Infrared matrix spectra, normal coordinate analysis and valence force field of six isotopomers of methyl nitrite

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(Received 15 June 1981)

Abstract—Infrared—spectra of the isotopic species ¹³CH₃ONO, CH₃¹⁸ONO, CH₃O¹⁵NO and CH₃ON¹⁸O, isolated in argon matrices, are reported. Spectral data together with earlier data on CH₃ONO are used for derivation of 22 parameter harmonic valence force fields for both the *cis* and *trans* conformers and assignments are presented for all isotopic species in the two conformations. The valence force field will be used to propose assignments of *cis* and *trans* CD₃ONO reported earlier by OGILVIE. A comparison of force constants of molecules with C–O, N–O, and N=O fragments and their dependence on conformation and structure is made.

1. INTRODUCTION

In a recent paper FELDER *et al.*[1] reported assignments for the vibrational spectrum of *cis* and *trans* methyl nitrite isolated in argon matrices. These authors used a thermal molecular beam technique for discrimination between the two conformers. By use of a photochemical isomerization of matrix isolated CH₃ONO Ogilvie has already been able to give partial assignments of the i.r. spectra of the two conformers[2]. The methyl nitrite molecule presents a favorable case for the study of the relation of the vibrational spectra and force fields of its two conformers:



As a consequence of the relatively low value of $\Delta H^{\circ}(T_0) \approx 623(11)$ cal/mol of the interconversion

$$-cis + trans = 0$$

both conformers may be studied simultaneously both in gaseous and matrix isolated states [3, 1].

In this paper we wish to report i.r. spectra of both conformers of the following isotopomers

isolated in Ar matrices. These spectral data and the matrix spectra available on $CH_3ONO[1]$ and $CD_3ONO[2]$ will be treated by normal coordinate analysis (NCA). Based on this analysis assignments will be presented for all observed fundamentals of both conformers in the mid i.r. region for the six isotopomers. Furthermore 22 parameter approximations to the valence force field of *cis* and *trans* methyl nitrite resulting from the normal coordinate analysis will be presented.

The only previous NCA has been reported by TRUE and BAUER[4], who used it as a coarse guideline for analysis of drift technique experiments.

2. EXPERIMENTAL

2.1. Substances

Methyl nitrite and methyl nitrite ¹³C were prepared according to published procedures [5, 6] from NaNO₂ and CH₃OH [or ¹³CH₃OH, 90% ¹³C enriched from Merck, Sharp and Dohme, Canada Ltd. The modifications CH₃¹⁸ONO, CH₃O¹⁵NO and CH₃ON¹⁸O were obtained from Professor A. P. Cox, Bristol. Isotopic purity of these species amounted approximately to enrichments of 10% ¹⁸O, 95% ¹⁵N and 40% ¹⁸O, respectively. The CH₃ON¹⁸O sample contained considerable concentrations of impurities like H₂O, CH₃OH, CO₂.

2.2. Instrumentation

Infrared matrix spectra were taken with a Perkin-Elmer spectrophotometer Model 325, equipped with a LHe cryostat of our own design. Matrices were prepared from separate inlet systems for Ar and the sample, the latter being kept at -80° to -100° C yielding vapor pressures between 20-25 torr. Deposition rate was measured by means of a small laser and amounted to approximately $150 \,\mu$ m/h. Mostly *M*/A ratios near 1000 were chosen. In order to enhance weak bands ordinate expansion (by 3-4) was applied. Furthermore particular matrix bands were measured with slit program 2, besides slit program 4 being normally used.

Calibration of frequencies in particular for measurements of small isotope shifts was based on spectra of the parent molecule; in the cases of the ¹⁵N species, where parent bands were too weak, calibration was made by the aid of CO_2 and H_2O lines in the matrix spectra.

Assignment of bands of particular isotopic species in mixtures with the parent molecule was based on preliminary isotope shift calculations and sorting-out of bands by comparison of peak intensity ratios. Usually the peak intensity ratio of adjacent band pairs of parent and isotopomer were found to be constant within a few percent over the full frequency range.

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3. RESULTS

In Fig. 1 overall matrix spectra of the ¹³C-, ¹⁵Nand the two ¹⁸O-species are reproduced. Impurities are marked by x and comprise mainly of H_2O , CO₂, CH₃OH. Parent molecule and isotopomer bands are denoted by p and h, respectively. Expanded sections of the spectra are given in Figs 2, 3, and 4 for regions exhibiting overlapping and complex band groups of the ¹³C- and both ¹⁸Ospecies. Observed matrix band frequencies for the two conformers of the six isotopomers considered in this paper are collected in Tables 1-6. Included in these tables are assignments and calculated frequencies as reproduced by the NCA as well as remarks on the mode description. All bands belonging to a particular species, whether assigned or not, are listed. Table 1 concerns the parent molecule and contains only the fundamentals given in the earlier work [1, 3]; it is included in this work for convenience and completeness. In Table 6 all bands reported by OGILVIE are listed including our assignments where such could be made.

