Far Infra-red Absorption of Disubstituted Propanes in Rotator, Solid and Liquid Phases

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Experimental observations of the far infra-red (f.i.-r.) absorption spectra of three polar disubstituted propanes (2,2-dichloro-, 2-chloro-2-nitro-, 2-methyl-2-nitro-propane) over the temperature range 133-303 K in the liquid, rotator and non-rotator solid phases are reported. The spectra in both the liquid and rotator phases are discussed in terms of two simple theoretical models of librational and relaxational motions : an acceptable fit to the experimental spectra is obtained on the basis of reasonable barriers and other parameters of the molecular motion. One of the models indicates that the molecular librational potential wells may become narrower with decreasing temperature and that there may be a distribution of potential well depths or shapes. The variation of potential barrier height with group substitution is also discussed.

1. THEORETICAL MODELS FOR MOLECULAR MOTIONS IN ROTATOR AND LIQUID PHASES

Theoretical models for the absorption of radiation in the f.i.-r. (10-200 cm⁻¹) and microwave regions have been developed for librational and relaxational molecular motions in rotator phase solids.¹⁻³ A rotator phase is characterized by a small entropy of fusion ($\Delta S_f \leq 21 \text{ J mol}^{-1}$),⁴ with a much higher entropy loss at the low temperature transition to the rigid lattice. It has been proposed ⁵ that the degree of local order of rigid molecules in the liquid phase near the melting point will not be much lower than that of the rotator phase, whence one might expect the absorption mechanism ^{1,2,6} in the liquid phase near the melting point to be similar to that of the rotator phase for which the models were developed. These two phases will be discussed together in terms of the two models outlined below.

The models used ^{1, 3, 7} in this work for the absorption of f.i.-r. radiation by polar molecules take account of both (a) the Debye relaxation process with the inclusion of the return to transparency at high frequencies due to molecular dipole inertial effects and (b) the "excess" or "Poley" absorption in the 20-150 cm⁻¹ region due to a damped librational motion.

These models will be discussed more fully elsewhere,⁷ but a brief description and an indication of the parameters follows. In both models, the librational angular frequency ω_0 of a polar molecule within a potential well of depth V (kJ mol⁻¹), semi-angular aperture ξ (radians) and of the assumed form

$$U(\theta) = V \sin^2\left(\frac{\pi}{2\xi}\theta\right) \tag{1}$$

has the small-angle (harmonic) solution

$$\omega_0 = \frac{\pi}{\xi} \left(\frac{V}{2I} \right)^{\frac{1}{2}},\tag{2}$$

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where *I* is the relevant moment of inertia of the librator. This harmonic frequency is similar to that derived from the Lennard-Jones-Devonshire potential used recently in molecular dynamics calculations for a cubic lattice.⁸

MODEL I, a classical autocorrelation function treatment by Brot *et al.*¹ of a librator within a crystal lattice: the width $1/\tau$ of the librational absorption is a function of both the frequency of weak thermal collisions $(1/\tau_i)$ perturbing the motion and of a "natural width", which is here assumed to include contributions from the anharmonicity of the potential well, its departure in practice from the assumed cylindrical symmetry, and other effects. Relaxational absorption occurs when the librator receives sufficient energy in a "strong "thermal collision to enable it to jump from one well to another. The mean times of residence (τ_r) within a potential well and of the duration of a jump from one well to another (τ_j) are functions of V, ξ , and temperature T, owing to the Boltzmann population of the potential wells,

$$\frac{\tau_{\rm r}}{\tau_{\rm i}} = \frac{1 - \exp\left(-\frac{V/kT}{}\right)}{\exp\left(-\frac{V/kT}{}\right)} \tag{3}$$

and $\tau_r \approx \tau_D$, the Debye relaxation time. Such a relaxational mechanism has been represented in common liquids ⁹ with $\tau_{i} \sim 0.4 \times 10^{-12}$ s and angle of jump 20-60°, values similar to those used in this work. Assuming the well-shape of eqn (1) with ξ deduced from section (2), reasonable trial values of the barrier height (V > kT) and collision frequency $(1/\tau_i \sim 1/\tau_i)$ are used in trial calculations of absorption spectra, τ_i being adjusted to fit the width of the observed librational absorption, and V being adjusted to fit both ω_0 and τ_p and to give the observed relative amplitudes of librational and relaxational absorptions.

