

# Calculation of Vibrational Relaxation Times in Polyatomic Gases

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Ultrasonic dispersion measurements are reported for  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{D}_2$  at 298 and 335°K, followed by theoretical calculations of the vibrational relaxation times of  $\text{CH}_4$ ,  $\text{CD}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{D}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{D}_2$ ,  $\text{CH}_3\text{F}$ ,  $\text{CD}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CD}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CD}_3\text{Br}$  and  $\text{SF}_6$ . The Schwartz, Slawsky, Herzfeld <sup>1</sup>-Tanczos <sup>2</sup> method is used and the results are compared with experiment over ranges of temperature. Within the limits set by the uncertainty of the intermolecular potential, agreement is good. For  $\text{C}_2\text{D}_2$ ,  $\text{CH}_3\text{F}$  and  $\text{CD}_3\text{Cl}$  the quickest route for relaxation is *not* via the lowest mode. Although single dispersion is predicted for all the molecules, the calculated absorption peaks for the ethylenes and methyl halides are slightly lower than expected for a single relaxation time due to the rapid exchange of energy between the upper modes. It is suggested that the effective exponential repulsion parameter is about  $5.5 \text{ \AA}^{-1}$  for all molecules. Except for the acetylenes, the ratios of the relaxation times for corresponding hydrogenated and deuterated molecules are incorrectly predicted; this is ascribed to the influence of rotation.

Recent work <sup>3, 25</sup> has shown that the theory of Schwartz, Slawsky and Herzfeld <sup>1</sup> (SSH) can successfully predict the vibrational relaxation times of diatomic molecules over wide ranges of temperature. Tanczos <sup>2</sup> has extended the theory for polyatomic molecules and this has been used to explain double dispersion,<sup>55, 56</sup> but otherwise few calculations have been carried out. This paper presents calculations of the relaxation times of several polyatomic molecules over the ranges of temperature so far covered by experiment in order that a comparison can be made between theory and experiment. New experimental dispersion results for the acetylenes are also given.

## EXPERIMENTAL

The wavelength of sound was measured in  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{D}_2$  using a 4 Mc/sec quartz crystal interferometer.<sup>5</sup> Measurements were made at 298 and 335°K over the pressure range 1-0.2 atm, and in all four cases half the dispersion zone was covered. The interferometer was surrounded by a thermostatted copper block which kept the temperature constant to within 0.1°C and calibration runs were carried out at each temperature using dry,  $\text{CO}_2$ -free air. The crystal frequency was measured to within 0.02 % and the velocity determinations are estimated to have an accuracy of 0.1 %.

Corrections to the velocity <sup>6</sup> were made, the second virial coefficients and their temperature derivatives being obtained from the critical data <sup>7</sup> using the Berthelot equation.<sup>22</sup> Values of the virial coefficient so calculated agree with the experimental results of Bottomley, Reeves and Seiflow.<sup>8</sup> It is assumed that  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{D}_2$  have the same virial coefficients. The relaxation times were obtained by fitting theoretical single dispersion curves to the experimental points, the necessary vibrational specific heats being calculated from spectroscopic data.<sup>18, 19</sup>

The sample of  $\text{C}_2\text{H}_2$  was the one used by Lambert and Salter.<sup>9</sup> The  $\text{C}_2\text{D}_2$  was prepared by Patterson,<sup>26</sup> and was shown by a mass-spectrometer analysis to contain 99.3

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atom % D. Both gases were further purified by passing them through an alumina-packed column, the alumina being modified by NaOH in order to remove polar molecules and halogenated hydrocarbons. The molecular weights were measured by a sensitive gas density balance and found to be  $26.18 \pm 0.03$  for  $C_2H_2$  and  $28.05 \pm 0.03$  for  $C_2D_2$ . Immediately prior to each set of readings the gas under investigation was passed over fresh phosphorus pentoxide spread on glass wool.

## RESULTS

### $C_2H_2$

The vibrational specific heats at 298 and 335°K are 3.56 and 4.18 cal mole<sup>-1</sup> deg.<sup>-1</sup> respectively, and the measured true relaxation times (Herzfeld and Litovitz 4 p. 82) are  $\beta = 0.082 \mu\text{sec}$  at 298°K,  $\beta = 0.079 \mu\text{sec}$  at 335°K. The result at 298°K is slightly longer than that of Lambert and Salter.<sup>9</sup>

### $C_2D_2$

The vibrational specific heats at 298 and 335°K are 4.78 and 5.30 cal mole<sup>-1</sup> deg.<sup>-1</sup>, and the measured true relaxation times are  $\beta = 0.072 \mu\text{sec}$  at 298°K,  $\beta = 0.072 \mu\text{sec}$  at 335°K.

## CALCULATIONS

### TRANSITION PROBABILITIES

The probability,  $P_{k \rightarrow l}^{i \rightarrow j}(a, b)$ , that during a binary collision vibrational mode  $a$  in one molecule will change its quantum state from  $i$  to  $j$ , while simultaneously a second mode  $b$  in the other molecule will change its state from  $k$  to  $l$ , is given by the SSH theory<sup>1, 2, 55</sup> as :

$$P_{k \rightarrow l}^{i \rightarrow j}(a, b) = P_0(a) \cdot P_0(b) [V(a)]^{i-j} [V(b)]^{k-l} 8(\mu/2kT) \exp(-(\phi_0/kT)) \\ \times \left( \frac{8\pi^3 \mu \Delta E}{h^2} \right)^2 \int_0^\infty f(u) du,$$

where

$$f(u) = \frac{u}{\alpha^4} \left( \frac{r_c}{r_0} \right)^2 \exp \left( \frac{-\mu u^2}{2kT} \right) \left\{ \frac{\exp(L-L')}{[1 - \exp(L-L')]^2} \right\}, \\ L = \frac{4\pi^2 \mu u}{\alpha h} \quad \text{and} \quad L' = \frac{4\pi^2 \mu v}{\alpha h}. \quad (1)$$

$\mu$  is the reduced mass of the colliding pair which approach each other with an effective relative velocity  $u$  and recede with a velocity  $v$ . The integration is over the thermal distribution (at  $T^\circ\text{K}$ ) of the molecular velocities assumed to be Maxwellian.  $h$  and  $k$  are the Planck and Boltzmann constants respectively.

