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Experiment versus Time Dependent Density Functional Theory Prediction of Fullerene Electronic Absorption

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Abstract: Time dependent density functional theory (TDDFT) was applied to a description of optically allowed electronic transitions for C_{60} (I_h), C_{70} (D_{5h}), C_{76} (D_2), C_{78} (C_{2v}), C_{78} ($C_{2v'}$), C_{78} (D_3), C_{78} (D_{3h}), C_{78} ($D_{3h'}$), and C_{80} (D_2). We present a detailed comparison of experiment (solution spectra in toluene and *n*-hexane) and theory (vibrationless/gas phase) for all fullerenes—except C_{78} (D_{3h}, $D_{3h'}$) which have not yet been isolated. The level of agreement is good enough to allow assignment of dominant spectral features.

I. Introduction

Since the first preparation of fullerenes in macroscopic amounts, their electronic absorption spectra have been of great interest. In the 0−7 eV energy range there is now a large data base of measurements for the most abundant fullerenes C_{60} (I_h) and C_{70} (D_{5h})—not only in room temperature solutions[1−8] but also in gas phase[9−12] and in solid state at various temperatures.[13−16] In contrast, the higher fullerenes have been less extensively characterized due to their lower abundance and the occurrence of multiple, spectrally distinguishable isolated pentagon ring (IPR) isomers.[17] The latter problem, which is encountered from C_{78} on up, makes isomer separation necessary.

While the acquisition of (isomer specific) fullerene electronic absorption spectra is straightforward once the materials have been prepared in sufficient quantity and purity, their assignment is problematic. This is a function of molecular size and extensive valence electron correlation which makes both detailed molecular spectroscopy and predictive level theory difficult. Even in the case of C_{60}, which due to its high symmetry is the simplest such problem, there is still literature controversy concerning the gross visible region assignment.[3,13] This is reflected by the numerous calculations of optically allowed transitions which have been performed at assorted levels of theory for this molecule.[8−23]

A common computational approach, which has also been applied to higher fullerenes, makes use of semiempirical quantum chemical procedures to describe excited states at the level of singles configuration interaction (CNDO/S, INDO/S). Absolute errors on peak positions of >0.5 eV with superimposed scatter of ±0.5 eV are not unusual.[24] Oscillator strengths appear even harder to calculate. For higher fullerenes, which generally have lower symmetry and higher excited state densities than C_{60}, accuracy is not good enough to allow unequivocal differentiation of isomers on the basis of such calculations.[24,25]

From a different perspective, the experimental data base of fullerene absorption spectra (C_{60}, C_{70}, C_{76}, ...) provides a series of benchmarks with varying valence electron count against which to optimize quantum chemical approaches for calculating dipole allowed electronic transitions in large organic molecules. Multiple isomer spectra at **one cage size** are particularly useful here in that they allow an additional sensitive test of the computational approximation. C_{78} is the best characterized multiple IPR isomer fullerene with three isolable forms generally produced in graphite/helium arc discharges.[17,24,26]

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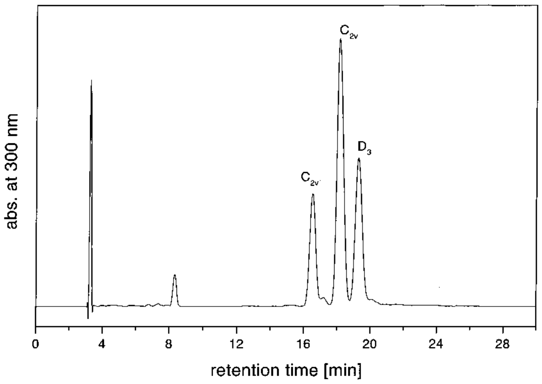

Figure 1. HPLC trace recorded at 300 nm for an C_{78} isomer mixture eluting from a Wakosil II $5C_{18}$ AR column at stage 2 of the isomer fractionation (see text). Note the presence of C_{78} (C_{2v}), C_{78} ($C_{2v'}$), and C_{78} (D_3).

The purpose of this paper is to demonstrate the utility of TDDFT calculations for an almost predictive level description of fullerene optical absorption measurements. This is unprecedented as yet. Specifically, the method is first used to calculate UV−vis region allowed transitions of C_{60} and C_{70}. After correction to take into account matrix effects as well as systematic error in the computational method, predictions are in good agreement with the solution spectra. The method is then applied to C_{76} (D_2), to the three known C_{78} isomers (C_{78}-C_{2v}, C_{78}-$C_{2v'}$, and C_{78}-D_3), and to C_{80} (D_2). Again good agreement is found between (corrected) prediction and the solution phase absorption spectra suggesting that the TDDFT approach will be of general utility for predicting optical response of even larger fullerene cages. Along these lines we also provide predictions for C_{78} (D_{3h}) and C_{78} ($D_{3h'}$) which have yet to be isolated/detected.

II. Experimental Methods

Fullerenes were generated by graphite arc discharge in helium according to the Krätschmer−Huffmann method.[27] They were extracted from the fullerene soot as has been previously described.[24,26] C_{78} isomers were separated from other fullerenes and each other by a three stage HPLC fractionation protocol which also generated pure C_{76} (D_2)—starting from soot extract. Stages 1 and 2 made use of a Cosmosil II Buckyprep column (toluene eluent) to generate a pure C_{76} fraction and a C_{78} isomer mixture fraction. Individual C_{78} isomers were separated from one another in the third stage using a Wakosil II 5C18 AR column (toluene/acetonitrile (3:2)).[26] Figure 1 shows a typical analytic scale HPLC obtained with a Wakosil column for a C_{78} isomer mixture after stage 2 fractionation. C_{80} (D_2) was isolated as has been previously described.[28]

Materials used for further study were pure >99% in each case (C_{60}, C_{70}, C_{76}, C_{78} (C_{2v}), C_{78} ($C_{2v'}$), C_{78} (D_3), and C_{80} (D_2)). This was checked by laser desorption time of flight mass spectroscopy (LD-TOFMS) and analytical HPLC. Absorption spectra were recorded at room temperature using a Varian Cary 5E UV−vis−NIR spectrophotometer (resolution 0.5 nm). C_{70}, C_{76}, all three C_{78} isomers, and C_{80} were studied in toluene solutions of known concentration using 1 or 5 mm path length cuvettes. For some fullerenes, hexane solutions were also studied to extend the UV range beyond the toluene cutoff. In all cases degassed solvents of purity, 98.5% for hexane and 99.8% for toluene, were used. Absolute absorption coefficients are good to ±1% or better for C_{60}, C_{70}, and C_{76}. For C_{78} (C_{2v}, C_{2v}, and D_3) as well as C_{80}, which we isolated and studied in significantly smaller quantities, extinction coefficients are accurate to ±10%.

