

*Approximate Potential Function for the Out-of-plane Vibrations of Ethylene, and of Aromatic Molecules such as Benzene and Naphthalene.*

By C. A. COULSON and S. SENENT.

[Reprint Order No. 51019.]

An approximate potential function is described for the out-of-plane vibrations of  $\pi$ -electron systems such as ethylene, benzene, naphthalene, and higher aromatic fused-ring hydrocarbon molecules. The advantage of this potential function, which can be tested and shown to give good results for ethylene, benzene, and certain vibrations of naphthalene, is that it requires only two force constants.

SATISFACTORY potential functions exist to describe the out-of-plane vibrations of simple  $\pi$ -electron molecules such as ethylene and benzene. These enable us to define the potential energy in terms of the perpendicular displacements  $z_r$  of the atoms from their mean plane provided that the  $z_r$  are supposed to be small. With relatively small molecules only a few force constants are required. But with large molecules there are so many force constants in a complete potential function that we have little hope of determining them all. It is of interest, therefore, to devise a simple potential function which will deal reasonably with simple molecules and can also be used, without further analysis, for large ones. The succeeding paper illustrates one of the ways in which such a potential function may be used; by its aid we have calculated the deformation and strain energy in the overcrowded molecule 3 : 4-5 : 6-dibenzophenanthrene: other similar applications are in progress and will be reported in due course. The potential function which we shall describe here involves only two force constants. But it would not be difficult to give it greater flexibility by allowing different values to the same force constant when it arises (see below) in a different molecular environment. The present discussion, however, will be given entirely in terms of just two such constants. A particular case of our potential function has already been used by Bell (*Trans. Faraday Soc.*, 1945, **41**, 292) in studying out-of-plane vibrations in benzene.

*Simplified Ethylene-type Potential.*—Let us consider first the ethylene-type system represented in Fig. 1, in which the valency angles are all assumed to be  $120^\circ$ . There are 6 atoms 1 . . . . . 6, and our object is to express the potential energy  $V$  as a function  $V(z_1 . . . . . z_6)$  of their normal displacements  $z_r$  from the equilibrium plane of the molecule. For simplicity let us suppose that all five bond lengths are identical ( $= a$ ). Later we shall remove this restriction. It is convenient to introduce  $M$  and  $M'$  (Fig. 1) which are the remaining vertices of the parallelograms shown. The lines 1- $M$  and 2- $M'$  bisect the angles 3-1-4 and 5-2-6 respectively. In equilibrium  $M$  and  $M'$  are in the plane of the whole molecule; but in the displaced configuration the displacements of  $M$  and  $M'$  are  $z_3 + z_4 - z_1$  and  $z_5 + z_6 - z_2$ .

Let us suppose that we are given the molecule in its displaced configuration, having non-zero  $z_r$ . And let us calculate how much energy is recovered when the molecule is brought back to its initial condition with all  $z_r = 0$ . This may be achieved in four stages:

(i) A uniform displacement,  $(z_1 + z_2)/2$ , brings the centre of the molecule to its correct position. No work is done since the shape of the molecule is unchanged.

(ii) A uniform rotation through an angle  $(z_1 - z_2)/a$  around the axis of symmetry perpendicular to the line 1-2 will bring atoms 1 and 2 into their correct positions. No work is done in this rigid-body rotation. The new co-ordinates of the four edge atoms are given by:

$$z'_3 = z_3 - \frac{3}{2}z_1 + \frac{1}{2}z_2, \text{ etc.}$$

(iii) Rotations around axes through atoms 1 and 2 will bring  $M$  and  $M'$  to their correct positions. The angle of twist around atom 1 will be  $(z'_3 + z'_4)/a$ , i.e.,  $(z_3 + z_4 + z_2 - 3z_1)/a$ . If we may suppose that the energies of these two deformations are additive, the energy recovered in this stage is

