

Theoretical prediction of vibrational spectra. Scaled quantum mechanical (SQM) force field for fluorobenzene

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Abstract—The complete harmonic force field of fluorobenzene has been determined from *ab initio* Hartree–Fock calculations using the 4–21 Gaussian basis set. As force constants are systematically overestimated at this level of theory, the directly calculated force field was scaled by empirical factors taken over from benzene and methylfluoride. Except for a slight overestimation of the C–F stretching frequency, the scaled quantum mechanical (SQM) force field obtained in this way reproduces the experimental fundamental frequencies of the parent molecule and two deuterated isotopomers within 20 cm^{-1} (with mean deviations below 12 cm^{-1}), and experimental assignments are analyzed on this basis. Theoretical i.r. intensities reproduce the main features of the spectra fairly well.

INTRODUCTION

Fluorobenzene, $\text{C}_6\text{H}_5\text{F}$, as one of the simplest substituted aromatic systems, has been the subject of numerous spectroscopic and structural studies. Still, with the advent of increasingly reliable quantum chemical methods, it is of interest to determine its force field according to present-day standards, and on this basis to reinvestigate previous assignments of its vibrational spectra.

After scattered early studies, the basic comprehensive work on the vibrational spectra of fluorobenzene was done by SMITH *et al.* [1]. Based on their results, assignment of the spectra was investigated in detail by SCOTT *et al.* [2] and by WHIFFEN [3]. The i.r. and Raman spectra of the penta-deutero-derivative were first measured and analyzed by STEELE *et al.* [4]. A more recent high-resolution i.r. study by LIPP and SELISKAR [5] has dealt with the parent molecule, the pentadeutero- and *p*-deuterioisotopomers. A comprehensive work on the vibrational spectra of benzene derivatives, including fluorobenzene, has been published in a book by VARSÁNYI [6].

The most complete studies for the determination of the force field from experimental frequencies are due to STEELE and co-workers [7–9]. Normal co-ordinate calculations based on simplified force fields have also been published by KOROSTELEV and SVERDLOV [10, 11] and by KAHANE-PAILLOUS [12]. The first quantum chemical attempt to determine the force field of fluorobenzene is due to TÖRÖK *et al.* [13], who calculated the out-of-plane force constants at the semiempirical CNDO/2 level.

Recently, as discussed in several reviews [14–18], it has become increasingly realistic to calculate molecular force constants by reasonably accurate *ab initio* quantum chemical methods. Although sophisticated electron correlation calculations are also emerging, for

molecules of medium complexity like fluorobenzene, it is the self-consistent-field (SCF) Hartree–Fock method—with the use of a medium-sized basis set—which can be applied more or less routinely at present. As has been pointed out several times, force constants at this level of theory are obtained with the modest accuracy of 10–30% (equivalent to about 5–15% in the frequencies), which is obviously insufficient for a purely theoretical prediction of vibrational spectra. However, the errors are fairly systematic and can be accounted for by simple empirical adjustments, as was realized already in the earliest studies by PULAY and co-workers [13, 19, 20] and by BLOM and ALTONA [21]; for details see especially Ref. [16]. For the sake of uniformity we have recently suggested a standardized procedure [22]. In this, selection of reference geometry, definition of internal co-ordinates and scaling is performed in a well-defined scheme. As to scaling, a few scale factors are assigned to the various types of co-ordinates involved in the force constants and the theoretical force field is fitted to the experimental frequencies. We call the result of this combined theoretical–experimental approach the scaled quantum mechanical (SQM) force field [22].

For a purely *a priori* prediction of vibrational spectra, the theoretical force field of the molecule under investigation is scaled by factors taken over from related molecules, with the underlying idea that relative errors are better transferable than force constants themselves. Several studies in this and other laboratories have proved the viability of this approach on a number of molecules. In the present context, the successful prediction of the vibrational spectra of benzene-related molecules such as pyridine [23], aniline [24], toluene [25] and benzonitrile [26] is worth mentioning. All these investigations made use of a basic study on benzene [27].

The strategy outlined above is used in this paper for fluorobenzene: its complete (in-plane and out-of-plane) harmonic force field is calculated quantum

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chemically and then scaled empirically by scale factors, taken over from benzene and methylfluoride, to obtain the SQM force field. Changes in the force field of fluorobenzene compared with that of benzene will be investigated. Because of some ambiguities concerning choice of the best reference geometry, the molecular structure of fluorobenzene is also discussed briefly. Assignment of the vibrational spectra of C_6H_5F , p - C_6H_4DF and C_6D_5F is discussed in the light of the theoretical results. Infrared intensities are also presented.

COMPUTATIONAL DETAILS

Our standard scheme [28] was used in performing the calculations. This scheme is based on the gradient method of PULAY [14, 29] and uses the split-valence 4-21 basis set [28]. The actual calculations were made by the program TEXAS [30]. The geometry was optimized by force relaxation technique. Some empirical corrections (see below) were applied on the theoretically calculated geometry to obtain the reference configuration around which the force constants were evaluated. The latter were determined by calculating the forces (first derivatives) analytically for appropriately distorted geometries, and evaluating the second derivatives numerically. Scaling of the force constants was done as described previously [22]. The i.r. intensities were calculated from the theoretical dipole moment derivatives, the latter obtained numerically from the dipole moment vectors at the distorted geometries.

The internal co-ordinates used in the vibrational analysis are listed in Table 1. These were selected according to the recommendations of Ref. [28] and are the same as used for benzene itself [27]. Note the use of individual local co-ordinates as far as possible, while

defining the ring deformation co-ordinates based on full D_{6h} symmetry; redundancy is easily eliminated this way.

RESULTS AND DISCUSSION

Geometry

The geometry of fluorobenzene has been discussed in several papers and a detailed analysis is not the purpose of this study. Still, since the calculation of force constants is quite sensitive to the reference geometry chosen, it seemed worthwhile to discuss a few points.

