(CCH ₃) (98)	220		
V24	τ(CNO ₂) (100)	0.3		

a) Based on quasirigid model with planar skeletal conformation.

b) Numbers in brackets indicate percentage potential energy distribution.

c) v_1 , δ_1 , γ_1 denote the modes which belong to the a" species in the symmetric isotopes.

computer program published by Hunziker [20] was applied which includes a least-square fit for refinement of force constants. The observed vibrational frequencies were not corrected for anharmonicity. As a rule force constants resulting from the fit process were considered non-significant, if their value did not exceed their standard deviation.

The significant force constants as resulting from the best fit are collected in table 6, together with their standard deviations. In total 68 fundamentals of the species d_0 , d_2 , d_3 , d_5 were included in the fit process, leading to 25 significant force constants. These allow reproduction of the frequencies with a standard deviation of 12.6 cm⁻¹. Calculated values of the normal modes are reproduced in tables 1-4 together with an approximate PED description of the normal modes.

4.2. Assignment of matrix spectra

4.2.1. Splittings of bands in the matrix spectra

The absorption bands of all three isotopic modifications feature unusually numerous splittings or unusually large line width. Though no definite explanation for individual bands is available, there exist several reasons, some of which are related to the low barrier of the NO_2 torsion:

- (i) site effects in the Ar matrix,
- (ii) association of molecules owing to insufficient isolation,
- (iii) existence of several conformations of the NO₂group frozen by the matrix crystal field.
- (iv) occurrence of combination tones with NO₂ torsional states.

Whereas little can be said about point (i), the presence of associated molecules in the matrix appears unlikely since it has been found experimentally that for M/A > 300 the spectra remain unchanged. Therefore, as a rule only spectra will be taken into account for which M/A > 300, cf. figs. 1–6. With respect to points (iii) and (iv) it should be remembered that the NCA yields distinct dependence of many normal frequencies on the NO₂ torsional angle τ . A typical example is afforded by the $v_a(NO_2)$ mode near 1560 cm⁻¹, which varies from 1584 cm⁻¹ for $\tau = 0^\circ$ to 1533 cm⁻¹ for $\tau = 90^\circ$ (d_0 species). In fig. 8 this dependence is shown for a few typical modes of the d_0 species. By the matrix crystal field a number of conformations



Fig. 6. Matrix and gas far infrared spectra of CH₃CH₂NO₂: top: Ar matrix, LHe temperature, crystal quartz wedge target, M/A = 50, 1850 µm, middle: Ar matrix, LHe temperature, Csl plate target, $M/A \approx 10, 225 \,\mu\text{m}$, bottom: gas spectra: b 8400 Torr cm, c ca. 1000 Torr cm, d 1000 Torr cm. e 250 Torr cm, a argon absorption, w window absorption.

may be frozen, each of which would contribute its own spectrum. Alternatively even a relatively weak matrix crystal field may lead to NO2 torsional levels lying only a few cm⁻¹ above the ground state which then could give rise to combination tones. The dependence of the $0 \rightarrow 1, 0 \rightarrow 2$ transition of the torsional mode on the effective torsional potential as expressed



Fig. 7. Molecular model for nitroethane, conformation and internal structural parameters. 1,2 (C), 3 (N), 4,5 (O) and 8 (H) are assumed to be in the same plane, 8 trans w.r.t. 3. Structural parameters: $r_{CC} = 1.54$ Å, $r_{CN} = 1.50$ Å, $r_{NO} = 1.22$ Å, $r_{CH} = 1.08 \text{ A}$. \preceq CNO = 116.5°, all other angles 109.47°.

by $V = \frac{1}{2}V_2$ (1-cos2 τ) is shown in fig. 9, which is based on semirigid rotor theory [21,22].

4.2.2. Assignment

In the following discussion only points of the assignment will be considered which appear to have some relevance in one respect or the other (cf. tables 1-5 and figs. 1-6).

