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Infrared Spectrum and Internal-Rotation Barrier of Nitroethylene

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The infrared spectra of nitroethylene- d_0 and 1-nitroethylene- d_1 have been obtained in the vapor phase over the range 4000–70 cm^{-1} . All fundamental frequencies have been observed and the NO_2 torsion was located at 103 and 95 cm^{-1} for the d_0 and d_1 isotopes, respectively. The barrier to internal rotation has been calculated to be 6510 ± 280 cal/mole for H_2CCHNO_2 and 5960 ± 280 cal/mole for H_2CCDNO_2 using the "semirigid" model with a $V_2(1-\cos 2\phi)$ potential. A normal-coordinate analysis has been carried out in order to clarify the nature of the fundamental vibrations. It shows that there is considerable mixing between the symmetry coordinates in the normal modes. The existence of this interaction indicates that the common assumption that the torsional mode is decoupled from the other modes of the same symmetry, the semirigid model, does not appear to be valid here. The effect of this on the barrier height is discussed.

NITROETHYLENE is of considerable interest because it is the simplest member of the nitro-olefin series and permits the study of the possible effects of conjugation between the ethylenic pi electrons and those on the nitro group. In particular, investigation of the far-infrared spectrum of the vapor leads to information about the barrier to internal rotation for the nitro group in this molecule. Figure 1 shows the structure of the nitroethylene molecule as determined by microwave spectroscopy.

The synthesis of nitroethylene- d_0 and 1-nitroethylene- d_1 was that of Hess, Bauder, and Günthard.¹ Infrared spectra were recorded on Perkin-Elmer 125 and 225 spectrometers from 4000 to 400 cm^{-1} and on a Perkin-Elmer 301 spectrometer from 600 to 70 cm^{-1} using a 70-cm path-length absorption cell. Intensity measurements at different temperatures were carried out on several hot bands with a 7-cm thermostatted cell.

INFRARED SPECTRUM AND FUNDAMENTAL VIBRATIONS

The infrared spectra of nitroethylene- d_0 and 1-nitroethylene- d_1 have been obtained in the vapor phase over the range 4000 to 70 cm^{-1} . Observed absorption bands for the two isotopes are listed in Tables I and II. All frequencies reported are accurate to at least ± 2 cm^{-1} . Representative spectra are shown in Figs. 2 and 3.

In order to clarify the assignment of the fundamental vibrations and to obtain an insight into the molecular force field a normal-coordinate calculation was carried out using the ALGOL program developed by Hunziker² on the CDC 1604A computer at the ETH Rechenzentrum. A microwave study¹ has shown that nitroethylene is a planar molecule of C_s symmetry with the largest moment of inertia about an axis perpendicular to the molecular plane. The internal symmetry coordinates used are shown in Table III. Force constants

were transferred from ethylene³ and nitromethane⁴ in a first approximation which was subsequently refined using at least-squares iteration. No realistic force field could be obtained without the introduction of a considerable number of off-diagonal interaction constants in the F matrix.

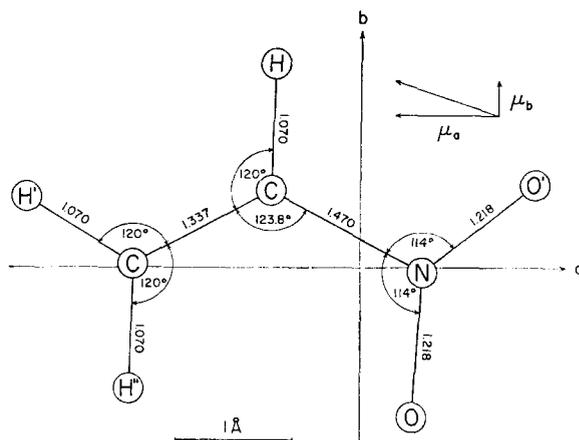


FIG. 1. Structure of nitroethylene molecule.