III. Computational Methods

Our computational method is based on the time dependent extension of density functional theory (see ref 29 for a review) which opens the way to the treatment of frequency dependent response functions such as dynamic dipole polarizabilities $\alpha(\omega)$. Excitation energies and, for the case of dipole allowed transitions, oscillator strengths are given as poles and residues of the response functions as function of the frequency. The working equations of the TDDFT method closely resemble those of the Hartree−Fock (HF) random phase approximation (RPA). One basically replaces the terms due to the exchange contribution to the total energy (in HF) by the corresponding ones arising from the exchange-correlation term E_{XC} of DFT. This allows us to apply an efficient computational scheme based on an auxiliary basis set expansion[30] to approximate electron densities. It is due to this scheme that the treatment of relatively large low-symmetry molecules such as C_{78} has been possible using an approach which does not belong to the field of semiempirical methods. For a detailed description of the TDDFT method and its implementation used in this work the reader is referred to refs 31 and 32. Our TDDFT approximation can only be expected to describe excitations which are dominated by (one or more) single replacements from the ground state since only the poles of linear response functions are considered. In this respect the state of affairs is similar to that of HF-RPA. For fullerenes, highly correlated "π-plasmon" like absorption features are found in the 6−8 eV range.[33] We would therefore expect the TDDFT approximation to run into problems as these energies are approached-dependent in detail on symmetry and electron count of the fullerene in question.

In ref 34 test calculations on small molecules (N_2, formaldehyde, ethene, and pyridine) were carried out using the TDDFT method. A total number of 31 excitation energies were calculated and compared with experimental values. It was found that the B3LYP (see e.g., ref 34 for a description of B3LYP) and the B-P86[35] functional led to the best results with a mean deviation from experiment of −0.44 eV/−0.53 eV and a root mean square deviation of −0.54 eV/−0.65 eV. The nearly equal modulus of the values for the mean and the root mean square deviation (for B3LYP and B-P86) indicate that the error in the TDDFT excitation energies mainly has the character of a constant shift. An analogous behavior has been observed in DFT band structure calculations and is attributed to the incomplete cancellation of the coulomb self-interaction by the approximations for the exchange correlation functionals currently used.[36] If a shift of computed excitation energies is applied for fullerenes to facilitate comparison with measured spectra, one should especially take into consideration trends found for pyridine and porphine[31] as well as benzene and naphthalene.[32] In these cases we find a relatively small scatter

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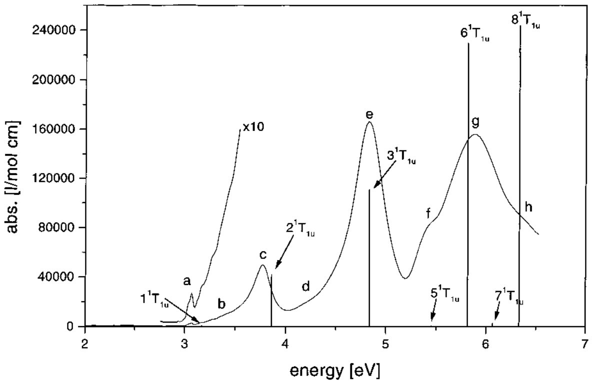

Figure 2. Absorption spectrum of C_{60} (I_h) in *n*-hexane solution at room temperature. Superimposed are TDDFT calculations of optically allowed transition energies corrected for systematic errors by adding 0.35 eV (see text). Oscillator strengths were normalized to experiment.

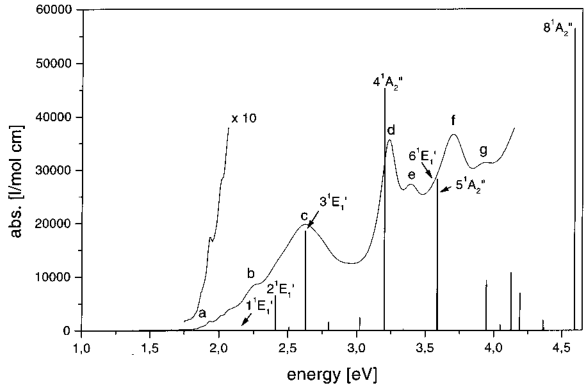

Figure 3. Toluene absorption spectrum and TDDFT calculation for C_{70} (D_{5h}) corrected and normalized as described for C_{60}.

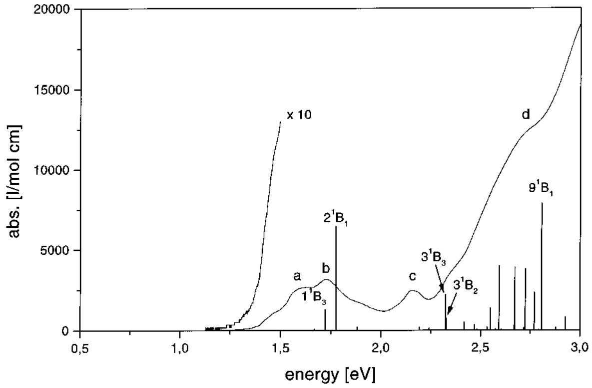

Figure 4. Absorption spectrum for C_{76} (D_2) recorded in toluene solution. Superimposed is the corrected TDDFT calculation.

for $\pi \rightarrow \pi$ transitions (deviations of less than 0.5 eV) and average shifts between about 0 eV (benzene) and −0.3 eV (pyridine).