4.2.2.1. CH-stretching region. Comparison of the $3050-2850 \text{ cm}^{-1}$ region of d_0 , d_2 and d_5 suggests that the two highest bands near 3023 and 3000 cm⁻¹ of d_0 and d_2 should be attributed to the E type methyl group stretching modes. The 2972 cm⁻¹ band of the d_0 species is not detectable in the d_2 spectrum, and may therefore be assigned to the a" stretching mode of the CH_2 group. The d_5 spectrum exhibits a weak band at 2924 cm⁻¹, which reliably on be excluded from originating from isotopic impuriti's and probably is a combination tone of the two NO₂ s retching. modes $v_4(a)$ and $v_5(a)$. Very probably this combination also contributes one of ne replaining absorption bands of the d_0 and d_2 modifications at approximately the same frequency. Tentatively the CH3-stretching mode $v_3(a)$ is attributed to bands at 2954 cm⁻¹ (d_0) and 2952 cm⁻¹ (d_7), respectively. One of the remain-

Table 6

List of internal coordinates and valence force constants of nitroethane

	Description	Internal coordinate	Internal coordinate	Force constant 2)		
				Notation	Value	Standard deviation
-	CH ₃ stretch	Δ <i>η</i>	Δ <i>r</i> _i	K _r	4.760	0.030
1 <u>1</u>		Δr_i	∆r _k k≠i	k _{IT}	0.034	0.008
	CH ₂ stretch	∆s;	Δs_i	Ks	4.883	0.021
	and the second second	Δs_i	∆s _k k≠i	k _{ss}	0.025	0.015
	CH ₃ bend	Δαί	$\Delta \alpha_i$	H_{α}	0.540	0.014
	CH3 rock	$\Delta \beta_{i}$	Δβί	HB	0.672	0.036
		Δβί	$\Delta \beta_k k \neq i$	h _{BB}	-0.016 b)	0.023
		Δαί	$\Delta \beta_k k \neq i$	had	0.017 b)	0.016
	CH ₂ bend	Δδ	Δδ	H _δ	0.634	0.016
	CH ₂ wag	$\Delta \gamma_{W}$	$\Delta \gamma_{W}$	Hym	0.631	0.029
	CH ₂ twist	Δγι	Δγι	H_{γ_1}	1.418	0.034
• 	CH ₂ rock	$\Delta \gamma_{\Gamma}$	$\Delta \gamma_{\Gamma}$	Hyr	0.626	0.041
		$\Delta \gamma_{\rm I}$	$\left\{ \Delta \beta_2 \atop \Delta \beta_2 \right\}$	h _{yr} B	-0.030	0.007
	CC stretch	AW	~ <u>~</u> µ ₃	Kw	4.711	0.208
•		AW	Δ.;; Δ.β.:	fwa	0.061	0.021
	and the factors of	AW	Δγ	J Wβ fWo	0.088	0.024
	CCN bend			H .	1.698	0.154
	CN stretch	Δ <i>P</i>	ΔP	Kp	3.052	0.403
	NO stretch	 Δ <i>R</i> ;	Δ <i>R</i> ;	Kp	8.280	0.453
		ΔR ;	$\Delta R_{\nu} k \neq i$	krr	1.008	0.290
		ΔR :	ΔP	kop	0.464	0.097
		$\Delta R;$	 ^~	fp.	0.182	0.058
. (†	NO ₂ bend	ΔΨ	-1w Aw	H.	2.441	0.348
	NO ₂ rock	ΔΩ	 	Ho	3.236	0.454
	NO ₂ wag	ΔΓ	<u></u> ΔΓ	Hr.	0.391	0.027
	CH ₂ torsion	Δ٤	Δt	Hr	0.083 c)	
	NO ₂ torsion	Δτ	Δτ	H _T	10 ⁻⁶ c)	

⁸⁾ In mdyn/A; angle coordinates are multiplied by 1 A.

b) Value of force constant \leq standard deviation.

c) Not adjusted in the fitting process.

ing bands of d_0 at 2925 cm⁻¹ may be interpreted as $\nu_3(a')$, the other one at 2919 cm⁻¹ as well as the two bands of d_2 at 2923 and 2916 cm⁻¹ as overtones and/or combination tones of the methyl bending modes $\nu_5(a')$ and $\nu_{18}(a'')$.