The final values of the force constants used in the calculation of the normal modes are listed in Table IV. Calculated frequencies and normal coordinates for both isotopes expressed as linear combinations of internal symmetry coordinates are shown in Tables V and VI. Observed frequencies were assigned to their respective symmetry species on the basis of Teller-Redlich product-rule calculations and band contours. Bands corresponding to in-plane vibrations have shapes corresponding to various mixtures of Type A and B contours, while the out-of-plane vibrations have Type C band contours.

It is clear from the results in Tables V and VI that considerable interaction between symmetry coordinates

¹H. D. Hess, A. Bauder, and Hs. H. Günthard, "The Microwave Spectrum of Nitroethylene" (to be published).

²H. Hunziker, *J. Mol. Spectry.* **7**, 131 (1965).

³S. Brodersen, *Kgl. Danske Videnskab. Selskab. Mat. Fys. Skrifter* **1**, 24 (1957).

⁴T. P. Wilson, *J. Chem. Phys.* **11**, 361 (1943).

TABLE I. Observed infrared bands of nitroethylene- d_0 .

Frequency cm^{-1}	Intensity	Assignment	Frequency cm^{-1}	Intensity	Assignment
3131 <i>R</i>			955.0 <i>Q</i>		$\nu_{11} + 2\nu_{18} - 2\nu_{18}$
3122 <i>Q</i>	w	ν_1	953.8 <i>Q</i>	s	$\nu_{11} + 3\nu_{18} - 3\nu_{18}$
3112 <i>P</i>			952.4 <i>Q</i>		$\nu_{11} + 4\nu_{18} - 4\nu_{18}$
3062 <i>R</i>			951.2 <i>Q</i>		$\nu_{11} + 5\nu_{18} - 5\nu_{18}$
3055 <i>Q</i>	w	ν_2	950.0 <i>Q</i>		$\nu_{11} + 6\nu_{18} - 6\nu_{18}$
3046 <i>P</i>			897 <i>R</i>		
3000 <i>R</i>	vw	ν_3	888 <i>Q</i>	s	ν_{12}
2985 <i>P</i>			878 <i>P</i>		
2906	m	$\nu_5 + \nu_6$	803.0 <i>Q</i>		ν_{13}
2890			801.5 <i>Q</i>		$\nu_{13} + \nu_{18} - \nu_{18}$
2710	w	$2\nu_6$	800.0 <i>Q</i>		$\nu_{13} + 2\nu_{18} - 2\nu_{18}$
2440	w	$\nu_5 + \nu_{12}$	798.5 <i>Q</i>		$\nu_{13} + 3\nu_{18} - 3\nu_{18}$
2330	vw	$\nu_8 + \nu_9$	797.0 <i>Q</i>		$\nu_{13} + 4\nu_{18} - 4\nu_{18}$
1918	m	$\nu_6 + \nu_{16}$	788	w	?
1740	w	$2\nu_{12}$	661 <i>R</i>		
1656 <i>R</i>	m	ν_4	649 <i>Q</i>	s	ν_{14}
1643 <i>P</i>			643 <i>P</i>		
1566 <i>R</i>			655 <i>R</i>	s	ν_{15}
1558 <i>Q</i>	vs	ν_5	647 <i>P</i>		
1550 <i>P</i>			549 <i>R</i>		
1386 <i>R</i>	vs	ν_6	541.0 <i>Q</i>		ν_{16}
1380 <i>P</i>			539.5 <i>Q</i>		$\nu_{16} + \nu_{18} - \nu_{18}$
1368 <i>R</i>			538.5 <i>Q</i>		$\nu_{16} + 2\nu_{18} - 2\nu_{18}$
1360 <i>Q</i>	s	ν_7	537.0 <i>Q</i>		$\nu_{16} + 3\nu_{18} - 3\nu_{18}$
1352 <i>P</i>			531 <i>P</i>		
1322 <i>R</i>			334 <i>R</i>		
1315 <i>Q</i>	m	$\nu_{14} + \nu_{16}$	323 <i>Q</i>	w	ν_{17}
1308 <i>P</i>			313 <i>P</i>		
1278 <i>R</i>			103 <i>Q</i>	vw	ν_{18}
1269 <i>Q</i>	s	ν_8			
1260 <i>P</i>					
962 <i>Q</i>	vs	ν_{10}			
957.5 <i>Q</i>		ν_{11}			
956.3 <i>Q</i>		$\nu_{11} + \nu_{18} - \nu_{18}$			

exists which makes it difficult to assign most of the fundamental vibrations to simple bond stretching or bond bending modes. This interaction is further demonstrated by the considerable frequency shifts of many of the vibrations upon deuteration. Perhaps the introduction of more interaction constants in the force field would give more localized normal-coordinate vectors and better agreement between the observed and calculated frequencies. However, this procedure seems unjustified since for the two isotopes there are already 33 parameters in the force field with 36 independent frequencies.

