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Bis-perfluorocycloalkenyl (PFCA) aryl ether monomers towards a versatile class of semi-fluorinated aryl ether polymers

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ABSTRACT

A unique class of perfluorocycloalkenyl (PFCA) aryl ether monomers was synthesized from commercially available perfluorocycloalkenes (PFCAs) and bisphenols in good yields. This facile one pot reaction of perfluorocycloalkenes, namely, octafluorocyclopentene (OFCP), and decafluorocyclohexene (DFCH), with bisphenols occurs at room temperature via an addition–elimination reaction in the presence of a base. The synthesis of PFCA monomers and their condensation with bisphenols lead to perfluorocycloalkenyl (PFCA) aryl ether homopolymers and copolymers with random and/or alternating polymer architectures.

Perfluorinated and semi-fluorinated polymers are continually sought due to their profound and exclusive properties in applied chemistry and biochemistry.[1–4] Innovative and efficient methods are highly desired to strategically incorporate fluorine into molecular architectures with outstanding and specifically designed performance. Incorporation of fluorine into polymeric systems results in a unique combination of properties such as excellent thermal stability, chemical inertness, unique surface properties, low refractive index, low dielectric constant, and low optical loss in telecom wavelength.[1,2,5–10] Such materials are potentially suitable as matrices for non-linear optics (NLO) or electro-optics (EO) applications as demonstrated by Iacono et al, and many other research groups including ours with perfluorocyclobutyl (PFCB) aryl ether polymers and other fluorinated vinylene derived polymers.[8–11]

Perfluorocycloalkenes (PFCA) are a general class of compounds comprising many commercially available perfluorocyclo-olefins including octafluorocyclopentene (OFCP) and decafluorocyclohexene (DFCH) (Fig. 1). As expected, PFCAs react with various nucleophiles including phenoxides,[12–15] alkoxide,[16–18] organometallic,[19–21] amines,[22–25] thiols,[26] azoles[27] and phosphonium ylides.[28] PFCA derivatives have thus shown a variety of applications including photochromic small molecules,[29–33] nonlinear optical activity,[34] lubricants,[21] and etching agents.[35] Herein we extend our recently published initial discovery of perfluorocyclopentenyl (PFCP) aryl ether polymers[5]––a new step growth Polycondensation and report the synthesis of bis-perfluorocycloalkenyl (PFCA) aryl ether monomers from perfluorocyclo-olefins, namely, OFCP and DFCH and bisphenols via an addition–elimination reaction in the presence of a base (Scheme 1).

Table 1 denotes the bisphenol and PFCA starting materials, monomers there from (**M1**–**M6**), and isolated yield of the condensation reaction. Further, the X-ray crystal structures of **M1** (Fig. 2) and **M6** (Fig. S22) were also solved.

With few exceptions such as, fluorinated vinylene derived Teflon, perfluorocyclco-olefins, in general, do not undergo homopolymerization via free radical mechanism.[36] Recently, we have

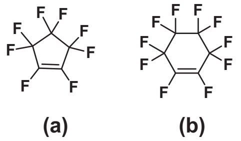
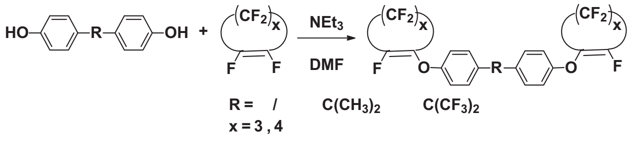


Figure 1. Commercially available perfluorocycloalkenes (a) OFCP and (b) DFCH.



Scheme 1. Perfluorocycloalkenyl (PFCA) aryl ether monomer synthesis.

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Table 1
Reaction of bisphenols with perfluorocycloalkenes

Entry	Bisphenol	PFCA	Yield[a] (%)
M1	Biphenol	OFCP	76
M2	Bisphenol-A	OFCP	71
M3	Bisphenol-AF	OFCP	72
M4	Biphenol	DFCH	69
M5	Bisphenol-A	DFCH	63
M6	Bisphenol-AF	DFCH	62

[a] Based on isolated product.