A potential well (such as that of eqn (1)) may become "narrower" with decreasing temperature (as predicted by Pardoe²³ for liquids) due to contraction of the lattice and decreasing amplitude of motion of the librator's neighbours; this narrowing will principally affect the lower parts of the wells due to their Boltzmann population, while the lattice structure maintains ξ constant. For ease of calculation, the "narrowed" well of fig. 4 is composed of two sections of the form of eqn (1): a narrowed lower portion (ξ of eqn (1) is replaced by $\xi_1 \leq \xi$) in which libration takes place, and a broadened barrier (phase shift $(\xi - \xi_1)$ is introduced to maintain a constant aperture, when ξ of eqn (1) becomes $(2\xi - \xi_1)$ which principally defines τ_j . This narrowed well is identical to that of eqn (1) when $\xi_1 = \xi$; if V cannot represent τ_D and ω_0 in this case, a value of ξ_1 for a narrow well may be used in the calculation either to decrease τ_r and increase the calculated low frequency absorption, or increase ω_0 the librational frequency. The range of values of V, τ_i and ξ_1 which gave a good fit to a typical spectrum is approximately ± 6 %.

The temperature variation of the spectra (other parameters being constant) can be seen as follows:

(a) the harmonic librational frequency ω_0 of eqn (2) is independent of T,

(b) τ_1 varies little with temperature and therefore, from eqn (3), τ_r is an exponential function of T.

MODEL II, an itinerant oscillator model of a librator with co-operative relaxation proposed by Hill² and partially developed by Wyllie³: a central dipole of moment of inertia I is performing damped librational motion (with damping coefficient r) within a cage of Z nearest neighbours, where the damping arises from lack of rigidity of the cage. The co-operative diffusional reorientation of the cage molecules about their centres of gravity is a function of the moment of inertia of the cage $I_{\rm c}$ and its damping coefficient ζ . In this work both the inertial term in the equation of motion of the cage and non-zero values of r have been included in the model and, owing to the flexibility of the model with its two damping coefficients, good agreement with experimentally observed spectra is obtained. If the lattice structure is not known precisely an estimate of the aperture angle ξ can be made from Z. Reasonable trial values of the barrier height V, the damping coefficients r and ζ (from eqn (4)) are then used in trial calculations of absorption spectra, these parameters being adjusted to obtain a good fit, with an uncertainty of approximately ± 5 % for a typical spectrum. The narrowing of the potential wells discussed above would not affect the calculated spectra if V were recalculated to keep ω_0 constant (as in table 3).

If the resistance ζ were of viscous origin and ζ/T decreased with increasing temperature, then both

$$1/\tau_{\rm D} \approx 2kT/\zeta \tag{4}$$

and the relative importance of the relaxational/librational absorptions would increase with temperature, as in model I above.

2. THE OBSERVED PARAMETERS OF THE ROTATOR PHASES OF THE MOLECULES STUDIED

Molecules which are sufficiently "spherical", e.g., those of the "spherical methanes" CX_4 , where X can be CH_3 , Cl, NO₂ or combinations of those groups,¹⁰ form a rotator phase of high symmetry, often f.c.c. Some parameters of those studied in this work (2,2-dichloro-, 2-chloro-2-nitro-, 2-methyl-2-nitro-propane) are shown in table 1 together with other molecules of this series for comparison, providing a value for the angular aperture ξ to be used in the models.

(i) 2-METHYL-2-NITROPROPANE

From the similar molecular symmetries of 2-methyl-2-nitropropane and 2-methyl-2-chloropropane (t-butyl chloride, which has a f.c.c. upper rotator phase ¹¹ [phase I] as have neopentane and carbon tetrachloride) one would expect a f.c.c. lattice in rotator phase I of 2-methyl-2-nitropropane. A value of $\xi = 0.62$ rad was therefore used in the analysis of the data.¹⁹ Two rotator phases were observed (c.f., methyl chloroform and t-butyl chloride), the transition point at approximately 250 K being notably different from that (258 K) reported by Crowe *et al.*,¹² who had difficulty in obtaining a pure sample : the melting point observed here (298-9 K) was, however, in good agreement with the literature value (299 K). The lower transition point observed here between 193 and 219 K has not been reported before.