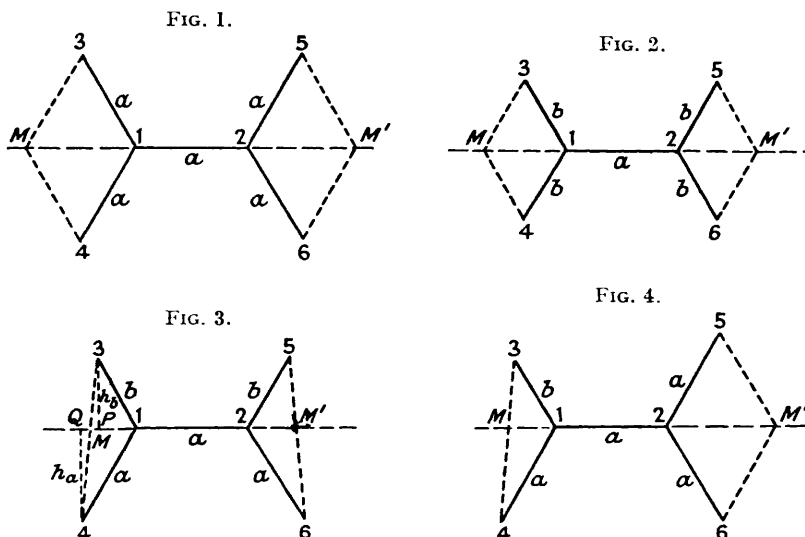
$$\frac{1}{2}k_1(z_2 + z_3 + z_4 - 3z_1)^2 + \frac{1}{2}k_1(z_1 + z_5 + z_6 - 3z_2)^2 \quad . \quad . \quad (1)$$

where  $k_1$  is some force constant yet to be determined. Strictly, we should add to (1) a cross-term proportional to  $(z_2 + z_3 + z_4 - 3z_1)(z_1 + z_5 + z_6 - 3z_2)$ , since otherwise the in-phase and the out-of-phase flapping frequencies of ethylene would be governed by the same force constant. We know that this is not so. But fortunately the difference is not great, and we shall find that this term may be omitted without serious loss of accuracy. In view of our intention to obtain the simplest worthwhile potential function, we shall neglect this cross-term completely, though it may be inserted quite easily if we wish to do so.

(iv) At the end of stage (iii) the displacements of the atoms 3, 4, 5, 6 are given by  $z_3'' = (z_3 - z_4)/2$ , etc. A torsion of the group 3-1-4 around the axis 1-2 by an amount  $2z_3''/a\sqrt{3}$  brings this end of the molecule into the required position. There is thus a total torsion in the bond 1-2 which amounts to  $2(z_3'' + z_6'')/a\sqrt{3}$ . An energy is recovered in the process, which is of the form

$$\frac{1}{2}k_2(z_3 - z_4 - z_5 + z_6)^2 \quad \dots \quad (2)$$

The total potential energy  $V(z_1 \dots z_6)$  is therefore the sum of the two expressions (1) and (2). We have already seen that (2) measures the torsion around the axis of the



molecule; but (1) is also recognised to have a simple physical interpretation as arising from the lack of planarity of the atoms around 1 and 2. This is because, for example,  $(z_2 + z_3 + z_4 - 3z_1)/3$  is precisely the distance by which atom 1 is separated from the plane containing atoms 2, 3, and 4. It is convenient to refer to (1) as the planarity terms and (2) as the torsion terms.

*More General Ethylene-type Potential.*—Formulæ (1) and (2) were obtained on the assumption that, as in Fig. 1, all the bond lengths were equal, with a value  $a$ . But it is not difficult to extend the analysis to cover the other cases with which we shall be concerned, represented by Figs. 2—4. Here certain of the “C-H type” bonds are supposed to have a different length  $b$ . The discussion, apart from the asymmetrical case in Fig. 3, is quite straightforward, and need not be reproduced in detail. In all cases the potential energy is the sum of planarity and torsion terms, though these are given by slightly more involved functions than in (1) and (2). They are:

$$\begin{aligned} \text{Planarity terms: Fig. 2, } & \frac{1}{2}k_1 \left\{ \frac{a}{b}z_3 + \frac{a}{b}z_4 + z_2 - \left(1 + \frac{2a}{b}\right)z_1 \right\}^2 \\ & + \frac{1}{2}k_1 \left\{ \frac{a}{b}z_5 + \frac{a}{b}z_6 + z_1 - \left(1 + \frac{2a}{b}\right)z_2 \right\}^2 \quad \dots \quad (3) \end{aligned}$$

$$\text{Fig. 3, } \frac{1}{2}k_1 \left\{ \frac{a}{b} z_3 + z_4 + z_2 - \left( 2 + \frac{a}{b} \right) z_1 \right\}^2 \\ + \frac{1}{2}k_1 \left\{ \frac{a}{b} z_5 + z_6 + z_1 - \left( 2 + \frac{a}{b} \right) z_2 \right\}^2 \quad \dots \quad (4)$$