$\alpha$  is the exponential repulsion parameter obtained by matching an exponential curve to a suitable intermolecular potential whose minimum value is  $\phi_0$ .  $\alpha$  is a function of  $u$  and its value for the velocity of approach with the highest probability is denoted by  $\alpha^*$ .  $(r_c/r_0)$  is a reference factor relating the distance of closest approach  $r_c$  to the separation  $r_0$  at zero energy. The collision rate  $Z$  is calculated from  $r_0$  using

$$Z = 4Nr_0^2(\pi kT/2\mu)^{\frac{1}{2}}, \quad (2)$$

where  $N$  is the number of molecules per cm<sup>3</sup>. Use of this reference factor avoids having to define exactly what is meant by a collision.<sup>27</sup>

$\Delta E$  is the energy exchanged between the vibrational and translational degrees of freedom :

$$\Delta E = h\nu_a(i-j) + h\nu_b(k-l) = (v^2 - u^2)\mu/2, \quad (3)$$

where  $\nu_a$  and  $\nu_b$  are the frequencies of the vibrational modes. If  $k = l$ , only one mode is involved and the transition is said to be a simple one; if two modes change their quantum states, this is a complex transition. When  $\Delta E$  is large the integration in eqn. (1) can be solved analytically in terms of  $\alpha^*$  to give the formula deduced by Tanczos.<sup>2</sup> In these calculations the integration is always performed numerically.

#### VIBRATIONAL FACTORS

The vibrational factors  $[V^{i,j}]^2$  are defined for zero, single and double quantum jumps by

$$[V^{i-i}]^2 = 1, \\ [V^{(i+1)-i}]^2 = [V^{i-(i+1)}]^2 = \alpha^2(\bar{A}^2)(i+1)/2\gamma$$

and

$$[V^{(i+2)-i}]^2 = [V^{i-(i+2)}]^2 = \alpha^4(\bar{A}^4)(i+1)(i+2)/16\gamma^2,$$

where

$$\gamma = 4\pi^2\nu/\hbar. \quad (4)$$

The expression for the double jump differs slightly from that given by Tanczos.<sup>2</sup>

$\bar{A}$  is the average Cartesian displacement of the surface atoms of the molecule for unit change of the normal co-ordinate. The averaging is carried out according to the "breathing sphere" model, i.e., the full displacements of the surface atoms are taken and the appropriate powers averaged. This assumes that the displacements are always normal to the surface and corresponds to the molecule having a favourable orientation at the collision. To allow for this, steric factors  $P_0$  are introduced for each vibration which changes its quantum state.  $P_0$  is taken to be  $\frac{1}{3}$  for a linear molecule (as discussed by Witteman<sup>28</sup> for  $\text{CO}_2$ ) while for non-linear molecules it is taken as  $\frac{2}{3}$  following Tanczos.

The Cartesian displacements are derived from a normal co-ordinate analysis of the molecular vibrations.<sup>41</sup> One of the products of this analysis is a transformation matrix  $L$ , which is the link between the internal co-ordinates  $R$  and the normal co-ordinates  $Q$ ,

$$R = LQ. \quad (5)$$

The Cartesian displacements  $x$  are related to the changes in the internal co-ordinates by the matrix  $B$ ,

$$R = Bx. \quad (6)$$

The squares of the Cartesian displacements are given by<sup>42, 43</sup>

$$x^2 = Q'L^{-1}H(L')^{-1}Q, \quad (7)$$

where the matrix  $H$  is defined as

$$H = BM^{-2}B', \quad (8)$$

$M$  being a diagonal matrix of the atomic masses. Comparison of eqn. (8) with the definition of Wilson's  $G$  matrix,<sup>40</sup>

$$G = BM^{-1}B', \quad (9)$$

shows that the elements of  $H$  are easily obtained from  $G$ . For unit change of the

$a$ th normal co-ordinate only, the sum of the squares of the Cartesian displacements of all the atoms is given by

$$\sum_{i=1}^{i=3N} x_i^2 = [L^{-1}H(L')^{-1}]_{aa}, \quad (10)$$

where  $N$  is the number of atoms in the molecule. In order to obtain the average displacement of the surface atoms, the movements of the various types of atom in the molecule need to be calculated separately. This is done by including only the required atomic masses in the diagonal matrix when  $H$  is computed according to eqn. (8).

TABLE 1.—DATA CONCERNING THE MOLECULAR VIBRATIONS

	mode	degeneracy	frequency, $\text{cm}^{-1}$	$(\overline{A^2})$ , (a.m.u.) $^{-1}$
CH <sub>4</sub> <sup>10</sup>	$\nu_1$	1	2915	·2480
	$\nu_2$	2	1534	·2480
	$\nu_3$	3	3019	·2481
	$\nu_4$	3	1306	·2092
CD <sub>4</sub> <sup>10</sup>	$\nu_4$	3	996	·0962
C <sub>2</sub> H <sub>4</sub> <sup>11, 13</sup>	$\nu_{10}$	1	810	·1605
C <sub>2</sub> D <sub>4</sub> <sup>12</sup>	$\nu_{10}$	1	589	·0802
C <sub>2</sub> H <sub>2</sub> <sup>18</sup>	$\nu_4$	2	612	·1523
	$\nu_5$	2	729	·2308
	$\nu_6$	2	511	·0629
C <sub>2</sub> D <sub>2</sub> <sup>19</sup>	$\nu_4$	2	539	·1093
	$\nu_5$	2	1049	·0220
	$\nu_6$	2	1200	·1972
CH <sub>3</sub> F <sup>14, 15</sup>	$\nu_3$	1	992	·0611
	$\nu_6$	2	912	·0962
CD <sub>3</sub> F <sup>14, 15</sup>	$\nu_3$	1	732	·0235
	$\nu_6$	2	1015	·2121
CH <sub>3</sub> Cl <sup>14, 15</sup>	$\nu_3$	1	699	·0305
	$\nu_6$	2	769	·1022
CD <sub>3</sub> Cl <sup>14, 15</sup>	$\nu_3$	1	611	·0308
	$\nu_6$	2	955	·2177
CH <sub>3</sub> Br <sup>14, 15</sup>	$\nu_3$	1	578	·0346
	$\nu_6$	2	712	·1054
CD <sub>3</sub> Br <sup>14, 15</sup>	$\nu_3$	1	344	·00877
	$\nu_6$	2		
SF <sub>6</sub> <sup>16, 17</sup>	$\nu_6$	3		