The ν (CD) stretching region 2300–2000 cm⁻¹ of both the d_2 and the d_5 species consists of a complex system of weak bands, which cannot be resolved at this time. The phenomenon goes back to a complicated system of Fermi type resonances between ν (CD) fundamentals and combination tones of fundamentals lying in the fingerprint region 1200–800 cm⁻¹. The mixing of the CD₂ and CD₃ bending modes with other group modes in this region increases drastically the possibility of Fermi-type resonances with the ν (CD) fundamentals. This is to be contrasted with the



Fig. 8. Dependence of normal modes on the NO₂ torsional angle τ . a $\nu_4(a', 0'')$, $\nu_{17}(a'', 90'')$; b $\nu_{12}(a', 0'')$, $\nu_{11}(a', 90'')$; c $\nu_{13}(a', 0'')$, $\nu_{12}(a', 90'')$; d $\nu_{14}(a', 0'')$, $\nu_{22}(a'', 90'')$.



Fig. 9. NO₂ internal rotation transitions. Semirigid model approximation, Boltzmann distribution for 4 K. a $v_{24} = 0 \rightarrow 1$, $J = 1 \rightarrow 1$ transition; b $v_{24} = 1 \rightarrow 2$, $J = 1 \rightarrow 1$ transition; c $v_{24} = 2 \rightarrow 3$, $J = 1 \rightarrow 1$ transition; d $v_{24} = 0 \rightarrow 2$, $J = 1 \rightarrow 1$ transition.

 H^1 modifications where only local resonances among CH₃ and CH₂ modes respectively should be expected.

For the normal coordinate analysis the two bands at 2230 and 2174 cm⁻¹ of the d_2 species were used.

4.2.2.2. $1600-1300 \text{ cm}^{-1}$ region. In this frequency range, the NO₂ stretching modes and the CH₃ and CH₂ bending modes are to be expected. Assignment of the bands of all three isotopic species does not appear to be problematic and will not be discussed in detail. As a common feature of all matrix spectra the splitting of the asymmetric NO2 stretching mode $v_4(a')$ into 3 or 4 components with small line width should be mentioned. According to the discussion presented in section 4.2.1 this mode is strongly τ dependent for d_0 , cf. fig. 8. The same holds however for the other isotopic species. A particular feature of the d_0 spectrum is the observation of only two bands in the 1450 cm⁻¹ range, where three HCH-bending modes should occur. Though only few spectra of ethyl compounds have been analyzed in detail, the absence of one of the three HCH bending modes seems to be a common feature of the gas spectra (C_2H_5F $[23], C_2H_5C[24], C_2H_5J[25], C_2H_5-CN[26]).$ However, for these molecules no matrix spectra have been reported.

4.2.2.3, 1300-250 cm⁻¹ range

(1) d_0 -species: the absorption bands above 700 cm⁻¹ appear to be attributable in a straightforward manner. The bands below 700 cm⁻¹ should originate from heavy atom vibrations approximately described as $\delta(NO_2)$, $\gamma_w(NO_2)$, $\gamma_r(NO_2)$ and $\delta(CCN)$ group modes. The assignment of the NO₂ modes has been based on rigid rotor model envelopes of gaseous nitromethane. Nitromethane may be considered as a C_{2v} frame- C_{3v} top type molecule. The kinetic energy tensor of the rotation internal rotation problem of this model does not depend on the internal rotation angle and the instantaneous principal inertia axes a, b, c coincide with the internal rotation axis and the normais to the symmetry planes of the NO2 group, respectively. Therefore, the assignment of the symmetrical bending, out-of-plane and in-plane rocking modes of the NO₂ group in nitromethane is not directly affected by internal rotation and may therefore be made in a straightforward manner [6]. The same order of these NO₂ group assignments was applied to nitroethane. As a particular feature of the matrix spectrum the large line width (20 cm^{-1}) of the 644 cm⁻¹ band

assigned as $\nu_{13} \delta(NO_2)$ (a') should be mentioned. It may bear a relation to the fact that the normal frequency of this mode calculated as a function of the NO₂ torsional angle τ exhibits the largest dependence of all normal modes on τ , cf. section 4.2.1.

