A Preliminary Study of Host-Guest Interactions in Polymeric Clathrates – An Ab Initio Study of the Model Complexes Benzene/X_2 (X = F, Cl, Br, I)

Giuseppe Milano[a], Gaetano Guerra[a], and Luigi Cavallo*[b]

Dipartimento di Chimica, Università di Salerno[a],
Baronissi, I-84081 Salerno, Italy

Dipartimento di Chimica, Università degli Studi di Napoli “Federico II”[b],
Via Mezzocannone 4, I-80134 Napoli, Italy
E-mail: cavallo@chemna.dichi.unina.it

Received May 7, 1998

Keywords: Arene complexes / Ab initio calculations / Polymeric clathrates / Host-guest chemistry

A systematic ab initio investigation of the complexes benzene/halogen molecules is presented. For the whole halogen series, the T-shaped geometry is clearly favored relative to the sandwich geometry. This preference is rationalized in terms of the electrostatic fields generated by the interacting molcules. Higher binding energies have been calculated on going from /F_2 to /I_2 molecular complexes.

Introduction

Van der Waals interactions of aromatic systems are of considerable interest because they often play an important structure-determining role. These interactions control such diverse phenomena as porphyrin aggregation, the packing of aromatic molecules, and the base-base interactions in DNA. For this reason, a large number of experimental as well as theoretical papers have been devoted to the study of the weak interactions in prototype systems of the type benzene/benzene, benzene/H_2O, benzene/NH_3, benzene/N_2, benzene/alkane, and benzene/hydrogen halide.[1][2]

Another phenomenon of considerable interest that is often controlled by these interactions is the sorption of small molecules in polymers,[3][4] the economic importance of which, e.g. in the packaging industry and in the field of membrane separation processes, is well known. For instance, systematic studies of the sorption of various molecules in amorphous polymeric materials based on atactic polystyrene have allowed correlations to be made between the structures of the small molecules and the relevant sorption parameters.[3] Moreover, studies of the sorption of halogenated aliphatic molecules have led to molecular models of absorption that involve interactions of the halogen atoms with the phenyl groups of the polymeric absorbents.[5] However, experimental and theoretical studies of the molecular interactions responsible for the sorption phenomena are made difficult by the dynamic intramolecular and intermolecular disorder that is characteristic of the swollen polymeric phases.

Recently, semicrystalline polymeric materials based on syndiotactic polystyrene that are able to absorb small molecules, not only in the amorphous phase but also in the cavities of suitable crystalline phases, have been described.[6][7][8][9] It has also been found that the same classes of molecules that are suitable for sorption into atactic polystyrene based samples,[3] are absorbed both into amorphous and crystalline phases of syndiotactic polystyrene samples.[6][7][8][9] Furthermore, it is remarkable that at low activities these small molecules are preferentially (or exclusively) absorbed as guests in the crystalline phase to form clathrates.[9] This suggests that the host-guest interactions in clathrate structures are similar to the interactions between the polymer and small molecules in the amorphous phase.

X-ray diffraction[10][11] and FT-IR-spectroscopic[9] studies on these clathrate samples can give detailed experimental information regarding the molecular interactions that occur between the guest molecules and the host polymer in the crystalline cavities. In particular, the number and distances of the intermolecular interactions, the preferred relative orientations of the guest and host, as well as possible preferential guest conformations can be established. Finally, it is worth noting that the study of host-guest interactions in these polymeric clathrates is also relevant due to the potential applications of nanoporous materials based on syndiotactic polystyrene for water and air purification and, more generally, for chemical separations.[6]

The clathrate structure of syndiotactic polystyrene incorporating two I_2 molecules per cavity has been well characterized by X-ray diffraction study.[7] The I_2 molecule interacts significantly with only two phenyl rings, and the I_2 molecular axis is almost perpendicular to the planes of the phenyl rings. Moreover, X-ray studies of the benzene/Cl_2[12] and benzene/Br_2[13] systems have shown that a T-shaped geometry (see Figure 1), with the halogen molecule almost aligned along the C_{6v} symmetry axis of the benzene, is preferred. Furthermore, IR-spectroscopic studies indicate that an axial or slightly bent structure is also adopted in nitrogen matrices.[14][15] However, despite the great interest in these complexes, a systematic theoretical description of

1434−1948/98/1010−1513 $ 17.50+.50/0

the benzene/X_2 (X = F, Cl, Br, I) series is still lacking. To the best of our knowledge, of this series only the benzene/I_2 complex has been studied in detail from a theoretical point of view.[16][17][18] For this reason, we have carried out a systematic study of the interactions occurring in the ground state of the model systems benzene/X_2 (X = F, Cl, Br, I) using the second-order Møller-Plesset (MP2) theory.