In table 1 are listed the important frequencies of the molecules, together with the sources of the spectral data and the calculated average squares of the Cartesian displacements for unit change of the normal co-ordinate ( $\overline{A^2}$ ). The non-surface atoms are the carbon atoms of the methanes and the methyl halides, and the sulphur atom of SF<sub>6</sub>. The necessary  $G$  and  $L$  matrices are taken from Bruton <sup>44</sup> for SF<sub>6</sub>, from Duncan <sup>45</sup> for the ethylenes and acetylenes, and from Mills <sup>46</sup> for the methanes and methyl halides. The vibrational modes are numbered according to the usual spectroscopic convention.

#### INTERMOLECULAR POTENTIAL

Herzfeld and Litovitz <sup>4</sup> have recommended two methods of matching in order to obtain  $\alpha$  from a suitable intermolecular potential whose force constants have been determined experimentally, usually from viscosity measurements. Method B gives slightly larger values of  $\alpha$  compared with method A, and has been used more widely.

Millikan and White<sup>47</sup> have found that use of method A reproduces well their shock tube results for O<sub>2</sub>, N<sub>2</sub> and CO. However, method B gives the better overall prediction<sup>25</sup> of the results of the shock tubes and the lower temperature acoustic measurements. Only method B is used here.

Matching is done against the Lennard-Jones 12—6 function for non-polar molecules. For polar ones the Monchick and Mason<sup>20</sup> potential is used where data are available. This potential is similar in form to the Krieger potential which has been used by earlier workers,<sup>2, 3</sup> but has since been found to be incorrect.<sup>20</sup> The necessary formulae for method B fitting have already been given.<sup>3</sup> Table 2 gives the intermolecular force constants which are assumed to be the same for the corresponding deuterated molecules. Two sets of force constants are used in the calculations for the acetylenes and methyl bromides in order to demonstrate the sensitive dependence of the calculated probabilities upon them.

TABLE 2.—INTERMOLECULAR FORCE CONSTANTS

	$r_0$ , Å	$\epsilon/k$ , °K	$\delta^*$	$\phi_0/k$ , °K	ref.
CH <sub>4</sub>	3.76	148	0	— 148	21
C <sub>2</sub> H <sub>4</sub>	4.23	205	0	— 205	22
C <sub>2</sub> H <sub>2</sub> I	4.21	185	0	— 185	22
C <sub>2</sub> H <sub>2</sub> II	3.84	294	0	— 294	23
CH <sub>3</sub> F	3.73	333	0	— 333	23
CH <sub>3</sub> Cl	3.94	414	·5	— 1044	20
CH <sub>3</sub> Br I	4.25	382	·4	— 841	20
CH <sub>3</sub> Br II	3.95	550	·5	— 1387	—
SF <sub>6</sub>	5.46	155	0	— 155	24

#### CALCULATION OF THE RELAXATION TIMES

The probabilities for the various processes have to be converted into the corresponding transition rates. The procedure has been described by Tanczos<sup>2</sup> but his formulae for the complex transitions contain an error as pointed out by Schofield.<sup>55</sup> They can be stated correctly by the general formula for the transition  $P_{0-y}^{x-0}(a, b)$  as

$$k_{0-y}^{x-0}(a, b) = g_b Z P_{0-y}^{x-0}(a, b) (x\theta_a/\theta_b^y) \exp [(x-1)(-h\nu_a/kT)]$$

$$k'_{0-y}^{x-0}(a, b) = (v_b/v_a) k_{0-y}^{x-0}(a, b) (\theta_b^{y-1}/\theta_a^{x-1}), \quad (11)$$

where  $g$  is the degeneracy of the mode and  $\theta$  is defined by

$$\theta_a = 1 - \exp [-h\nu_a/kT].$$

The transition rates are then combined,

$$k_{aa} = k^{1-0}(a) + \sum_{b \neq a} [k_{0-1}^{1-0}(a, b) + k_{0-2}^{1-0}(a, b) + k_{0-1}^{2-0}(a, b) + \dots]$$

$$k_{ab} = k'_{0-1}^{1-0}(a, b) + k'_{0-2}^{1-0}(a, b) + k'_{0-1}^{2-0}(a, b) + \dots, \quad b \neq a,$$

where  $k^{1-0}(a)$  ( $= ZP^{1-0}(a)\theta_a$ ) is the transition rate for a simple process.  $k_{aa}$  and the  $k_{ab}$  are the coefficients of the temperature relaxation equation of the  $a$ th mode. There is a relaxation equation for each vibration considered, so that the coefficients form a square matrix with all the off-diagonal elements negative.<sup>2</sup> Account is only taken of those modes which contribute appreciably to the specific heat, and calculations are carried out for transitions concerning these modes if they have a significant probability, e.g., for the acetylenes two modes and three transitions are considered, while for C<sub>2</sub>H<sub>4</sub> the probabilities of fifteen transitions concerning eight modes have to be computed.