Attempts to calculate the three CH stretching frequencies using only one force constant were unsuccessful and a lower value was required for the lone CH bond stretching constant. The intensity of this vibration at

2995 cm^{-1} was considerably less than that of the other CH stretching modes, and, indeed, considerably less than the combination band $\nu_5 + \nu_6$ occurring at 2898 cm^{-1} .

The carbon-carbon double-bond stretching mode occurs as a well localized normal coordinate at 1650 and 1626 cm^{-1} in the d_0 and d_1 isotopes. However, all the lower-lying frequencies correspond to normal coordinates which are considerably mixed. This is true even for the strong bands at 1558 and 1382 cm^{-1} of the d_0 isotope, and 1557 and 1381 cm^{-1} of the d_1 isotope which would be expected to be the symmetric and antisymmetric NO_2 stretching vibrations. In both isotopes these bands appear to contain considerable contributions from the C-C and CN stretching coordinates. Curiously enough, the vibration at 958 cm^{-1} appears to

TABLE II. Observed infrared bands of 1-nitroethylene-*d*₁.

Frequency cm ⁻¹	Intensity	Assignment	Frequency cm ⁻¹	Intensity	Assignment
3130 <i>R</i>			955 <i>Q</i>		$\nu_{10} + 2\nu_{18} - 2\nu_{18}$
3120 <i>Q</i>	w	ν_1	954 <i>Q</i>	s	$\nu_{10} + 3\nu_{18} - 3\nu_{18}$
3110 <i>P</i>			952 <i>Q</i>		$\nu_{10} + 4\nu_{18} - 4\nu_{18}$
3058 <i>R</i>			951 <i>Q</i>		$\nu_{10} + 5\nu_{18} - 5\nu_{18}$
3048 <i>Q</i>	w	ν_2	950 <i>Q</i>		$\nu_{10} + 6\nu_{18} - 6\nu_{18}$
3038 <i>P</i>			897 <i>Q</i>	s	ν_{11}
2900	m	$\nu_5 + \nu_6$	873 <i>Q</i>	s	ν_{12}
2886			768 <i>Q</i>		ν_{13}
2250	vw	ν_3	765 <i>Q</i>		$\nu_{13} + \nu_{18} - \nu_{18}$
1916	w	$\nu_6 + \nu_{16}$	763 <i>Q</i>	s	$\nu_{13} + 2\nu_{18} - 2\nu_{18}$
1820	vw	$\nu_9 + \nu_{12}, \nu_{10} + \nu_{12}$	761		$\nu_{13} + 3\nu_{18} - 3\nu_{18}$
1710	vw	$\nu_4 + \nu_{18}, \nu_{10} + \nu_{13}$	760		$\nu_{13} + 4\nu_{18} - 4\nu_{18}$
1630 <i>R</i>			657 <i>R</i>		
1622 <i>Q</i>	m	ν_4	643 <i>Q</i>	m	ν_{14}
1614 <i>P</i>			640 <i>P</i>		
1559 <i>R</i>			598 <i>R</i>		
1553 <i>Q</i>	vs	ν_5	589 <i>Q</i>	w	ν_{15}
1544			580 <i>P</i>		
1496 <i>R</i>			552 <i>R</i>		
1481 <i>Q</i>	m	$\nu_{10} + \nu_{14}$	546 <i>Q</i>		ν_{16}
1474 <i>P</i>			543 <i>Q</i>		$\nu_{16} + \nu_{18} - \nu_{18}$
1385 <i>R</i>			540 <i>Q</i>	w	$\nu_{16} + 2\nu_{18} - 2\nu_{18}$
1376 <i>Q</i>	vs	ν_6	537 <i>Q</i>		$\nu_{16} + 3\nu_{18} - 3\nu_{18}$
1365 <i>P</i>			534 <i>Q</i>		$\nu_{16} + 4\nu_{18} - 4\nu_{18}$
1356 <i>R</i>			324 <i>R</i>		
1350 <i>Q</i>	s	ν_7	315 <i>Q</i>	w	ν_{17}
1342 <i>P</i>			300 <i>P</i>		
1142 <i>R</i>			95 <i>Q</i>	vw	ν_{18}
1135 <i>Q</i>	m	ν_8			
1126 <i>P</i>					
962 <i>Q</i>	vs	ν_9			
958 <i>Q</i>		ν_{10}			
956 <i>Q</i>		$\nu_{10} + \nu_{18} - \nu_{18}$			