Methods

The interaction energy, ΔE, of the complexes was evaluated as the sum of the self-consistent field interaction energy, ΔE_{SCF},[19] and the correlation interaction energy, ΔE_{COR},[19] where ΔE_{COR} was calculated using MP2 theory.[19] We applied the supermolecule approach.[1] Thus, the interaction energy was obtained as the difference between the energy of the complex and the energies of the free benzene and halogen molecules. All the calculated interaction energies were basis set superposition error (BSSE) free.[19] For the BSSE evaluation, the counterpoise method of Boys and Bernardi was used.[20] All the calculations were performed using the GAMESS package.[21]

The geometries of the benzene (R_{C-C} = 1.406 and R_{C-H} = 1.08 Å) and halogen molecules (R_{F-F} = 1.34, R_{Cl-Cl} = 1.99, R_{Br-Br} = 2.28, R_{I-I} = 2.68 Å) were kept rigid, and only the distance between the centres of mass of the benzene and halogen molecules, R, was varied. To locate the BSSE-free minimum energy geometries, the potential energy surface was scanned simply by varying the distance R. To save computer time, we used the 6-31G basis set for the C and H atoms,[22] augmented with single d and p polarization functions,[22] respectively, and the SBK effective core potential (ECP) and valence basis set, augmented with a d polarization function, for the halogens.[23] To assess the dependence of the interaction energy on the particular basis set used, single-point energy calculations were performed on the minimum energy geometries obtained from the potential energy surface scan. In these cases, a double-ζ basis set, DZ, augmented with two d polarization functions on the C atoms, was adopted for the benzene.[24] Finally, test calculations were performed using the SBK ECP basis set on the C atoms of the benzene as well. Due to the fact that envisaged extensions of this work will focus on systems of considerably larger size (polymer cavities containing guest molecules), we decided to use basis sets of moderate size only.

Results

As already suggested by other authors,[1] for benzene-containing molecular complexes the total interaction energy is mainly determined by the electrostatic (quadrupole-quadrupole) interaction, essentially included in the ΔE_{SCF} contribution, and by the dispersion energy, essentially included in the ΔE_{COR} contribution. For this reason, the selection of suitable basis sets requires that one-electron properties, in particular the quadrupole moment, Q_{zz}, be reproduced with good accuracy.

Table 1 shows the Hartree-Fock quadrupole moments of the molecules considered in the present study. As reported previously,[1] for the benzene molecule the 6-31G basis set, even augmented by two polarization functions on the carbon atoms, underestimates the quadrupole moment. On the other hand, with the DZ basis set reasonable values for the quadrupole moment are obtained, even in the absence of polarization functions.

Table 1. Quadrupole moments of the benzene and halogen molecules at the Hartree-Fock level

Molecule	Basis set	Polarization exponents	Q_{zz} [a.u.]
C_6H_6	6-31G		−6.59
	6-31G d, p	C: 0.80, H: 1.10	−6.52
	6-31G 2d	C: 1.60, 0.40	−6.36
	DZ		−7.19
	DZ 2d	C:1.5, 0.375	−7.38
	DZ 2d, 2p	C:1.5, 0.375; H: 2.0, 0.5	−7.20
	SBK d	C: 0.80	−6.30
	Experimental[a]		−7.4
F_2	SBK		−0.09
	SBK d	0.80	+0.40
	SBK 2d	1.60, 0.40	+0.48
	Extended basis set[b]		+0.41
	Extended basis set[c]		+0.56
	Experimental[d]		+0.65
Cl_2	SBK		+0.78
	SBK d	0.750	+1.97
	SBK 2d	1.500, 0.375	+2.73
	DZ		+0.95
	DZ 2d	1.500, 0.375	+2.74
	Extended basis set[b]		+2.51
	Extended basis set[e]		+2.26
	Experimental[f]		+2.40
Br_2	SBK		+1.88
	SBK d	0.389	+3.85
	SBK 2d	0.778, 0.195	+4.24
	Extended basis set[b]		+3.55
I_2	SBK		+3.08
	SBK d	0.266	+6.06
	SBK 2d	0.532, 0.133	+6.21
	Extended basis set[b]		+4.17
	Extended basis set[g]		+4.49