The eigenvalues of the matrix of coefficients  $k$  are the reciprocal heat-bath relaxation times.<sup>29</sup> The effective ultrasonic relaxation times  $\tau_i$  and the associated relaxation constants  $D_i$  are obtained from the  $k$  matrix after division by a matrix whose elements are related directly to the specific heats of the modes.<sup>2</sup> If there are  $n'$  relaxation equations, there are  $n'$  values of  $\tau_i$  and  $D_i$ , and from these the dispersion curve is calculated using

$$\left(\frac{W}{W_0}\right)^2 = 1 + \sum_{i=1}^{i=n'} \frac{D_i(\omega\tau_i)^2}{1 + (\omega\tau_i)^2}, \quad (12)$$

where  $W$  is the velocity of sound (angular frequency  $\omega$ ), the subscript 0 referring to zero frequency. Usually one relaxation constant is very much larger than the rest and so the dispersion is governed by only one relaxation time  $\tau$ . This is single dispersion when all the vibrational specific heat relaxes together. Single dispersion curves have been fitted to most experimental results, and in this case there is a simple relation between the true relaxation time  $\beta$  and the effective one,

$$\beta = \tau(C_0/C_\infty). \quad (13)$$

$C_\infty$  is the specific heat at high frequencies above the dispersion zone; at the inflection point of a single dispersion curve,  $\tau\omega = 1$ . Corresponding to eqn. (12), the absorption curve is given by

$$\alpha\lambda = \pi \left(\frac{W_0}{W}\right)^2 \sum_{i=1}^{i=n'} \frac{D_i\omega\tau_i}{1 + (\omega\tau_i)^2}, \quad (14)$$

where  $\alpha\lambda$  is the amplitude absorption coefficient per wavelength  $\lambda$ .

The calculations give relaxation times which can be compared directly with experiment, and these relaxation times can be identified with certain rate-controlling transitions. All the calculations were carried out on the Oxford University Ferranti computer Mercury, using a programme based upon the one written by Schofield.<sup>55</sup>

## RESULTS OF THE CALCULATIONS

### METHANES

The results for  $\text{CH}_4$  and  $\text{CD}_4$  are set out in table 3 and compared with experiment. A wide temperature range is covered and in all cases single dispersion is predicted in agreement with experiment; the rate-determining step is the deactivation of the lowest mode for which the probabilities and values of  $\alpha^*$  are given. For  $\text{CH}_4$  at 298°K, the value of  $\alpha^*$  is a little larger than that calculated by Tanczos ( $\alpha^* = 4.82 \text{ \AA}^{-1}$ ). This is because he used method A fitting<sup>4</sup> and a different value of  $r_0$ . The predicted magnitudes of the relaxation times are in good agreement with experiment. The calculated temperature dependence is greater than that found by Eucken and Aybar,<sup>31</sup> but less than that measured by Cottrell and Matheson.<sup>32</sup> The relaxation time of  $\text{CD}_4$  has been measured at two temperatures by Cottrell and Matheson.<sup>32</sup> They found the relaxation time to be twice as long as their result for  $\text{CH}_4$  whereas the theory predicts it should be half as long. This is in spite of the fact that the vibrational amplitude for the lowest mode  $\nu_4$  is twice as large for  $\text{CH}_4$  (table 1), but this is outweighed by  $\Delta E$  being  $310 \text{ cm}^{-1}$  larger for the simple deactivation of the lowest mode of  $\text{CH}_4$ . However, the theory does predict the correct temperature dependence for  $\text{CD}_4$ .

Cottrell, Hunter and Read<sup>33</sup> reported the measurement of the relaxation time of the  $\nu_3$  mode of  $\text{CH}_4$ . They obtained a value of  $100 \mu\text{sec}$  using two methods, one being the spectrophone. In order to compare this with the theory, the heat-

bath relaxation times have been calculated for CH<sub>4</sub>, and are also given in table 3. The four relaxation times ( $\beta_1$ - $\beta_4$ ) are given in ascending order of magnitude. They can be related to the different modes by inspection of the rates of the various processes. Thus the largest relaxation time  $\beta_4$  is associated with the relaxation of the lowest mode, because it very nearly equals the reciprocal of  $k^{1-0}(v_4)$ . It is also close to the ultrasonic relaxation time for the lowest mode. The relaxation time for  $v_3$  is  $\beta_3$  and is associated with the transition  $P_{0-1}^{2-0}(v_3, v_2)$ .  $v_2$  exchanges energy rapidly with  $v_4$  and has the shortest relaxation time  $\beta_1$ . The relaxation time  $\beta_2$  is associated with  $v_1$ , the important transition for this mode being  $P_{0-1}^{1-0}(v_1, v_3)$ .

TABLE 3.—CALCULATED AND EXPERIMENTAL RELAXATION TIMES OF THE METHANES

ULTRASONIC RELAXATION TIMES						
	$T$ (°K)	$Z$ (nsec <sup>-1</sup> )	$\alpha^*$ (Å <sup>-1</sup> )	$P^{1-0}(v_4) \times 10^4$	$\beta$ (μsec)	
					calc.	expt.
CH <sub>4</sub>	298	9.70	5.22	0.873	1.38	2.03 (a)
	348	8.98	5.20	1.43	0.932	1.10 (a)
	382	8.57	5.18	1.95	0.731	.84 (b)
	475	7.68	5.15	4.05	0.409	.66 (b)
	574	6.99	5.13	7.76	0.246	.58 (b)
	626	6.69	5.12	10.5	0.196	.49 (b)
CD <sub>4</sub>	298	8.68	5.24	2.07	0.656	3.90 (a)
	348	8.03	5.22	3.34	0.446	2.50 (a)

(a) Cottrell and Matheson; <sup>32</sup> (b) Eucken and Aybar.<sup>31</sup>

#### HEAT-BATH RELAXATION TIMES FOR CH<sub>4</sub>

relaxation times (μsec)	$T = 290^\circ\text{K}$ associated with mode	$Z = 9.84 \text{ nsec}^{-1}$	process
$\beta_1 = 0.00149$	$v_2$	$P_{0-1}^{1-0}(v_2, v_4) = 1.86 \times 10^{-2}$	
$\beta_2 = 0.00268$	$v_1$	$P_{0-1}^{2-0}(v_3, v_2) = 1.26 \times 10^{-3}$	
$\beta_3 = 0.0564$	$v_3$	$P_{0-1}^{1-0}(v_1, v_3) = 7.84 \times 10^{-3}$	
$\beta_4 = 1.484$	$v_4$	$P^{1-0}(v_4) = 8.02 \times 10^{-5}$	

Since Cottrell *et al.*<sup>33</sup> measure the time lag between the input of light and its emergence as translational energy of the molecules, the slowest relaxation time  $\beta_4$  is the most important, because  $v_3$  relaxes via the lowest mode using transitions which involve little exchange of energy between vibration and translation. Thus they appear to have overestimated the relaxation time by a factor of sixty.\* The spectrophone will only give fresh information about the relaxation of an upper mode if its heat-bath relaxation time is longer than those of the lower modes through which it relaxes, or if it exchanges a significant amount of energy direct with translation.

