Chapter 5.
Ground-state Molecular Structure

5.1 Chlorobenzene

Electron diffraction was conducted on the ground state of chlorobenzene in the UED apparatus at 428 K. The ratio image, $R^N(x,y)$, is shown in Fig. 5-1. A fit of experimental and theoretical CO_2 diffraction data was used to find a camera length of 13.52 cm. The data in the range of s = 4.24 – 17.68 Å^{-1} were used in the refinement. It was found that data below s = 4.24 Å^{-1} caused problems with the modeling of the polynomial background by introducing an oscillation. Chlorobenzene was chosen as a candidate for experimentation because of the possibility of seeing the detachment of the chlorine atom after photoexcitation. Furthermore, it contains a heavy atom (chlorine) with a large scattering cross-section that would show clearly its presence (or lack thereof) in a molecule. Due to an insufficient absorption cross-section, the time-resolved UED experiment was not successful.

The theoretical model used in the structural refinement was in z-matrix format:

C1						
C2	C1	r1				
C3	C2	r2	C1	a1		
C4	C3	r3	C2	a2	C1	d1
C5	C4	r3	C3	a3	C2	d2
C6	C5	r2	C4	a2	C3	d3
H7	C2	r4	C1	a4	C6	d4
H8	C3	r5	C2	a5	C1	d5
H9	C4	r6	C5	a6	C6	d6
H10	C5	r5	C6	a5	C1	d5
H11	C6	r4	C1	a4	C2	d4
Cℓ	C1	r7	C6	a7	C2	d7

Parameters for the initial geometry were taken from density functional theory (DFT) calculations at the B3LYP/6-311G(d,p) level. During the refinement a data scale factor [λ in Eq. (4-15)] of 0.6393 was obtained. The refinement was conducted independently three times to ensure that the results were reproducible. One of the three refinements produced bond parameters that were not consistent with the structure of an aromatic ring in a ground-state molecule. The refinement chosen as the best representative of the structure was the one with the smallest error bars.

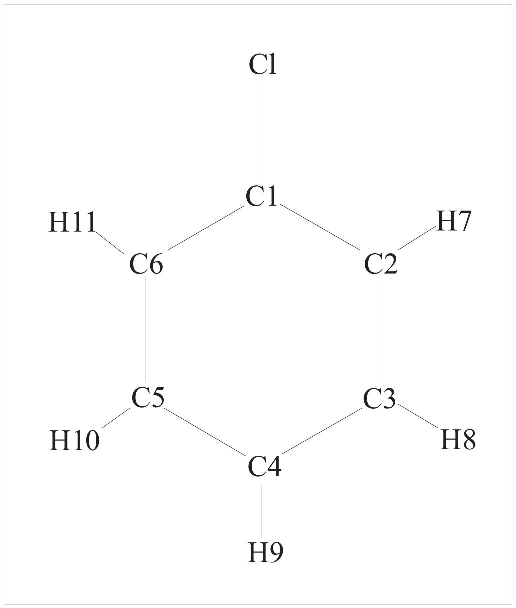

Fig. 5-2 shows the refined theoretical $sM(s)$ and $f(r)$ along with the experimental data. The refinement resulted in a χ^2 value of 233.021 and $R = 0.110$, both reasonable values for a UED ground-state refinement. The $sM(s)$ curve is difficult to dissemble intuitively, but the $f(r)$ curve shows some interesting features. The heavy chlorine atom makes the direct C–Cl bond at ~1.7 Å, the next-nearest-neighbor distance at ~2.7 Å, and the third-nearest-neighbor distance at ~4 Å quite obvious. The bars shown in the $f(r)$ plot are proportional to $\frac{n_{ij}Z_iZ_j}{r_{ij}}$ [see Eq. (2-14)]. Discrepancy between theoretical and experimental curves is not easily explained, but may be a consequence of the model that was held at near-C_{2v} symmetry as suggested by DFT. It's possible that, because of the large Z possessed by the Cl atom, effects such as effective distance shrinkage played a larger role and were not accounted for by the UED theoretical methodology.

Table 5-1. The refined structure of chlorobenzene

Parameters (Å, º)	UED	Ref. 1	Ref. 2 (r_g)	Theoretical
r(C1-C2)	1.391±0.060	1.391	1.400	1.391
r(C1-C6)	1.400*	1.391	1.400	1.391
r(C2-C3), r(C5-C6)	1.393±0.023	1.394	1.400	1.393
r(C3-C4), r(C4-C5)	1.393±0.033	1.400	1.400	1.393
r(C1-Cl)	1.724±0.004	1.739	1.737	1.762
r(C2-H7), r(C6-H11)	-	1.078	1.083	1.082
r(C3-H8), r(C5-H10)	-	1.087	1.083	1.084
r(C4-H9)	-	-	1.083	1.084
a(C6-C1-C2)	121.2*	121.7	121.7	121.4
a(C1-C2-C3)	119.1±3.1	119.1	-	118.9
a(C5-C6-C1)	118.9*	119.1	-	118.9
a(C2-C3-C4), a(C4-C5-C6)	120.3±2.7	120.2	-	120.4
a(C3-C4-C5)	120.1±1.6	119.8	120.4	119.8
a(Cl-C1-C6)	119.2±11.2	-	-	119.3
a(H7-C2-C1), a(H11-C6-C1)	-	119.7	-	120.0
a(H8-C3-C2), a(H10-C5-C6)	-	120.4	-	119.4
a(H9-C4-C5)	-	-	-	120.1

Table 5-1 presents the refined structural parameters of chlorobenzene along with those obtained through DFT calculations and by previous electron diffraction experiments.[1,2] Error bars reported herein are 3σ. One previous published account of the structure of chlorobenzene is based on a model refined to electron diffraction, microwave, and solution-phase NMR data.[1] The authors note that the structures obtained for each method were nearly identical, regardless. The agreement between Cradock *et al.*'s results, Penionzhkevich *et al.*'s results, the UED results, and the DFT structure is good, with nearly all parameters falling within error bars of one another. The exception is the C–Cl distance. Its weight in the UED data furnishes it with a small uncertainty in the refinement – too small to cover the deviation with both the value reported by previous electron diffractionists and that of DFT. It is interesting to note, however, that both UED and the other electron diffraction experiments favor a C–Cl bond significantly shorter than that predicted by DFT, pointing out a shortcoming of the theory.[1,2] Although seemingly not available in the literature, it would be interesting to explore this overestimation using different theoretical methods and basis sets.

In addition to χ^2 and R, quality of the fit is also rated by the dependent parameters. In this molecule r(C1-C6), a(C6-C1-C2), and a(C5-C6-C1) were not explicitly fit, but instead allowed to drift with the changes in the other parameters (marked with asterisks in Table 5-1). If an incorrect model is used, these dependent parameters often change to unphysical values. In the refinement of the chlorobenzene molecular structure, the dependent parameters remained consistent with DFT. Cradock *et al.* also used dependent parameters in their structural refinement. Their dependent bonds were derived from a single refined average ring C–C distance, a frequent strategy in electron diffraction.[1] Penionzhkevich *et al.*'s refinement was further constrained simply using one value for all C–C distances.[2]

5.2 Bromobenzene

Picked as a candidate for UED inquiry for the same reasons as chlorobenzene above, bromobenzene provided an even more exaggerated look at diffraction from an organic molecule containing a heavy atom, bromine being twice as massive as chlorine. Bromobenzene was introduced into the UED apparatus through the effusive jet nozzle held at 438 K. The ratio image is shown in Fig. 5-1. A fit of experimental and theoretical CO_2 diffraction data was used to find a camera length of 13.37 cm. The data in the range of s = 3.04 – 14.65 Å^{-1} were used in the refinement. Both the upper and lower bounds of the s range are typical numbers in UED experiments. The upper bound was set because, at larger *s*, the polynomial background failed to correct the data to the theoretical baseline. A higher upper bound was initially attempted in the refinement (16.16 Å^{-1}) but the resulting structure differed significantly (two C–C bonds shrunk by 0.06 Å).

As in chlorobenzene, a C_{2v} z-matrix was used in the refinement. For this molecule it was retooled in order to reflect true C_{2v} symmetry instead of the "shortcut" z-matrix implemented above.

