

## A valence force field for the amide group

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**Abstract**—A valence force field is presented for the grouping  $R-CO-NH-R'$  where  $R$  and  $R'$  are  $CH_2$  or  $CH_3$ , derived from the frequencies of  $N$ -methylacetamide, nylons, and some of the deuteroderivatives. By refining all experimental data simultaneously,<sup>2</sup> the overall agreement between the experimental and calculated frequencies is good.

### INTRODUCTION

DURING the last decade extensive experimental data have been collected on infrared spectra of molecules with the amide group [1–14]. An assignment of characteristic frequencies of the amide group was soon established [2] and later work led to an understanding of the origin of other bands in  $N$ -methylacetamide [11, 12] and in polyamides made from  $\omega$ -aminoacids [9]. Along with the assignment of spectra, normal coordinate calculations for these molecules were being performed. The first of these was that for  $N$ -methylacetamide [2] in which methyl groups were taken as mass points and a Urey–Bradley force field was used. This calculation was later refined to the complete molecular model of  $N$ -methylacetamide [12, 15] using, in addition, experimental frequencies of molecules with deuterated methyl groups. A calculation of the out-of-plane vibrations of polyamides in the planar form was done with a valence force field neglecting torsion coordinates and the amide VII vibration [16]. A similar attempt with in-plane vibrations [17], using a Urey–Bradley force field for the amide group, was not

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successful due to a very poor computer used in this calculation (Russian Ural 2). However, it showed the probable necessity of using a valence force field for the amide group. With the Urey-Bradley force field, reproduction of the fine structure of the  $\text{CH}_2$  wagging vibrations in the region  $1150\text{--}1300\text{ cm}^{-1}$  (see [9]) was not possible. Recently, a calculation was done for the dimer of polyglycine ( $\text{CH}_3\text{NHCOCH}_2\text{NHCOCH}_3$ ) and was used for an estimation of the rotation angles of the central  $\text{CO—CH}_2$  and  $\text{CH}_2\text{—NH}$  bonds [14]. A calculation on nylon 6, in which methylene groups were taken as mass points [13], showed that such a calculation may serve as a good tool in understanding far infrared spectra below  $600\text{ cm}^{-1}$ , where there is no essential contribution from hydrogen atom motions.

In this paper we present a valence force field for the grouping  $\text{R—CO—NH—R}'$ , where R and R' are  $\text{CH}_2$  or  $\text{CH}_3$ , which was derived from the frequencies of N-methylacetamide, nylons, and some of their deuteroderivatives. In the nylons, n-paraffin force constants were used for the  $(\text{CH}_2)_{n-1}$  chain (with the exception of some constants for the first and last methylene groups). The force constants of the amide group were assumed to be transferable between nylons and N-methylacetamide. In out-of-plane blocks, torsion coordinates were included. In deriving this force field, we started from NEEDHAM'S force field [12] and refined it using experimental frequencies of polyamides. When the refined force field was applied back to the N-methylacetamide, some frequencies were about  $100\text{ cm}^{-1}$  off their experimental values. Therefore, it was necessary to refine all experimental data simultaneously. After doing this, the overall agreement between experimental and calculated frequencies was good, and most of the frequencies were reproduced to within  $7\text{ cm}^{-1}$ , although some greater deviations do occur (e.g. in the C—C stretching region in nylon 3). If this force field is applied to similar molecules [18], the agreement goes down only slightly; one frequency which seems to be systematically off about  $15\text{ cm}^{-1}$  is the  $\text{CH}_2$  wagging mode in the  $\text{CH}_3\text{—CH}_2\text{—CO—}$  group.

#### THE FORCE FIELD

In view of the bad experience in the past with the Urey-Bradley force field for the amide group [17], we decided to introduce a valence force field instead. However, a unique result for this kind of force field cannot be expected, since the problem is expected to be ill-conditioned because of the large number of force constants. Therefore, measures must be taken to ensure the convergence of the refinement. These measures should express mathematically the physical requirements on the force constants, viz., that cross terms between remote coordinates should be small and that similar force constants should be close, and also the requirement that in each refinement cycle the differences between the initial and refined force constants should be small.

In our belief, the best way to do this is to add to the sum of the squares of frequency errors, i.e.

$$\sum_i P_i [\omega_i(\text{calc}) - \omega_i(\text{exp})]^2$$

the sum of squares of all linear combinations of force constants which we wish to keep close to zero, properly weighted according to the accuracy with which we wish to do

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so. Thus, if the force constant  $f_i$  should lie between  $-0.2$  and  $0.2$ , we add  $(f_i/0.2)^2$ ; if the constants  $f_i$  and  $f_j$  should be close to each other with an accuracy of  $0.1$ , we add  $[(f_i - f_j)/0.1]^2$ . In our refinement program, we have introduced three types of such requirements: that a force constant be close to a predefined value, that the difference between two force constants be close to a predefined value (usually zero), and that the difference between a force constant before and after refinement in each cycle be close to zero. In addition, we permitted the corrections to any two chosen force constants to be kept exactly equal in each cycle. This was done to facilitate introducing more transferability among force constants than was assumed during the original coding of the  $F$  matrices (otherwise it is necessary to recode the  $F$  matrices).

The final values of the force constants are listed in Table 1. Of the 99 force constants in the polyamides (76 for the in-plane block and 23 for the out-of-plane block), 22 were transferred from *n*-paraffins, two torsion force constants were transferred from SHIMANOUCI [22], and the force constant for the N—H stretching vibration was estimated to be 5.98 in order to lead to the value of about  $3300\text{ cm}^{-1}$  for the N—H stretching frequency. Twelve more force constants are required for *N*-methylacetamide, of which 2 constants for C—H stretching were transferred from *n*-paraffins. The remaining 84 force constants, 60 for the in-plane block, 14 for the out-of-plane block, and 10 new constants for *N*-methylacetamide, were refined by least squares. The cross terms involving coordinates C—C(—CO)—H, C—C—C(=O), H—C—C(=O), N—C—H, N—C(=H<sub>2</sub>)—C, and H—C(—N)—C not shown in Table 1 were also transferred from *n*-paraffins, neglecting the difference between C(=O), N, and C(=H<sub>2</sub>) atoms in these cross terms. Moreover, in the in-plane block 10 of the force constants were forced to the values of the similar force constants in *n*-paraffins with an accuracy of  $0.1$ , and 6 with an accuracy of  $0.2$ , as shown in Table 1. At first sight, the values of the force constants seem to be reasonable, although the value of the cross term between C—C(=O) and C=O may seem to be too high. But we must keep in mind that this set of force constants certainly is not unique, and we are convinced that other sets, in which some of the force constants may differ by as much as  $0.5$  from those in Table 1, may reproduce the experimental data equally well.