(ii) 2,2-DICHLOROPROPANE

By comparison with 2,2-dinitropropane,^{13, 14} one would have expected a f.c.c. lattice for the rotator phase. The structure has been reported, however, as being rhombohedral ¹¹ (approximately primitive cubic, with 21 molecules per unit cell: this lattice had previously been reported as optically isotropic,¹⁵ but slight anisotropy¹¹ indicates that $\alpha \approx 90.0^{\circ}$). To estimate the well aperture ξ of this lattice, one may compare this with the similar rhombohedral lattice parameter is equal to the body diagonal of the f.c.c. lattice ¹¹ and the density change of 1.7 % may be due to thermal expansion (c.f. table 1). These similarities suggest a value of $\xi = 0.62$ rad, as for an f.c.c. lattice. The transition point observed here was in good agreement with the literature value of 187-8 K.

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DATA	
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TABLE	

173	2	F.	IR	. ABSO	RPT	ION	IN SOLI) AND	LIQUID PH	IASES	VIEW	Alucie Ol
2,2-dinitro- propane ^t	1.3 at 298 K b	326 K		f.c.c. a = 8.78 Å	4		1.32(calc.) 1.30(expt.) 2.2 × 10^{-4} K ⁻¹ <i>j</i>				267 K	atrony (ref. (11)) .
2-methyl-2- nitropropane	0.9525- 1.07 × 10 ⁻³ × (T-301) ø	299 K,h 298.9 Kf 206 5 K e	AN C.067				$ \begin{array}{c} 1.022-8 \times 10^{-4} \\ \times (T-273) g \\ 2.7 \times 10^{-4} \mathrm{K}^{-1} g \end{array} $	258 K,e 250 K f			193 to 219 K.	1971) · c clicht anic
2-chloro-2- nitropropane	1.23 at 293 K b 1.22-1.22 × 10 ⁻³ ×(T-273) g	251.5 K,e 253 K f	5.14 e								214 K,e 208 K, 44.7	رآمدهام مام مرام مرام
2,2-dichloro- propane ^a	1.112 at 293 K b	239 K	13.7	228 K rhombohedral a = 14.68 Å c,d	α = 90.0 ⁻ 21	151	1.25				187 K > 16.7	nirol Buther Co
achloride ^a	ıt 293 K b	0 K	10	229 K rhombohedral a = 14.42 Å c	α = 90.0 ⁻ 21	143	1.79(calc.)	15 K 10.3	3 K oclinic b = 11.6 Å $\beta = 111^{\circ}$	17 1.87		3 K oclinic et ed (Dubl Cher
carbon tetra 1.595 a	1.595 a	25		238 K f.c.c. <i>a</i> = 8.34 Å	4	145	1.774(expt.) 1.76 (calc.)	22	a = 20.3 Å $c = 19.9 Å$	13		10 mon more D C West
t-buty ¹ chloride ^a	0.847 at 288 K b	246 K	8	228 Kf.c.c. a = 8.62 Å	4	160	0.96(calc.)	219 K 27	213 K tetragonal a = 7.08 Å b = 7.08 Å c = 6.14 Å	154 1.00		aicters and Dhy
	density/ g cm ⁻³	melting point	$\Delta S/J \text{ mol}^{-1} \text{ K}^{-1}$	temp. lattice parameters	molecules/	volume/ molocita/83	density/ density/ g cm ⁻³ linear expansion coefficient	temp. ΔS/J mol ⁻¹ K ⁻¹	temp. lattice parameters	volume/ molecule/ų density/g cm ⁻³	temp. $\Delta S/J \mod^{-1} \mathrm{K}^{-1}$	temp. lattice Handbook of Chem
	liquid phase			upper rotator phase				upper/lower rotator phase transition	lower rotator phase		transition point	non-rotator phase solid a ref (11) · b

(iii) 2-CHLORO-2-NITROPROPANE

In the absence of crystallographic data, a value of $\xi = 0.62$ rad was adopted for this molecule as in (i) and (ii) above.

The observed transition temperature (208 K) was notably different from the literature value (214 K), although the transition entropy greatly exceeded that of fusion and the observed melting point (253 K) was in good agreement with the literature value (251.5 K).