(2) d_2 -species: The isotopic substitution at the CH₂-group leads to a considerable complication of the fingerprint spectrum. This necessitates more intense use of NCA results in the assignment process and leads to some unexplained features of the matrix spectrum. It should be noted that the latter exhibits a number of multiple bands, which impede a reliable assignment noticeably. Some of the difficulties seem to be related to the localization of the CH₃ rocking modes in the matrix spectrum. As indicated by the NCA the a' CH₃ rocking mode is strongly intermixed with skeletal vibrations. The assignment proposed in table 2 was found to be the best compromise, however it does not explain all observed bands. In particular the band triplet near 1043, 1033 and 1022 cm⁻¹ has now to be considered as representing the fundamental $\nu_{10}(a')$. On the other hand the two modes $v_8(a')$ and $v_{20}(a'')$ are calculated near 1239 and 918 cm⁻¹ respectively, where no absorptions were detactable. According to the NCA $v_{10}(a')$ is nearly independent of the NO2 torsional angle. Hence, the only way to interpret the band triplet seems to be to consider it as arising from combinations of $v_{10}(a')$ with NO₂ torsional transitions. $\nu_8(a')$ is found to be a mixture of essentially 5 group modes (cf. table 2), whereas $v_{20}(a'')$ approaches nearly a pure $\gamma_t(CD_2)$ group vibration. Again $\nu_{13}(a')$ assigned to the broad band at 629 cm⁻¹ is composed of several heavy atom group vibrations and depends markedly on the NO₂ conformation. The lowest skeletal modes near 537/528 and 497 cm⁻¹ feature large band width and low intensity; but their assignments appear reasonably reliable $(v_{22}(a''), v_{14}(a'))$.

(3) d_5 -species: The matrix spectrum of this molecule is complicated by the fact that 15 fundamentals should be located within the 1300-250 cm⁻¹ range. The NCA predicts most of the normal modes to be mixtures of several group modes (cf. table 3). The doublet near 1305/1302 cm⁻¹ is attributed to $\nu_6(a')$, ($\nu(CC)$, $\gamma_w(CD_2)$) which has not been observed either in the d_2 spectrum or in the ethyl chloride spectrum [24]. Similarly the band triplet near 1195 cm⁻¹ considered as $\nu_7(a')$ is now a mixture involving mainly the $\delta(CD_2)$ group mode. Surprisingly the fundamental $\nu_{13}(a')$, assigned to the absorption band at 587 cm⁻¹, does not show unusually large line width, though it is found by NCA to depend sensitively on the NO₂ conformation. This is in contrast to the fundamentals $\nu_{13}(a')$ of the d_0 and d_2 species, whose large line width may possibly be related to the dependence on the conformation. It should be noted, however, that this fundamental varies its composition by group modes markedly in the series $d_0 - d_2 - d_5$.

4.2.2.4. $250-20 \text{ cm}^{-1}$ range. In this range only the d_0 modification has been studied. Only one very weak band at 221 cm⁻¹ has been found so far, though its detection requires thick matrices (up to 2 mm) and low M/A, cf. fig. 6. This band has been attributed to $v_{23}(a'')$, i.e. the methyl torsional mode. No indication of the NO₂ torsional mode has been observed above 20 cm^{-1} . According to fig. 9 the $v_{24} = 0 \rightarrow 1$ transition is expected to occur below 20 cm⁻¹ for barrier values $V_2 \leq 90 \text{ cm}^{-1}$, cf. subsect. 4.1.2. The absence of the NO₂ torsional band above 20 cm^{-1} , therefore indicates the absence of matrix crystal field contributions of the order of 100 cm⁻¹ to the NO₂ barrier V_2 .