In Table 2 several experimental [31, 32] and theoretical [33, 34] results are compiled. The last column designated as reference is the geometry used in this study for the evaluation of the force constants. In essentially a reproduction of the results of BOGGS *et al.* [33], this reference configuration was obtained in the following way. Using the same theoretical model as for the calculation of the force constants (Hartree-Fock model, 4-21 basis set) the theoretical equilibrium geometry was determined by complete optimization. Then, as suggested earlier, empirical corrections were used to estimate the true equilibrium distances from the theoretical results. Offset values of +0.011 Å and +0.005 Å were applied on the C-C and C-H bonds, respectively [28]. To obtain a similar correction for the C-F bond length we have also determined the theoretical geometry for methylfluoride, with the result of $r_e = 1.413$ Å. The best experimental estimate by DUNCAN [35] is $r_e = 1.382$ Å, which is also supported by high-level theoretical calculations including electron correlation either by Møller-Plesset perturbation theory [36] or by configuration interaction [37]. Comparison of the two values gives a difference of 0.031 Å, which was assumed to be transferable to

Table 1. Internal co-ordinates for fluorobenzene*

| No. | Internal co-ordinate | Description |
|--------------|---|---------------------------------|
| In-plane | | |
| 1 | r_1 | C-F stretching (C-F) |
| 2-6 | r_2, \dots, r_6 | C-H stretchings (C-H) |
| 7-12 | R_1, \dots, R_6 | C-C stretchings (C-C) |
| 13 | $\beta_1 = 2^{-1/2}(\varphi_1 - \varphi'_1)$ | C-F deformation (β C-F) |
| 14-18 | β_2, \dots, β_6 | C-H deformations (β C-H) |
| 19 | $q_{19} = 6^{-1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$ | b_{1u} ring deformation |
| 20 | $q_{20a} = 12^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$ | e_{2g} ring deformation |
| 21 | $q_{20b} = 1/2(\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6)$ | e_{2g} ring deformation |
| Out-of-plane | | |
| 22 | γ_1 | C-F wagging (γ C-F) |
| 23-27 | $\gamma_2, \dots, \gamma_6$ | C-H waggings (γ C-H) |
| 28 | $q_{28} = 6^{-1/2}(\delta_1 - \delta_2 + \delta_3 - \delta_4 + \delta_5 - \delta_6)$ | b_{2g} ring deformation |
| 29 | $q_{29a} = 1/2(-\delta_1 + \delta_3 - \delta_4 + \delta_6)$ | e_{2u} ring deformation |
| 30 | $q_{29b} = 12^{-1/2}(-\delta_1 + 2\delta_2 - \delta_3 - \delta_4 + 2\delta_5 - \delta_6)$ | e_{2u} ring deformation |

* See Fig. 1. γ_1 is the angle of the C-F bond with the $C_6C_1C_2$ plane, etc. All waggings are positive if the X (X = F/H) atom moves toward the positive z direction. δ_1 is the $C_6C_1C_2C_3$ dihedral angle, and so on cyclically. The sign of the torsional co-ordinates is defined according to E. B. WILSON, JR, J. C. DECIUS and P. C. CROSS, *Molecular Vibrations*, p. 60. McGraw-Hill, New York (1955).

Table 2. Structural results for fluorobenzene*

| Parameter | Experimental† | | Theoretical | | Reference‡ |
|---------------------|---------------|----------|-------------|--------------|------------|
| | MW [31] | ED [32] | 4-21 [33]‡ | 6-31G** [34] | |
| $r(C_1C_2)$ | 1.383 | 1.387 | 1.3746 | 1.3782 | 1.3856 |
| $r(C_2C_3)$ | 1.395 | 1.399 | 1.3833 | 1.3854 | 1.3943 |
| $r(C_3C_4)$ | 1.397 | 1.401 | 1.3848 | 1.3860 | 1.3958 |
| $r(C_1F_7)$ | 1.354 | 1.356(4) | 1.369 | 1.3311 | 1.339 |
| $r(C_2H_8)$ | 1.081 | 1.100(4) | 1.0693 | 1.0741 | 1.0743 |
| $r(C_3H_9)$ | 1.083 | | 1.0714 | 1.0757 | 1.0764 |
| $r(C_4H_{10})$ | 1.080 | | 1.0711 | 1.0747 | 1.0764 |
| $\angle(C_6C_1C_2)$ | 123.4 | 123.4(4) | 122.35 | 122.40 | 122.35 |
| $\angle(C_1C_2C_3)$ | 117.9 | 118.0(2) | 118.58 | 118.44 | 118.58 |
| $\angle(C_2C_3C_4)$ | 120.5 | 120.2(3) | 120.32 | 120.48 | 120.32 |
| $\angle(C_3C_4C_5)$ | 119.8 | 120.2(4) | 119.85 | 119.76 | 119.85 |
| $\angle(H_8C_2C_3)$ | 122.1 | — | 121.80 | 121.93 | 121.80 |
| $\angle(H_9C_3C_4)$ | 119.9 | — | 120.09 | 120.06 | 120.09 |

* Distances (r) in Ångströms, angles (\angle) in degrees. For numbering of atoms see Fig. 1.

† The following abbreviations are used: MW—microwave spectroscopy, ED—electron diffraction. The MW results are hybrid r_s and r_o values, the attachable uncertainties are probably less than 0.006 Å and 0.5° (e.g. the assumed shortening of 5×10^{-5} Å for both C–C and C–F bonds on ^{13}C substitution resulted in $r(\text{C–F}) = 1.348$ Å and $r(\text{C}_1\text{–C}_2) = 1.386$ Å). The ED distances are of r_p type, the differences between the C–C bond lengths were fixed, taken from the MW study.

‡ For comparison, the corresponding values in benzene, taken from Ref. [27], are: $r(\text{C–C}) = 1.3845$ Å, $r(\text{C–H}) = 1.0721$ Å.

§ Corrected theoretical geometry used in the force constant calculations; see text.

fluorobenzene in the form of a correction of -0.03 Å. This correction is in line with the offset value suggested by BOGGS *et al.* [33] based on vinylfluoride (-0.026 Å).

Inspection of Table 2 shows the familiar trends observed in the ring by fluorine substitution: the $C_6C_1C_2$ angle opens by $2-3^\circ$, while the $C_1\text{–}C_2$ bond is about 0.01 Å shorter than the other C–C distances or that in benzene at the same theoretical level (1.385 Å, Ref. [27]). Less attention has been paid in earlier theoretical results to the C–H bond lengths. At the 4-21 level the *ortho* C–H bond is about 0.002 Å shorter than the other two, these latter being practically equal. This is in complete accord with the experimental information obtained from overtone C–H stretching frequencies by GOUGH and HENRY [38].

