J. Phys. Chem. A **2004,** *108,* 3723−3726

Photodissociation Pathways of the 2,3-Benzofluorene Cation

John Banisaukas, Jan Szczepanski, John Eyler, and Martin Vala*

Department of Chemistry and Center for Chemical Physics, University of Florida,
Gainesville, Florida 32611-7200

Received: February 4, 2004

Benzofluorene ($C_{17}H_{12}$) cations have been studied in the vapor phase by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The identification of certain fragmented species from electron impact/matrix optical experiments (see Banisaukas, J.; Szczepanski, J.; Vala, M.; Hirata, S. *J. Phys. Chem. A* **2004**, *108*, 3713) provided the background for the present detailed studies of the dissociation pathways of the cation via FT-ICR mass spectrometry. Both hydrogen and acetylene loss pathways along various photodissociation routes have been identified.

I. Introduction

Polycyclic aromatic hydrocarbons (PAHs) in neutral, ionized, fragmented, and/or hydrogenated forms are widely considered to be the carriers of the unidentified infrared (UIR) emission bands.[1−4] Although the possibility that PAHs may fragment in the vicinity of stellar sources has been discussed for some time,[5] only recently have experimental studies begun to appear. Boissel and co-workers were the first to show that PAH cations were susceptible to fragmentation upon (short) exposure to visible radiation.[6] The primary step in this photodestruction was shown to be sequential multiphoton absorption.[7] The photofragmentation of a large class of PAH cations was investigated by Ekern et al. via FT-ICR mass spectrometry.[8,9] These PAHs were classified as either photostable, losing hydrogen only, losing carbon and hydrogen, or photodestroyed for particular photon fluxes. All PAHs classified as photostable contained at least one four- or five-membered ring. The photostability of PAH cations as related to their structure, degree of ionization, and dehydrogenation have been studied by Leach and co-workers.[10,11]

However, the relationship between PAH size and photostability is still not completely understood. Large PAHs contain a high density of vibrational states into which absorbed energy can be distributed. Thus, for large PAHs, radiative IR emission should dominate dissociation as the relaxation mechanism. In FT-ICR photodissociation experiments, both hydrogen and acetylene loss were observed from the cation of fluorene ($C_{13}H_{10}^+$), a PAH in which two six-membered rings are fused to a central pentagonal ring.[9,12]

The present study focuses on the photodissociation of the 2,3-benzofluorene (BZF) cation. It extends previous studies on fluorene and determines the effect of the addition of an additional aromatic ring on photostability and photoreactivity.

II. Computational Methods

Optimized geometries and fragmentation energies were calculated using the Gaussian 98 platform.[13] Hybrid density functional theory (B3LYP) was applied with the 6-31G** basis set. The B3LYP/4-31G level of theory accurately predicts the C−H bond energy of C_6H_6 and thus has been widely applied to PAH systems.[14] In a comprehensive study of PAHs with six-membered rings, Langhoff demonstrated that the B3LYP/4-31G and B3LYP/6-31G** levels of theory predicted harmonic frequencies and relative intensities reasonably well.[15]

Carbon−hydrogen bond energies were calculated by subtracting zero-point-corrected ground-state energies before and after hydrogen removal. Zero-point energies were scaled by 0.978. Because no energy barrier for H removal is expected, on the basis of the zero energy barrier calculated for fluorene and 1-hydronaphthalene cations,[14,16] the energy difference between the parent molecule energy and the sum of the fragment molecule and atomic hydrogen energies is taken as the energy of the C−H bond.

III. Experimental Methods

Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry was used to investigate the photofragmentation of the BZF cation. All experiments were performed on a 2-T FT-ICR mass spectrometer[17] equipped with a modular ICR data acquisition system (MIDAS).[18] Gas-phase BZF (IE = 7 eV) was ionized by bombardment with low-energy electrons (17 eV). Ions were trapped in an open-ended cylindrical cell located at the center of the magnetic field. Because significant fragmentation occurred during ionization, the parent ion was isolated using a stored waveform inverse Fourier transform (SWIFT),[19] and any fragment ions or ^{13}C isotope-containing ions were ejected. The isolated parent ion was then irradiated for 0.1−10.0 s with the continuous output (250−1100 nm) of a 300-W collimated xenon arc lamp (ILC Technology, model LX300UV) to create the photoproducts of interest. Photofragmentation pathways were investigated by two methods. In the first, each fragment ion was isolated with a second SWIFT waveform and then photolyzed to determine its fragmentation pattern. In the second method, individual fragment ions were ejected during the lamp irradiation steps.