4.2.2.5. Matrix spectra of the d_1 and d_3 species. As has been mentioned in section 3 it has been possible to extract fragments of the matrix spectra of these two isotopic modifications, as given in tables 4 and 5. The d_3 data have been included in the NCA and proved relevant for the assignment of the CH₂-group modes. The force field derived from the combined data was then used to predict the d_1 spectrum. As may be seen from table 5, the observed 13 d_3 fundamentals are fairly well predicted with the largest deviation amounting to 36 cm⁻¹. This result may be considered as an indication of the correctness of the assignment given in tables 1-4.

4.3. Gas phase spectra

4.3.1. Model envelope calculations

For the assignment of polyatomic quasirigid molecule spectra model envelope calculations have proven to be a powerful aid [27-29].

Application of this technique to nitroethane spectra may be critical since the nearly free NO₂ internal rotation should be expected to lead to marked deviations

Table 7

from quasirigid rotor band envelopes. There is nevertheless considerable motivation to compare such model envelopes to experimental band contours in order to separate out bands which still follow the quasirigid rotor pattern, i.e. bands which are not noticeably influenced by internal rotation transitions. It also should be mentioned that the present state of rotation-internal rotation theory does not allow computation of the approximate rotation-internal rotation structure of vibrational transitions. On the one hand it cannot be extended to J values of the order of 100 [22], as would be required for a molecule like nitroethane [13]. On the other hand realistic band envelope calculation would require the inclusion of the vibration-internal rotation interaction in sufficient detail. The molecular data of CH₃CH₂NO₂ required for computation of quasirigid rotor bands should be commented upon briefly. For this molecule the kinetic energy matrix coefficients [22] depend strongly on the NO2 internal rotation angle, furthermore in the interval $0 < \tau < \frac{1}{2}\pi$ the b and c principal inertia axes are interchanged. Table 7 gives a collection of rotational constants and asymmetry parameters for various NO₂ conformations of the d_0 species and clearly demonstrates the τ dependence. Qualitatively the same behavior has been found for the deuterated molecules. Quasirigid band contours have been calculated for an extended set of models. In fig. 10 two typical examples are reproduced. The following comments should be made:

- (i) The limitation of J values to $J \le 80$ produces in the wings of both the B and C type bands artificial discontinuities located at 15-20 cm⁻¹ from the band center.
- (ii) For both conformations the band contours are alike. The A type bands for both the 0° and 90° conformation belong to a' fundamentals but may be hybridized with B and C type bands, respectively. B type bands either belong to a' or a'' modes, and in the first case may be hybridized with A type bands. C type contours alternatively belong to a'' and a', respectively, the latter being possibly involved in hybrids with A type bands.

Comparison of the model envelopes with the experimental data (cf. figs. 1-3, 10) at once reveals pronounced discrepancies. Fig. 11 shows bands which follow approximately the model contours. Nearly all other bands cannot be classified by means of the model

Nitroethane-do: dependence	of rotational constants on the
NO_2 torsional angle r^{2}	

т	A b)	<i>B</i> (cm ⁻¹)	С	_к с)
0°	0.3636	- 0.1423	0.1063	-0.721
30°	0.3474	0.1419	0.1080	-0.716
60°	0.3175	0.1408	0.1120	-0.720
90°	0.3035	0.1400	0.1143	-0.728

a) Based on the model used in ref. [13] and subsect. 4.1.

b) a inertia axis approximately directed from H-atom 8 to N atom; b inertia axis approximately parallel to the NO₂ plane, cf. fig. 7.

c) Asymmetry parameter $\kappa = (-A+2B-C)/(A-C)$.



Fig. 10. Quasirigid model band contours of nitroethane- d_0 for planar (0°) and perpendicular (90°) conformation. For rotational constants cf. table 7. Max. J value included in computation: 80. Frequency interval between two marks: 5 cm⁻¹.

envelopes, either because of overlapping with neighbouring bands or because of strong deviations. Typical examples in the d_0 spectrum are afforded by the band complex near 1250 cm⁻¹ or the unstructured absorption between 750 and 550 cm⁻¹, which embrace bands lacking all typical features.