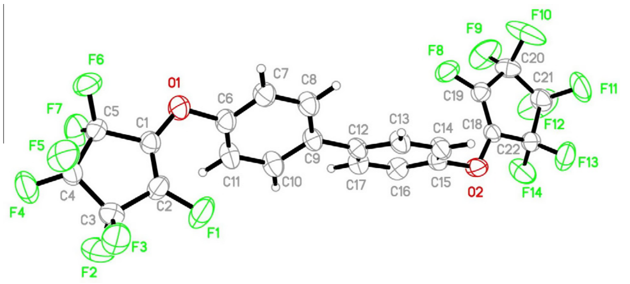
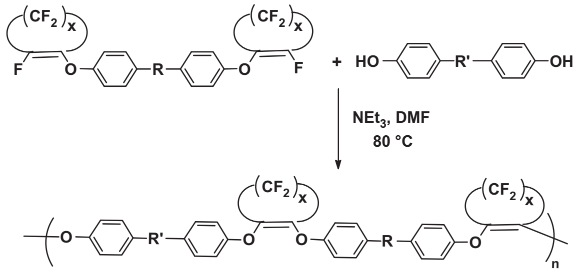


Figure 2. ORTEP representation of M1 crystal structure.

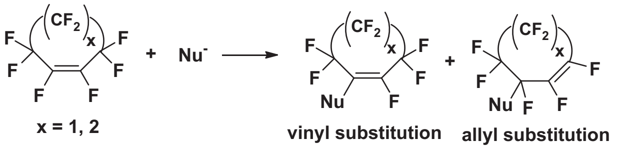


Scheme 2. General synthesis of PFCA aryl ether polymers from PFCA aryl ether monomers.

published the first polymerization of PFCAs using a novel step growth condensation with bisphenols.[5] PFCA aryl ether polymers are highly thermally stable and show variable thermal properties depending upon the functional spacer group, R (Scheme 2).

Due to the volatility of perfluorocycloalkenes, the stochiometry ratio is difficult to sustain during polymerization. However, bis-PFCA aryl ether monomers reported here, not only precludes the stochiometry ratio issue, but also provides a new synthetic versatility which can afford a variety of random and/or alternating copolymers with specific design control to be published elsewhere (Scheme 2).[5] These monomers also provide the option of synthesizing copolymers containing both, OFCP and DFCP moieties.

Attack of the nucleophile on the PFCA double bond generates a carbanion which can eliminate fluoride resulting in vinyl substituted and allyl substituted products (Scheme 3). The ratio of vinylic to allylic products depends on the ring size, reaction conditions and nucleophile.[26] The vinylic product would be the major product unless the allyl position has a more favored leaving group.[26] The allylic product was noticeable in case of DFCH (**M3**–**M6**) as evident by three signals with identical molecular weight in the GC–MS spectra (Fig. S23). Allyl substitution was not observed in case of OFCP (**M1**–**M3**) as evidenced by NMR and GC–MS. The presence of allylic products for **M4**–**M6** also explains the unaccounted signals in the ^{1}H, ^{19}F and ^{13}C NMR (Figs. 3 and S13–S20). Interestingly, there were no other addition products, as has previously been reported with fluorinated arylene vinylene ether (FAVE) polymers.[37,38]



Scheme 3. General reaction representation for addition–elimination reactions on perfluorocycloalkenes.

^{13}Carbon (^{19}F-coupled) NMR has been proved to be a very helpful technique to determine structural properties of **M1**–**M6**. ^{19}Fluorine coupled ^{13}Carbon NMR of perfluorocycloalkenes and their products show short range as well as long range coupling, and each carbon of PFCA ring shows a splitting pattern due to each fluorine atom present on the ring. For example, in OFCP the β carbon, a, with two fluorine atoms shows a tquint.t with $J = 1375.0$, 120.0, 25.4 Hz, and the α carbon, b, shows a tqm, $J = 1287.5$, 116.8 Hz (Fig. S2). As expected, DFCH and its products show a more complicated and unresolved splitting pattern in their ^{13}C NMR spectra due to the higher number of fluorine atoms (Figs. S4, S15, S18 and S20).