4. ANALYSIS AND ASSIGNMENTS

If internal rotation in the two conformations of CH₃ONO is disregarded, their normal modes classify with respect to symmetry as

A preliminary assignment of the parent molecule

based on empirical rules [7] and on the information derived from the gas phase spectra has been proposed earlier [1, 3]. For the heavy isotopic modifications this applies in a straightforward way. The normal coordinate treatment may therefore be started from a rather reliable zeroth order approximation.

4.1. Normal coordinate analysis (NCA)

In Fig. 5 the internal coordinates used in this work are labelled schematically. The structural parameters of TURNER, CORKILL and Cox[8] are listed in the figure caption. For the methyl group the following symmetry coordinates were used

a'-block:

$$S_1 = 6^{-1/2} [2\Delta r_1 - \Delta r_2 - \Delta r_3]$$

CH-stretching [ν (CH)]
$$S_2 = 3^{-1/2} [\Delta r_1 + \Delta r_2 + \Delta r_3]$$

$$S_6 = 6^{-1/2} [2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3], \quad CH_3\delta \text{-rocking} \\ [\gamma_{\parallel}(CH_3)]$$

$$S_7 = 6^{-1/2} [\Delta \alpha_1 + \Delta \alpha_2 + \Delta \alpha_3 - \Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3], CH_3-deformation [\delta'(CH_3)]$$

$$S_8 = 6^{-1/2} [2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3], CH_3-$$

bending [$\delta''(CH_3)$]

$$S_{11} = 6^{-1/2} [\Delta \alpha_1 + \Delta \alpha_2 + \Delta \alpha_3 + \Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3], CH_3-redundant [\delta''(CH_3)]$$
(1)

Cis			s	Trans			
Assignment	Freque obs.*	ency(cm ⁻¹) cal.	Potential Energy Distribution [†]		Freque obs.*	ncy(cm ⁻¹) cal.	Potential Energy Distribution†
ν ₁ (a')	3031	3033.0	ν (CH) [98]		2913	2916.6	v (CII) [92]
$v_2(a')$	2952	2952.6	V (CH) [98]	,	2823	2826.2	∨ (CH) [94]
v ₃ (a')	1613	1612.5	∪ (N=O) [92]		1665	1665.6	v(N=O)[92]
v ₄ (a')	1455	1458.4	δ'(CH ₃)[34]+δ"(CH ₃)[52] +γ ₀ (CH ₃)[13]		1467	1469.3	δ'(CH ₃)[29]+δ"(CH ₃)[58] + _{Υμ} (CH ₃)[12]
ν ₅ (a')	1408	1408.8	δ' (CH3) [46] -δ" (CH3) [49]		1424	1423.5	δ' (CH ₃) [32] -δ" (CH ₃) [72]
v ₆ (a')	1231	1227.6	γ_{c} (CH ₃) [58] - δ' (CH ₃) [15] + δ (CON) [12]		1180	1178.0	γ ₁ (CH ₃) [62]
ν ₇ (a')	985	985.4	ν (CO) [50]+Υ, (CH ₃) [15] -δ' (CH ₃) [10]+δ (ONO) [13]		1043	1042.8	ν (C-O) [62] +γ; (CH ₃) [10] -δ (ONO) [16]
v ₈ (a')	838	836.4	δ (ONO) [36]-ν(N-O) [26] -ν (C-O)[30]		807	806.8	ν (C-O) [13] -ν (N-O) [34] +δ (ONO) [39]
∨ ₉ (a')	625	623.7	ν (N-O) [66]-ν (N=O) [12] -δ (CON) [13]		565	563.6	ν (N-O) [68] +ν (C-O) [15)
v ₁₀ (a')	351	341.6	δ (ONO) [21]+δ (CON) [62]		370	369.5	δ (CON) [82]-δ (ONO) [18]
v ₁₁ (a")	3002	2998.6	V(CH)[99]		2883	2875.2	v(CH)[100]
v ₁₂ (a")	1438	1436.1	δ (CH ₃) [100]		1447	1445.5	δ (CH ₂) [94]
v ₁₃ (a")	994	996.0	γ ₁ (CH ₃) [100]		1031	1031.9	Y (СH ₂) [92]
v14 (a")	-	333.7	τ (NO) [94]		-	196.3	τ ^Î (NO) [100]
v ₁₅ (a")	-	118.1	γ(CH ₃)[95]		-	136.0	Y(CH ₃)[100]

Table 1. Cis and trans methyl nitrite (CH₃ONO): Ar matrix i.r. spectrum

*Ref. 1.

†Numbers in square brackets represent percentage of potential energy distribution. Signs represent relative phases. Contributions less than 10% are not included.