[a] J. Vrbancich, G. L. D. Ritchie, *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 648. – [b] P. A. Straub, A. D. McLean, *Theo. Chim. Acta* **1974**, *32*, 227. – [c] G. Maroulis, A. J. Thakkar, *J. Chem. Phys.* **1989**, *90*, 366. – [d] G. H. Cheeseman, A. J. T. Finney, *Theo. Chim. Acta* **1970**, *15*, 33. – [e] G. Maroulis, *Chem. Phys. Lett.* **1992**, *199*, 244. – [f] A. D. Buckingham, L. Graham, J. H. Williams, *Mol. Phys.* **1983**, *49*, 703. – [g] G. Maroulis, A. J. Thakkar, *Mol. Phys.* **1991**, *73*, 1235.

On the contrary, for the halogen molecules, both with DZ (for F_2 and Cl_2) and ECP (for the whole series) basis sets, the quadrupole moments are clearly underestimated in the absence of polarization functions. For F_2 and Cl_2, the DZ and ECP basis sets augmented with two polarization functions provide reasonable values of Q_{zz}, whereas for the heavier Br_2 and I_2 halogen molecules Q_{zz} is overestimated.

Table 2 shows the calculated minimum energy distances, BSSE-free, and the interaction energy contributions for the benzene/X_2 molecular complexes. Clearly, the T-shaped geometry is preferred for each of the halogens. This result is in

Table 2. Energy contributions to the total interaction energy, BSSE-free, for the benzene/X_2 molecular complexes in the T-shaped and sandwich geometries

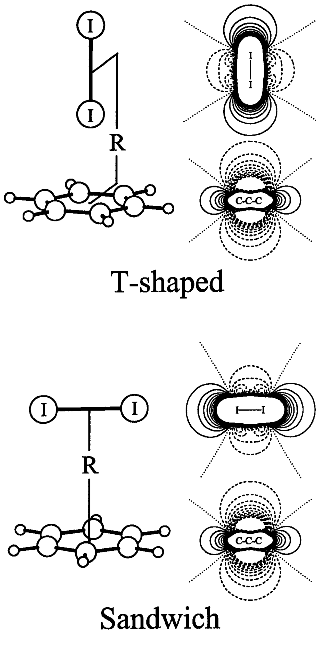
/X_2	Geometry	C_6H_6 Basis Set	Halogen Basis Set	R[a] [Å]	ΔE_{SCF} [kcal/mol]	ΔE_{COR} [kcal/mol]	ΔE_{TOT} [kcal/mol]
/F_2	T-shaped	6-31G d,p	SBK d	3.9	+0.33	−1.00	−0.67
	T-shaped	DZ 2d	SBK 2d		+0.36	−1.38	−1.02
	T-shaped	SBK d	SBK d		+0.55	−0.98	−0.43
	Sandwich	6-31G d,p	SBK d	3.8	+0.27	−0.48	−0.21
	Sandwich	DZ 2d	SBK 2d		+0.30	−0.77	−0.47
	Sandwich	SBK d	SBK d		+0.30	−0.52	−0.22
/Cl_2	T-shaped	6-31G d,p	SBK d	4.6	−0.01	−1.10	−1.11
	T-shaped	DZ 2d	SBK 2d		−0.27	−1.99	−2.26
	T-shaped	DZ 2d	DZ 2d		−0.20	−2.00	−2.20
	T-shaped	SBK d	SBK d		+0.21	−1.12	−0.91
	Sandwich	6-31G d,p	SBK d	4.4	+0.38	−0.58	−0.20
	Sandwich	DZ 2d	SBK 2d		+0.46	−1.10	−0.64
	Sandwich	DZ 2d	DZ 2d		+0.48	−1.16	−0.68
	Sandwich	SBK d	SBK d		+0.35	−0.62	−0.27
/Br_2	T-shaped	6-31G d,p	SBK d	4.7	−0.20	−1.88	−2.08
	T-shaped	DZ 2d	SBK 2d		−0.36	−3.06	−3.42
	T-shaped	SBK d	SBK d		+0.18	−1.95	−1.77
	Sandwich	6-31G d,p	SBK d	4.4	+0.71	−1.03	−0.32
	Sandwich	DZ 2d	SBK 2d		+0.64	−1.79	−1.15
	Sandwich	SBK d	SBK d		+0.62	−1.19	−0.57
/I_2	T-shaped	6-31G d,p	SBK d	4.9	+0.17	−2.71	−2.54
	T-shaped	DZ 2d	SBK 2d		+0.05	−4.28	−4.23
	T-shaped	SBK d	SBK d		+0.84	−2.81	−1.97
	Sandwich	6-31G d,p	SBK d	4.6	+0.86	−1.29	−0.43
	Sandwich	DZ 2d	SBK 2d		+0.73	−2.06	−1.33
	Sandwich	SBK d	SBK d		+0.71	−1.40	−0.69