IV. Results and Discussion

A. Calculated Fragmentation Energies. *1. Sequential Hydrogen Loss*. C−H bond energies for the BZF neutral and cation were calculated using the B3LYP/6-31G** functional/basis set and are displayed in Figure 1 of the previous paper.[22]

---

* To whom correspondence should be addressed. E-mail: mvala@chem.ufl.edu.

10.1021/jp040100h CCC: $27.50

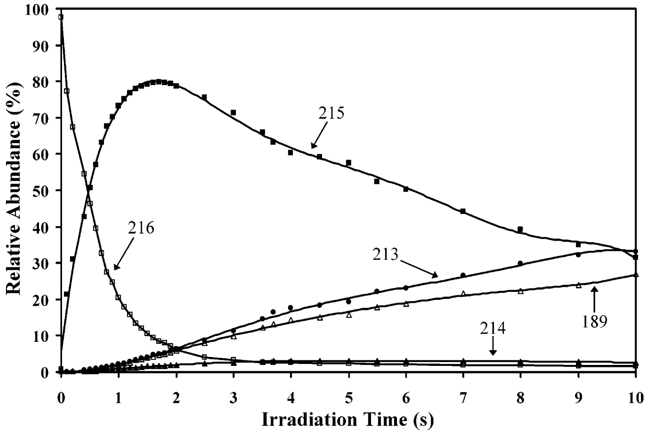

Figure 1. Relative abundance (%) of the 2,3-benzofluorene (*m*/*z* 216) parent ion and the *m*/*z* 215, 214, 213, and 189 fragment ions as a function of irradiation time (s).

In both cases, one of the hydrogens attached to the five-membered ring is the easiest to remove: 3.32 eV for the neutral (closed-shell system) and 2.60 eV for the cation (open-shell system). All other C−H bond energies are approximately 45% higher for the neutral and 96% higher for the cation. After the removal of the first hydrogen from the BZF cation, the abstraction of each of the remaining hydrogens requires approximately 4.90 eV, yielding 11 possible structures for the doubly dehydrogenated fragment ion. The multiple possibilities for hydrogen removal prevent the definitive structural identification of the doubly dehydrogenated ion.

2. Acetylene Loss. On the basis of earlier PAH photofragmentation studies,[9,12,20,21] acetylene (C_2H_2) removal is also a probable photofragmentation route for the BZF cation. For the fluorene cation ($C_{13}H_{10}^+$), Dibben et al. observed the loss of acetylene following the removal of one hydrogen from the parent ion.[12] Energies for acetylene loss were calculated for the singly dehydrogenated BZF ion at the B3LYP/4-31G level of theory. In BZF, acetylene loss can occur only from the exterior six-membered rings. The three acetylene units farthest from the five-membered ring ($H_6C_6C_7H_7$, $H_7C_7C_8H_8$, and $H_8C_8C_9H_9$) are the easiest to abstract, with removal energies of 5.40 eV. This is a lower energy limit because no energy barrier for the removal of C_2H_2 was calculated. The two acetylene units directly attached to the five-membered ring ($H_1C_1C_2H_2$ and $H_3C_3C_4H_4$) have slightly higher removal energies (5.59 eV). Thus, all five of these acetylene units are equally likely to be removed from the singly dehydrogenated fragment ion. The energy required for the removal of the sixth acetylene unit ($H_2C_2C_3H_3$) is 18% higher (6.35 eV). Its removal is not expected to be a major photofragmentation route.