<u>,</u>		Cis			Trans			
Ass ignment	Frequency(cm ⁻¹) obs. cal.		Potential Energy Distribution [#]	Frequency(cm ⁻¹) obs. cal.		Potential Energy Distribution*		
2v, (A')	3200	_	_	3295	-	-		
√ ₁ (a')	3022	3019.3	v (CH) [97]	2908	2904.5	v(CH)[91]		
v_(a')	2949	2949.4	v (CH) [98]	2816	2822.0	v (CH) [92]		
v, (a')	1613	1612.3	v (N=O) [92]	1665	1665.4	∨ (N=O) [100]		
v4 (a')	1453	1454.9	δ' (CH ₃) {31}+δ" (CH ₃) [55] +γ ₁ (CH ₃) [14]	1465 1467.4 ბ'(CH + Υ"		δ'(CH ₃) [26]+δ"(CH ₃ [60] +γ (CH ₃ [13]		
ν _ε (a')	1403	1401.7	δ' (CH ₂) [46]-δ" (CH ₂) [49]	1420 1419.2		δ" (CH3) [27]-δ' (CH3) [70]		
5 ν _a +ν _a (a')	_	-		1358	-	-		
v ₆ (a')	1228	1220.9	$\gamma_{ }$ (CH ₃) [57] - δ' (CH ₃) [14] + δ (CON) [12]	1171.5	1169.1	Υ (CH ₃) [60]		
2Va (A')	-	-	-	1112	-	-		
v7(a')	976	974.6	ν (CO) [44] + Υ ₀ (CH ₃) [14] -δ' (CH ₃) [11] +δ (ONO) [15]	1031	1030.6	ν (CO) [39] +γ (CH ₃) [10] -δ (ONO) [19]		
ν ₈ (a')	831	827.6	δ (ONO) [33] -ν (N-0) [24] -ν (CO) [36]	803	802.7	ν (CO) [10] -ν (N-O) [34] +δ (ONO) [37]		
ν _g (a')	625	623.3	ν (N-O) [66] -ν (N=O) [12] -δ (ONO) [14]	561	558.9	ν (N-O) [68] +ν (CO) [17]		
v10 (a')	348	337.6	δ (ONO) [21] +δ (CON) [62]	366.5	366.6	δ (CON) [69] -δ (ONO) [19]		
$v_{1}, (a^{*})$	2992	2985.9	v(CH)[99]	2877	2863.0	v (CH) [99]		
$v_{12}(a^{"})$	1437	1431.3	δ (CH ₂) [100]	1446	1443.7	δ (CH3) [94]		
$v_{12}(a^{"})$	988	991.7	ү, (СН ₃) (100]	-	1025.0	Y (CH) [92]		
⊥⊃ ∨ ₁₄ (a")	-	333.2	τ (NO) [94]	-	195.6	τ (NO) [100]		
$v_{15}^{(a^*)}$	-	118.1	y (CH ₃) [95]	-	135.9	Y (CH ₃) [100]		

Table 2. Cis and trans methyl nitrite (13CH3ONO): Ar matrix i.r. spectrum

*See footnote †(b) of Table 1.

Cis			.8	Trans			
Assignment	Frequen obs.	cy(cm ⁻¹) cal.	Potential Energy Distribution [#]	Frequen obs.	cy(cm ⁻¹) cal.	Potential Energy Distribution [#]	
2v ₃ (A')	3140	-	-	3245	-	-	
v₁(a')	3030	3033.0	v(CH)[98]	2912	2916.6	∨(CH)[92]	
v_(a')	2950	2952.6	v(CH)[98]	2822	2826.2	v(CH)[94]	
v_3(a')	1586.5	1585.0	v(N=O)[91]	1636	1636.8	v(N=O)[100]	
∨ ₄ (a')	1454	1457.9	δ' (CH ₃) [33]+δ" (CH ₃) [52] +γ ₁₁ (CH ₃) [13]	1467	1469.1	δ' (CH ₃) [29]+δ" (CH ₃) [58] +γ (CH ₃) [12]	
∨ _⊂ (a')	1407.5	1408.6	δ' (CH ₃) [46]-δ" (CH ₃) [49]	1424	1423.5	δ" (CH ₃)[32]-δ' (CH ₃) [72]	
ν ₈ +ν ₉ (A')	-	-	-	1348	-	-	
ັ _{ບ6} (a')	1231	1226.2	Υ (CH ₃) [58]-δ'(CH ₃) [15] +δ (CON) [12]	1178	1176.9	Υ ₁₁ (CH ₃) [62]	
2∵ _q (A¹)	-	-	-	1112	-	-	
$v_7(a')$	983.5	983.2	ν (CO) [52] - γ _ι (CH ₃) [14] -δ' (CH ₃) [10] +δ (ONO) [12]	1040	1041.2	ν (CO) [63] +γ, (CH ₃) [10] -δ (CON) [13]	
ν ₈ (a ')	823	821.6	δ (ONO) [40] -ν (N-O) [24] -ν (CO) [27]	794	793.5	ν (CO) [13] -ν (N−Ο) [32] +δ (ONO) [41]	
∨ ₉ (a')	619	618.4	ν (N-O) [68]-ν (N=O) [12] -δ (ONO) [12]	560.5	559.8	v (N−O) {70}+v (CO) [50]	
ν ₁₀ (a')	343.5	341.6	δ (ONO) [21]+δ (CON) [62]	366.0	366.9	δ (CON) [68] –δ (ONO) [20]	
$v_{11}^{(a'')}$	3000	2998.6	v (CH) [99]	2882	2875.1	v (CH) [99]	
$v_{12}^{(a'')}$	1438	1436.1	δ (CH3) [100]	1447	1447.0	δ (CH ₃) [94]	
$v_{13}^{-}(a^{*})$	991	9.96.0	Y, (CH3) [100]	1031	1031.9	ү ₁ (СН ₃) [92]	
v14 (a")		328.4	τ (NO) [94]	-	193.9	τ (NO) [100]	
$v_{15}^{-}(a^{*})$		118.1	γ(CH ₃)[95]	-	135.5	ү (СН ₃) [100]	

Table 3. Cis and trans methyl nitrite (CH₃O¹⁵NO): Ar matrix i.r. spectrum

*See footnote † of Table 1.