In the case of **M1**, the ^{1}H NMR spectrum (Fig. S5) shows a doublet of doublet (at 7.41 and 7.67 with $J = 8.2$ Hz), representing a symmetric environment. The ^{19}F NMR (Fig. S6) shows well integrated four fluorine peaks, where peak at −150.45 ppm represents the terminal vinyl fluorine indicating the addition–elimination reaction product. The ^{13}C NMR (^{19}F coupled) spectrum (Fig. 4) shows singlets for the phenylene carbons whereas PFCP ring carbon signals undergo short range as well as long range coupling and therefore a complex pattern is observed. For example, the allylic carbon, f, shows ttd with $J = 1032.1$, 98.5, 27.7 Hz whereas the β carbon, e, shows a broad splitting pattern overlapping with adjacent carbon, g's, signals.

To further establish the structures and understand the solid-state nature of these monomers, X-ray analysis was conducted. Bis-PFCA monomers were purified using column chromatography with hexanes as the eluent. The purified monomers, **M1**, **M4** and **M6** were obtained as white crystalline solids, while other monomers were highly viscous clear liquids. Attempts to crystallize **M1**, **M4** and **M6** from a multitude of polar and non-polar solvents were unsuccessful. Finally, recrystallization of **M1** and **M6** from chlorobenzene and a mixture of toluene and bromobenzene, respectively, with a slow evaporation, resulted in the afforded X-ray quality crystalline solids. Crystal structures for **M1** and **M6** are shown in Figures 2 and S22, and selected crystal properties including dihedral bond angles (°) for **M1** and **M6** are reported in Tables 2 and S1, respectively.

Figure 2 shows the ORTEP representation for **M1**. Crystal structure measurements were carried out at 193 K. The crystal shows the monoclinic, P21/n space group with no sign of thermal atomic displacement. Both PFCP rings show a presence of a double bond (C1–C2 and C18–C19) with a bond length of 1.32 Å. Two phenyl rings stand with a torsion angle (C8-C9-C12-C13) of 30.8°. The PFCP ring (with higher numbered carbon) inclined to the phenyl ring with 90.3°, but the other PFCP ring inclined with 56.6° to the corresponding phenyl ring. Interestingly, the former PFCP ring is almost planar, but PFCP ring (with lowered numbered carbon) shows an envelope conformation with the flap atom, C4.

Figure S22 shows the ORTEP representations for molecule A and molecule B, two conformation structures of **M6** crystal. Crystal data were recorded at 188 K. The crystal shows triclinic, P-1 space group and a significant amount of thermal displacements, resulting in the asymmetry in molecules. **M6** crystal properties are very different from **M1** crystal structural properties because of two extra trifluoromethyl groups and a bigger PFCA rings. Both molecules A and B show the $C\equiv C$ bond length of 1.32 Å in PFCH rings as we