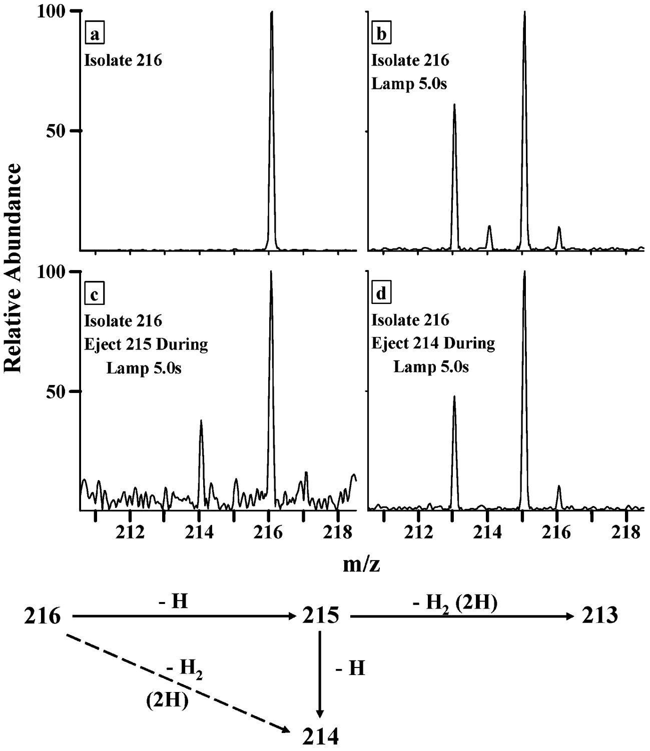

Figure 2. Dehydrogenation of the 2,3-benzofluorene cation (*m*/*z* 216). Solid arrows represent primary pathways. The dashed arrow represents a secondary pathway. (a) FT-ICR mass spectrum of isolated *m*/*z* 216. (b) FT-ICR mass spectrum after Xe lamp irradiation (5.0 s). (c) FT-ICR mass spectrum after Xe lamp irradiation (5.0 s) with the simultaneous ejection of *m*/*z* 215. (d) FT-ICR mass spectrum after Xe lamp irradiation (5.0 s) with the simultaneous ejection of *m*/*z* 214.

B. FT-ICR Photodissociation Pathways. Prior to lamp irradiation, the BZF parent ion (*m*/*z* 216) was isolated using a SWIFT waveform. Irradiation of the isolated *m*/*z* 216 ion with a xenon arc lamp yielded two fragmentation routes: dehydrogenation to form the *m*/*z* 215, 214, and 213 ions and carbon loss to form the *m*/*z* 190, 189, 188, 187, and 163 ions. The relative abundances of the major BZF fragment ions (*m*/*z* 216, 215, 214, 213, and 189) as a function of irradiation time are shown in Figure 1. The relative abundance of the *m*/*z* 216 parent cation rapidly decreased to 3% during 3.0 s of irradiation. The *m*/*z* 215 ion initially increased proportionately with the *m*/*z* 216 ion decrease, reaching a maximum relative abundance of 80% at 1.7 s. After 1.7 s, the decrease of the *m*/*z* 215 ion was accompanied by an increase in the abundances of the *m*/*z* 213 and 189 ions, indicating that the *m*/*z* 213 and 189 ions were fragmentation products of *m*/*z* 215. The *m*/*z* 214 fragment ion exhibited a slow, relatively small increase for the 10.0-s irradiation period and thus could not be correlated exclusively with either the *m*/*z* 216 parent ion or the *m*/*z* 215 fragment ion.

1. Hydrogen Loss. During irradiation, the *m*/*z* 216 parent ion lost a maximum of three hydrogen atoms. To distinguish between single- and double-hydrogen loss pathways, specific ions were ejected during photolysis. Ejection of the *m*/*z* 215 ion during 5.0 s of lamp irradiation resulted in a 60% reduction of *m*/*z* 214 (Figure 2). Thus, the predominant pathway for the formation of *m*/*z* 214 is single-hydrogen loss from *m*/*z* 215. However, because 40% of the *m*/*z* 214 ion remained after the ejection of *m*/*z* 215, double-hydrogen loss from the *m*/*z* 216 parent ion is also a significant pathway for *m*/*z* 214 formation. Ejection of *m*/*z* 215 eliminated the *m*/*z* 213 ion; however, the ejection of the *m*/*z* 214 ion had no significant effect on *m*/*z* 213. Thus, the pathway for *m*/*z* 213 formation must involve double-hydrogen loss from *m*/*z* 215 rather than single-hydrogen loss from *m*/*z* 214.