Force field

Our results for the complete harmonic in-plane and out-of-plane force fields of fluorobenzene are compiled in Tables 3 and 4. To conserve space, in the construction of these tables we tried to avoid redundancy as far as possible; therefore several columns which follow from symmetry have been omitted. We emphasize again that, from the point of view of fluorobenzene, this SQM force field represents *a priori* results: the theoretical force constants were scaled by the scale factors of benzene (set II in Table VIII of Ref. [27]) using no experimental data on fluorobenzene itself. For force constants involving the C–F bond, only one new factor was introduced, that of scaling the C–F stretching. For this a value of 0.75 was obtained from separate force constant calculations on methylfluoride (see below), and this value was assumed to be

transferable to the aromatic system. The resulting force constant $F_{1,1}$ still may be slightly overestimated; this will be discussed in the section on frequencies. For the C–F in-plane bending and out-of-plane wagging the corresponding C–H scale factors were taken over from benzene (0.797 and 0.739, respectively), rounded off to 0.80 and 0.74, respectively.

In the following, we investigate the major changes occurring in fluorobenzene as compared with the parent benzene molecule. (For easier comparison, force constants of benzene obtained by the same method [27] are given in parentheses in Tables 3 and 4.) Qualitative comparison with the results of STEELE *et al.* [7-9] will also be discussed. Steele's results, derived by the "overlay" technique fitting a model force field simultaneously to several fluoroderivatives of benzene, represent the most general harmonic force field obtained on an experimental basis. Exact comparison of the two force fields is made difficult by their treatment of redundancy (they use a redundant system of co-ordinates and eliminate redundancy by constraining selected force constants to zero), but the main trends of the two results can be compared without difficulty.

Not surprisingly, fluorine substitution has a quite appreciable effect on the force constants of the ring skeleton. The C–C stretching force constant in *ortho* position, $F_{7,7}$ (Table 3) changes from 6.58 aJ \AA^{-2} in benzene to 6.77 aJ \AA^{-2} in fluorobenzene, an increase of $\Delta F \sim 0.2$, or about 3%. It is interesting to observe that this change is only about half of what could be expected from the change in the bond length: as compared with benzene $\Delta R = -0.010$ Å (see Table 2), from which—using the cubic anharmonicity of $f_{RRR} \sim$

Table 3. In-plane SQM force field of fluorobenzene*

| No.† | 1 (rC-F) | 2 (rC-H) | 3 (rC-H) | 4 (rC-H) | 7 (rC-C) | 8 (rC-C) | 9 (rC-C) | 13 (β C-F) | 14 (β C-H) | 15 (β C-H) | 16 (β C-H) | 19 (ring) | 20 (ring) | 21 (ring) |
|------|-------------|--------------------|-------------|-------------|--------------------|-------------|-------------|----------------------|----------------------|----------------------|----------------------|--------------|--------------|--------------|
| 1 | 6.198 | | | | | | | | | | | | | |
| 2 | 0.004 | 5.284 (5.176) | | | | | | | | | | | | |
| 3 | 0.013 | 0.012 (0.016) | 5.194 | | | | | | | | | | | |
| 4 | 0.001 | 0.002 (0.005) | 0.014 | 5.201 | | | | | | | | | | |
| 5 | 0.013 | 0.001 (0.001) | 0.003 | 0.014 | | | | | | | | | | |
| 6 | 0.004 | 0.002 (0.005) | 0.001 | 0.002 | | | | | | | | | | |
| 7 | 0.402 | 0.050 (0.079) | -0.008 | -0.024 | 6.771 (6.578) | | | | | | | | | |
| 8 | 0.003 | 0.070 (0.079) | 0.079 | -0.005 | 0.700 (0.710) | 6.589 | | | | | | | | |
| 9 | -0.102 | -0.005 (-0.002) | 0.078 | 0.079 | -0.423 (-0.407) | 0.718 | 6.524 | | | | | | | |
| 10 | -0.102 | -0.017 (-0.022) | -0.003 | 0.079 | 0.410 (0.425) | -0.400 | 0.715 | | | | | | | |
| 11 | 0.003 | -0.025 (-0.022) | -0.024 | -0.005 | -0.410 (-0.407) | 0.434 | -0.400 | | | | | | | |
| 12 | 0.402 | -0.005 (-0.022) | -0.020 | -0.024 | 0.712 (0.710) | -0.410 | 0.410 | | | | | | | |

Table 4. Out-of-plane SQM force field of fluorobenzene*

| No. | 22 (γ C-F) | 23 (γ C-H) | 24 (γ C-H) | 25 (γ C-H) | 28 (ring) | 29 (ring) | 30 (ring) |
|-----|-----------------------|-----------------------|-----------------------|-----------------------|------------------|------------------|------------------|
| 22 | 0.615 | | | | | | |
| 23 | -0.085 | 0.419 (0.439) | | | | | |
| 24 | -0.006 | -0.071 (-0.069) | 0.442 | | | | |
| 25 | -0.020 | 0.001 (-0.0003) | -0.068 | 0.432 | | | |
| 26 | -0.006 | -0.012 (-0.018) | -0.002 | -0.068 | | | |
| 27 | -0.085 | -0.001 (-0.0003) | -0.012 | 0.001 | | | |
| 28 | -0.186 | 0.141 (0.145) | -0.141 | 0.147 | 0.370 (0.376) | | |
| 29 | 0.193 | -0.070 (-0.073)† | -0.074 | 0.148 | 0.0005 (0.0) | 0.318 (0.316) | |
| 30 | 0.0 | -0.130 (-0.127)† | 0.133 | 0.0 | 0.0 (0.0) | 0.0 (0.0) | 0.334 (0.316) |

* See footnotes * and † to Table 3. Values in parentheses are the corresponding benzene force constants [27]. For a comparison with recent results on toluene [25], note that, apparently, the relative signs of the wagging and torsional coordinates are not always the same as those used here and in benzene.

† In the original paper [27] the force constant $\gamma_{1q_{29a}}$, which defines these terms, was quoted with the wrong sign.

-40 aJ Å⁻³, obtained as part of our present calculations—one would obtain $\Delta F \sim 0.4$ aJ Å⁻². Apparently, there is an inherent change in the form of the potential curve, which partly compensates for the increase caused by the shortening of the bond. In his results, derived from experimental frequencies, Steele lists four slightly different force fields (Table II of Ref. [9]). From chemical intuition, he also prefers those two force fields which show the expected increase in the C-C force constant upon fluorination; still, the result is less clear-cut because two other models—in which a reversed effect is found in this force constant—give equally good fit to the frequencies. The quantum chemical calculation proves now that Steele's choice was correct. The C-C force constants in *meta* and *para* positions, $F_{8,8}$ and $F_{9,9}$, respectively, change much less (< 1%).