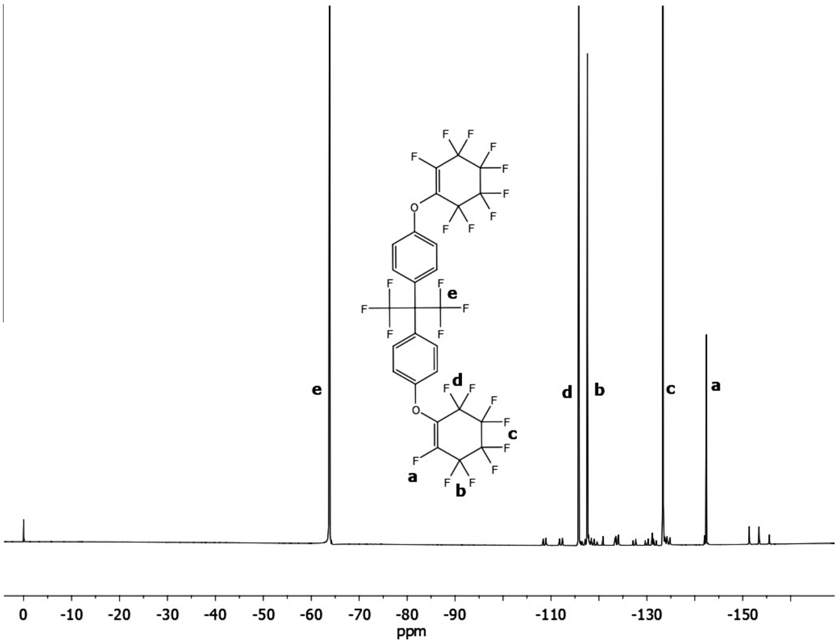


Figure 3. ^{19}F NMR of monomer **M6**. Minor peaks represent the allyl substituted products.

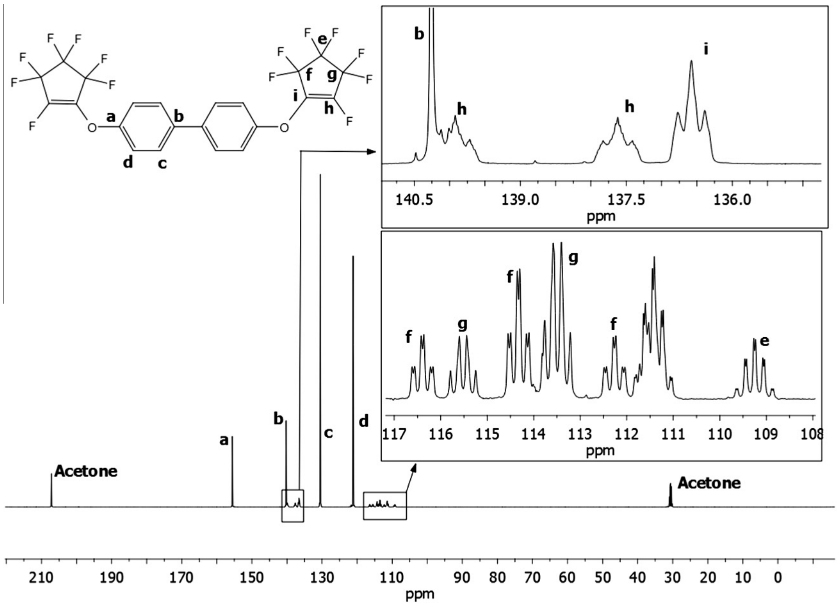


Figure 4. ^{13}C NMR (^{19}F-coupled) of monomer **M1**. Insets: expanded signals of PFCP ring carbons.

Table 2
Selected crystal data and structure refinements for monomer **M1**

Parameters	**M1** (°)
C8-C9-C12-C13	30.8
C1-O1-C6-C11	56.6
C18-O2-C15-C14	90.3
C2-C1-C5-C4	10.2
C18-C19-C20-C21	−1.5

see in **M1** crystal. The PFCH rings inclined to the corresponding phenyl rings with an angle ranging from 62° to 74°. In molecule A the high numbered PFCH rings shows half chair geometry with no sign of atomic displacement whereas the low numbered PFCH ring shows distorted chair to distorted half chair conformation with atom C14 distorted over two sites (C14 and C14A), and concomitant disorder of F atoms on the ring. In molecule B, both PFCH rings show the half chair conformation; with the high numbered PFCH ring showing the atomic thermal displacement (F23′ and F23B).

These PFCA monomers (**M1**–**M6**) were also characterized with ATR-FTIR. Figures 5 and S21 show the IR spectrum for monomers **M1**–**M6**. A strong peak at 830 cm^{-1} represents the typical, out of plane, aromatic C–H bending mode.[39] These spectra show the characteristic bands from 1080 to 1285 cm^{-1} due to CF$_2$ and C–O–C asymmetric stretching.[35,40] Peaks at 1499 and 1600 cm^{-1} (strong and medium intensities respectively) are associated with C=C stretching for the aromatic rings in these spectra. Figures 5 and