For all fullerenes, studied structures were optimized using the DFT-SCF (self-consistent field) method with the B-P86 functional[35] and a basis set with SVP (split valence plus polarisation)[37] quality on carbon. For the C_{60} molecule this treatment leads to C−C distance of 145.9 pm/140.8 pm for the long and the short C−C bond which compares favorably with the experimentally determined values of 144.5 pm/139.9 pm[38] and 145.8 pm/140.1 pm.[39] All excitation energies reported in this work were calculated using B-P86 (SVP)-optimized molecular structures.

For the calculation of excitation energies at first a basis set proposed by Spackman[40] for the efficient calculation of molecular polarizabilities was used. It consists of a 6-31G basis which was augmented by a diffuse s- and a diffuse d-function. Exploratory calculations on C_{60} showed that the error introduced by omitting the diffuse d-function is smaller than 0.1 eV for the first eight dipole allowed excitations which range up to 6 eV. Since with five functions on every carbon atom the d-functions add substantially to the total amount of basis functions, the reduced basis set which will subsequently be called 6-31G+s was used throughout this work. In connection with this primary basis set a "TZVP (triple-ζ valence plus polarization) auxiliary basis"[41] was used as described in ref 14. In a number of test calculations it was confirmed that the error introduced by the auxiliary basis set expansion is insignificant.

The TDDFT calculations were carried out using the B-P86 functional. As observed in ref 31 and verified in calculations on C_{60}, the influence of the particular functional on the excitation energies is rather small as long as only nonhybrid functionals are considered. For the first five dipole allowed transitions of C_{60} the difference in excitation energies calculated using B-P86 functional and the classical LDA as proposed by Vosko, Wilk, and Nusair[42] was found to be less than 0.03 eV. Hybrid functionals as for example B3LYP[34] lead to excitation energies which generally interpolate between RPA results and results obtained by nonhybrid functionals. Since the efficiency of the auxiliary basis set expansion is lost if HF exchange is included, as in hybrid functionals, we did not use this type of functional in the present work.

IV. Results

(a) Experimental Data. Figure 2 shows an absorption spectrum for C_{60} in hexane solution. The concentration was approximately 2.5×10^{-5} mol/L. Figures 3−8 show absorption spectra obtained for toluene solutions of C_{70}, C_{76}, C_{78} (C_{2v}, $C_{2v'}$ and D_3), and C_{80}, respectively. Concentrations were approximately 10^{-4} mol/L for all toluene measurements. Included as inserts in Figures 5−7 are measurements in hexane solution for which concentrations were lower but not accurately known. In all spectra we have labeled pronounced local absorption maxima/shoulders in alphabetical order from low to high energies.

(b) Calculated Transitions. The energies, oscillator strengths, and excited state symmetries of selected dipole allowed transitions calculated for the known IPR cages of C_{60}, C_{70}, C_{76},[43] C_{78}, and C_{80} are listed in Tables 1−5. These are tabulated together with experimental peak maxima/shoulders and their previous literature assignment—insofar as this has been possible in a comprehensive fashion. In the case of C_{60} we tabulate all calculated transitions. For the lower symmetry fullerenes C_{70}, C_{76}, C_{78} (C_{2v}, $C_{2v'}$, and D_3), and C_{80} we list only those (generally dominant) transitions relevant to the experimental assignment. A comprehensive listing of **all** dipole allowed transitions for these molecules as well as C_{78} (D_{3h} and $D_{3h'}$) is given in footnote 44.

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(43) C_{76} has two IPR forms (D_2 and Jahn-Teller instable T_d). Only the D_2 form has been observed, and we have only calculated its spectrum.

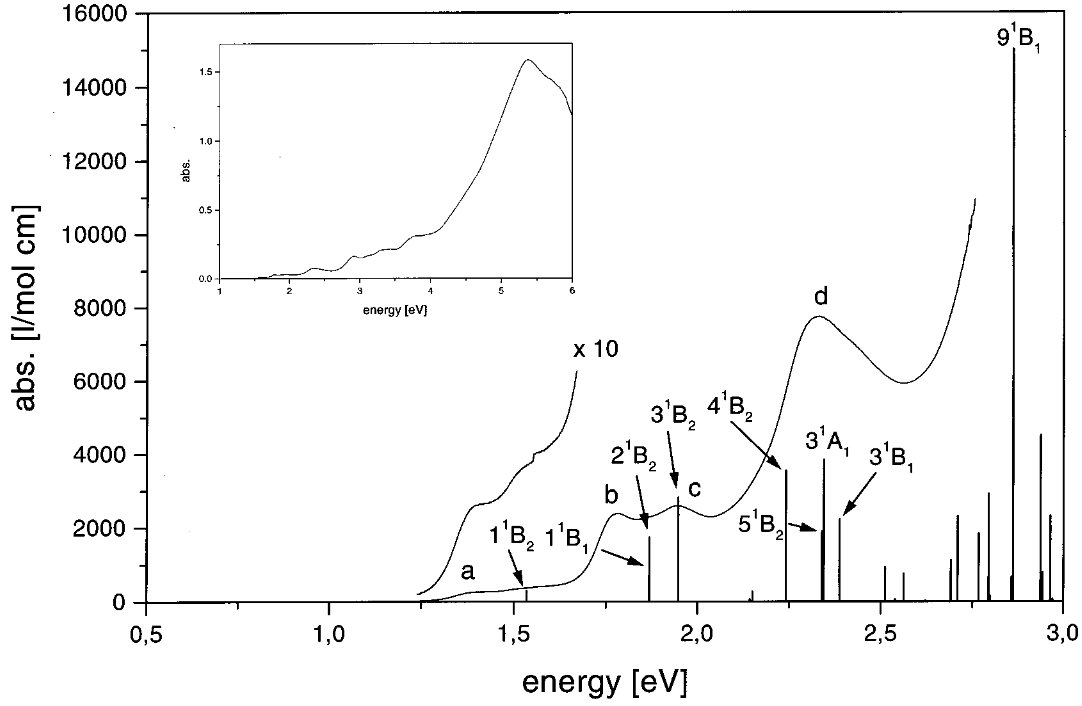

Figure 5. Absorption spectrum for C_{78} (C_{2v}) recorded in toluene solution. Superimposed is the corrected TDDFT calculation. The insert contains a measurement in hexane solution.