[a] Optimized intermolecular distance, BSSE-free.

agreement with X-ray structural investigations of benzene/Cl_2[12] and benzene/Br_2[13] complexes, which have shown that the T-shaped geometry is the most probable. The minimum energy distances R, between the centres of mass of the benzene and halogen molecules for the T-shaped structures are 3.9, 4.6, 4.7, and 4.9 Å for F_2, Cl_2, Br_2, and I_2, respectively. The calculated values of R are overestimated by roughly 0.3 Å (4.27 and 4.34 Å in the crystalline structures of the benzene/Cl_2 and benzene/Br_2 complexes, respectively). The T-shaped geometry for the benzene/X_2 complexes is also in agreement with the structures indicated by infrared absorption spectra of the Cl_2, Br_2 and I_2 complexes with benzene in nitrogen matrices,[14][15] and with previous ab initio studies on the benzene/I_2 complex.[16][17][18]

As already outlined,[1] the rationalization of the preferred geometry in molecular complexes with benzene is essentially related to the electrostatic interaction (quadrupole-quadrupole) between the two molecules. In order to rationalize the preferred geometry in terms of electrostatic interactions, the electrostatic fields generated by the two interacting molecules are depicted in Figure 1. In the T-shaped geometry, negative and positive regions of the electrostatic potential of the benzene and halogen molecules face each other, whereas in the sandwich geometry regions of electrostatic potential of the same sign face each other. As a consequence, the electrostatic interactions clearly favour the T-shaped geometry relative to the sandwich geometry.

Figure 1. Schematic representation of the T-shaped and sandwich geometries for the benzene/I_2 complex; the distance R between the centres of mass of the two molecules, which was varied during the potential energy surface scan, is indicated; the electrostatic fields generated by the two molecules are also indicated; starting from the 0.0 contours (dotted lines), positive and negative contours of the electrostatic field (continuous and dashed lines, respectively) are shown; the isopotential curves are spaced by 1 kcal/mol



Our analysis is in agreement with the previously reported rationalization based on the quadrupole-quadrupole electrostatic interaction. In order to optimize this interaction, and depending on the sign of the quadrupole moment of the two molecules that form the molecular complex, either T-shaped (benzene/benzene and benzene/I_2) or sandwich (benzene/N_2) geometries are adopted. Considering that all the halogen molecules have quadrupole moments of the same sign, it is reasonable to assume that the T-shaped structure is the preferred geometry throughout the benzene/X_2 series.