#### ETHYLENES

Holmes and Tempest<sup>39</sup> measured the molecular absorption in C<sub>2</sub>H<sub>4</sub> and obtained at 298°K a peak which is about 4 % lower than the one expected for a single relaxation time. They interpreted this as being due to double dispersion. The calculated effective relaxation times associated with the three largest relaxation

\* In a private communication Prof. Cottrell has stated that his latest spectrophone experiments show that the original result <sup>33</sup> is far too long.



constants are given in table 4. One relaxation time governs 97 % of the absorption or dispersion, the remaining 3 % being associated with two much shorter relaxation times. This would fit the experimental results, but differs from the interpretation of Holmes and Tempest who postulated two relaxation times of similar magnitude.

TABLE 4.—CALCULATED AND EXPERIMENTAL RELAXATION TIMES  
OF THE ETHYLENES

	$T(^{\circ}\text{K})$	$Z$ (nsec <sup>-1</sup> )	$\alpha^*$ (Å <sup>-1</sup> )	$P^{1-0}(v_{10})$ $\times 10^4$	calc.	$\beta$ ( $\mu\text{sec}$ )	expt.	
$\text{C}_2\text{H}_4$	263	9.89	4.74	1.61	1.35	.287 (a)		
	298	9.29	4.72	2.46	1.01	.226 (a)	.39 (b)	.26 (c)
	353	8.54	4.69	4.43	.670	.183 (a)		
	573	6.70	4.62	24.7	.204		.126 (b)	
$\text{C}_2\text{D}_4$	298	8.69	4.76	15.1	.211			.14 (c)

(a) Holmes and Tempest ; <sup>39</sup> (b) Corran, Lambert, Salter and Warburton ; <sup>38</sup> (c) Hudson, McCoubrey and Ubbelohde.<sup>48</sup>

EFFECTIVE RELAXATION TIMES AND CONSTANTS FOR  $\text{C}_2\text{H}_4$

$T = 298^{\circ}\text{K}$		$T = 353^{\circ}\text{K}$	
$\tau_i$ ( $\mu\text{sec}$ )	$D_i$	$\tau_i$ ( $\mu\text{sec}$ )	$D_i$
.726	$7.27 \times 10^{-2}$	.418	$9.97 \times 10^{-2}$
.018	$9.4 \times 10^{-4}$	.037	$1.7 \times 10^{-3}$
.039	$8.1 \times 10^{-4}$	.016	$1.57 \times 10^{-3}$
$\Sigma D_i = 7.50 \times 10^{-2}$		$\Sigma D_i = 1.040 \times 10^{-1}$	

As the temperature increases, the calculated percentage of the absorption associated with the major relaxation time decreases, in agreement with experiment. The small fraction of the absorption associated with the two minor relaxation times will be found above  $10 \text{ Mc sec}^{-1} \text{ atm}^{-1}$ , where it may be obscured by the rotational and classical absorption. Excess absorption has been detected for  $\text{C}_2\text{H}_4$  in this region, but was attributed to experimental error.<sup>30</sup> The slight double dispersion predicted for  $\text{C}_2\text{H}_4$  is due to the exchange of energy between the closely spaced upper modes being very much *faster* than the simple deactivation of the lowest mode.<sup>49</sup> The opposite is true for previous cases of double dispersion, e.g.,  $\text{CH}_2\text{Cl}_2$ .<sup>2</sup> With  $\text{C}_2\text{H}_4$  the amount of double dispersion is barely detectable by velocity measurements and for comparison with other experimental results it can be treated as single dispersion.

Hudson, McCoubrey and Ubbelohde<sup>48</sup> calculated that for  $\text{C}_2\text{D}_4$  the probability of exchange between the two lowest modes was only three times greater than the probability for the simple deactivation of the lowest mode, and they suggested that the complex exchange might not be fast enough for single dispersion. In these calculations the ratio of the rates is found to be ten not three, and single dispersion is predicted for  $\text{C}_2\text{D}_4$  with the largest relaxation constant accounting for 98 % of the dispersion. The measurements of Hudson *et al.* only cover half the dispersion zone and are fitted to a single dispersion curve. With both  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$  the rate-determining step for vibrational relaxation is the deactivation of the lowest mode ( $v_{10}$ ). Details of this transition together with the calculated and experimental relaxation times are given in table 4.

The predicted relaxation time for  $\text{C}_2\text{H}_4$  is 3.4 times too long at room temperature, and the temperature dependence is 50 % steeper than that found experimentally; both of these disagreements could be due to  $\alpha^*$  being too small. It is calculated that the relaxation time of  $\text{C}_2\text{D}_4$  should be 4.75 times shorter than that of  $\text{C}_2\text{H}_4$ .



This agrees with the estimate of Hudson *et al.* of between 3.5 and 7 times shorter. Experimentally they found it was only twice as short. If  $\alpha^*$  was larger, this would reduce the calculated ratio a little, because the values of the transition probabilities relative to each other are slightly dependent upon the intermolecular potential.

#### ACETYLENES

The results of the calculations for  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{D}_2$  at two temperatures are presented in table 5 and compared with the experimental results given above. Single dispersion is indicated in all cases. Dickens and Ripamonti<sup>3</sup> performed a similar calculation for  $\text{C}_2\text{H}_2$  at 298°K only, using the set I of force constants. They obtained a relaxation time half that reported here because they used a steric factor of  $\frac{2}{3}$  following Tanczos.<sup>2</sup> With the set I of force constants the relaxation times are very close to the measured values, though their temperature dependence is steeper.