3. EXPERIMENTAL

The spectra were obtained from repeated measurements by Fourier spectroscopy using an N.P.L. mark II modular cube interferometer under a pressure of 2-3 Torr, covering the range 10-200 cm⁻¹ with a Golay SP 50 detector. The sample, placed before the detector, was contained between polypropylene windows and the temperature of the copper cell attached to the cold finger of a Dewar vessel was measured by a chromel-alumel thermocouple. The temperature range 133-303 K was covered using dry ice/acetone mixture above 205 K, acetone cooled by liquid air in the region 173-203 K, and liquid air below 173 K : temperature variations were less than 1.5 K.

MATERIALS

(i) 2,2-dichloropropane was prepared 16 from acetone and PCl₅ and purified by fractional distillation.

(ii) 2-methyl-2-nitropropane was prepared from t-butylamine following Kornblum *et al.*¹⁷ and purified by fractional distillation. B.p. 399-401 K (lit. 400-401 K).

(iii) 2-chloro-2-nitropropane. A commercial sample from Phase Separations (Rock Ferry, Cheshire) was used without further purification: refractive index $n^{25} = 1.4231$ (lit. $n^{26} = 1.4231$).

4. DISCUSSION AND ANALYSIS OF ABSORPTION SPECTRA

Clemett *et al.*¹⁸ measured only part of the Debye absorption for the compounds studied here; nevertheless their data show a good approximation to the simple Debye relations which have been accepted in constructing the high-frequency (i.e., 1-8 cm⁻¹) contours of this absorption. This "extrapolated microwave absorption" is shown with the f.i.-r. spectra in fig. 1-3 and "excess" absorption is observed in the f.i.-r. region. An attempt has been made to reproduce these spectra using the theoretical models of section 2 in the simple case of a single potential well of depth V. This is the mean of a distribution of well depths which may be expected in a real liquid or rotator phase solid, as demonstrated in a calculation of potential well depths for the upper rotator phase of t-butyl chloride.¹⁹ The occurrence of slight "shoulders" on some of the experimental spectra may indicate such a distribution in well depths, shapes or angular apertures : this will be discussed later. It may be seen from table 3 that these simple models give very reasonable estimates of the parameters of molecular motion, e.g., $V \sim 3-14$ kJ mol⁻¹, $\tau_r \sim \zeta/2kT \sim \tau_p$, $\tau_i \sim \tau_i \sim 0.5 \times 10^{-12}$ s, etc.

(i) 2-METHYL-2-NITROPROPANE SPECTRA

The positions of the non-rotator phase lattice modes seen in absorption are 42, 68, 82 and 92 cm⁻¹ at 133 K, and 43, 65 and 90 cm⁻¹ at 193 K (fig. 1*a*). Those of t-butyl chloride and methylchloroform, of the same $C_{3\nu}$ symmetry group, have been partly identified by deuteration,²⁰ the strongest being due to libration about the axis of symmetry. The band at 65 cm⁻¹ and 193 K may therefore be due to librational motion about the C—NO₂, $C_{3\nu}$, axis.



FIG. 1.—Absorption coefficient of 2-methyl-2-nitropropane. Extrapolated microwave observations (continuous lines), f.i.-r. observations (dashed lines), model I (open circles) and II (crosses) calculations with parameters of table 3. (a) Phase II (219 K (dotted line) and 244 K (dashed line)), non-rotator phase (mixed line), (b) phase I at 273 K, (c) liquid at 303 K and phase I at 294 K.

Table 2.—Variation with temperature of the integrated absorption, I over the F.I.-R. band

$I^a = \int \alpha(\tilde{v}) \mathrm{d}\tilde{v}.$								
phase	2-methyl-2-nitropropane/ 10 ³ cm ⁻²	2,2-dichloropropane/ 10 ³ cm ⁻²	2-chloro-2-nitropropane/ 10 ³ cm ⁻²					
liquid		295 K : 3.3	293 K : 7.6					
liquid	303 K : 9.9	241 K : 3.4	253 K : 7.2					
rotator	(I): 9.9	235 K : 3.1	208 K : 7.7					
rotator	(II) : 10.2	192 K : 3.9						
non-rotator	193 K : 12.2	182 K : 4.4	193 K : 7.3					

^a The low wavenumber end of the f.i.-r. spectrum was extrapolated to the origin through the anticipated Debye limit of the microwave data, and the high wavenumber end of the f.i.-r. absorption was extrapolated by continuing the observed falling absorption curve smoothly to zero: the uncertainty in such extrapolations appeared to contribute possible errors in the total area of ± 8 %.