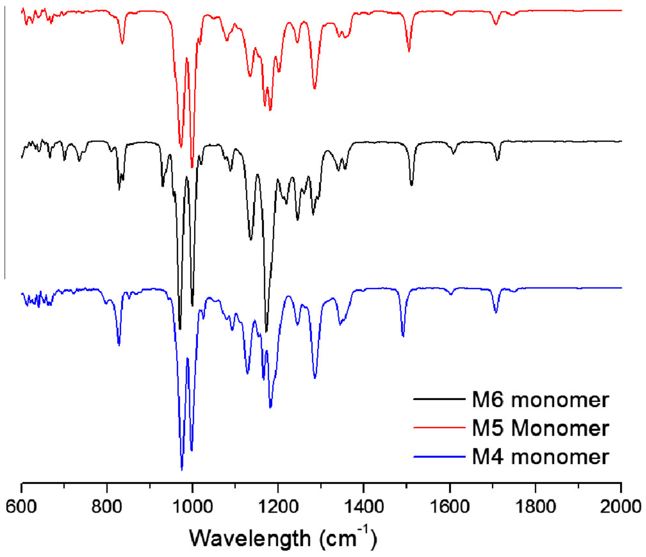


Figure 5. FTIR-IR spectra for **M4**–**M6**.

S21 show C═C stretching peaks of the PFCP and PFCH rings at 1724 and 1707 cm^{-1}, respectively.[18,41] Also Figure 5 shows a small peak at 1747 cm^{-1} (easily visible for **M4** and **M6**) which belongs to characteristic C═C stretching for a allylic substituted PFCH ring (minor products).[18] Further, the GC–MS and elemental analyses showed the expected molecular weight and elemental composition for all the products **M1**–**M6**.

In conclusion, we have developed a new class of PFCA aryl ether monomers from commercially available feedstocks via an addition–elimination reaction, in a good isolated yield. These monomers are a substantial step for the synthesis of a wide range of PFCA homo and copolymers of variable randomness or blockiness.

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Supplementary data

Supplementary data (crystallographic data for the structures reported in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 927350 (**1**) and 927351 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1233 336 033: e-mail: deposit@ccdc.cam.ac.uk). A list of detailed experimental procedures, instrumentation and characterization data (NMR, IR, GC/MS) for all the new compounds) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.04.087.