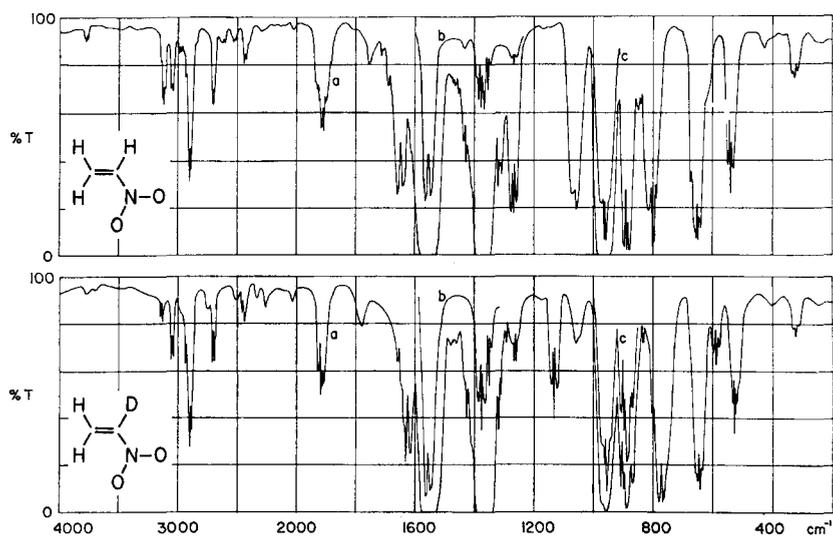
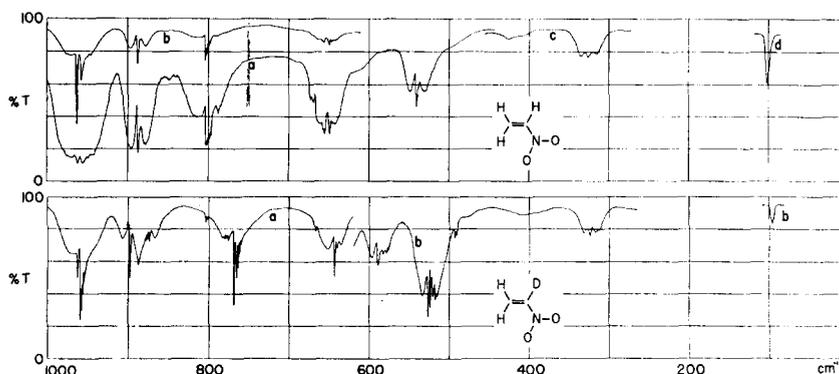
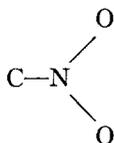


FIG. 2. Infrared spectrum of nitroethylene gas, 4000–1000 cm⁻¹ upper curve H₂C-CHNO₂, lower curve H₂C-CDNO₂. (a) 20 mm Hg/70-cm path length; (b) 5 mm Hg/10-cm path length; (c) 5 mm Hg/70-cm path length.