The low temperature rotator phase (phase II) displays a broad absorption band whose maximum occurs at a frequency near 65 cm⁻¹, that of the rigid lattice (fig. 1*a*); the integrated absorption intensity decreased (see table 2) on transition. This may arise either from increased higher electric moment contributions with the increased density of the rigid lattice or from the appearance of another mode of absorption in the non-rotator phase. In phase II, rotation about the symmetry axis alone is



FIG. 2.—Absorption coefficient of 2,2-dichloropropane, key as fig. 1. (a) Rotator phase at 192 K, non-rotator phase (mixed line) at 182 K; (b) rotator phase at 235 K; (c) liquid at 241 K; (d) liquid at 295 K.

indicated by the low permittivity measurements of Crowe *et al.*¹² and by comparison with the n.m.r. measurements of Gutowsky *et al.*²¹ on t-butyl chloride. The absorption is unchanged throughout this phase and is centred at 65 cm^{-1} , the maximum of the non-rotator phase.

The absorption maximum shifts to a lower frequency on transition to the upper rotator phase (phase I) near 250 K, the spectrum then remaining constant through this phase and past the melting point into the liquid phase, indicating no change of degree of molecular order in this region. Assuming that the shape of the potential wells remains constant, the temperature dependence of the models discussed in section

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2 would thus indicate a constant barrier height V in the region 253-300 K, the change in the observed microwave absorption occurring through the temperature dependence of τ_r or ζ . Calculated spectra are shown together with their parameters (table 3) for comparison with the observed spectra in fig. 1b. The n.m.r. measurements of Gutowsky et al.²¹ on the similar molecule, t-butyl chloride, indicate that molecular



FIG. 3.—Absorption coefficient of 2-chloro-2-nitropropane, key as fig. 1. (a) Rotator phase at 209 K, non-rotator (mixed line) at 193 K; (b) rotator phase at 233 K; (c) liquid at 253 K; (d) liquid at 293 K.

reorientation about all axes is taking place above the upper transition point and that self-diffusion becomes important as the melting point is approached : the models used here take no account of this effect, but good agreement between experimental and calculated spectra is observed in the upper rotator and liquid phases.

(ii) 2,2-DICHLOROPROPANE SPECTRA

The lattice modes of the non-rotator phase (fig. 2a) shift from 61 and 78 cm⁻¹ at 133 K to 56 and 68 cm⁻¹ at 182 K, with decreasing absorption magnitude. No evidence was found of the limited amount of dipole reorientation in the region of 170-185 K reported by Roeder et al.²² from n.m.r. measurements.

Above the transition point, the rotator phase exhibits a broader band of reduced integrated intensity (table 2) as in (i) above. The frequency of maximum absorption shifts to lower frequencies with increasing temperature within each phase (fig. 2) and on phase transition, although the observed shift is quite small at the melting point, as expected if the rotator phase models are to be meaningful in the liquid state. This frequency shift over the rotator and liquid phases would indicate (other parameters remaining constant) a large increase in V with decreasing temperature. Approximate calculations after Brot ¹⁹ would indicate that such a variation would be reasonable.