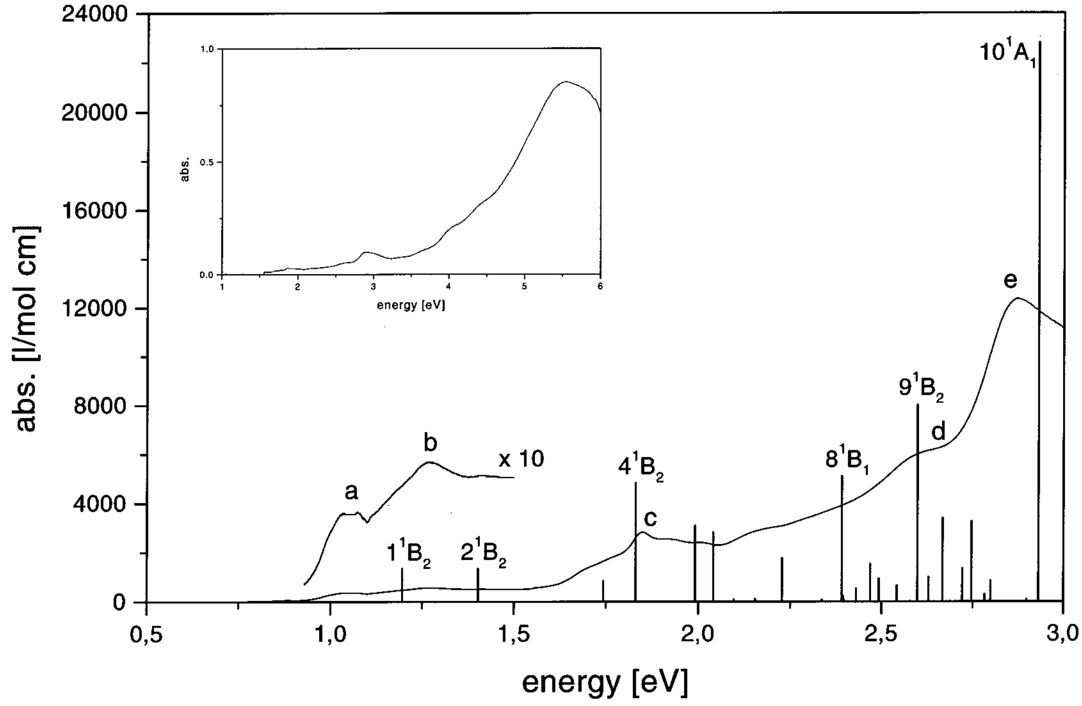

Figure 6. Absorption spectrum for C_{78} ($C_{2v'}$) recorded in toluene solution. Superimposed is the corrected TDDFT calculation. The insert contains a measurement in hexane solution.

V. Discussion

(a) Comparison of Measurements and Calculations: Energy Offset. Due to its high symmetry C_{60} has the lowest (energy) density of allowed transitions among fullerenes studied here. This facilitates comparison between experiment and theory. Based on the assignment of Table 1, which we discuss in more detail below, it appears that individual TDDFT excited state predictions are systematically lower than experiment. The "statistical" data base is not large enough to determine whether this deviation is itself a function of excitation energy. However, on the basis of test calculations for smaller molecules we expect a constant offset (see above). For C_{60}, over the energy range studied, the average deviation is −0.35 eV. In the absence of extensive test calculations for molecules of this size we therefore uniformly blue shift **all** calculated transition energies by adding 0.35 eV to TDDFT predictions. This is documented in Figures 2−8 which show stick plot representations of calculated oscillator strengths and corrected transition energies superimposed on the experimental data. A uniform offset of 0.35 eV is justifiable "after the fact" by the uniformly good agreement