$$\text{Fig. 4, } \frac{1}{2}k_1 \left\{ \frac{a}{b} z_3 + z_4 + z_2 - \left( 2 + \frac{a}{b} \right) z_1 \right\}^2 \\ + \frac{1}{2}k_1 \left\{ z_5 + z_6 + z_1 - 3z_2 \right\}^2 \quad \dots \quad (5)$$

$$\text{Torsion terms: Fig. 2, } \frac{1}{2}k_2 \left\{ z_3 - z_4 - z_5 + z_6 \right\}^2 \quad \dots \quad (6)$$

$$\text{Fig. 3, } \frac{1}{2}k_2 \left\{ \frac{a}{b} z_3 - z_4 - \frac{a}{b} z_5 + z_6 + \left( 1 - \frac{a}{b} \right) (z_1 - z_2) \right\}^2 \quad \dots \quad (7)$$

$$\text{Fig. 4, } \frac{1}{2}k_2 \left\{ \frac{a}{b} z_3 - z_4 - z_5 + z_6 + \left( 1 - \frac{a}{b} \right) z_1 \right\}^2 \quad \dots \quad (8)$$

The physical significance of these terms remains unchanged from what it was in the simpler cases (1) and (2). It should be noted that we have used the same force constants  $k_1$  and  $k_2$  in all the expressions (1)–(8). Strictly there should be four distinct  $k_1$  and four distinct  $k_2$ . It would be possible to introduce all these. But we shall see that a surprisingly good approximation is obtained by giving all the  $k_1$  constants the same value, and also all the  $k_2$  constants.

*Final Potential Function.*—We are now in a position to write down the complete potential function for any of the molecules which are covered by this type of analysis. This is the sum of a planarity term for any atom around which there are three other bonded atoms, and a torsion term for any bond each of whose ends are attached to two other atoms. Thus for benzene (Fig. 5) there are six planarity terms for the carbon atoms, and six torsion terms for the carbon-carbon bonds. The planarity terms are of the same form as the first half of (4), the torsion terms are as in (7) where  $a$  denotes the C-C distance and  $b$  the C-H distance. In ethylene we have the situation of Fig. 2. In naphthalene (Fig. 6) there are two planarity terms of type (1) corresponding to  $C_{(9)}$  and  $C_{(10)}$ ; eight planarity terms as in benzene, corresponding to  $C_{(1)} \dots C_{(8)}$ ; one torsion term (2) associated with  $C_{(9)}-C_{(10)}$ ; four torsion terms (8) associated with  $C_{(9)}-C_{(1)}$ ,  $C_{(9)}-C_{(8)}$ ,  $C_{(10)}-C_{(4)}$  and  $C_{(10)}-C_{(5)}$ ; and six torsion terms (7) associated with the remaining carbon-carbon bonds. The potential energy function for any other molecule can be written down equally easily.

The only bonds around which torsion occurs are C-C bonds. The appropriate force constant  $k_2$  would therefore be expected to vary with the degree of double-bond character, going from a very small value for near-single bonds to a maximum for the pure double bond of ethylene. In the aromatic molecules for which this analysis is chiefly intended, the variations in bond order are relatively small. This is the ground on which we justify a single value of  $k_2$ , except, of course, for ethylene where obviously a different and larger value will be needed.

The justification for a single planarity force constant  $k_1$  is less convincing. However, apart from highly condensed molecules such as ovalene, the number of internal carbon atoms all of whose neighbours are other carbon atoms, is quite small. Most of the carbon atoms are secondary ones.\* We might expect that there would be different  $k_1$  values for primary, secondary, and tertiary atoms. Once again, therefore, with the exception of ethylene, we shall not introduce a great error in the planarity contributions to the total potential by treating all the carbon atoms as secondary, with a common value of  $k_1$ .

\* The convention is adopted that a primary, secondary, or tertiary carbon atom is one which has one, two, or three adjacent carbon atoms within the  $\pi$ -electron framework of the molecule.