TABLE 5.—CALCULATED AND EXPERIMENTAL RELAXATION TIMES  
OF THE ACETYLENES

	$T(^{\circ}\text{K})$	$Z(\text{nsec}^{-1})$	$\alpha^*(\text{\AA}^{-1})$	$P^{1-0}(\nu_4) \times 10^3$	$\alpha^*(\text{\AA}^{-1})$	$P^{1-0}(\nu_5) \times 10^3$	$\beta(\mu\text{sec})$ calc.	$\beta(\mu\text{sec})$ expt.
set I of force constants								
$\text{C}_2\text{H}_2$	298	9.55	4.77	1.96	4.74	.638	.0742	.0820
	336	8.99	4.75	2.73	4.72	.932	.0579	.0790
$\text{C}_2\text{D}_2$	298	9.20	4.79	2.61	4.78	3.06	.0419	.0719
	336	8.66	4.77	3.54	4.76	4.20	.0336	.0725
set II of force constants								
$\text{C}_2\text{H}_2$	298	7.94	5.37	7.61	5.34	2.90	.0224	.0820
	336	7.48	5.35	9.76	5.32	3.86	.0190	.0790
$\text{C}_2\text{D}_2$	298	7.65	5.40	9.07	5.39	11.08	.0142	.0719
	336	7.21	5.38	11.36	5.37	14.02	.0124	.0725

Inspection of the transition probabilities for  $\text{C}_2\text{D}_2$  shows that the simple deactivation of the lowest mode  $\nu_4$  is *slower* than that of the next mode up ( $\nu_5$ ). This is because the modes have nearly equal frequencies and the vibrational factor (represented by  $\overline{A^2}$  in table 1) is larger for  $\nu_5$ . With  $\text{C}_2\text{H}_2$ ,  $\nu_5$  also has the larger vibrational factor but this is outweighed by  $\nu_4$  having a much lower frequency than  $\nu_5$ . Thus  $\text{C}_2\text{D}_2$  is an exception to the generally accepted postulate that, with single dispersion, vibrational relaxation occurs via the lowest mode. The calculated ratio of the relaxation times for  $\text{C}_2\text{D}_2$  and  $\text{C}_2\text{H}_2$  is 1 : 1.75 whereas the experimental result is 1 : 1.15.

Use of the set II force constants gives values of  $\alpha^*$  which are  $0.5 \text{ \AA}^{-1}$  larger. This decreases the calculated relaxation times by a factor of three and predicts a less steep temperature dependence. The calculated ratio of the relaxation times for  $\text{C}_2\text{D}_2$  and  $\text{C}_2\text{H}_2$  is 1 : 1.55.

#### METHYL HALIDES

Methyl halides are similar to the ethylenes in that a small yet significant proportion of the absorption or dispersion is governed by a relaxation time which is much shorter than the major one. With  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$  at room temperature this proportion is calculated to be about 4 %, while for  $\text{CH}_3\text{Cl}$  and  $\text{CD}_3\text{Cl}$  the figures are 5 % and 3 % respectively. For both fluorides it is only around 1 %. Again the proportion increases with temperature, e.g., for  $\text{CH}_3\text{Cl}$  at 475°K it is 10 %, but at this temperature the two relaxation times have magnitudes differing only

TABLE 6.—CALCULATED AND EXPERIMENTAL RELAXATION TIMES OF THE METHYL HALIDES

	$T(^{\circ}\text{K})$	$Z$ (msec $^{-1}$ )	$\alpha^*$ (Å $^{-1}$ )	$P^{1-0}(v_2) \times 10^5$	$\alpha^*$ (Å $^{-1}$ )	$P^{1-0}(v_2) \times 10^5$	calc.	$\beta$ ( $\mu$ sec)	expt.
CH <sub>3</sub> F	298	6.56	5.44	.721	5.42	1.20	19.3	2.66 (a)	
	373	5.86	5.40	1.58	5.38	2.85	9.86	3.2 (b)	
CD <sub>3</sub> F	298	6.28	5.44	2.42	5.46	10.2	2.88	2.28 (a)	
	373	5.62	5.40	5.37	5.42	21.5	1.64	—	
CH <sub>3</sub> Cl	294	6.05	5.42	53.3	5.36	8.12	.495	.220 (c)	.204 (d)
	375	5.35	5.38	75.2	5.32	14.5	.469	.218 (c)	.196 (d)
	475	4.76	5.33	118.6	5.28	28.8	.391	.215 (c)	.230 (d)
	294	5.87	5.42	86.8	5.40	98.4	.230	.596 (a)	
I. CH <sub>3</sub> Br	291	5.16	4.94	3.33	4.86	.0171	10.2	.075 (d)	.072 (e)
	373	4.55	4.90	7.37	4.83	.0599	6.99	.101 (d)	.107 (e)
	470	4.06	4.86	16.5	4.79	.205	4.64	.110 (d)	.135 (e)
	291	5.08	4.94	6.60	4.91	.991	7.96	.142 (f)	
II. CH <sub>3</sub> Br	291	4.45	5.45	81.3	5.38	.739	.462	.075 (d)	.072 (e)
	373	3.93	5.41	108.0	5.34	1.49	.510	.101 (d)	.107 (e)
	470	3.50	5.37	164.0	5.30	3.31	.485	.110 (d)	.135 (e)
	291	4.38	5.46	154.3	5.43	29.4	.343	.142 (f)	

(a) Lambert, Parks-Smith and Stretton;<sup>36</sup> (b) Fogg, Hanks and Lambert;<sup>34</sup> (c) Edwards;<sup>35</sup> (d) Amme and Legvold;<sup>37</sup> (e) Corran, Lambert, Salter and Warburton;<sup>38</sup> (f) Lambert and Salter.<sup>9</sup>

by a factor of three. Unfortunately, accurate absorption measurements are not yet available to test these predictions, and so the methyl halides are treated as showing single dispersion, the results of the calculations on six methyl halides being presented in table 6.