Some attention should also be paid to the transferring of force constants from *n*-paraffins. We calculated frequencies of some longer *n*-paraffins and observed that a few of the C—C stretching frequencies and several C—C—C bending frequencies were over  $10\text{ cm}^{-1}$  off their calculated values. Deviations of up to  $7\text{ cm}^{-1}$  were also observed in the CH<sub>2</sub> wagging frequencies, and here they were determined almost exclusively by phase differences associated with the corresponding modes. This dependence was also observed in the C—C stretching and C—C—C bending regions, although the interaction of both branches of the dispersion curves interferes somewhat with this. Such errors are expected to be transferred to the amide force constants. That is, by keeping the *n*-paraffin force constants fixed during refinement, other constants which are being refined are forced to change so as to compensate for the errors caused by the fixed force constants. This compensation should probably work best for molecules with about five methylene groups, from which most of the data in the refinement were used. On this basis, we can explain some large errors in the C—C stretching frequencies in nylon 3 and in the CH<sub>2</sub> wagging frequency of the CH<sub>3</sub>CH<sub>2</sub>CO group. The application of this force field to other similar molecules with

Table 1. Force constants for the  $\text{CH}_2\text{CONHCH}_2$  group

| (a) Force constants involving coordinates symmetric to the skeletal plane  |           |                     |          |              |              |              |                     |          |                        |                      |   |
|--|-----------|---------------------|----------|--------------|--------------|--------------|---------------------|----------|------------------------|----------------------|---|
|  | C-C(CO)   | C-C-C(O)            | C-C(O)   | C=C=O        | C=O          | C-C(O)-N     | C(O)-N              | C-N-C    | H-N-C(H <sub>2</sub> ) | N-C(H <sub>2</sub> ) | N-C(H <sub>2</sub> )-C (N/C(H <sub>2</sub> ))-C |
| C-C(CO)  | 4.532††   |                     |          |              |              |              |                     |          |                        |                      |   |
| C-C-C(O)   | 0.3155*   | 1.5985              |          |              |              |              |                     |          |                        |                      |   |
| C-C(O)   | 0.0890*   | 0.3134†             | 5.1744   |              |              |              |                     |          |                        |                      |   |
| C-C=O  | 0         | -0.0314†            | 0.2584   | 2.8251       |              |              |                     |          |                        |                      |   |
| C=O  | 0         | 0                   | 0.7637   | -0.1167      | 8.7802       |              |                     |          |                        |                      |   |
| C-C(O)-N   | 0         | -0.2082††           | 0.0207   | 1.4945       | -0.4954      | 2.5393       |                     |          |                        |                      |   |
| C(O)-N   | 0         | 0                   | 0.6382   | -0.0838      | 0.2304       | 0.4377       | 6.1175              |          |                        |                      |   |
| C-N-C  | 0         | 0                   | 0        | -0.0121      | 0            | -0.1291      | -0.4826             | 2.3231   |                        |                      |   |
| H-N-C(H <sub>2</sub> )   | 0         | 0                   | 0        | 0.1308       | 0            | 0            | -0.3746             | 0.8481   | 1.1542                 |                      |   |
| N-C(H <sub>2</sub> )   | 0         | 0                   | 0        | 0            | 0            | 0            | 0.3522              | 0.6152   | 0.3241                 | 5.2782               |   |
| N-C(H <sub>2</sub> )-C   | 0         | 0                   | 0        | 0            | 0            | 0            | 0                   | 0.0150†† | -0.1433†               | 0.3116†              | 1.5625  |
| (N/C(H <sub>2</sub> ))-C   | 0         | 0                   | 0        | 0            | 0            | 0            | 0                   | 0        | 0                      | 0.0830*              | 0.3247*   |
|  |           |                     |          |              |              |              |                     |          |                        |                      | 4.532††   |
| $K_{\text{NH}} = 5.98^{**}$ .  |           |                     |          |              |              |              |                     |          |                        |                      |   |
| (b) Force constants involving antisymmetric and/or unsymmetric coordinates |           |                     |          |              |              |              |                     |          |                        |                      |   |
|  | C-C(CO)-H | H-C-C(O)            | H-C-C(O) | CO o.p. bend | C(O)-N tors. | NH o.p. bend | N-C-H               | H-C(N)-C |                        |                      |   |
| C-C(CO)-H  | 1.1532    |                     |          |              |              |              |                     |          |                        |                      |   |
| C-C(CO)-H'   | 0.5161    |                     |          |              |              |              |                     |          |                        |                      |   |
| H-C-C(O)   | 0.4747    | 1.0665 <sub>s</sub> |          |              |              |              |                     |          |                        |                      |   |
| H'-C-C(O)  | 0.5168    | 0.4707 <sub>s</sub> |          |              |              |              |                     |          |                        |                      |   |
| CO o.p. bend   | 0         | 0.0346              | 0.5797   |              |              |              |                     |          |                        |                      |   |
| C(O)-N tors.   | 0         | 0                   | 0.1400   | 0.6706       |              |              |                     |          |                        |                      |   |
| NH o.p. bend   | 0         | 0                   | 0.0256   | 0.0287       |              |              |                     |          |                        |                      |   |
| N-C-H  | 0         | 0                   | 0        | 0            | 0.0800       |              |                     |          |                        |                      |   |
| N-C-H'   | 0         | 0                   | 0        | 0            | -0.0009      |              | 1.2175              |          |                        |                      |   |
| H-C(N)-C   | 0         | 0                   | 0        | 0            | 0.3780       |              | 0.3780              | 1.1975   |                        |                      |   |
| H'-C(N)-C  | 0         | 0                   | 0        | 0            | 0.0009       |              | 0.4894 <sub>s</sub> |          |                        |                      |   |
|  |           |                     |          |              | 0            |              | 0.3619 <sub>s</sub> | 0.5177   |                        |                      |   |

$\tau_{\text{C-O}} = 0.037^{**}$ ,  $\tau_{\text{H-O(H}_2\text{)}} = 0.037^{**}$

Table 1 (cont.)