```
C1
Br   C1   r1
C2   C1   r2   Br   a1
C3   C1   r2   C2   360-2*a1    Br   d1
C4   C2   r3   C1   a2          Br   d2
C5   C3   r3   C1   a2          Br   d3
C6   C1   r4   C2   180-a1      Br   d4
H7   C2   r5   C1   (360-a2)/2  C4   d5
H8   C3   r5   C1   (360-a2)/2  C5   d6
H9   C4   r6   C2   a3          C6   d7
H10  C5   r6   C3   a3          C6   d7
H11  C6   r7   C1   a4          Br   d8
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Parameters defining the initial geometry were taken from DFT calculations at the B3LYP/6-311G(d,p) level. The refinement was conducted seven independent times to ensure a robust minimum configuration. In this case, two minima were found that were close enough to the geometry predicted by theory that both are reported here. An experimental data scaling factor of $\lambda = 1.0364$ was obtained.

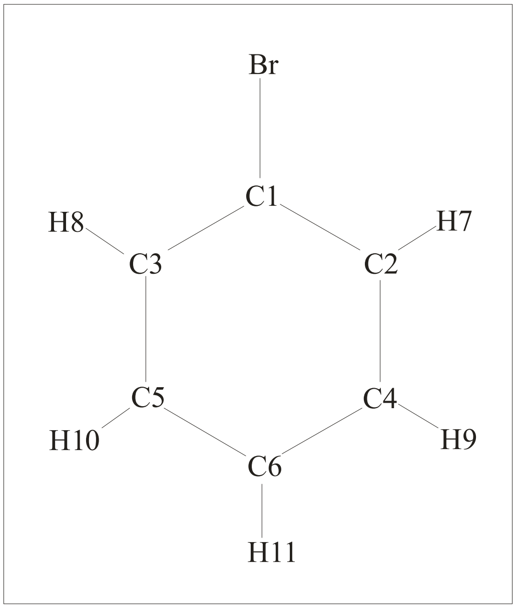


Table 5-2 shows the UED refined structural parameters of bromobenzene (Minimum A and Minimum B) along with the results of a previous gas-phase electron diffraction experiment.[3] Almenningen *et al.*'s values are r_a values [see Eq. (2-9)], but the comparison with UED's r_e will be valid since the differences ($r_e < r_a$) are in the third decimal place and beyond the precision of UED. Both Minimum A and Minimum B fit the data with $\chi^2 = 70.166$ and $R = 0.061$. This is an interesting example of the ambiguity present in electron diffraction data analysis. Since the molecular intensity data are made up of broad peaks composed of numerous sinusoidal interference components, multiple solutions always exist. In every set of data there normally exists one minimum that makes physical and chemical sense (the correct solution) and at least one minimum that is wildly different than the expected structure and can be discarded from further consideration immediately. In the case outlined here for bromobenzene, the choice is somewhat less clear.

Table 5-2. The refined structure of bromobenzene

parameters	Minimum A value (Å, º)	Minimum B value (Å, º)	Ref. 3	Theoretical
r(C1-C2), *r*(C1-C3)	1.375±0.005	1.392±0.007	1.394	1.391
r(C2-C4), *r*(C3-C5)	1.362±0.008	1.393±0.008	1.395	1.394
r(C1-C6)	2.798±0.014	2.796±0.015	-	2.773
r(C4-C6), *r*(C5-C6)	1.407*	1.358*	1.394	1.393
r(C1-Br)	1.845±0.004	1.844±0.004	1.898	1.920
r(C2-H7), *r*(C3-H8)	-	-	1.098	1.082
r(C4-H9), *r*(C5-H10)	-	-	1.087	1.084
r(C6-H11)	-	-	1.086	1.083
a(C3-C1-C2)	116.9±0.9	119.2±0.8	121.4	121.5
a(C1-C2-C4), *a*(C1-C3-C5)	123.1±1.0	118.9±1.1	119.0	118.9
a(C2-C4-C6), *a*(C3-C5-C6)	119.1*	122.5*	-	120.5
a(C4-C6-C5)	118.7*	118.1*	-	119.8
a(H7-C2-C1), *a*(H8-C3-C1)	118.5*	120.6*	122.2	120.3
a(H9-C4-C3), *a*(H10-C5-C3)	-	-	120.9	119.3
a(H11-C6-C1)	-	-	-	180.0

The parameters in Minimum B are closer to both the results from the previous diffraction experiment as well as the DFT structure. The exceptions are the *r*(C4-C6) and *r*(C5-C6) distances in the ring and the C–Br distance. *r*(C1-Br) is robust amongst the various UED refinements so its deviation from prior GED results and DFT must be related to either the model or the data itself. *r*(C4-C6) and *r*(C5-C6) vary with the minimum chosen. In Minimum B, this distance falls considerably short of what is expected. Such an issue, often referred to as a correlation problem, is common in diffraction and is a consequence of refinement of a structure with multiple similarly valued parameters. Such correlation problems in other molecules often lead to switching of double and single bonds, sp^2 and sp^3 bond angles, etc. Correlation problems may be eliminated from the refinement by introducing constraints on the model – explicitly defining one parameter with respect to another such that it will not vary far from its expectation.

Where chlorobenzene demonstrated the effect of a heavy atom on the diffraction signal, bromobenzene shows it further. Fig. 5-3(a) shows the fit of the DFT derived structure with the data – no structural refinement. Here χ^2 = 1137.568 and R = 0.241, admittedly a poor match when considering ground-state data where the initial guess is based on a well-founded quantum chemical method. However, the bromine atom has such a considerable effect on the diffraction pattern that if only r(C1-Br) is refined there is marked improvement in the fit quality [see Fig. 5-3(b)]. The refinement causes r(C1-Br) to shrink from 1.920 Å to 1.862 Å with the new χ^2 and R equal to 201.465 and 0.104, respectively. Quite a change!

The final refined theoretical and experimental $sM(s)$ and $f(r)$ curves are shown in Fig. 5-4. Only the theory corresponding to Minimum B is shown, although that of Minimum A is essentially indistinguishable. The effect of the bromine atom is clearly illustrated in the $f(r)$ curve where distinct peaks appear where C–Br distances occur. The tallest bars under the $f(r)$, each proportional to $\frac{n_{ij}Z_iZ_j}{r_{ij}}$ mark the direct bond to Br, the next nearest neighbor distances, the third nearest neighbor distances, and the single cross ring C–Br distance.

5.3 Iodobenzene

The final halogenated benzene studied by UED, and the most severe in the heavy atom scattering regime, is iodobenzene. Like its predecessors it was chosen in the hopes that detachment of the iodine atom could be seen in the time-resolved diffraction data.

And, also like its predecessors, its absorption cross-section proved too low to produce enough signal for its reaction to be resolved. However, it also provides an excellent example of ground-state electron diffraction performed with UED; iodine is a very distinct atom in a molecule otherwise consisting of carbons and hydrogens.

The initial geometry was taken from DFT calculations at the B3LYP/6-311G(d,p) level with an electron core potential treatment at the LANL2DZ level for the iodine atom. The z-matrix used to model iodobenzene was fixed in C_{2v} symmetry consistent with these theoretical results as well as the results of a prior electron diffraction experiment.[4]

C1						
C2	C1	r1				
C3	C1	r1	C2	a1		
C4	C2	r2	C1	a2	C3	d1
C5	C3	r2	C1	a2	C2	d1
C6	C1	r3	C2	a1/2	C3	d2
H7	C2	r4	C1	180-a2/2	C4	d3
H8	C3	r4	C1	180-a2/2	C5	d3
H9	C4	r5	C2	a5	C6	d4
H10	C5	r5	C3	a5	C6	d4
H11	C6	r6	C1	a6	C2	d5
I12	C1	r7	C2	180-a1/2	C3	d6

Iodobenzene was introduced into the scattering chamber through a nozzle maintained at 473 K. This was the first molecule to test the all-metal inlet manifold that allowed vaporizing and transporting samples with high boiling points (see Section 3.1.3). A camera distance of 13.45 cm was obtained using the CO_2 comparison method (see Section 3.2.7). The data range used in the refinement procedure was $s = 3.09 – 16.05$ Å^{-1}

based on the quality of the data. One hundred diffraction patterns were obtained and averaged. Each pattern was collected using a 4 minute exposure time with about 25000 electrons/pulse (at 1 kHz), or about 4 pA for 400 minutes of exposure time. The ratio image is shown in Fig. 5-5. The data scaling factor (λ) was 1.509. Four separate refinements were conducted and the one with the most reasonable structural parameters (closest to DFT and prior electron diffraction results) was chosen as the best and reported here.