Among the in-plane ring bending deformations (q_{19} - q_{21}) the force constant $F_{19,19}$, connected with the b_{1u} co-ordinate—a deformation which, by alternating changes in the angles, brings the ring from hexagonal to trigonal symmetry—is unchanged. The e_{2g} deformation force constant of benzene is split by +4% and -2% ($F_{20,20}$ and $F_{21,21}$, respectively) in the fluoroderivative.

As to the out-of-plane ring deformations (Table 4) the most significant change is found for $F_{30,30}$ (e_{2u}^2), which increases from 0.316 to 0.334, by 6%.

From the point of view of electronic structure of an aromatic system, the CC-CC coupling force constants are of special interest. In fluorobenzene these are practically the same as those in benzene, and show the trend *ortho* > *meta* ~ *para*. While in the first empirical force field of EATON and STEELE [7] the "Kekulé-constraint" *ortho* = *meta* = *para* was assumed, in the

refined force field [9], lifting these constraints, they obtained already the above trend. (It is interesting to note that in benzene itself this trend was questioned in a recent experimental study by OZKABAK *et al.* [39a] giving negligible *para* coupling; high-level quantum chemical calculations by PULAY [40] confirmed the earlier theoretical results on benzene, and, indeed, the discrepancy turned out to be the consequence of redundancy in the co-ordinate system chosen by OZKABAK *et al.* [39b].)

It is notable that changes outside the ring are comparable with those inside the ring. The C-H stretching force constant in *ortho* position, $F_{2,2}$, increases from 5.18 to 5.28 aJ Å⁻², or by 2%. In contrast to the C-C stretching, discussed above, this change can be explained purely by the change in the bond length (Table 2): $\Delta r = -0.003$ Å with a cubic constant $f_{rrr} = -35$ aJ Å⁻³ gives $\Delta F_{rr} \sim 0.1$ aJ Å⁻², in agreement with the explicit calculation. This trend was already correctly stated on an experimental basis by STEELE *et al.* [41]: from a study of the C-H stretching frequencies in a number of fluoroaromatics they suggested that fluorine substitution increases the *ortho* C-H stretching force constants by 1%. Our result suggests a stronger effect, which is indirectly supported by the spectroscopic work of GOUGH and HENRY [38]. They studied overtone ($\nu = 2-5$) C-H frequencies and, rather than calculating force constants, estimated the bond shortening from empirical correlation between frequencies and bond lengths. Their result of $\Delta r = -0.0026$ Å is in excellent accord with the theoretical result.

While the *ortho* C-H bond became shorter and stronger, it is interesting to see that it has become less stiff against both in-plane and out-of-plane angle

deformations. The in-plane bending force constant $F_{14,14}$ (Table 3) has decreased by about 8%, the out-of-plane wagging force constant $F_{23,23}$ (Table 4) by about 5%. In the empirical force field this effect was already recognized. In the in-plane field of STEELE [9], the average decrease is about 7%, in accord with our results. In the out-of-plane field [8] it is about 10%, qualitatively correct but apparently overestimated.

Although all of the above effects of fluorine substitution are relatively small, the excellent reproduction of the frequencies by our force field gives support to the above conclusions.

Frequencies and assignment

The theoretical frequencies obtained from the SQM force field of Tables 3 and 4 are compared with several assignments of the experimental spectra in Table 5. Similar results for the *p*-deutero and pentadeutero isotopomers are compiled in Table 6. The vibrational modes are numbered simply according to the order of frequencies obtained in this study. Reference to the "parent" modes in benzene—a practice used by some authors—is omitted because it would be too arbitrary in many cases. Characterization is based on the present theoretical results (using the *M* matrix criterion $M_{ip} = L_{ip}^{-1} L_{pi}$ [42], where *i* refers to a normal mode and *p* to an internal co-ordinate). The dominant internal co-ordinates are indicated by their serial numbers defined in Table 1.

Inspection of Tables 5 and 6 shows excellent overall agreement between theoretical and experimental frequencies. Before going into details of the assignment, however, we have to discuss a slight discrepancy concerning the C–F stretching frequency ν_6 . Based on experience of other molecules, we consider reproduction as good within about 20 cm^{-1} . This is fulfilled throughout the spectra except for some ambiguity in ν_6 . The calculated value of 1260 cm^{-1} in the parent molecule (Table 5) is definitely too high if we accept SMITH's assignment of 1220 cm^{-1} [1]. LIPP and SELISKAR [5] put the band origin already higher, to 1232 cm^{-1} , and, in addition, this was obtained after an estimated Fermi-resonance correction while their direct measured value was 1238 cm^{-1} . Taking this latter experimental value, our result is much better. (It should be noted at this point that in a recent review [17] we gave some preliminary results on fluorobenzene quoting a value of 1299 cm^{-1} for the C–F stretching frequency with the remark that the problem of such a serious overestimation was being investigated; we have indeed detected an error in the C–F force constant of our first calculations which caused the erroneous frequency.)

Still, considering all three isotopomers (see also Table 6) the C–F stretching frequency seems slightly overestimated in our calculations. This is not surprising because both adjustments in our procedure (geometry correction and force constants scaling) were based on methylfluoride, a system relatively far from fluorobenzene.

The C–F stretching scale factor was obtained in the following way. At the equilibrium bond length of $r_e = 1.382\text{ \AA}$ in methylfluoride, we calculated the C–F stretching force constant the same way as for fluorobenzene and obtained a value of $F_{th} = 7.32\text{ aJ \AA}^{-2}$. The average best experimental force constant is $F_{exp} = 5.65\text{ aJ \AA}^{-2}$ [43, 44], using harmonically corrected frequencies. Because in this study we consider direct measured (anharmonic) frequencies, the methylfluoride force constant corresponding to uncorrected frequencies should be used; this can be estimated from the previous value as $F = 5.50$. The latter compared with the theoretical value gave the scale factor $c = 5.50/7.32 \sim 0.75$. This is noticeably lower than typical stretching scale factors (values from 0.82 to 0.92 were found in Ref. [22]). When transferred to fluorobenzene, however, even this gives a slightly overestimated frequency.