| (c) Cross terms between symmetric and unsymmetric coordinates |                |                |                |                        |          |                      |  |                         |       |
|---|----------------|----------------|----------------|------------------------|----------|----------------------|--|-------------------------|-------|
|   | C—C(OO)        | O—C—C(O)       | C—C(O)         | skew                   | C—C—O    | cis                  | gauche                                       | C—C(O)—N                | trans |
| C—C(CO)—H   | 0.174††        | 0.5232*        | -0.0730*       | 0                      | 0        | 0                    | 0  | 0                       | 0     |
| H—C—C(O)  | -0.0923*       | 0.4920†        | 0.2074†        | 0.1317                 | -0.1936§ | -0.0229              | 0.0278§                                      |                         |       |
| (d) Methyl group force constants in N-methylacetamide         |                |                |                |                        |          |                      |  |                         |       |
|   | gauche         | trans          | skew           | H—N—C(H <sub>3</sub> ) | cis      | N—C(H <sub>3</sub> ) | N—C(H <sub>3</sub> )—C                       | (N)C(H <sub>3</sub> )—C |       |
| N—C—H   | -0.0099        | -0.0938§       | 0.0580         | -0.0083§               | 0.3655†  | 0.4895†              | -0.1418*                                     |                         |       |
| H—C(N)—C  | 0              | 0              | 0              | 0                      | -0.1086* | 0.4991*              | 0.174††                                      |                         |       |
| (e) Symmetrized force constants                               |                |                |                |                        |          |                      |  |                         |       |
|   | H <sub>α</sub> | H <sub>β</sub> | F <sub>β</sub> | n-paraffin             |          |                      | H—C—N  |                         |       |
|   | H—C—C(O)       | H—C(CO)—C      | H—C(N)—C       | H—C(N)—C               | H—C—N    | H—C—N                | H—C—N  | H—C—N                   | H—C—N |
| H <sub>γ</sub> + F <sub>γ</sub> + 2H <sub>δ</sub>             | 1.5373         | 1.6743         | 1.710          | 1.7162                 | 1.5955   | 1.5955               | f <sub>γγ</sub> + f <sub>γ'γ'</sub> = 0.015  |                         |       |
| H <sub>γ</sub> - F <sub>γ</sub>                               | 0.5958         | 0.6421         | 0.682          | 0.6798                 | 0.8395   | 0.8395               | f <sub>γγ</sub> - f <sub>γ'γ'</sub> = -0.131 |                         |       |
| F <sub>γ</sub> + 2H <sub>δ</sub>                              | 0.9915         | 0.9915         | 1.087          | 0.8714                 | 0.8714   | 0.8714               | f <sub>γγ</sub> + f <sub>γ'γ'</sub> = -0.013 |                         |       |
| F <sub>γ'</sub>   | -0.0421        | -0.0421        | 0.021          | 0.1075                 | 0.1075   | 0.1075               | f <sub>γγ</sub> - f <sub>γ'γ'</sub> = 0.005  |                         |       |
|   |                |                |                |                        |          |                      | f <sub>γγ</sub> + f <sub>γ'γ'</sub> = 0.022  |                         |       |
|   |                |                |                |                        |          |                      | f <sub>γγ</sub> - f <sub>γ'γ'</sub> = 0.002  |                         |       |

\* Kept close to the corresponding force constant in the polymethylene chain with an accuracy of 0.01.

† As in \*, with an accuracy of 0.02.

‡ cis.

§ From N-methylacetamide (this calculation).

\*\* Assumed (no refinement).

†† Transferred from n-paraffins [21].

‡‡ trans.

Every H atom lies on the upper side of the skeletal plane and every H' atom on the lower side. The positive direction of the CO and NH out-of-plane (o.p.) bending coordinates corresponds to the situation in which the CO or NH bond enters the upper side of the skeletal plane. The positive direction of a torsion coordinate corresponds to the situation in which the outer skeletal atoms (i.e. C or N) involved in this coordinate enter the upper side of the skeletal plane. All zero values of force constants were assumed.

the amide group showed the force field to be a powerful means of understanding and assigning their spectra [18]. But it also showed clearly that a further refinement of this force field to remove some of the uncertainty caused by ill-conditioning would be possible and desirable if new experimental data, and/or a more refined set of n-paraffin force constants, were available.

#### ASSUMED STRUCTURES AND COORDINATES

In the calculations we used the following bond lengths [19]:  $d_{\text{CH}} = 1.093 \text{ \AA}$ ,  $d_{\text{CC}} = 1.54 \text{ \AA}$ ,  $d_{\text{NH}} = 1.01 \text{ \AA}$ ,  $d_{\text{CO}} = 1.23 \text{ \AA}$ ,  $d_{\text{C(=O)-N}} = 1.34 \text{ \AA}$ ,  $d_{\text{C(-H)-N}} = 1.47 \text{ \AA}$ . All angles in the methylene and methyl groups were assumed tetrahedral, and angles in the C—CO—NH—C group were assumed trigonal ( $120^\circ$ ). Mass values used were  $m_{\text{H}} = 1.007825$ ,  $m_{\text{C}} = 12$ ,  $m_{\text{N}} = 14.00307$ ,  $m_{\text{O}} = 15.99491$ , and  $m_{\text{D}} = 2.01410$ . For the velocity of light and Avogadro's number we used the values  $2.997925 \times 10^{10} \text{ cm/sec}$  and  $6.02257 \times 10^{23} \text{ mol}^{-1}$  respectively.

The internal coordinates were bond lengths, bond angles, out-of-plane bend angles, and torsion angles. The first two kinds were used in the usual way: a + 1 value of the coordinate means an increase by 1 Å, or 1 rad., respectively. For defining the next two types, let us call one side of the carbon skeleton the upper side and the other the lower side. The value + 1 for the coordinate C=O (or N—H) out-of-plane bend means the C=O (N—H) bond is rotated by 1 rad. perpendicular to the C—C—N (C—N—C) plane and moves into the upper side of this plane. In the internal torsion coordinates we follow the FUKUSHIMA convention [20]: if atom X has  $m$  adjacent atoms and atom Y has  $n$  adjacent atoms,  $(n - 1)(m - 1)$  dihedral angles about the X—Y bond may be defined. For the torsion coordinate about this bond we take the sum of the changes of all of these dihedral angles divided by  $(m - 1)(n - 1)$ . The plus sign for a dihedral angle is chosen in a direction such that the change of the skeletal dihedral angle (i.e. the angle involving the C and N atoms only) moves both outer skeletal atoms into the upper side of the skeletal plane. This convention has the disadvantage that it changes the direction of the torsion coordinate about adjacent skeletal bonds from clockwise to counterclockwise; on the other hand, we found it very convenient for setting up the  $B$  matrix elements. If the rotation angles in the molecule differ from those of the standard all-*trans* for the skeleton (e.g. the  $\gamma$  form of nylon 6), we first rotate it to the standard conformation for determining the positive direction of the out-of-plane bending and torsion coordinates.

We decided to remove the local redundancy in each methylene group by omitting the H—C—H bending coordinate and in the amide group by omitting the H—N—C(=O) and O=C—N coordinates. The omission of the H—C—H bending coordinate leads to an increase by the value of  $H_s$  of all diagonal and cross terms between the remaining five angle coordinates around this carbon atom. This change is included in Table 1, where final refined values of force constants are listed. In the actual coding of the  $F$  matrices, we further changed our force constant set in the case of the CCH

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bending, NCH bending, and CH stretching coordinates to some sums and differences of force constants yielding in-plane and out-of-plane blocks in polyamides which are mutually independent. Even in the case where complete independence is not obtained, it is worth doing so since the conditioning of the in-plane and out-of-plane blocks may be different, requiring a different approach to ensuring convergence. This is difficult to do without having separated the force constants influencing the individual blocks. For the convenience of those who would wish to follow this approach, we also include the symmetrized combinations of force constants in Table 1. Note only that in forming out-of-plane coordinates, the internal coordinate containing the hydrogen atom on the *upper* side of the skeletal plane always enters with a + sign.