2. Acetylene Loss. Irradiation of the *m*/*z* 216 parent ion also yielded ions of *m*/*z* 190, 189, 188, 187, and 163, indicating the loss of carbons as well as hydrogens. As reported in earlier PAH photofragmentation studies,[9,12] such carbon loss most likely occurs as the loss of acetylene. Ejection of the *m*/*z* 215 ion during irradiation eliminated the *m*/*z* 189, 188, and 187 ions, indicating that these ions are photolysis products of the *m*/*z* 215 ion. Because the *m*/*z* 190 fragment ion remained, its formation pathway must involve acetylene loss from the *m*/*z* 216 parent ion. Similarly, the *m*/*z* 189 fragment ion is produced by acetylene loss from the *m*/*z* 215 fragment ion. Isolation and photolysis of the *m*/*z* 215 fragment ion produced the *m*/*z* 189 and 187 fragment ions (Figure 3). Ejection of the *m*/*z* 214 and 213 ions

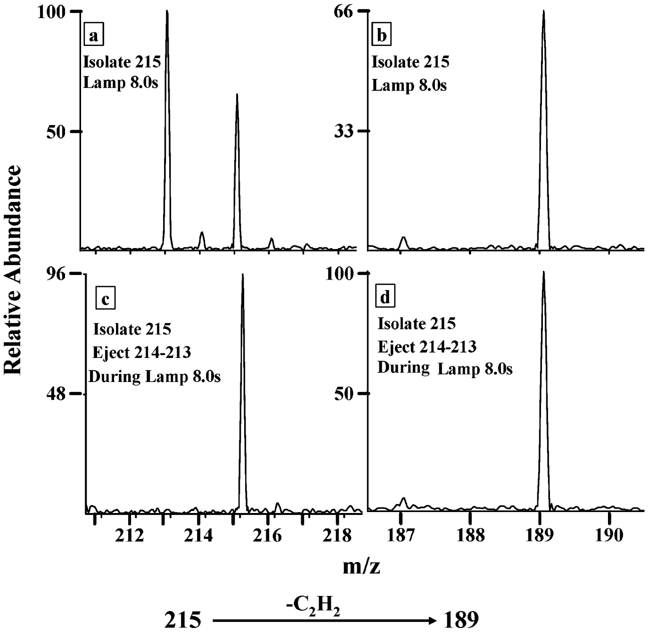

Figure 3. Acetylene loss pathway for the *m*/*z* 215 fragment ion. (a) FT-ICR mass spectrum after Xe lamp irradiation (8.0 s) of isolated *m*/*z* 215 (*m*/*z* 211−218 range). (b) FT-ICR mass spectrum after Xe lamp irradiation (8.0 s) of isolated *m*/*z* 215 (*m*/*z* 187−190 range). (c) FT-ICR mass spectrum after Xe lamp irradiation (8.0 s) of isolated *m*/*z* 215 with the simultaneous ejection of *m*/*z* 214−213 (*m*/*z* 211−218 range). (d) FT-ICR mass spectrum after Xe lamp irradiation (8.0 s) of isolated *m*/*z* 215 with the simultaneous ejection of *m*/*z* 214−213 (*m*/*z* 187−190 range).

during lamp photolysis had no effect on the *m*/*z* 189 and 187 ions, indicating that no acetylene loss occurs from either *m*/*z* 214 or 213. The only possible pathway for *m*/*z* 188 and 187 ion formation is therefore the loss of hydrogen from *m*/*z* 189. Ejection of the *m*/*z* 188 ion during the photolysis of isolated *m*/*z* 189 eliminated the *m*/*z* 187 ion, indicating that the *m*/*z* 187 ion is formed by single-hydrogen loss from the *m*/*z* 188 ion. Photolysis of the isolated *m*/*z* 189 fragment ion also initiated acetylene loss to form the *m*/*z* 163 fragment ion.