The other uncertainty arises from the geometry correction, as stretching force constants are very sensitive to the selection of the reference bond length at which the force field is evaluated [16]. As mentioned above, our strategy for the selection of the reference C–F bond length was that, rather than accepting simply the microwave and electron diffraction results, we estimated it from our own theoretical calculations, using a correction of -0.03 \AA based on methylfluoride. This procedure resulted in $r = 1.339\text{ \AA}$ (Table 2). Considering that at this value the force constant (as judged from the frequency) is slightly too high, the true equilibrium bond length may be somewhere between this value and the experimental result of $1.356(4)\text{ \AA}$ [31, 32]. Thus our estimate is $r_e = 1.34\text{--}1.35\text{ \AA}$.

The above slight uncertainty concerning the C–F stretching does not affect the assignments as a whole. We start the discussion with $\text{C}_6\text{H}_5\text{F}$ and consider the other two isotopomers separately.

The first complete assignment for fluorobenzene- d_0 was given long ago by SMITH *et al.* [1]. Soon afterwards, reassignments were given by SCOTT *et al.* [2] and by WHIFFEN [3] (see Table 5). The latter two agree, except for ν_{16} in species b_2 , where Whiffen suggests a higher frequency at $1280\text{--}1290\text{ cm}^{-1}$, a weak i.r. band unassigned in Ref. [1], while Scott preserves the original assignment with ν_{16} at 1236 cm^{-1} (shoulder). Our calculated value of 1271 cm^{-1} is closer to Whiffen's suggestion. It may be noted about its character, however, that this is a fairly well-defined C–C stretching mode, rather than βCH given in Ref. [3]. According to the present calculation, it is the next highest frequency at $1310\text{--}1320\text{ cm}^{-1}$, which is predominantly a C–H bending.

In general, the calculated results clearly support the reassignments [2, 3]. The most striking point is ν_{14} , for which Smith's value of 874 cm^{-1} is far too low. Both Scott and Whiffen omitted this latter frequency among the fundamentals and used the 1156 cm^{-1} band twice (species a_1 and b_2). This is also confirmed by the calculation, as we calculate ν_5 and ν_{15} practically in

Table 5. Fundamental vibrational frequencies of fluorobenzene (in cm^{-1})

| No. | Calculated (SQM)* | | | Experimental assignment† | | | |
|--------------------------------------|-------------------|---------------------------------------|--|--------------------------|-----------|-------------|----------|
| | Frequency | i.r. int. (km mol^{-1}) | Characterization | SMITH [1] | SCOTT [2] | WHIFFEN [3] | LIPP [5] |
| <i>A</i> ₁ (in-plane) | | | | | | | |
| 1 | 512 | 3.61 | 20 (ring) | 519 | | | 517, m |
| 2 | 807 | 19.53 | 1 (C-F), 19 (ring), 8(C-C) | 808 | | | 809, s |
| 3 | 997 | 0.00 | 19 (ring) | 1008 | | | 1009, m |
| 4 | 1015 | 2.76 | 9(C-C), 19 (ring) | 1022 | | | 1023, m |
| 5 | 1161 | 3.61 | 14 (β C-H), 15 (β C-H) | 1157 | | | 1156, s |
| 6 | 1260 | 54.19 | 1 (C-F) | 1220 | | | 1238, vs |
| 7 | 1501 | 69.53 | 15 (β C-H), 1 (C-F) | 1499 | | | 1500, vs |
| 8 | 1616 | 54.01 | 8 (C-C), 7 (C-C) | 1596 | | | 1605, vs |
| 9 | 3064 | 0.02 | 4 (C-H), 3 (C-H) | 3044 | | 3036 | 3061 |
| 10 | 3090 | 17.43 | 4 (C-H), 3 (C-H) | 3067 | | 3049 | 3080 |
| 11 | 3109 | 0.01 | 2 (C-H) | 3101 | | 3065 | 3094 |
| <i>B</i> ₂ (in-plane) | | | | | | | |
| 12 | 387 | 3.90 | 13 (β C-F) | 405 | | | 400, m |
| 13 | 617 | 0.05 | 21 (ring) | 614 | | | 614 § |
| 14 | 1067 | 4.85 | 8 (C-C), 14 (β C-H) | 874 | 1066 | 1065 | 1066, m |
| 15 | 1163 | 0.65 | 16 (β C-H), 15 (β C-H), 9 (C-C) | 1066 | 1157‡ | 1156‡ | 1128, vw |
| 16 | 1271 | 0.24 | 7 (C-C), 9 (C-C) | 1236 | | 1282 | 1301, vw |
| 17 | 1314 | 1.00 | 14 (β C-H), 15 (β C-H) | 1323 | | | — |
| 18 | 1456 | 2.96 | 16 (β C-H), 8 (C-C) | 1460 | | | 1460 |
| 19 | 1607 | 13.17 | 7 (C-C), 9 (C-C) | 1603 | | 1592 | 1605 § |
| 20 | 3075 | 11.12 | 3 (C-H) | 3058 | | 3049‡ | 3069 |
| 21 | 3107 | 4.53 | 2 (C-H) | 3091 | | 3065‡ | — |
| <i>B</i> ₁ (out-of-plane) | | | | | | | |
| 22 | 237 | 0.80 | 22 (γ C-F) | 242 | | | 249, s |
| 23 | 493 | 4.07 | 22 (γ C-F), 29 (δ ring) | 500 | | | 498, s |
| 24 | 683 | 23.15 | 28 (δ ring) | 685 | | | 687, s |
| 25 | 748 | 92.78 | 25 (γ C-H), 22 (γ C-F) | 754 | | | 754, vs |
| 26 | 900 | 18.22 | 23 (γ C-H), 25 (γ C-H) | 826 | 894 | 896 | 895, s |
| 27 | 985 | 0.86 | 25 (γ C-H), 24 (γ C-H) | 894 | 997 | 982 | 978, w |
| <i>A</i> ₂ (out-of-plane) | | | | | | | |
| 28 | 411 | — | 30 (δ ring) | (330) | 405‡ | (400) | 414 |
| 29 | 826 | — | 23 (γ C-H), 24 (γ C-H) | 818 | 826 | 831 | 818 |
| 30 | 967 | — | 24 (γ C-H), 23 (γ C-H) | 955 | 970 | 955 | 957 |

* Results of the present study, obtained from the force field given in Tables 3 and 4. In the approximate characterization of a normal mode, co-ordinates dominant according to the *M*-matrix [42] criterion are indicated by their serial number defined in Table 1.