FIG. 3. Infrared spectrum of nitroethylene, 1000–50 cm^{-1} . Upper curve: $\text{H}_2\text{C}-\text{CHNO}_2$ (a) 10 mm Hg, 70-cm path length; (b) 5 mm Hg, 10-cm path length; (c) 20 mm Hg, 70-cm path length; (d) 50 mm Hg (45°C), 70-cm path length. Lower curve: $\text{H}_2\text{C}-\text{CDNO}_2$ (a) 20 mm Hg, 10-cm path length; (b) 20 mm Hg, 70-cm path length; (c) 20 mm Hg, 70-cm path length.



be a symmetric skeletal



stretching.

Although the torsional vibration is relatively low lying and considerably removed from the next-lowest frequency in the A'' block its normal coordinate is a linear combination of the torsional coordinate and the CH(CD) out-of-plane wagging coordinate as Tables V and VI show. In general one does not expect such interaction between vibrations whose frequencies are normally so far apart from one another and the existence of such an interaction is of some importance. If this low-lying vibration were independent of all other coordinates besides the torsional coordinate then a “freezing” of all the other vibrational coordinates in the same symmetry block ought to result in the same value for the calculated torsional frequency as obtained in the case where all the coordinates are free. This is not the

case as shown in Table VII. The “freezing” of all the other coordinates results in a shift of several wavenumbers for the torsion in both isotopes, and the “freezing” of just the CH(CD) out-of-plane wagging coordinate results in virtually the same shift. Apparently the out-of-plane motion of the light atom is excited by the torsion of the heavy NO_2 group about the CN bond. The significance of this interaction is further discussed in the section on internal rotation.

TABLE IV. Force constants for nitroethylene in 10^6 dyn cm^{-1} (number refers to symmetry coordinate).

Force constant	Value
K_1	4.88
$K_2 = K_3$	5.09
K_4	9.86
K_5	4.74
$K_6 = K_7$	8.21
K_8	0.66
K_9	0.92
K_{10}	0.80
K_{11}	2.23
K_{12}	2.51
K_{13}	2.27
K_{14}	0.055
K_{15}	0.41
K_{16}	0.56
K_{17}	0.60
K_{18}	0.20
$k_{1,2} = k_{1,3}$	-0.06
$k_{2,3}$	0.12
$k_{2,6} = k_{3,6}$	-0.12
$k_{2,7} = k_{3,7}$	0.32
$k_{4,5}$	0.75
$k_{5,6} = k_{5,7}$	0.77
$k_{6,7}$	2.71
$k_{4,8}$	-0.82
$k_{4,10}$	0.30
$k_{5,10}$	0.20
$k_{5,12}$	0.10
$k_{6,12} = k_{7,12}$	0.20
$k_{10,12}$	-0.17
$k_{14,15}$	0.01
$k_{15,14}$	0.06
$k_{15,17}$	-0.16
$k_{16,18}$	0.06

TABLE III. Symmetry coordinates for nitroethylene.

Symmetry coordinate	Description
S_1	CH stretching of lone CH
S_2	CH stretching in CH_2 group
S_3	CH stretching in CH_2 group
S_4	CC stretching
S_5	CN stretching
S_6	NO stretching
S_7	NO stretching
S_8	CH_2 deformation
S_9	CH_2 in-plane rocking
S_{10}	CH in-plane wagging
S_{11}	CCN deformation
S_{12}	NO_2 deformation
S_{13}	NO_2 in-plane rocking
S_{14}	NO_2 torsion
S_{15}	CH out-of-plane wagging
S_{16}	torsion about the C-C bond
S_{17}	NO_2 out-of-plane rocking
S_{18}	CH_2 out-of-plane rocking

TABLE V. Calculated frequencies and normal coordinates for nitroethylene- d_0 .^a