For all the methyl halides except  $\text{CD}_3\text{F}$ ,  $\nu_3$  is the mode with the lowest frequency. This mode is essentially a stretching of the carbon-halogen bond and involves only a slight movement of the lighter hydrogen or deuterium atoms. However, the next mode  $\nu_6$  does involve extensive movement of these atoms and so it has a much larger vibrational factor compared to  $\nu_3$ . For two of the halides,  $\text{CH}_3\text{F}$  and  $\text{CD}_3\text{Cl}$ , this outweighs the effect of  $\nu_3$  having the lower frequency and thus, similar to  $\text{C}_2\text{D}_2$ , the quickest route for the relaxation of the vibrational energy is via the second lowest mode.

The intermolecular force constants are most reliable for methyl chloride, and the relaxation times calculated for  $\text{CH}_3\text{Cl}$  with the Monchick and Mason potential are in good agreement with the experimental results. A slight decrease of the relaxation time with temperature is predicted, whereas the experimental results indicate that the relaxation time is almost independent of temperature. The theoretical relaxation time for  $\text{CD}_3\text{Cl}$  is half that predicted for  $\text{CH}_3\text{Cl}$  at room temperature, but the measured values are the other way around, similar to the methanes.

For  $\text{CH}_3\text{Br}$ , using the Monchick and Mason (set I) force constants, the calculated relaxation times are too long by about two orders of magnitude, and the predicted temperature dependence is wrong. Since Monchick and Mason report that their constants for methyl bromide are based on "scanty or insufficient data", it was decided to alter the force constants arbitrarily and recalculate.  $r_0$  and  $\delta^*$  are brought into line with the values for methyl chloride while  $\epsilon/k$  is increased in view of the larger dispersion forces to be expected with the bromine atom (table 2). With these set II force constants, the predicted relaxation times are 25 times smaller than before, and only 4.5 times larger than the experimental results. The decrease by a factor of 25 has been achieved in two ways. First,  $\alpha^*$  has increased from 4.94 to 5.45  $\text{\AA}^{-1}$ , which increases the probabilities 5 times. Secondly, deepening the well by 600°K produces another factor of 5. Both changes decrease the temperature dependence, particularly the latter. The predicted temperature dependence using the set II force constants is almost correct, with the relaxation time increasing slightly with temperature. It is predicted that, at room temperature,  $\text{CD}_3\text{Br}$  should have a relaxation time shorter than that of  $\text{CH}_3\text{Br}$  by about 30 %. The only available result for  $\text{CD}_3\text{Br}$  is that of Lambert and Salter,<sup>9</sup> who made measurements on a sample containing 21 %  $\text{CHD}_2\text{Br}$ . They found the relaxation time to be double that of  $\text{CH}_3\text{Br}$ .

Only Lennard-Jones parameters are available for methyl fluoride, and for  $\text{CH}_3\text{F}$  the calculated relaxation times are too long and their temperature dependence is the wrong way round, although the experimental result for the upper temperature is doubtful. Both discrepancies could be due to the well depth being too small. For both  $\text{CH}_3\text{F}$  and  $\text{CD}_3\text{F}$  the most rapid way for the vibrational energy to relax is via  $\nu_6$  even though this is the second lowest mode of  $\text{CH}_3\text{F}$ . Thus in comparing their relaxation times, one is comparing the deactivation rates of modes with frequencies of 1200 and 912  $\text{cm}^{-1}$ , and this is why it is predicted that  $\text{CD}_3\text{F}$  is 6 times faster. However, the experimental values for the fluorides are about equal.

#### SULPHUR HEXAFLUORIDE

Single dispersion is predicted with a relaxation time of 205  $\mu\text{sec}$  at room temperature. Experimentally<sup>6</sup> the single dispersion relaxation time is 0.7  $\mu\text{sec}$ . The

rate-determining step is the deactivation of the lowest mode with a probability of  $2.17 \times 10^{-6}$  and  $\alpha^* = 3.59 \text{ \AA}^{-1}$ . This value of  $\alpha^*$  is very low and for agreement between theory and experiment a value of about  $5.5 \text{ \AA}^{-1}$  is required, but then the corresponding value of  $r_0$  would bear no relation to that obtained from viscosity measurements.

## DISCUSSION

Single dispersion is correctly predicted for all the molecules considered in this paper, though with the ethylenes and methyl halides rapid exchange of energy between the upper modes leads to absorption peaks slightly lower than expected for a single relaxation time. Further experimental work is required to investigate this effect. Quantitative prediction of the relaxation times for the non-polar hydrocarbons is good, with the calculated values being within a factor of 5 of the experimental results. For the polar methyl halides agreement is not so good, but neither are the force constants so reliable. Generally, the predicted relaxation times are too long and their temperature dependence is a little too steep.

Where there is good agreement between the measured and calculated relaxation times,  $\alpha^*$  has a value of about  $5.5 \text{ \AA}^{-1}$ . This has also been found for diatomic<sup>3, 25</sup> and triatomic molecules.<sup>4, 55</sup> There are only two results available for non-hydrogen containing polyatomic molecules. Tanczos<sup>2</sup> calculated a value of  $4.15 \text{ \AA}^{-1}$  for  $\alpha^*$  with  $\text{CCl}_4$ , but the predicted relaxation time was ten times too long. Similarly here a value of  $3.6 \text{ \AA}^{-1}$  calculated for  $\text{SF}_6$  results in too long a relaxation time. In both cases a value of about  $5.5 \text{ \AA}^{-1}$  for  $\alpha^*$  would give agreement with the experimental relaxation times.