3. Photofragmentation Pathways. The complete photofragmentation route for the BZF cation is depicted in Figure 4. Percentages represent the relative importance in cases where multiple pathways are available for photodissociation. Irradiation of the *m*/*z* 216 parent ion yields single-hydrogen loss to form *m*/*z* 215 (96.5% yield), double-hydrogen loss to form *m*/*z* 214 (1.8% yield), and acetylene loss to form *m*/*z* 190 (1.5% yield). The high yield of the *m*/*z* 215 fragment ion is consistent with the low calculated energy (2.60 eV) for the removal of a hydrogen from the five-membered ring. Because of the low yields of *m*/*z* 214 and 190, further fragmentation of these ions remains undetermined. The *m*/*z* 215 fragment ion photodissociates to form *m*/*z* 214 via single-hydrogen loss (4.8% yield), *m*/*z* 213 via double-hydrogen loss (55.7% yield), and *m*/*z* 189 via acetylene loss (39.5% yield). The low yield of the *m*/*z* 214 ion (4.8%) correlates well with the predicted high energy (∼5 eV) required for this fragmentation route. The observed double-hydrogen loss to form the photostable *m*/*z* 213 ion (55.7% yield) must be more energetically favorable than single-hydrogen loss to form the *m*/*z* 214 ion. If double-hydrogen loss occurs as the loss of an H_2 molecule, then the two hydrogens removed are likely attached to adjacent carbons. Such double-hydrogen loss is therefore limited to one of the exterior six-membered rings. The observed acetylene loss from the *m*/*z* 215 fragment ion to form the *m*/*z* 189 ion must occur from one of the exterior six-membered rings containing C_2H_2 units. Calculated energies for acetylene loss were similar for all available acetylene units. However, the removal of acetylene molecules furthest from the five-membered ring required slightly lower energies (5.40 eV) than for those nearest the five-membered ring (5.59−6.35 eV). Because double-hydrogen loss from the *m*/*z* 215 ion yields the photostable *m*/*z* 213 ion, this simultaneous hydrogen loss must prevent the subsequent removal of acetylene. Therefore, the double-hydrogen loss pathway and the acetylene loss pathway most likely involve the six-membered ring furthest from the five-membered ring. However, because three acetylene positions are still equally likely, which specific hydrogens or acetylene units are removed remains undetermined.

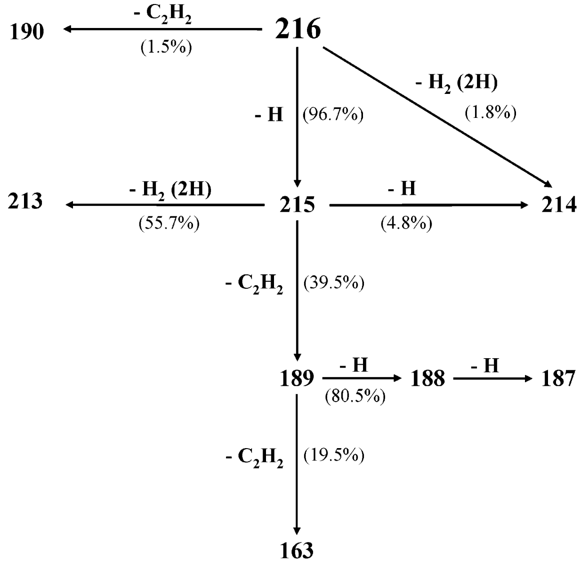

Figure 4. Overall observed photodissociation pathways for the 2,3-benzofluorene cation (*m*/*z* 216). Percentages represent the importance of relative pathways.