References and notes

1. Ameduri, B., Boutevin, B., Eds.Well-Architectured Fluoropolymers: Synthesis, Properties and Applications; Elsevier Science: San Diego, 2004.
2. Scheirs, J., Ed.Modern Fluoropolymers: High Performance Polymers for Diverse Applications; Wiley: Chichester, 1997.
3. Feiring, A. E., Ed.Organofluorine Chemistry: Principles and Commercial Applications; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum Press: New York, 1994.
4. *Biomedicinal Aspects of Fluorine Chemistry*; Filler, R., Kobayashi, Y., Eds.; Elsevier: Amsterdam, 1982.
5. Cracowski, J.-M.; Sharma, B.; Brown, D. K.; Cristensen, K.; Lund, B. R.; Smith, D. W., Jr. *Macromolecules* **2012**, *45*, 766.
6. Hougham, G. G.; Cassidy, P. E.; Johns, K.; Davidson, T. *Fluoropolymers: Synthesis*; Plenum Pub Corp: New York, 1999.
7. Keck, S.; Knoerzer, T. A.; Smith, D. W., Jr.; Iacono, S. T. *Polym. Int.* **2013**. http://dx.doi.org/10.1002/pi.4447.
8. Kettwich, S. C., Lund, B. R., Smith, D. W., Jr., Iacono, S. T., Eds.Advances in Fluorine-Containing Polymers; American Chemical Society: Washington, DC, 2012; Vol. 1106, p 9.
9. Iacono, S. T.; Budy, S. M.; Moody, J. D.; Smith, R. C.; Smith, D. W., Jr. *Macromolecules* **2008**, *41*, 7490.
10. For a review see: Iacono, S. T.; Budy, S. M.; Jin, J.; Smith, D. W., Jr. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5705.
11. Ma, H.; Jen, A. K. Y.; Dalton, L. R. *Adv. Mater.* **2002**, *14*, 1339.
12. Lindner, P. E.; Lemal, D. M. *J. Org. Chem.* **1996**, *61*, 5109.
13. Bayliff, A. E.; Bryce, M. R.; Chambers, R. D. *J. Chem. Soc., Perkin Trans. 1* **1987**, 763.
14. Stockel, R. F.; Beachem, M. T.; Megson, F. H. *J. Org. Chem.* **1965**, *30*, 1629.
15. Stockel, R. F.; Beachem, M. T.; Megson, F. H. *Can. J. Chem.* **1964**, *42*, 2880.
16. Plevey, R. G.; Talbot, R. E. *J. Fluorine Chem.* **1977**, *10*, 577–584.
17. Plevey, R. G.; Sparrow, D. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 573–577.
18. Clayton, A. B.; Roylance, J.; Sayers, D. R.; Stephens, R.; Tatlow, J. C. *J. Chem. Soc.* **1965**, 7358.
19. Yamada, S.; Konno, T.; Ishihara, T.; Yamanaka, H. *J. Fluorine Chem.* **2005**, *126*, 125–133.
20. Han, M.; Lee, S.; Jung, J.; Park, K.; Kwon, S.; Ko, J.; Lee, P. H.; Kang, Y. *Tetrahedron* **2006**, *62*, 9769–9777.
21. Organometallic derivatives of perfluorocycloalkenes. U.S. Patent 3,787,461, 1974.
22. Powers, G. A.; Stephens, R.; Tatlow, J. C. *J. Fluorine Chem.* **1982**, *20*, 555–558.
23. McBee, E. T.; Turner, J. J.; Morton, C. J.; Stefani, A. P. *J. Org. Chem.* **1965**, *30*, 3698–3705.
24. Cullen, W. R.; Dhaliwal, P. S. *Can. J. Chem.* **1967**, *45*, 719.
25. Mir, Q. C.; Guo, C. Y.; Kirchmeier, R. L.; Shreeve, J. M. *J. Org. Chem.* **1994**, *59*, 173.
26. Timperley, C. M. *J. Fluorine Chem.* **2004**, *125*, 685–693.
27. Garg, S.; Twamley, B.; Zhuo, Z.; Shreeve, J. M. *Chem. Eur. J.* **2009**, *15*, 10554.
28. Yamada, S.; Ishii, E.; Konno, T.; Ishihara, T. *Org. Biomol. Chem.* **2007**, *5*, 1442.
29. Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305.
30. Wigglesworth, T. J.; Sud, D.; Norsten, T. B.; Lekhi, V. S.; Branda, N. R. *J. Am. Chem. Soc.* **2005**, *127*, 7272.
31. Malval, J.-P.; Gosse, I.; Morand, J.-P.; Lapouyade, R. *J. Am. Chem. Soc.* **2002**, *124*, 904.
32. Yamada, T.; Muto, K.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2001**, *66*, 6164.
33. Yamada, T.; Kobatake, A.; Muto, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 1589.
34. Matsui, M.; Tsuge, M.; Funabiki, K.; Shibata, K.; Muramatsu, H.; Hirota, K.; Hosoda, M.; Tai, K.; Shiozaki, H.; Kim, M.; Nakatsu, K. *J. Fluorine Chem.* **1999**, *97*, 207–212.
35. Takahashi, K.; Itoh, A.; Nakamura, T.; Tachibana, K. *Thin Solid Films* **2000**, *374*, 303.
36. Beale, J. H.; Schwartz, N. N.; Mantell, G. J. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 67.
37. Moody, J. D.; VanDerveer, D.; Smith, D. W., Jr.; Iacono, S. T. *Org. Biomol. Chem.* **2011**, *9*, 4842.
38. Iacono, S. T.; Budy, S. M.; Ewald, D.; Smith, D. W., Jr. *Chem. Commun.* **2006**, 4844.
39. Silverstein, R. M.; Webster, F. X. *Spectroscopic Identification of Organic Compounds*; Wiley: India, 2006.
40. Cotthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1964.
41. Vasekova, E.; Drage, E. A.; Smith, K. M.; Mason, N. J. *J. Quant. Spectrosc. Radiat. Transfer* **2006**, *102*, 418.