4.3.2. Assignment of gas phase absorption bands 4.3.2.1. $3500-2000 \text{ cm}^{-1}$ region. In the typical ν (CH) stretching band complex of both d_0 and d_2 two band centers may be recognized at 3000 and 2957 cm⁻¹ possibly belonging to hybrids with dominant C and A type, respectively (cf. fig. 5). A more complete assignment may be achieved by comparison of spectra taken at higher resolution with matrix spectra; this is



Fig. 11. Nitroethane- d_0 : Comparison of experimental and computed band contours: left: Envelope at 1577 cm⁻¹ and computed B-type contour, middle: Absorption at 1120 cm⁻¹ and computed B-type (1136 cm⁻¹) and C-type (1102 cm⁻¹) contours, right: Envelope at 876 cm⁻¹ and computed A-type contour, dashed lines: vertical: band center frequencies of computed envelopes; horizontal: 0% transmission for the (shifted) upper traces.

given in tables 1, 2. Since the gas spectra of the two species are quite similar, the CH₂-stretching modes appear to have low intensity. In the spectra of d_0 , d_2 , d_5 weak bands near 3220, 3210 and 3140, near 2750, 2750 and 2750, and near 2440, 2445 and 2435 cm⁻¹ were detected, w.i.ch are assigned tentatively as $2\nu_4(a') (d_0, d_2, d_5), 2\nu_7(a', d_0), 2\nu_6(a', d_2),$ $2\nu_5(a', d_5), \nu_4(a') + \nu_{12}(a') (d_0), \nu_4(a') + \nu_{11}(a') (d_2)$ and $\nu_4(a') + \nu_{10}(a') (d_5)$, respectively.

This phenomenon yields a further example for the hypothesis that anharmonicity effects in polyatomic molecules may be interpreted mainly in terms of anharmonic force constants of typical groups. As may be seen from tables 1-3 these overtones may be traced back to NO₂ fundamentals. The majority of these bands has also been detected in the matrix spectra.

Similar to the matrix spectrum the gas spectrum of d_5 exhibits a strong absorption at 2933 cm⁻¹ assigned to the combination tone $\nu_4(a') + \nu_5(a')$.

The ν (CD) stretching bands lack nearly all structure with the exception of a unidentified a_5 band with its Q branch near 2085 cm⁻¹. Obviously this goes back to Fermi type resonances as discussed in connection with the matrix spectra (cf. subsetc. 4.2.2.1).

4.3.2.2. Region $1600-1300 \text{ cm}^{-1}$. The only band in this region recognizable w.r.t. the band contour is $v_4(a') v_s(NO_2)$ near 1570 cm⁻¹, which shows an ap-

proximate B type envelope for all 3 isotopic species. This is in agreement with the expectation for B-type bands. As discussed in section 4.3.1 and table 7 the b inertia axis remains nearly parallel to the NO_2 plane for all conformations of the NO₂ group. One might therefore expect the asymmetric NO2 stretching mode to give rise to a sort of B type envelope in spite of the fact that its frequency is strongly dependent on the NO₂ conformation (cf. fig. 8). By comparison with the matrix spectra the Q branches of almost all other fundamentals lying in this frequency range may be located, leading to the assignments given in tables 1-3. The width of the Q branches turns out to be 5-10 times larger than predicted by the quasirigid model envelopes. Again the similarity of the d_0 and d_2 spectra should be noted, with the exception of the $\delta(CH_2)$, $\nu_6(a')$ and $\gamma_w(CH_3)$, $\nu_9(a')$ modes which may be located by weak absorption peaks in the d_0 spectrum.