Irradiation of the *m*/*z* 189 ion results in single-hydrogen loss to form *m*/*z* 188 (80.5% yield) and acetylene loss to form *m*/*z* 163 (19.5% yield). The *m*/*z* 188 ion can undergo single-hydrogen loss to form *m*/*z* 187. No fragments lower than *m*/*z* 163 were observed in the mass spectrum. The sequential rather than simultaneous hydrogen loss from the *m*/*z* 189 ion may indicate that the hydrogens that are removed are not on adjacent carbons. However, because the actual structure of *m*/*z* 189 is ambiguous, the specific hydrogens that are lost remain undetermined.

V. Conclusions

From this gas-phase photodissociation study of the BZF cation (*m*/*z* 216), the main photofragmentation pathway is single-H loss (96.7% yield, likely H_{11} from the five-membered ring) and marginal C_2H_2 (acetylene) loss (1.5% yield). However, high yields of 39.5 and 19.5% for acetylene loss from the closed-shell *m*/*z* 215 and 189 BZF fragment cations, respectively, were also determined.

Acknowledgment. We gratefully acknowledge the National Aeronautics and Space Administration and donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research.

References and Notes

(1) Gillett, F. C.; Forrest, W. J.; Merrill, K. M. *Astrophys. J.* **1973**, *183*, 87.

(2) Duley, W. W.; Williams, D. A. *Mon. Not. R. Astron. Soc.* **1981**, *196*, 269.

(3) Leger, A.; Puget, J. L. *Astron. Astrophys.* **1984**, *137*, L5.

(4) Allamandola, L. J.; Tielens, A. G. G. M.; Barker, J. R. *Astrophys. J.* **1985**, *290*, L25.

(5) Pauzat, F.; Talbi, D.; Ellinger, Y. *Astron. Astrophys.* **1997**, *319*, 318.

(6) Boissel, P.; Lefevre, G.; Thiebot, P. *Molecules and Grains in Space*; Nenner, I., Ed.; American Institute of Physics Press: New York, 1993; p 667.

(7) Boissel, P.; de Parseval, P.; Marty, P.; Lefevre, G. *J. Chem. Phys.* **1997**, *106*, 4973.

(8) Ekern, S. P.; Marshall, A. G.; Szczepanski, J.; Vala, M. *Astrophys. J.* **1997**, *488*, L39.

(9) Ekern, S. P.; Marshall, A. G.; Szczepanski, J.; Vala, M. *J. Phys. Chem. A* **1998**, *102*, 3498.

(10) Joachims, H. W.; Baumgärtel, H.; Leach, S. *Astrophys. J*. **1996**, *512*, 500.

(11) Allain, T.; Leach, S.; Sedlmayr, E. *Astron. Astrophys*. **1996**, *305*, 616.

(12) Dibben, M. J.; Kage, D.; Szczepanski, J.; Eyler, J. R.; Vala, M. *J. Phys. Chem. A* **2001**, *105*, 6024.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(14) Bauschlicher, C. W. *Astrophys. J.* **1998**, *509*, L125.

(15) Langhoff, S. R. *J. Phys. Chem.* **1996**, *100*, 2819.

(16) Szczepanski, J.; Dibben, M. J.; Pearson, W.; Eyler, J. R.; Vala, M. *J. Phys. Chem. A* **2001**, *105*, 9388.

(17) Yang, Y.; Linnert, H. V.; Riveros, J. M.; Williams, K. R.; Eyler, J. R. *J. Phys. Chem. A* **1997**, *101*, 2371.

(18) Senko, M. W.; Canterbury, J. D.; Guan, S.; Marshall, A. G. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 1839.

(19) Marshall, A. G.; Wang, T. C. L.; Ricca, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 7893.

(20) Allain, T.; Leach, S.; Sedlmayr, E. *Astron. Astrophys*. **1996**, *305*, 602.

(21) Ling, Y.; Martin, J. M. L.; Lifshitz, C. *J. Phys. Chem. A* **1997**, *101*, 219.

(22) Banisaukas, J.; Szczepanski, J.; Vala, M.; Hirata, S. *J. Phys. Chem. A* **2004**, *108*, 3713.