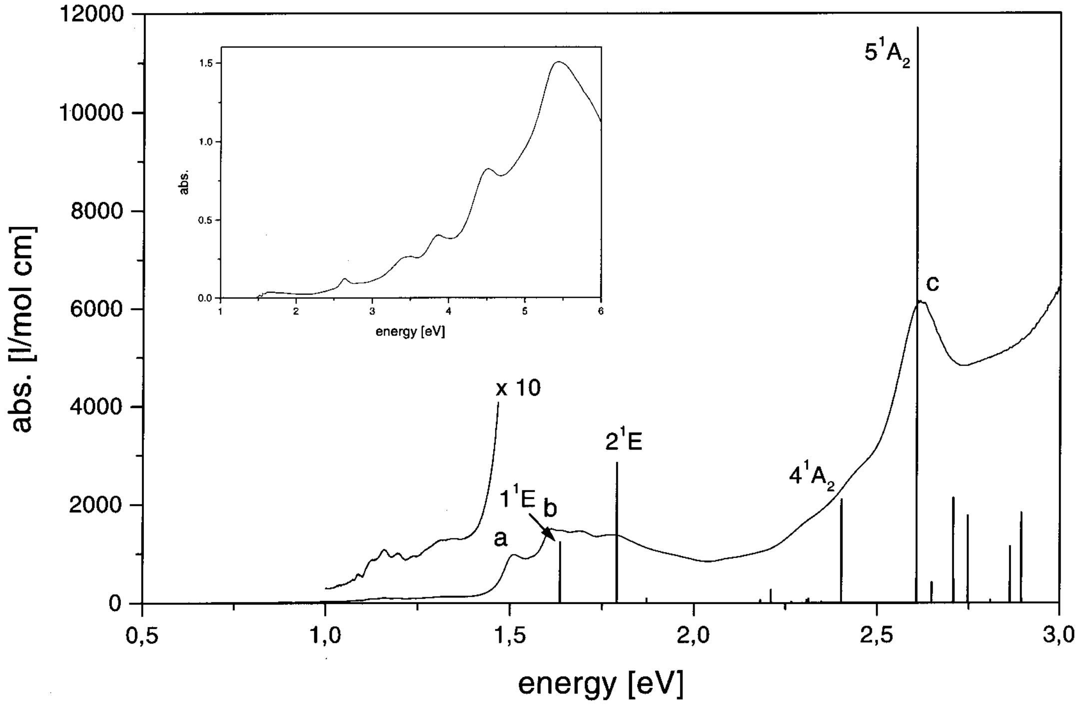

Figure 7. Absorption spectrum and corrected TDDFT calculation for C_{78} (D_3) recorded in toluene solution. The insert contains a measurement in hexane solution.

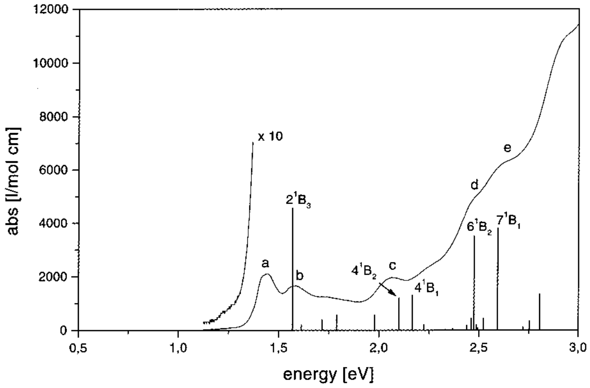

Figure 8. Absorption spectrum and corrected TDDFT calculation for C_{80} (D_2) recorded in toluene solution.

between experiment and corrected theory apparent in the figures. Oscillator strengths calculated for C_{60} were normalized to give best agreement to the spectrum. The corresponding scaling factor was thereafter used consistently for all other spectra. Rough estimates show that the spectral regions experimentally probed always contain ±50% of the integrated oscillator strength expected on the basis of calculations.

Note that while the experiment probes the optical response of fullerene molecules subject to differing degrees of solvent pertubation in ground and excited state, the calculation refers to isolated ("gas phase") species with zero vibrational excitation. In the case of C_{60}, systematic studies have indicated that at room temperature, solvent interactions generally cause red shifts of transitions relative to gas phase.[7] Depending on the excited state, this can be as much as 500 cm^{-1} for toluene solutions. Roughly the same red shift relative to gas phase has been derived for C_{70} in toluene solutions.[7] Smaller shifts are observed for hexane solutions. The effect is rationalized primarily in terms of differences between ground and excited state static polarizabilities and corresponding changes to the interaction between chromophore and solvent environment. Solvatochromism has not been systematically studied for larger fullerenes. On the basis of photoacoustic probes of C_{76} and C_{78} microcrystalline powders[45] and extrapolations analogous to those of ref 7 we expect C_{76}, C_{78}, and C_{80} toluene solution spectra to be red shifted