	,c	is	Trans				
Assignment	Frequency(cm ⁻¹) obs. cal.		Potential Energy Distribution [#]	Frequency(cm ⁻¹) obs. cal.		Potential Energy Distribution [*]	
v, (a')	3031	3033.0	v(CH)[98]	2913	2916.6	v (CH) [92]	
$v_2^{(a')}$	2952	2952.6	v(CH)[98]	2823	2826.2	V(CH)[94]	
∨_3 (a')	1610.5	1609.1	v (N=O) [93]	1663.0	1663.5	v (N=O) [100]	
√ <mark>4</mark> (a')	1453	1458.1	δ' (CH ₃) [34]+δ" (CH ₃) [52] +γ (CH ₃) [13]	+δ"(CH ₃)[52] 1467 1468.6 [13]		δ'(CH ₃)[28]+δ"(CH ₃)[59] +γ (CH ₃)[12]	
∨ ₅ (a')	1406.5	1408.5	δ' (CH ₃) [47]-δ" (CH ₃) [49]	1424	1422.7	δ" (CH ₃) [30] -δ' (CH ₃) [70]	
∨ ₆ (a')	-	1211.6	$\begin{array}{c} & (CH_3) [62] - \delta' (CH_3) [16] \\ & + \delta (CON) [11] \end{array}$	1176	1166.4	γ _{II} (CH ₃) [66]	
v ₇ (a')	960	962.3	v (CO) [49] + $\gamma_{ }$ (CH ₃) [12] + δ (ONO) [16]	1013	1013.0	ν (CO) [63] -δ (ONO) [18]	
∨ _g (a')	833.5	835.7	δ (ONO) [35] ~ν (N-O) [25] -ν (CO) [33]	801	800.8	ν (CO) [15] -ν (N-O) [32] +δ (ONO) [41]	
∨ ₉ (a')	605	604.5	ν (N-O) [67] -ν (N=O) [12] -δ (ONO) [12]	556	553.2	v (N-O) [75] +v (CO) [12]	
∨ ₁₀ (a')	~	339.7	οδ (ONO) [20]+δ (CON) [62]	-	364.2	δ (CON) [70] –δ (ONO) [19]	
v ₁₁ (a")	3002	2998.6	V(CH)[99]	2883	2875.1	V(CH)[99]	
$v_{12}^{(a'')}$	1437	1436.0	δ (CH3) [100]	1446	1445.6	δ (CH3) [94]	
v13 ^(a")	~	993.0	Y ₁ (CH ₃) [100]	-	1029.1	Y (CH ₃) [93]	
$v_{14}^{}(a'')$	-	328.4	τ (NO) [94]	-	194.9	τ (NO) [100]	
v ₁₅ (a")	~	118.0	ү (СН ₃) [95]	-	134.9	Y (CH ₃) [100]	

Table 4. Cis and trans methyl nitrite (CH3¹⁸ONO): Ar matrix i.r. spectrum

*See footnote † of Table 1.