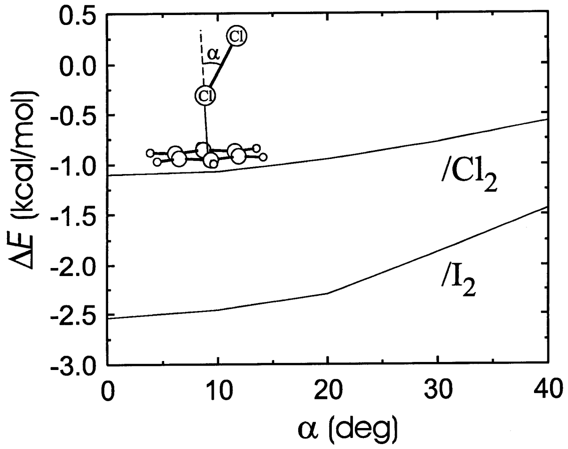
This rationalization is also supported by the fact that the ΔE_{SCF} contribution always favours the T-shaped geometry. Moreover, the repulsive electrostatic interaction in the sandwich geometry pushes the two molecules far apart, and this reduces the strength of the attractive dispersion interactions. As a consequence, the ΔE_{COR} energy contribution also favours the T-shaped geometry.

As regards the total binding energy, more stable complexes are observed on going from the very weakly bound F_2 to I_2, both for T-shaped and sandwich geometries. The calculated value for the T-shaped benzene/I_2 complex, 2.54 kcal/mol, is in fair agreement with the heat of formation of this complex in the gas phase, as determined by spectrometric methods (2.0−2.6 kcal/mol).[25] Previous ab initio calculations led to binding energies of 1.91[16] and 2.07[18] kcal/mol. By using the DZ basis set for benzene and the SBK ECP set for the halogens, and augmenting these basis sets with two standard polarization functions on the C and halogen atoms, the same trend is observed, i.e. higher binding energies on going from F_2 to I_2. With this basis set, which should be of better quality, the binding energies are probably overestimated. In fact, for the T-shaped benzene/I_2 complex this basis set gives a binding energy of 4.23 kcal/mol. Finally, by using the SBK ECP basis set for the C atoms of benzene as well, results fairly similar to those obtained using the 6-31G basis set are obtained. However, there is a decrease in the energy difference between the sandwich and the more stable T-shaped geometry [ΔE(sandwich − T-shaped) = 0.46, 0.89, 1.76, and 2.11 kcal/mol using the 6-31G basis set for the benzene, and 0.21, 0.52, 1.20, and 1.28 kcal/mol using the SBK ECP basis set for the benzene, for F_2, Cl_2, Br_2, and I_2, respectively].

The results shown in Table 2 clearly indicate that the ΔE_{SCF} contribution is virtually independent of the basis set used, and that the increase in the binding energy is essentially due to the dispersion term, ΔE_{COR}. It is also apparent that the ΔE_{COR} contribution is not yet converged. Due to the fact that we have mixed a DZ basis set with a split-valence ECP basis set, we checked the reasonability of this mixing by using, for the Cl_2 complex only, a DZ all-electron basis set. The results obtained with the ECP were in very good agreement with the all-electron results. Thus, we believe that the basis set mixing that we have used represents a reasonable approximation.

In the last part of our study, we investigated the feasibility of oblique structures. In Figure 2, the BSSE-free interaction energies of the oblique geometries of the benzene/Cl_2 and benzene/I_2 complexes are plotted as a function of the angle α between the halogen−halogen bond and the C_{6v} symmetry axis of the benzene. Since in the bent structures the distance R is not re-optimized, we confined our analysis to structures close to the T-shaped geometry, that is, to values of $\alpha \leq 40°$. The geometries at $\alpha = 0°$ correspond to the minimum energy T-shaped geometries of the Cl_2 and I_2 complexes. It is clear that the T-shaped geometries of the two complexes represent only shallow minima, and that large oscillations might easily be achieved. In fact, α deformations of 20−30° require less than 0.5 kcal/mol. Our results support the hypothesis that in photoexcitation experiments the excitation process occurs in bent conformations, i.e. the conformations with the largest transition moment.[18]

Figure 2. MP2 BSSE-free interaction energy as a function of α for the benzene/Cl_2 and benzene/I_2 complexes; the 6-31G d,p and ECP SBK 2d basis sets were used for the benzene and halogen molecules, respectively



Conclusions

A systematic investigation of benzene/halogen molecule complexes in the ground state has indicated that the T-shaped geometry is preferred relative to the sandwich geometry for each of the halogens. The calculated minimum energy distances for the benzene/Cl_2 and benzene/Br_2 complexes (for which X-ray structures are available) overestimate the experimental values by roughly 0.3 Å. Moreover, irrespective of the particular basis set used, higher binding energies have been calculated on going from benzene/F_2 to benzene/I_2 molecular complexes. The relative stability of the T-shaped and sandwich geometries is essentially determined by the electrostatic quadrupole-quadrupole interaction. This can clearly be visualized in terms of the electrostatic potential generated by the interacting molecules. Finally, we note that the T-shaped geometry represents only a shallow minimum, and that environmental effects (i.e. crystal packing or inert matrices) can reasonably force the adoption of oblique geometries.