† In the case of Scott's and Whiffen's assignments, since they are based on Smith's data, only the changes relative to Smith's assignment are indicated. Note that early papers used different convention for species notation which means interchanging *B*₁ and *B*₂. Qualitative i.r. intensities are indicated by the usual notation, taken from Lipp. Values in parentheses were estimated in the original papers.

‡ Frequency used a second time.

§ Taken from Ref. [45].

|| H-bending mode in benzene.

coincidence (1161 and 1163 cm^{-1} , respectively). The strongest contributions to these modes are given by C-H bendings. As to the out-of-plane modes, again we agree with the reassignments which added a frequency around 990 cm^{-1} to the *b*₁ fundamentals (ν_{27} in Table 5), while putting the 826 cm^{-1} band into species *a*₂.

A more recent, high-resolution study by LIPP and SELISKAR [5] has proposed several reassignments. As noted above, they put the band origin for ν_6 at a somewhat higher frequency than previous studies. More significantly, they suggest some changes in the medium-frequency range in species *b*₂. Rather than using the 1156 cm^{-1} band twice (see above), they suggest a very weak band at 1128 cm^{-1} to be a

fundamental. As another significant change, they emphasize that their 1327 cm^{-1} band appears to exhibit an A-type contour and thus should belong to species *a*₁. Correspondingly, they assign it to a combination, as $517 + 809 \text{ cm}^{-1}$. Note that Smith *et al.* already introduced this combination as a component contributing to the band structure in this region, but they, as well as Scott and Whiffen later, assigned here a fundamental, too. From our calculation one conclusion is clear: a *b*₂ fundamental (ν_{17}) is expected—with fairly low intensity—in this region. Lipp and Seliskar also list the *b*₂ fundamental around 1600 cm^{-1} (ν_{8b} based on the benzene notation, ν_{19} here) as unobserved, while previous studies listed this frequency

Table 6. Fundamental vibrational frequencies of *p*-C₆H₄DF and C₆D₅F (in cm⁻¹)*

| No. | <i>p</i> -C ₆ H ₄ DF | | C ₆ D ₅ F | | |
|--------------------------------------|--|----------|---------------------------------|------------------|------|
| | Calc. | Exp. [5] | Calc. | Experimental [4] | [5] |
| <i>A</i> ₁ (in-plane) | | | | | |
| 1 | 507 | 513 | 498 | 505 | 503 |
| 2 | 805 | 807 | 747 | 753 | 753 |
| 3 | 979 | 991 | 819 | 817 | 820 |
| 4 | 1013 | 1022 | 868 | 880 | 877 |
| 5 | 1161 | 1156 | 954 | 959 | 964 |
| 6 | 1260 | 1239 | 1184 | 1163 | 1172 |
| 7 | 1494 | 1493 | 1404 | 1389 | 1396 |
| 8 | 1613 | 1600 | 1585 | 1578 | 1579 |
| 9 | 2278 | 2274† | 2260 | 2270‡ | — |
| 10 | 3075 | — | 2288 | 2275‡ | 2291 |
| 11 | 3108 | — | 2305 | 2295 | — |
| <i>B</i> ₂ (in-plane) | | | | | |
| 12 | 386 | 400‡ | 369 | 388 | 385 |
| 13 | 611 | 608§ | 592 | 590 | 592§ |
| 14 | 871 | 1036‡ | 807 | 806 | 807 |
| 15 | 1097 | 1093 | 844 | 843 | 843 |
| 16 | 1265 | 1289 | 1031 | 1035 | 1035 |
| 17 | 1300 | — | 1264 | 1281 | — |
| 18 | 1409 | 1415 | 1330 | 1311 | 1312 |
| 19 | 1601 | — | 1574 | 1564 | — |
| 20 | 3075 | 3062 | 2274 | 2266‡ | 2281 |
| 21 | 3107 | — | 2301 | 2276‡ | — |
| <i>B</i> ₁ (out-of-plane) | | | | | |
| 22 | 228 | 248 | 223 | 229 | 234 |
| 23 | 485 | 492 | 425 | 438 | 427 |
| 24 | 597 | 603 | 542 | 563 | 553 |
| 25 | 717 | 716 | 620 | 627 | 625 |
| 26 | 851 | 851 | 757 | 717 | 759 |
| 27 | 953 | 922 | 828 | 825‡ | — |
| <i>A</i> ₂ (out-of-plane) | | | | | |
| 28 | 411 | 414 | 358 | 350 | 362 |
| 29 | 826 | 818 | 642 | 682¶ | 636 |
| 30 | 967 | 957 | 786 | 789‡ | 776 |

* See footnotes to Table 5.

† See text.

‡ Approximate value.

§ Data taken from Ref. [45].

|| According to the inequality rule this frequency was estimated as lying between 789 and 711 cm⁻¹, then a very weak type C band at 717 cm⁻¹ was assigned.

¶ Absent in the vapour spectrum, appears only in liquid phase.

twice, in both in-plane symmetry species. Although there is no basic difference between the two points of view, it is of interest to observe that, according to the calculations, the splitting is indeed small, with $\nu_8 = 1616$ and $\nu_{19} = 1607$ cm⁻¹.

In conclusion, the reassignments of SCOTT *et al.* [2] and WHIFFEN [3], as compared with Smith *et al.*'s result [1], are confirmed by the present study, while the further modifications suggested by LIPP and SELISKAR [5] are not supported.

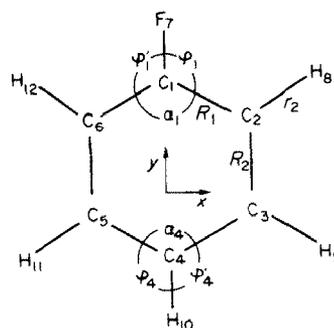
As to *p*-deuteriofluorobenzene (Table 6), the present calculations support the fundamentals selected by LIPP and SELISKAR [5], with the only exception of ν_{14} : the calculations suggest a band at around 871 cm⁻¹,

while they gave 1036 cm⁻¹. It is even qualitatively clear that there must be a β CD frequency somewhere below 900 cm⁻¹, so the selection of LIPP and Seliskar must have been a mistake. Indeed, the above estimation of ν_{14} was omitted in their paper on the vibronic spectrum of fluorobenzene [45].

The perdeuterated isotopomer C₆D₅F has been measured, with a complete assignment given, by STEELE *et al.* [4]. In the more recent reinvestigation by LIPP and SELISKAR [5], there are only two noticeable differences: the assignments of ν_{26} and ν_{29} (in our notation) have been slightly modified. In both cases our calculation supports the modifications, but otherwise confirms that Steele's early assignment was already correct.