		Ci	S	Trans				
Assignment	Frequen obs.	cy(cm ⁻¹) cal.	Potential Energy Distribution [*]	Frequen obs.	cy(cm ⁻¹) cal.	Potential Energy Distribution [#]		
2v3(A')	3120	-	-	3218		-		
v, (a')	3031	3033.1	v(CH)[98]	2913	2916.6	v(CH)[92]		
$v_{2}(a')$	2952	2052.6	V(CH)[98]	2823	2826.2	v(CH)[94]		
∨(a')	1575	1574.1	∨ (N=O) [89]	1623.5	1624.0	v (N=O) [99]		
v₄(a')	1455	1457.4	δ'(CH ₃)[32]+δ"(CH ₃)[53] +γ (CH ₃)[13]	1467	1467.0	δ' (CH3) [29] + δ" (CH3) [58]+ γ (CH3) [12]		
ν _ς (a')	1408	1408.5	δ' (CH3) [46]-δ" (CH3) [48]	1424	1423.5	δ" (CH ₃) [30] -δ' (CH ₃) [70]		
v ₆ (a')	1229	1224.6	$\gamma_{(CH_3)}$ [59] - δ' (CH ₃) [15] - δ (CON) [12]	1179	1175.3	γ _{II} (CH ₃) [62]		
2∨ _q (A')	-	-	-	1115	-	-		
v ₇ (a')	981.5	981.7	ν (CO) [52]+γ (CH ₃) [13] +δ (ONO) [12]	1040.5	1040.0	v (CO) [65] + γ_{c} (CH ₃) [10] - δ (ONO) [15]		
∨ ₈ (a')	830.0	830.8	δ (ONO) [36] -ν (N−O) [29] -ν (CO) [27] +ν (N=O) [11]	799	799.7	ν (CO) [11] -ν (N-O) [35] +δ (ONO) [39]		
v ₉ (a')	620.0	619.0	ν (N-O) [65] +ν (N=O) [11] -δ (CON) [14]	556	555.5	v (N≁O) [68]+v (CO) [15]		
v ₁₀ (a')	347	334.2	δ (ONO) [22]+δ (CON) [62]	367	366.2	δ (CON) [69] -δ (ONO) [20]		
v, (a")	3002	2998.6	V (CH) [99]	2883	2375.1	∨(CH)[99]		
$v_{12}^{(a'')}$	1438	1436.1	ն (CH ₃) [100]	1447	1445.5	δ (CH ₃) [94]		
$v_{13}^{2}(a^{*})$	994	996.0	Y, (CH ₃) (100]	1031	1031.9	Υ ₁ (CH ₃) (92)		
$v_{14}^{}(a'')$	-	331.1	τ (NO) [94]	-	192.9	T (NO) [100]		
v ₁₅ (a")	-	117.7	ү(СН ₃) (95]	-	135.9	Y1(CH3)[100]		

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*See footnote † of Table 1.

Cis				Trans				
Assignment	Frequen obs .*	cy(cm ⁻¹) cal.†	Potential Energy Distribution ‡	Frequen obs .*	cy(cm ⁻¹) cal.†	Potential Energy Distribution‡		
ν, (a')	2275.0	2276.6	v (CD) [97]	-	2180.2	v (CD) [96]		
v_(a')	-	2119.0	v (CD) [99]	-	2038.0	(دی) ۷ [97]		
v_(a')	1610.5	1609.5	v (N=O) [95]	1664.0	1663.2	v(N=O) [100]		
√4(a')	-	1114.9	Υ (CD ₃) [18] +δ' (CD ₃) [27) -ν (CO) [28] +δ (CON) [12]	1095.0	1094.9	ν (CO) [28]-δ' (CD ₃) [53]		
∨ ₅ (a')	-	1091.2	δ' (CD ₃) [49]+δ" (CD ₃) [26] +δ (ONO) [10]	-	1055.5	ν (CO) [17]+δ' (CD ₃) [18] +δ" (CD ₃) [28]-δ (ONO) [18]		
ν ₆ (a')	1024	1023.9	δ' (CD ₃) [10]-δ" (CD ₃) [70] +δ (ONO)[10]	1019.0	1037.2	δ" (CD ₃) [67]-δ' (CD ₃) [17]		
ν ₇ (a')	-	897.1	v (CO) [41] + γ_{II} (CD ₃) [35] -v (N-O) [11]	-	949.9	v (CO) [25] - v (N-O) [16] + γ_{ii} (CD ₃) [40]		
∨ ₈ (a')	798	785.7	δ (ONO) [26]-ν (N-O) [37] -ν (CO) [12]+ν (N=O) [10]	775.0	757.0	$v(N-0)[25]+\gamma_{H}(CD_{3})[20]$ - $\delta(ONO)[41]$		
∨ ₀ (a')	595.8	599.1	∨ (N-O) [61]-∨ (N=O) [11]	551.0	547.6	v (N-O) [70] +v (CO) [15]		
v10 (a')	-	307.2	δ (ONO) [16]+δ (CON) [61]	-	335.5	δ (CON) [68] -δ (ONO) [16]		
v ₁₁ (a")	-	2238.5	v (CD) [98]	-	2145.6	v(CD)[98]		
v _{1.5} (a")	1045	1057.7	δ (CD ₃) [94]	-	1039.8	δ (CD ₃) [97]		
$v_{13}^{12}(a'')$	-	752.2	Υ ₁ (CD ₃) [95]	-	796.6	Y, (CD3) [95]		
v14 (a")	-	322.8	τ (NO) [93]	-	189.6	τ (NO) [99]		
v ₁₅ (a")	-	86.7	γ(CD ₃)[95]	-	106.1	Y (CD3) [100]		

Table 6. Cis and trans methyl nitrite (CD₃ONO): Ar matrix i.r. spectrum

*Ref. [2].

tNot used in the NCA force constant calculations. \$See footnote † of Table 1.



Fig. 2. Expanded spectra of ¹³CH₃ONO in the CH stretching region. c: *cis*, t: *trans* of the ¹³C species; p refers to the corresponding parent molecule lines where detectable.

a"-block:

$$S_{12} = 2^{-1/2} (\Delta r_1 - \Delta r_2), \quad \text{CH-stretching} [\nu(\text{CH})]$$

$$S_{13} = 2^{-1/2} (\Delta \alpha_2 - \Delta \alpha_3), \quad \text{CH}_3\text{-rocking} [\gamma_{\perp}(\text{CH}_3)]$$

$$S_{14} = 2^{-1/2} (\Delta \beta_2 - \Delta \beta_3), \quad \text{CH}_3\text{-bending} [\delta(\text{CH}_3)].$$
(2)

The expressions for the internal coordinates (stretching, bending and torsional coordinates) were taken according to WILSON, DECIUS and CROSS[9].