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	TAB	LE 3.—	-FARAME	TERS OF	MODELS	I AND II			
T/K	V/ kJ mol−1	r	$\zeta/2kT/10^{-12}$ s	$10^{\tau_{\rm D}^d/}$ s	10^{-12} s	${ extstyle au _{ extstyle au } ^{ au _{ extstyle au } / } ex$	$10^{\tau_1/12}$ s	$r/10^{-12}$ s rad ⁻¹	ω ₀ /1012 rad s ⁻¹
2-nitro	propane								
300	5.5 all	2.4	12	8					5.8
and									
294	7.3 ^{aI}			8	10	0.53	0.65	0.15	6.7
273	6.3 all	2.4	28	14					6.1
	8.3 ^a l			14	21	0.54	0.72	0.16	7.1
oropro	pane								
295	2.8 ^{aII}	2.4	8	6.5					4.0
	5.9 ^{aI}			6.5	5.7	0.58	1.60	0.30	5.8
241	5.6 ^{aII}	1.8	14	13					5.7
	6.3 ^a l			13	15.6	0.60	0.87	0.20	6.2
235	8.5 ^a II	1.2	14	15					7.1
	6.0 ^{b11}	1.2	14	15					7.1
	6.5 ^{bI}			15	16	0.60	1.20	0.22	7.3
192	14.2 ^{all}	1.2	51	28					9.0
	6.8 ^{cII}	1.2	51	28					9.0
	6.4 ^{cI}			28	35	0.64	1.30	0.23	8.6
	12 ^e								
-2-nitr	opropane								
293	6.8 ^{all}	2.2	16	12					6.2
	8.0 al			12	17	0.53	0.54	0.13	7.0
253	11.8 all	1.4	18	20					8.2
	5.7 cll	1.4	18	20					8.2
	7.6 ^{cl}			20	20	0.57	0.60	0.16	9.4
233	16 all	1.2	41	30					9.7
	7.7 cli	1.2	41	30					9.7
	7.7 ^{cl}			30	31	0.58	0.86	0.16	9.5
209	17.6 all	1.2	72	40					10.0
	8.5 cll	1.2	72	40					10.0
	7.5 cl			40	42	0.60	0.91	0.17	9.3
	<i>T</i> /К 2-nitrc 300 and 294 273 oropro 295 241 235 192 -2-nitr 293 253 233 233 209	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	TABLE 3.—PARAME $V'_{T/K}$ kJ mol ⁻¹ r $\frac{\zeta/2kT'}{10^{-12}s}$ 22-nitropropane 300 5.5 all 2.4 12 and 294 7.3 al 2.4 12 and 294 7.3 al 2.4 12 and 294 7.3 al 2.4 28 8.3 all 2.4 28 8.3 al 24 oropropane 295 2.8 all 2.4 8 241 5.6 all 1.8 14 6.3 al 235 8.5 all 1.2 14 6.0 bil 1.2 14 6.0 bil 1.2 14 6.5 bi 192 14.2 all 1.2 51 192 14.2 all 1.2 51 6.4 cl 12 e 12 e 293 6.8 all 2.2 16 8.0 al 2.2 16 233 16 all 1.2 2.1 14 14 18 7.6 cl 233 16 all 1.2 41 7.7 cl 209 17.6 all	TABLE 3.—FARAMETERS OF 1 $V/T/K$ kJ mol ⁻¹ r $\frac{\zeta/2kT/}{10^{-12} \text{ s}}$ $10^{\frac{r}{12}/2} \text{ s}$ 22-nitropropane 300 5.5 all 2.4 12 8 and 294 7.3 al 8 273 6.3 all 2.4 28 14 oropropane 295 2.8 all 2.4 8 6.5 5.9 al 6.5 241 5.6 all 1.8 14 13 6.3 al 13 235 8.5 all 1.2 14 15 6.5 5.9 al 15 192 14.2 all 1.2 14 15 15 192 14.2 all 1.2 51 28 6.4 cl 28 22 16 12 28 12 28 12 28 12 20 233 16 all 1.2 14 18 20 7.6 cl 20 233 16 all 1.2 72 40 7.7 cl 30 209 17.6 all 1.2 72 40 7.5 cl 40	TABLE 3.—FARAMETERS OF MODELS $V'_{T/K}$ kJ mol ⁻¹ r $\sqrt[5]{2kT/}$ $10^{\frac{r_0^2}{-12}}$ $10^{\frac{r_0^2}{-12}}$ 10^{-12} 10^{-12} s 11^{-12} 14^{-12} 11^{-12} 14^{-12} 11^{-12} 11^{-12} 11^{-12} 11^{-12} 11^{-12} 11^{-12} 11^{-12} 11^{-12} <td>TABLE 3.—FARAMETERS OF MODELS I AND II $V/T/K$ kJ mol-1 r $\zeta_{10}^{2}LKT/T$ $10^{-12}s$ $10^{-12}s$</td> <td>$\begin{array}{cccccccccccccccccccccccccccccccccccc$</td> <td>$\begin{array}{c ccccccccccccccccccccccccccccccccccc$</td>	TABLE 3.—FARAMETERS OF MODELS I AND II $V/T/K$ kJ mol-1 r $\zeta_{10}^{2}LKT/T$ $10^{-12}s$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

 $a \xi_1 = \xi = 0.6$ rad; $b \xi_1 = 0.52$ rad; $\xi = 0.62$ rad; $c \xi_1 = 0.43$ rad, $\xi = 0.62$ rad; (I) model I, (II) model II; d ref. (18); e ref. (21).