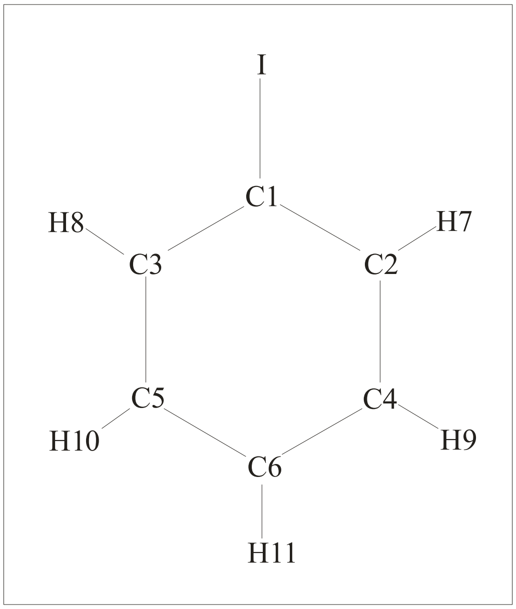


Fig. 5-6 shows the match (scale factor and polynomial background corrected) between the $sM(s)$ curves derived from both the DFT structure of iodobenzene and the UED data (χ^2 = 259.793; R = 0.173). Features at s = 3, 6, and 11 Å^{-1} are clearly mismatched in either phase or amplitude. With only an adjustment of the C–I distance, 2.141 to 2.090 Å, those features show a considerable visual improvement and χ^2 and R

become 88.392 and 0.102, respectively. Like seen in bromobenzene, internuclear distances involving the heavy atom are by far the most important to the diffraction signal.

The structural parameters obtained in the final refinement are listed in Table 5-3 with those of previous diffraction (diffraction and microwave)[4] and DFT. Brunvoll *et al.*'s structure is nearly identical to that given by DFT except for the C–I distance (shorter by ~0.05 Å) and the hydrogen angles. The UED structure shows more deviation. Likely due to correlation issues between similar C–C bond distances in the ring, a diversion of bond lengths has occurred. *r*(C2-C4) and *r*(C3-C5) have become longer than DFT by nearly 0.04 Å while *r*(C4-C6) and *r*(C5-C6), the dependent distances, have become shorter by about the same amount. This is a common (and annoying) problem. Diffractionists typically deal with it by introducing further structural constraints into their refinement. Since the power of UED is not in the determination of extremely accurate ground-state structures, but in the elucidation of excited-state pathways, the problem often receives only rough treatment.

Table 5-3. The refined structure of iodobenzene

Parameters	Minimum A value (Å, °)	Previous GED	Theoretical
r(C1-C2), *r*(C1-C3)	1.406±0.012	1.394	1.391
r(C2-C4), *r*(C3-C5)	1.431±0.010	1.391	1.394
r(C1-C6)	2.806±0.024	-	2.776
r(C4-C6), *r*(C5-C6)	1.350*	1.393	1.393
r(C1-I)	2.071±0.007	2.095	2.141
r(C2-H7), *r*(C3-H8)	-	1.094	1.082
r(C4-H9), *r*(C5-H10)	-	1.092	1.084
r(C6-H11)	-	1.090	1.084
a(C3-C1-C2)	120.2±1.3	121.2	121.3
a(C1-C2-C4), *a*(C1-C3-C5)	117.9±1.5	118.9	119.0
a(C2-C4-C6), *a*(C3-C5-C6)	121.9*	-	120.4
a(C4-C6-C5)	120.1*	-	119.8
a(H7-C2-C1), *a*(H8-C3-C1)	121.1*	122.3	120.7
a(H9-C4-C3), *a*(H10-C5-C3)	-	120.2	119.3
a(H11-C6-C1)	-	-	180.0

Fig. 5-7 shows the final refined theoretical $sM(s)$ and $f(r)$ curves with χ^2 = 69.192 and R = 0.089. The $f(r)$ curve shows clearly the positions of internuclear distances involving the iodine marked by the tallest bars under the curve. The direct C–I bond is actually swallowed by the next-nearest-neighbor C–C peak and the next-nearest-neighbor C··I peak is mixed with the long C···C distance peak, but the farther C···I peaks are obvious. The shape is actually more like the chlorobenzene $f(r)$ (Fig. 5-2) where C–Cl peaks are coincident with C–C peaks. Only the bromobenzene is truly exceptional in that its C–Br distances can be readily predicted directly from the $f(r)$ (Fig. 5-4).

The iodobenzene $sM(s)$ may also be compared with the $sM(s)$ curves for chlorobenzene and bromobenzene to see clear differences. There are unique features in each curve due to the presence of heavy atoms. It will be seen in the next sections where only light (F, at the heaviest) atoms are incorporated in the molecules that the $sM(s)$ curves all appear quite similar. But here, halogenated benzenes show that structural differences can be directly seen in the scattering intensity itself. First, one can compare the 2D images shown in Figs. 5-1 and 5-5. In the $sM(s)$ curves chlorobenzene (Fig. 5-2) shows a peak at s = 8 Å^{-1} that is nearly washed out in the bromobenzene $sM(s)$ (Fig. 5-4) by the shoulder at s = 7 Å^{-1}. Neither peak has any noticeable evidence in the iodobenzene $sM(s)$ (Fig. 5-7), which instead has a large peak at s = 5 Å^{-1}. Furthermore, the features at s ~ 10 Å^{-1} show some significant differences. In addition to the mass of the heavy atoms in each halogenated benzene studied herein, the C–X distance is also quite variable between the molecules: 1.724 Å in chlorobenzene, 1.845 Å in bromobenzene, and 2.071 Å in iodobenzene, also altering the scattering intensity.

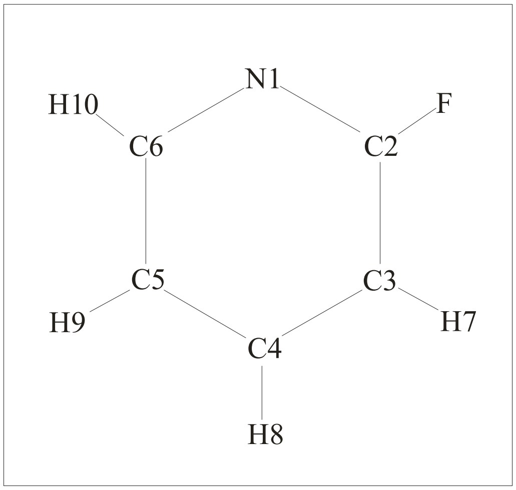
5.4 2-fluoropyridine

2-fluoropyridine is a poorly studied molecule for which there exists (to the author's knowledge) no experimental structural information. The motivation behind applying UED to this molecule was to explore its relatively unknown photophysics and photochemistry[5] and to compare it to the methyl substituted pyridines well-studied by UED.[6]

2-fluoropyridine has only C_s symmetry making it very much a challenge for structural refinement (likely the reason an electron diffraction structure of this molecule has not been reported). Multiple distances of similar value lead to numerous problems in the refinement procedure (correlations), which can only be remedied by introducing dependencies into the model z-matrix.

N1						
C2	N1	r1				
C3	C2	r2	N1	a1		
C4	C3	r3	C2	a2	N1	d1
C5	C4	1.005*r3	C3	a3	C2	d2
C6	C5	0.9979*r2	C4	1.0127*a2	C3	d3
F7	C2	r4	N1	180-a1/2	C6	d4
H8	C6	r5	N1	a4	C2	d5
H9	C3	r6	C2	a5	N1	d6
H10	C4	r7	C5	a6	C6	d7
H11	C5	r8	C6	a7	N1	d8

The geometrical parameters for the initial guess geometry were taken from DFT calculations at the B3LYP/6-311G(d,p) level. The temperature of the molecule (nozzle temperature) was 408 K and mean amplitudes of vibration were fixed at the values obtained using empirical calculations [see Eqs. (4-27) and (4-28)]. The ground state ratio image is shown in Fig. 5-5. The camera distance for this experiment (13.34 cm) was independently determined by fitting a theoretical CO_2 model to experimental CO_2 data taken before the 2-fluoropyridine sample was introduced. A data scaling factor (λ) of 0.4426 was used over the range of $s = 3.12 – 16.18$ Å^{-1}.