Infrared intensities

Infrared intensities are based on the calculated dipole moment derivatives. From the structural point of view the most interesting analysis could be done at the level of these derivatives, rather than in terms of intensities. However, derivatives are very difficult to determine experimentally, so that a detailed analysis is not possible and we have not compiled them. Still, with reference to pioneering works of STEELE and WHIFFEN [46], a few points are worth mentioning. These authors have determined the basic dipole moment derivatives of several fluorobenzenes (fluorobenzene itself was not treated) from experimental i.r. intensities. For the C–F stretching they obtained a dipole gradient ranging from -5.0 to -6.5 D/Å in the various fluorobenzenes. (Negative sign indicates C⁺F⁻ polarity in terms of bond moment hypothesis.) Our result is -5.3 D/Å. The C–H stretching dipole moment derivatives of Steele and Whiffen are in the range from ~ 0.0 to -0.45 D/Å (the latter value is for benzene). Our values are as follows: *ortho* = -0.21 , *meta* = -0.42 , *para* = -0.45 D/Å. The basic results of the early experimental study are thus confirmed. It is of general interest to note that the polarity of the C–H bonds is C⁺H⁻ in stretchings, and C⁻H⁺ in all (in- and out-of-plane) bendings. This has already been observed in simple hydrocarbons as, for example, in ethylene [47]. A detailed analysis of M–H bond



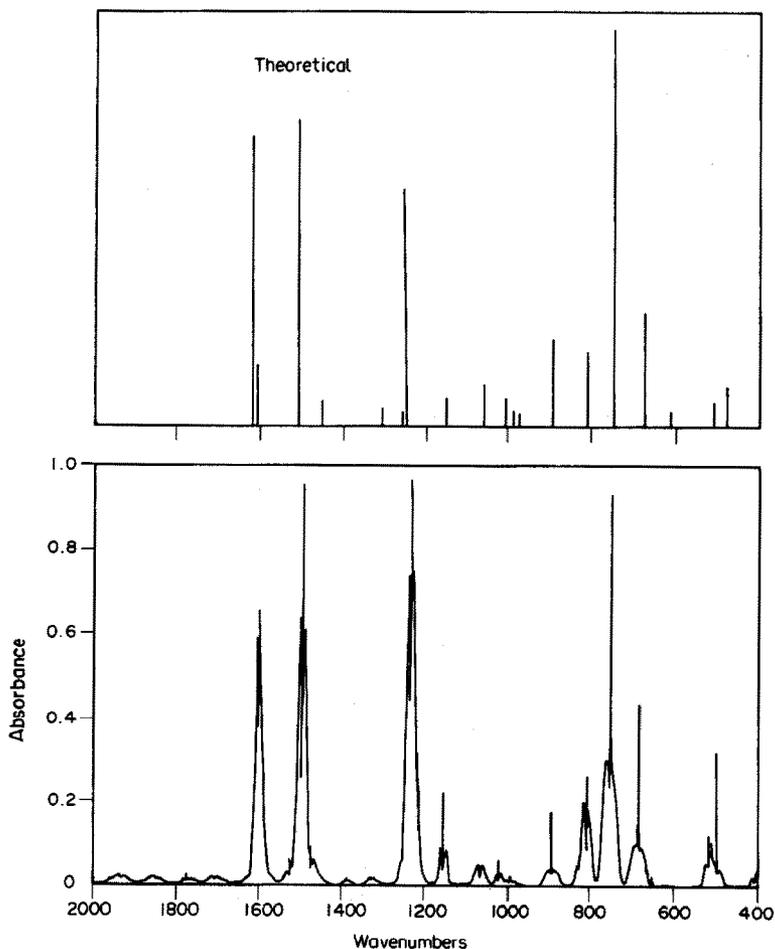


Fig. 2. Experimental and theoretical i.r. spectrum of fluorobenzene.

moments has been given recently by WIBERG and WENDOLOSKI [48].

The i.r. intensities, calculated from the theoretical (unadjusted) dipole moment derivatives and the scaled theoretical force field of Tables 3 and 4, are listed as part of Table 5. To give a better view we have also compared the theoretical and measured spectra in Fig. 2. As can be seen, the main features—relative intensities on a semiquantitative scale as normally used in spectroscopy—are very well reproduced. Specifically, it can be noticed that among the in-plane vibrations the a_1 modes are generally more intense than the b_2 modes, obviously due to a mixing in of the strongly polar C–F stretching. As an even more characteristic feature, the high intensity of the out-of-plane vibrations is also reproduced. Thus, although the calculated intensities are approximate—notably they are very sensitive to basis set truncation—they certainly can help to make assignments more reliable.

CONCLUSION

The present study is hoped to have demonstrated again that *ab initio* quantum chemical calculations are

of practical use for vibrational spectroscopy. The scaled quantum mechanical (SQM) force field of fluorobenzene, obtained from the direct calculated values by scaling them with empirical scale factors taken over from benzene and methylfluoride, may be considered as the best harmonic force field available. Steele's pioneering results based on detailed experimental work are basically confirmed. The calculated frequencies of the parent molecule support the classic assignments of SCOTT *et al.* [2] and of WHIFFEN [3], but do not confirm the modifications suggested recently by LIPP and SELISKAR [5]. Assignments for two deuterated isotopomers are also basically confirmed.