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(44) Calculated optically allowed transitions (energies in eV (oscillator strengths)) ordered by symmetry: (i) C_{70} (D_{5h}) A_2'': 2.16 (0.002), 2.45 (0.005), 2.67 (0.008), 2.85 (0.151), 3.24 (0.087), 3.84 (0.023), 4.01 (0.006), 4.24 (0.188); E_1': 1.79 (0.0003), 2.06 (0.022), 2.28 (0.062), 2.80 (0.000), 2.99 (0.001), 3.24 (0.094), 3.60 (0.031), 3.70 (0.004), 3.78 (0.036), 4.02 (0.002), 4.04 (0.005), 4.15 (0.005). (ii) C_{76} (D_2), B_1: 1.32 (0.000), 1.43 (0.022), 1.89 (0.000), 2.10 (0.000), 2.13 (0.000), 2.20 (0.005), 2.32 (0.001), 2.37 (0.001), 2.46 (0.026), 2.58 (0.003); B_2: 1.13 (0.000), 1.53 (0.001), 1.98 (0.002), 2.12 (0.001), 2.18 (0.001), 2.24 (0.013), 2.32 (0.000), 2.38 (0.013), 2.44 (0.000), 2.53 (0.001); B_3: 1.37 (0.004), 1.84 (0.001), 1.97 (0.007), 2.07 (0.002), 2.13 (0.000), 2.22 (0.000), 2.25 (0.000), 2.32 (0.013), 2.42 (0.008), 2.65 (0.001). (iii) C_{78} (C_{2v}) A_1: 1.79 (0.000), 1.88 (0.000), 2.00 (0.013), 2.23 (0.000), 2.31 (0.000), 2.34 (0.004), 2.42 (0.006), 2.51 (0.002), 2.59 (0.003), 2.61 (0.008); B_1: 1.52 (0.002), 1.80 (0.001), 2.04 (0.007), 2.19 (0.000), 2.21 (0.003), 2.27 (0.000), 2.36 (0.008), 2.45 (0.001), 2.51 (0.050), 2.62 (0.002); B_2: 1.19 (0.001), 1.52 (0.006), 1.60 (0.009), 1.89 (0.012), 1.99 (0.006), 2.16 (0.003), 2.26 (0.000), 2.29 (0.000), 2.44 (0.010), 2.59 (0.015). C_{78} (C_{2v}') A_1: 1.69 (0.009), 2.05 (0.000), 2.08 (0.002), 2.14 (0.003), 2.19 (0.002), 2.23 (0.000), 2.30 (0.000), 2.37 (0.005), 2.40 (0.011), 2.58 (0.076); B_1: 1.75 (0.000), 1.80 (0.000), 1.93 (0.000), 1.99 (0.000), 2.04 (0.017), 2.25 (0.000), 2.28 (0.003), 2.32 (0.011), 2.43 (0.001), 2.45 (0.003); B_2: 0.85 (0.005), 1.05 (0.005), 1.39 (0.003), 1.48 (0.016), 1.64 (0.010), 1.88 (0.006), 2.04 (0.001), 2.12 (0.005), 2.25 (0.027), 2.55 (0.000). C_{78} (D_3) A_2: 0.80 (0.000), 1.83 (0.000), 1.96 (0.000), 2.05 (0.007), 2.26 (0.039), 2.36 (0.007), 2.51 (0.004), 2.55 (0.000), 2.66 (0.000), 2.81 (0.001); E: 1.29 (0.004), 1.44 (0.010), 1.52 (0.000), 1.86 (0.001), 1.92 (0.000), 1.96 (0.000), 2.00 (0.000), 2.30 (0.001), 2.36 (0.002), 2.40 (0.006), 2.46 (0.000), 2.54 (0.006). C_{78} (D_{3h}) A_2'': 1.93 (0.006), 2.18 (0.009), 2.31-(0.001), 2.50 (0.032), 2.68 (0.005), 3.08 (0.181), 3.54 (0.000), 3.71 (0.009); E': 1.86 (0.000), 2.02 (0.003), 2.29 (0.000), 2.33 (0.001), 2.36 (0.003), 2.50 (0.011), 2.68 (0.000), 2.69 (0.002), 2.82 (0.000), 3.02 (0.014), 3.11 (0.051), 3.27 (0.000), 3.32 (0.001), 3.36 (0.023), 3.53 (0.044), 3.59 (0.005). C_{78} ($D_{3h'}$) A_2'': 0.80 (0.001), 1.15 (0.044), 2.07 (0.001), 2.35 (0.078), 2.70 (0.019) 3.12 (0.001), 3.28 (0.008), 3.35 (0.038); E': 1.87 (0.012), 2.02 (0.000), 2.07 (0.002), 2.11 (0.001), 2.21 (0.002), 2.24 (0.018), 2.36 (0.005), 2.50 (0.008), 2.68 (0.130), 3.26 (0.013), 3.31 (0.000), 3.40 (0.005). C_{80} (D_2) B_1: 0.56 (0.000), 1.44 (0.002), 1.72 (0.000), 1.82 (0.004), 2.09 (0.001), 2.14 (0.001), 2.24 (0.013), 2.40 (0.000); B_2: 1.26 (0.001), 1.37 (0.013), 1.63 (0.002), 1.75 (0.004), 2.02 (0.000), 2.13 (0.012), 2.17 (0.001), 2.40 (0.001); B_3: 1.13 (0.000), 1.22 (0.015), 1.87 (0.001), 1.98 (0.000), 2.11 (0.001), 2.14 (0.000), 2.37 (0.000), 2.45 (0.004).

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Table 1. Calculated TDDFT Excitation Energies and Oscillator Strengths for Optically Allowed Transitions in C_{60} in Comparison to Previous Assignments in Experimental Absorption Spectra[e]

	exp. 1[a]			exp. 2[b]		this work		
spectral feature[c]	assignmt	E_{obs}	f_{obs}	assignmt	E_{obs}	assignmt	E_{calc}	f_{calc}
a	1^1T_{1u}	3.04	0.015	($^1T_{2u}$	3.02)	1^1T_{1u}	2.82	0.002
b	2^1T_{1u}	3.30				*d*		
c	3^1T_{1u}	3.78	0.37	$^1T_{1u}$	3.81	2^1T_{1u}	3.51	0.139
d	4^1T_{1u} 5^1T_{1u}	4.06 4.35	0.10	($^3T_{1u}$	4.22)	*d*		
e	6^1T_{1u}	4.84	2.27	$^1T_{1u}$	4.90	3^1T_{1u}	4.48	0.369
f	7^1T_{1u}	5.46	0.22	($^3T_{1u}$	5.52)	4^1T_{1u} 5^1T_{1u}	5.02 5.10	0.000 0.003
g	8^1T_{1u}	5.88	3.09	$^1T_{1u}$	5.96	6^1T_{1u}	5.47	0.765
h	9^1T_{1u}	6.36				7^1T_{1u} 8^1T_{1u}	5.72 5.98	0.008 0.812

[a] Absorption spectrum of C_{60} in *n*-hexane at 300 K [5]. [b] Absorption spectrum of C_{60} in an argon matrix at 5 K [6]. [c] See Figure 2. [d] See text for tentative assignment. [e] Values in parentheses indicate nominally dipole forbidden transitions. All energies in eV.

Table 2. Assignment of C_{70} Absorption Spectrum by Comparison to TDDFT Excitation Energies for Optically Allowed Transitions[e]

		this work			CNDO/S[c]	
spectral features	E_{obs}	assignmt	E_{calc}	f_{calc}	assignmt	E_{calc}
a	1.95	$1^1E_1'$	1.79	0.0003		
b	2.27	$2^1E_1'$	2.06	0.022		
c	2.62	$3^1E_1'$	2.228	0.062	$^1E_1'$ [d]	2.37
d	3.24	$4^1A_2''$	2.85	0.151	$^1E_1' + A_2''$	3.00
e	3.4				$^1E_1'$	3.52
f	3.7	$6^1E_1'$ $5^1A_2''$	3.24 3.24	0.094 0.087	A_2''	3.75
g	3.92					

[a] See Figure 3 for comparison to corrected TDDFT enegies. [b] See footnote 44 for all optically allowed transitions in energy range. [c] Comparison to assignment based on CNDO/S. See ref 21. [d] State numbering not given; see Figure 2 in ref 21 for a rough estimate of relative f_{calc}. [e] All energies in eV.