Ten separate and independent refinements were conducted with different adjusted z-matrices in order to determine the most reasonable solution. Since 2-fluoropyridine is only of C_s symmetry and refinement of all the degrees of freedom caused serious correlation problems, successive trials involved additional constrained structural parameters. The z-matrix shown herein was used as a final model and it, too, suffered some serious problems. The constraints introduced in the bond distances and angles are scaling factors based on the structure predicted by DFT. The refined parameters are listed along with the DFT values in Table 5-4.

Table 5-4. The refined structure of 2-fluoropyridine

Parameters	Refined value (Å, º)	Theoretical
r(N1-C2)	1.318±0.015	1.310
r(C2-C3)	1.409±0.007	1.392
r(C3-C4)	1.383±0.008	1.388
r(C4-C5)	1.390*	1.396
r(C5-C6)	1.406*	1.389
r(C6-N1)	1.299*	1.340
r(C2-F)	1.284±0.009	1.344
r(C3-H7)	-	1.082
r(C4-H8)	-	1.084
r(C5-H9)	-	1.083
r(C6-H10)	-	1.086
a(N1-C2-C3)	124.3±0.4	125.8
a(C2-C3-C4)	114.7±0.7	116.7
a(C3-C4-C5)	122.3±1.2	119.2
a(C4-C5-C6)	116.2*	118.2
a(C5-C6-N1)	123.1*	123.3
a(C6-N1-C2)	119.5*	116.8
a(F-C2-N1)	117.9*	116.2
a(H7-C3-C2)	-	120.5
a(H8-C4-C5)	-	120.7
a(H9-C5-C6)	-	120.4
a(H10-C6-N1)	-	115.8

Agreement between UED-refined parameters and those from DFT is fair. In a molecule with so many independent parameters (low symmetry) many constraints were necessary and the ones employed were perhaps not enough. The deviation between the UED and DFT C–F distances is striking (0.06 Å); much greater than expected or normally seen in a ground state structural refinement. The reason for the deviation is not clear as *r*(C2–F) is a terminal bond, one that affects only the distances associated with the fluorine atom, and presumably less influenced by correlation with other bonds. Other parameters, although nearly all outside of error bars (3σ) from DFT values, are reasonable. Including the three halo-benzenes previously discussed, this molecule is the fourth example of a structural refinement involving a C–X (X = F, Cl, Br, I) bond that UED finds to be significantly shorter than DFT. Without other electron diffraction data to compare it to, little more can be said, but a comparison between bond distances predicted by various methods and levels of theory may prove interesting and useful.

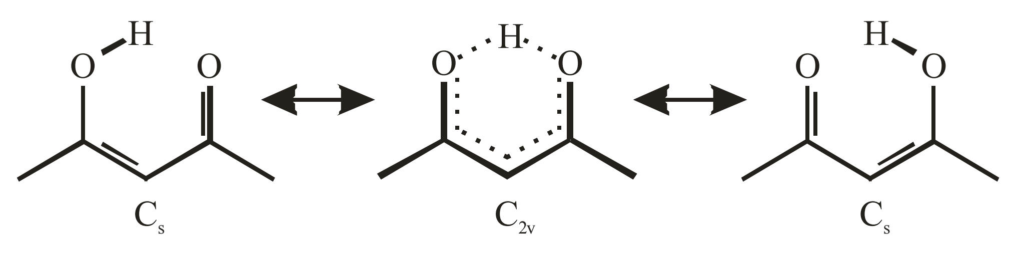
The refined theoretical $sM(s)$ and $f(r)$ curves are shown with the experimental data in Fig. 5-8. The refinement matched the data with a χ^2 and R of 89.686 and 0.035, respectively. Fluorine, an atom of a size with carbon and nitrogen, shows none of the prominent features displayed in the diffraction data collected from the heavier halogenated compounds. Like most molecules, the $f(r)$ shows peaks corresponding to direct bonds, next-nearest neighbors, and longer cross-ring distances. The visual match between experimental and theoretical curves is quite good as both peak positions and amplitudes are aligned nearly perfectly.

5.5 Acetylacetone

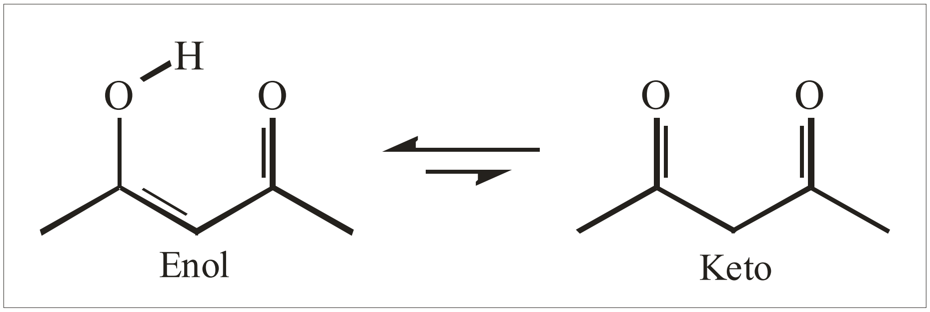
Acetylacetone was successfully explored by UED in both its ground state and following UV excitation. The ground-state result was perhaps the most interesting as it allowed UED to solve an old problem tossed between diffractionists as they attempted to determine the geometry of this molecule. The source of the problem is its intramolecular hydrogen bond and to what degree it influences the remainder of the molecular structure. The further complication lies in its tautomeric reaction as enol and keto conformers interconvert. This section was derived from the account of UED results previously published in Ref. 7.

The dissociation energies of hydrogen bonds span more than two orders of magnitude (about 0.2–40 kcal/mol) with the “classical” hydrogen bond lying around 3–5 kcal/mol. These energies vary as a function of the bond's electrostatic, covalent, and dispersion contributions.[8] While weak hydrogen bonds are due to van der Waals interactions, moderate hydrogen bonds are primarily electrostatic in nature, and strong hydrogen bonds have substantial covalent character. In the extreme limit, for symmetric hydrogen bonds X–H–X, the H-atom is equally shared.[9] Such unusually strong interactions can result either from charge-assisted hydrogen bonds in polarized systems or from resonance-assisted hydrogen bonds in neutral systems.[10]

Enolones, the enol tautomers of β-diketones, contain two neutral donor and acceptor oxygen atoms connected by a system of conjugated double bonds and can lead to strong intramolecular homonuclear resonance-assisted O–H···O hydrogen bonds. Increasing delocalization transforms the hydrogen bond from an asymmetric (double-well) O–H···O electrostatic interaction to a symmetric (single-well) O–H–O covalent bond, with the O···O distance being a measure of the degree of covalence. In the limit of complete resonance delocalization, the C–C and C=C bonds as well as the C–O and C=O bonds become equal to each other, the O···O distance becomes very short and the H-atom lies midway between the two oxygens.



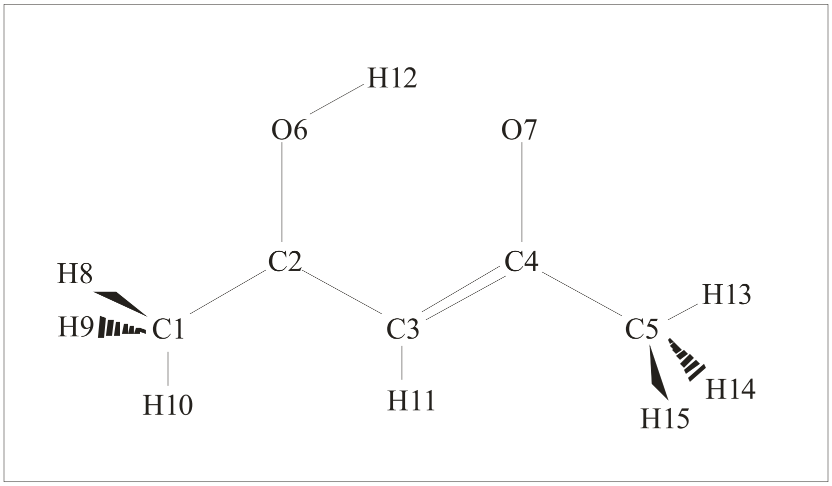
Acetylacetone, a prototypical enolone, has been the subject of numerous experimental[11,12] and theoretical[13] efforts to understand the nature of such strong hydrogen bonds. Acetylacetone consists of two tautomeric forms in dynamic equilibrium, with the enol form dominating in the gas phase at room temperature (and colder temperatures) due to stabilization by the internal hydrogen bonds.