All calculations were performed on an IBM 360 computer using a computer program written by one of us (J. J.). In coding this program, care was taken to save computer time and storage space in handling large matrices. The method of calculation was essentially the same as in the previous work [15, 16].

#### EXPERIMENTAL DATA

Extensive experimental data on infrared frequencies of molecules with the amide group were collected in Prague in the early sixties [4, 5, 9, 11]. These data were used in the present refinement, complemented by some data in the region below  $400\text{ cm}^{-1}$  [10, 13]. Although other data are available in the literature [1, 7, 8], there is an advantage in using experimental data from a single source, since systematic errors in a given region of the spectrum are then the same for all the frequencies. This is important for a successful simultaneous refinement of a transferable set of force constants, since accurate frequency shifts are much more relevant than accurate frequencies. This is so because such a refinement is in reality an extrapolation from frequency shifts to unknown eigenvectors, and in some cases changes in such frequency shifts of as little as  $3$  to  $5\text{ cm}^{-1}$  can lead to drastic changes in eigenvectors.

The experimental frequencies are listed in Table 2 together with their statistical weights and calculated values. In our coding, 1273/3 means that the contribution to the sum of error squares was  $(\omega_{\text{calc}} - 1273)/3^2$ ; i.e. rather than statistical weights  $P_i$ , the values  $P_i^{-1}$  are listed. Because of the small difference between the starting and refined set of force constants in the last refinement cycle, we did not repeat the frequency calculations with the final set in Table 1 for all molecules. Only the frequencies of nylon 6 and nylon 66 listed in Table 2 are those obtained with the set of force constants in Table 1; the other calculated frequencies are those obtained with the next-to-last set of force constants.

In Table 2, *B*, *W*, *T*, *R*, and *S* mean  $\text{CH}_2$  bending, wagging, twisting, rocking, and C—C stretching modes respectively. Where the assignment is shown between two lines, it relates to both of them (in the case of splitting of the monomer unit modes). The indices in the *B*, *W*, *T*, *R*, and *S* modes are sequence indices of the progression and are related to the phase differences in the polymethylene portion of the chain [23, 24]. Compared to the previous assignment [9], we now denote one band in the  $\text{CH}_2$  wagging progression as amide III, although the selection of the proper one is

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Table 2 (cont.)

| Nylon 66 (cont.) |       |       |       |       |                           | N-deuterated nylon 4 (cont.) |       |             |       |                           |  |
|------------------|-------|-------|-------|-------|---------------------------|------------------------------|-------|-------------|-------|---------------------------|--|
| Exp. [4]         | $A_g$ | $B_g$ | $B_u$ | $A_u$ | Assignment                | Exp. [9]                     | $A_1$ | Calc. $B_2$ | $B_1$ | Assignment                |  |
| 988/2            |       |       |       | 993   | $R_5(\text{NH})$          | 1092/4                       | 1087  |             |       |                           |  |
|                  | 960   |       |       |       | C—CO stretch              | 1079/2                       |       |             | 1078  | $S_2$                     |  |
| 934/2            |       |       | 935   |       | C—CO stretch              |                              |       | 1079        |       | $R_3$                     |  |
| 908/2            |       |       |       | 904   | $R_3(\text{CO})$          |                              | 1034  |             | 1059  | $S_2$                     |  |
|                  |       | 888   |       |       | $R_4(\text{NH})$          | 984/4                        | 989   |             | 986   | Amide III                 |  |
|                  |       | 803   |       |       | $R_2(\text{CO})$          | 940/4                        | 939   |             | 939   | C—CO stretch              |  |
| 798/2            |       |       |       | 798   | $R_3(\text{NH})$          | 869/2                        |       | 872         |       | $R_2$                     |  |
|                  |       |       | 745   |       | Amide IV                  | 754/2                        |       | 743         |       | $R_1$                     |  |
|                  |       |       |       | 743   | $R_2(\text{NH})$          |                              | 770   |             | 687   | Amide IV                  |  |
|                  |       |       |       | 741   | $R_1(\text{CO})$          |                              |       | 604         |       | Amide VI                  |  |
|                  | 726   |       |       |       | Amide IV                  | 495/3                        |       | 502         |       | Amide V                   |  |
| 732/3            |       |       |       | 721   | $R_1(\text{NH})$          |                              | 532   |             |       |                           |  |
|                  |       | 697   |       |       | Amide V                   | 449/2                        |       |             | 450   |                           |  |
| 695/3            |       |       |       | 695   |                           |                              | 393   |             | 366   | Skeletal bend             |  |
| 583/3            |       |       |       | 582   | Amide VI                  |                              |       |             | 334   |                           |  |
|                  |       | 581   |       |       |                           |                              |       |             | 242   |                           |  |
| 535/2            |       |       | 539   |       |                           |                              |       | 202         |       | Amide VII                 |  |
|                  | 522   |       |       |       |                           |                              |       | 107         |       |                           |  |
|                  | 472   |       |       |       |                           |                              | 103   |             |       | Skeletal bend and torsion |  |
| 405/3            |       |       | 394   |       | Skeletal bend             |                              | 97    |             |       |                           |  |
| 358/3            |       |       | 356   |       |                           |                              |       |             | 93    |                           |  |
|                  |       | 351   |       |       |                           |                              |       |             | 48    |                           |  |
| 330/3            |       |       | 318   |       |                           |                              |       |             |       |                           |  |
| 230/3            |       |       |       | 214   | Amide VII                 |                              |       |             |       |                           |  |
|                  |       | 214   |       |       |                           |                              |       |             |       |                           |  |
|                  |       |       | 183   |       |                           |                              |       |             |       |                           |  |
|                  | 178   |       |       |       |                           |                              |       |             |       |                           |  |
|                  |       | 129   |       |       |                           |                              |       |             |       |                           |  |
|                  |       |       | 128   |       |                           |                              |       |             |       |                           |  |
|                  |       |       | 112   |       |                           |                              |       |             |       |                           |  |
|                  |       | 107   |       | 74    | Skeletal bend and torsion |                              |       |             |       |                           |  |
|                  |       |       |       | 72    |                           |                              |       |             |       |                           |  |
|                  |       | 60    |       | 60    |                           |                              |       |             |       |                           |  |
|                  |       | 53    |       | 51    |                           |                              |       |             |       |                           |  |
|                  |       |       |       | 44    |                           |                              |       |             |       |                           |  |
|                  |       |       |       | 22    |                           |                              |       |             |       |                           |  |
|                  |       |       |       | 19    |                           |                              |       |             |       |                           |  |