We thank Prof. *V. Barone* of the University of Naples and Dr. *A. Peluso* of the University of Salerno for useful discussions. The financial support of the *Ministero dell' Università e della Ricerca Scientifica e Tecnologica* and of the *Consiglio Nazionale delle Ricerche* of Italy is gratefully acknowledged.

---

[1] P. Hobza, H. L. Selzle, E. W. Schlag, *Chem. Rev.* **1994**, *94*, 1767.
[2] H. J. Neusser, H. Krause, *Chem. Rev.* **1994**, *94*, 1829.
[3] L. A. Errede, *Adv. Polym. Sci.* **1991**, *99*, 1.
[4] L. A. Errede, *J. Phys. Chem.* **1996**, *100*, 9918.

[5] L. A. Errede, *J. Phys. Chem.* **1991**, *95*, 1836.
[6] G. Guerra, C. Manfredi, M. Rapacciuolo, P. Corradini, G. Mensitieri, M. A. Del Nobile. *Ital. CNR RM94A00030 (21/1/94)*.
[7] C. De Rosa, G. Guerra, V. Petraccone, B. Pirozzi, *Macromolecules* **1997**, *30*, 4147.
[8] C. Manfredi, M. A. Del Nobile, G. Mensitieri, G. Guerra, M. Rapacciuolo, *J. Polym. Sci., Polym. Phys. Ed.* **1997**, *35*, 133.
[9] G. Guerra, C. Manfredi, P. Musto, S. Tavone, *Macromolecules* **1998**, *31*, 1329.
[10] Y. Chatani, T. Inagaki, Y. Shimane, H. Shikuma, *Polymer* **1993**, *34*, 4841.
[11] C. De Rosa, P. Rizzo, O. Ruiz de Ballesteros, V. Petraccone, G. Guerra, *Polymer*, in press.
[12] O. Hassel, K. O. Strømme, *Acta Chem. Scand.* **1959**, *13*, 1781.
[13] O. Hassel, K. O. Strømme, *Acta Chem. Scand.* **1958**, *12*, 1146.
[14] L. Fredin, B. Nelander, *Mol. Phys.* **1974**, *27*, 885.
[15] L. Fredin, B. Nelander, *J. Am. Chem. Soc.* **1974**, *96*, 1672. A. Engdahl, B. Nelander, *J. Chem. Phys.* **1983**, *78*, 6563.
[16] E. Kochanski, J. Prissette, *Nouv. J. Chim.* **1980**, *4*, 509.
[17] I. Jano, *Theor. Chim. Acta.* **1985**, *66*, 341.
[18] E. Lenderink, K. Duppen, F. P. X. Everdij, J. Mavri, R. Torre, D. A. Wiersma, *J. Phys. Chem.* **1996**, *100*, 7822.
[19] W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, New York, **1986**.
[20] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553.
[21] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347.
[22] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213. M. M. Francl, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654.
[23] W. J. Stevens, H. Basch, M. Krauss, *J. Chem. Phys.* **1984**, *81*, 6026. W. J. Stevens, H. Basch, M. Krauss, *Can. J. Chem.* **1992**, *70*, 612.
[24] T. H. Dunning, *J. Chem. Phys.* **1970**, *53*, 2823.
[25] D. Atack, O. K. Rice, *J. Phys. Chem.* **1954**, *58*, 1017. F. T. Lang, R. L. Strong, *J. Am. Chem. Soc.* **1965**, *87*, 2345. W. K. Duerksen, M. Tamres, *J. Am. Chem. Soc.* **1968**, *90*, 1379. T. D. McLean, B. B. Ratcliff, J. Z. Pastalan, K. K. Innes, *J. Quant. Spectrosc. Radiat. Transfer* **1989**, *42*, 445.

[98140]