Previous gas-phase electron diffraction experiments present conflicting evidence on the acetylacetone structure: Lowrey *et al.*[14] and Andreassen *et al.*[15] report a symmetric (C_{2v}) structure with a symmetric, linear hydrogen bond) while Iijima *et al.*[16] support an asymmetric (C_s) structure with an asymmetric, bent hydrogen bond. Surprisingly, the two experiments reporting a symmetric structure give very different O···O distances, (2.381 Å[14] vs. 2.514 Å[14,15]). The situation is further complicated by theoretical investigations on the relative energies of these structures,[17] which place C_{2v} anywhere from slightly below[18] to >20 kcal/mol above[19] the C_s structure.

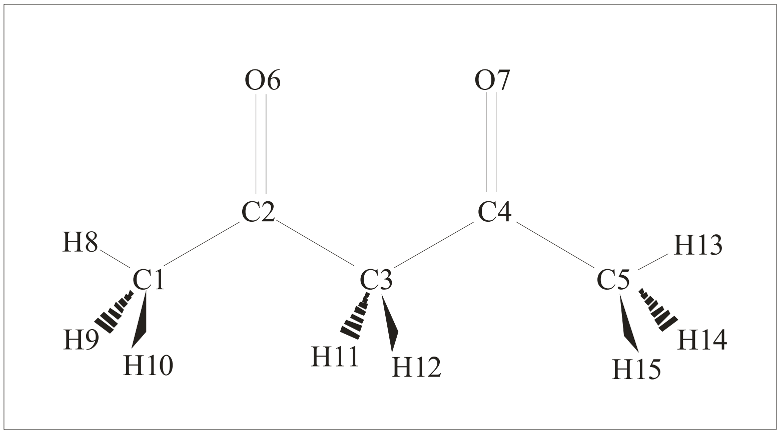
Acetylacetone (2,4-pentanedione, 99+%, Aldrich) was introduced into the UED scattering chamber through the nozzle set at 428 K. The ground-state ratio image, $R^N(x,y)$, is shown in Fig. 5-9. A data scaling factor (here, 1/λ, see Section 4.8) of 2.197 was used to match with theory. The camera distance was 13.49 cm. A z-matrix written for C_s symmetry lacking any constrained parameters was used for the refinement of the enol structure. Refinement was conducted over the data range of s = 3.00 to 15.28 $Å^{-1}$.

C1						
C2	C1	r1				
C3	C2	r2	C1	a1		
C4	C3	r3	C2	a2	C1	d1
C5	C4	r4	C3	a3	C2	d2
O6	C2	r5	C1	a4	C3	d3
O7	C4	r6	C5	a5	C3	d4
H8	C1	r7	C2	a6	C3	d5
H9	C1	r8	C2	a7	H8	d6
H10	C1	r9	C2	a8	H8	d7
H11	C3	r10	C2	a9	C1	d8
H12	O6	r11	C2	a10	C1	d9
H13	C5	r12	C4	a11	C3	d10
H14	C5	r13	C4	a12	H13	d11
H15	C5	r14	C4	a13	H13	d12



The keto structure was also necessary in the refinement as previous spectroscopic experiments predict a significant population at 428 K (see below). The same z-matrix used to model the enol tautomer was also used for keto acetylacetone except that H12 was defined from C3 rather than O6. As is customary in UED experiments, the initial geometries were taken from DFT calculations at the B3LYP/6-311G(d,p) level and the mean amplitudes of vibration were fixed at values calculated at the experimental temperature.

Figure 5-10 shows the experimental data and refined theoretical $sM(s)$ and $f(r)$ curves. The fit was completed with $\chi^2 = 41.676$ and $R = 0.030$. The first peak at ~1.5 Å corresponds to direct bond distances in both the enol and keto forms, the peak at ~2.5 Å to second nearest-neighbor distances and the peaks at longer distances to the unique O···O and C···O distances in the enol and keto tautomers. Comparing these curves to those of the halogenated benzenes in Figs. 5-2, 5-4, and 5-7 shows the striking differences a heavy atom can make.



The $f(r)$ curve is also broken down in Fig. 5-10 to show the contributions of the tautomeric structures. Structural determination of acetylacetone tautomers requires an accurate estimate of the relative populations of the enol and keto forms at the experimental temperature. Initial fitting of the populations of the raw DFT structures yielded an enol-keto ratio of 88:12 ± 1, which is in stark contrast to that expected at 428 K; thermodynamic equilibrium constants obtained by a wide variety of techniques (NMR, UV, IR) predict a ratio between 71:29 and 79:21.[20-22] However, the fractional contributions of each tautomer change as the structures are refined. The complete C_s structure of the enol was refined while the smaller population of keto tautomer was fixed at DFT values (to simplify the procedure). However, since the keto tautomer is free to undergo internal rotation about its C–C single bonds, the skeletal (and methyl) torsion angles were refined.[18,23]

The refined enol and partially refined keto structures resulted in a tautomeric ratio of 78:22 ± 4, in excellent agreement with the results of gas-phase NMR[22] and IR absorption.[20] DFT predicts a 99:1 ratio at 428 K due to a serious underestimation of the entropic term (2.4 vs. 8.3 cal/mol/K [21,22]) resulting from the facile internal rotation in keto acetylacetone.

The refined parameters of the enol and keto tautomers are listed in Table 5-5 and Table 5-6, respectively, along with those parameters determined by prior electron diffraction work and DFT. The refined enolic structure is asymmetric, with all bond distances and angles being within ~0.02 Å and ~3° of the DFT values, respectively. Differences between the C–C distances (0.084 Å) and C–O distances (0.059 Å) are far greater than the corresponding standard deviations (3σ) and unambiguously distinguish between single and double bonds: a clear manifestation of structural asymmetry. This asymmetric C_s enol structure is complemented by neutron scattering,[12] x-ray diffraction,[24,25] and electron diffraction[16]—all report an asymmetric hydrogen bond, as do some spectroscopic studies.[26] The O···O distance is 2.592 Å, somewhat longer than the DFT value (2.541 Å) and longer than those previously reported by electron diffraction

(2.519 Å[15] and 2.512 Å[16]) and x-ray crystallography (2.535 Å[24] and 2.547 Å[25]). In the UED fit, the O–H, H···O distances and the O–H···O angle were held at DFT values (1.003 Å, 1.683 Å and 148.4 °, respectively) in sharp contrast to fit values of Lowrey *et al.* (O–H and H···O ~ 1.19 Å; ∠OHO ~ 180 °)[14] and Andreassen *et al*. (O–H and H···O ~ 1.99 Å; ∠OHO ~ 180 °).[15] Moreover, the H-atom was constrained to be in the plane unlike in the work of Iijima *et al*. who report a significantly out-of-plane H-atom (∠HOCC = 26 °).[16] The partially refined keto structure is quite different from that reported in the literature—the oxygen atoms are much farther apart (~3.520 Å; dihedral ∠OCCO = 104.7°) compared to that previously reported (~2.767 Å; dihedral ∠OCCO = 48.6 °).[14]

Table 5-5. The refined structure of enol-acetylacetone

Parameters (Å, º)	UED	Ref. 16	Ref. 15	Ref. 14	DFT
	C_s	C_s	C_{2v}	C_{2v}	C_s
r(C1-C2)	1.504±0.021	1.518	1.504	1.493	1.495
r(C2-C3)	1.359±0.034	1.376	1.397	1.412	1.370
r(C3-C4)	1.443±0.019	1.424	1.397	1.412	1.444
r(C4-C5)	1.518±0.023	1.486	1.504	1.493	1.513
r(C2-O6)	1.321±0.021	1.313	1.275	1.310	1.325
r(C4-O7)	1.262±0.005	1.238	1.275	1.310	1.244