  

| N-deuterated nylon 6 |       |             |       |              |
|----------------------|-------|-------------|-------|--------------|
| Exp. [9, 13]         | $A_1$ | Calc. $B_2$ | $B_1$ | Assignment   |
| 1637/6               | 1630  |             | 1630  | Amide I      |
|                      | 1486  |             | 1487  | Amide II     |
|                      | 1478  |             | 1476  | $B_2$        |
|                      | 1471  |             | 1471  | $B_4$        |
|                      | 1459  |             | 1460  | $B_3$        |
|                      | 1443  |             | 1443  | $B_5$        |
| 1419/2               | 1420  |             | 1420  | $B_1$        |
| 1371/4               |       |             | 1376  | $W_5$        |
| 1381/4               | 1376  |             |       | $W_5$        |
|                      | 1367  |             | 1372  | $W_4$        |
| 1349/4               | 1339  |             |       | $W_4$        |
|                      |       |             | 1330  | $W_3$        |
|                      |       | 1305        |       | $T_2$        |
| 1303/3               |       | 1304        |       | $T_1$        |
| 1278/2               |       | 1281        |       | $T_3$        |
|                      | 1276  |             | 1281  | $W_3$        |
| 1243/2               |       | 1237        |       | $T_4$        |
| 1227/2               | 1220  |             |       | $W_1$        |
|                      |       |             | 1214  |              |
| 1173/2               |       | 1175        |       | $T_5$        |
|                      |       |             | 1127  |              |
|                      |       |             |       | $S_1$        |
| 1122/2               | 1125  |             |       |              |
|                      | 1102  |             |       | $S_2$        |
|                      |       | 1098        |       | $R_5$        |
| 1090/2               |       |             | 1095  | $S_5$        |
|                      | 1064  |             | 1067  | $S_5$        |
|                      | 1055  |             | 1035  | $S_8$        |
|                      | 1004  |             | 1023  | $S_4$        |
| 981/4                | 983   |             | 990   | Amide III    |
| 961/2                |       |             | 945   | C—CO stretch |
| 951/2                |       | 954         |       | $R_4$        |
| 923/2                | 926   |             |       | C—CO stretch |
| 837/2                |       | 836         |       | $R_3$        |
| 773/2                |       | 762         |       | $R_2$        |

  

| N-deuterated nylon 4 |       |             |       |            |
|----------------------|-------|-------------|-------|------------|
| Exp. [9]             | $A_1$ | Calc. $B_2$ | $B_1$ | Assignment |
| 1629/6               | 1630  |             | 1630  | Amide I    |
| 1473/4               | 1490  |             |       | Amide II   |
|                      |       |             | 1481  |            |
| 1464/4               | 1471  |             | 1475  | $B_2$      |
| 1448/4               | 1451  |             | 1451  | $B_2$      |
|                      |       |             | 1418  | $B_1$      |
| 1419/2               | 1417  |             |       | $W_3$      |
| 1384/4               | 1374  |             | 1371  | $W_3$      |
| 1359/4               |       |             | 1346  | $W_4$      |
| 1334/4               | 1331  |             |       | $W_4$      |
|                      |       | 1302        |       | $T_1$      |
| 1263/3               |       | 1266        |       | $T_2$      |
| 1251/2               | 1247  |             |       | $W_1$      |
|                      |       |             | 1240  | $W_1$      |
| 1192/2               |       | 1192        |       | $T_2$      |
|                      |       |             | 1132  | $S_1$      |
| 1121/2               | 1118  |             |       | $S_1$      |

Table 2 (cont.)

| N-deuterated nylon 6 (cont.) |                |                         |                |                              | N-deuterated nylon 7 (cont.) |     |              |               |
|------------------------------|----------------|-------------------------|----------------|------------------------------|------------------------------|-----|--------------|---------------|
| Exp.<br>[9, 13]              | A <sub>1</sub> | Calc.<br>B <sub>2</sub> | B <sub>1</sub> | Assignment                   | Exp.<br>[9]                  | A'  | Calc.<br>A'' | Assignment    |
| 734/2                        | 736            |                         | 730            | Amide IV                     |                              |     |              | Amide IV      |
|                              |                | 723                     |                | B <sub>1</sub>               |                              |     |              | Amide VI      |
| 496/3                        |                | 604                     |                | Amide VI                     | 493/3                        |     | 604          | Amide VI      |
|                              |                | 502                     |                | Amide V                      |                              |     | 502          | Amide V       |
| 512/2                        | 541            |                         | 513            | Skeletal bend                | 435/4                        | 508 | 214          | Skeletal bend |
| 442/2                        | 440            |                         |                |                              |                              | 467 |              |               |
| 429/2                        |                |                         | 431            |                              |                              | 443 |              |               |
| 365/2                        | 365            |                         | 332            |                              |                              | 337 |              |               |
| 345/4                        |                |                         | 263            |                              |                              |     |              | 134           |
| 294/2                        | 298            |                         | 217            | Amide VII                    |                              |     | 125          |               |
| 220/3                        |                |                         | 195            |                              | 153                          |     | 83           |               |
| 195/2                        |                |                         | 165            | Skeletal bend<br>and torsion |                              | 139 |              | 59            |
| 170/2                        |                |                         | 126            |                              |                              |     |              | 52            |
|                              |                |                         | 97             |                              |                              |     |              |               |
|                              |                |                         | 71             |                              |                              |     |              |               |
|                              |                |                         | 61             |                              |                              |     |              |               |
|                              | 53             |                         |                |                              |                              |     |              |               |
|                              | 53             |                         |                |                              |                              |     |              |               |
|                              |                | 40                      |                |                              |                              |     |              |               |

  