Thus it appears that the effective value of  $\alpha^*$  is almost independent of the type of molecule, and that the repulsion forces encountered at collision energies necessary for vibrational energy transfer are roughly the same for all molecules. This was first suggested by Herzfeld and Litovitz for di- and tri-atomic molecules, and from the calculations presented here it appears to be a general result. Thus molecules cannot be divided into "hard" and "soft", a suggestion that has been made to explain the Lambert-Salter plot.<sup>9</sup> There is independent evidence for the exponential repulsion parameter having a value around  $5.5 \text{ \AA}^{-1}$ . Salem<sup>51</sup> has calculated the repulsion forces between two colliding helium atoms, and his results fit an exponential curve with  $\alpha = 4.8 \text{ \AA}^{-1}$ , thus confirming earlier reported calculations.<sup>22</sup>

The repulsion parameter can be deduced from measurements of the temperature dependence of the relaxation time. This is straightforward for diatomic molecules,<sup>3</sup> but doubtful for polyatomic ones. First, the relaxation time has to be related to some definite transition. Holmes and Tempest<sup>39</sup> assumed that the temperature dependence of the reciprocal relaxation time for  $\text{C}_2\text{H}_4$  was directly proportional to the transition rate for the simple deactivation of the lowest mode,  $k^{1-0}(\nu_{10})$ . This is incorrect; between 263 and 353°K the calculations show that  $(1/\beta)$  increases 2.02 times while  $k^{1-0}(\nu_{10})$  increases by a factor of 2.67. Thus the temperature dependence was underestimated and hence  $\alpha^*$  overestimated. Using these calculations to give the relation between  $(1/\beta)$  and  $k^{1-0}(\nu_{10})$ , one obtains  $\alpha^* = 6.1 \text{ \AA}^{-1}$  from the results of Holmes and Tempest, as against their value of  $6.72 \text{ \AA}^{-1}$ . Another common approach is to assume simple series activation of the upper modes via the lowest.<sup>6</sup> For this to be valid the energy exchange between the upper modes must be rapid compared with the deactivation of the lowest mode, and there must be no similar processes in parallel with this, as with, e.g.,  $\text{C}_2\text{D}_2$ , where both modes exchange energy directly with translation at comparable rates (table 5).

In eqn. (1) the term  $\exp[-\phi_0/kT]$  represents the implicit treatment of the attractive forces<sup>52</sup> and must be allowed for when obtaining a value of  $\alpha^*$  from temperature dependence measurements. Therefore the value obtained for the repulsion parameter is dependent to some extent on the value assumed for the well depth of the potential, e.g., for  $C_2H_4$  a change in  $(\epsilon/k)$  of  $100^\circ K$  alters the value of  $\alpha^*$  by about  $0.6 \text{ \AA}^{-1}$  and, as was shown with the methyl bromides, the attractive forces considerably influence the temperature dependence.

Values of  $\alpha^*$  for polyatomic molecules obtained from temperature dependence measurements can be much larger than  $5.5 \text{ \AA}^{-1}$ , e.g.,  $CF_4$  and cyclopropane.<sup>50</sup> Further work is required to determine whether these are indeed correct values for the repulsion forces or due to incorrect assumptions made either in the theory or, as discussed above, in interpreting the experimental results; in particular, since reliable temperature dependence measurements are few and the results obtained by different workers for one substance often disagree, more experimental measurements of both absorption and dispersion over as wide a range of  $T^{-1}$  as possible are needed to obtain precise values with which to test the theory.

If  $\alpha^*$  is approximately the same for all molecules, then with due allowance being made for the differing molecular weights and vibration frequencies, one would expect that the relaxation times of diatomic molecules would be given as a function of temperature by a reduced formula. Such has been found empirically by Millikan and White<sup>47</sup> for these molecules and their mixtures with inert gases. For polyatomic molecules at one temperature there is a correlation between the frequency of the lowest mode ( $\nu_{\min}$ ) and  $1/P^{1-0}(\nu_{\min})$ . Lambert and Salter<sup>9</sup> found that there were two broad groups, those with two or more hydrogen atoms (class I) which exchange energy more rapidly than those with less than two (class II). Comparison between the two classes at similar frequencies shows that those in class I have lower masses and bigger vibrational factors, or else they have large dipole moments, all of which enhance the probability of energy exchange. Most of the calculations so far have been done for class I molecules, more are now required for class II.

The predicted ratios of the relaxation times for hydrogenated and deuterated molecules are generally not in agreement with the experimental results. Defining  $Q$  as  $\beta$  for the hydrogenated molecule divided by  $\beta$  for the corresponding deuterated one, the experimental and calculated values of  $Q$  are compared in table 7, and except

TABLE 7.—CALCULATED AND EXPERIMENTAL VALUES  
OF  $Q$  AT ROOM TEMPERATURE

$X \equiv H \text{ OR } D$		
	$Q_{\text{calc.}}$	$Q_{\text{expt.}}$
$CX_4$	2.1	.5
$C_2X_4$	4.8	1.9
$C_2X_2$	1.75	1.15
$CX_3F$	6.7	1.2
$CX_3Cl$	2.1	.37
$CX_3Br$	1.3	.50

for the acetylenes, the calculations overestimate  $Q$  by a factor of 3-5. This effect was pointed out for the methanes by Cottrell and Matheson<sup>32</sup> who suggested that, since the moments of inertia are very small, the peripheral velocities are correspondingly high and this aids vibrational energy exchange and would favour  $CH_4$  which has a velocity  $\sqrt{2}$  times greater than that of  $CD_4$ . The results presented here support the view that rotation is involved because the ethylenes and methyl

halides all have one axis about which the moment of inertia is close to that of the methanes, and in these cases the predicted values of  $Q$  are incorrect. Further evidence is provided by the acetylenes. Because the comparatively heavy carbon atoms are directly involved in the rotations, the peripheral velocities of  $C_2H_2$  and  $C_2D_2$  are much slower and relatively closer compared with the other pairs in table 7, and so the calculated and experimental values of  $Q$  are in better agreement. The suggestion<sup>32</sup> that rotation might explain the more rapid exchange of energy shown by Lambert and Salter's class I is unlikely because class I contains some molecules with comparatively large moments of inertia, e.g.,  $CH_2Cl_2$  and two cyclic compounds  $C_3H_6$  and  $C_2H_4O$ .

Cottrell *et al.*<sup>53, 54</sup> have extended their measurements on the methanes to other hydrides of groups 4 and 5, and have found that they can correctly predict the values of  $Q$  using a one-dimensional model for the interaction between a classical rotator and a vibrator. However, they have made no calculations of the actual relaxation times which the SSH theory is reasonably successful in doing. A full treatment of the interaction between a vibrator and rotator is needed. This would require abandoning the breathing sphere model and the assumption of an angular dependent intermolecular potential.

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