Frequency cm^{-1}		S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}	S_{16}	S_{17}	S_{18}	
Obs	Calc																			
3122	3124	2	-8	8						-1										
3055	3055	4	-8	-9	1															
2995	2999	12	4	1	-1															
1650	1652	1	1	1	27	-5	3	2	-4		-1	-2	-1	-3						
1558	1563	2		1	9	12	-6	-17		1	3	-5	6	-3						
1382	1397	1		1		1	22	7	4	2	4	-5	-6	-4						
1360	1360		-2	-1	-8	2	12	2	-7	1	2	-2	-2	-1						
1269	1259	-1		-1	-10	-5	10	-17	1	-2	-8		2	-4						
958	991				-2	-15	-23	-30		-3	6	2	15							
888	911		-2	1	-8	-6	-14	-5		14	-5	-7	-6	-1						
655	665	-2			-7	-16	16	-9		10	5	20	15	10						
541	531		-1		-24	-39	-15	12	2	-2	3	-15	23	-21						
325	326		-2	1	-3	-22	8	-13		-6	-2	-44	10	58						
1060	1086															1	7	-7	-4	-1
963	947															5	5	1	7	
803	791															2	1	14	-3	
649	645															10	13	-8	-4	
103	104.5															-37	12	-5	-4	-3

^a The columns headed by S_n represent the columns of the matrix L relating symmetry coordinates and normal coordinates, $S=LQ$.

TABLE VI. Calculated frequencies and normal coordinates for 1-nitroethylene- d_1 .^a

Frequency cm^{-1}		S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}	S_{16}	S_{17}	S_{18}		
Obs	Calc																				
3120	3122		-8	8						-1											
3048	3050		-9	-9	1																
2250	2261	15			5	2						2		1							
1626	1635	3	1	1	26	-8	3	4	-4		-1	-1	-2	-2							
1557	1531	5		1	12	11	-8	-19	-1	1	1	-4	7	-3							
1381	1378	-3		-2	-2		-17	-1	-7	-1	-1	4	3	4							
1354	1353	-1	2		10	-2	-20		5	-1	-2	4	3	4							
1135	1152	4	-1	2	9	11	1	22	1	5	7	-5	-1	3							
958	958		-1	-1	-5	-13	-27	-25		5	4	-3	-18								
873	832		1	-1	8	7	-2	-4	-1	-14	10	1	-8								
584	614	-4	1	1	15	-8	18	-14	-1	7	9	24	8	16							
520	513		-1		-2	-4	-1	1			1	-11	25	-17							
324	324		-2	1	-3	-20	9	-13		-6	-3	-46	9	59							
962	956																-1	-8	-3	-7	
897	887																8	-7	-7	3	
768	778																4	-3	13	-2	
637	635																-1	-12	-12	8	4
95	96.5																40	10	4	4	3

^a The columns headed by S_n represent the columns of the matrix L relating symmetry coordinates and normal coordinates, $S=LQ$.

TABLE VII. Torsional frequencies calculated by normal-coordinate treatment for several models.

Molecule	Observed (cm^{-1})	Unrestricted vibrations (cm^{-1})	All vibrations frozen except torsion (cm^{-1})	CH(CD) out-of-plane frozen (cm^{-1})
H_2CCHNO_2	103	104.5	106.5	106.3
H_2CCDNO_2	95	96.5	97.9	97.8

TABLE VIII. Thermodynamic functions of nitroethylene- d_0 in calories per degree mole.

T ($^{\circ}\text{K}$)	C_p°	$(H^{\circ}-H_0^{\circ})/T$	$-(G^{\circ}-H_0^{\circ})/T$	S°
298.16	17.35	11.88	58.58	70.46
300	17.43	11.91	58.65	70.56
400	21.50	13.81	62.33	76.15
500	24.91	15.70	65.62	81.33
600	27.67	17.47	68.65	86.12
700	29.89	19.09	71.46	90.56
800	31.71	20.56	74.11	94.67
900	33.23	21.89	76.61	98.50
1000	34.50	23.09	78.98	102.07
1100	35.57	24.17	81.23	105.41
1200	36.48	25.16	83.38	108.54
1300	37.27	25.06	85.43	111.49
1400	37.94	26.89	87.39	114.28
1500	38.52	27.64	89.27	116.92

Using the above assignment of the fundamentals and the rotational constants given in Ref. 1 the thermodynamic properties of nitroethylene- d_0 and 1-nitroethylene- d_1 have been calculated for the harmonic-oscillator rigid-rotor model and are listed in Tables VIII and IX.