| N-deuterated nylon 8 |                |                         |                |                |
|----------------------|----------------|-------------------------|----------------|----------------|
| Exp.<br>[9]          | A <sub>1</sub> | Calc.<br>B <sub>2</sub> | B <sub>1</sub> | Assignment     |
| 1637/6               | 1630           |                         | 1630           | Amide I        |
|                      | 1487           |                         | 1486           | Amide II       |
|                      | 1478           |                         | 1477           | B <sub>7</sub> |
|                      | 1474           |                         | 1474           | B <sub>6</sub> |
|                      | 1471           |                         | 1471           | B <sub>5</sub> |
|                      | 1463           |                         | 1463           | B <sub>4</sub> |
|                      | 1451           |                         | 1451           | B <sub>3</sub> |
|                      | 1441           |                         | 1441           | B <sub>2</sub> |
|                      | 1420           |                         | 1420           | B <sub>1</sub> |
| 1420/2               | 1381           |                         | 1382           | W <sub>7</sub> |
|                      | 1372           |                         | 1374           | W <sub>6</sub> |
|                      | 1366           |                         | 1360           | W <sub>5</sub> |
|                      | 1328           |                         | 1335           | W <sub>4</sub> |
| 1307/3               |                | 1308                    |                | T <sub>3</sub> |
|                      |                | 1306                    |                | T <sub>2</sub> |
|                      |                | 1302                    |                | T <sub>1</sub> |
|                      | 1294           |                         | 1290           | W <sub>3</sub> |
| 1288/2               |                | 1288                    |                | T <sub>4</sub> |
| 1253/2               |                | 1259                    |                | T <sub>5</sub> |
|                      | 1249           |                         | 1253           | W <sub>2</sub> |
| 1219/3               |                | 1219                    |                | T <sub>6</sub> |
| 1211/2               | 1208           |                         |                | W <sub>1</sub> |
|                      |                |                         | 1204           | T <sub>6</sub> |
| 1164/2               |                | 1167                    |                | S <sub>1</sub> |
|                      |                |                         | 1128           | S <sub>2</sub> |
| 1124/2               | 1126           |                         |                | S <sub>3</sub> |
| 1096/3               | 1109           |                         | 1104           | R <sub>7</sub> |
|                      |                | 1105                    |                | R <sub>7</sub> |
|                      | 1068           |                         | 1066           | S <sub>7</sub> |
|                      | 1064           |                         | 1064           | S <sub>6</sub> |
|                      | 1036           |                         | 1059           | S <sub>5</sub> |
|                      |                |                         | 1036           | S <sub>5</sub> |
| 1022/3               | 1032           |                         |                | S <sub>5</sub> |
|                      | 1009           |                         | 993            | S <sub>4</sub> |
|                      |                | 995                     |                | R <sub>6</sub> |
| 999/2                |                | 980                     |                | Amide III      |
| 978/3                |                | 980                     |                | Amide III      |
| 978/2                |                |                         | 974            | Amide III      |
| 934/2                | 940            |                         | 931            | C—CO stretch   |
|                      |                | 903                     |                | R <sub>5</sub> |
| 911/3                |                | 828                     |                | R <sub>4</sub> |
| 828/2                |                | 766                     |                | R <sub>3</sub> |
| 770/2                |                |                         |                | R <sub>3</sub> |

  

| N-deuterated nylon 7 |      |              |  |                |
|----------------------|------|--------------|--|----------------|
| Exp.<br>[9]          | A'   | Calc.<br>A'' |  | Assignment     |
| 1632/6               | 1630 |              |  | Amide I        |
|                      | 1487 |              |  | Amide II       |
|                      | 1476 |              |  | B <sub>6</sub> |
|                      | 1474 |              |  | B <sub>5</sub> |
|                      | 1467 |              |  | B <sub>4</sub> |
|                      | 1454 |              |  | B <sub>3</sub> |
|                      | 1442 |              |  | B <sub>2</sub> |
|                      | 1420 |              |  | B <sub>1</sub> |
| 1421/2               | 1380 |              |  | W <sub>6</sub> |
| 1374/2               | 1373 |              |  | W <sub>5</sub> |
|                      | 1348 |              |  | W <sub>4</sub> |
| 1355/4               | 1314 |              |  | W <sub>3</sub> |
| 1323/2               |      | 1307         |  | T <sub>3</sub> |
|                      |      | 1305         |  | T <sub>1</sub> |
| 1302/3               |      | 1296         |  | T <sub>2</sub> |
| 1289/3               |      | 1269         |  | T <sub>4</sub> |
| 1262/2               |      |              |  | W <sub>2</sub> |
|                      | 1260 |              |  | T <sub>5</sub> |
| 1230/2               |      | 1229         |  | W <sub>1</sub> |
| 1219/2               | 1213 |              |  | T <sub>6</sub> |
| 1168/2               |      | 1166         |  | S <sub>1</sub> |
| 1127/2               | 1125 |              |  | S <sub>1</sub> |
| 1110/4               |      | 1105         |  | R <sub>5</sub> |
| 1095/4               | 1105 |              |  | S <sub>2</sub> |
| 1066/3               | 1065 |              |  | S <sub>6</sub> |
|                      | 1055 |              |  | S <sub>5</sub> |
|                      | 1036 |              |  | S <sub>2</sub> |
| 1021/4               | 1016 |              |  | S <sub>4</sub> |
| 973/2                | 980  |              |  | Amide III      |
| 973/3                |      | 975          |  | R <sub>5</sub> |
| 937/2                | 935  |              |  | C—CO stretch   |
| 878/2                |      | 878          |  | R <sub>4</sub> |
| 793/2                |      | 791          |  | R <sub>3</sub> |
|                      |      | 744          |  | R <sub>2</sub> |
|                      |      | 721          |  | R <sub>1</sub> |



Table 2 (cont.)