Table 3. Assignment of C_{76} Absorption Spectrum by Comparison to TDDFT Excitation Energies for Optically Allowed Transitions[d]

		this work[b]			CNDO/S[c]		
spectral features[a]	E_{obs}	assignmt	E_{calc}	f_{calc}	assignmt	E_{calc}	f_{calc}
a	1.60	1^1B_3	1.37	0.004	1^1B_3	1.72	0.0000
b	1.73	2^1B_1	1.43	0.022	1^1B_2	1.86	0.0412
c	2.17	3^1B_3 3^1B_2	1.97 1.98	0.007 0.002	1^1B_1 2^1B_3 2^1B_1 3^1B_3	1.98 2.03 2.32 2.37	0.0296 0.0047 0.0047 0.0052
d	2.75	6^1B_2 8^1B_3 8^1B_2 9^1B_1	2.24 2.32 2.38 2.46	0.013 0.013 0.013 0.026	7^1B_3	2.92	0.1023

[a] See Figure 4 for comparison to corrected TDDFT energies. [b] See footnote 44 for all optically allowed transitions in energy range. [c] Assignment based on Table 2 of ref 54. [d] All energies in eV.

relative to room temperature gas phase by about the same amount as C_{60}, i.e., not significantly more than 500 cm^{-1}. Except for hot band complications, the differences between room temperature and low temperature gas phase peak positions are expected to be much smaller than effects due to solvatochromism.[7] Consequently, in comparing measurements to TDDFT prediction, an energy shift of at most +0.05 to +0.07 eV must be applied to the experimental data (to account for solvatochromism). The calculations then appear to be systematically off by about −0.40 to −0.42 eV. This is somewhat more than found in our previous test calculations on small molecules (see above) but comparable with offsets observed in a recent LDA-SCC study of C_{60} optical response (see below).

(b) Assignment and Comparison to Previous Work. (i) C_{60} (I_h). Figure 2 is in quantitative agreement with previous measurements of C_{60} optical absorption in hexane solutions at room temperature.[3] This is not the case for the positions and oscillator strengths of calculated transitions cf. previous calculations. For example, CNDO/S calculations including over 930 configurations—still state of the art for this method-locate the first five excited $^1T_{1u}$ states between 3.36 ($^1T_{1u}$) and 4.97 eV (5 $^1T_{1u}$).[18] In contrast TDDFT calculations yield a wider separation of these states as well as significantly different relative intensities. Consequently we propose a UV-region spectral assignment deviating slightly from that of the classic study of ref 3 (which was itself based on an earlier CNDO/S calculation with smaller single excitation configuration space). While the symmetry assignment of dominant features a, c, e, and g remains, c now corresponds to 2 $^1T_{1u}$ − 1 ^1A_g rather than 3 $^1T_{1u}$ − 1 ^1A_g, e to 3 $^1T_{1u}$ − ^1A_g, rather than 6 $^1T_{1u}$ − 1 ^1A_g, and so on (see Table 1). Minor features b and d previously assigned to 2 $^1T_{1u}$ and 4/5 $^1T_{1u}$, respectively, must then be reassigned. We propose 1

Table 4. Assignment of C_{78} Isomer Absorption Spectra by Comparison to TDDFT Excitation Energies for Optically Allowed Transitions[b]

isomer	spectral features[a]	E_{obs}	assignmt	E_{calc}	f_{calc}
C_{2v}	a	1.39	1^1B_2	1.19	0.001
	b	1.78	1^1B_1	1.52	0.002
			2^1B_2	1.52	0.006
	c	1.95	3^1B_2	1.60	0.009
			4^1B_2	1.89	0.012
	d	2.33	5^1B_2	1.99	0.006
			3^1A_1	2.00	0.013
			3^1B_1	2.04	0.007
$C_{2v'}$	a	1.04	1^1B_2	0.85	0.005
	b	1.27	2^1B_2	1.05	0.005
	c	1.85	4^1B_2	1.48	0.016
	d	2.60	9^1B_2	2.25	0.027
	e	2.87	10^1A_1	2.58	0.076
D_3	a	1.51	1^1E	1.29	0.004
	b	1.61	2^1E	1.44	0.010
	c	2.62	5^1A_2	2.26	0.039

[a] See Figure 5 for comparison to corrected TDDFT energies. See footnote 44 for all optically allowed transitions in energy range. [b] All energies in eV.

Table 5. Assignment of C_{80} Absorption Spectrum by Comparison to TDDFT Excitation Energies for Optically Allowed Transitions[b]

spectral features[a]	E_{obs}	assignmt	E_{calc}	F_{calc}
a	1.43	2^1B_3	1.22	0.015
b	1.57			
c	2.06	4^1B_2	1.75	0.004
		4^1B_1	1.82	0.004
d	2.47	6^1B_2	2.13	0.012
e	2.61	7^1B_1	2.24	0.013

[a] See Figure 5 and footnote 44 for comparison to corrected TDDFT energies. [b] All energies in eV.

$^1T_{1u} + a_g\ (1) + h_g\ (4)$ for b and for d tentatively resurrect spin-orbit mixed 2 $^3T_{1u} - 1\ ^1A_g$ as originally suggested in ref 13 to explain MCD spectra obtained in argon matrices.

It is of interest to note that a recent LDA-SCC study of C_{60} response, which bears methodological similarities to our calculation, comes to quantitatively similar conclusions—including roughly the same energy offset.[22] This study contains an illuminating detailed comparison of LDA-SCC prediction and various competing computational approaches.

(ii) C_{70} (D_{5h}). Spectral features and their relative intensities as shown in Figure 3 agree with previous measurements. Our absolute absorption coefficients are lower than determined in an early toluene solution study (e.g., $\epsilon_{382} \cong 37\,500$ (ref 46) versus $35\,000$ L mol^{-1} cm^{-1}) but larger than obtained for analogous band maxima in a more recent benzene solution measurement (e.g., $\epsilon_{381} = 29\,400$ L mol^{-1} cm^{-1} [47]).