HOT BANDS

Several of the observed fundamentals in the mid infrared showed complicated satellite structure which could be attributed to hot bands, or transitions originating in excited states of the low-lying torsion.⁵ In order to check this interpretation measurements were made at 300° and 350°K on the sharp Q branch at 803 cm^{-1} of nitroethylene- d_0 which is accompanied by a series of four satellites. The results are seen in Fig. 4. Calculated values for the normalized population of several states of the torsion at these temperatures are given in Table X and show that the satellites can be accounted for by this hypothesis.

 TABLE IX. Thermodynamic functions of 1-nitroethylene- d_1 in calories per degree mole.

T ($^{\circ}\text{K}$)	C_p°	$(H^{\circ}-H_0^{\circ})/T$	$-(G^{\circ}-H_0^{\circ})/T$	S°
298.16	17.95	12.13	58.93	71.06
300	18.03	12.17	59.00	71.18
400	22.16	14.17	62.78	76.94
500	25.59	16.12	66.15	82.27
600	28.36	17.94	69.25	87.19
700	30.58	19.59	72.14	91.73
800	32.40	21.08	74.86	95.94
900	33.89	22.43	77.42	99.85
1000	35.14	23.64	79.85	103.48
1100	36.18	24.73	82.15	106.88
1200	37.05	25.72	84.35	110.07
1300	37.80	26.62	86.44	113.07
1400	38.43	27.44	88.45	115.89
1500	38.98	28.20	90.37	118.56

⁵ G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Co., Inc., New York, 1947), Vol. 2, p. 267.

 TABLE X. Normalized populations of torsion levels for nitroethylene- d_0 at two different temperatures.

$\nu_{18} =$	0	1	2	3
300°K	39.0	23.8	14.5	8.9
350°K	34.5	22.6	14.8	9.7

Although other bands also exhibited satellite structure no intensity measurements were carried out on them because the underlying rotational envelope would have complicated the interpretation. It is assumed that such satellites are due to upper stage transitions from the torsion.

INTERNAL-ROTATION BARRIER

The far-infrared spectra of both isotopes show only one band which evidently is the NO_2 torsion occurring at 103 cm^{-1} for nitroethylene, and at 95 cm^{-1} for 1-nitroethylene- d_1 . This band is relatively narrow in both cases, having a half-width of about 1 cm^{-1} , and consists of a superposition of several transitions. Since the upper levels of the vibration are appreciably populated at room temperature the transitions 1 \leftarrow 0, 2 \leftarrow 1, 3 \leftarrow 2 will have comparable intensities. The absence of any other transitions in the far infrared indicate that the vibration is more nearly harmonic than most other torsions which generally show either broad unresolved absorption⁶ or bands corresponding to the resolved upper transitions.⁷

The internal-rotation potential for the NO_2 group may be written as:

$$V = V_2(1 - \cos 2\phi) + \dots$$

For the case of a harmonic oscillator and a high barrier, the barrier height is given by the following expression:

$$V_2 = 2\pi^2 c^2 \bar{\nu}^2 I_r,$$

where c is the speed of light, $\bar{\nu}$ the torsional frequency in cm^{-1} , and I_r the reduced moment of inertia of the NO_2 group, calculated as follows:

$$I_r = I_t \left[1 - I_t \sum_{n=1,2,3} (\cos^2 \phi_n / I_n) \right],$$

TABLE XI. Internal-rotation barrier heights.

Molecule	Harmonic approx		Mathieu treatment	
	cm^{-1}	cal/mole	cm^{-1}	cm^{-1}
H_2CCHNO_2	2320 \pm 100	6620 \pm 280	2280 \pm 100	6510 \pm 280
H_2CCDNO_2	2120 \pm 100	6050 \pm 280	2087 \pm 100	5960 \pm 280

⁶ K. R. Loos and R. C. Lord, *Spectrochim. Acta* **21**, 119 (1965).

⁷ W. G. Fateley and F. A. Miller, *Spectrochim. Acta* **17**, 857 (1961).