| $\text{CH}_2\text{CONHCH}_3$ (cont.) |      |           |                                   | $\text{CD}_2\text{CONHCH}_3$ (cont.) |        |           |                          |                          |
|--------------------------------------|------|-----------|-----------------------------------|--------------------------------------|--------|-----------|--------------------------|--------------------------|
| Exp. [11]                            | A'   | Calc. A'' | Assignment                        | Exp. [11]                            | A'     | Calc. A'' | Assignment               |                          |
| 1161/3                               | 1163 |           |                                   | 715/3                                |        | 699       | Amide V                  |                          |
|                                      |      | 1134      | $\text{CH}_2(\text{NH})$ rock     | 592/3                                | 587    |           | Amide IV                 |                          |
| 1096/6                               | 1105 |           | N— $\text{CH}_2$ stretch          | 537/3                                |        | 536       | Amide VI                 |                          |
| 1044/3                               |      | 1054      | $\text{CH}_2(\text{CO})$ rock     | 407/3                                | 404    |           | Skeletal bend            |                          |
| 991/2                                | 987  |           | C—C stretch                       | 288/3                                | 282    |           |                          |                          |
| 883/2                                | 884  |           | $\text{CH}_2(\text{CO})$ rock     | 182/3                                |        | 189       | Amide VII                |                          |
| 725/3                                |      | 726       | Amide V                           |                                      |        | 140       | $\text{CH}_2$ torsion    |                          |
| 628/2                                | 634  |           | Amide IV                          |                                      |        | 104       | $\text{CD}_2$ torsion    |                          |
| 600/3                                |      | 597       | Amide VI                          |                                      |        |           |                          |                          |
| 439/3                                | 442  |           | Skeletal bend                     |                                      |        |           |                          |                          |
| 289/3                                | 295  |           |                                   |                                      |        |           |                          |                          |
| 192/3                                |      | 195       | Amide VII                         |                                      |        |           |                          |                          |
|                                      |      | 147       | $\text{CH}_2$ torsion             |                                      |        |           |                          |                          |
|                                      |      | 136       |                                   |                                      |        |           |                          |                          |
| $\text{CH}_2\text{CONDCH}_3$         |      |           |                                   | $\text{CD}_2\text{CONDCH}_3$         |        |           |                          |                          |
| Exp. [11]                            | A'   | Calc. A'' | Assignment                        | Exp. [11]                            | A'     | Calc. A'' | Assignment               |                          |
| 1647/6                               | 1648 |           | Amide I                           | 1647/6                               | 1634   |           | Amide I                  |                          |
| 1485/6                               | 1496 |           | Amide II                          | 1480/6                               | 1488   |           | Amide II                 |                          |
| 1471/4                               | 1459 |           | $\text{CH}_2(\text{ND})$ as bend  | 1452/6                               |        | 1465      |                          |                          |
|                                      |      | 1465      |                                   |                                      |        |           |                          |                          |
|                                      |      | 1452      | $\text{CH}_2(\text{CO})$ as bend  |                                      | 1451   |           | $\text{CH}_2$ as bend    |                          |
| 1440/6                               |      |           | $\text{CH}_2(\text{ND})$ sym bend | 1408/2                               | 1407   |           | $\text{CH}_2$ sym bend   |                          |
| 1446/4                               | 1439 |           |                                   |                                      | 1198/4 | 1200      |                          | $\text{CH}_2$ rock       |
| 1406/2                               | 1408 |           | $\text{CH}_2(\text{CO})$ sym bend |                                      |        | 1133      |                          |                          |
| 1372/2                               | 1365 |           |                                   |                                      | 1125/4 | 1126      |                          | N— $\text{CH}_2$ stretch |
| 1185/3                               | 1186 |           | $\text{CH}_2(\text{ND})$ rock     |                                      |        | 1045      | $\text{CD}_2$ as bend    |                          |
|                                      |      | 1134      |                                   |                                      |        |           | 1044                     | $\text{CD}_2$ sym bend   |
| 1123/3                               | 1114 |           | N— $\text{CH}_2$ stretch          | 976/4                                | 968    |           | Amide III                |                          |
| 1045/3                               |      | 1052      | $\text{CH}_2(\text{CO})$ rock     | 910/3                                |        | 899       | $\text{CD}_2$ rock       |                          |
| 1000/2                               | 993  |           | Amide III                         | 861/3                                | 857    |           | C—C stretch              |                          |
| 965/3                                | 967  |           |                                   |                                      | 795/4  | 798       |                          | $\text{CD}_2$ rock       |
| 872/2                                | 872  |           | C—C stretch                       | 588/3                                | 583    |           | Amide IV                 |                          |
|                                      |      | 635       | Amide VI                          |                                      |        | 559       | Amide VI                 |                          |
| 628/2                                | 628  |           | Amide IV                          | 505/3                                |        | 498       | Amide V                  |                          |
| 510/3                                |      | 504       | Amide V                           | 402/3                                | 402    |           | Skeletal bend            |                          |
| 439/3                                | 439  |           | Skeletal bend                     | 280/3                                | 281    |           |                          |                          |
| 292/3                                | 294  |           |                                   |                                      | 173/3  |           | 189                      | Amide VII                |
| 189/3                                |      | 195       | Amide VII                         |                                      |        | 140       | $\text{CH}_2$ torsion    |                          |
|                                      |      | 147       | $\text{CH}_2$ torsion             |                                      |        | 103       | $\text{CD}_2$ torsion    |                          |
|                                      |      | 136       |                                   |                                      |        |           |                          |                          |
| $\text{CD}_2\text{CONHCH}_3$         |      |           |                                   | $\text{CH}_2\text{CONHCD}_3$         |        |           |                          |                          |
| Exp [11]                             | A'   | Calc. A'' | Assignment                        | Exp. [11]                            | A'     | Calc. A'' | Assignment               |                          |
| 1647/6                               | 1651 |           | Amide I                           | 1647/6                               | 1662   |           | Amide I                  |                          |
| 1567/6                               | 1550 |           | Amide II                          | 1564/6                               | 1549   |           | Amide II                 |                          |
| 1462/2                               | 1460 |           | $\text{CH}_2$ as bend             | 1447/3                               | 1446   |           | $\text{CH}_2$ as bend    |                          |
| 1446/6                               |      | 1465      |                                   |                                      | 1437/6 |           | 1452                     |                          |
| 1416/2                               | 1415 |           | $\text{CH}_2$ sym bend            | 1373/2                               | 1380   |           | $\text{CH}_2$ sym bend   |                          |
| 1326/2                               | 1320 |           | Amide III                         | 1302/2                               | 1304   |           | Amide III                |                          |
| 1161/3                               | 1165 |           | $\text{CH}_2$ rock                | 1145/3                               | 1144   |           | N— $\text{CH}_2$ stretch |                          |
|                                      |      | 1133      |                                   |                                      |        | 1051      | 1059                     | $\text{CH}_2$ rock       |
| 1120/3                               | 1121 |           | N— $\text{CH}_2$ stretch          |                                      | 1030   | 1044      | $\text{CD}_2$ as bend    |                          |
|                                      | 1048 | 1046      | $\text{CD}_2$ as bend             |                                      | 1019   |           | $\text{CD}_2$ sym bend   |                          |
|                                      | 1039 |           | $\text{CD}_2$ sym bend            | 968/4                                | 967    |           | C—C stretch              |                          |
|                                      | 865  |           | C—C stretch                       | 890/4                                |        | 884       | $\text{CD}_2$ rock       |                          |
| 871/4                                |      | 908       | $\text{CD}_2$ rock                |                                      | 781    |           |                          |                          |
| 907/3                                |      |           |                                   |                                      | 725/3  |           | 724                      | Amide V                  |
| 800/3                                | 803  |           |                                   |                                      | 606/4  | 610       |                          | Amide IV                 |
|                                      |      |           |                                   | 600/3                                |        | 595       | Amide VI                 |                          |

Table 2 (cont.)