As a torsional coordinate for the CH_3 group the sum

$$S_{15} = \frac{1}{3} (\Delta \tau_{H_1 \text{CON}} + \Delta \tau_{H_2 \text{CON}} + \Delta \tau_{H_3 \text{CON}})$$
(3)

is used and for the torsion around the O-N bond

$$S_{16} = \Delta \tau_{\rm CONO} \tag{4}$$

has been chosen.



Fig. 3. Expanded spectra of 90% CH₃ONO and 10% CH₃¹⁸ONO in four different frequency regions. p: parent molecule; h: heavy isotope; x: impurity bands.



Fig. 4. Expanded spectra of 60% CH₃ONO and 40% CH₃ON¹⁸O in five different frequency regions. p: parent molecule; h: heavy isotope; x: impurity bands. a: without ordinate expansion; b: with ordinate expansion.

In order to define the force constants the potential function will be given

$$2V = K_{R}(\Delta R)^{2} + K_{S}(\Delta S)^{2} + K_{D}(\Delta D)^{2} + K_{r}[(\Delta r_{1})^{2} + (\Delta r_{2})^{2}] + K_{r}[(\Delta r_{1})^{2} + (\Delta r_{2})^{2} + (\Delta r_{3})^{2}] + K_{r}'(\Delta r_{1})^{2} + H_{\phi}(\Delta \phi)^{2} + H_{\theta}(\Delta \phi)^{2} + H_{\alpha}[(\Delta \alpha_{1})^{2} + (\Delta \alpha_{2})^{2} + (\Delta \alpha_{3})^{2}] + H_{\alpha}'(\Delta \alpha_{1})^{2} + H_{\beta}[(\Delta \beta_{1})^{2} + (\Delta \beta_{2})^{2} + (\Delta \beta_{3})^{2}] + H_{\tau}(\Delta \tau)^{2} + H_{\tau}(\Delta \gamma)^{2} + 2K_{RS}(\Delta R)(\Delta S) + 2K_{SD}(\Delta S)(\Delta D)$$

 $+ K_{rr}[(\Delta r_{1})(\Delta r_{2}) + (\Delta r_{2})(\Delta r_{3}) + (\Delta r_{3})(\Delta r_{1})]$ $+ 2l_{R\phi}(\Delta R)(\Delta \phi) + 2l_{S\phi}(\Delta S)(\Delta \phi) + 2l_{S\theta}(\Delta S)(\Delta \theta)$ $+ 2l_{D\theta}(\Delta D)(\Delta \theta) + 2l_{D\alpha}(\Delta D)(\Delta \alpha_{1} + \Delta \alpha_{2} + \Delta \alpha_{3})$ $+ 2h_{\theta\phi}(\Delta \theta)(\Delta \alpha_{1} + \Delta \alpha_{2} + \Delta \alpha_{3}) + 2h'_{\theta\alpha}(\Delta \theta)(\Delta \alpha_{1})$ $+ 2h_{\alpha\beta}[(\Delta \alpha_{1})(\Delta \beta_{1}) + (\Delta \alpha_{2})(\Delta \beta_{2}) + (\Delta \alpha_{3})(\Delta \beta_{3})]$ $+ 2h_{\alpha\alpha}[(\Delta \alpha_{1})(\Delta \alpha_{2}) + (\Delta \alpha_{2})(\Delta \alpha_{3}) + (\Delta \alpha_{3})(\Delta \alpha_{1})]$ (5)



Fig. 5. Geometry and internal coordinates of methyl nitrite. cis: R = 1.164 Å, S = 1.398 Å, D = 1.437 Å, $r_1 = 1.09$ Å, $r_2 = r_3 = 1.10$ Å, $\phi = 114.8^\circ$, $\theta = 114.7^\circ$, $\alpha_1 = 101.8^\circ$, $\alpha_2 = \alpha_3 = 109.9^\circ$. $\beta_1 = \beta_2 = \beta_3 = 108.1^\circ$, trans: R = 1.164 Å, S = 1.415 Å, D = 1.436 Å, $r_1 = r_2 = r_3 = 109.5^\circ$, $\beta_1 = \beta_2 = \beta_3 = 109.5^\circ$. The internal coordinates for torsion of CH₃ and NO groups are defined in the text.



Fig. 6. Force constant-bond distance graph for N=O fragment for a few related molecules. (a) ONF, (b) *trans* CH₃ONO, (c) *trans* HONO, (d) *cis* CH₃ONO, (e) *cis* HONO, (f) HNO₃ (anti) and (g) HNO₃(syn).

which features 25 a priori force constants. It has been chosen by analogy with valence force fields used for methanol[10] and for nitrous acid[11] and has been completed with some off-diagonal terms. As is seen from expression (5) no interaction constants of the ν (CH) coordinates with other internal coordinates and no interaction constants of the two torsional coordinates with other coordinates have been taken into consideration. In the above equation the redundancy S_{11} has to be taken into account by retaining only the independent force constant parameters. Normal coordinate calculations were carried out by means of the computer program written by HUNZIKER [12].