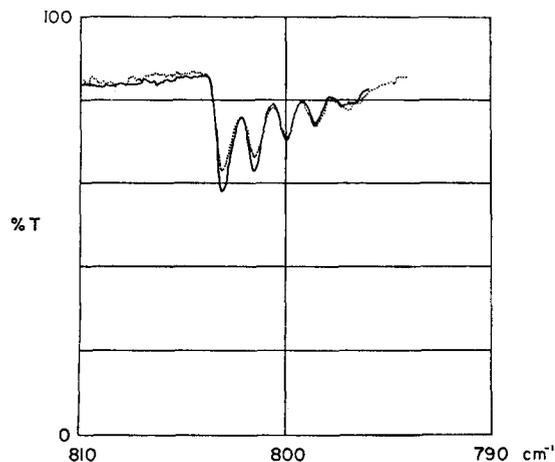


FIG. 4. Q branch of 803-cm^{-1} band. 20 mm Hg, 7-cm path length; solid line, 20°C ; dotted line, 75°C .

where I_t is the moment of inertia of NO_2 about its symmetry axis, the CN bond, ϕ_n is the angle between this axis and the n th principal axis of inertia, and I_n is the n th principal moment of nitroethylene. From the structural data of the microwave study¹ the reduced moment of inertia for the NO_2 group is calculated to be $14.75 \text{ a.m.u.} \cdot \text{\AA}^2$ for the d_0 isotope and $15.78 \text{ a.m.u.} \cdot \text{\AA}^2$ for the d_1 isotope.

The more exact treatment requires the solution of the Mathieu equation for the internal-rotation problem⁸

$$[F_p^2 + \frac{1}{2}V_2(1 - \cos 2\phi)]u = Eu,$$

where

$$F = \hbar^2/2I_r, \quad p = -i(\partial/\partial\phi).$$

Here $V_2 = Fs$, where s is a parameter in the standard form of the Mathieu equation. Using the CDC 1604A computer a table of Mathieu eigenvalues has been calculated for functions having a period $\cos 2\phi$, and s values of 1916 and 1880 were obtained for the d_0 and d_1 isotopes, respectively.

Barrier heights calculated for both isotopes using the two methods are listed in Table XI for comparison, the difference between the two approaches being well within the error bounds of the calculation. The results compare favorably with the only other work reported

⁸ D. R. Herschbach, *J. Chem. Phys.* **31**, 91 (1959).

on a twofold nitro barrier, that of Dixon and Wilson⁹ who found a barrier of $9100 \pm 2700 \text{ cal/mole}$ for methyl nitrate. The large barrier in nitroethylene probably arises from the conjugation of the ethylenic pi electrons with those on the nitro group, leading to a considerable amount of double-bond character in the C-N bond.

In calculating internal-rotation barriers from microwave or far-infrared data one usually assumes a semi-rigid model^{7,8} neglecting any interaction of the torsion with other normal modes. It is generally assumed that such interaction is negligible if no other low-lying fundamental exists in the same symmetry species as the torsion. As shown above in the case of nitroethylene the torsional mode shifts about 2 cm^{-1} if all normal modes are frozen, most of this shift coming from interaction with the out-of-plane wagging vibration of the hydrogen atom in the 1 position. In calculating the barrier V_2 the observed frequency should be corrected for this effect. This would result in a barrier value of approximately 6900 cal/mole for nitroethylene- d_0 , an increase of almost 300 cal/mole over the values given in Table XI. In view of the incomplete knowledge of the force field a more precise correction was not carried out.

It is interesting to note in this connection that for the case of trifluoroacetaldehyde the torsion was found in the far-infrared spectrum at 60 cm^{-1} by Berney¹⁰ while the value calculated from the microwave data is 75 cm^{-1} .¹¹ The microwave value is obtained from an analysis of internal-rotation splittings using the semi-rigid model and the considerable discrepancy may be caused by the interaction of the torsion with the out-of-plane wagging of the CF_3 group.

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⁹ W. B. Dixon and E. B. Wilson, Jr., *J. Chem. Phys.* **35**, 191 (1961).

¹⁰ C. V. Berney (to be published).

¹¹ R. C. Woods III, *Proc. Intern. Symp. Mol. Struct. Spectry*, Ohio State University 1964, Paper J-9 (1964); and private communication.