Almost all calculations of C_{70} electronically excited states relevant to global spectral assignment have been performed at the CNDO/S or INDO/S level. A recent CNDO/S calculation including an MO space of 47 × 35 is representative of the level of accuracy obtained.[21] Based on this calculation, the C_{70} spectrum has been partially assigned as indicated in Table 2. The TDDFT calculation makes possible a more comprehensive assignment as also indicated in Table 2. As in all subsequent tables we list only states relevant to spectral assignment (i.e., with significant one-photon oscillator strength near pronounced experimental features). For all other optically allowed states see footnote 44.

Our assignment is consistent with a recent experimental determination of fluorescence polarization, which concludes that all optically allowed transitions from the absorption threshold to beyond 470 nm are xy polarized.[48] Note, however, that a recent semiempirical calculation specifically directed toward modeling C_{70} emission spectra[15] suggests that the first absorption feature of C_{70} may be complicated by a quasi-degeneracy and associated vibronic coupling with forbidden states.[49]

(iii) C_{76} (D_2). Room temperature absorption spectra of C_{76} solutions have been reported for various solvents including hexane,[50] dichloromethane,[51] methylcyclohexane,[52] and toluene.[53] Figure 4 is in good qualitative agreement with these measurements. Only in the case of dichloromethane solutions have absolute absorption coefficients been previously reported.[51] Corresponding band maxima in toluene solution appear roughly 25% larger than in the latter study.

There are only a limited number of previous excited state calculations. Most extensive are CNDO/S and INDO/S predictions of electronic absorption and magnetic circular dichoism spectra.[54] Table 3 compares the latter CNDO/S calculations to this work. Again TDDFT appears to do somewhat better at describing the experiment. We therefore tentatively assign the spectrum as indicated. This assignment is consistent with circular dichoism spectra of kinetically resolved C_{76} (D_2).[53]

(iv) C_{78} is the smallest fullerene for which separate cage isomers have been isolated. It can be shown on the basis of topological arguments (ring spiral algorithm) that C_{78} has five possible isolated pentagon ring isomers (IPR).[24] Of these, three have been detected and isolated: C_{2v}, $C_{2v'}$, and D_3.[17,26] Comparative computational studies of the ground states of all five C_{78} IPR forms[25,55,56] generally come to the conclusion that the three most stable isomers are being produced. Conceivably it will prove possible to interconvert C_{78} isomers and in so doing generate the "missing" IPR forms. In order to prepare for this eventuality, it was of interest to perform excited state calculations not only for the three known isomers but also for the two remaining D_{3h} isomers.[25]

Figures 5−7 contain absorption spectra obtained in toluene and hexane solutions for C_{78} (C_{2v}), C_{78} ($C_{2v'}$), and C_{78} (D_3), respectively. For toluene solutions we also report absolute absorption coefficients. Each IPR form is readily distinguishable on the basis of its fingerprints. We discuss each in turn. Figure 5 is in qualitative agreement with previous measurements of C_{78} (C_{2v}) in CH_2Cl_2 solution.[57] However, our absorption cross sections are about 25% larger. The only previous experimental study of C_{78} ($C_{2v'}$)—other than a preliminary measurement by our group in CS_2[24]—was carried out in methylcyclohexane solution.[52] It is in qualitative agreement with this study but does not contain extinction coefficients. C_{78} (D_3) absorption

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has been studied in CH_2Cl_2 with no extinction coefficients given.[57] Furthermore, circular dichoism spectra have been obtained for kinetically resolved C_{78} (D_3) in toluene.[58] We are in qualitative agreement with these experiments.

There are only a small number of excited state calculations for C_{78} isomers. Of these the only ones relevant to spectral assignment are again at the semiempirical CI-singles level. Agreement with experiment is generally modest.[24,25] In particular, C_{78} isomers **cannot** be distinguished on the basis of predicted spectra.[25] In contrast, Figures 5−7 (+ footnote 44) show near quantitative agreement between TDDFT calculation and experiment—thus allowing isomer distinction. Table 4 lists tentative spectral assignments on the basis of our calculations. We choose not to provide a detailed comparison of TDDFT excitation energies with previous semiempirical prediction—similar global trends as apparent in Tables 1−3 apply. From TDDFT calculations of C_{78} (D_{3h} and $D_{3h'}$) it is apparent that these forms should have characteristic fingerprints allowing their assignment form solution spectra, should it prove possible to generate and purify them.

(v) C_{80} (D_2). We have recently reported the isolation and partial characterization of C_{80}.[28] This included an absorption spectrum in CH_2Cl_2 solution, together with a rough estimate (±40%) of the extinction coefficients. Figure 8 contains an absorption spectrum in toluene solution obtained for a larger quantity of C_{80} (+ more concentrated solution) than in our previous work. Extinction coefficients are now good to ±10% and appear somewhat larger than found by us in CH_2Cl_2 solutions.[28] There are no other experimental determinations of C_{80} solution spectra. Similarly, there are no relevant excited state calculations. Figure 8 and Table 5 contrast experiment and TDDFT calculations of C_{80}(D_2). Agreement is again satisfactory allowing tentative assignment of dominant spectral features as indicated. The level of agreement is itself further confirmation of our original D_2—symmetry structural inference based on ^{13}C-NMR measurements.[24]

VI. Summary and Outlook

TDDFT calculations allow near quantitative prediction of dipole allowed transitions for C_{60} (I_h), C_{70} (D_{5h}), C_{76} (D_2), C_{78} (C_{2v}), C_{78} ($C_{2v'}$), C_{78} (D_3), and C_{80} (D_2). Comparison to experiment shows that after correction for systematic error the accuracy is high enough to allow (i) (re)assignment of spectra and (ii) isomer discrimination in the case of all IPR forms of C_{78}. Detailed analysis of excited state wave functions for these and as yet experimentally unstudied larger fullerenes will allow insight into the nature and degree of localization of specific excitations. On the experimental side, it will be of interest to perform absorption measurements at lower temperatures in order to (further) assign vibronic fine structure.

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