| CH <sub>2</sub> CONHCD <sub>2</sub> (cont.) |      |          |                               | CD <sub>2</sub> CONHCD <sub>2</sub> (cont.) |      |          |                               |
|---|------|----------|-------------------------------|---|------|----------|-------------------------------|
| Exp. [11]                                   | A'   | Calc. A" | Assignment                    | Exp. [11]                                   | A'   | Calc. A" | Assignment                    |
| 430/3                                       | 430  |          | Skeletal bend                 | 1027/3                                      | 1015 |          | CD <sub>2</sub> (NH) as bend  |
|   | 275  |          |                               | 979/3                                       | 969  |          | CD <sub>2</sub> (NH) sym bend |
|   |      | 181      |                               | 911/3                                       |      | 916      | CD <sub>2</sub> (CO) rock     |
|   |      | 144      |                               | 821/6                                       | 826  |          |                               |
|   |      | 101      | CD <sub>2</sub> torsion       |   |      | 874      | CD <sub>2</sub> (NH) rock     |
|   |      |          |                               | 750/6                                       | 746  |          | Amide V                       |
|   |      |          |                               | 716/3                                       |      | 698      | Amide IV                      |
|   |      |          |                               | 574/3                                       | 570  |          | Amide VI                      |
|   |      |          |                               | 526/3                                       |      | 534      | Skeletal bend                 |
|   |      |          |                               | 394/3                                       | 392  |          | Amide VII                     |
|   |      |          |                               | 266/3                                       | 264  |          | CD <sub>2</sub> torsion       |
|   |      |          |                               |   |      | 175      |                               |
|   |      |          |                               |   |      | 109      |                               |
|   |      |          |                               |   |      | 96       |                               |
| CH <sub>2</sub> CONDCD <sub>2</sub>         |      |          |                               | CD <sub>2</sub> CONDCD <sub>2</sub>         |      |          |                               |
| Exp. [11]                                   | A'   | Calc. A" | Assignment                    | Exp. [11]                                   | A'   | Calc. A" | Assignment                    |
| 1640/6                                      | 1647 |          | Amide I                       |   |      |          |                               |
| 1480/6                                      | 1484 |          | Amide II                      |   |      |          |                               |
| 1432/4                                      | 1440 |          | CH <sub>2</sub> as bend       |   |      |          |                               |
| 1473/6                                      |      | 1452     | CH <sub>2</sub> as bend       |   |      |          |                               |
| 1367/2                                      | 1365 |          | CH <sub>2</sub> sym bend      |   |      |          |                               |
| 1160/3                                      | 1167 |          | N—CH <sub>2</sub> stretch     |   |      |          |                               |
|   | 1065 |          | Amide III                     |   |      |          |                               |
|   |      | 1056     | CH <sub>2</sub> rock          |   |      |          |                               |
|   | 1045 |          | CD <sub>2</sub> as bend       |   |      |          |                               |
|   | 1009 |          | CD <sub>2</sub> sym bend      |   |      |          |                               |
| 966/4                                       | 992  |          | CH <sub>2</sub> rock          |   |      |          |                               |
|   | 937  |          | C—C stretch                   |   |      |          |                               |
| 773/3                                       | 777  |          | CD <sub>2</sub> rock          | 1635/6                                      | 1633 |          | Amide I                       |
| 890/4                                       |      | 884      | Amide VI                      | 1473/2                                      | 1468 |          | Amide II                      |
|   |      | 632      | Amide IV                      | 1174/6                                      | 1184 |          | N—CH <sub>2</sub> stretch     |
| 606/3                                       | 605  |          | Amide V                       | 1110/6                                      | 1097 |          |                               |
| 516/4                                       |      | 503      | Skeletal bend                 |   |      | 1048     |                               |
| 428/3                                       | 428  |          | Amide VII                     |   | 1047 |          | CD <sub>2</sub> bend,         |
|   | 274  |          | CH <sub>2</sub> torsion       |   | 1046 |          | C—C stretch,                  |
|   |      | 181      | CD <sub>2</sub> torsion       |   |      | 1045     | and Amide III                 |
|   |      | 144      | (strongly mixed)              | 1010/4                                      | 1022 |          |                               |
|   |      | 101      |                               | 980/4                                       | 991  |          |                               |
|   |      |          |                               | 950/4                                       | 931  |          |                               |
|   |      |          |                               | 912/3                                       |      | 910      | CD <sub>2</sub> (CO) rock     |
|   |      |          |                               | 815/4                                       | 825  |          |                               |
|   |      |          |                               |   |      | 873      | CD <sub>2</sub> (ND) rock     |
|   |      |          |                               | 746/4                                       | 741  |          |                               |
|   |      |          |                               | 573/3                                       | 566  |          | Amide IV                      |
|   |      |          |                               |   |      | 556      | Amide VI                      |
|   |      |          |                               | 506/3                                       |      | 498      | Amide V                       |
|   |      |          |                               | 396/3                                       | 390  |          | Skeletal bend                 |
|   |      |          |                               | 268/3                                       | 263  |          |                               |
|   |      |          |                               |   |      | 175      | Amide VII                     |
|   |      |          |                               |   |      | 109      | CD <sub>2</sub> torsion       |
|   |      |          |                               |   |      | 96       |                               |
| CD <sub>2</sub> CONHCD <sub>2</sub>         |      |          |                               | CD <sub>2</sub> CONDCD <sub>2</sub>         |      |          |                               |
| Exp. [11]                                   | A'   | Calc. A" | Assignment                    | Exp. [11]                                   | A'   | Calc. A" | Assignment                    |
| 1645/6                                      | 1650 |          | Amide I                       |   |      |          |                               |
| 1555/6                                      | 1540 |          | Amide II                      |   |      |          |                               |
| 1326/2                                      | 1323 |          | Amide III                     |   |      |          |                               |
| 1147/3                                      | 1140 |          | N—CH <sub>2</sub> stretch     |   |      |          |                               |
| 1098/4                                      | 1091 |          | CD <sub>2</sub> (CO) sym bend |   |      |          |                               |
|   | 1046 |          | C—C stretch                   |   |      |          |                               |
|   |      | 1048     | CD <sub>2</sub> (NH) as bend  |   |      |          |                               |
|   | 1046 | 1045     | CD <sub>2</sub> (CO) as bend  |   |      |          |                               |

quite ambiguous since amide III contributes significantly to several bands in the CH<sub>2</sub> wagging region. On the other hand, the previous notation, where we included the amide III band with the wagging sequence, was rather confusing. Further, we now denote the band at about 940 cm<sup>-1</sup> as C—C(=O) stretch instead of its previous inclusion with the *S* progression.

There are some frequencies which were not experimentally observed. Of greatest significance is the amide IV in polyamides, whose absence has for a long time been discussed by those studying the infrared spectra of polyamides. The present calculations show the somewhat surprising fact that this mode should lie in the 700 cm<sup>-1</sup>

region, rather than in the  $600\text{ cm}^{-1}$  region where it was expected. In the former region it is masked by the strong amide V band, and in the deuterated molecules an ambiguity occurs as to whether some unpronounced shoulders in the vicinity of  $R_1$  may belong to the remnants of nondeuterated molecules or to a weak amide IV' band. No amide VI' band was observed; calculation places it at  $604\text{ cm}^{-1}$  in nylons and at  $628\text{ cm}^{-1}$  in N-methylacetamide. The bands  $R_{n-1}$  in nylons are masked by C—C stretching bands and could not be located with certainty. The dependence of these frequencies on force constants is somewhat similar to that of the  $1045\text{ cm}^{-1}$  band of nylon 66, and since the latter is well assigned, we can have some confidence in the calculated values of the former frequencies. No data for skeletal torsions (with the exception of amide VII), and for skeletal bends below  $150\text{ cm}^{-1}$ , are available.

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