## 1816 Coulson and Senent: Approximate Potential Function for the

It is not difficult to relate our force constants to more conventional ones. A single example suffices. In benzene (Fig. 5) if we suppose that all the  $z_r = 0$  except  $z_1$ , our potential energy function takes the form

$$\frac{1}{2}k_1\left(\frac{a}{b}z_1\right)^2 + \frac{1}{2}k_2\left(\frac{a}{b}z_1\right)^2 = \frac{1}{2}kz_1^2$$

where  $k = (k_1 + k_2)a^2/b^2$ . This constant  $k$  governs the separate flapping of a single C-H bond. Other correlations follow similarly. An advantage of our potential function is that it takes account of certain interactions between the flapping of nearby bonds, and the buckling of the carbon framework, in a particularly simple physical fashion.

*Application to Ethylene.*—The out-of-plane vibrations of ethylene have been studied very fully (*e.g.*, by Bernard and Manneback, *Ann. Soc. sci. Bruxelles*, 1939, **59**, 113; Arnett and Crawford, *J. Chem. Phys.*, 1950, **18**, 118; Herzberg, "Molecular Spectra and Molecular Structure, Vol. II, Polyatomic Molecules," Van Nostrand, New York, 1954, especially pp. 150, 183, 189). As Sutherland and Dennison (*Proc. Roy. Soc.*, 1935, *A*, **148**, 250) have shown, the out-of-plane vibrations require three force constants, and fall into the symmetry classes  $A_{1u}$ ,  $B_{1u}$ , and  $B_{2g}$ . There is just one normal mode in each class. The  $A_{1u}$  mode is the internal torsion mode,  $B_{1u}$  represents flapping in phase, and  $B_{2g}$  flapping out of phase. The conventional numbering of these frequencies is  $\nu_4$ ,  $\nu_7$ , and  $\nu_8$  respectively. Table 1 shows some of the assignments that have been made by various authors. If we take

TABLE 1. Frequencies of out-of-plane vibrations in ethylene.

Symmetry	Label	Frequency (cm. <sup>-1</sup> )				Calc. frequency
		(a)	(b)	(c)	(d)	
$A_{1u}$	$\nu_4$	825	—	950	1027	1027
$B_{1u}$	$\nu_7$	949.2	949.2	949.2	950	889
$B_{2g}$	$\nu_8$	950	—	943	943	1021

(a) Gallaway and Barker, *J. Chem. Phys.*, 1942, **10**, 88. (b) Thorndike, Wells, and Wilson, *ibid.*, 1947, **15**, 157. (c) Rasmussen and Brattain, *ibid.*, p. 120. (d) Arnett and Crawford, *ibid.*, 1950, **18**, 118.

1.34 and 1.08 Å for the C=C and C-H bond lengths, we find that the frequency  $\nu_4$  determines a unique value  $k_2 = 0.157 \times 10^5$  dyne cm.<sup>-1</sup>. With only one remaining parameter we cannot satisfy both  $\nu_7$  and  $\nu_8$ . Taking the mean of the two values of  $k_1$  which would be required to give these two frequencies leads to a magnitude  $k_1 = 0.131 \times 10^5$  dyne cm.<sup>-1</sup>, and calculated frequencies as shown in the last column of the Table. It is gratifying that the complete neglect of the cross-term in the potential function referred to on p. 1814 leaps to an error nowhere greater than 8%.

*Application to Benzene.*—The potential function for benzene has been studied by many writers, *e.g.*, Wilson (*Phys. Rev.*, 1934, **45**, 706), Manneback (*Ann. Soc. sci. Bruxelles*, 1935, **55**, *B*, 129, 237), Lord and Andrews (*J. Phys. Chem.*, 1937, **41**, 149), Duchesne and Penney (*Bull. Soc. Roy. Sci. Liège*, 1939, **8**, 514), Bell (*Trans. Faraday Soc.*, 1945, **41**, 293), Bak (*Kgl. Danske Vid. Sels. Mat. Phys. Medd.*, 1945, **28**, No. 9), Miller and Crawford (*J. Chem. Phys.*, 1946, **14**, 282; 1949, **17**, 249), and Ingold and his collaborators (*J.*, 1936, 971). The last three of these are the most complete, but they require no less than eight force constants to deal with the out-of-plane vibrations. These vibrations have total symmetry  $A_{2u} + 2B_{2g} + 2E_{2u} + 2E_{2g}$ . Ingold and his collaborators (*loc. cit.*) assign these to the frequencies  $\nu_{11}$ ,  $\nu_4$ ,  $\nu_5$ ,  $\nu_{16}$ ,  $\nu_{17}$ , and  $\nu_{10}$  as in Table 2.