No significant convergence problems were encountered, but it should be mentioned that the two cross constants K_{SD} and $h_{\theta\phi}$ for the *cis* conformation appear to be highly correlated. The valence force field was determined by fitting the 13 fundamentals of the parent molecule CH₃ONO and 47 isotope shifts of all singly substituted ¹³C, ¹⁵N and ¹⁸O isotopic modifications. The fundamental frequencies of the modification CD₃ONO reported by OGILVIE[2] were not included in the fit.

The valence force constants resulting from the fitting process are listed in Table 7. Normal frequencies for the parent molecule and all 5 isotopomers as reproduced from the harmonic force field given in Table 7 are included in Tables 1–6. From the force field in Table 7 observed

Table 7. Valence force field (VFF) of cis and trans methyl nitrite (mdyn/Å)

	cis	trans
к _R	11.936(406)	12.832(318)
к _s	3.809(591)	2,596(243)
K _{RS}	3.135(719)	2.240(701)
к _D	4.336(220)	4.435(257)
к _{sd}	0.834(252)	0.0
^K r	4.862(28)	4.452(21)
к'r	0.095(61)	0.151(42)
K rr	0.082(15)	0.059(13)
н _ф	2.296(268)	2.397 (200)
^ℓ R¢	0.797(368)	1.227(354)
^ℓ S¢	0.725(374)	0.822(141)
н _ө	1.939(359)	1.420(181)
^l s0	1.206(488)	0.135(167)
ℓ _D θ	0.273(272)	0.364(294)
h _{0¢}	0.0	0.276(180)
h _{ea}	-0.192(77)	-0.012(161)
$h_{\theta \alpha}^{*}$	0.197(134)	0.186(118)
² Dα	0.363(105)	0.480(99)
на	0.562(35)	0.675(56)
н'α	0.398(109)	0.185(64)
haa	-0.044(41)	0.002(34)
h _{αβ}	-0.084(31)	-0.013(41)
н	0.532(8)	0.531(22)
н _т	0.167*	0.131*
н _ү	0.026†	0.026†

*Ref. [11]. †Ref. [10].

Molecule	C-O bond distance (A)	Force constant (mdyn/A)	N-O bond distance (A)	Force constant (mdyn/A)	N=O bond distance (Å)	Force constant (mdyn/A)
cis CH ₃ ONO ^a	1.437	4.34	1.398	3.81	1.182	11.94
trans CH ₃ ONO ^a	1.436	4.43	1.415	2.60	1.164	12.83
снзон р	1.424	5.30	-	-	-	-
снзсоон с	1.364	5.55	-	-	-	-
сн,сосоон d	1.328	5.76	-	-	-	-
(CH ₃) ₂ 0 ^e	1.410	5.19	-	-	-	-
cis HONO f	-	-	1.399	2.73	1.186	11.18
trans HONO ^f	-	-	1.442	2.22	1.169	12.28
нио 3 а	-	-	1.406	3.60	1.211(syn) 1.199(anti)	7.90
ONF h	-	-			1.13	15.9

Table 8. Force constant-bond distance data for few molecules

^(a)This work. ^(b)Ref. [10]. ^(c)Ref. [15]. ^(d)Ref. [16]. ^(e)Ref. [17]. ^(f)Ref. [11]. ^(g)Ref. [18]. ^(h)Ref. [19].

frequencies are reproduced with an RMS deviation of 3.2 and 3.8 cm^{-1} and the isotope shifts with an RMS deviation of 1.9 and 1.5 cm^{-1} for *cis* and *trans* conformers, respectively.

4.2.1. Assignment and discussion. In Tables 1-6 the composition of normal modes from internal coordinates (group modes) is given in terms of the potential energy distribution (PED). For the CHstretching modes the higher frequency of the a'block corresponds to the *e*-type [i.e. symmetry coordinate S_1 of equation (1)] and the lower frequency corresponds to the *a*-type [i.e. symmetry coordinate S_2 of equation (1)]. From this information it is obvious that, besides ν (CH), ν (N=O) and torsional modes, all normal modes are complex combinations of the remaining group modes.