4.3.2.3. 1300-259 cm⁻¹ range. With few exceptions the gas phase spectra of all 3 isotopic species feature unstructured though highly complex bands. Exceptions are the A-type bands observed at 995, 876 cm⁻¹ of d_0 , at 1031 and 886 cm⁻¹ of d_2 and at 1060 and 880 cm⁻¹ of d_5 . According to tables 1-3 the higher of these fundamentals correspond to rather different mixtures of group modes, whereas the lower ones contain similar contributions of $v_s(NO_2)$ and $\delta(NO_2)$. It should be pointed out that this fundamental is involved in overtones in the 2440 cm⁻¹ region as mentioned in subsect. 4.3.2.1. Again assignments of the gas absorption bands in this range can be made only by comparison with the matrix spectra, which in many cases allow a posteriori location of Q branches. All 3 isotopes possess quite similar gas phase spectra in the 750-500 cm⁻¹ range, in particular strong structureless absorption near 600 cm⁻¹. For the peculiar strength and contour of the latter band no explanation seems available at this time.

4.3.2.4. 250-100 cm⁻¹ range. Since the FIR absorption spectrum below 60 cm⁻¹ of the d_0 species has been discussed in an earlier paper [13], the analysis is restricted to the upper FIR range, in which the methyl torsional mode is expected. As shown by fig. 6 a sequence of 5, eventually 6 sharp Q branches is observed, whose frequencies are listed in table 8. It appears difficult to give a complete analysis of these Q branches, but a partial interpretation may be given if they are ordered into doublets according to table 8. If the sequence of the doublet center frequencies is analysed by rotation-internal rotation theory of the semirigid C_s frame- C_{3v} top model one may derive an approximate value of the barrier V_3 to internal rotation of the CH₃-group. The application of the CsF-C3vT model requires freezing of the NO2 internal rotation. Since the kinetic coefficient g^{55} depends only slightly on the internal rotation angle τ of the nitro group, its average value may be used in the internal rotation hamiltonian [30], leading to a

Table 8

Nitroethane-do: methyl torsion Q-branch sequence

U23	Frequencies (cm ⁻¹)			
(CH3-torsion)	Obs.	Center	Calc. a)	
0 → 1	223.2 218.4 }	220.8	220.8	
1 - 2	207.2 204.3	205.8	205.9	
2→3	189.1 188.2 }	188.7	189.3	

a) Using a value of g⁵⁵ = 2F/h² ≈ 169 GHz and of V₃ ≈ 1080 cm⁻¹.

barrier value $V_3 \approx 1080 \pm 3 \text{ cm}^{-1}$. If the g^{55} value for the planar and perpendicular conformation of the nitrogroup is used, one finds $V_3 \approx 1100$ and $V_3 \approx$ 1060 cm^{-1} , respectively. Though no solution of the rotation-internal rotation problem of a semirigid $C_sF-C_{2v}T-C_{3v}T$ model is available at the present time, this finding suggests that the observed doublets may originate from a splitting of the CH₃-torsional levels by interaction of the two torsional modes. It may be stated that the CH₃ torsional barrier of nitroethane is comparable to values reported for other ethyl compounds [31].

5. Concluding remarks

Based on the results of this paper the nitroethane spectra may be considered as a typical example of molecular spectra which require for interpretation the explicit inclusion of the interaction of vibration with the low barrier internal rotation. Many features of both matrix and gas phase spectra cannot be explained satisfactorily in terms of a quasirigid molecular model. The strong dependence of the kinetic energy matrix coefficients of the NO₂ internal rotational angle combined with the low rotational barrier render perturbation type treatments rather uncertain. On the other hand its correct consideration in the rotation internal rotation vibration problem very sensibly complicates the solution of the latter.

An attempt was made to calculate the NO₂ internal rotational vibrational spectrum by a method used earlier for $CH_2 = CCl - CH_2D$ [32]. The results for nitroethane, where the CH₃ torsion was treated as a vibration, produced unsatisfactory agreement with experimental data, however, and are therefore not reported here. The main obstacle to explaining the spectra in these terms was the large complexity arising from unknown dependence of vibrational force constants and transition moments on the NO₂ torsional angle and from intrinsic coupling with over all rotation due to the low internal rotational barrier.

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