r(O6-H12)	-	1.030	1.240	1.192	1.003
r(O6-O7)	2.592*	2.481	2.498	2.371	2.541
r(C1-H8), *r*(C1-H9)	-	1.087	1.075	1.090	1.094
r(C1-H10)	-	1.087	1.075	1.090	1.089
r(C3-H11)	-	1.081	1.075	1.090	1.081
r(C5-H13)	-	1.087	1.075	1.090	1.089
r(C5-H14), *r*(C5-H15)	-	1.087	1.075	1.090	1.095
a(C1-C2-C3)	123.6±1.1	124.1	122.0	120.0	124.1
a(C2-C3-C4)	120.5±1.0	119.7	118.3	118.0	120.4
a(C3-C4-C5)	118.2±2.7	118.1	122.0	120.0	118.6
a(O6-C2-C1)	112.9±2.7	114.9	114.8	120.0	113.7
a(O7-C4-C5)	118.7±3.1	118.9	114.8	120.0	119.7
a(C2-O6-H12)	-	81.0	86.9	88.0	105.8
a(H8-C1-C2), *a*(H9-C1-C2)	-	-	110.2	109.3	109.6
a(H10-C1-C2)	-	-	110.2	109.3	111.7
a(H11-C3-C2)	-	-	120.9	121.0	119.5
a(H13-C5-C4)	-	-	110.2	109.3	109.6
a(H14-C5-C4), *a*(H15-C5-C4)	-	-	110.2	109.3	110.6
φ(H12-O6-C2-C1)	-	154.0	180.0	180.0	180.0
φ(H10-C1-C2-C3)	–57.2±16.5	-	30.7	0.0	0.0
φ(H14-C5-C4-C3)	–19.3±4.8	-	30.7	0.0	-63.2

Table 5-6. The refined structure of keto-acetylacetone

Parameters (Å, º)	UED	Ref. 14	DFT
r(C1-C2), r(C4-C5)	-	1.525	1.511
r(C2-C3), r(C3-C4)	-	1.525	1.536
r(C2-O6), r(C4-O7)	-	1.218	1.209
r(O6-O7)	-	2.731	
r(C1-H10), r(C5-H13)	-	1.090	1.089
r(C1-H8), r(C1-H9), r(C5-H14), r(C5-H15)	-	1.090	1.095
r(C3-H11), r(C3-H12)		1.090	1.091
a(C1-C2-C3), a(C3-C4-C5)	-	125.0	116.0
a(C2-C3-C4)	-	114.0	107.7
a(O6-C2-C1), a(O7-C4-C5)	-	115.0	123.3
a(H11-C3-C2)	-	109.3	108.0
a(H12-C3-C2)	-	109.3	111.1
a(H8-C1-C2), a(H9-C1-C2), a(H14-C5-C4), a(H15-C5-C4)	-	109.3	110.0
a(H10-C1-C2), a(H13-C5-C4)	-	109.3	109.5
φ(C4-C3-C2-C1)	43.0±1.4	152.3	–89.5
φ(C5-C4-C3-C2)	87.4±1.9	152.3	–89.6
φ(H10-C1-C2-C3)	–11.3±20.0	–60.0	–68.9
φ(H14-C5-C4-C3)	51.1±13.0	–60.0	–68.8

In light of previous reports of a symmetric structure, a C_{2v} acetylacetone enolic model was also tested extensively as a candidate structure. The refinement consistently led to a somewhat inferior fit, and more importantly, to a fraction of 68:32 ± 3 compared to the thermodynamically expected value of 79:21 at 428 K. This error in the enol-keto ratio can be directly attributed to the assumption of C_{2v} symmetry in the acetylacetone enol—Lowrey *et al.*, who first suggested the C_{2v} structure, also seriously underestimate the enol-keto fraction (66:34 ± 5 at 105°C)[14] when thermodynamics would have predicted ~85:15—thereby bringing into question the validity of the C_{2v} model. Fig. 5-11 shows the variation of the tautomeric component ratio with enol symmetry and structure.

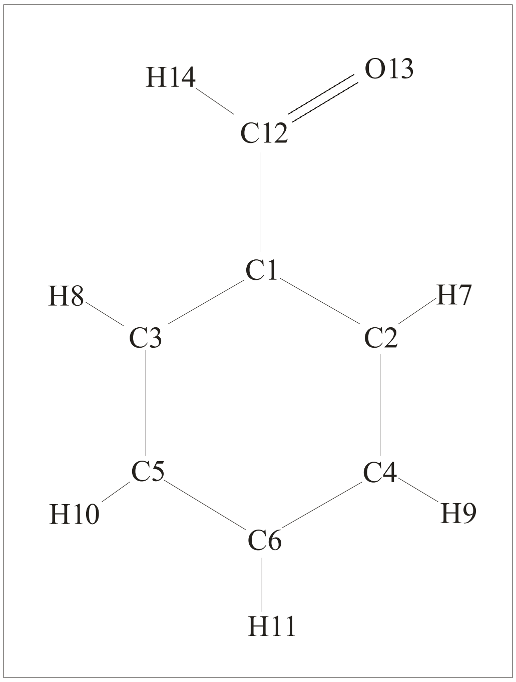
The diffraction results reported here shed new light on the nature of the hydrogen bond in resonant tautomeric structures. The keto structure with its large internal rotation at high temperature exhibits a rotation-averaged dihedral angle of ~105° between the carbonyls. The enolic structure clearly indicates that acetylacetone does not exhibit aromatic ring characteristics with a symmetric intramolecular hydrogen bond, but rather adopts a discrete enolone configuration with an O–H···O hydrogen bond that is asymmetric. This asymmetry of the skeletal geometry and the long O···O distance reflects weak π-resonance delocalization in acetylacetone, which in turn, implies that the nature of the hydrogen bond in acetylacetone is localized and electrostatic rather than delocalized and covalent.

However, and it is noted here as a postscript, the authors of a more recent analysis of microwave spectra of gas-phase acetylacetone have claimed that the structure is actually C_{2v}.[27] Their data are consistent with a single state and not two states separated by a tunneling barrier. It is hard to understand the reasons why these experimental results differ from those obtained through UED.

5.6 Benzaldehyde

The experiments on time-resolved diffraction of benzaldehyde proved to be one of UED's most exciting results. The ground-state structure was also refined and compared with theory and prior diffraction data to confirm UED's accuracy. This section revisits work published in Refs. 28 and 29 that also describe the excited-state dynamics. Benzaldehyde was admitted to the diffraction chamber using the metal-valve inlet system and a nozzle maintained at 483 K. The camera distance was determined to be 13.50 cm. The data range used for refinement was $s = 4.7 – 15.4$ Å^{-1} (60 – 200 pixels), the center of the detector's range. The initial guess geometry was obtained from the DFT optimized structure at the B3LYP/6-311G(d,p) level and the mean amplitudes of vibration for the internuclear distances were calculated during each fitting cycle following the methodology outlined in Section 4.5.2. The scale factor (here, 1/λ, see Section 4.8) was optimized at 2.094. The model for structural refinement was in z-matrix format fixed in C_{2v} symmetry (DFT predicts nearly C_{2v} symmetry). This approximation was also used in a previous diffraction experiment on benzaldehyde[30] and needed for simplification of the refinement.

C1						
C2	C1	r1				
C3	C1	r1	C2	a1		
C4	C2	r2	C1	a2	C3	d1
C5	C3	r2	C1	a2	C2	d2
C6	C1	r3	C2	a1/2	C3	d3
H7	C2	r4	C1	180-a2/2	C4	d4
H8	C3	r5	C1	180-a2/2	C5	d5
H9	C4	r6	C2	a3	C6	d6
H10	C5	r7	C3	a3	C6	d7
H11	C6	r8	C1	a4	C2	d8
C12	C1	r9	C3	180-a1/2	C2	d9
O13	C12	r10	C1	a5	C2	d10
H14	C12	r11	O13	180-a5/2	C1	d11



The two-dimensional ratio pattern of the ground state diffraction is shown in Fig. 5-9. The experimental $sM(s)$ (scale factor and polynomial background optimized) was compared with that of the initial guess geometry; χ^2 = 67.127 and R = 0.043. The structure of benzaldehyde was subsequently refined using the C_{2v} constraint. The refined ground state benzaldehyde structural parameters are listed in Table 5-7. Refined bond distances and angles are within 0.01 Å and 1 º, respectively, of the structure derived by Borisenko *et al.*[30] The carbonyl torsional angle was tested in preliminary fitting and found to remain nearly planar. For the final refinement, it was fixed in the plane of the ring. In addition, bond distances and angles involving hydrogen atoms were fixed at values given by DFT. Values in Table 5-7 marked with asterisks are dependent and change in value as other "fittable" parameters are refined.