A good fit to the observed spectra (fig. 2) is obtained on model II for the potential function of eqn (1) due to the independence of ζ and r on V, yielding a barrier height V of the order of that obtained by Gutowsky *et al.*²¹ by n.m.r. measurements.

The dependence of τ_r and ω_0 on V in model I, together with the small variation ¹⁸ of τ_D with temperature, indicates that the barrier height V will not change as much as much as suggested above and that the potential wells may become "narrower" on

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contraction of the lattice with decreasing temperature.²³ The arbitrarily modified potential is shown in fig. 4, increasing the calculated value of ω_0 at 192 K from 6×10^{12} rad s⁻¹ to 8.6×10^{12} rad s⁻¹, while maintaining $\tau_r \sim \tau_D$. Thus the observed



FIG. 4.—Symmetrical and narrowed ($\xi_1 = 0.7 \xi$) potential wells. Solid line as eqn (1); dashed line, $U(\theta) = V \sin^2 \left(\frac{\pi}{2\xi_1} \theta\right), 0 < \theta < \xi_1/2; \text{ mixed line, } U(\theta) = V \sin^2 \left(\frac{\pi}{2(2\xi - \xi_1)} [\theta + \xi - \xi_1]\right), \xi_1/2 < \theta < \xi_1/2;$

liquid and rotator phase spectra of 2,2-dichloropropane may be fitted on both models by variations in the barrier height and in the shape of the potential wells at low temperatures (less than 30 % change), as can be seen from fig. 2 and table 3.

(iii) 2-CHLORO-2-NITROPROPANE SPECTRA

In the non-rotator phase, lattice modes appear at 40 cm⁻¹ and 63 cm⁻¹ at 133 K, the former having disappeared at 193 K (fig. 3a), the latter having reduced intensity at 58 $\rm cm^{-1}$ at this temperature. There is no significant change in integrated intensity (table 2) throughout the temperature range of observations, and there is very little movement of the frequency of maximum absorption from 58 cm^{-1} at 193 K (just below the transition point) through the rotator phase into the liquid phase (56 cm⁻¹) at 253 K, as shown in fig. 3a-c. The temperature variation of τ_D is qualitatively as described in section 2. As in section 4(ii), all the spectra of the rotator and liquid phases may be fitted by model II with the potential function of eqn (1) but model I again indicates that the potential wells should become narrower with decreasing temperature (as $\tau_r \gg \tau_D$ for $\xi_1 = \xi$ at low T). A good fit to the observed spectra may then be obtained on both models for these narrower wells (see table 3 and fig. 3).

An alternative analysis of the spectra is obtained by observing that the feature near

58 cm⁻¹ described earlier for the rotator and liquid phases is present in all spectra, although it is dominated in the high temperature liquid phase by a low wavenumber absorption process (fig. 3). The origin of this absorption may either be different from those discussed so far, or may be accounted for by a spread in the shape or depth of potential wells, the distribution functions $\rho(\xi_1, T)$ and $\rho(V, T)$ being temperaturedependent.

The analysis of these spectra in terms of identical wells whose depth and/or shape varies with T (as shown in fig. 2-3) would thus represent the mean values of these parameters at temperature T, whereas a distribution is to be expected in reality.

Although the microwave spectra of Clemett *et al.*¹⁸ indicate the possibility of two well depths separated by 4 kJ/mol in methylnitropropane, no such indication was observed for chloronitropropane. It should be noted that, for a particular distribution of well depths or shapes, a distribution of the latter will affect the librational absorption spectrum far more than the former owing to the Boltzmann population of the wells.