We have used the potential function, with only two parameters, as described earlier. The bond lengths were taken to be 1.40 Å (C-C) and 1.08 Å (C-H). We used the two frequencies  $\nu_{10}$  and  $\nu_{11}$  to determine the appropriate values of  $k_1$  and  $k_2$ , and found them to be  $k_1 = 0.1474 \times 10^5$  dyne cm.<sup>-1</sup>,  $k_2 = 0.0553 \times 10^5$  dyne cm.<sup>-1</sup>. The remaining four frequencies shown in the last column of Table 2 followed from these values of  $k_1$  and  $k_2$ . It is most gratifying to see that the accuracy thus obtained is of the same order as in ethylene.

Indeed, if we had chosen  $k_1$  and  $k_2$  to give the best all-round agreement, instead of the correct values of  $\nu_{10}$  and  $\nu_{11}$ , we could doubtless have done better than in Table 2.

TABLE 2. Frequencies ( $\text{cm}^{-1}$ ) for benzene vibrations.

Symmetry	Label	Wave-number				
		(a)	(b)	(c)	(d)	(e)
$A_{2u}$	$\nu_{11}$	671	671	668	671	(671)
$B_{2g}$	$\nu_4$	—	664	638	685	638
	$\nu_5$	1000	1048	1060	993	1110
$E_{2u}$	$\nu_{16}$	—	406	403	404	413
	$\nu_{17}$	890	845	873	985	1049
$E_{2g}$	$\nu_{10}$	849	950	858	850	(850)

(a) Angus, Bailey, Hale, Ingold, Leckie, Raisin, Thompson, and Wilson, *J.*, 1936, 971. (b) Langseth and Lord, *Kgl. danske, Vid. Sels. Mat.-fys. Medd.*, 1938, **16**, No. 6. (c) Bak, *ibid.*, 1945, **28**, No. 9. (d) Crawford and Miller, *J. Chem Phys.*, 1946, **14**, 282. (e) Calc. in present paper. Figures in parentheses were used to fix parameters  $k_1$  and  $k_2$ .

A word needs to be said concerning our use of the C-C bond distance 1.40 Å. We have chosen this value rather than the recent X-ray value of 1.375 Å (Cox and Smith, *Nature*, 1954, **173**, 75) because it has recently been confirmed in accurate high-dispersion Raman studies by Stoicheff (*Canad. J. Phys.*, 1954, **32**, 339). A satisfactory decision between these two divergent values does not seem possible at present. We have preferred the

FIG. 5. Numbering of atoms in benzene.

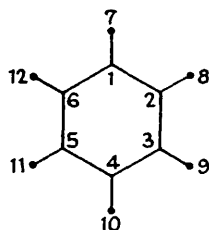
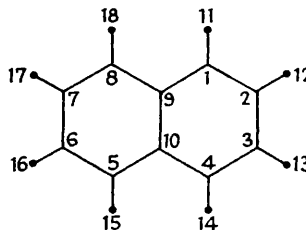


FIG. 6. Numbering of atoms in naphthalene.



Raman value both because it relates to the molecule in the gas phase and because it is essentially spectroscopic. Our comparisons with experiment must also be wholly spectroscopic.

Before leaving benzene, it is interesting to compare our values of  $k_1$  and  $k_2$  and the associated force constant  $k$  (p. 1816) for displacement of a single H atom, with the value calculated in the detailed work of Miller and Crawford (*J. Chem. Phys.*, 1946, **14**, 282) where this particular constant is called  $A$ . We find a value  $k = 0.340 \times 10^5$  dyne  $\text{cm}^{-1}$ , whereas Miller and Crawford obtain a value  $A = 0.378 \times 10^5$  dyne  $\text{cm}^{-1}$ . The agreement is satisfactory. It is also satisfactory that the torsion force constant  $k_2$  for benzene is distinctly smaller than that for ethylene.