Table 5-7. The refined structure of ground state benzaldehyde

Parameters	UED	Ref. 30 (r_e)	DFT
r(C1-C2), r(C1-C3)	1.388 ± 0.004	1.393	1.401, 1.398
r(C2-C3), r(C3-C5)	1.381 ± 0.004	1.385	1.388, 1.392
r(C1-C6)	2.785 ± 0.010	2.781	2.785
r(C4-C6), r(C5-C6)	1.417*	1.392	1.397, 1.394
r(C1-C12)	1.480 ± 0.005	1.472	1.481
r(C12-O13)	1.200 ± 0.002	1.206	1.209
r(C12-H14)	-	1.094	1.113
r(C2-H7), r(C3-H8)	-	1.076	1.083, 1.086
r(C4-H9), r(C5-H10)	-	-	1.084, 1.084
r(C6-H11)	-	-	1.084
a(C2-C1-C3)	120.0 ± 0.7	119.9	119.9
a(C1-C2-C5), a(C1-C3-C5)	121.0 ± 0.9	120.2	119.9, 120.2
a(C2-C4-C6), a(C3-C5-C6)	119.1*	119.5	120.0, 119.7
a(C4-C6-C5)	119.9*	120.7	120.3
a(C2-C1-C12)	120.0*	120.9	120.3
a(C1-C12-O13)	126.4 ± 0.3	123.6	124.9
a(H7-C2-C1), a(H8-C3-C1)	119.5*	-	118.5, 119.6
a(H9-C4-C2), a(H10-C5-C3)	-	-	120.1, 120.2
a(H11-C6-C1)	-	-	180.0
a(H14-C12-C1)	116.8*	115.1	114.4
φ(C2-C1-C12-O13)	-	7	0

Six separate refinements were performed of which the "best" was selected and reported here. In addition to possessing the lowest χ^2 value, the final fit also was closest to known structural information. It should be noted that this refinement was conducted starting with the new UED_2004 refinement software and then transferred to the Uedana (older) refinement software, which produced the final fit. Results were robust between the two programs and conducted in the way reported here for consistency with previous UED publications. The final refined $sM(s)$ and $f(r)$ curves are shown in Fig. 5-12. Structural refinement converged at the minimum with χ^2 = 34.291 and R = 0.031.

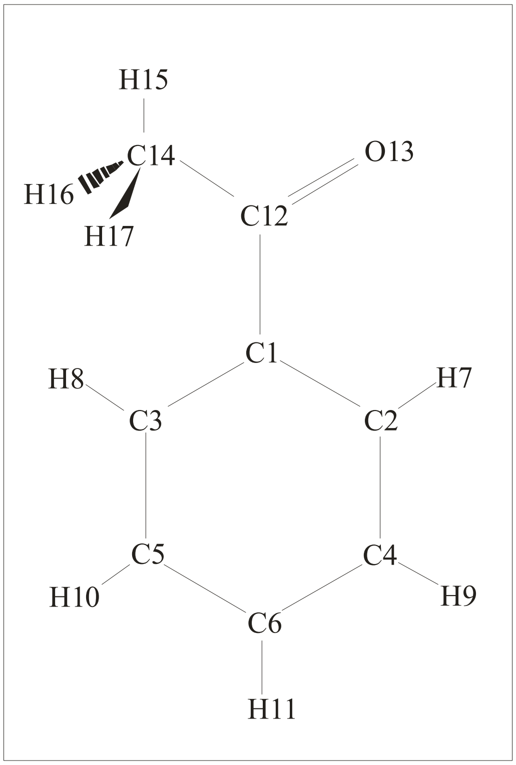
5.7 Acetophenone

The molecular structure of acetophenone has been determined for the first time (to the author's knowledge) by UED, the summary of which has been published.[28,29] The combination of a high boiling point and reactivity in the apparatus made working with acetophenone a challenge; coating of the inlet window occurred rapidly, the vacuum was difficult to maintain, and sample reacted in the nozzle. Moreover, acetophenone has numerous similar structural parameters (45 degrees of freedom) which make the analysis non-trivial. The ratio pattern derived from the raw diffraction pattern is shown in Fig. 5-13.

The initial guess for the structural refinement was taken from the result of a DFT calculation at B3LYP/6-311G(d,p). As with other molecules, the mean amplitudes of vibration were calculated at 483 K using the nozzle temperature as the temperature of the sample. The camera distance was determined to be 13.43 cm. The polynomial background and theory scaling factor ($\lambda = 0.535$) were optimized for the best fit. The data range used for refinement was $s = 3.48–14.58$ Å^{-1} (45–190 pixels).

C1						
C2	C1	r1				
C3	C1	r1	C2	a1		
C4	C2	r2	C1	a2	C3	d1
C5	C3	r2	C1	a2	C2	d2
C6	C1	r3	C2	a1/2	C3	d3
H7	C2	r4	C1	180-a2/2	C4	d4
H8	C3	r5	C1	180-a2/2	C5	d5
H9	C4	r6	C2	a3	C6	d6
H10	C5	r7	C3	a3	C6	d7
H11	C6	r8	C1	a4	C2	d8
C12	C1	r9	C3	180-a1/2	C2	d9
O13	C12	r10	C1	a5	C2	d10
C14	C12	r11	O13	180-a5/2	C1	d11
H15	C14	r12	C12	a6	O13	d12
H16	C14	r13	C12	a7	H15	d13
H17	C14	r14	O12	a8	H15	d14

In order to simplify the refinement process, a C_{2v} symmetry was imposed for the aryl ring, however, the acetyl group was permitted unhindered rotation. Refinement was conducted slightly differently than in previous cases. Only one average value for acetophenone's aromatic bonds and single bonds was refined. Then a set of deviation values were refined such that, for example, each aromatic C–C bond is dependent on the average aromatic bond value and its deviation. The refined parameters were: one average single bond, one average aromatic bond, five bond deviations, the C–O double bond distance, two ring angles, two angles defining the carbonyl group, and the methyl group torsional angle. The structure was derived from these values.



The refined structural parameters of ground state acetophenone ($\chi^2 = 39.069$; $R = 0.028$) are listed in Table 5-8. Bond lengths and angles agree with the theoretical values (from DFT) within 0.02 Å and 2 º, respectively. A relatively large discrepancy with DFT values was seen in the refined parameters related to the carbonyl and methyl groups: –0.017 Å and +0.029 Å for the C=O and C–CH_3 distances, respectively, and +3.5 º and –2.8 º for the carbonyl and methyl angles with respect to the aryl skeleton. The orientation of the methyl hydrogen atoms is observed to deviate from the planar symmetric starting condition, reflecting the freedom of its torsional motion.

Table 5-8. The structure of ground state acetophenone

Parameters	UED	DFT
r(C1-C2), *r*(C1-C3)	1.407 ± 0.017	1.401, 1.400
r(C2-C3), *r*(C3-C5)	1.401 ± 0.019	1.388, 1.393
r(C1-C6)	2.806 ± 0.028	2.798
r(C4-C6), *r*(C5-C6)	1.380*	1.396, 1.393
r(C1-C12)	1.488 ± 0.034	1.502
r(C2-H7), *r*(C3-H8)	-	1.083, 1.083
r(C4-H9), *r*(C5-H10)	-	1.084, 1.083
r(C6-H11)	-	1.085
r(C12-O13)	1.198 ± 0.003	1.214
r(C12-C14)	1.548 ± 0.016	1.518
r(C14-H15)	-	1.088
r(C14-H16) , *r*(C14-H17)	-	1.094, 1.094
a(C2-C1-C3)	118.7 ± 1.4	119.1
a(C1-C2-C4), *a*(C1-C3-C5)	120.0 ± 1.1	120.6, 120.4
a(C2-C4-C6), *a*(C3-C5-C6)	120.7*	120.0, 120.0
a(C4-C6-C5)	120.0*	120.0
a(C2-C1-C12)	120.5*	118.1
a(C1-C12-O13)	124.1 ± 0.4	120.6
a(C1-C12-C14)	116.0 ± 0.4	118.8
a(H7-C2-C1), *a*(H8-C3-C1)		118.1, 120.4
a(H9-C4-C2), *a*(H10-C5-C3)	-	120.0, 119.9
a(H11-C6-C1)	-	180.0
a(H15-C14-C12)	-	108.5
a(H16-C14-C12), *a*(H17-C14-C12)	-	111.0, 111.0
φ(C2-C1-C12-O13)	-	0.0
φ(H15-C14-C12-O13)	29.5 ± 3.0	0.0

The refined theoretical and experimental $sM(s)$ and $f(r)$ curves are shown in Fig. 5-14. The data are modeled well by the refined theoretical model. Comparison between these curves and the curves in Fig. 5-12 for the benzaldehyde ground state is also worth comment. Here the difference between acetophenone and benzaldehyde can be seen in the $f(r)$ curves. Structurally speaking, acetophenone only differs from benzaldehyde in that a methyl group replaces the aldehydic hydrogen. That, in diffraction, simply adds amplitude to a few molecular interference terms (recall that hydrogen contributions are very small in electron diffraction). This is reflected in the

$f(r)$ by the growth in peak size experienced by acetophenone. When carbon replaces hydrogen, $\frac{nZ_iZ_j}{r_{ij}}$ for the internuclear distances is multiplied by 6.