5. VARIATION OF POTENTIAL BARRIER HEIGHT WITH SUB-STITUTED GROUPS

Powles *et al.*²⁴ suggested that group substitution in "spherical" molecules involving increased dipole moment and/or decreased symmetry would result in increased potential barrier heights, and the n.m.r. observations of Gutowsky *et al.*²¹ on the series C Me_nCl_{4-n} indicated that this was so.

Intermolecular potential calculations by Brot *et al.*¹⁹ for t-butyl chloride in the rotator phase indicate that, owing to the quasi-isotropy of the phase, the principal contribution to the barrier height is from the Lennard-Jones potential with only a minor contribution from polar interactions. Rothschild's analysis ⁹ has led to similar observations in common liquids.

The values of the barrier heights deduced from the rotator phase spectra observed here for varying well depth and shape are in agreement with this discussion :

increasing V chloronitropropane ($\mu = 11.7 \times 10^{-30}$ C m) (low symmetry) methylnitropropane ($\mu = 12.4 \times 10^{-30}$ C m) dichloropropane ($\mu = 7.6 \times 10^{-30}$ C m) t-butyl chloride ¹⁹ ($\mu = 7.2 \times 10^{-30}$ C m) (high symmetry)

6. CONCLUSION

Using the simple models described in section 2 with a single potential well depth and shape in each case, a good fit may be obtained to the observed spectra of the three compounds studied here through both the liquid and rotator phases, which indicates only slightly lower order in the liquid than in the rotator phase. Table 3 shows that the models give reasonable parameters for these phases, e.g., $V \sim 3$ to 9 kJ mol⁻¹, relaxational jumps through approximately 0.62 rad in times of 0.5×10^{-12} s (c.f. the mean time between collisions) as observed in common liquids,⁹

$$\zeta/2kT \sim \tau_{\rm r} \sim \tau_{\rm D}.$$

It has been observed ⁹ that dipole-dipole forces are not important in orientational jump relaxation in common liquids; calculations ¹⁹ show that the Lennard-Jones potential is a good approximation in the rotator phase, as indicated by the change in potential barrier height with group substitution observed in this work.

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Although model II could fit all observed spectra, due to the independence of parameters ζ and r on V, with a variation in barrier height which can be shown to be reasonable, model I indicated that, at low temperatures, the potential well shapes become narrower due to the decreased amplitude of molecular motion as proposed by Pardoe²³ for liquids. A good fit to the observed spectra could thus be obtained on both models assuming a narrowing of potential wells of less than 30 % and a small variation in barrier height as shown in table 3. The mean difference in the barrier heights deduced from the two models is ± 10 %. These barrier heights will be similar to those which would be calculated to fit microwave spectra on an $\alpha(\tilde{v})/\log(\tilde{v})$ plot⁸ where the calculated librational frequency may be in error by a factor of 2+0.4.

In general, both the width $(1/\tau \text{ or } r)$ of the librational absorption and the apparent collision frequency $(1/\tau_i)$ are seen from table 3 to increase with temperature as expected; over the observed temperature range the variation is less than 100 %.

The low-wavenumber shoulder on the high temperature liquid chloronitropropane absorption spectrum may indicate either a mode of absorption, other than the relaxation and high frequency libration of the rotator phase, or a distribution of well depths or shapes, the latter being preferred due to the Boltzmann weighting of the population of the wells, although both distributions are likely to occur.

Although only transient local order ⁵ is to be expected in the liquid phase of spherical molecules, even at temperatures just above the melting point, the models do give a fair representation of the observed liquid spectra in terms of relaxational ⁹ and librational motion in accordance with recent observations of librational motion in liquids.²⁵ As the potential wells become shallower with respect to thermal energy (kT), and less defined with increasing temperature in the liquid phase, the molecular motion would become that of a perturbed free rotator.

Reasons for the calculated absorptions exceeding those observed at high wavenumbers may include :

(a) the classical a.c.f. of model I is not truly an even function of time,

(b) anharmonicity in the potential wells and distribution of barrier heights can be reflected in the width parameter (τ or r) without, however, incorporating the form of the distribution of librational frequencies.

For a more detailed analysis, one would require more detailed knowledge of the rotator phase structure. It would be interesting to attempt to reproduce the " narrowing" of potential wells with decreasing temperature and to see the effects of distributions of potential wells with the use of molecular dynamics calculations for the systems studied here.

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