*Application to Naphthalene.*—The complete potential function for naphthalene (Fig. 6) is not known, nor are complete and final assignments made for all the fundamental frequencies. Our approach to this molecule must therefore be different from that for ethylene and benzene where all the frequencies were known and an agreed assignment exists. There are 15 out-of-plane modes of vibration belonging to the representation  $4A_u + 4B_{1u} + 3B_{2g} + 4B_{3g}$  of the symmetry group  $D_{2h}$ . The  $A_u$  type are inactive in both infra-red and Raman spectra,  $B_{1u}$  are active in both,  $B_{2g}$  and  $B_{3g}$  are active in Raman only. The assignments of these fifteen frequencies to the four symmetry classes have varied from one writer to another (cf., e.g., Pimentel and McClellan, *J. Chem. Phys.*, 1952, **20**, 270; Manneback, *J. Chim. phys.*, 1949, **46**, 49; Barrow and McClellan, *J. Amer. Chem. Soc.*, 1951, **73**, 573) but the most satisfactory solution appears to be that of McClellan and Pimentel (in the press; we acknowledge the kindness of the authors in providing us with an advance copy of the manuscript) who studied both  $C_{10}H_8$  and  $C_{10}D_8$ , and attempted a full

allocation of all the 48 fundamental frequencies of these two molecules. In this allocation only the  $B_{1u}$  group seems completely reliable: the difficulties associated with a search for the four inactive  $A_u$  frequencies are obviously great. For that reason the comparison with experiment shown in Table 3 must be treated with some reserve, apart from the  $B_{1u}$  group of frequencies.

In making our calculations we have used the potential function described on p. 1815, with only two force constants. We have taken the bond lengths to be the same in naphthalene as in benzene (Coulson, Daudel, and Robertson, *Proc. Roy. Soc.*, 1951, *A*, 207, 306) and have therefore adopted the numerical values of  $k_1$  and  $k_2$  previously obtained from benzene. It is worth mention, therefore, that no empirical quantities whatever for naphthalene are used in the calculations of the last column in this Table. Without doubt we could have improved the agreement for the important  $B_{1u}$  vibrations, while still adhering to only two distinct force constants, if we had been prepared to modify the benzene values of  $k_1$  and  $k_2$ . Further, by using two separate  $k_1$  and  $k_2$  for the secondary and the tertiary carbon atoms, we could have done better still. We have not done this because our object in this paper is to show how good a potential function can be found for this—and larger—molecules by the simple expedient of carrying-over the two force constants for benzene. The agreement for the  $B_{1u}$  vibrations in  $C_{10}H_8$  is within 10%, a situation which seems to us eminently satisfactory both in showing that the potential function is good and also in confirming the experimental assignments. The agreement for the higher frequencies in the  $B_{2g}$  and  $B_{3g}$  classes is only a little worse than for the  $B_{1u}$  class. But the lower frequencies are less satisfactory, and so are the more difficult  $A_u$  modes. It is not possible at this stage to say whether the lack of agreement here is the result of false assignments or the importance of neglected cross-terms in the potential function. Certainly the very low frequencies must be very sensitive to the values of such terms.

TABLE 3. *Frequencies in naphthalene.*

Symmetry	Label	(a)	(b)	(c)	Symmetry	Label	(a)	(b)	(c)
$A_u$	$\nu_{10}$	1146	1307	1143	$B_{2g}$	$\nu_{26}$	1254	1167	1040
	$\nu_{11}$	841	1094	917		$\nu_{27}$	1168	715	722
	$\nu_{12}$	726	842	549		$\nu_{28}$	191	191	365
	$\nu_{13}$	586	(400)	222	$B_{3g}$	$\nu_{37}$	1624	1099	1107
$B_{1u}$	$\nu_{22}$	949	956	1053		$\nu_{38}$	972	774	937
	$\nu_{23}$	821	780	776		$\nu_{39}$	742	588	687
	$\nu_{24}$	747	475	422		$\nu_{40}$	406	285	436
	$\nu_{25}$	80	176	183					

(a) Barrow and McClellan, *loc. cit.* (b) McClellan and Pimentel, in the press. (c) Calc. in the present paper.

In conclusion, we believe that our simple potential function should be useful for more complicated molecules such as anthracene or pyrene, or the dibenzophenanthrene discussed in the following paper. We also, once more, thank Drs. A. L. McClellan and G. C. Pimentel for valuable correspondence and information concerning the experimental assignments of frequencies in naphthalene.

MATHEMATICAL INSTITUTE, OXFORD.

LABORATORIO DE QUÍMICA FÍSICA,

SECCION DEL INSTITUTO "A. DE G. ROCASOLANO," DEL C.S.I.C.,

VALLADOLID, SPAIN.

[Received, December 31st, 1954.]