Since the assignment of nearly all fundamentals appears fairly straightforward, only a few comments seem to be necessary:

- (i) As a whole the NCA gives indication of only few Fermi resonances. As a noteworthy example $\nu_{10}(a')$ of cis CH₃ONO near 351 cm⁻¹ should be mentioned, which can be reproduced only with a deviation of 9.4 cm^{-1} ($\simeq 3 \text{ times the}$ RMS deviation). This seems to originate from a Fermi resonance $\nu_{10}(a')$, $2\nu_{15}(A')$, though only one member of the Fermi resonance doublet seems to be detectable. The fundamental $\nu_{10}(a')$, however, is rather weak for itself and possibly the other member escapes detection. Another example is afforded by the ν (CH) modes $\nu_1(a')$ and $\nu_{11}(a'')$ of the trans conformation of ¹³CH₃ONO, of which the isotope shifts cannot be fitted within two RMS deviations. Ouite probably the usual type of Fermi resonance (ν (CH), 2δ (CH₃)) causes these discrepancies.
- (ii) The assignment of the matrix spectra of CH₃ONO and CD₃ONO reported by OGILVIE[2] presents a number of difficulties. First, this data appears rather incomplete since only few of the fundamentals in Table 6 may be located in the reported spectra. Second, the six fundamentals attributed to the *cis* conformer are predicted satisfactorily, cf. Table 6. For the trans species three of the six fundamentals attributed to this conformer by OGILVIE are predicted rather closely by the NCA, whereas among the three remaining bands one probably belongs to the cis form (2252 cm^{-1}) , and the other two can be predicted only with a relatively large error $(\nu_6(a'), 1019 \text{ cm}^{-1} \text{ and } \nu_8(a'), 775 \text{ cm}^{-1})$. The assignment of the 2252 cm⁻¹ band rests on the fact that it is very close to $\nu_{11}(a'')$ of the cis species and further on the fact that all ν (CH) normal modes of the *cis* conformer are predicted to be higher in frequency than those of the trans species, in agreement with the observed fundamental frequencies.

4.2.2. Valence force field. A number of comments should also be made with respect to the valence force field. The main force constants associated with the heavy atom chain in both conformers appear to be of particular interest since, as already pointed out, almost all normal modes are strongly intermixed group modes. First, as shown in Table 7, some of the interaction constants are not determined by our set of data, i.e. they are not significantly different from zero. Second, it should be remarked that the two conformers feature a few significantly different force constants which mainly concern the heavy atom skeleton, e.g. the stretching force constant associated with the N=O and N-O and their interaction constant. A further drastic difference is afforded by the interaction constant of N-O stretching and CON bending coordinates which is about one order of magnitude higher for the cis conformers. Third, it appears surprising that the value of the C-O stretching force constant (4.4 mdyn/Å) of both conformers is considerably lower than in methanol (5.3 mdyn/Å). On the other hand the N-O stretching constant is higher for both trans and cis conformers in comparison to HONO. Also the interaction constant associated with the N-O and N=O stretching coordinates is higher than for HONO. The increase is higher for the cis conformer, which appears to feature in general noticeably higher interaction constants.

Finally, the unusually high value of the interaction constant K_{RS} for both conformers should be pointed out (3.14 and 2.24 mdyn/Å for *cis* and *trans*), only relatively little lower than the value of the diagonal constant K_S (3.81 and 2.60 mdyn/Å, respectively). High values of this off diagonal constant have earlier been found for HONO (1.80 and 1.67 mdyn/Å for *cis* and *trans* conformers, respectively)[11].

4.2.3. Relation between valence force constants and structural parameters. The data provided by this work on CH₃ONO may be combined with data on further similar molecules for investigation of correlations between valence force constants and bond length like BADGER's rule [13, 14]. A relationship of this sort for N-O bonds has been considered earlier by JONATHAN[15] in which only NO_x species were included. Available data on molecules containing C-O, N-O and N=O fragments are collected in Table 8. Based on these data one may construct graphs illustrating a bond length-force constant relationship. The graph for N=O fragments is shown in Fig. 6 and is approximately linear. For the N-O fragments one finds wide scattering and no obvious bond lengthforce constant relation seems to exist. This lack might originate from inclusion of too widely different molecules, e.g. from the fact that for some of the species included in Table 8 large offdiagonal force constants have been found, implying that the heavy atom skeleton C-O-N=O has to be considered as a whole. This is corroborated by the fact that the skeletal modes are complicated mixtures of group modes according to PED, as

already pointed out in section 4.2.1. Similarly for the C-O fragment no simple relationship results from the data given in Table 8 and similar remarks as those made for the N-O fragment seem to apply. It should be kept in mind that the valence force field found in this work does not necessarily represent a unique solution to the normal coordinate problem, and there might exist another solution featuring diagonal force constants associated with the C-O-N=O fragment yielding less scatter in the bond length-force constant plots for O-N and C-O fragments. However, there is no indication of such a second solution at this time.

Acknowledgements—The authors wish to thank the ETHZ Administration for a research grant (13.223/41) and the Swiss National Foundation (Project No. 2.19.079/2.612.080) and Messrs SANDOZ for financial support. The authors are also grateful to Professor A. P. Cox of the University of Bristol, U.K. for granting the isotopic species $CH_3^{18}ONO$, $CH_3O^{15}NO$ and $CH_3ON^{18}O$. We also thank Mr G. GRASSI for preparing the species $^{13}CH_3ONO$. Furthermore we wish to thank Mr R. GUNDE for technical assistance and Drs H. HOLLENSTEIN and P. FELDER for helpful discussions. Finally we thank the ETHZ Computer Center for granting free computation time.

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