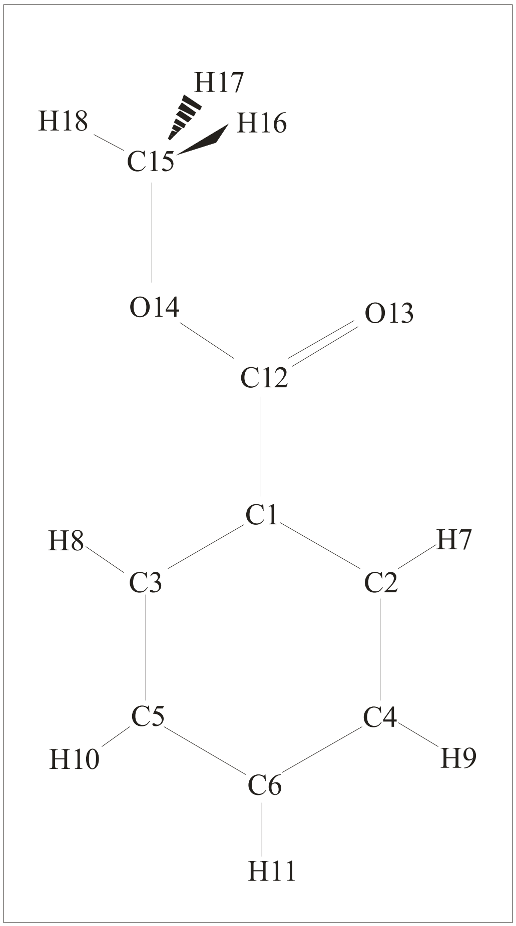
5.8 Methylbenzoate

In the series of aromatic carbonyls, UED first studied an aldehyde (benzaldehyde), then a ketone (acetophenone), and finally tackled an ester, methylbenzoate. With 18 atoms and 48 structural degrees of freedom, it is the largest molecule ever studied by UED. Also due to its size and similar internuclear distances, its structure has not been previously determined. The account here represents the first published record of the structure of methylbenzoate.

Methylbenzoate was introduced into the UED scattering chamber using the metal inlet system and through a nozzle at 493 K. The experiment was repeated several times due to clogging or other sample pressure instability. The two-dimensional ground-state diffraction pattern shown in Fig. 5-13. Using a camera length determined to be 13.43 cm, the intensity was converted to *s* space and analyzed. Due to the large number of "fittable" parameters, ground-state refinement was tested using several different approaches. The final refinement fixed the structure of the aryl ring and refined only the structure of the ester functional group. Refinement attempts using parameters to describe the ring caused problems that resulted in an unphysical structure; bond distances deviated >0.2 Å from reasonable numbers.

C1						
C2	C1	r1				
C3	C2	r2	C1	a1		
C4	C3	r3	C2	a2	C1	d1
C5	C4	r4	C3	a3	C2	d2
C6	C5	r5	C4	a4	C3	d3
H7	C2	r6	C1	a5	C3	d4
H8	C3	r7	C2	a6	C4	d5
H9	C4	r8	C5	a7	C3	d6
H10	C5	r9	C6	a8	C4	d7
H11	C6	r10	C1	a9	C5	d8
C12	C1	r11	C6	a10	C2	d9
O13	C12	r12	C1	a11	C2	d10
O14	C12	1.11799*r12	O13	a12	C1	d11
C15	O14	0.964168*r11	C12	a13	C1	d12
H16	C15	r15	O14	a14	C12	d13
H17	C15	r16	O14	a15	H16	d14
H18	C15	r17	O14	a16	H17	d15

The ester functional group itself had to be further constrained to prevent unphysical distances that emerged even with the ring parameters eliminated from the fit. All distances and angles containing hydrogen atoms were fixed at the values supplied by the DFT calculation of the methylbenzoate structure (B3LYP/6-311G(d,p) level). The mean amplitudes of vibration at 493 K were calculated for each internuclear separation following the standard UED methodology.



The ground-state refinement was conducted numerous times using data taken during several experiments. The breakdown of the fitting if the proper parameters weren't constrained was found to be robust with regard to data set and *s* range employed. The final refinement was performed using the range s = 3.49 to 16.08 Å^{-1} (45 – 210 pixels). The scale factor was optimized during the refinement; λ = 0.606.

Table 5-9. The structure of ground state methylbenzoate

Parameters	UED	DFT
r(C1-C2), *r*(C1-C3)	-	1.399, 1.399
r(C2-C3), *r*(C3-C5)	-	1.390, 1.391
r(C1-C6)	-	2.789
r(C4-C6), *r*(C5-C6)	-	1.395, 1.394
r(C1-C12)	1.508 ± 0.003	1.491
r(C2-H7), *r*(C3-H8)	-	1.083, 1.082
r(C4-H9), *r*(C5-H10)	-	1.084, 1.084
r(C6-H11)	-	1.084
r(C12-O13)	1.206 ± 0.002	1.209
r(C12-O14)	1.349*	1.351
r(C14-C15)	1.454*	1.437
r(C14-H16) , *r*(C14-H17)	-	1.091
r(C14-H18)	-	1.088
a(C2-C1-C3)	-	119.8
a(C1-C2-C4), *a*(C1-C3-C5)	-	120.1, 119.9
a(C2-C4-C6), *a*(C3-C5-C6)	-	120.0, 120.1
a(C4-C6-C5)	-	120.1
a(C2-C1-C12)	-	117.8
a(C1-C12-O13)	-	124.6
a(H7-C2-C1), *a*(H8-C3-C1)	-	118.6, 119.4
a(H9-C4-C2), *a*(H10-C5-C3)	-	119.9, 119.8
a(H11-C6-C1)	-	180.0
a(O14-C12-O13)	125.3 ± 0.7	123.0
a(C15-O14-C12)	118.8 ± 0.9	115.5
a(H16-C15-O14), *a*(H17-C15-O14)	-	110.5
a(H18-C15-O14)	-	105.5
φ(O13-C12-C1-C2)	14.8 ± 2.4	0.0
φ(C15-O14-C12-C1)	−210.7 ± 6.1	180.0
φ(H16-C15-O14-C12)	-	180.0

The refined structural parameters of ground state methylbenzoate are listed with DFT derived values in Table 5-9. With the constraints imposed, agreement between theory and experiment is good. However, certain parameters showed significant deviation. The torsional angles strayed somewhat from the planarity predicted by DFT; not surprising with the elevated temperature of the gas. The $sM(s)$ and $f(r)$ curves derived from the experiment and the refined theory are shown in Fig. 5-15. Agreement in the $sM(s)$ is fair but shows some mismatch at s ~10 Å^{-1}. This feature is matched by the refinement if a model with full structural freedom is used – this, of course, produces a refinement result that is highly unphysical. It is interesting to note that this region at s ~10 Å^{-1} is approximately where the filter on the detector ends (Section 3.1.4) and despite the treatment to be rid of its contribution (Section 4.2.1) it may still be having an effect. The curves shown match with a χ^2 of 224.746 and R of 0.056. Although χ^2 scales with the intensity of the data, R values may be compared between experiments. The higher value of R for this fit compared to those described in previous sections demonstrates that the structural refinement of methylbenzoate was not of the highest quality. If the analysis problems lie with the molecule itself, a distinct possibility given its size and similar distances, it would explain why its structure is absent from the literature of electron diffraction.

5.9 References

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