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REFERENCES

- [1] D. C. SMITH, E. E. FERGUSON, R. L. HUDSON and J. R. NIELSEN, *J. chem. Phys.* **21**, 1475 (1953).
- [2] D. W. SCOTT, J. P. McCULLOUGH, W. D. GOOD, J. F. MESSERLY, R. E. PENNINGTON, T. C. KINCHELOE, I. A. HOSSENLOPP, D. R. DOUSLIN and G. WADDINGTON, *J. Am. chem. Soc.* **78**, 5457 (1956).
- [3] D. H. WHIFFEN, *J. chem. Soc.* 1350 (1956).
- [4] D. STEELE, E. R. LIPPINCOTT and J. XAVIER, *J. chem. Phys.* **33**, 1242 (1960).
- [5] E. D. LIPP and C. J. SELISKAR, *J. molec. Spectrosc.* **73**, 290 (1978).
- [6] GY. VARSÁNYI, *Vibrational Spectra of Benzene Derivatives*. Akadémiai Kiadó, Budapest, and Academic Press, New York (1969).
- [7] V. J. EATON and D. STEELE, *J. molec. Spectrosc.* **48**, 446 (1973).
- [8] R. A. R. PEARCE, D. STEELE and K. RADCLIFFE, *J. molec. Struct.* **15**, 409 (1973).
- [9] V. J. EATON and D. STEELE, *J. molec. Spectrosc.* **54**, 312 (1975).
- [10] YU. S. KOROSTELEV and L. M. SVERDLOV, *Zh. Prikl. Spekt.* **XVI**, 850 (1972).
- [11] YU. S. KOROSTELEV, N. A. KOROSTEVA and L. M. SVERDLOV, *Zh. Prikl. Spekt.* **XXXI**, 1082 (1979).
- [12] J. KAHANE-PAILLOUS, *J. Chim. phys.* **57**, 1048 (1960).
- [13] F. TÖRÖK, HEGEDŰS, K. KÓSA and P. PULAY, *J. molec. Struct.* **32**, 93 (1976).
- [14] P. PULAY, in *Modern Theoretical Chemistry*, (edited by H. F. SCHAFER III), Vol. 4, pp. 153–185. Plenum, New York (1977).
- [15] G. FOGARASI and P. PULAY, in *Annual Review of Physical Chemistry* (edited by B. S. RABINOVITCH), Vol. 35, pp. 191–213. Annual Reviews, Palo Alto (1984).
- [16] G. FOGARASI and P. PULAY, in *Vibrational Spectra and Structure* (edited by J. R. DURIG), Vol. 14, pp. 125–219. Elsevier, Amsterdam (1985).
- [17] G. FOGARASI and P. PULAY, *J. molec. Struct.* **141**, 145 (1986).
- [18] B. A. HESS, JR, L. J. SCHAAD, P. ČÁRSKY and R. ZAHRADNÍK, *Chem. Rev.* **86**, 709 (1986).
- [19] P. PULAY and W. MEYER, *Molec. Phys.* **27**, 473 (1974).
- [20] G. FOGARASI and P. PULAY, *J. molec. Struct.* **39**, 275 (1977) and references therein.
- [21] C. E. BLOM and C. ALTONA, *Molec. Phys.* **31**, 1377 (1976).
- [22] P. PULAY, G. FOGARASI, G. PONGOR, J. E. BOGGS and A. VARGHA, *J. Am. chem. Soc.* **105**, 7037 (1983).
- [23] (a) G. PONGOR, P. PULAY, G. FOGARASI and J. E. BOGGS, *J. Am. chem. Soc.* **106**, 2765 (1984); (b) G. PONGOR, G. FOGARASI, J. E. BOGGS and P. PULAY, *J. molec. Spectrosc.* **114**, 445 (1985).
- [24] Z. NIU, K. M. DUNN and J. E. BOGGS, *Molec. Phys.* **55**, 421 (1985).
- [25] Y. XIE and J. E. BOGGS, *J. comput. Chem.* **7**, 158 (1986).
- [26] A. G. CSÁSZÁR and G. FOGARASI, to be published.
- [27] P. PULAY, G. FOGARASI and J. E. BOGGS, *J. chem. Phys.* **74**, 3999 (1981).
- [28] P. PULAY, G. FOGARASI, F. PANG and J. E. BOGGS, *J. Am. chem. Soc.* **101**, 2550 (1979).
- [29] P. PULAY, *Molec. Phys.* **17**, 197 (1969).
- [30] P. PULAY, *Theor. chim. Acta* **50**, 299 (1979).
- [31] (a) B. BAK, D. CHRISTENSEN, L. HANSEN-NYGAARD and E. TANNENBAUM, *J. chem. Phys.* **26**, 134 (1957); (b) L. NYGAARD, I. BOJESEN, T. PEDERSEN and J. RASTRUP-ANDERSEN, *J. molec. Struct.* **2**, 209 (1968).
- [32] G. PORTALONE, GY. SCHULTZ, A. DOMENICANO and I. HARGITTAI, *J. molec. Struct.* **118**, 53 (1984).
- [33] J. E. BOGGS, F. PANG and P. PULAY, *J. comput. Chem.* **3**, 344 (1982).
- [34] (a) C. W. BOCK, M. TRACHTMAN and P. GEORGE, *J. molec. Struct. (Theochem)* **122**, 155 (1985); (b) C. W. BOCK, M. TRACHTMAN and P. GEORGE, *J. comput. Chem.* **6**, 592 (1985).
- [35] J. L. DUNCAN, *J. molec. Struct.* **6**, 477 (1970).
- [36] S. KONDO, Y. KOGA and T. NAKANAGA, *J. chem. Phys.* **81**, 1951 (1984).
- [37] G. FOGARASI and P. PULAY, unpublished results; see related partial results in [16], p. 201.
- [38] K. M. GOUGH and B. R. HENRY, *J. Am. chem. Soc.* **106**, 2781 (1984).
- [39] (a) A. G. OZKABAK, L. GOODMAN, S. N. THAKUR and K. KROGH-JESPERSEN, *J. chem. Phys.* **83**, 6047 (1985); (b) Erratum: *J. chem. Phys.* **85**, 2346 (1986).
- [40] P. PULAY, *J. chem. Phys.* **85**, 1703 (1986).
- [41] E. B. GILL, D. STEELE and N. D. PERKINS, *J. molec. Struct.* **38**, 33 (1977).
- [42] (a) P. PULAY and F. TÖRÖK, *Acta chim. hung.* **44**, 287 (1965); (b) G. KERESZTURY and G. JALSOVSZKY, *J. molec. Struct.* **10**, 304 (1971).
- [43] C. E. BLOM and A. MULLER, *J. molec. Spectrosc.* **70**, 449 (1978).
- [44] J. L. DUNCAN, D. C. MCKEAN and G. K. SPEIRS, *Molec. Phys.* **24**, 553 (1972).
- [45] E. D. LIPP and C. J. SELISKAR, *J. molec. Spectrosc.* **87**, 255 (1981).
- [46] (a) D. STEELE and D. H. WHIFFEN, *J. chem. Phys.* **29**, 1194 (1958); (b) D. STEELE and D. H. WHIFFEN, *Trans. Faraday Soc.* **56**, 177 (1960).
- [47] G. FOGARASI and P. PULAY, *Acta chim. hung.* **108**, 55 (1981).
- [48] K. B. WIBERG and J. J. WENDOLOSKI, *J. phys. Chem.* **88**, 586 (1984).